Heterocycle Annulation of Enolizable Vinyl Quinone Imides. Dihydroquinolines and Quinolines from Thermal 6 π -Electrocyclizations and Indoles from Photochemical Cyclizations

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2. General Methods

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Infrared and UV/Visible spectra were recorded with a Perkin-Elmer 1600 Series FT-IR and with a HP-8453 UV/Visible spectrometer respectively.

Nuclear magnetic resonance spectra were recorded with a Bruker 300 or 400 MHz spectrometer with the corresponding solvent signals as internal standard. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (0.00 ppm). Values of the coupling constant, J , are given in Hertz (Hz); 2J refers to geminal, 3J to vicinal and nJ to corresponding long-range proton-proton couplings. To clarify the assignments of NMR-signals, the authors have numbered the carbon atoms of the structures. The following abbreviations are used in the experimental section for the description of ^1H -NMR spectra: singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublets

(dd), doublet of triplet (dt), broad singlet (bs), broad doublet (bd) and broad triplet (bt). The chemical shifts of complex multiplets are given as the range of their occurrence. ^{13}C -Signals were assigned by means of Bruker standard DEPT-experiments and the following abbreviations are used in the experimental part: quaternary carbons (quart. C), methylene carbons (CH) and (CH_2) respectively and methyl signals (CH_3). Further assignment of NMR-signals was achieved using D_2O -exchange experiments and two-dimensional NMR experiments (COSY, NOE, HMQC and HMBC).

Low-resolution mass spectra were recorded with a Kratos MS80RFA (LRFAB, NBA / NaI) or with a HPGCD (LRGC-MS).

All air- and moisture sensitive reactions were performed under argon in flame-dried glassware. All experiments were monitored by thin layer chromatography (tlc) performed on EM Science precoated silica gel 60 F-254 glass supported plates with 0.25 mm thickness. Spots were visualized by exposure to ultraviolet light or by staining with either a 10 % solution of phosphomolybdenic acid (PMA) or anisaldehyde 5% in ethanol followed by heating. Flash chromatography was performed with Fisher brand silica gel (170-400mesh). Preparative TLC was performed on Analtech precoated silica gel GF-1000 Microns glass plates (20 x 20 cm).

Ether refers to diethyl ether. Ether and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl and dichloromethane was distilled from calcium hydride. Pyridine and dimethylformamide (DMF) were distilled and stored over molecular sieves. Commercially available reagents were used as supplied and all other used solvents were dried over molecular sieves prior to use unless stated otherwise.

3. Experimental Procedures

Stille coupling of the described aromatic bromo-compounds with *cis-trans* mixtures of vinyl stannane **6** yielded *cis/trans* product mixtures with the *trans* isomer as the major component. Those mixtures did not need to be separated and were carried throughout the syntheses to the corresponding annulation products. Some mixtures of *cis/trans* isomers provided complex NMR spectra with overlapping proton and/or carbon signals with dominant resonances of the major *trans* isomer.

3.1 Synthesis of 6-Amino Dihydroquinolines **9a** and **9b** and 6-Amino Quinoline **11**

Scheme 1: (a) For **5a**: Ac₂O, py; (b) For **5b**: SESCl, py; (c) 10 mol% (Ph₃P)₄Pd, toluene, reflux; (d) Pb(OAc)₄, CHCl₃; (e) 5 mM in toluene, 5 % HMPA, rt; (f) From **9b**: *Method A*: CsF, DMF (97 %); *Method B*: TBAF, THF (98 %); *Method C*: K₂CO₃, DMF (97%); (g) 50 % H₂SO₄.

Synthesis of Diacetate 5a. Diamine **4** (374 mg, 2.00 mmol; Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797-11810) was dissolved in pyridine (4.0 mL) and acetic anhydride (3.8 mL, 4.08 g, 40.0 mmol) was added dropwise at 0-5 °C. After stirring at rt for 2 h, the white suspension was diluted with ethyl acetate (20 mL) and heated to reflux. The warm solution was decanted from insoluble parts and precipitated from hexane (200 mL). Filtration at 0 °C gave diacetate **5a** as a white powder (520 mg, 96 %): mp 198-200 °C; IR (nujol) ν 3260, 1659, 1540, 1299, 1042 cm⁻¹; ¹H-NMR (DMSO-d₆) δ 10.08 (s, 1H, NH), 9.40 (s, 1H, NH), 8.01 (s, 1H), 7.42 (s, 2H), 2.04 (s,

6H, 2Me) ppm; ^{13}C -NMR (DMSO- d_6) δ 168.61, 168.56, 137.75, 131.33 and 118.35 (quart. C); 127.80, 122.28 and 118.33 (CH); 24.02 and 23.12 (CH_3) ppm; LRGC-MS: m/z = 272 (calc. for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2\text{Br}$: 272).

Synthesis of SES-Protected Diamide 5b. A solution of diamine **4** (187 mg, 1.0 mmol) in pyridine (1 mL) was slowly added at 0 °C to a solution of SESCOl (1.00 g, 5 mmol; Weinreb, S. M.; Demko, D. M.; Lessen, T. A. *Tetrahedron Lett.* **1986**, 27 (19), 2099-2102; For a more reliable procedure for the preparation of SESCOl see: Weinreb, S. M.; Chase, C. E.; Wipf, P.; Venkatraman, S. *Org. Synth.* **1998**, 75, 161-165) in pyridine (1 mL). The dark solution was stirred at rt over night and then poured into 1N HCl (50 mL). The mixture was extracted with ethyl acetate (3 x 25 mL). The organic layers were washed with water (2 x 20 mL) and then combined, dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:3) yielding SES-protected diamide **5b** as a yellow oil (330 mg, 64 %): IR (neat) ν 3257, 2955, 1604, 1494, 1382, 1325, 1253, 1145, 842 cm^{-1} ; ^1H -NMR (CD_2Cl_2) δ 7.63 (d, 1H, 3J = 8.8 Hz, C_2H), 7.52 (d, 1H, 4J = 2.5 Hz, C_5H), 7.16 (dd, 1H, 3J = 8.8 Hz, 4J = 2.5 Hz, C_3H), 6.69 and 6.54 (each bs, each 1H, 2NH), 3.08-2.95 (m, 4H, 2 CH_2), 1.09-0.98 (m, 4H, 2 CH_2), 0.01 and 0.00 (each s, each 9H, 2TMS) ppm; ^{13}C -NMR (CD_2Cl_2) δ 135.39, 133.01 and 116.33 (quart. C); 125.24, 123.42 and 121.62 (CH); 49.33, 48.76, 11.07 and 10.96 (CH_2); -1.85 (CH_3) ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+$ = 539 (calc. for $\text{C}_{16}\text{H}_{31}\text{N}_2\text{O}_4\text{S}_2\text{Si}_2\text{BrNa}$: 539).

Synthesis of Stille Coupling Product 7a. Diacetate **5a** (244 mg, 0.90 mmol) was suspended in toluene (90 mL) and stannane **6** (cis / trans mixture, 420 mg, 1.08 mmol; Collins, P. W.; Kramer, S. W.; Gasiecki, A. F.; Weier, R. M.; Jones, P. H.; Gullikson, G. W.; Bianchi, R. G.; *J. Med. Chem.* **1987**, *30*, 193-197), tetrakis (triphenylphosphine) palladium (0) (156 mg, 0.14 mmol) and a few crystals 2,6-di-tert.-butyl-4-methylphenol (radical scavenger) were added. The reaction mixture was stirred at reflux for 7 h, cooled and filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with ethyl acetate / methanol (30:1). Recrystallization from toluene (40 mL) and filtration of the product at 0 °C gave a cis/trans-mixture of Stille coupling product **7a** (cis / trans 1:2) as a beige solid (131 mg, 50 %): mp 168-175 °C; IR (KBr) ν 3265, 3036, 1735, 1665, 1549, 1516, 1270 cm^{-1} ; ¹H-NMR (DMSO-d₆) δ 9.92 and 9.83 (each bs, total 1H, NH, trans / cis 2:1 in the order given), 9.37 and 9.18 (each bs, total 1H, NH, trans / cis 2:1 in the order given), 7.78 (d, 0.66H, ⁴J = 2.0 Hz, C₅H *trans*-isomer), 7.55-7.30 (m, total 1.66H, C₅H *cis*-isomer, C₁H *cis*-isomer and C₂H), 7.24 (d, 0.66H, ³J = 8.6 Hz, C₁H *trans*-isomer), 6.62 and 6.57 (each d, total 1H, ³J = 15.7 Hz and ³J = 11.7 Hz respectively, C₇H trans / cis 2:1 in the order given), 6.13 and 5.87 (each dt, total 1H, ³J = 15.7 Hz, 7.2 Hz and ³J = 11.6 Hz, 7.2 Hz respectively, C₈H trans / cis 2:1 in the order given), 3.64 and 3.61 (each s, total 3H, OMe trans / cis 2:1 in the order given), 3.30 and 3.17 (each dd, total 2H, ³J = 7.2 Hz, ⁴J = 1.0 Hz and ³J = 7.2 Hz, ⁴J = 1.5 Hz respectively, CH₂ trans / cis 2:1 in the order given), 2.01 and 2.00 (each s, total 3H, Me cis / trans 1:2 in the order given) ppm; ¹³C-NMR (DMSO-d₆) δ 171.47, 171.34, 168.62, 168.26, 136.85, 135.96, 131.42, 131.07, 130.27, 130.18 and 119.36 (quart. C); 128.39, 128.00, 126.94, 125.72, 124.84, 123.49, 119.52, 118.58, 118.36 and 115.48 (CH); 37.57 and 33.33 (CH₂); 51.63, 23.94 and 23.19 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 313 (calc. for C₁₅H₁₈N₂O₄Na: 313).

Synthesis of Stille Coupling Product 7b. Diamide **5b** (103 mg, 0.20 mmol) was dissolved in toluene (20 mL) and stannane **6** (cis / trans mixture, 93 mg, 0.24 mmol), tetrakis (triphenylphosphine) palladium (0) (23 mg, 0.02 mmol) and a few crystals 2,6-di-tert.-butyl-4-methylphenol (radical scavenger) were added. The reaction mixture was stirred at reflux for 12 h, cooled and filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:3). Traces of stannane contaminants were removed by the following procedure: The product was dissolved in ethyl acetate (0.1 mL), added to hexane (10 mL) and the resulting emulsion was let in the freezer over night. Whilst stannane-impurities remained in solution, pure cis/trans-mixture (cis / trans 1:4) of Stille coupling product **7b** oiled out from the mixture as a pale yellow oil (62 mg, 58 %): IR (neat) ν 3261, 2955, 1740, 1703, 1496, 1324, 1251, 1144, 861, 843 cm^{-1} ; ^1H -NMR (acetone- d_6) δ 8.64 and 8.55 (each bs, total 1H, NH cis / trans 1:4 in the order given), 7.94 and 7.67 (each bs, total 1H, NH trans / cis 4:1 in the order given), 7.56 (d, 0.8H, $^4J = 2.5$ Hz, C_5H *trans*-isomer), 7.53-7.45 (m, 0.2H, C_5H *cis*-isomer), 7.42 (d, 0.8H, $^3J = 8.7$ Hz, C_2H *trans*-isomer), 7.39-7.30 (m, 0.4H, C_2H *cis*-isomer and C_3H *cis*-isomer), 7.27 (dd, 0.8H, $^3J = 8.7$ Hz, $^4J = 2.5$ Hz, C_3H *trans*-isomer), 7.05 and 6.84 (each dt, total 1H, $^3J = 15.8$ Hz, $^4J = 1.5$ Hz and $^3J = 11.4$ Hz, $^4J = 1.7$ Hz respectively, C_7H trans / cis 4:1 in the order given), 6.29 and 6.06 (each dt, total 1H, $^3J = 15.8$ Hz, 7.1 Hz and $^3J = 11.4$ Hz, 7.3 Hz respectively, C_8H trans / cis 4:1 in the order given), 3.67 and 3.66 (each s, total 3H, OMe trans / cis 4:1 in the order given), 3.32 and 3.24 (each dd, total 2H, $^3J = 7.1$ Hz, $^4J = 1.5$ Hz and $^3J = 7.3$ Hz, $^4J = 1.7$ Hz respectively, CH_2 trans / cis 4:1 in the order given), 3.15-2.90 (m, 4H), 1.05-0.95 (m, 4H), 0.33, 0.02, 0.01 and 0.00 (each s, total 18H, 2 SiMe_3) ppm; ^{13}C -NMR (acetone- d_6) δ 172.41, 138.35, 137.62, 137.23, 135.41, 132.75 and 131.89 (quart. C); 129.70, 129.18, 128.81, 128.17,

126.82, 126.64, 123.98, 121.95, 121.17 and 118.92 (CH); 50.17, 49.30, 48.60, 48.33, 38.97, 34.84, 11.60, 11.53, 11.49 and 11.25 (CH₂); 52.61, 52.50, 0.09, 0.07, 0.00 and – 0.05 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 557 (calc. for C₂₁H₃₈N₂O₆Si₂Na: 557).

Synthesis of Quinone Diimide 8a. Stille coupling product **7a** (cis / trans 1:2, 29.0 mg, 0.10 mmol) was dissolved in chloroform (5 mL) and lead tetraacetate (665 mg, 1.5 mmol) was added. The reaction mixture was stirred at rt for 30 min during which a white precipitate was formed (Pb(OAc)₂). The suspension was then filtered through Celite[®] and the filtrate was washed with water (2 x 5 mL). The aqueous phases were extracted with chloroform (2 x 5 mL) and the organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure to give a cis/trans-mixture (cis/trans 1:2) of pure quinone diimide **8a** as a brown oil (27 mg, 94 %): IR (neat) ν 2956, 1737, 1697, 1604, 1207, 985 cm⁻¹; ¹H-NMR (CDCl₃) δ 6.88-6.57 (m, 4H), 6.46 (dt, 0.66H, ³J = 16.0 Hz, 7.0 Hz, C₈H *trans*-isomer), 6.15-6.00 (m, 0.33H, C₈H *cis*-isomer), 3.73 and 3.70 (each s, total 3H, Ome trans / cis 2:1 in the order given), 3.29-3.24 (m, 2H, CH₂), 2.32, 2.31, 2.24 and 2.25 (each s, total 6H, 2Me) ppm; ¹³C-NMR (CDCl₃) δ 185.72, 185.58, 171.00, 153.35, 152.12, 141.96, 133.28, 129.14, 128.65, 128.52, 126.18, 125.39, 52.19, 52.05, 38.27, 25.44, 25.32 ppm; LRGC-MS: m/z = 288 (calc. for C₁₅H₁₆N₂O₄: 288); UV/Vis (toluene) λ_{max} = 291 nm.

Synthesis of Quinone Diimide 8b. Protected diamide **7b** (cis/trans 1:4, 27 mg, 0.05 mmol) was dissolved in chloroform (2 mL) and lead tetra acetate (22 mg, 0.05 mmol) were added. The reaction mixture was stirred at rt for 20 min during which a white precipitate was formed ($\text{Pb}(\text{OAc})_2$). The suspension was then filtered through Celite[®] and the filtrate was washed with water (2 x 3 mL). The aqueous phases were extracted with chloroform (2 x 5 mL) and the organic layers were combined, dried over MgSO_4 and concentrated under reduced pressure to give a cis/trans-mixture (1:4) of pure quinone diimide **8b** as an orange oil (26 mg, 98 %): IR (neat) ν 2954, 1742, 1568, 1420, 1324, 1251, 1171, 1138, 858 cm^{-1} ; ^1H -NMR (CDCl_3) δ 7.95-7.80 (m, 2H), 7.05-6.50 (m, 3H), 3.73 and 3.72 (each s, total 3H, OMe, cis / trans 1:4 in the order given), 3.31-3.10 (m, 6H, 3 CH_2), 1.20-1.10 (m, 4H, 2 CH_2), 0.11, 0.10, 0.09 and 0.04 (each s, total 18H, 2 SiMe_3) ppm; ^{13}C -NMR (CDCl_3) δ 170.99, 170.70, 164.00, 163.79, 163.33, 163.09, 144.19 and 143.87 (quart. C); 138.72, 132.20, 132.03, 130.37, 130.24, 129.62, 129.25, 125.88, 125.52 and 123.41 (CH); 51.88, 51.83, 51.71, 51.64, 38.79, 38.44, 10.10, 9.98, 9.92 and 9.89 (CH_2); 52.35, 0.00 and -0.04 (CH_3) ppm; LRGC-MS and LRFAB-MS: no $[\text{M}]^+$ observed; UV/Vis (toluene) $\lambda_{(\text{max})}$ = 316 nm.

Synthesis of 6-Acetamide Dihydroquinoline 9a. Quinone diimide **8a** (cis / trans 1:2, 29 mg, 0.10 mmol) was dissolved in toluene (20 mL, 5 mM) and HMPA (1 mL, 5 %) was

added. The reaction mixture was let at rt for 8 h. The solution was washed with water (2 x 10 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. Flash chromatography of the crude product on silica gel with ethyl acetate yielded 6-acetamide dihydroquinoline **9a** as a yellow oil (16.5 mg, 57 %): IR (neat) ν 3302, 3068, 2953, 1725, 1666, 1641, 1548, 1449, 1320, 1252, 836 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.40 (d, 1H, ⁴*J* = 2.1 Hz, C₅H), 7.38 (bs, 1H, NH), 7.23 (dd, 1H, ³*J* = 8.4 Hz, ⁴*J* = 2.1 Hz, C₃H), 7.03 (d, 1H, ³*J* = 8.4 Hz, C₂H), 6.94 (dd, 1H, ³*J* = 15.6 Hz, 5.3 Hz, C₈H), 5.95 (dd, 1H, ³*J* = 15.6 Hz, ⁴*J* = 1.5 Hz, C₇H), 5.86 (bd, 1H, ³*J* = 5.3 Hz, C₉H), 3.71 (s, 3H, OMe), 2.09 (s, 6H, 2Me) ppm; ¹³C-NMR (CD₂Cl₂) δ 168.64, 166.50, 158.66, 137.22, 134.93 and 122.93 (quart. C); 144.31, 125.46, 122.55, 120.72, 116.30 and 75.02 (CH); 52.27, 24.86 and 21.70 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 311 (calc. for C₁₅H₁₆N₂O₄Na: 311).

Synthesis of SES-protected 6-Amino Dihydroquinoline 9b. Quinone diimide **8b** (cis/trans 1:4, 27 mg, 0.05 mmol) was dissolved in toluene (10 mL, 5 mM) and HMPA (0.5 mL, 5 %) was added. The reaction mixture was stirred at rt for 18 h. The solution was washed with water (2 x 10 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. Flash chromatography of the crude product on silica gel with ethyl acetate / hexane (1:5) yielded SES-protected 6-amino dihydroquinoline **9b** as a yellow oil (16 mg, 60 %): IR (neat) ν 3258, 2954, 1754, 1490, 1328, 1252, 1145, 837 cm⁻¹; ¹H-NMR (acetone-d₆) δ 8.61 (bs, 1H, NH), 7.64 (d, 1H, *J* = 9.8 Hz), 7.25-7.18 (m, 2H), 6.74 (d, 1H, ³*J* = 9.5 Hz, C₇H), 6.31 (dd, 1H, ³*J* = 9.5 Hz, 6.5 Hz, C₈H), 5.59 (dd,

^1H , $^3J = 6.5$ Hz, $^4J = 1.1$ Hz, C_9H) 3.65 (s, 3H, OMe), 3.08-2.98 (m, 4H, 2CH_2), 1.05-0.95 (m, 2H, CH_2), 0.93-0.85 (m, 2H, CH_2), -0.01 and -0.03 (each s, each 9H, 2 SiMe_3) ppm; ^{13}C -NMR (acetone- d_6) δ 170.05, 136.91, 131.88 and 128.49 (quart. C); 127.15, 125.89, 125.40, 121.22, 119.54 and 57.39 (CH); 48.84, 47.85, 11.19 and 11.00 (CH_2); 52.91, -1.78 and -1.95 (CH_3) ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+ = 555$ (calc. for $\text{C}_{21}\text{H}_{36}\text{N}_2\text{O}_6\text{S}_2\text{Si}_2\text{Na}$: 555).

Synthesis of Mono-Protected 6-Amino Quinoline 10. Dihydroquinoline **9b** (5.5 mg, 0.01 mmol) was converted to mono-protected 6-amino quinoline **10** by three different methods. *Method A:* The substrate was dissolved in DMF (1 mL) and cesium fluoride (4.5 mg, 0.03 mmol) was added. The reaction mixture was stirred at rt for 20 min and the resulting bright-yellow solution was then poured into water (5 mL). The mixture was extracted with ethyl acetate (3 x 5 mL) and the organic layers were washed with water (2 x 5 mL). The aqueous phases were extracted with ethyl acetate (2 x 5 mL). The organic layers were combined, dried over MgSO_4 and concentrated under reduced pressure. *Method B:* The substrate was dissolved in THF (1 mL) and TBAF (1M in THF, 30 μL , 0.03 mmol) was added. After stirring at rt for 3 h, the reaction mixture was diluted with ether (5 mL) and washed with water (2 x 10 mL). The aqueous phases were extracted with ether (2 x 5 mL), combined, dried over MgSO_4 and concentrated under reduced pressure. *Method C:* The substrate was dissolved in DMF (1 mL) and K_2CO_3 (4.2 mg, 0.03 mmol) was added. The reaction mixture was stirred at rt for 20 min and the then poured into water (5 mL). The mixture was extracted with ethyl acetate (3 x 5 mL) and the organic layers were washed with water (2 x 5 mL). The aqueous phases were

extracted with ethyl acetate (2 x 5 mL). The organic layers were combined, dried over MgSO_4 and concentrated under reduced pressure.

The crude products were purified by flash chromatography on silica gel with ethyl acetate / hexane (2:3) to give mono-protected 6-amino quinoline **10** as a colorless oil in quantitative yields for each of the described methods (3.7 mg, 100 %): IR (neat) ν 3241, 2955, 1727, 1625, 1481, 1381, 1310, 1146, 841 cm^{-1} ; ^1H -NMR (acetone- d_6) δ 9.15 (bs, 1H, NH), 8.43 (d, 1H, $^3J = 8.6$ Hz), 8.14 (d, $^3J = 9.1$ Hz, C_2H), 8.13 (d, 1H, $^3J = 8.6$ Hz), 7.90 (d, 1H, $^4J = 2.5$ Hz, C_5H), 7.83 (dd, 1H, $^3J = 9.1$ Hz, $^4J = 2.5$ Hz, C_3H), 3.41 (s, 3H, OMe), 3.25-3.15 (m, 2H), 1.08-1.00 (m, 2H), -0.05 (s, 9H, TMS) ppm; ^{13}C -NMR (acetone- d_6) δ 166.25, 148.00, 145.52, 139.97 and 131.05 (quart. C); 137.35, 132.70, 124.93, 122.67 and 114.58 (CH); 48.12 and 11.04 (CH_2); 52.87 and -2.02 (CH_3) ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+ = 389$ (calc. for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4\text{SSiNa}$: 389).

Synthesis of 6-Amino Quinoline 11. Mono-protected 6-amino quinoline **10** (3.6 mg, 0.01 mmol) was dissolved in 50 % H_2SO_4 (0.1 mL) and stirred at rt for 20 h. The reaction mixture was poured into 5 % NaHCO_3 (20 mL) and the mixture was extracted with ethyl acetate (3 x 5 mL). The organic layers were combined, dried over MgSO_4 and concentrated under reduced pressure. Flash chromatography of the crude product on silica gel with ethyl acetate / hexane (1:1) afforded deprotected 6-amino quinoline **11** as a yellow oil (1.6 mg, 80 %): IR (neat) ν 3357, 3220, 2925, 1720, 1624, 1478, 1285, 1236, 1114 cm^{-1} ; ^1H -NMR (acetone- d_6) δ 8.03 (d, 1H, $^3J = 8.6$ Hz), 7.94 (d, 1H, $^3J = 8.6$ Hz), 7.86 (d, 1H, $^3J = 9.1$ Hz, C_2H), 7.34 (dd, 1H, $^3J = 9.1$ Hz, $^4J = 2.5$ Hz, C_3H), 6.96 (d, 1H, $^4J = 2.5$ Hz, C_5H), 5.49 (bs, 2H, NH_2), 3.92 (s, 3H, OMe), ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+ = 225$ (calc. for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$: 225).

3.2 Synthesis of 6-Hydroxy Dihydroquinolines 16a and 16b, 6-Hydroxy Quinoline 17 and 5-Hydroxy Indoles 18a, 18b and 19

Scheme 2: (a) Fe, HCl, EtOH (87 %); (b) Ac₂O, MeOH (87 %); (c) BnBr, K₂CO₃, DMF (86 %); (d) Fe, conc. HCl (88 %); (e) SESCl, py (84 %); (f) H₂, Pd/C 10 %, ethyl acetate / conc. HCl (80 %); (g) TESOTf, imidazol, DMF (93 % **12a**, 91 % **12b**); (h) 10-15 mol% (Ph₃P)₄Pd, toluene, reflux (76 % **13a**, 50 % **13b**); (i) 50 % AcOH, THF (94 % **14a**, 90 % **14b**); (j) Pb(OAc)₄, CHCl₃ or CHCl₃ / MeOH (98 % **15a**, 100 % **15b**); (k) For **16a**: 5 mM in toluene, 5 % HMPA, rt, darkness (73 %); For **16b**: 2 mM in toluene, 2.5 % HMPA, reflux, darkness (58 %); (l) From **16b**: *Method A*: CsF, DMF (99 %); *Method B*: K₂CO₃, DMF, 50 °C (98 %); (m) For **15a**: 5 mM in toluene, 0.5 % HMPA, rt, light (69 %); For **15b**: 2 mM in toluene, 0.5 % HMPA, rt, light (59 %); (n) From **18a**: NaOMe, MeOH (95 %); From **18b**: CsF, DMF (97 %).

Synthesis of Bromo Amino Phenol 21. 3-Bromo-4-nitrophenol **20** (44 mg, 0.20 mmol; from nitration of 3-bromophenol according to Sasamoto, K.; Deng, G.; Ushijima, T.; Ohkura, Y.; Ueno, K. *Analyst UK* **1995**, 120 (6), 1709-1714) and iron powder (56 mg, 1.00 mmol) were suspended in ethanol (1 mL) and 37 % HCl (0.5 mL) was added. The reaction mixture was stirred at reflux for 1.5 h, cooled and poured into 1N NaOH (20 mL). The resulting mixture was extracted with ethyl acetate (5 x 10 mL). The organic layers were washed with water (2 x 10 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure. The residue was dissolved in ethyl acetate (0.2 mL) and precipitated from hexane (30 mL). Filtration at 0 °C afforded bromo amino phenol **21** as a beige solid (33 mg, 87 %): mp 141-143 °C; IR (KBr) ν 3348, 2761, 1649, 1602, 1499, 1446, 1206 cm⁻¹; ¹H-NMR (acetone-d₆) δ 7.83 (bs, 1H, OH), 6.92 (d, 1H, ⁴J = 2.6 Hz, C₅H), 6.74 (d, 1H, ³J = 8.6 Hz, C₂H), 6.65 (dd, 1H, ³J = 8.6 Hz, ⁴J = 2.6 Hz, C₃H) ppm; ¹³C-NMR (acetone-d₆) δ 150.34, 139.33 and 109.25 (quart. C); 119.51, 117.42 and 116.82 (CH) ppm; LRGC-MS: m/z = 189 (calc. for C₆H₆NOBr: 189).

Synthesis of Mono-Acetate 22. Bromo aminophenol **21** was converted into mono-acetate **22** by a modified Schotten-Baumann procedure according to Werbel, L. M. et al *J. Med. Chem.* **1986**, 29, 924-934. The substrate (188 mg, 1.00 mmol) was dissolved in methanol (4 mL) and acetic anhydride (102 mg, 1.00 mmol) was added. The reaction mixture was stirred at reflux for 30 min and then evaporated under reduced pressure. The

residue was dissolved in ethyl acetate (20 mL) and the resulting solution was washed with water (2 x 20 mL). The aqueous phases were extracted with ethyl acetate (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:1) to give mono-acetate **22** as a pale pink solid (200 mg, 87 %): mp 112-114 °C; IR (KBr) ν 3258, 2784, 1658, 1606, 1528, 1496, 1432, 1281, 1037 cm⁻¹; ¹H-NMR (DMSO-d₆) δ 9.77 (bs, 1H), 9.27 (bs, 1H), 7.23 (d, 1H, ³*J*=8.7 Hz, C₂H), 7.01 (d, 1H, ⁴*J*=2.6 Hz, C₅H), 6.75 (dd, 1H, ³*J*=8.7 Hz, ⁴*J*=2.6 Hz, C₃H), 2.00 (s, 3H, Me) ppm; ¹³C-NMR (DMSO-d₆) δ 168.40, 155.89, 127.79 and 119.69 (quart. C); 129.03, 118.50 and 114.84 (CH); 22.88 (CH₃) ppm; LRGC-MS: *m/z* = 231 (calc. for C₈H₈NO₂Br: 231).

Synthesis of Benzyl Ether 23. 3-Bromo-4-nitrophenol **20** (327 mg, 1.50 mmol) was dissolved in DMF (5 mL) and K₂CO₃ (415 mg, 3.00 mmol) and benzylbromide (282 mg, 1.65 mmol) were added. The reaction mixture was stirred at rt for 1 h and then poured into water (20 mL). The mixture was extracted with ethyl acetate (2 x 10 mL). The organic layers were washed with water (2 x 20 mL), combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:20) to give benzyl ether **23** as pale yellow crystals (380 mg, 86 %): mp 68-71 °C; IR (KBr) ν 2933, 1580, 1511, 1328, 1232, 1023 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.97 (d, 1H, ³*J*=9.1 Hz, C₂H), 7.47-7.35 (m, 5H, aromatic protons), 7.34 (d, 1H, ⁴*J*=2.7 Hz, C₅H), 7.01 (dd, 1H, ³*J*=9.1 Hz, ⁴*J*=2.7 Hz, C₃H), 5.14 (s, 2H, CH₂) ppm; ¹³C-NMR (CD₂Cl₂) δ 162.50, 143.15, 135.88 and 117.07 (quart. C); 129.30, 129.10, 128.51, 128.20, 121.62 and 114.80 (CH); 71.55 (CH₂) ppm; LRGC-MS: *m/z* = 309 (calc. for C₁₃H₁₀NO₃Br: 309).

Synthesis of Amino Benzyl Ether 24. Benzyl ether **23** (370 mg, 1.25 mmol) and iron powder (349 mg, 6.25 mmol) were suspended in ethanol (5 mL) and 37 % HCl (1.5 mL) was added. The reaction mixture was stirred at reflux for 1 h, cooled and poured into 1N NaOH (60 mL). The resulting mixture was extracted with ethyl acetate (3 x 20 mL). The organic layers were washed with water (2 x 20 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure to give pure amino benzyl ether **24** as a white solid (334 mg, 96 %): mp 60-61 °C; IR (KBr) ν 3431, 3346, 3032, 1599, 1497, 1227, 1021 cm⁻¹; ¹H-NMR (DMSO-d₆) δ 7.42-7.26 (m, 5H, aromatic protons), 7.04 (d, 1H, ⁴*J* = 2.7 Hz, C₅H), 6.80 (dd, 1H, ³*J* = 8.7 Hz, ⁴*J* = 2.7 Hz, C₃H), 6.73 (d, 1H, ³*J* = 8.7 Hz, C₂H), 4.96 (s, 2H, CH₂), 4.83 (bs, 2H, NH₂) ppm; ¹³C-NMR (DMSO-d₆) δ 150.28, 140.39, 137.69 and 107.86 (quart. C); 128.75, 128.11, 128.03, 118.60, 116.62 and 116.51 (CH); 70.39 (CH₂) ppm; LRGC-MS: *m/z* = 279 (calc. for C₁₃H₁₂NOBr: 279).

Synthesis of SES-Protected Amino Benzyl Ether 25. Amino benzyl ether **24** (300 mg, 1.08 mmol) was dissolved in pyridine (1.5 mL) and a solution of SES-chloride (260 mg, 1.30 mmol; Weinreb, S. M.; Chase, C. E.; Wipf, P.; Venkatraman, S. *Org. Synth.* **1998**, 75, 161-165) in pyridine (0.2 mL) was added slowly. The resulting yellow solution was stirred at rt for 1 h and evaporated under reduced pressure. The residue was dissolved in ethyl acetate (15 mL) and washed with water (1 x 20 mL), 5 % CuSO₄ (1 x 20 mL) and again with water (1 x 20 mL). The aqueous layers were extracted with ethyl acetate

(2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:8) yielding SES-protected amino benzyl ether **25** as a pale yellow oil (370 mg, 84 %): IR (neat) ν 3268, 2953, 1600, 1493, 1331, 1149, 858 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.56 (d, 1H, ³J = 9.0 Hz, C₂H), 7.48-7.30 (m, 5H, aromatic protons), 7.23 (d, 1H, ⁴J = 2.8 Hz, C₅H), 6.97 (dd, 1H, ³J = 9.0 Hz, ⁴J = 2.8 Hz, C₃H), 6.51 (bs, 1H, NH), 5.05 (s, 2H, benzyl-CH₂), 3.08-2.90 (m, 2H, CH₂), 1.10-0.99 (m, 2H, CH₂), 0.01 (s, 9H, SiMe₃) ppm; ¹³C-NMR (CD₂Cl₂) δ 157.45, 136.89, 129.01 and 117.58 (quart. C); 129.17, 128.76, 128.12, 125.37, 119.55 and 115.87 (CH); 71.14, 49.11 and 10.93 (CH₂); -1.86 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 466 (calc. for C₁₈H₂₄NO₃BrSSiNa: 466).

Synthesis of SES-Protected Amino Phenol 26. Attempted hydrogenation of SES-protected bromo aminobenzyl ether **25** in THF, CH₂Cl₂ or ethyl acetate left the substrate unchanged whereas the debenzylated *and* debrominated product was obtained quantitatively in methanol within minutes. The employment of blends of ethyl acetate / methanol (1:2 to 1:10) resulted in the formation of product mixtures. The reaction conditions as described below are a modification of a reported procedure for the hydrogenolytic cleavage of aryl benzyl ether bearing bromo substituents (Sala, T.; Sargent, M. V. *J. Chem. Soc. Perkin Trans 1* **1981**, 3, 849-854).

SES-protected amino benzyl ether **25** (752 mg, 1.70 mmol) was dissolved in ethyl acetate (20 mL) and 37 % HCl (0.5 mL) was added. Under argon, the palladium catalyst (75mg, 10% on coal) was added and the resulting suspension was stirred in a H₂-atmosphere (balloon) for 7.5 h. During the reaction, new catalyst (10 mg) was added every hour (total amount of catalyst: 145 mg = 20 % g/g with respect to the substrate). After

completed debenzylation, the mixture was filtered through Celite®. The filtrate was washed with 5 % NaHCO₃ (2 x 30 mL) and water (1 x 20 mL). The aqueous layers were extracted with ethyl acetate (2 x 20 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:5 → 1:3) yielding SES-protected amino phenol **26** as white crystals (479 mg, 80 %): mp 123-125 °C; IR (KBr) ν 3412, 2953, 1496, 1320, 1142, 854 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.48 (d, 1H, ³J = 8.8 Hz, C₂H), 7.12 (d, 1H, ⁴J = 2.8 Hz, C₅H), 6.82 (dd, 1H, ³J = 9.0 Hz, ⁴J = 2.8 Hz, C₃H), 6.48 (bs, 1H), 5.78 (bs, 1H), 3.04-2.96 (m, 2H, CH₂), 1.10-1.01 (m, 2H, CH₂), 0.00 (s, 9H, SiMe₃) ppm; ¹³C-NMR (CD₂Cl₂) δ 155.01, 128.43 and 118.03 (quart. C); 126.07, 120.08 and 116.46 (CH); 49.25 and 10.89 (CH₂); -1.87 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 376 (calc. for C₁₁H₁₈NO₃BrSSiNa: 376).

Synthesis of TES-Protected Bromo Amino Phenol 12a. Mono-acetate **22** (118 mg, 0.75 mmol) was dissolved in DMF (0.5 mL) and imidazol (255 mg, 3.75 mmol) and triethylsilyltriflate (0.20 mL, 238 mg, 0.90 mmol) were added at 0 °C. The reaction mixture was stirred at rt for 30 min and then poured into water (50 mL). The mixture was extracted with ether (3 x 20 mL) and the organic layers were washed with water (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:4) yielding TES-protected bromo amino phenol **12a** as a pale pink oil that solidified upon standing at rt (240 mg, 93 %): mp 39-40 °C; IR (KBr) ν 3260, 2954, 1736, 1495, 1399, 1323, 1252, 1143, 841 cm⁻¹; ¹H-NMR (DMSO d₆) δ 9.34 (bs, 1H, NH), 7.37 (d, 1H, ³J = 8.7 Hz, C₂H), 7.09 (d, 1H, ⁴J = 2.6 Hz, C₅H), 6.86 (dd, 1H, ³J = 8.7 Hz, ⁴J = 2.6 Hz, C₃H), 2.03 (s, 3H, Me), 1.00-0.90 (m, 9H), 0.78-0.65 (m, 6H) ppm; ¹³C-NMR (DMSO-d₆) δ 168.39, 153.06, 130.22 and 129.88

(quart. C); 128.60, 123.07, 118.98 (CH); 4.32 (CH₂); 22.98 and 6.40 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 368 (calc. for C₁₄H₂₂NO₂SiBrNa: 368).

Synthesis of TES-Protected Bromo Amino Phenol 12b. SES-protected aminophenol **26** (150 mg, 0.43 mmol) was dissolved in DMF (1.0 mL) and imidazol (59 mg, 0.86 mmol) and triethylsilyltriflate (0.12 mL, 141 mg, 0.53 mmol) were added at 0 °C. The reaction mixture was stirred at rt for 1 h and then poured into water (10 mL). The mixture was extracted with ether (3 x 10 mL) and the organic layers were washed with brine (1 x 10 mL). The organic phases were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:10) yielding TES-protected bromo amino phenol **12b** as a colorless oil (181 mg, 91 %): IR (neat) ν 3267, 2957, 2881, 1599, 1490, 1332, 1151, 930, 747 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.52 (d, 1H, ³J = 8.9 Hz, C₂H), 7.11 (d, 1H, ⁴J = 2.7 Hz, C₅H), 6.84 (dd, 1H, ³J = 8.9 Hz, ⁴J = 2.7 Hz, C₃H), 6.63 (bs, 1H, NH), 3.06-2.93 (m, 2H, CH₂), 1.10-0.92 (m, 11H), 0.82-0.69 (m, 6H), -0.01 (s, 9H, SiMe₃) ppm; ¹³C-NMR (CD₂Cl₂) δ 154.67, 129.47 and 117.14 (quart. C); 125.10, 124.57 and 120.75 (CH); 48.96, 10.99 and 5.41 (CH₂); 6.91 and -1.86 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 490 (calc. for C₁₇H₃₂NO₃BrSi₂SNa: 490).

Synthesis of Stille Coupling Product 13a. TES-Protected bromo aminophenol **12a** (230 mg, 0.67 mmol) was dissolved in toluene (30 mL) and stannane **6** (cis / trans mixture, 313 mg, 0.80 mmol; Collins, P. W.; Kramer, S. W.; Gasiiecki, A. F.; Weier, R. M.; Jones, P. H.; Gullikson, G. W.; Bianchi, R. G.; *J. Med. Chem.* **1987**, *30*, 193-197), tetrakis (triphenylphosphine) palladium (0) (78 mg, 0.07 mmol) and a few crystals 2,6-di-tert.-butyl-4-methylphenol (radical scavenger) were added. The reaction mixture was stirred at reflux for 2 h, cooled and filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was purified by two sequential flash chromatographies on silica gel with ethyl acetate / hexane (1:2 → 1:1) to give a cis/trans-mixture (1:3) of Stille coupling product **13a** as a brown oil (185 mg, 76 %). The product still contained traces of organotin-impurities, which did not influence the following step and could easily be separated from the deprotected phenol **14a** (see below: *Synthesis of Deprotected Vinyl Aminophenol 14a*). IR (neat) ν 3274, 2956, 2878, 1742, 1663, 1552, 1492, 1417, 1283, 1248, 1210, 1166, 1002, 747 cm^{-1} ; ^1H -NMR (CD_2Cl_2) δ 7.80 and 7.58 (each bs, total 1H, NH trans / cis 3:1 in the order given), 7.73 and 7.34 (each d, total 1H, $^3J = 8.7$ Hz and $^3J = 8.6$ Hz respectively, C_2H cis / trans 1:3 in the order given), 6.95 (d, 0.75H, $^4J = 2.6$ Hz, C_5H trans-isomer), 6.82-6.62 (m, 1.5H), 6.53 (d, 0.75H, $^3J = 15.6$ Hz, C_7H trans-isomer), 6.16 and 5.97 (each dt, total 1H, $^3J = 15.6$ Hz, 7.1 Hz and $^3J = 11.2$ Hz, 7.4 Hz respectively, C_8H trans / cis 3:1 in the order given), 3.69 and 3.67 (each s, total 3H, OMe trans / cis 3: 1 in the order given), 3.24 and 3.11 (each bd, total 2H, $^3J = 7.1$ Hz and $^3J = 7.4$ Hz respectively, CH_2 trans / cis 3:1 in the order given), 2.07 and 2.06 (each s, total 3H, CH_3 trans / cis 3:1 in the order given), 1.11-0.95 (m, 9H), 0.82-0.67 (m, 6H) ppm; ^{13}C -NMR (CD_2Cl_2) δ 172.54, 172.30, 169.63, 168.95, 153.97, 152.71, 133.15, 130.20, 129.93 and 128.93 (quart. C); 129.18, 129.04, 127.41, 127.22,

125.41, 124.91, 120.71, 119.90, 119.82 and 117.71 (CH); 38.65, 34.22, 5.33 and 5.27 (CH₂); 52.39, 52.30, 24.33, 23.93, 6.80 and 6.78 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 386 (calc. for C₁₉H₂₉NO₄SiNa: 386).

Synthesis of Stille Coupling Product 13b. Protected bromo aminophenol **12b** (500 mg, 1.07 mmol) was dissolved in toluene (45 mL) and stannane **6** (cis / trans mixture, 502 mg, 1.29 mmol), tetrakis (triphenylphosphine) palladium (0) (186 mg, 0.16 mmol) and a few crystals 2,6-di-tert.-butyl-4-methylphenol (radical scavenger) were added. The reaction mixture was stirred at reflux for 18 h, cooled and filtered through Celite[®]. The filtrate was concentrated under reduced pressure. The residue was purified by two sequential flash chromatographies on silica gel with ethyl acetate / hexane (1:5) to give a cis/trans-mixture (trans-enriched, trans isomer > 90 %) of Stille coupling product **13b** as a yellow oil (260 mg, 50 %). The product still contained traces of tin-impurities, which did not influence the following step and could easily be separated from the deprotected phenol **14b** (see below: *Synthesis of Deprotected Vinyl Aminophenol 14b*). IR (neat) ν 3268, 2956, 1740, 1491, 1148, 845 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.36 and 7.25 (each d, total 1H, ³*J* = 8.8 Hz and ³*J* = 8.7 Hz respectively, C₂H cis / trans 1:10 in the order given), 6.99 (d, 0.9H, ⁴*J* = 2.7 Hz, C₅H *cis*-isomer), 6.82-6.67 (m, 2H), 6.60 (bd, 0.1H, ³*J* = 11.2 Hz, C₇H *cis*-isomer), 6.50 and 6.41 (each bs, total 1H, NH cis / trans 1:10 in the order given), 6.22 and 6.05 (each dt, total 1H, ³*J* = 15.8 Hz, 7.1 Hz and ³*J* = 11.2 Hz, 7.5 Hz respectively, C₈H trans / cis 10:1 in the order given), 3.70 and 3.68 (each s, total 3H, OMe trans / cis 10:1 in the order given), 3.29 and 3.11 (each dd, total 2H, ³*J* = 7.1 Hz, ⁴*J* = 1.1 Hz and ³*J* = 7.5 Hz, ⁴*J* = 1.3 Hz respectively, CH₂ trans / cis 10:1 in the order given), 3.02-2.92 (m, 2H, CH₂), 1.07-0.95 (m, 11H), 0.82-0.69 (m, 6H), 0.03 and 0.01 (each s, total 9H, SiMe₃ cis / trans 1:10 in the order given) ppm; ¹³C-NMR

(CD₂Cl₂) (dominant signals of the major *trans* isomer) δ 172.04, 155.01, 134.76 and 127.46 (quart. C); 128.83, 127.60, 126.49, 120.48 and 118.40 (CH); 48.75, 38.59, 10.89 and 5.47 (CH₂); 52.39, 6.94 and -1.87 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 508 (calc. for C₂₂H₃₉NO₅SSi₂Na: 508).

Synthesis of Deprotected Vinyl Amino Phenol 14a. Stille coupling product **13a** (*cis* / *trans* 1:3, 182 mg, 0.50 mmol) was dissolved in THF (8 mL) and 50 % acetic acid (8 mL) was added. The solution was stirred at rt for 18 h and then poured into 5 % NaHCO₃ (100 mL). The mixture was extracted with ethyl acetate (6 x 20 mL). The organic layers were washed with water (2 x 25 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate yielding a *cis/trans*-mixture (1:3) of deprotected vinyl amino phenol **14a** as a white solid (117 mg, 94 %): mp 126-134 °C; IR (KBr) ν 3276, 2954, 1730, 1662, 1532, 1498, 1443, 1296, 1212, 1167 cm⁻¹; ¹H-NMR (acetone-d₆) δ 8.57, 8.34 and 8.31 (each bs, total 2H, OH and NH), 7.53 and 7.28 (each d, total 1H, ³*J* = 8.7 Hz, C₂H *cis* / *trans* 1:3 in the order given), 6.97 (d, 0.75H, ⁴*J* = 2.7 Hz, C₅H *trans*-isomer), 6.75-6.60 (m, 2H), 6.55 (d, 0.25H, ³*J* = 11.4 Hz, C₇H *cis*-isomer), 6.17 and 5.89 (each dt, total 1H, ³*J* = 15.8 Hz, 7.1 Hz and ³*J* = 11.4 Hz, 7.3 Hz respectively, C₈H *trans* / *cis* 3:1 in the order given), 3.65 and 3.63 (each s, total 3H, OMe *trans* / *cis* 3:1 in the order given), 3.23 and 3.15 (each dd, total 2H, ³*J* = 7.1 Hz, ⁴*J* = 1.4 Hz and ³*J* = 7.3 Hz, ⁴*J* = 1.6 Hz respectively, CH₂ *trans* / *cis* 3:1 in the order given), 2.07 and 2.04 (each s, total 3H, Me *trans* / *cis* 3:1 in the order given) ppm; ¹³C-NMR (acetone-d₆) δ 172.40, 172.26, 169.47, 169.00, 156.09, 155.14, 133.77, 131.90 and 128.42 (quart. C); 129.61, 129.28, 128.58, 126.80, 126.40, 124.75, 116.41, 115.80,

115.42 and 112.62 (CH); 38.63 and 34.35 (CH₂); 52.09, 52.02, 23.73 and 23.52 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 272 (calc. for C₁₃H₁₅NO₄Na: 272).

Synthesis of Deprotected Vinyl Amino Phenol 14b. Stille coupling product **13b** (trans isomer > 90 %; 55 mg, 0.11 mmol) was dissolved in THF (2 mL) and 50 % acetic acid (2 mL) was added. The solution was stirred at rt for 20 h and then poured into 5 % NaHCO₃ (60 mL). The mixture was extracted with ether (3 x 20 mL). The organic layers were washed with brine (2 x 20 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by preparative tlc with ethyl acetate / hexane (3:2) yielding a cis/trans-mixture (trans isomer > 90 %) of deprotected vinyl amino phenol **14b** as a yellow oil (37 mg, 90 %): IR (neat) ν 3405, 3286, 2955, 1736, 1720, 1495, 1316, 1254, 1208, 1142, 842 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.29 and 7.16 (each d, total 1H, ³J = 8.7 Hz and ³J = 8.6 Hz respectively, C₂H cis / trans 1:10 in the order given), 6.97 (d, 0.9H, ⁴J = 2.7 Hz, C₅H *trans*-isomer), 6.78 (dt, 0.9H, ³J = 15.8 Hz, ⁴J = 1.4 Hz, C₇H *trans*-isomer), 6.71 (dd, 0.9H, ³J = 8.6 Hz, ⁴J = 2.8 Hz, C₃H trans isomer), 6.79-6.58 (m, 0.3H), 6.40-6.26 (bs, 2H, OH and NH), 6.21 and 6.02 (each dt, total 1H, ³J = 15.8 Hz, 7.1 Hz and ³J = 11.2 Hz, 7.5 Hz respectively, C₈H trans / cis 10:1 in the order given), 3.71 and 3.69 (each s, total 3H, OMe trans / cis 10:1 in the order given), 3.28 and 3.13 (each dd, total 2H, ³J = 7.1 Hz, ⁴J = 1.4 Hz and ³J = 7.5 Hz, ⁴J = 1.5 Hz respectively, CH₂ trans / cis 10:1 in the order given), 3.05-2.90 (m, 2H, CH₂), 1.11-0.98 (m, 2H, CH₂), 0.02 and 0.01 (each s, total 9H, SiMe₃ trans / cis 10:1 in the order given) ppm; ¹³C-NMR (CD₂Cl₂) (dominant signals of the major trans isomer) δ 172.84, 155.81, 135.80 and 126.20 (quart. C); 129.04, 128.91, 125.90, 116.20 and 113.58 (CH); 48.97, 38.54 and 10.82 (CH₂); 52.61 and -1.83 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 394 (calc. for C₁₆H₂₅NO₅SSiNa: 394).

Synthesis of Quinone Monoimide 15a. Vinyl aminophenol **14a** (cis / trans 1:3, 30 mg, 0.12 mmol) was suspended in chloroform (8 mL) and methanol (ca. 0.1 mL) was added dropwise until a clear solution resulted (ca. 5 drops). Lead tetraacetate (53 mg, 0.12 mmol) was added and the reaction mixture was stirred in the dark at rt for 20 min. The resulting bright yellow suspension (lead diacetate precipitated) was filtered, poured into water (10 mL) and the mixture was extracted with chloroform (3 x 20 mL). The organic layers were washed with water (2 x 10 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure affording a cis/trans-mixture (1:3) of pure quinone monoimide **15a** as a yellow oil (29 mg, 98 %): IR (neat) ν 2951, 1736, 1705, 1640, 1625, 1582, 1209, 979 cm⁻¹; ¹H-NMR (CDCl₃) δ 6.89 and 6.85 (each d, total 1H, ³J = 10.0 Hz, cis / trans 1:3 in the order given), 6.76 (d, 0.75H, ⁴J = 1.9 Hz), 6.62-6.45 (m, 3H), 6.19 (dt, 0.25H, ³J = 12.1 Hz, 7.5 Hz, C₈H *cis*-isomer), 3.74 and 3.73 (each s, total 3H, Ome cis / trans 1:3 in the order given), 3.32-3.25 (m, 2H, CH₂), 2.30 and 2.29 (each s, total 3H, Me trans / cis 3:1 in the order given) ppm; ¹³C-NMR (CDCl₃) δ 186.52, 186.31, 185.40, 171.07, 153.22, 152.82, 144.60 and 144.13 (quart. C); 134.94, 134.79, 132.33, 131.19, 130.66, 130.30, 129.88, 128.13, 125.94 and 125.20 (CH); 38.49 and 34.58 (CH₂); 52.37, 52.29, 25.59 and 25.53 (CH₃) ppm; LRGC-MS and LRFAB-MS: no [M]⁺ observed; UV/Vis (toluene) $\lambda_{(\text{max})}$ = 285 nm.

Synthesis of Quinone Monoimide 15b. Vinyl aminophenol **14b** (trans isomer > 90 %, 19 mg, 0.05 mmol) was dissolved in chloroform (3 mL) and lead tetraacetate (24 mg, 0.06 mmol) was added. The reaction mixture was stirred in the dark at rt for 20 min. The resulting bright yellow suspension (lead diacetate precipitated) was poured into water (10 mL) and the mixture was extracted with chloroform (3 x 10 mL). The organic layers were washed with water (2 x 10 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure yielding a cis/trans-mixture (trans isomer > 90 %) of pure quinone monoimide **15b** as a brown oil (19 mg, 100 %): IR (neat) ν 2956, 1739, 1641, 1637, 1556, 1323, 1139, 857 cm⁻¹; ¹H-NMR (CDCl₃) δ 8.02 and 8.00 (each d, total 1H, ³*J* = 10.2 Hz and ³*J* = 10.3 Hz respectively, cis / trans 1:10 in the order given), 6.79 (d, 0.9H, ⁴*J* = 2.1 Hz, C₅H trans isomer), 6.72-6.55 (m, 2.1H), 6.51 and 6.22 (each dt, total 1H, ³*J* = 16.0 Hz, 7.0 Hz and ³*J* = 12.0 Hz, 7.4 Hz respectively, C₈H trans/cis 10:1 in the order given), 3.75 and 3.74 (each s, total 3H, OMe cis/trans 1:10 in the order given), 3.35-3.19 (m, 4H, 2CH₂), 1.22-1.09 (m, 2H, CH₂), 0.12 and 0.11 (each s, total 9H, SiMe₃ trans / cis 10:1 in the order given) ppm; ¹³C-NMR (CDCl₃) (dominant signals of the major trans isomer) δ 186.11, 170.69, 164.52 and 144.86 (quart. C); 134.76, 130.78, 130.41, 128.55 and 125.30 (CH); 51.72, 38.31 and 9.73 (CH₂); 52.16 and -1.99 (CH₃) ppm; LRGC-MS and LRFAB-MS: no [M]⁺ observed; UV/Vis (toluene) λ_{max} = 284 nm.

Synthesis of 6-Hydroxy Dihydroquinoline 16a. Quinone monoimide **15a** (cis / trans 1:3, 12.5 mg, 0.05 mmol) was dissolved in toluene (10 mL, 5 mM). Addition of HMPA (0.5 mL, 5 %) resulted in the typical color change from yellow to red-brown indicating the formation of a quinone methide intermediate. The reaction mixture was stirred at rt in darkness for 1.5 h. The resulting brown solution was washed with water (2 x 10 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:1) to give 6-hydroxy dihydroquinoline **16a** as a beige solid (9 mg, 73 %): mp 141-144 °C; IR (KBr) ν 3212, 2923, 1726, 1642, 1499, 1458, 1302, 1248, 1198, 1173, 985 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.0-6.85 (bs, 1H, OH), 6.97 (d, 1H, ³J = 8.4 Hz, C₂H), 6.94 (dd, 1H, ³J = 15.6 Hz, ³J = 5.4 Hz, C₈H), 6.73 (dd, 1H, ³J = 8.4 Hz, ⁴J = 2.6 Hz, C₃H), 6.49 (d, 1H, ⁴J = 2.6 Hz, C₅H), 5.97 (dd, 1H, ³J = 15.6 Hz, ⁴J = 1.5 Hz, C₇H), 5.82 (bd, 1H, ³J = 5.4 Hz, C₉H), 3.72 (s, 3H, OMe), 2.11 (s, 3H, Me) ppm; ¹³C-NMR (CD₂Cl₂) δ 166.56, 157.74, 155.70, 131.42 and 123.51 (quart. C); 144.26, 126.11, 122.58, 116.59, 111.91 and 75.07 (CH); 52.30 and 21.46 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 270 (calc. for C₁₃H₁₃NO₄Na: 270).

Synthesis of 6-Hydroxy Dihydroquinoline 16b. Quinone monoimide **15b** (trans isomer > 90 %, 11 mg, 0.03 mmol) was dissolved in toluene (15 mL, 2 mM). Addition of

HMPA (0.375 mL, 2.5 %) resulted in the typical color change from yellow to red-brown indicating the formation of a quinone methide intermediate. The reaction mixture was stirred at reflux in darkness for 1 h. The resulting brown solution was washed with water (2 x 10 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:2) yielding aminophenol **14b** (40 %) and 6-hydroxy dihydroquinoline **16b** as a beige foam (4 mg, 58 %; yield based on reacted quinone monoimide **15b** with respect to isolated reduction product **14b**): IR (neat) ν 3436, 2955, 1737, 1493, 1339, 1253, 1208, 1146, 835 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 7.53 (d, 1H, ³J = 8.7 Hz, C₂H), 6.70 (dd, 1H, ³J = 8.7 Hz, ⁴J = 2.9 Hz, C₃H), 6.63 (d, 1H, ⁴J = 2.9 Hz, C₅H), 6.57 (d, 1H, ³J = 9.5 Hz, C₇H), 6.19 (dd, 1H, ³J = 9.5 Hz and 6.5 Hz, C₈H), 5.49 (d, 1H, ³J = 6.5 Hz, C₉H), 5.42 (bs, 1H, OH), 3.66 (s, 3H, OMe), 2.95-2.80 (m, 2H, CH₂), 1.00-0.91 (m, 2H, CH₂), 0.07 (s, 9H, SiMe₃) ppm; ¹³C-NMR (CD₂Cl₂) δ 170.13, 154.44, 128.54 and 127.50 (quart. C); 127.19, 126.50, 124.42, 116.10, 114.12 and 57.10 (CH); 48.29 and 10.78 (CH₂); 53.24 and -1.94 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 392 (calc. for C₁₆H₂₃NO₅SSiNa: 392).

Synthesis of 6-Hydroxy Quinoline 17. SES-Protected 6-hydroxy dihydroquinoline **16b** (7.4 mg, 0.02 mmol) was deprotected and aromatized by two methods. *Method A:* The substrate was dissolved in DMF (0.5 mL) and CsF (6.1 mg, 0.04 mmol) was added. The resulting bright yellow solution was stirred at rt for 30 min and then poured into water (5 mL). The mixture was extracted with ethyl acetate (5 x 5 mL). The organic layers were washed with water (2 x 5 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure. *Method B:* The substrate was dissolved in DMF

(0.5 mL) and K₂CO₃ (5.5 mg, 0.04 mmol) was added. The pale yellow suspension was stirred at 50 °C for 4 h during which the color turned into a bright yellow. The suspension was poured into water (5 mL) and the resulting mixture was extracted with ethyl acetate (5 x 5 mL). The organic layers were washed with water (2 x 5 mL) and then combined, dried over MgSO₄ and concentrated under reduced pressure.

The crude products were purified by flash chromatography on silica gel with ethyl acetate / hexane (1:1) yielding 6-hydroxy quinoline **17** as white crystals in quantitative yields for both of the described methods (4 mg, 100 %): mp 191-193 °C; IR (KBr) ν 3119, 2954, 1726, 1619, 1475, 1305, 1229, 1113, 838 cm⁻¹; ¹H-NMR (acetone-d₆) δ 9.32 (bs, 1H, OH), 8.27 (d, 1H, ³*J* = 8.5 Hz), 8.05 (d, 1H, ³*J* = 8.5 Hz), 8.04 (d, 1H, ³*J* = 9.2 Hz, C₂H), 7.48 (dd, 1H, ³*J* = 9.2 Hz, ⁴*J* = 2.7 Hz, C₃H), 7.30 (d, 1H, ⁴*J* = 2.7 Hz, C₅H), 3.96 (s, 3H, OMe) ppm; ¹³C-NMR (acetone-d₆) δ 166.75, 158.39, 146.24, 144.02 and 131.98 (quart. C); 136.01, 133.01, 123.91, 122.03 and 109.25 (CH); 52.70 (CH₃) ppm; LRFAB-MS: [M+Na]⁺ = 226 (calc. for C₁₁H₉NO₃Na: 226).

Synthesis of Protected 5-Hydroxy Indole 18a. Quinone monoimine **15a** (cis / trans 1:3, 25 mg, 0.10 mmol) was dissolved in toluene (20 mL, 5 mM) and HMPA (0.1 mL, 0.5 %) was added. The reaction mixture was stirred at rt in light for 20 min. The resulting yellow-brown solution was washed with water (2 x 20 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (2:3) yielding protected 5-hydroxy indole **18a** as a beige solid (17 mg, 69 %): mp 152-154 °C; IR (KBr) ν 3402, 2955, 1700, 1622, 1460, 1434, 1369, 1339, 1310, 1207 cm⁻¹; ¹H-NMR (acetone-d₆) δ 8.40-8.00 (bs, 1H, OH), 7.66 (d, 1H, ³*J* = 9.0 Hz, C₂H), 6.96 (d, 1H, ⁴*J* = 2.5 Hz, C₅H),

6.84 (dd, 1H, $^3J = 9.0$ Hz, $^4J = 2.5$ Hz, C₃H), 6.49 (s, 1H, C₇H), 4.01 (s, 2H, CH₂), 3.63 (s, 3H, OMe), 2.72 (s, 3H, Me) ppm; $^1\text{H-NMR}$ (acetone-d₆) δ 171.15, 170.74, 154.44, 136.39, 131.97 and 131.05 (quart. C); 116.35, 113.54, 111.99 and 106.43 (CH); 36.98 (CH₂); 51.99 and 27.24 (CH₃) ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+ = 270$ (calc. for C₁₃H₁₃NO₄Na: 270).

Synthesis of Protected 5-Hydroxy Indole 18b. Quinone monoimine **15b** (trans isomer > 90 %, 18.5 mg, 0.05 mmol) was dissolved in toluene (25 mL, 2 mM) and HMPA (0.13 mL, 0.5 %) was added. The reaction mixture was stirred at rt in light for 45 min. The resulting yellow-brown solution was washed with water (2 x 20 mL) and the aqueous phases were extracted with toluene (2 x 10 mL). The organic layers were combined, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:3) yielding protected 5-hydroxy indole **18b** as a brown oil (18.5mg, 59 %): IR (neat) ν 3448, 2953, 1740, 1465, 1362, 1216, 1155, 858 cm⁻¹; $^1\text{H-NMR}$ (CD₂Cl₂) δ 7.74 (d, 1H, $^3J = 8.9$ Hz, C₂H), 6.95 (d, 1H, $^4J = 2.5$ Hz, C₅H), 6.83 (dd, 1H, $^3J = 8.9$ Hz, $^4J = 2.5$ Hz, C₃H), 6.47 (s, 1H, C₇H), 4.98 (bs, 1H, OH), 4.00 (s, 2H, CH₂), 3.72 (s, 3H, OMe), 3.24-3.05 (m, 2H, CH₂), 1.00-0.85 (m, 2H, CH₂), -0.02 (s, 9H, SiMe₃) ppm; $^{13}\text{C-NMR}$ (CD₂Cl₂) δ 171.44, 152.82, 135.42, 132.01 and 130.68 (quart.C); 115.19, 113.87, 111.30 and 106.19 (CH); 50.26, 35.21 and 9.84 (CH₂); 52.71 and -1.94 (CH₃) ppm; LRFAB-MS: $[\text{M}+\text{Na}]^+ = 392$ (calc. for C₁₆H₂₃NO₅SSiNa: 392).

Synthesis of Deprotected 5-Hydroxy Indole 19. *From acetate-protected 5-hydroxy indole 18a:* Protected 5-hydroxy indole **18a** (2.50 mg, 0.01 mmol) was dissolved in methanol (0.2 mL) and sodium methylate (5.40 mg, 0.10 mmol) was added. After stirring at rt for 15 min the reaction mixture was purified by preparative tlc with ethyl acetate / hexane (2:1) yielding 5-hydroxy indole **19** as a pale yellow oil (2.0 mg, 95 %).

From SES-protected 5-hydroxy indole 18b: Protected 5-hydroxy indole **18b** (5.0 mg, 0.014 mmol) was dissolved in DMF (0.2 mL) and CsF (6.2 mg, 0.04 mmol) was added. The suspension was stirred at rt for 4 h and then poured into water (5 mL). The mixture was extracted with ethyl acetate (4 x 5 mL). The organic layers were washed with water (2 x 5 mL) and then combined, dried over MgSO₂ and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel with ethyl acetate / hexane (1:2) affording 5-hydroxy indole **19** as a pale yellow oil (2.7 mg, 97 %): IR (neat) ν 3391, 2923, 1724, 1456, 1175, 1015, 797 cm⁻¹; ¹H-NMR (CD₂Cl₂) δ 8.55 (bs, 1H), 7.21 (d, 1H, ³*J* = 8.6 Hz, C₂H), 6.92 (d, 1H, ⁴*J* = 2.3 Hz, C₅H), 6.69 (dd, 1H, ³*J* = 8.6 Hz, ⁴*J* = 2.3 Hz, C₃H), 6.22 (dd, 1H, ⁴*J* = 2.0 Hz and 0.9 Hz, C₇H), 4.63 (bs, 1H), 3.82 (bs, 2H, CH₂), 3.73 (s, 3H, OMe) ppm; ¹³C-NMR (CD₂Cl₂) δ 171.40, 150.29, 132.51, 132.18 and 129.58 (quart. C); 111.89, 111.74, 104.94 and 101.72 (CH); 34.23 (CH₂); 52.79 (CH₃) ppm; LRFAB-MS: [M+H]⁺ = 223 (calc. for C₁₁H₁₁NO₃Na: 223).

3.3 Selection of NMR Spectra of Intermediates and Annulation Products

^1H and ^{13}C NMR of 6-Amino Dihydroquinoline Diacetate 9a.

¹H and ¹³C NMR of di-SES-Protected 6-Amino Dihydroquinoline 9b.

¹H and ¹³C NMR of SES-Protected 6-Amino Quinoline 10.

¹H-NMR of 6-Amino Quinoline 11.

¹H and ¹³C NMR of 6-Hydroxy Dihydroquinoline Acetate 16a.

Current Data Parameters
NAME MT-606
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010603
Time 19.50
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 406.4
DM 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 7.40 usec
PL1 -6.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300151 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 210.06825 Hz/cm

Current Data Parameters
NAME MT-606
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010603
Time 19.57
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 19500
DS 0
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 4096
DM 19.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 6.25 usec
PL1 -5.00 dB
SFO1 100.6216290 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
P2 116.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 100.6127105 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 20122.54 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 10.25000 ppm/cm
HZCM 1031.28040 Hz/cm

¹H and ¹³C NMR of SES-Protected 6-Hydroxy Dihydroquinoline 16b.

¹H and ¹³C NMR of 6-Hydroxy Quinoline 17.

Current Data Parameters
NAME MT-788
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020106
Time 14.11
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 28
DS 2
SWH 6172.833 Hz
FIDRES 0.094190 Hz
AQ 5.3084560 sec
RG 912.3
OW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 7.50 usec
PL1 -3.00 dB
SF01 300.1318534 MHz

F2 - Processing parameters
SI 262144
SF 300.1300041 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm

Current Data Parameters
NAME MT-788
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20020106
Time 15.47
INSTRUM spect
PROBHD 5 mm BBO BB-1
PULPROG zgpg30
TD 32768
SOLVENT Aceton
NS 2416
DS 0
SWH 19723.805 Hz
FIDRES 0.601925 Hz
AQ 0.8307188 sec
RG 2648
OW 25.350 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 7.00 usec
PL1 -4.00 dB
SF01 75.4743947 MHz

***** CHANNEL f2 *****
CPDPRG2 wait1216
NUC2 1H
PCPD2 105.000 usec
PL2 -3.00 dB
PL12 21.00 dB
SF02 300.1315007 MHz

F2 - Processing parameters
SI 16384
SF 75.4676741 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 15693.54 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 10.50000 ppm/cm
HZCM 732.41058 Hz/cm

¹H and ¹³C NMR of 5-Hydroxy Indole Acetate 18a.

Current Data Parameters
NAME MT-605-2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010604
Time 15.58
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT Aceton
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 455.1
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 7.40 usec
PL1 -6.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 10.500 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 210.06825 Hz/cm

Current Data Parameters
NAME MT-605-2
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20010604
Time 17.07
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 65536
SOLVENT Aceton
NS 1000
DS 0
SWH 26315.789 Hz
FIDRES 0.401547 Hz
AQ 1.2452340 sec
RG 256
DW 19.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 6.25 usec
PL1 -6.00 dB
SFO1 100.6216290 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 116.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 400.1300007 MHz

F2 - Processing parameters
SI 32768
SF 100.6126698 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 20102.54 Hz
F2P -5.000 ppm
F2 -503.05 Hz
PPMCM 10.25000 ppm/cm
HZCM 1031.27991 Hz/cm

¹H and ¹³C NMR of SES-Protected 5-Hydroxy Indole 18b.

¹H and ¹³C NMR 5-Hydroxy Indoleacetic Acid Methylster 19.