Electronic Supporting Information

Synthesis of the Pyrrolo[2,3-*c*]carbazole Core Containing in Dictyodendrins Skeleton

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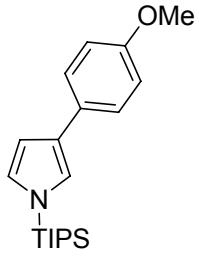
General Remarks: Melting points of crystallized compounds were determined in open capillary tubes. NMR spectra were recorded in $CDCl_3$ in the following spectrometers: ^1H NMR (400 MHz), ^{13}C NMR (100.5 MHz). Chemical shits (δ) are reported in ppm related to internal tetramethylsilane (TMS). Assignments given for the NMR spectra are based on DEPT, COSY $^1H/^1H$, HETCOR $^1H/^{13}C$ (HSQC and HMBC sequences for one bond and long range $^1H/^{13}C$ heterocorrelations, respectively) and NOESY experiments for selected compounds. For HPLC analysis a C18 column [4.6 × 150 mm, 5 μm, CH_3CN/H_2O 60:40 till CH_3CN/H_2O 90:10 (15 min), then CH_3CN 100% (1 min), flow of 1 ml/min] was used. For semipreparative HPLC analysis a C18 column [7.8 × 100 mm, 5 μm, CH_3CN/H_2O 60:40 isocratic, flow of 3 ml/min] was used. For the routine MS were obtained using ESI (+) techniques. Only significant ions are given: those with higher relative abundance, except for the ions with higher *m*/*z* values. Accurate mass measurements were obtained using ESI (+) or CI techniques. Absorption values in the IR spectra are given as wave-numbers (cm^{-1}). Column chromatography was performed on silica gel 60 Å (35-70 mesh). Thin layer chromatography (TLC) was performed with aluminium-backed sheets with silica gel 60 F_{254} and spots were visualized with UV light.

1-(Triisopropylsilyl)-3-(4-methoxyphenyl)pyrrole, 6

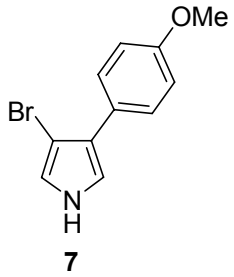


6

A solution of *n*-BuLi (2.5 M in hexane, 8.0 mL, 19.84 mmol) was added dropwise to a solution of **4** (3.0 g, 9.92 mmol) in dry THF (50 mL) at cooled −78 ºC. The reaction mixture was stirred for 25 min at −78 ºC and then a solution of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.2 mL, 59.52 mmol) in dry THF (200 mL) was added. The mixture was stirred at −78 ºC for 1 h, allowed to warm to room temperature and then quenched with saturated aqueous NH_4Cl solution (60 mL). The aqueous solution was extracted with diethyl ether (3 × 120 mL) and the combined organic phases were dried (anhydrous Na_2SO_4) and concentrated at reduced pressure to give a colorless oil (10.23 g). $Pd(PPh_3)_4$ (1.15 g, 0.99 mmol) was added to a stirred mixture of the above colorless oil (10.23 g), 4-bromoanisole (2.5 mL, 19.84 mmol) in toluene (200 mL), aqueous Na_2CO_3 solution (2 M, 10 mL, 19.84 mmol) and MeOH (40 mL) under an argon atmosphere and the mixture was heated at reflux temperature for 16 h. After cooling, the solvent was evaporated under reduced pressure and the aqueous layer was extracted with AcOEt (3 x 300 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure to give an orange oil (10.54 g) which was submitted to flash silica gel column chromatography (hexane / AcOEt 95:5) to give pure **6** (2.66 g, 81% yield) as a yellow oil. Compounds **6** was characterized by comparing their ^1H-RMN spectra to the previously reported data described in the literature.[1]

[1] A. Álvarez, A. Guzmán, A. Ruiz, and E. Velarde, *J. Org. Chem.*, 1992, **57**, 1653.

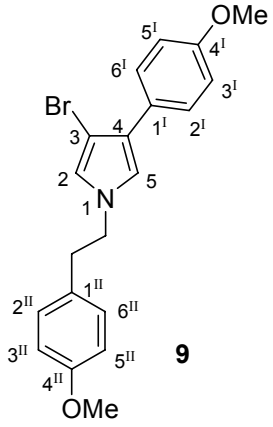
3-Bromo-4-(4-methoxyphenyl)-1*H*-pyrrole, 7



7

NBS (110 mg, 0.61 mmol) was added to a stirred solution of **6** (200 mg, 0.61 mmol) in dry THF (2 mL) at cooled −78 ºC. The reaction mixture was kept at −78 ºC for 2 h and then left to reach room temperature for 2 h. CH_2Cl_2 (20 mL) was added, the resulting suspension was filtered through a plug of neutral alumina and the filtrate was evaporated under reduced pressure to give a brown oil (248 mg). A solution of TBAF in THF (1.0 M, 0.65 mL, 0.65 mmol) was added to a stirred solution of the above brown oil (248 mg) in THF (3 mL). After stirring at room temperature for 45 min, water (20 mL) was added. The resulting solution was extracted with AcOEt (3 × 20 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure to give a black oil (256 mg) which was submitted to flash silica gel column chromatography (hexane / AcOEt 80:20) to give pure **7** (80.3 mg, 52% yield) as a brown oil. Compounds **7** was characterized by comparing their ^{1}H-RMN spectra to the previously reported data described in the literature.[2]

3-Bromo-1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-pyrrole, 9



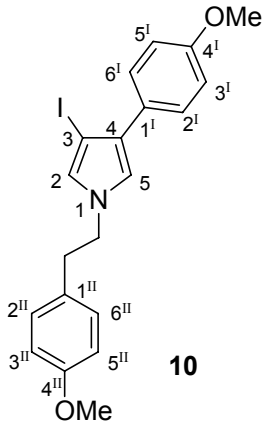
9

K_2CO_3 (120 mg, 0.88 mmol) was added to a stirred solution of **7** (40.6 mg, 0.16 mmol) in dry DMF (1.5 mL) at room temperature and the reaction mixture was maintained for 30 min at the same temperature. After this time, 4-methoxyphenetyl bromide (140 μL, 0.88 mmol) was added and the reaction mixture was heated at 80 ºC for 17 h. The solvent was evaporated under reduced pressure to give a yellow solid (453 mg) which was submitted to flash silica gel column chromatography (hexane / AcOEt 95:5) to give pure **9** (55.4 mg, 90% yield) as a yellow oil; IR (NaCl) ν 2925, 1610, 1512, 1245, 1178, 1030, 835, 789 cm^{-1}; ^{1}H NMR δ: 3.00 (t, 2 H, J = 7.2 Hz, CH_2-Ar), 3.80 (s, 3 H, $4^{II}OCH_3$), 3.83 (s, 3 H, $4^{I}OCH_3$), 4.02 (t, 2 H, J = 7.2 Hz, CH_2-N), 6.59 (d, 1 H, J = 2.8 Hz, H5), 6.66 (d, 1 H, J = 2.8 Hz, H2), 6.85 (d, 2 H, J = 8.8 Hz, $H3^{II}$ and 5^{II}), 6.93 (d, 2 H, J = 8.8 Hz, $H3^{I}$ and 5^{I}), 7.02 (d, 2 H, J = 8.8 Hz, $H2^{II}$ and 6^{II}), 7.46 (d, 2 H, J = 8.8 Hz, $H2^{I}$ and 6^{I}). ^{13}C NMR δ: 37.2 (t, CH_2-Ar), 52.0 (t, CH_2-N), 55.2 (2q, OCH_3), 94.7 (s, C3), 113.7 (d, $C3^{I}$ and 5^{I}), 114.0 (d, $C3^{II}$ and 5^{II}), 118.6 (d, C5), 121.1 (d, C2), 123.4 (s, C4), 126.9 (s, $C1^{I}$), 128.9 (d, $C2^{I}$ and 6^{I}), 129.6 (d, $C2^{II}$ and 6^{II}), 129.9 (s, $C1^{II}$), 158.2 (s, $C4^{I}$), 158.4 (s, $C4^{II}$); MS (ESI+), *m*/*z* (%): 388 (33) and 386 (32) ([M+H]$^+$), 324

[2] L. B. Snyder, Z. Meng, R. Mate, S. V. D'Andrea, A. Marinier, C. A. Quesnelle, P. Gill, K. L. DenBleyker, J. C. Fung-Tomc, M. Frosco, A. Martel, J. F. Barrett and J. J. Bronson, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 4735.

(94), 308 ([M–Br+2H]$^+$, 34), 282 (100). HRMS (ESI+) calcd for [$C_{20}H_{20}BrNO_2$+H]$^+$: 386.0750. Found: 386.0748.

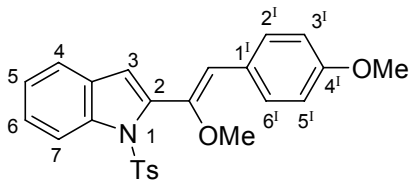
3-Iodo-1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-pyrrole, 10



10

A solution of iode (460 mg, 1.82 mmol) in dry CH_2Cl_2 (80mL) was added dropwise to a stirred solution of **6** (0.60 mg, 1.82 mmol) in dry CH_2Cl_2 (40 mL) containing $Hg(OAc)_2$ (610 mg, 1.91 mmol) cooled at –78 ºC. The reaction mixture was stirred at –78 ºC for 1 h and then the solvent was evaporated under reduced pressure. Hexane (100 mL) was added to the residue, the mixture was filtered through a Celite® pad and the filtrate was evaporated under reduced pressure to give the iodide (860 mg) as an orange oil. A solution of TBAF in THF (1.0 M, 1.9 mL, 1.9 mmol) was added to a stirred solution of the above orange oil (860 mg) in THF (8 mL). After stirring at room temperature for 30 min, water (30 mL) was added. The resulting solution was extracted with AcOEt (3 × 50 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure to give **8** as a brown oil. K_2CO_3 (1.38 g, 10.01 mmol) was added to a stirred solution of the above brown oil in dry DMF (16 mL) at room temperature and the reaction mixture was maintained for 30 min at the same temperature. After this time, 4-methoxyphenetyl bromide (1.6 mL, 10.01 mmol) was added and the reaction mixture was heated at 80 ºC for 17 h. The solvent was removed in vacuum to give an orange solid (5.71 g) which was submitted to flash silica gel column chromatography (hexane / AcOEt 95:5) to give pure **10** (388 mg, 49% overall yield) as a yellow oil; IR (NaCl) ν 2931, 2834, 1611, 1512, 1247, 1179, 1034, 832 cm^{-1}; ^{1}H NMR δ: 3.00 (t, 2 H, J = 7.2 Hz, CH_2-Ar), 3.80 (s, 3 H, C4^{II}-OCH_3), 3.83 (s, 3 H, C4^{I}-OCH_3), 4.04 (t, 2 H, J = 7.2 Hz, CH_2-N), 6.57 (d, 1 H, J = 2.2 Hz, H5), 6.73 (d, 1 H, J = 2.2 Hz, H2), 6.84 (d, 2 H, J = 8.8 Hz, H3^{II} and 5^{II}), 6.92 (d, 2 H, J = 8.8 Hz, H3^{I} and 5^{I}), 7.02 (d, 2 H, J = 8.8 Hz, H2^{II} and 6^{II}), 7.41 (d, 2 H, J = 8.8 Hz, H2^{I} and 6^{I}). ^{13}C NMR δ: 37.3 (t, CH_2-Ar), 51.9 (t, CH_2-N), 55.2 and 55.3 (2q, OCH_3), 61.3 (s, C3), 113.6 (d, C3^{I} and 5^{I}), 114.0 (d, C3^{II} and 5^{II}), 119.1 (d, C5), 126.4 (d, C2), 126.8 (s, C4), 127.9 (s, C1^{I}), 129.3 (d, C2^{I} and 6^{I}), 129.6 (d, C2^{II} and 6^{II}), 129.9 (s, C1^{II}), 158.3 (s, C4^{I}), 158.5 (s, C4^{II}); MS (ESI+), *m*/*z* (%): 434 ([M+H]$^+$, 47), 307 ([M–I+H]$^+$, 27), 282 (21), 149 (10), 135 (100). HRMS (ESI+) calcd for [$C_{20}H_{20}INO_2$+H]$^+$: 434.0611. Found: 434.0609.

(*Z*)-2-[1-Methoxy-2-(4-methoxyphenyl)vinyl]-*N*-tosyl-1*H*-indole, (*Z*)-13

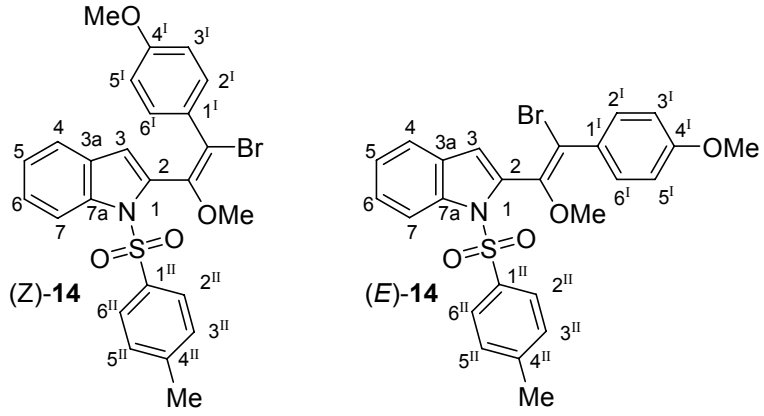


(*Z*)-**13**

A solution of **12** (501 mg, 1.19 mmol) in dry DMF (4 mL) was added to a suspension of NaH (190 mg, 4.76 mmol) in dry DMF (6 mL) cooled at 0 ºC. The reaction mixture was allowed to warm to room temperature and was stirred for 10 min. Dimethyl sulphate (0.34 mL, 3.57 mmol) was then added and stirring continued for another 10 min. After

completion of the reaction, water (25 mL) was added and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated at reduced pressure to give an orange oil (652 mg) which was submitted to flash silica gel column chromatography (hexane / AcOEt 95:5) to give pure (*Z*)-**13** (403 mg, 78% yield) as a white solid. mp (hexane / AcOEt) 134−136 ºC; IR (KBr) ν 2932, 1640, 1571, 1508, 1248, 1175, 750, 656 cm^{-1}; ^1H NMR δ: 2.31 (s, 3 H, CH_3 Ts), 3.62 (s, 3 H, OCH_3 enol), 3.84 (s, 3 H, OCH_3), 5.51 (s, 1 H, CH-Ar), 6.70 (s, 1 H, H3), 6.91 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.10 (d, *J* = 8.3 Hz, 2 H, Ts), 7.27 (ddd, *J* = 8.3, 7.3 and 1.2 Hz, 1 H, H5), 7.39 (ddd, 1 H, *J* = 8.3, 7.3 and 1.2 Hz, H6), 7.49 (br d, *J* = 8.3 Hz, 1 H, H4), 7.65 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 7.67 (d, *J* = 8.3 Hz, 2 H, Ts), 8.29 (br d, *J* = 8.3 Hz, 1 H, H7). ^{13}C NMR δ: 21.5 (q, CH_3 Ts), 55.3 (q, OCH_3), 56.9 (q, OCH_3 enol), 112.7 (d, CH-Ar), 113.7 (d, $C3^I$ and 5^I), 115.0 (d, C3), 115.7 (d, C7), 121.2 (d, C4), 124.0 (d, C5), 125.5 (d, C6), 127.2 (d, Ts), 128.5 (s), 129.3 (d, Ts), 129.5 (s), 130.0 (d, $C2^I$ and 6^I), 135.2 (s), 136.0 (s), 137.5 (s), 144.8 (s), 146.1 (s), 158.3 (s); MS (ESI+), *m*/*z* (%): 889 ($[2M+Na]^+$, 76), 886 (22), 885 (53), 884 ($[2M+NH_4]^+$, 100), 451 ($[M+NH_4]^+$, 46), 435 (24), 434 ($[M+H]^+$, 93), 402 ($[M–OMe]^+$, 8). HRMS (ESI+) calcd for $[C_{25}H_{23}NO_4S+H]^+$: 434.1420. Found: 434.1430.

(*Z*)-2-[2-Bromo-1-methoxy-2-(4-methoxyphenyl)vinyl]-*N*-tosyl-1*H*-indole, (*Z*)-14 and (*E*)-2-[2-bromo-1-methoxy- -2-(4-methoxyphenyl)vinyl]-*N*-tosyl-1*H*-indole, (*E*)-14



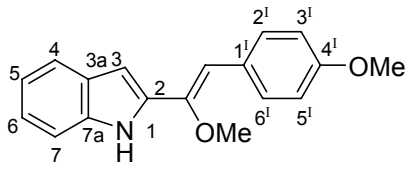
NBS (210.0 mg, 1.19 mmol) was added to a solution of (*Z*)-**13** (431.6 mg, 1.0 mmol) in dry THF (5 mL) cooled at −78 ºC and the solution was allowed to reach room temperature for 1h. CH_2Cl_2 (50 mL) was added and the solution was filtrated over an alumina plug and concentrated at reduced pressure to obtain a stereoisomeric mixture of (*Z*)-**14** and (*E*)-**14** (483.9 mg, in a 2.6:1 ratio determinated by HPLC and ^1H-NMR). The above mixture (*Z*)-**14** and (*E*)-**14** (483.9 mg) was crystallized with acetonitrile (3 mL) to obtain (*Z*)-**14** pure (259.3 mg, 51% yield) as a white solid and a mixture of (*Z*)-**14** and (*E*)-**14** (180.3 mg, 35% yield, in a 1:1 ratio determinated by HPLC) as a yellow pale foam. Purification of 30 mg of the stereoisomeric mixture of (*Z*)-**14** and (*E*)-**14** using semipreparative HPLC with a C18 column [7.8 × 100 mm, 5 μm, CH_3CN/H_2O 60:40 isocratic, flow of 3 ml/min] allowed to obtain 15.5 mg of (*Z*)-**14** as a white solid and 6 mg of (*E*)-**14** as a yellow oil.

(*Z*)-**14**: mp 160−161 ºC (CH_3CN / H_2O); IR (KBr) ν 2933, 1605, 1508, 1372, 1239, 1175, 827, 748, 679 cm^{-1}; ^1H NMR δ: 2.38 (s, 3 H, CH_3 Ts), 3.14 (s, 3 H, OCH_3 enol), 3.71 (s, 3 H, OCH_3), 6.41 (s, 1 H, H3), 6.67 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.20 (td, *J* = 8.2 and 1.2 Hz, 1 H, H5), 7.24 (d, *J* = 8.2 Hz, 2 H, $H3^{II}$ and 5^{II}), 7.33 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 7.35 (td, 1 H, *J* = 8.2 and 1.2 Hz, H6), 7.40 (dd, *J* = 8.2 and 1.2 Hz, 1 H, H4), 7.89 (d, *J* = 8.2 Hz, 2 H, $H2^{II}$ and 6^{II}), 8.12 (dd, *J* = 8.2 and 1.2 Hz, 1 H, H7); ^{13}C NMR δ: 21.6 (q, CH_3 Ts), 55.1 (q, OCH_3), 56.7 (q, OCH_3 enol), 111.5 (C, C-Ar), 113.4 (d, $C3^I$ and 5^I), 114.4 (d, C7), 115.1 (d, C3), 121.4 (d, C4), 123.3 (d, C5), 125.4 (d, C6), 127.4 (d, $C2^{II}$ and 6^{II}), 128.1 (s, C3a), 129.5 (d, $C3^{II}$ and 5^{II}), 130.3 (s, $C1^I$), 131.0 (d, $C2^I$ and 6^I) and (s, C2), 136.2 (s, $C4^{II}$), 136.6 (s, C7a), 144.1 (s, C-OMe), 144.8 (s, $C1^{II}$), 159.1 (s, $C4^I$). MS (ESI+), *m*/*z* (%): 514 (8) and 512 (8) ($[M+H]^+$), 433 ($[M–Br+H]^+$, 93), 401 ($[M–Br–MeO]^+$, 25), 359 (36), 357 (18), 341 (21), 293 (10), 278 (100), 247 (22). HPLC-PDA analysis (CH_3CN/H_2O 60:40 till CH_3CN/H_2O 90:10 (15 min), then CH_3CN 100% (1 min), flow of 1 ml/min) (retention time): 8.87 min. HRMS (CI) calcd for $[C_{25}H_{22}BrNO_4S+2H]^+$: 514.42. Found: 514.50.

(*E*)-**14**: IR (NaCl) ν 2931, 1604, 1507, 1374, 1252, 1175, 678, 578 cm^{-1}; ^1H NMR δ: 2.32 (s, 3 H, CH_3 Ts), 3.38 (s, 3 H, OCH_3 enol), 3.86 (s, 3 H, OCH_3), 6.87 (s, 1 H, H3), 6.93 (d, *J* = 9.0 Hz, 2 H, $H3^I$ and 5^I), 7.18 (d, *J* = 8.4 Hz, 2 H, $H3^{II}$ and 5^{II}), 7.28 (td, *J* = 8.2 and 0.8 Hz, 1 H, H5), 7.40 (td, 1 H, *J* = 8.2 and 1.2 Hz, H6), 7.57 (dd, *J* = 8.2 and 1.2 Hz, 1 H, H4), 7.68 (d, *J* = 9.0 Hz, 2 H, $H2^I$ and 6^I), 7.89 (d, *J* = 8.4 Hz, 2 H, $H2^{II}$ and 6^{II}), 8.21 (dd, *J* = 8.2 and 0.8 Hz,1 H, H7); ^{13}C NMR δ: 21.6 (q, CH_3 Ts), 55.3 (q, OCH_3), 57.8 (q, OCH_3 enol), 110.5 (s, C-Ar), 113.3 (d, $C3^I$ and 5^I), 114.9 (d, C7), 115.5 (d, C3), 121.5 (d, C4), 123.7 (d, C5), 125.6 (d, C6), 127.6 (d, $C2^{II}$ and 6^{II}), 128.8 (s, C3a), 129.6 (d, $C3^{II}$ and 5^{II}), 131.1 (d, $C2^I$ and 6^I), 132.8 and 136.5 (s, C7a∗) and (s, C2∗), 135.4 (s, $C4^{II}$), 144.7 (s, C-OMe), 144.9 (s, $C1^{II}$), 159.4 (s, $C4^I$). MS (EI), *m*/*z* (%): 514 (10) and 512 (10) ($[M+H]^+$), 433 ($[M–Br+H]^+$, 100), 401 ($[M–Br–MeO]^+$, 20), 359 (29), 357 (42), 341 (19), 337 (21), 278 (89), 247 (24), 234 (25). HPLC-PDA analysis (CH_3CN/H_2O 60:40 till CH_3CN/H_2O 90:10 (15 min), then CH_3CN 100% (1 min), flow of 1 ml/min) (retention time): 9.69 min. HRMS (ESI+) calcd for $[C_{25}H_{22}BrNO_4S+NH_4]^+$: 529.0791. Found: 529.0775.

∗Interchangeable C

(*Z*)-2-[1-Methoxy-2-(4-methoxyphenyl)vinyl]-1*H*-indole, (*Z*)-15

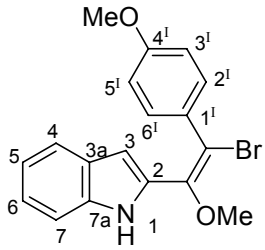


(*Z*)-**15**

A suspension of (*Z*)-**13** (756.4 mg, 1.74 mmol), Cs_2CO_3 (1.89 g, 5.74 mmol) in a 2:1 mixture of THF and MeOH (87 mL) was stirred at 60 ºC for 24 h. The reaction mixture was allowed to cool to room temperature. Water (70 mL) was added and the aqueous layer was extracted with AcOEt (70 mL). The organic layer was washed with water (40 mL) and brine (40 mL) and was dried (anhydrous Na_2SO_4). Elimination of solvent at reduced pressure gave pure (*Z*)-**15** (477.0 mg, 98% yield) as a palle yellow solid. An analytical sample was obtained by trituration from diethyl ether giving (*Z*)-**15** as a white solid, mp 157−159 ºC (diethyl ether); IR (KBr) ν 3325, 3296,

1653, 1513, 1341, 1246, 1161 cm^{-1}; ^1H NMR δ: 3.76 (s, 3 H, OCH_3 enol), 3.85 (s, 3 H, OCH_3), 6.28 (s, 1 H, CH-Ar), 6.73 (d, *J* = 1.2 Hz, 1 H, H3), 6.92 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.12 (td, 1 H, *J* = 8.0 and 0.8 Hz, H5), 7.20 (td, *J* = 8.0 and 0.8 Hz, 1 H, H6), 7.37 (br d, *J* = 8.0 Hz, 1 H, H7), 7.61 (br d, *J* = 8.0 Hz, 1 H, H4), 7.66 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 8.31 (br s, 1 H, NH); ^{13}C NMR δ: 55.3 (q, OCH_3), 58.9 (q, OCH_3 enol), 110.9 (d, C3), 110.8 (d, C7), 112.4 (d, CH-Ar), 114.0 (d, $C3^I$ and 5^I), 120.2 (d, C5), 120.6 (d, C4), 122.5 (d, C6), 127.8 (s, $C1^I$), 128.8 (C, C7a), 130.0 (d, $C2^I$ and 6^I), 134.8 (s, C2), 136.2 (s, C3a), 147.5 (s, C-OMe), 158.6 (C, $C4^I$). MS (ESI+), *m*/*z* (%): 280 ($[M+H]^+$, 5), 267 (18), 266 (100), 121 (24). HRMS (ESI+) calcd for $[C_{18}H_{17}NO_2+H]^+$: 280.1332. Found: 280.1339.

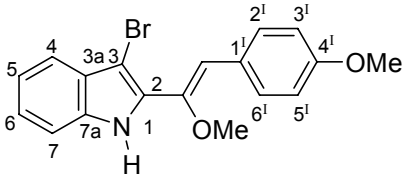
(*Z*)-2-[2-Bromo-1-methoxy-2-(4-methoxyphenyl)vinyl]-1*H*-indole, (*Z*)-16



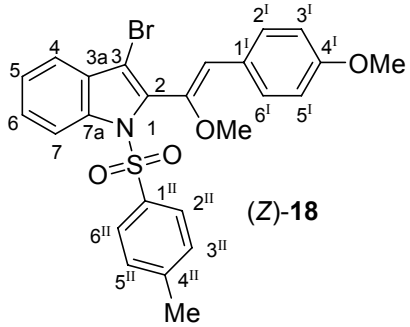
(*Z*)-**16**

A suspension of (*Z*)-**14** (10.0 mg, 0.02 mmol), Cs_2CO_3 (22.0 mg, 0.066 mmol) in a 2:1 mixture of THF and MeOH (1 mL) was stirred at 60 ºC for 24 h. The reaction mixture was allowed to cool to room temperature. Water (10 mL) was added and the aqueous layer was extracted with AcOEt (10 mL). The organic layer was washed with water (5 mL) and brine (5 mL) and was dried (anhydrous Na_2SO_4). Elimination of solvent at reduced pressure gave pure (*Z*)-**16** (0.07 mg, quantitative yield) as a yellow oil; IR (NaCl) ν 3364, 2924, 2853, 1601, 1506, 1452, 1294, 1242 cm^{-1}; ^1H NMR δ: 3.78 (s, 3 H, OCH_3 enol), 3.83 (s, 3 H, OCH_3), 6.32 (d, *J* = 1.6 Hz, 1 H, H3), 6.87 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.05 (td, *J* = 8.0 and 1.2 Hz, 1 H, H5), 7.14 (td, *J* = 8.0 and 1.2 Hz, 1 H, H6), 7.17 (m, 1 H, H7), 7.33 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 7.49 (dd, *J* = 8.0 and 1.2 Hz, 1 H, H4), 7.74 (br s, 1 H, NH); ^{13}C NMR δ: 55.3 (q, OCH_3), 59.3 (q, OCH_3 enol), 105.2 (d, C3), 110.0 (s, C-Ar), 110.9 (d, C7), 114.3 (d, $C3^I$ and 5^I), 120.2 (d, C5), 120.9 (d, C4), 123.0 (d, C6), 127.8 (s, C3a), 130.1 (s, $C1^I$), 130.3 (s, C2), 131.4 (d, $C2^I$ and 6^I), 135.8 (s, C7a), 146.1 (s, C-OMe), 159.9 (s, $C4^I$). MS (ESI+), *m*/*z* (%): 360 (98) i 358 (100) ($[M+H]^+$), 326 (26), 282 (40), 240 (47), 130 (55). HRMS (ESI+) calcd for $[C_{18}H_{16}BrNO_2+H]^+$: 358.0437. Found: 358.0430.

(*Z*)-3-Bromo-2-[1-methoxy-2-(4-methoxyphenyl)vinyl]-1*H*-indole, (*Z*)-17 and (*Z*)-3-bromo-2-[1-methoxy-2-(4-methoxyphenyl)vinyl]-*N*-tosyl-1*H*-indole, (*Z*)-18



(*Z*)-**17**



(*Z*)-**18**

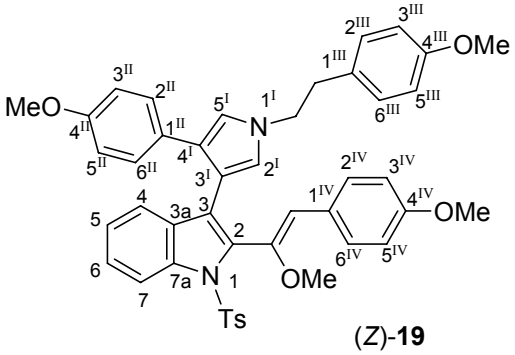
NBS (350 mg, 1.99 mmol) and (*Z*)-**15** (550 mg, 1.97 mmol) were added to a suspension of MeONa, prepared from Na (50.0 mg, 2.17 mmol) and MeOH (15 mL) cooled at 0 ºC. The reaction mixture was allowed to react to room temperature and was stirred for 2 h. The solvent was evaporated under reduced pressure, water (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum to give (*Z*)-**17** as an orange foam (720 mg). A solution of the above orange oil (720 mg) in dry THF (6 mL) was added, dropwise, to a stirred suspension cooled at 0 ºC of NaH (130 mg, 3.15 mmol) in dry THF (2 mL). When hydrogen evolution ceased, TsCl (450 mg, 2.36 mmol) was added and the mixture was allowed to heat to room temperature and was stirred for 17 h. H_2O (20 mL) was added and the mixture was stirred for more 10 minutes. The solvent was removed under reduced pressure, AcOEt (50 mL) was added and the organic phase was washed with saturated aqueous $NaHCO_3$ solution (3 × 20 mL), H_2O (3 × 20 mL) and brine (2 × 20 mL). The organic phase was dried (anhydrous Na_2SO_4) and concentrated at reduced pressure to give an orange residue (1.05 g) which was submitted to flash silica gel column chromatography (hexane / AcOEt 97:3) to give pure (*Z*)-**18** (720 mg, 72% overall yield) as a brown pale foam.

(*Z*)-**18**: mp 152−154 ºC (hexane / AcOEt); IR (KBr) ν 2932, 1605, 1551, 1378, 1297, 1175, 661, 607 cm^{-1}; ^1H NMR δ: 2.34 (s, 3 H, CH_3 Ts), 3.58 (s, 3 H, OCH_3 enol), 3.85 (s, 3 H, OCH_3), 5.36 (s, 1 H, CH-Ar), 6.93 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.13 (d, *J* = 8.4 Hz, 2 H, $H3^{II}$ and 5^{II}), 7.38 (td, *J* = 7.6 and 0.4 Hz, 1 H, H5), 7.48 (td, 1 H, *J* = 8.4 and 1.2 Hz, H6), 7.54 (br d, *J* = 7.6 Hz, 1 H, H4), 7.67 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 7.69 (d, *J* = 8.4 Hz, 2 H, $H2^{II}$ and 6^{II}), 8.33 (br d, *J* = 8.4 Hz, 1 H, H7); ^{13}C NMR δ: 21.6 (q, CH_3 Ts), 55.3 (q, OCH_3), 56.6 (q, OCH_3 enol), 105.9 (s, C3), 113.8 (d, $C3^I$ and 5^I), 115.4 (d, C7), 115.5 (d, CH-Ar), 120.5 (d, C4), 124.4 (d, C5), 126.8 (d, C6), 127.3 (d, $C2^{II}$ and 6^{II}), 128.1 (s, $C1^I$), 128.9 (s, C3a), 129.5 (d, $C3^{II}$ and 5^{II}), 130.3 (d, $C2^I$ and 6^I), 132.4 (s, C2), 135.3 (s, $C4^{II}$), 135.9 (s, C7a), 142.6 (s, C-OMe), 145.2 (s, $C1^{II}$), 158.5 (s, $C4^I$). MS (ESI+), *m/z* (%): 531 (65) and 529 (61) ($[M+NH_4]^+$), 514 (48) and 512 (46) ($[M+H]^+$). HRMS (ESI+) calcd for $[C_{25}H_{22}BrNO_4S+H]^+$: 512.0525. Found: 512.0528.

(*Z*)-**17**: ^1H NMR δ: 3.69 (s, 3 H, OCH_3 enol), 3.85 (s, 3 H, OCH_3), 6.67 (s, 1 H, CH-Ar), 6.93 (d, *J* = 8.8 Hz, 2 H, $H3^I$ and 5^I), 7.20-7.28 (m, 2 H, H5 and H6), 7.35 (br d, *J* = 8.0 Hz, 1 H, H4∗), 7.60 (br d, *J* = 8.0 Hz, 1 H, H7∗), 7.70 (d, *J* = 8.8 Hz, 2 H, $H2^I$ and 6^I), 8.51 (br s, 1 H, NH).

∗ Interchangeable H

(*Z*)-2-[1-Methoxy-2-[4-methoxyphenyl)vinyl]-3-[1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-pyrrol-3-yl]-*N*-tosyl-1*H*-indole, (*Z*)-19

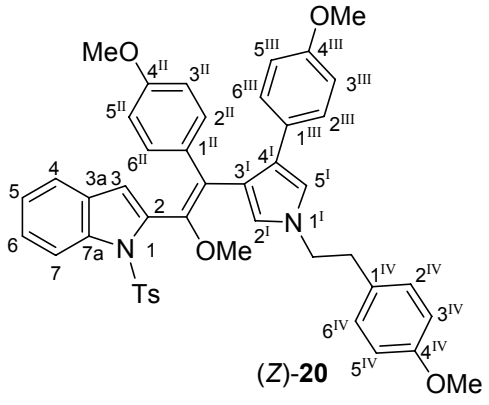


(*Z*)-**19**

A solution of *n*-BuLi (2.5 M in hexane, 0.75 mL, 1.86 mmol) was added dropwise to a solution of **10** (403 mg, 0.93 mmol) in dry THF (5 mL) at −78 ºC. The reaction mixture was stirred for 25 min at −78 ºC and

then a solution of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.95 mL, 5.58 mmol) in dry THF (20 mL) was added. The mixture was stirred at −78 ºC for 1 h, allowed to warm to room temperature and then quenched with saturated aqueous NH_4Cl solution (20 mL). The aqueous solution was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated at reduced pressure to give **2** as an orange oil (1.14 g). $Pd(PPh_3)_4$ (72.0 mg, 0.062 mmol) was added to a stirred mixture of the above orange oil (1.14 g), (*Z*)-**18** (320 mg, 0.62 mmol), aqueous Na_2CO_3 solution (2 M, 0.62 mL, 1.24 mmol) and DMF (16 mL) under an argon atmosphere and the mixture was heated at reflux temperature for 16 h. After cooling, the solvent was evaporated under reduced pressure and the aqueous layer was extracted with AcOEt (3 × 60 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure to give an orange oil (1.34 g) which was submitted to flash silica gel column chromatography (hexane / AcOEt 75:25) to give a brown solid which was purified by trituration in *n*-pentane to give pure (Z)-**19** (270 mg, 59% yield) as a brown pale foam, mp 72−74 ºC (*n*-pentane); IR (KBr) ν 2933, 2836, 1677, 1608, 1510, 1372, 1247, 1175, 1035 cm^{-1}; ^1H NMR δ: 2.38 (s, 3 H, CH_3 Ts), 2.92 (t, 2 H, *J* = 6.8 Hz, CH_2-Ar), 3.49 (s, 3 H, OCH_3), 3.72 (s, 3 H, $C4^{II}$-OCH_3), 3.75 (s, 3 H, $C4^{III}$-OCH_3), 3.79 (s, 3 H, $C4^{IV}$-OCH_3), 4.00 (t, 2 H, *J* = 6.8 Hz, CH_2-N), 4.84 (s, 1 H, CH-Ar), 6.42 (d, 1 H, *J* = 2.4 Hz, $H2^{I}$), 6.49 (d, *J* = 8.8 Hz, 2 H, $H3^{III}$ and 5^{III}), 6.62 (d, 1 H, *J* = 2.4 Hz, $H5^{I}$), 6.65 (d, 2 H, *J* = 8.4 Hz, $H2^{II}$ and 6^{II}), 6.80 (d, 2 H, *J* = 8.8 Hz, $H2^{III}$ and 6^{III}), 6.82 (d, 2 H, *J* = 8.4 Hz, $H3^{II}$ and 5^{II}), 6.84 (d, *J* = 8.8 Hz, 2 H, $H3^{IV}$ and 5^{IV}), 7.09 (d, *J* = 8.4 Hz, 2 H, H3 and 5 Ts), 7.18-7.24 (m, 2 H, H4 and H5), 7.37-7.40 (m, 3 H, H6 and $H2^{IV}$ and 6^{IV}), 7.60 (d, *J* = 8.4 Hz, 2 H, H2 and 6 Ts), 8.33 (br d, *J* = 8.4 Hz, 1 H, H7); ^{13}C NMR δ: 21.5 (q, CH_3 Ts), 37.3 (t, CH_2-Ar), 51.7 (t, CH_2-N), 55.16 (q, OCH_3), 55.19 (q, OCH_3), 55.20 (q, OCH_3), 56.1 (q, OCH_3), 111.5 (s, $C3^{I}$), 113.4 (d, $C3^{II}$ and 5^{II}), 113.7 (d, $C3^{III}$ and 5^{III}), 113.75 (d, CH-Ar), 113.8 (d, $C2^{II}$ and 6^{II}), 115.5 (d, C7), 118.5 (d, $C5^{I}$), 121.1 (d, $C2^{I}$), 121.4 (d, C5), 122.9 (s, C3a), 123.8 (d, C4), 125.0 (s, $C1^{II}$), 125.5 (d, C6), 127.2 (d, C2 and 6 Ts), 127.8 (d, $C2^{III}$ and 6^{III}), 128.8 (s, C3), 128.9 (s, $C1^{III}$), 129.2 (d, C3 and 5 Ts), 129.6 (d, $C3^{IV}$ and 5^{IV}), 130.0 (d, $C2^{IV}$ and 6^{IV}), 130.2 (s, $C4^{I}$), 132.0 (2s, $C1^{IV}$ and C2), 135.8 (s, C4 Ts), 136.5 (s, C7a), 143.9 (s, C-OMe), 144.5 (s, C1 Ts), 157.3 (s, $C4^{III}$), 157.9 (s, $C4^{IV}$), 158.3 (s, $C4^{II}$). MS (ESI+), *m*/*z* (%): 1499 ($[2M+Na]^+$, 29), 739 ($[M+H]^+$, 66), 325 (20), 324 (100), 141 (14), 125 (31). HRMS (ESI+) calcd for $[C_{45}H_{42}N_2O_6S+H]^+$: 739.2836. Found: 739.2833.

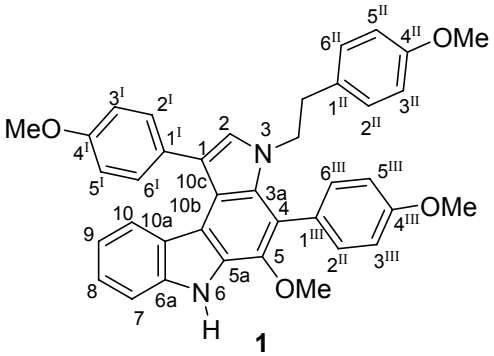
(*Z*)-2-[1-Methoxy-2-(4-methoxyphenyl)-2-[1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-pyrrol-3-yl]vinyl]-*N*-tosyl-1*H*-indole, (*Z*)-20



A solution of *n*-BuLi (2.5 M in hexane, 0.52 mL, 1.3 mmol) was added dropwise to a solution of **10** (280 mg, 0.65 mmol) in dry THF (3 mL) cooled at −78 ºC. The reaction mixture was stirred for 25 min at −78 ºC and then a solution of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.7 mL, 3.9 mmol) in dry THF (13 mL)

was added. The mixture was stirred at −78 ºC for 1 h, allowed to warm to room temperature and then quenched with saturated aqueous NH_4Cl solution (10 mL). The aqueous solution was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated at reduced pressure to give **2** as an orange oil (750 mg). $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) was added to a stirred mixture of the above orange oil (750 mg), (*Z*)-**14** (0.22 mL, 0.43 mmol), aqueous Na_2CO_3 solution (2 M, 0.4 mL, 0.87 mmol) and DMF (11 mL) under an argon atmosphere and the mixture was heated at reflux temperature for 16 h. After cooling, the solvent was evaporated under reduced pressure and the aqueous layer was extracted with AcOEt (3 × 20 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure to give an orange oil (850 mg) which was submitted to flash silica gel column chromatography (hexane / AcOEt 80:20) to give a brown solid which was purified by trituration in *n*-pentane to give pure (*Z*)-**20** (210 mg, 67% yield) as a brown pale solid, mp 64−66 ºC (*n*-pentane); IR (KBr) ν 2933, 1511, 1369, 1246, 1175, 749, 681 cm^{-1}; ^1H NMR δ: 2.33 (s, 3 H, CH_3 Ts), 2.51 (s, 3 H, OCH_3), 3.02 (t, 2 H, *J* = 7.2 Hz, CH_2-Ar), 3.65 (s, 3 H, $C4^{II}$-OCH_3), 3.74 (s, 3 H, $C4^{III}$-OCH_3), 3.77 (s, 3 H, $C4^{IV}$-OCH_3), 4.04 (t, 2 H, *J* = 7.2 Hz, CH_2-N), 6.30 (s, 1 H, H3), 6.47 (d, 1 H, *J* = 2.4 Hz, $H2^I$), 6.54 (d, 2 H, *J* = 9.2 Hz, $H3^{II}$ and 5^{II}), 6.71 (d, 1 H, *J* = 2.4 Hz, $H5^I$), 6.80 (d, 2 H, *J* = 8.8 Hz, $H3^{III}$ and 5^{III}), 6.81 (d, 2 H, *J* = 8.4 Hz, $H3^{IV}$ and 5^{IV}), 7.02 (d, 2 H, *J* = 8.4 Hz, $H2^{IV}$ and 6^{IV}), 7.13-7.18 (m, 5 H, H5, H3 and 5 Ts and $H2^{II}$ and 6^{II}), 7.29 (td, 1 H, *J* = 8.8 and 1.2 Hz, H6), 7.36 (br d, 1 H, *J* = 7.6 Hz, H4), 7.45 (d, 2 H, *J* = 8.8 Hz, $H2^{III}$ and 6^{III}), 7.93 (d, 2 H, *J* = 8.4 Hz, H2 and 6 Ts), 8.10 (br d, 1 H, *J* = 8.8 Hz, H7); ^{13}C NMR δ: 21.5 (q, CH_3 Ts), 37.2 (t, CH_2-Ar), 51.6 (t, CH_2-N), 54.9 (q, $C4^{II}$-OCH_3), 55.2 (2q, $C4^{III}$-OCH_3 and $C4^{IV}$-OCH_3), 56.6 (q, OCH_3), 112.8 (d, $C3^{II}$ and 5^{II}), 113.4 (2d, C3 and $C3^{III}$ and 5^{III}), 113.9 (d, $C3^{IV}$ and 5^{IV}), 114.3 (d, C7), 118.0 (d, $C5^I$), 120.6 (s, $C3^I$), 121.2 (d, C4), 121.7 (d, $C2^I$), 122.1 (s, C-Ar), 122.9 (d, C5), 124.3 (s, $C4^I$), 124.6 (d, C6), 127.4 (d, C2 and 6 Ts), 128.3 (d, $C2^{III}$ and 6^{III}), 128.7 (s, C3a), 129.4 (d, C3 and 5 Ts), 129.7 (d, $C2^{IV}$ and 6^{IV}), 130.4 (2s, $C1^{III}$ and $C1^{IV}$), 130.6 (d, $C2^{II}$ and 6^{II}), 134.3 (s, $C1^{II}$), 135.6 (s, C2), 136.5 (s, C7a), 136.7 (s, C4 Ts), 142.4 (s, C-OMe), 144.4 (s, C1 Ts), 157.6 (s, $C4^{III}$), 157.7 (s, $C4^{II}$), 158.3 (s, $C4^{IV}$). MS (ESI+), *m*/*z* (%): 1499 ($[2M+Na]^+$, 10), 1495 ($[2M+NH_4]^+$, 10), 761 ($[M+Na]^+$, 13), 740 (25), 739 ($[M+H]^+$, 54), 217 (12), 203 (12), 141 (18), 108 (14), 106 (100). HRMS (ESI+) calcd for $[C_{45}H_{42}N_2O_6S+H]^+$: 739.2836. Found: 739.2835.

5-Methoxy-3-(4-methoxyphenethyl)-1,4-bis(4-methoxyphenyl)-3,6-dihydropyrrolo[2,3-*c*]carbazole, 1

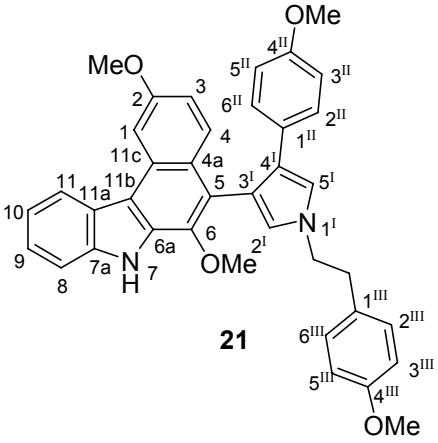


1

A solution of (*Z*)-**19** (50.1 mg, 0.068 mmol) and nitrobenzene (105 μL) in MeCN (6 mL) was introduced in a water-cooled photoreactor and purged with argon for 30 min. After this time, Pd/C (10%, 36 mg, 0.034 mmol) was added and the resulting suspension was irradiated with a medium pressure Hg-lamp (125 W) (cooled by a

stream of cold water) for 4 h. The suspension was filtered through a Celite® pad, which was carefully rinsed with EtOH / toluene (1:1, 20 mL). The organic solution was evaporated and the residue was submitted to flash silica gel column chromatography (hexane / AcOEt 92:8) to give **1** (15 mg) as a yellow solid. The solid was purified by trituration in MeCN to give pure **1** (10 mg, 25% yield) as a white solid , mp 249–250 ºC (MeCN); IR (KBr) ν 3441, 2922, 2850, 1608, 1512, 1460, 1244, 1172, 1029 cm^{-1}; ^1H NMR δ: 2.63 (m, 2 H, CH_2-Ar), 3.64 (s, 3 H, C5-OCH_3), 3.75 (s, 3 H, $C4^{II}$-OCH_3), 3.85 (m, 2 H, CH_2-N), 3.93 (2s, 6 H, $C4^{I}$-OCH_3 and $C4^{III}$-OCH_3), 6.62 (d, 2 H, *J* = 8.8 Hz, $H2^{II}$ and 6^{II}), 6.67 (br d, 1 H, *J* = 7.6, H7), 6.70 (d, 2 H, *J* = 8.8 Hz, $H3^{II}$ and 5^{II}), 6.85 (td, 1 H, *J* = 7.6 and 0.8 Hz, H8), 6.91 (s, 1 H, H2), 7.02 (d, 2 H, *J* = 8.8 Hz, $H3^{I}$ and 5^{I}), 7.08 (d, 2 H, *J* = 8.8 Hz, $H3^{III}$ and 5^{III}), 7.26 (br b, 1 H, H9), 7.45 (br d, 1 H, *J* = 7.6 Hz, H10), 7.46 (d, 2 H, *J* = 8.8 Hz, $H2^{I}$ and 6^{I}), 7.55 (d, 2 H, *J* = 8.8 Hz, $H2^{III}$ and 6^{III}), 8.31 (br s, 1 H, NH); ^{13}C NMR δ: 37.0 (t, CH_2-Ar), 50.2 (t, CH_2-N), 55.2 (q, $C4^{II}$-OCH_3), 55.4 and 55.5 (2q, $C4^{I}$-OCH_3 and $C4^{III}$-OCH_3), 61.3 (q, C5-OCH_3), 110.2 (d, C10), 113.4 (d, $C3^{I}$ and 5^{I}), 113.6 and 113.7 (2d, $C3^{II}$ and 5^{II} and $C3^{III}$ and 5^{III}), 114.8 (s), 117.0 (s), 117.9 (s), 118.6 (d, C8), 119.4 (s), 123.8 (s), 124.0 (d, C9), 124.7 (d, C7), 127.6 (s, $C1^{III}$), 128.9 (d, C2), 129.2 (s), 129.6 (d, $C2^{II}$ and 6^{II}), 130.1 (s), 130.4 (s, $C1^{II}$), 132.0 (d, $C2^{I}$ and 6^{I}), 132.2 (d, $C2^{III}$ and 6^{III}), 132.9 (s), 139.0 (s), 140.1 (s, C5), 158.1 (s, $C4^{II}$), 158.8 (s, $C4^{I}$), 159.3 (s, $C4^{III}$). MS (ESI+), *m*/*z* (%): 583 ($[M+H]^+$, 94), 582 (M^{+}, 34), 326 (100), 311 (40), 304 (61), 301 (77), 242 (30), 191 (47), 135 (46), 130 (98). HRMS (ESI+) calcd for $[C_{38}H_{34}N_2O_4+H]^+$: 583.2591. Found: 583.2600.

2,6-Dimethoxy-5-[1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-pyrrol-3-yl]-7*H*-benzo[*c*]carbazole, 21

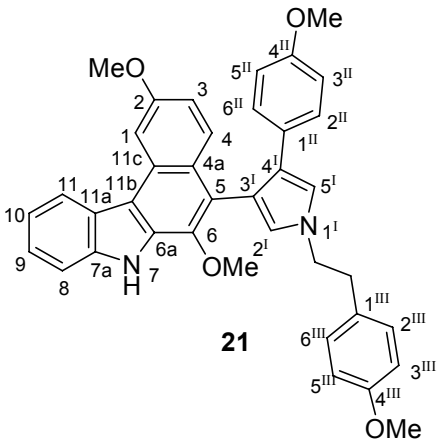


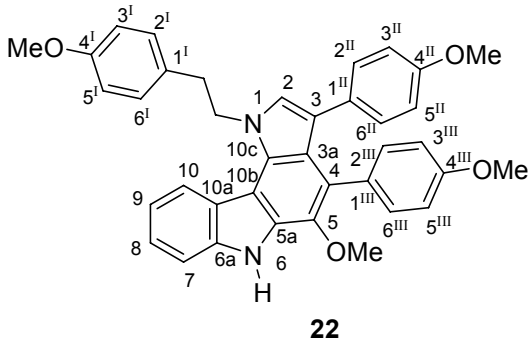
A solution of (*Z*)-**20** (56.1 mg, 0.076 mmol) and nitrobenzene (120 μL) in MeCN (6 mL) was introduced in a water-cooled photoreactor and was purged with argon for 30 min. After this time, Pd/C (10%, 43 mg, 0.04 mmol) was added and the resulting suspension was irradiated with a medium pressure Hg-lamp (125 W) (cooled by a stream of cold water) for 3 h. The suspension was filtered through a Celite® pad, which was carefully rinsed with EtOH / toluene (1:1, 20 mL). The organic solution was evaporated and the residue was submitted to flash silica gel column chromatography (hexane / AcOEt 86:14) to give **21** (7.7 mg, 17% yield) as an orange waxy; IR (NaCl) ν 3347, 2931, 1616, 1512, 1370, 1246, 1178, 1034, 826 cm^{-1}; ^1H NMR δ: 3.11 (t, 2 H, *J* = 7.2 Hz, CH_2-Ar), 3.61 and 3.62 (2s, 6 H, $C4^{II}$-OCH_3 and C6-OCH_3), 3.79 (s, 3 H, $C4^{III}$-OCH_3), 4.06 (s, 3 H, C2-OCH_3), 4.13-4.26 (m, 2 H, CH_2-N), 6.54 (d, 2 H, *J* = 9.2 Hz, $H3^{II}$ and 5^{II}), 6.60 (d, 1 H, *J* = 2.6 Hz, $H2^{I}$), 6.85 (d, 2 H, *J* = 8.4 Hz, $H3^{III}$ and 5^{III}), 6.96 (d, 1 H, *J* = 2.6 Hz, $H5^{I}$), 6.99 (dd, 1 H, *J* = 9.2 and 2.8 Hz, H3), 7.01 (d, 2 H, *J* = 9.2 Hz, $H2^{II}$ and 6^{II}), 7.09 (d, 2 H, *J* = 8.4 Hz, $H2^{III}$ and 6^{III}), 7.38 (td, 1 H, *J* = 8.0 and 0.8 Hz, H10), 7.44 (td, 1 H, *J* = 8.0 and 0.8 Hz, H9),7.58 (br d, 1 H, *J* = 8.0 Hz, H8), 7.80 (d, 1 H, *J* = 9.2 Hz, H4), 8.06 (d, 1 H, *J* = 2.8 Hz, H1), 8.48 (br d, 1 H, *J* = 8.0

Hz, H11), 8.61 (br s, 1 H, NH); ^{13}C NMR δ: 37.4 (t, CH_2-Ar), 51.6 (t, CH_2-N), 55.0 (q, OCH_3), 55.2 (q, $C4^{III}$-OCH_3), 55.4 (q, C2-OCH_3), 60.3 (q, OCH_3), 103.4 (d, C1), 111.3 (d, C8), 113.6 (d, $C3^{II}$ and 5^{II}), 113.8 (d, C3), 114.0 (d, $C3^{III}$ and 5^{III}), 115.2 (s, $C3^{I}$), 115.5 (s, C11b), 118.0 (d, $C5^{I}$), 120.1 (d, C10), 121.5 (d, C11), 122.0 (s, C5*), 122.5 (d, $C2^{I}$), 124.1 (d, C9), 124.6 and 124.7 (2s, $C4^{I}$ and C11a), 125.8 (s, C11c), 127.1 (d, $C2^{II}$ and 6^{II}), 128.3 (s, C4a*), 128.8 (s, $C1^{II}$), 129.2 (d, C4), 129.7 (d, $C2^{III}$ and 6^{III}), 130.3 (s, $C1^{III}$), 132.9 (s, C6a), 138.2 (s, C7a), 142.3 (s, C6), 157.2 (s, $C4^{II}$), 157.5 (s, C2), 158.4 (s, $C4^{III}$). MS (ESI+), *m*/*z* (%): 583 ([M+H]$^+$, 54), 514 (36), 456 (30), 428 (42), 164 (81), 150 (100), 149 (42), 135 (39), 130 (59), 116 (42). HRMS (ESI+) calcd for $[C_{38}H_{34}N_2O_4+H]^+$: 583.2591. Found: 583.2595.

* Interchangeable C

2,6-Dimethoxy-5-[1-(4-methoxyphenethyl)-4-(4-methoxyphenyl)-1*H*-3-pyrrolyl]-7*H*-benzo[*c*]carbazole, 21 and 5-methoxy-1-(4-methoxyphenethyl)-3,4-bis(4-methoxyphenyl)-1,6-dihydropyrrolo[3,2-*c*]carbazole, 22





A solution of *n*-BuLi (2.5 M in hexane, 0.12 mL, 0.30 mmol) was added dropwise to a solution of **10** (64 mg, 0.148 mmol) in dry THF (1 mL) at −78 ºC. The reaction mixture was stirred for 25 min at −78 ºC and then a solution of 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.15 mL, 0.89 mmol) in dry THF (3 mL) was added. The mixture was stirred at −78 ºC for 1 h, allowed to warm to room temperature and then quenched with saturated aqueous NH_4Cl solution (5 mL). The aqueous solution was extracted with diethyl ether (3 × 5 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated at reduced pressure to give **2** as a yellow oil (203 mg). $Pd(PPh_3)_4$ (9.0 mg, 0.008 mmol) was added to a stirred mixture of the above yellow oil (203 mg), a stereoisomeric mixture of (*Z*)-**14** and (*E*)-**14** in a 2.6:1 ratio determinated by HPLC and ^{1}H-NMR (39 mg, 0.077 mmol), aqueous Na_2CO_3 solution (2 M, 77 μL, 0.154 mmol) and DMF (2 mL) under an argon atmosphere and the mixture was heated at reflux temperature for 16 h. After cooling, the solvent was evaporated under reduced pressure and the aqueous layer was extracted with AcOEt (3 × 10 mL). The combinated organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated at reduced pressure to give a stereoisomeric mixture of (*Z*)-**20** and (*E*)-**20** as an orange oil (185 mg). A solution of the stereoisomeric mixture of (*Z*)-**20** and (*E*)-**20** (185 mg) and

nitrobenzene (115 μL) in MeCN (6 mL) was introduced in a water-cooled photoreactor and was purged with argon for 30 min. After this time, Pd/C (10%, 43 mg, 0.04 mmol) was added and the resulting suspension was irradiated with a medium pressure Hg-lamp (125 W) (cooled by a stream of cold water) for 3 h. The suspension was filtered through a Celite® pad, which was carefully rinsed with EtOH / toluene (1:1, 20 mL). The organic solution was evaporated and the residue was submitted to flash silica gel column chromatography (hexane / AcOEt 90:10) to give **22** (2.1 mg, 4% yield) as a white solid and (hexane / AcOEt 86:14) to give **21** (6.2 mg, 13% yield) as an orange waxy. **22**: IR (KBr) ν 3341, 2925, 2853, 1610, 1560, 1246, 1176, 1034 cm^{-1}; ^{1}H NMR δ: 3.32 (m, 2 H, CH_2Ar), 3.53 (s, 3 H, C5-OCH_3), 3.74, 3.75 and 3.81 (3s, 3 OCH_3), 4.97 (m, 2 H, CH_2-N), 6.49 (d, 2 H, *J* = 8.8 Hz, ArH), 6.57 (d, 2 H, *J* = 8.8 Hz, ArH), 6.74 (d, 2 H, *J* = 8.8 Hz, ArH), 6.82 (s, 1 H, H2), 6.86 (d, 2 H, *J* = 8.8 Hz, ArH), 7.07 (d, 2 H, *J* = 8.4 Hz, ArH), 7.10 (d, 2 H, *J* = 8.4 Hz, ArH), 7.26 (t, 1 H, *J* = 8.0 Hz, H8∗), 7.45 (t, 1 H, *J* = 8.0 Hz, H9∗), 7.60 (br d, 1 H, *J* = 8.0 Hz, H10), 8.37 (br d, *J* = 8.0 Hz, 1 H, H7), 8.60 (br s, 1H, NH); ^{13}C NMR δ: 37.5 (t, CH_2-Ar), 51.9 (t, CH_2-N), 55.21 (q, OCH_3), 55.25 (q, OCH_3), 55.28 (q, OCH_3), 60.8 (q, C5-OCH_3), 111.1 (d, C10), 112.5 (d), 112.6 (d), 114.0 (d and s), 119.4 (d and s), 120.1 (s), 122.2 (s), 122.6 (d, C7), 124.2 (d), 125.1 (s), 126.2 (d, C2), 127.3 (s), 127.7 (s), 128.1 (s) and 128.9 (s), 130.0 (d), 130.1 (s), 130.5 (d), 131.8 (d), 137.7 (s), 138.7 (s), 157.1 (s), 158.3 (s) and 158.4 (s). MS (ESI+), *m*/*z* (%): 583 ($[M+H]^+$, 53), 447 (32), 440 (67), 413 (21), 327 (25), 311 (26), 309 (24), 301 (44), 297 (21), 191 (22), 175 (36), 135 (100). HRMS (ESI+) calcd for $[C_{38}H_{34}N_2O_4+H]^+$: 583.2591. Found: 583.2588.

∗Interchangeable H