SUPPORTING INFORMATION

A Directed *ortho* Metalation Approach to C-7 Substituted Indoles. Suzuki-Miyaura Cross Coupling and the Synthesis of Pyrrolophenanthridone Alkaloids

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General. Tetrahydrofuran, toluene and ether were freshly distilled from sodium benzophenone ketyl under argon prior to use. DMF, diisopropylamine and TMEDA were distilled over CaH₂. *n*-, *sec*- and *tert*-butyllithium were purchased from Aldrich as solutions in hexanes, stored in resealable containers and titrated periodically against *sec*-butanol. All experiments were carried out under argon in flame dried glassware, using syringe-septum cap techniques. Flash column chromatography was carried out using Merck silica gel 60 (particle size: 32-63). GC-MS analyses were performed with a *Varian CP-800* GC coupled with a *Varian Saturn 2000*-Quadrupole MS under EI (70 eV) conditions. The purity of the products was determined by a *HP 6890* GC. The melting points are uncorrected and represent values obtained on recrystallized materials.

General Procedure I: Metalation of 2-TMS-*N*-DMG-Indoles at C-7

A solution of 2-TMS-*N*-DMG-indole and TMEDA in anhydrous THF (3 ml per mmol) is cooled to -78 °C and *s*-BuLi (1.5-2.5 equiv) is added dropwise. After stirring for two to three hours, the electrophile (1.2 to 10 equiv, either neat or as a solution in anhydrous THF) is added and the reaction mixture is allowed to warm to room temperature over night. For preparative work-up, saturated NH₄Cl-solution is added and the resulting solution extracted three times with EtOAc or Et₂O. Washing the combined organic layers with water and brine, drying over MgSO₄ or Na₂SO₄ and evaporation of the solvent in vacuum delivers the crude product that can be purified by column chromatography on silica gel or by recrystallization.

General Procedure II: Metalation of *N*-P(O)*t*Bu₂-Indoles at C-7

To a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole in anhydrous THF at -40 °C was added a solution of *n*-BuLi. After 2 h of stirring at -40 °C the electrophile was added and the reaction mixture was allowed to warm to room temperature. After addition of saturated NH₄Cl-solution, the resulting mixture is extracted three times with CH₂Cl₂. Washing the combined organic layers with water and brine, drying over MgSO₄ and evaporation of the solvent in vacuum delivers the crude product that can be purified by column chromatography on silica gel or by recrystallization.

General Procedure III: Cleavage of Urea Based Directing Groups on Indoles

- IIIa** The corresponding *N*-DMG indole derivative is dissolved in ethanolic KOH (25% KOH in EtOH) and refluxed until TLC analysis shows complete consumption (1-16 h). After adding saturated NH₄Cl-solution, the reaction mixture is extracted with diethylether for three times, the combined organic layers washed with water and brine, dried over MgSO₄ and the solvent evaporated under reduced pressure. The crude product can be purified by column chromatography on silica gel.
- IIIb** The corresponding *N*-DMG indole derivative (100 mg) is dissolved in 25% aq NaOH (1.5 ml) and EtOH (5 ml) and refluxed until TLC analysis shows complete consumption (5-16 h). After evaporation of the solvents, saturated NH₄Cl-solution is added, if necessary set to neutral pH, the reaction mixture extracted with EtOAc for three times, the combined organic layers washed with brine, dried over MgSO₄ and the solvent evaporated under reduced pressure. The crude product can be purified by column chromatography on silica gel or recrystallization.
- IIIc** The corresponding *N*-DMG indole derivative is dissolved in THF and treated with 5-10 equiv KO^tBu at rt until TLC analysis shows complete consumption (1.5-16 h). After adding saturated NH₄Cl-solution, the reaction mixture is extracted with EtOAc for three times, the combined organic layers washed with water and brine, dried over MgSO₄ and the solvent evaporated under reduced pressure. The crude product can be purified by column chromatography on silica gel or recrystallization.
- IIId** The corresponding *N*-DMG indole derivative is dissolved in THF and treated with 1 equiv NBu₄F (solution in THF) for 2 h at rt and afterwards with 2.2 equiv KO^tBu until TLC analysis shows complete consumption (2 h). After adding saturated NH₄Cl-solution, the reaction mixture is extracted with EtOAc for three times, the combined organic layers washed with water and brine, dried over MgSO₄ and the solvent evaporated under reduced pressure. The crude product can be purified by column chromatography on silica gel or recrystallization.

Indole and 7-bromoindole, obtained by cleavage of 2-trimethylsilyl-indole-1-carboxylic acid diethylamide or 2-trimethylsilyl-indole-1,7-dicarboxylic acid bis-diethylamide with KO^tBu, respectively, were compared with commercially bought authentic samples (Aldrich) and showed identical spectroscopic and chromatographic properties.

General Procedure IV: Suzuki-Miyaura Cross Coupling of 7-I-, 7-Br- and 7-B(OR)₂-Substituted Indole Derivatives

A degassed solution of the 7-substituted indole derivative, the ArX compound, 2-10 mol% Pd(PPh₃)₄ and the base is stirred at 80 °C for the specified time. The reaction mixture is treated with 1 M HCl in water and extracted three times with CH₂Cl₂ or EtOAc. Washing the combined organic layers with water and brine, drying over MgSO₄ and evaporation of the solvent delivered the crude product, which was purified by column chromatography.

Preparation of specific compounds

Preparation of Indole-1-carboxylic acid diethylamide (12)

To a suspension of 1.2 equiv NaH (60% in mineral oil, 1.92 g, 48 mmol) in 50 ml THF a solution of indole (4.7 g, 40 mmol) in 40 ml THF is added at 0 °C and the mixture stirred for 1 h at room temperature. After recooling to 0 °C 1.1 equiv *N,N*-diethylcarbonylchloride (5.58 ml, 44 mmol) are added and the mixture is stirred at rt over night. A saturated solution of NH₄Cl is carefully added and the resulting mixture extracted three times with Et₂O. The combined organic layers are washed with water and brine, dried over MgSO₄ and the solvent evaporated in vacuum. Kugelrohr distillation gives the title compound¹ in quantitative yield as a colourless oil (decomposition with time under air to form a yellow oil).

Isol. yield: >99%.

bp.: ~120 °C / 0.4 Torr.

¹H-NMR (300 MHz, acetone-d₆): δ = 1.23 (t, *J* = 7.1 Hz, 6H, CH₃), 3.50 (q, *J* = 7.1 Hz, 4H, CH₂), 6.64 (dd, *J* = 3.5 & 0.8 Hz, 1H, 3-H), 7.16 (ddd, *J* = 7.8 & 7.2 & 1.7 Hz, 1H, 5-H), 7.26 (ddd, *J* = 8.2 & 7.2 & 1.1 Hz, 1H, 6-H), 7.45 (d, *J* = 3.5 Hz, 1H, 2-H), 7.62 (ddd, *J* = 7.8 & 1.1 & 0.8 Hz, 1H, 4-H), 7.66 (dd, *J* = 8.2 & 1.7 Hz, 1H, 7-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = 13.3 (CH₃), 42.7 (CH₂), 105.1 (C-3), 113.4 (C-7), 121.2 (C-6), 121.7 (C-4), 123.5 (C-5), 126.6 (C-2), 129.7 (C-3a), 136.2 (C-7a), 154.2 (C=O).

MS (EI, 70 eV): *m/z* (%) = 216 (100) [M]⁺, 100 (87) [CONEt₂]⁺.

C₁₃H₁₆N₂O (216.28).

¹ Castells, J.; Troin, Y.; Diez, A.; Rubiralta, M.; Grierson, D. S.; Husson, H. P. *Tetrahedron* **1991**, 47, 7911-7924.

Preparation of Indole-1-carboxylic acid diisopropylamide

To a suspension of 1.2 equiv NaH (60% in mineral oil, 2.05 g, 51 mmol) in 50 ml THF a solution of indole (5.0 g, 42.7 mmol) in 40 ml THF is added at 0 °C and the mixture stirred for 1 h at room temperature. After recooling to 0 °C 1.1 equiv *N,N*-diisopropylcarbamoylchloride (8.38 ml, 46 mmol) are added and the mixture is stirred at rt over night. A saturated solution of NH₄Cl is carefully added and the resulting mixture extracted three times with Et₂O. The combined organic layers are washed twice with water and brine, dried over MgSO₄ and the solvent evaporated in vacuum. The title compound is obtained as colourless crystals after crystallization from EtOAc / hexanes.

Isol. yield: 95%.

mp.: 88.5 °C (EtOAc / hexanes).

¹H-NMR (300 MHz, acetone-d₆): δ = 1.39 (d, *J* = 6.7 Hz, 12H, CH₃), 3.77-3.86 (m, 2H, N-CH), 6.58 (d, *J* = 3.4 Hz, 1H, 3-H), 7.12 (t, *J* = 7.6 Hz, 1H, 5-H), 7.22 (t, *J* = 8.2 Hz, 1H, 6-H), 7.37 (d, *J* = 3.4 Hz, 1H, 2-H), 7.50-7.70 (m, 2H, 4-H, 7-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = 29.8 (CH₃), 42.0 (N-CH), 104.7 (C-3), 113.2 (C-7), 121.3 (C-6), 121.6 (C-4), 123.4 (C-5), 126.3 (C-2), 129.6 (C-3a), 136.6 (C-7a), 154.7 (C=O).

MS (EI, 70 eV): *m/z* (%) = 244 (100) [M]⁺, 128 (33) [CON^{*i*}Pr₂]⁺.

HRMS: calcd for C₁₅H₂₀N₂O: 244.1576, found: 293.1583.

C₁₅H₂₀N₂O (244.16).

Preparation of Indole-1-carboxylic acid diphenylamide

To a suspension of 1.2 equiv NaH (60% in mineral oil, 1.24 g, 31 mmol) in 30 ml THF a solution of indole (3.0 g, 25.6 mmol) in 20 ml THF is added at 0 °C and the mixture stirred for 1 h at room temperature. After recooling to 0 °C 1.1 equiv *N,N*-diphenylcarbamoylchloride (7.71 g, 28.2 mmol) are added and the mixture is stirred at rt over night. A saturated solution of NH₄Cl is carefully added and the resulting mixture extracted three times with Et₂O. The combined organic layers are washed with water and brine, dried over MgSO₄ and the solvent evaporated in vacuum. The title compound is obtained as colourless crystals after crystallization from EtOAc / hexanes.

Isol. yield: 86%.

mp.: 157 °C (EtOAc / hexanes).

¹H-NMR (300 MHz, acetone-d₆): δ = 6.36 (d, *J* = 3.7 Hz, 1H, 3-H), 7.03 (d, *J* = 3.7 Hz, 1H, 2-H), 7.24 (t, *J* = 7.6 Hz, 1H, 5-H), 7.34 (t, *J* = 7.8 Hz, 1H, 6-H), 7.14- 7.42 (m, 10H, C₆H₅), 7.52 (d, *J* = 7.8 Hz, 1H, 7-H), 8.14 (d, *J* = 7.6 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = 106.0 (C-3), 114.5 (C-7), 120.6 (C-4, C-6), 122.3 (C-4), 123.6 (C-5), 126.2 (C_o of Ph), 126.3 (C_p of Ph), 126.7 (C-3a), 129.3 (C_m of Ph), 135.9 (C-7a), 143.9 (C_i of Ph), 153.5 (C=O).

MS (EI, 70 eV): m/z (%) = 312 (100) $[M]^+$, 196 (23) $[\text{CONPh}_2]^+$, 168 (20) $[\text{NPh}_2]^+$.

C₁₃H₁₆N₂O (312.13).

Preparation of Indol-1-yl-pyrrolidin-1-yl-methanone

To a suspension of 1.2 equiv NaH (60% in mineral oil, 1.64 g, 41 mmol) in 40 ml THF a solution of indole (4.0 g, 34 mmol) in 40 ml THF is added at 0 °C and the mixture stirred for 1 h at room temperature. After recooling to 0 °C 1.1 equiv *N*-pyrrolidinecarbamoylchloride (5.0 g, 37 mmol) are added and the mixture is stirred at rt over night. A saturated solution of NH₄Cl is carefully added and the resulting mixture extracted three times with Et₂O. The combined organic layers are washed with water and brine, dried over MgSO₄ and the solvent evaporated in vacuum. Recrystallization from hexanes gives the title compound as colourless crystals.

Isol. yield: 95%.

mp.: 91-93 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 1.93-2.01 (m,), 3.59-3.68 (m,), 6.60 (d, J = 3.5 Hz, 1H, 3-H), 7.18-7.27 (m, 1H, 5-H), 7.27-7.37 (m, 1H, 6-H), 7.39 (d, J = 3.5 Hz, 1H, 2-H), 7.62 (d, J = 8.7 Hz, 1H, 4-H), 7.85 (d, J = 8.3 Hz, 1H, 7-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 25.6, 48.8, 105.6, 114.3, 121.0, 121.9, 123.6, 125.5, 129.4, 135.8, 153.5.

MS (EI, 70 eV): m/z (%) = 214 (100) $[M]^+$, 98 (12) $[\text{CON}(\text{CH}_2)_4]^+$, 89 (6), 70 (5) $[\text{N}(\text{CH}_2)_4]^+$.

Elemental Analysis: calcd for C₁₃H₁₄N₂O: C, 72.87; H, 6.59; N, 13.07. found: C, 73.02; H, 6.65; N, 13.06.

C₁₃H₁₄N₂O (214.27).

Preparation of 2-Trimethylsilyl-indole-1-carboxylic acid diethylamide (6)

At -78 °C 1.1 equiv *tert*-butyllithium (solution in hexane, 20.4 mmol) are added dropwise to a solution of indole-1-carboxylic acid diethylamide (4.0 g, 18.5 mmol) and 1.1 equiv trimethylsilylchloride (2.6 ml, 20.4 mmol) in 60 ml anhydrous THF. The resulting yellow solution is stirred for three hours at -78 °C. The reaction mixture is quenched by the addition of saturated NH₄Cl-solution at low temperature and extracted three times with EtOAc or Et₂O. The combined organic layers are washed with water and brine, dried over MgSO₄ and the solvent evaporated in vacuum. The crude product can be crystallized from EtOAc / hexanes or purified by Kugelrohr distillation. The crude product of high purity (>97% yield) could also be used without further purification. After crystallization from EtOAc / hexanes colourless crystals were obtained, Kugelrohr distillation gives a colourless oil which solidifies upon standing.

Isol. yield: 84% (after Kugelrohr distillation).

bp.: ~130-140 °C / 1.7 Torr.

mp.: 59 °C (EtOAc / hexanes)

¹H-NMR (300 MHz, acetone-d₆): δ = 0.36 (s, 9H, SiMe₃), 1.22 (t, *J* = 7.1 Hz, 6H, CH₃), 3.36-3.58 (m, 4H, CH₂), 6.56 (s, 1H, 3-H), 7.13 (t, *J* = 7.6 Hz, 1H, 5-H), 7.20-7.32 (m, 1H, 6-H), 7.38 (d, *J* = 8.2 Hz, 1H, 7-H), 7.62 (d, *J* = 7.6 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = 0.3 (SiMe₃), 14.3 (CH₃), 43.3 (CH₂), 112.0 (C-7), 116.2 (C-3), 121.6 (C-5), 121.7 (C-4), 123.9 (C-6), 129.9 (C-2), 138.3 (C-3a), 142.0 (C-7a), 155.7 (C=O).

MS (EI, 70 eV): *m/z* (%) = 288 (7) [M]⁺, 274 (100), 100 (10) [CONEt₂]⁺.

Elemental Analysis: calcd for C₁₆H₂₄N₂OSi: C, 66.62; H, 8.39; N, 9.71. found: C, 66.69; H, 8.36; N, 9.74.

C₁₆H₂₄N₂OSi (288.46).

Preparation of 2-Trimethylsilyl-indole-1-carboxylic acid diisopropylamide

Indole-1-carboxylic acid diisopropylamide (100 mg, 409 μmol) was dissolved in 1 ml of anhydrous THF and a solution of 2.5 equiv *s*-BuLi / TMEDA (1:1, 1.02 mmol, premixed at 0 °C) was added dropwise at -78 °C. After stirring at this temperature for 2 h, 3.0 equiv TMSCl (156 μl, 1.23 mmol) were added and the reaction mixture allowed to warm to room temperature. Workup with NH₄Cl-solution, extraction with Et₂O, drying over MgSO₄ and evaporation of the solvent under reduced pressure followed by column chromatography on silica gel (hexanes / EtOAc = 20:1) delivered the title compound as colorless crystals.

Isol. yield: 92%.

mp.: 129 °C (EtOAc / hexanes).

¹H-NMR (300 MHz, acetone-d₆): δ = 0.38 (s, 9H, SiMe₃), 1.37 (d, *J* = 6.7 Hz, 6H, CH₃), 1.47 (d, *J* = 6.7 Hz, 6H, CH₃), 3.62-3.71 (m, 2H, N-CH), 6.84 (s, 1H, 3-H), 7.12 (t, *J* = 7.9 Hz, 1H, 5-H), 7.24 (t, *J* = 8.2 Hz, 1H, 6-H), 7.44 (d, *J* = 8.2 Hz, 1H, 7-H), 7.61 (d, *J* = 7.9 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = -0.2 (SiMe₃), 29.6 (CH₃), 49.2 (N-CH), 111.6 (C-3), 115.2 (C-7), 121.3 (C-6), 121.5 (C-4), 123.4 (C-5), 129.5 (C-2), 138.6 (C-3a), 141.2 (C-7a), 153.7 (C=O).

MS (EI, 70 eV): *m/z* (%) = 316 (74) [M]⁺, 301 (100) [M - CH₃]⁺, 273 (28), 259 (31), 143 (19), 231 (22), 217 (15), 174 (20), 158 (26), 128 (42) [COⁱNPr₂]⁺, 86 (61).

C₁₆H₂₄N₂OSi (316.20).

Preparation of 2-Trimethylsilyl-1*H*-indole

According to the General Procedure I, for the metalation of 2-TMS-*N*-DMG-indoles trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μ mol) is reacted with 3.0 equiv of *s*-BuLi (solution in hexanes, 1.0 mmol) and 3.0 equiv TMEDA (151 μ l, 1.0 mmol) for 3 h at -78 °C. Without the addition of an electrophile the reaction mixture is allowed to warm to rt over night. The title product is isolated as a yellow oil by column chromatography on silica gel (EtOAc / hexanes 40:1).

Yield: quant. (GC).

¹H-NMR (300 MHz, CDCl₃): δ = 0.44 (s, 9H, SiMe₃), 6.83 (s, 1H, 3-H), 7.20 (t, J = 7.6 Hz, 1H, 5-H), 7.28 (t, J = 7.8 Hz, 1H, 6-H), 7.47 (d, J = 7.6 Hz, 1H, 4-H), 7.74 (d, J = 7.8 Hz, 1H, 7-H), 8.20 (s_{br}, 1H, NH).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.9, 111.0, 111.5, 119.9, 120.7, 122.5, 128.9, 138.4, 138.9.

MS (EI, 70 eV): m/z (%) = 190 (96) [M + H]⁺, 174 (100) [M – CH₃]⁺, 131 (30), 75 (20).

C₁₁H₁₅NSi (189.33).

Preparation of 2,7-Bis-trimethylsilyl-indole-1-carboxylic acid diethylamide (7f)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μ mol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μ mol) and 2.5 equiv TMEDA (131 μ l, 868 μ mol) for 3 h at -78 °C and quenched with 2.5 equiv trimethylsilylchloride (110 μ l, 868 μ mol). After workup and column chromatography on silica gel (hexanes / Et₂O = 50:1 to 10:1) the bis-silylated compound could be isolated as a colourless solid.

Isol. yield: 82%.

mp.: 74-76 °C (EtOAc / hexanes).

¹H-NMR (300 MHz, acetone-d₆): δ = 0.33 (s, 9 H, SiMe₃), 0.35 (s, 9 H, SiMe₃), 0.52 (s_{br}, 3H, CH₃), 1.32 (s_{br}, 3H, CH₃), 2.36 (s_{br}, 1H, CH₂), 2.83 (d, J = 10.2 Hz, 1H, CH₂), 3.19 (s_{br}, 1H, CH₂), 3.96 (s_{br}, 1H, CH₂), 6.91 (s, 1H, 3-H), 7.15 (dd, J = 7.1 & 7.7 Hz, 1H, 5-H), 7.49 (d, J = 7.1 Hz, 1H, 6-H), 7.66 (d, J = 7.7 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = -0.4, 1.1, 13.0, 14.5, 43.8, 43.9, 116.7, 121.3, 123.2, 123.5, 129.4, 132.8, 141.5, 143.8, 156.8.

MS (CI, isobutane): m/z (%) = 361 (100) [M + H]⁺, 345 (12) [M – CH₃]⁺.

HRMS: calcd for C₁₉H₃₂N₂OSi₂: 360.2053, found: 360.2059.

C₁₉H₃₂N₂OSi₂ (360.64).

Preparation of 7-Methyl-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (7b)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μmol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μmol) and 2.5 equiv TMEDA (131 μl , 868 μmol) for 3 h at -78°C and quenched with 1.2 equiv methyl iodide (28 μl , 416 μmol). Column chromatography on silica gel (hexanes / EtOAc = 20:1) delivered the pure product as a pale yellow oil.

Isol. yield: 81%.

$^1\text{H-NMR}$ (300 MHz, acetone- d_6): δ = 0.35 (s, 9H, SiMe $_3$), 0.86 (t, J = 7.2 Hz, 3H, NCH $_2$ CH $_3$), 1.36 (t, J = 7.2 Hz, 3H, NC'H $_2$ C'H $_3$), 2.47 (s, 3H, 7-CH $_3$), 2.70 (dq, J = 14.4 & 7.2 Hz, 1H, CH $_2$), 2.82 (dq, J = 14.4 & 7.2 Hz, 1H, CH $_2$), 3.59 (dq, J = 14.2 & 7.1 Hz, 1H, CH $_2$), 3.65 (dq, J = 14.2 & 7.1 Hz, 1H, CH $_2$), 6.23 (s, 1H, 3-H), 7.00-7.05 (m, 2H, 5-H, 6-H), 7.44-7.47 (m, 1H, 4-H).

$^{13}\text{C-NMR}$ (75 MHz, acetone- d_6): δ = -0.8, 12.3, 13.3, 17.7, 42.2, 43.5, 114.8, 119.2, 121.1, 121.5, 125.7, 129.2, 137.9, 139.5, 155.9.

MS (EI, 70 eV): m/z (%) = 302 (35) [M] $^+$, 287 (26) [M - CH $_3$] $^+$, 230 (8), 188 (5) [M - C $_9$ H $_7$] $^+$, 130 (5) [C $_9$ H $_8$ N] $^+$, 100 (100) [CONEt $_2$] $^+$.

C $_{17}$ H $_{26}$ N $_2$ OSi (302.48).

Preparation of 7-Methylindole

Following the General Procedure IIIa, 7-methyl-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (48 mg, 159 μmol) was dissolved in 10 ml 25% KOH in ethanol and refluxed for 12 h. Column chromatography (hexanes / EtOAc = 10:1) provided the title compound as a colourless solid. The sample was identified by comparison with a commercially bought authentic sample of 7-methylindole (Aldrich).

Isol. yield: 75%.

$^1\text{H-NMR}$ (300 MHz, CDCl $_3$): δ = 2.54 (s, 3H, CH $_3$), 6.60 (dd, J = 3.0 & 2.2 Hz, 1H, 3-H), 7.03 (d, J = 7.3 Hz, 1H, 6-H), 7.08 (dd, J = 7.5 & 7.3 Hz, 1H, 5-H), 7.24 (d, J = 3.0 Hz, 1H, 2-H), 7.54 (d, J = 7.5 Hz, 1H, 4-H), 8.10 (s_{br}, 1H, NH).

$^{13}\text{C-NMR}$ (75 MHz, acetone- d_6): δ = 16.8 (CH $_3$), 102.5 (C-3), 118.5 (C-5), 119.9 (C-4), 121.0 (C-7), 122.3 (C-2), 124.9 (C-6), 128.5 (C-3a, C-7a).

C $_9$ H $_9$ N (131.17).

Preparation of 7-Ethyl-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (7c)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μmol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μmol) and 2.5 equiv TMEDA (131 μl , 868 μmol) for 3 h at -78°C and quenched with 1.2 equiv ethyl iodide (43 μl , 416 μmol). Column chromatography on silica gel (hexanes / EtOAc = 15:1) delivered the pure product as a pale yellow oil.

Isol. yield: 70%.

$^1\text{H-NMR}$ (300 MHz, acetone- d_6): δ = 0.34 (s, 9H, SiMe₃), 0.83 (t, J = 7.2 Hz, 3H, NCH₂CH₃), 1.27 (t, J = 7.5 Hz, 3H, 7-CH₂CH₃), 1.37 (t, J = 7.1 Hz, 3H, NC'H₂C'H₃), 2.63 (dq, J = 14.4 & 7.2 Hz, 1H, CH₂), 2.72-2.87 (m, 2H, CH₂), 2.97 (dq, J = 15.0 & 7.5 Hz, 1H, CH₂), 3.53 (dq, J = 14.2 & 7.1 Hz, 1H, CH₂), 3.71 (dq, J = 14.2 & 7.1 Hz, 1H, CH₂), 6.84 (s, 1H, 3-H), 7.06-7.08 (m, 2H, 5-H, 6-H), 7.44-7.47 (m, 1H, 4-H).

$^{13}\text{C-NMR}$ (75 MHz, acetone- d_6): δ = -0.9, 12.2, 13.3, 14.2, 24.2, 42.2, 43.5, 115.0, 119.2, 121.3, 123.4, 128.0, 129.5, 137.1, 139.7, 156.0.

MS (EI, 70 eV): m/z (%) = 316 (10) [M]⁺, 301 (15) [M – CH₃]⁺, 201 (9), 186 (12), 184 (12), 173 (14), 170 (7), 156 (7), 144 (6), 130 (17), 115 (5), 102 (6), 100 (100) [CONEt₂]⁺.

C₁₈H₂₈N₂OSi (316.51).

Preparation of 7-(3-Methyl-but-2-enyl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (7d)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) was lithiated with 1.5 equiv of *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (453 μl , 3.0 mmol) for 2 h at -78°C and quenched with 1.5 equiv 1-bromo-3-methylbut-2-ene (346 μl , 3.0 mmol). Column chromatography on silica gel (hexanes / EtOAc = 80:1) delivered the pure product as a colourless oil.

Isol. yield: 66%.

$^1\text{H-NMR}$ (300 MHz, CDCl₃): δ = 0.38 (s, 9H, SiMe₃), 0.88 (t, J = 7.2 Hz, 3H, NCH₂CH₃), 1.39 (t, J = 7.2 Hz, 3H, NC'H₂C'H₃), 1.73 (s, 3H, CH₃), 1.83 (s, 3H, CH₃), 2.64 (sext, J = 7.2 Hz, 1H, CH₂), 2.81 (sext, J = 7.2 Hz, 1H, CH₂), 3.45-3.74 (m, 4H, CH₂), 5.42 (m, 1H, CH), 6.83 (s, 1H, 3-H), 7.04-7.14 (m, 2H, 5-H, 6-H), 7.48 (d, J = 7.2 Hz, 1H, 4-H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl₃): δ = 0.1, 13.1, 14.2, 18.6, 26.5, 29.6, 42.8, 44.0, 115.6, 119.5, 121.6, 122.3, 124.0, 125.8, 129.7, 134.3, 137.7, 140.3, 157.0.

MS (EI, 70 eV): m/z (%) = 356 (48) [M]⁺, 341 (100) [M – CH₃]⁺, 287 (10), 268 (14), 100 (33) [CONEt₂]⁺, 72 (10) [NEt₂]⁺.

HRMS: calcd for C₂₁H₃₂N₂OSi: 356.2284, found: 356.2288.

C₂₁H₃₂N₂OSi (356.58).

Preparation of 2-Trimethylsilyl-1*H*-indole-7-carbaldehyde (8)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μ mol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μ mol) and 2.5 equiv TMEDA (131 μ l, 868 μ mol) for 3 h at -78 °C and quenched with 20 equiv anhydrous DMF (537 μ l, 7.0 mmol). Column chromatography of the crude mixture on silica gel (hexanes / EtOAc = 15:1) delivered the title compound as a colourless solid.

Isol. yield: 40%.

mp.: 98 °C (hexanes).

¹H-NMR (300 MHz, acetone-*d*₆): δ = 0.42 (s, 9H, SiMe₃), 6.85 (d, *J* = 2.2 Hz, 1H, 3-H), 7.27 (t, *J* = 7.8 Hz, 1H, 5-H), 7.70-7.81 (m, 1H, 6-H), 7.91-7.99 (m, 1H, 4-H), 10.15 (s, 1H, CHO), 10.54 (s_{br}, 1H, NH).

¹³C-NMR (75 MHz, acetone-*d*₆): δ = -0.9, 111.9, 119.4, 121.2, 127.9, 129.4, 130.6, 137.1, 139.7, 193.4.

MS (EI, 70 eV): *m/z* (%) = 217 (19) [M]⁺, 202 (10) [M – CH₃]⁺, 154 (28), 138 (13), 136 (13), 136 (26), 111 (10), 107 (14), 95 (21), 91 (23), 83 (30), 73 (100), 69 (66), 57 (94).

HRMS: calcd for C₁₂H₁₅NOSi: 217.0923, found: 217.0926.

C₁₂H₁₅NOSi (217.34).

Preparation of 2-Trimethylsilyl-indole-1,7-dicarboxylic acid bis-diethylamide (7e)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) was lithiated with 1.5 equiv *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (450 μ l, 3.0 mmol) and quenched with 1.5 equiv ClCONEt₂ (380 μ l, 3.0 mmol). Column chromatography on silica gel (hexanes / EtOAc = 10:1 → 5:1) delivered the pure title compound as a colourless solid.

Isol. yield: 72%.

mp.: 73-75 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 0.35 (s, 9H, SiMe₃), 0.86-0.95 (m, 6H, CH₃), 1.24-1.35 (m, 6H, CH₃), 2.75-3.00 (m, 2H, CH₂), 3.06 (q, *J* = 7.1 Hz, 2H, CH₂), 3.28 (sext, *J* = 7.0 Hz, 1H, CH₂), 3.43 (sext, *J* = 6.9 Hz, 1H, CH₂), 3.62-3.77 (m, 2H, CH₂), 6.83 (d, *J* = 1.0 Hz, 1H, 3-H), 7.12-7.17 (m, 2H, 5-H, 6-H), 7.58-7.63 (m, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 0.18, 13.6, 13.8, 14.5, 14.6, 40.2, 43.2, 44.0, 44.8, 115.4, 121.3, 122.2, 122.6, 123.1, 129.8, 134.0, 141.7, 155.3, 169.4.

MS (EI, 70 eV): m/z (%) = 387 (42) $[M]^+$, 372 (35) $[M - CH_3]^+$, 314 (100), 287 (10), 271 (25), 241 (64), 216 (10), 200 (8), 172 (4), 100 (22) $[CONEt_2]^+$, 72 (20) $[NEt_2]^+$.

HRMS: calcd for $C_{21}H_{33}N_3O_2Si$: 387.2342, found: 387.2328.

$C_{21}H_{33}N_3O_2Si$ (387.59).

Preparation of 2-Trimethylsilanyl-indole-1-carboxylic acid (1-diethylcarbamoyl-ethyl)-ethyl-amide (9)

In the reaction described for 2-trimethylsilanyl-indole-1,7-dicarboxylic acid bis-diethylamide the title compound was isolated as a side product (colourless oil) after column chromatography on silica gel (hexanes / EtOAc = 10:1 $\rightarrow$ 5:1).

NMR signals are split up because of two different rotamers.

Isol. yield: 10%.

1H -NMR (300 MHz, $CDCl_3$): δ = 0.34, 0.39 (2x s, 9H, $SiMe_3$), 0.89-1.22 (m, 9H, CH_2CH_3), 1.52, 1.57 (2x d, J = 7.0 Hz, 3H, $CHCH_3$), 2.94-3.85 (n, 6H, CH_2), 5.12-5.30 (m, 1H, NCH), 6.82, 6.84 (2x s, 3-H), 7.08-7.29 (m, 3H, 5-H, 6-H, 7-H), 7.54-7.62 (m, 1H, 4-H).

^{13}C -NMR (75 MHz, $CDCl_3$): δ = -0.1, 12.2, 13.0, 13.4, 14.4, 15.6, 16.2, 16.5, 17.6, 40.2+40.3, 40.6+40.8, 42.0+42.4, 51.4+52.1, 111.1+111.9, 116.1+116.4, 121.2+121.3, 121.4+121.4, 123.6, 129.6+129.7, 137.4, 141.6, 155.3+155.8, 170.4+170.5.

MS (EI, 70 eV): m/z (%) = 387 (35) $[M]^+$, 372 (100) $[M - CH_3]^+$, 314 (88), 298 (55), 287 (55), 271 (16), 241 (75), 216 (32), 199 (78), 171 (28), 144 (8), 100 (30) $[CONEt_2]^+$, 72 (40) $[NEt_2]^+$.

$C_{21}H_{33}N_3O_2Si$ (387.59).

Preparation of 2,6-Bis-trimethylsilanyl-indole-1,7-dicarboxylic acid bis-diethylamide (13)

Following the General Procedure I, 2-trimethylsilanyl-indole-1,7-dicarboxylic acid bis-diethylamide (150 mg, 387 μ mol) was lithiated with 1.2 equiv *s*-BuLi (solution in hexanes, 464 μ mol) and 1.2 equiv TMEDA (70 μ l, 464 μ mol) and quenched with 1.2 equiv TMSCl (60 μ l, 464 μ mol). Column chromatography on silica gel (hexanes / EtOAc = 10:1) delivered the pure title compound as a colourless solid.

Isol. yield: 90%.

mp.: 142-143 $^{\circ}C$ (hexanes).

1H -NMR (300 MHz, $CDCl_3$): δ = 0.33 (s, 9H, $SiMe_3$), 0.36 (s, 9H, $SiMe_3$), 0.73 (t, J = 7.3 Hz, 3H, CH_3), 0.85 (t, J = 7.2 Hz, 3H, CH_3), 1.26-1.33 (m, 6H, CH_2), 2.46-2.68 (m, 2H, CH_2), 2.88 (q,

$J = 7.3$ Hz, 2H, CH₂), 2.88 (sext, $J = 7.1$ Hz, 1H, CH₂), 3.37 (sext, $J = 7.2$ Hz, 1H, CH₂), 3.77 (m, 2H, CH₂), 6.79 (s, 1H, 3-H), 7.38 (d, $J = 7.9$ Hz, 1H, 5-H), 7.60 (d, $J = 7.9$ Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): $\delta = -0.1, 1.1, 13.5, 13.6, 13.7, 14.3, 39.8, 43.4, 43.6, 44.0, 114.8, 121.1, 127.7, 127.8, 130.2, 132.9, 135.1, 142.8, 155.1, 169.4$.

MS (EI, 70 eV): m/z (%) = 459 (15) [M]⁺, 444 (100) [M – CH₃]⁺, 386 (31), 343 (8), 313 (30), 100 (10) [CONEt₂]⁺, 72 (9) [NEt₂]⁺.

Elemental Analysis: calcd for C₂₄H₄₁N₃O₂Si₂: C, 62.70; H, 8.99; N, 9.14. found: C, 62.83; H, 9.05; N, 9.08.

C₂₄H₄₁N₃O₂Si₂ (459.77).

Preparation of 1*H*-Indole-7-carboxylic acid diethylamide

Following the General Procedure IIIc, 2-trimethylsilyl-indole-1,7-dicarboxylic acid bis-diethylamide (109 mg, 0.28 mmol) in 3 ml THF was treated with 6 equiv KO^tBu (159 mg, 1.69 mmol) and stirred at rt over night. Column chromatography on silica gel (hexanes / EtOAc = 2:1) afforded the pure product as a colourless solid.

Isol. yield: 82%.

mp.: 92-94 °C (hexanes/EtOAc).

¹H-NMR (300 MHz, CDCl₃): $\delta = 1.24$ (t, $J = 7.1$ Hz, 6H, CH₃), 3.53 (q, $J = 7.1$ Hz, 4H, CH₂), 6.52 (dd, $J = 3.0$ & 2.2 Hz, 1H, 3-H), 7.06 (t, $J = 7.7$ Hz, 1H, 5-H), 7.16-7.23 (m, 2H, 2-H, 4-H), 7.67 (d, $J = 7.7$ Hz, 1H, 6-H), 9.26 (s_{br}, 1H, NH).

¹³C-NMR (75 MHz, CDCl₃): $\delta = 13.9$ (s_{br}), 41.8 (s_{br}), 102.6, 118.5, 118.6, 120.1, 122.8, 125.3, 129.3, 134.9, 170.3.

MS (EI, 70 eV): m/z (%) = 216 (65) [M]⁺, 144 (100) [M – NEt₂]⁺, 116 (47) [M – CONEt₂]⁺, 89 (19).

C₁₃H₁₆N₂O (216.28).

Preparation of 7-Iodo-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (7i)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) is lithiated with 1.5 equiv *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (450 μ l, 3.0 mmol) and quenched with 1.5 equiv iodine (774 mg, 3.0 mmol) as a solution in 3 ml THF. Crystallization from hexanes afforded the pure product as colorless crystals.

Isol. yield: 75%.

mp.: 107-109 °C (hexanes).

¹H-NMR (300 MHz, acetone-d₆): $\delta = 0.36$ (s, 9 H, SiMe₃), 0.92 (t, $J = 7.2$ Hz, 3H, CH₃), 1.41 (t, $J = 7.2$ Hz, 3H, CH₃), 2.62-2.80 (m, 2H, CH₂), 3.49 (sext, $J = 7.0$ Hz, 1H, CH₂), 3.81 (sext, $J = 7.1$ Hz,

1H, CH₂), 6.89 (dd, *J* = 7.8 & 7.4 Hz, 1H, 5-H), 6.90 (s, 1H, 3-H), 7.67 (d, *J* = 7.8 Hz, 1H, 4-H), 7.73 (d, *J* = 7.4 Hz, 1H, 6-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 0.0, 13.3, 14.1, 43.2, 44.3, 75.3, 115.4, 121.8, 122.9, 130.8, 135.6, 138.7, 142.1, 154.4.

MS (EI, 70 eV): *m/z* (%) = 414 (3) [M]⁺, 399 (9) [M – CH₃]⁺, 287 (8), 271 (5), 216 (9), 173 (5), 170 (5), 156 (6), 144 (7), 130 (6), 101 (23), 100 (100) [CONEt₂]⁺.

Elemental Analysis: calcd for C₁₆H₂₃IN₂OSi: C, 46.38; H, 5.59; N, 6.76. found: C, 46.56; H, 5.51; N, 6.75.

C₁₆H₂₃IN₂OSi (414.36).

Preparation of 7-Bromo-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (7h)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) is lithiated with 1.5 equiv *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (450 μl, 3.0 mmol) and quenched with 1.5 equiv of 1,2-dibromoethane (259 μl, 3.0 mmol) as a solution in 3 ml THF. Column chromatography on silica gel (hexanes / EtOAc = 40:1) delivered the product as a pale yellow oil.

Isol. yield: 69%.

¹H-NMR (300 MHz, acetone-d₆): δ = 0.36 (s, 9H, SiMe₃), 0.93 (t, *J* = 7.2 Hz, 3H, CH₃), 1.38 (t, *J* = 7.2 Hz, 3H, CH₃), 2.67-2.91 (m, 2H, CH₂), 3.62 (sext, *J* = 7.2 Hz, 2H, CH₂), 6.92 (s, 1H, 3-H), 7.04 (dd, *J* = 7.9 & 7.6 Hz, 1H, 5-H), 7.44 (dd, *J* = 7.6 & 0.8 Hz, 1H, 6-H), 7.65 (dd, *J* = 7.9 & 0.8 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = -0.7, 12.2, 13.2, 42.4, 43.7, 104.3, 114.9, 120.9, 122.1, 127.9, 131.4, 141.8, 153.9.

MS (EI, 70 eV): *m/z* (%) = 368/366 (23) [M]⁺, 354/352 (100), 288 (5) [M – Br]⁺, 244 (6), 100 (87) [CONEt₂]⁺.

HRMS: calcd for C₁₆H₂₃BrN₂OSi: 366.0763, found: 366.0759.

C₁₆H₂₃BrN₂OSi (367.34).

Preparation of 2-Ethyl-1-methyl-5-trimethylsilyl-1,2-dihydro-pyrrolo[3,2,1-*ij*]quinazolin-3-one (11)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) was lithiated 3.0 equiv *s*-BuLi (solution in hexanes, 6.0 mmol) and 3.0 equiv TMEDA (0.9 ml, 6.0 mmol) quenched with 3.0 equiv of iodine (1.52 g, 6.0 mmol) as a solution in 5 ml THF.

Column chromatography on silica gel (hexanes / EtOAc = 60:1) delivered the product as a yellow oil (decomposition on standing).

Yield: 50% (GC).

¹H-NMR (300 MHz, CDCl₃): δ = 0.41 (s, 9H, SiMe₃), 1.30 (t, *J* = 7.1 Hz, 3H, NCH₂CH₃), 1.60 (d, *J* = 6.5 Hz, 3H, NCHCH₃), 3.28-3.45 (m, 1H, NCH₂CH₃), 3.86-4.04 (m, 1H, NCH₂CH₃), 4.96 (q, *J* = 6.5 Hz, 1H, NCHCH₃), 6.77 (s, 1H, 6-H), 6.98 (d, *J* = 7.3 Hz, 1H, 7-H), 7.17 (dd, *J* = 7.8 & 7.3 Hz, 1H, 8-H), 7.42 (d, *J* = 7.8 Hz, 1H, 9-H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.3, 13.6, 24.6, 41.1, 56.2, 117.2, 118.2, 119.0, 121.7, 123.1, 127.9, 140.8, 149.4, 153.9.

MS (EI, 70 eV): *m/z* (%) = 286 (6) [M]⁺, 272 (100), 228 (50).

C₁₆H₂₂N₂OSi (286.46).

Preparation of 7-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (7j)

Following the General Procedure I, 2-trimethylsilyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) was lithiated with 1.5 equiv *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (450 μl, 3.0 mmol) and quenched slowly with 1.5 equiv of B(O*i*Pr)₃ (692 μl, 3.0 mmol). The reaction mixture was allowed to warm to rt over night. After addition of 10 ml of saturated NH₄Cl solution and 10 ml of EtOAc the organic layer was separated and the aqueous layer once extracted with 10 ml EtOAc. 1.5 equiv pinacol (355 mg, 3.0 mmol) were added to the combined organic layers and the solvent evaporated in vacuum. The residue was dissolved in EtOAc, dried over MgSO₄ for 1 h and evaporated in vacuum. Column chromatography on silica gel (hexanes / EtOAc = 10:1) afforded the pure product as a colourless solid.

Isol. yield: 60%.

mp.: 122-124 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 0.33 (s, 9H, SiMe₃), 1.07 (s_{br}, 6H, NCH₂CH₃), 1.32 (s, 12 H, CH₃), 2.80 (s_{br}, 3H, CH₂), 4.13 (s_{br}, 1H, CH₂), 6.80 (s, 1H, 3-H), 7.10 (dd, *J* = 7.8 & 7.1 Hz, 1H, 5-H), 7.67 (dd, *J* = 7.8 & 1.3 Hz, 1H, 6-H), 7.73 (dd, *J* = 7.1 & 1.3 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.2, 13.1, 25.0, 42.7, 83.9, 115.4, 120.3, 124.4, 128.6, 132.7, 140.2, 141.3, 155.9, (C-7 not detected).

MS (EI, 70 eV): *m/z* (%) = 414 (44) [M]⁺, 400 (100), 356 (9), 314 (7), 284 (10), 100 (12) [CONEt₂]⁺.

HRMS: calcd for C₂₂H₃₅BN₂O₃Si: 414.2510, found: 414.2510.

C₂₂H₃₅BN₂O₃Si (414.42).

Preparation of 2-Trimethylsilanyl-indole-1-carboxylic acid ethyl-[1-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-ethyl]-amide (10)

In the reaction described for 7-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide the title compound was isolated as a side product (yellow oil) after column chromatography on silica gel (hexanes / EtOAc = 10:1).

Isol. yield: 16%.

¹H-NMR (300 MHz, CDCl₃): δ = 0.42 (s, 9H, SiMe₃), 1.07 (t, *J* = 7.2 Hz, 3H, NCH₂CH₃), 1.27 (s, 12 H, CH₃), 1.39 (d, *J* = 7.2 Hz, 3H, NCHCH₃), 2.99 (q, *J* = 7.2 Hz, 1H, NCHCH₃), 3.14-3.49 (m, 2H, CH₂), 6.86 (s, 1H, 3-H), 7.10-7.29 (m, 3H, 5-H, 6-H, 7-H), 7.59 (d, *J* = 7.6 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.3, 13.4, 14.7, 25.1, 25.5, 25.4, 41.9, 81.1, 82.2, 111.7, 117.4, 121.3, 122.6, 123.9, 129.6, 137.6, 141.8, 159.4.

MS (EI, 70 eV): *m/z* (%) = 414 (15) [M]⁺, 399 (31) [M – CH₃]⁺, 385 (22), 355 (16), 341 (100), 298 (13), 283 (10), 270 (8), 216 (5), 144 (25), 83 (8).

C₂₂H₃₅BN₂O₃Si (414.42).

Preparation of 7-Hydroxy-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (7k)

Following the General Procedure I, 2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (577 mg, 2.0 mmol) was lithiated with 1.5 equiv *s*-BuLi (solution in hexanes, 3.0 mmol) and 1.5 equiv TMEDA (450 μl, 3.0 mmol) and quenched slowly with 1.5 equiv of B(O*i*Pr)₃ (692 μl, 3.0 mmol). The reaction mixture was allowed to warm to rt over night. After addition of 2.5 equiv H₂O₂ (30% solution in water, 0.7 ml, 5 mmol) at 0 °C and stirring for 1 h at rt, 10 ml of saturated NH₄Cl solution were added and the mixture extracted with EtOAc (3 x 30 ml). Column chromatography on silica gel (hexanes / EtOAc = 5:1) afforded the pure product as a slightly pink crystals.

Isol. yield: 58%.

mp.: 182-186 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 0.36 (s, 9H, SiMe₃), 1.13 (t, *J* = 7.2 Hz, 3H, CH₃), 3.20-3.40 (m, 4H, CH₂), 4.82 (s_{br}, 1H, OH), 6.71 (dd, *J* = 7.6 & 0.9 Hz, 1H, 6-H), 6.80 (s, 1H, 3-H), 6.99 (dd, *J* = 7.9 & 7.6 Hz, 1H, 5-H), 7.15 (dd, *J* = 7.9 & 0.9 Hz, 1H, 6-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 0.3, 13.6, 44.0, 111.1, 113.6, 117.3, 122.7, 128.2, 131.9, 140.7, 143.3, 158.2.

MS (EI, 70 eV): *m/z* (%) = 304 (44) [M]⁺, 289 (100) [M – CH₃]⁺, 260 (15), 189 (8), 174 (16), 159 (7), 100 (70) [CONEt₂]⁺, 72 (35) [NEt₂]⁺.

HRMS: calcd for C₂₆H₂₄N₂O₂Si: 304.1607, found: 304.1607.

C₂₆H₂₄N₂O₂Si (304.46).

Preparation of 7-Tributylstannanyl-2-trimethyl-silanyl-indole-1-carboxylic acid diethylamide (7g)

Following the General Procedure I, 2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μ mol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μ mol) and 2.5 equiv TMEDA (131 μ l, 868 μ mol) for 3 h at -78 °C and quenched with 1.5 equiv tributyltinchloride (140 μ l, 521 μ mol). Column chromatography on silica gel (hexanes / EtOAc = 20:1) delivered the pure product as a pale yellow oil. In larger scales, distillation under reduced pressure is also a possible way of purification.

Isol. yield: 33%.

¹H-NMR (300 MHz, acetone-d₆): δ = 0.34 (s, 9H, SiMe₃), 0.87-1.58 (m, 37H, alkyl-H), 6.86 (s, 1H, 3-H), 7.09 (dd, *J* = 7.8 & 6.9 Hz, 1H, 5-H), 7.35 (dd, *J* = 6.9 & 1.2 Hz, 1H, 6-H), 7.57 (dd, *J* = 7.8 & 1.2 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, acetone-d₆): δ = 0.0, 12.2, 14.0, 27.9, 44.5, 116.7, 121.5, 121.9, 123.5, 129.1, 134.2, 140.7, 145.3, 153.9.

C₂₈H₅₀N₂OSiSn (577.51).

Preparation of 7-Phenyl-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (14a)

1. Following the General Procedure I, 2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (100 mg, 347 μ mol) was lithiated with 2.5 equiv of *s*-BuLi (solution in hexanes, 868 μ mol) and 2.5 equiv TMEDA (131 μ l, 868 μ mol) for 3 h at -78 °C and quenched with 2.7 equiv ZnBr₂ (1.62 M solution in anhydrous THF, 578 μ l, 937 μ mol). After stirring and warming to room temperature over night, 5 mol% Pd(PPh₃)₄ (20 mg, 17 μ mol) and 1.2 equiv iodobenzene (47 μ l, 416 μ mol) were added and the resulting mixture refluxed over night. Column chromatography on silica gel (hexanes / EtOAc = 20:1), gave the pure title compound as a colourless oil.
2. Following the General Procedure IV, a solution of 7-iodo-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (50 mg, 121 μ mol), 1.1 equiv phenylboronic acid (16.2 mg, 133 μ mol), 2 mol% Pd(PPh₃)₄ (3 mg, 2.4 μ mol) and 1.5 equiv Na₂CO₃·H₂O (22.4 mg, 181 μ mol) in 0.6 ml DME and 0.12 ml H₂O was stirred at 80 °C for 16 h. Column chromatography on silica gel (hexanes / EtOAc = 20:1), gave the pure title compound as a colorless oil.

Isol. yield: 17% (after procedure 1), 90% (after procedure 2).

¹H-NMR (300 MHz, acetone-d₆): δ = 0.36 (s, 9H, SiMe₃), 0.62 (t, *J* = 7.2 Hz, 3H, CH₃), 0.82 (t, *J* = 7.2 Hz, 3H, CH₃), 2.31 (sext, *J* = 7.2 Hz, 1H, CH₂), 2.41 (sext, *J* = 7.1 Hz, 1H, CH₂), 2.59 (sext, *J* = 7.2 Hz, 1H, CH₂), 2.81 (sext, *J* = 7.1 Hz, 1H, CH₂), 6.93 (s, 1H, 3-H), 7.12 (dd, *J* = 7.3 & 1.2 Hz,

1H, 6-H), 7.22 (dd, $J = 7.8$ & 7.3 Hz, 1H, 5-H), 7.35-7.51 (m, 5H, Ph), 7.64 (dd, $J = 7.8$ & 1.2 Hz, 1H, 4-H).

$^{13}\text{C-NMR}$ (75 MHz, acetone- d_6): $\delta = -0.6, 12.8, 14.3, 42.5, 43.6, 115.3, 120.9, 121.7, 126.5, 127.9, 128.0, 128.9, 129.2, 130.6, 135.6, 139.9, 141.5, 155.0$.

MS (EI, 70 eV): m/z (%) = 364 (17) $[\text{M}]^+$, 349 (100) $[\text{M} - \text{CH}_3]^+$, 262 (8), 100 (32) $[\text{CONEt}_2]^+$, 72 (18) $[\text{NEt}_2]^+$.

C₂₂H₂₈N₂OSi (364.56).

Preparation of 7-Phenyl-indole-1-carboxylic acid diethylamide (14f)

Following the General Procedure IV, a solution of 7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (75 mg, 181 μmol), 1.2 equiv bromobenzene (23 μl , 217 μmol), 5 mol% $\text{Pd}(\text{PPh}_3)_4$ (11 mg, 9 μmol) and 3 equiv K_3PO_4 (115 mg, 543 μmol) in 2.5 ml DMF was stirred at 80 °C for 17 h. Column chromatography on silica gel (hexanes / EtOAc = 8:1), gave the pure title compound as a colorless solid.

Isol. yield: 94%.

mp.: 63-65 °C (hexanes).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 0.87$ (t, $J = 7.2$ Hz, 6H, CH_3), 2.85 (sbr, 2H, CH_2), 2.99 (sbr, 2H, CH_2), 6.69 (d, $J = 3.4$ Hz, 1H, 3-H), 7.18 (dd, $J = 7.3$ & 1.2 Hz, 1H, 6-H), 7.27 (d, $J = 3.4$ Hz, 1H, 2-H), 7.27 (dd, $J = 7.7$ & 7.3 Hz, 1H, 5-H), 7.31-7.38 (m, 1H, p -PhH), 7.39-7.51 (m, 4H, o -Ph-H, m -Ph-H), 7.64 (dd, $J = 7.7$ & 1.2 Hz, 1H, 4-H).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 12.7, 42.1, 104.7, 120.2, 121.4, 125.3, 127.1, 127.1, 127.7, 128.2, 128.2, 130.1, 132.7, 139.7, 153.6$.

MS (EI, 70 eV): m/z (%) = 292 (100) $[\text{M}]^+$, 191 (21), 163 (6), 100 (95) $[\text{CONEt}_2]^+$, 72 (28) $[\text{NEt}_2]^+$.

HRMS: calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$: 292.1576, found: 292.1580.

C₁₉H₂₀N₂O (292.37).

Preparation of 7-Phenyl-1H-indole

Following the General Procedure IIIc, 7-phenyl-indole-1-carboxylic acid diethylamide (30 mg, 0.1 mmol) in 2 ml THF was treated with 5 equiv KO^tBu (112 mg, 0.5 mmol) and stirred under reflux over night. Column chromatography on silica gel (hexanes / EtOAc = 10:1) afforded the pure product as a colourless oil.

Isol. yield: 71%.

$^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 6.65$ (dd, $J = 2.6$ & 1.3 Hz, 1H, 3-H), 6.76 (t, $J = 7.6$ Hz, 1H, 5-H), 7.20-7.73 (m, 7H, 2-H, 6-H, $\text{CH}_{\text{Phenyl}}$), 8.01 (dd, $J = 8.1$ & 1.3 Hz, 1H, 4-H), 8.46 (sbr, 1H, NH).

¹³C-NMR (75 MHz, CDCl₃): δ = 103.8, 120.7, 121.0, 122.6, 125.0, 126.3, 128.1, 128.9, 129.8, 130.0, 140.0, 155.3.

MS (EI, 70 eV): *m/z* (%) = 193 (100) [M]⁺, 165 (12).

C₁₄H₁₁N (193.24).

Preparation of 7-(7-Methoxy-benzo[1,3]dioxol-5-yl)-indole-1-carboxylic acid diethylamide (14e)

Following the General Procedure IV, a solution of 7-bromo-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (175 mg, 476 μmol), 1.2 equiv 3-methoxy-4,5-methylenedioxyphenyl boronic acid² (112 mg, 570 μmol), 5 mol% Pd(PPh₃)₄ (55 mg, 47 μmol) and 3 equiv K₃PO₄ (303 mg, 1.43 mmol) in 5 ml DMF was stirred at 80 °C for 44 h. Column chromatography on silica gel (hexanes / EtOAc = 20:1), gave the pure title compound as a colourless oil.

Isol. yield: 83%.

¹H-NMR (300 MHz, acetone-d₆): δ = 0.94 (t, *J* = 7.1 Hz, 6H, CH₃), 3.09 (s_{br}, 4H, CH₂), 3.90 (s, 3H, OCH₃), 6.00 (s, 2H, OCH₂O), 6.59 (d, *J* = 1.5 Hz, 1H, 2'-H), 6.64 (d, *J* = 1.5 Hz, 1H, 6'-H), 6.67 (d, *J* = 3.4 Hz, 1H, 2-H), 7.12 (dd, *J* = 7.3 & 1.3 Hz, 1H, 6-H), 7.16 (t, *J* = 7.3 Hz, 1H, 5-H), 7.36 (d, *J* = 3.4 Hz, 1H, 3-H), 7.59 (dd, *J* = 7.7 & 1.3 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 12.3, 14.3, 41.7, 42.9, 56.5, 101.5, 102.3, 104.9, 108.0, 120.3, 121.6, 125.1, 127.3, 127.5, 130.3, 132.8, 134.2, 134.5, 143.6, 148.8, 153.9.

MS (EI, 70 eV): *m/z* (%) = 366 (100) [M]⁺, 295 (8), 237 (6), 209 (6), 100 (40) [CONEt₂]⁺, 72 (19) [NEt₂]⁺.

HRMS: calcd for C₂₁H₂₂N₂O₄: 366.1580, found: 366.1583.

C₂₁H₂₂N₂O₄ (366.41).

Preparation of 7-(7-Methoxy-benzo[1,3]dioxol-5-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide

Following the General Procedure IV, a solution of 7-iodo-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (152 mg, 367 μmol), 1.2 equiv 3-methoxy-4,5-methylenedioxyphenyl boronic acid (86 mg, 440 μmol), 10 mol% Pd(PPh₃)₄ (43 mg, 37 μmol) and 3 equiv K₃PO₄ (234 mg, 1.1 mmol) in

² 3-Methoxy-4,5-methylenedioxyphenyl boronic acid was prepared via the known 3-methoxy-4,5-methylenedioxyphenyl bromide (Magnus, P.; Sebhat, I. K. *Tetrahedron* **1998**, 54, 15509-15524) and halogen-lithium exchange / B(OMe)₃ quench (41%, not optimized).

4 ml DMF was stirred at 80 °C for 16 h. Column chromatography on silica gel (hexanes / EtOAc = 20:1), gave the pure title compound as a slightly yellow foam.

Isol. yield: 75%.

¹H-NMR (300 MHz, acetone-*d*₆): δ = 0.34 (s, 9H, SiMe₃), 0.62 (t, *J* = 7.2 Hz, 3H, CH₃), 0.90 (t, *J* = 7.2 Hz, 3H, CH₃), 2.38 (sext, *J* = 7.2 Hz, 1H, CH₂), 2.59 (sext, *J* = 7.2 Hz, 1H, CH₂), 2.77 (sext, *J* = 7.0 Hz, 1H, CH₂), 2.99 (sext, *J* = 7.2 Hz, 1H, CH₂), 3.92 (s, 3H, OCH₃), 6.01 (s, 2H, OCH₂O), 6.67, 6.68 (2× s, 2H, 2'-H, 6'-H), 6.90 (s, 1H, 3-H), 7.12 (dd, *J* = 7.3 & 1.5 Hz, 1H, 6-H), 7.17 (dd, *J* = 7.5 & 7.3 Hz, 1H, 5-H), 7.59 (dd, *J* = 7.5 & 1.5 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.4, 12.9, 14.4, 42.5, 43.5, 56.6, 101.7, 102.3, 108.4, 114.9, 120.3, 121.3, 125.7, 127.1, 129.7, 130.0, 133.8, 134.7, 135.3, 143.6, 148.8, 155.1.

MS (EI, 70 eV): *m/z* (%) = 438 (23) [M]⁺, 425 (100), 100 (16) [CONEt₂]⁺, 72 (10) [NEt₂]⁺.

C₂₄H₃₀N₂O₄Si (438.60).

Preparation of 7-(2-Fluoro-phenyl)-indole-1-carboxylic acid diethylamide (14b)

Following the General Procedure IV, a solution of 7-iodo-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (123 mg, 296 μmol), 1.2 equiv 2-fluorophenylboronic acid (50 mg, 355 μmol), 5 mol% Pd(PPh₃)₄ (17 mg, 15 μmol) and 3 equiv K₃PO₄ (189 mg, 888 μmol) in 3.5 ml DMF was stirred at 80 °C for 16 h. Column chromatography on silica gel (hexanes / EtOAc = 10:1 → 5:1), gave the pure title compound as a colourless oil.

Isol. yield: 82%.

¹H-NMR (300 MHz, CDCl₃): δ = 0.96 (s_{br}, 6H, CH₃), 3.09 (s_{br}, 4H, CH₂), 6.63 (d, *J* = 3.4 Hz, 1H, 3-H), 7.02-7.44 (m, 7H, 2-H, 5-H, 6-H, 3'-H, 4'-H, 5'-H, 6'-H), 7.63 (dd, *J* = 7.7 & 1.4 Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 13.3 (s_{br}), 41.9 (s_{br}), 105.1, 115.4 (d, *J* = 21 Hz), 121.1, 121.5, 121.6, 124.4 (s_{br}), 126.4, 127.1, 127.9 (d, *J* = 16 Hz), 129.1 (d, *J* = 8 Hz), 130.5, 131.4 (s_{br}), 133.6, 153.6, 159.8 (d, *J* = 246 Hz).

MS (EI, 70 eV): *m/z* (%) = 310 (100) [M]⁺, 209 (22), 100 (96) [CONEt₂]⁺, 72 (38) [NEt₂]⁺.

HRMS: calcd for C₁₉H₁₉FN₂O: 310.1481, found: 310.1483.

C₁₉H₁₉FN₂O (310.37).

Preparation of 7-(2-Methoxy-phenyl)-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (14c)

Following the General Procedure IV, a solution of 7-iodo-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (150 mg, 366 μ mol), 1.2 equiv 2-methoxy boronic acid (67 mg, 439 μ mol), 10 mol% Pd(PPh₃)₄ (43 mg, 37 μ mol) and 3 equiv K₃PO₄ (234 mg, 1.1 mmol) in 4 ml DMF was stirred at 80 °C for 15 h. Column chromatography on silica gel (hexanes / EtOAc = 40:1), gave the pure title compound as a yellow oil.

NMR signals are split up because of two different rotamers.

Isol. yield: 70%.

¹H-NMR (300 MHz, CDCl₃): δ = 0.33 (s, 9H, SiMe₃), 0.58, 0.66, 0.86 (3x t, J = 7.2 Hz, 6H, CH₃), 2.25, 2.27, 2.39, 2.62, 2.81, 2.84 (6x sext, J = 7.2 Hz, 4H, CH₂), 3.63, 3.81 (2x s, 3H, OCH₃), 6.80-7.41 (m, 7H), 7.52-7.63 (m, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = -0.4+0.3, 13.0+13.1, 14.7+14.9, 42.6+42.9, 43.5+43.6, 55.2+55.5, 110.0+111.1, 114.5+114.8, 120.0+120.1, 120.5+120.6, 120.7+121.8, 122.7+124.1, 126.2+127.1, 127.4+128.4, 128.8+129.1, 129.3+130.1, 131.9+132.3, 135.7+136.0, 141.1+141.3, 154.6+154.8, 156.1+157.2.

MS (EI, 70 eV): m/z (%) = 394 (17) [M]⁺, 380 (100), 100 (8) [CONEt₂]⁺.

HRMS: calcd for C₁₉H₁₉FN₂O: 394.2077, found: 394.2083.

C₂₃H₃₀N₂O₂Si (394.58).

Preparation of 7-(3,4-Dimethoxy-phenyl)-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (14d)

Following the General Procedure IV, a solution of 7-iodo-2-trimethylsilanyl-indole-1-carboxylic acid diethylamide (77.5 mg, 187 μ mol), 1.2 equiv 3,4-dimethoxy boronic acid (41 mg, 224 μ mol), 5 mol% Pd(PPh₃)₄ (11 mg, 9 μ mol) and 3 equiv K₃PO₄ (119 mg, 561 μ mol) in 2.5 ml DMF was stirred at 80 °C for 15 h. Column chromatography on silica gel (hexanes / EtOAc = 8:1), gave the pure title compound as a colourless solid.

Isol. yield: 99%.

mp.: 123-125 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 0.38 (s, 9H, SiMe₃), 0.65 (t, J = 7.2 Hz, 3H, CH₂CH₃), 0.89 (t, J = 7.2 Hz, 3H, CH₂CH₃), 2.29 (sext, J = 7.2 Hz, 1H, CH₂), 2.53 (sext, J = 7.0 Hz, 1H, CH₂), 2.64 (sext, J = 7.2 Hz, 1H, CH₂), 2.97 (sext, J = 7.2 Hz, 1H, CH₂), 3.94 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃),

6.89 (s, 1H, 3-H), 6.96 (d, $J = 8.2$ Hz, 1H, 5'-H), 7.07-7.29 (m, 4H, 5-H, 6-H, 2'-H, 6'-H), 7.52-7.63 (m, 1H, 4-H), 7.60 (d, $J = 7.6$ Hz, 1H, 4-H).

^{13}C -NMR (75 MHz, CDCl_3): $\delta = -0.3, 12.8, 14.3, 42.4, 43.4, 56.2, 56.3, 111.4, 112.3, 114.9, 120.1, 121.3, 125.9, 127.3, 130.0, 132.4, 135.4, 141.5, 144.7, 148.6, 148.8, 155.1$.

MS (EI, 70 eV): m/z (%) = 424 (81) $[\text{M}]^+$, 410 (100), 352 (5), 336 (5), 278 (9), 264 (5), 207 (5), 100 (62) $[\text{CONEt}_2]^+$, 72 (40) $[\text{NEt}_2]^+$.

HRMS: calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}$: 424.2182, found: 424.2184.

$\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}$ (424.61).

Preparation of 2-(1-Diethylcarbamoyl-1*H*-indol-7-yl)-benzoic acid ethyl ester (16c)

Following the General Procedure IV, a solution of 7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (75 mg, 181 μmol), 1.2 equiv 2-bromo-benzoic acid ethyl ester (50 mg, 217 μmol), 5 mol% $\text{Pd}(\text{PPh}_3)_4$ (11 mg, 9 μmol) and 3 equiv K_3PO_4 (115 mg, 543 μmol) in 2.5 ml DMF was stirred at 80 $^\circ\text{C}$ for 40 h. Column chromatography on silica gel (hexanes / EtOAc = 8:1 $\rightarrow$ 5:1), gave the pure title compound as a colorless oil.

Isol. yield: 76%.

^1H -NMR (300 MHz, CDCl_3): $\delta = 0.78$ (t, $J = 7.1$ Hz, 3H, OCH_2CH_3), 0.86 (s_{br}, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 2.67-2.98 (m, 2H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 3.08 (s_{br}, 2H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 3.93 (q, $J = 7.1$ Hz, 2H, OCH_2CH_3), 6.61 (d, $J = 3.4$ Hz, 1H, 3-H), 6.99 (dd, $J = 7.2$ & 0.8 Hz, 1H, 6-H), 7.12 (d, $J = 3.4$ Hz, 1H, 2-H), 7.18 (dd, $J = 7.9$ & 7.2 Hz, 1H, 5-H), 7.35-7.48 (m, 2H, 4'-H, 6'-H), 7.48-7.62 (m, 2H, 4-H, 5'-H), 7.96 (d, $J = 7.6$ Hz, 1H, 3'-H).

^{13}C -NMR (75 MHz, CDCl_3): $\delta = 13.2, 13.5, 41.8, 60.5, 104.6, 120.1, 120.9, 125.0, 126.5, 127.1, 127.2, 129.6, 130.3, 130.3, 131.3, 131.4, 133.1, 140.2, 153.4, 167.4$.

MS (EI, 70 eV): m/z (%) = 364 (59) $[\text{M}]^+$, 318 (8), 248 (100), 222 (32), 191 (13), 163 (5), 100 (42) $[\text{CONEt}_2]^+$, 72 (28) $[\text{NEt}_2]^+$.

$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3$ (364.44).

Preparation of Pyrrolo[3,2,1-de]phenanthridin-7-one³ (17)

In the reaction described for 2-(1-diethylcarbamoyl-1*H*-indol-7-yl)-benzoic acid ethyl ester the title compound was isolated as a side product (colourless solid) after column chromatography on silica gel (hexanes / EtOAc = 8:1 → 5:1).

Isol. yield: 13%.

mp.: 146-147 °C (hexanes) [Lit. 3: 145-147 °C].

¹H-NMR (300 MHz, CDCl₃): δ = 6.95 (d, *J* = 3.5 Hz, 1H, 4-H), 7.52 (t, *J* = 7.7 Hz, 1H, 2-H), 7.60-7.69 (m, 1H, 9-H), 7.77-7.88 (m, 2H, 10-H, 11-H), 8.06-8.13 (m, 2H, 5-H, 1-H), 8.33 (d, *J* = 8.0 Hz, 1H, 3-H), 8.64 (d, *J* = 7.6 Hz, 1H, 8-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 111.3, 116.8, 116.9, 118.8, 122.9, 123.2, 123.7, 124.3, 125.7, 128.4, 128.9, 129.8, 133.4, 134.8, 160.9.

MS (EI, 70 eV): *m/z* (%) = 219 (100) [M]⁺, 191 (12), 163 (8).

HRMS: calcd for C₁₅H₉NO: 219.0684, found: 219.0675.

C₁₅H₉NO (219.24).

Preparation of 6-(1-Diethylcarbamoyl-1*H*-indol-7-yl)-benzo[1,3]dioxole-5-carboxylic acid ethyl ester (16b)

Following the General Procedure IV, a solution of 7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (15 mg, 36 μmol), 1.2 equiv 6-bromo-benzo[1,3]dioxole-5-carboxylic acid ethyl ester⁴ (12 mg, 43 μmol), 5 mol% Pd(PPh₃)₄ (2 mg, 1.8 μmol) and 3 equiv K₃PO₄ (23 mg, 108 μmol) in 1 ml DMF was stirred at 80 °C for 16 h. Column chromatography on silica gel (hexanes / EtOAc = 8:1 → 5:1), gave the pure title compound as a colorless solid.

Isol. yield: 90%.

mp.: 108-110 °C (CHCl₃).

¹H-NMR (300 MHz, CDCl₃): δ = 0.74 (t, *J* = 7.1 Hz, 3H, OCH₂CH₃), 0.96 (s_{br}, 6H, N(CH₂CH₃)₂), 2.90-3.10 (m, 2H, N(CH₂CH₃)₂), 3.19 (s_{br}, 2H, N(CH₂CH₃)₂), 3.86 (q, *J* = 7.1 Hz, 2H, OCH₂CH₃),

³ Tsuge, O.; Hatta, T., Tsuchiyama, H. *Chem. Lett.* **1998**, 155-156.

⁴ 6-Bromo-benzo[1,3]dioxole-5-carboxylic acid ethyl ester was synthesized from piperonylic acid via acid chloride formation and conversion with ethanol (92%: 1. SOCl₂ / reflux; 2. EtOH / NEt₃ / rt) and subsequent bromination (94%: NBS / CH₃CN / rt).

6.01-6.07 (m, 2H, OCH₂O), 6.60 (d, $J = 3.3$ Hz, 1H, 3-H), 6.85 (s, 1H, 6'-H), 6.97 (d, $J = 7.3$ Hz, 1H, 6-H), 7.09 (d, $J = 3.3$ Hz, 1H, 2-H), 7.16 (dd, $J = 7.9$ & 7.3 Hz, 1H, 5-H), 7.44 (s, 1H, 3'-H), 7.57 (d, $J = 7.9$ Hz, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): $\delta = 13.6, 13.7$ (br.), 42.5 (br.), 60.6, 102.1, 104.9, 110.3, 112.4, 120.3, 121.3, 125.0, 126.6, 127.6, 128.0, 129.9, 142.5, 147.1, 150.4, 153.6, 160.2, 166.6.

MS (EI, 70 eV): m/z (%) = 408 (60) [M]⁺, 362 (15), 292 (100), 281 (25), 264 (49), 235 (12), 207 (43), 177 (12), 100 (37) [CONEt₂]⁺, 72 (27) [NEt₂]⁺.

C₂₃H₂₄N₂O₅ (408.45).

Preparation of [1,3]Dioxolo[4,5-*j*]pyrrolo[3,2,1-*de*]phenanthridin-7-one (hippadine)⁵ (2b)

In the reaction described for 6-(1-diethylcarbamoyl-1*H*-indol-7-yl)-benzo[1,3]dioxole-5-carboxylic acid ethyl ester the title compound was isolated as a side product (colourless solid) after column chromatography on silica gel (hexanes / EtOAc = 8:1 → 5:1).

Isol. yield: 7%.

mp.: 217 °C (hexanes) [Lit. 3: 218-219 °C (EtOH); Lit 5e: 217-218 °C].

¹H-NMR (300 MHz, CDCl₃): $\delta = 6.15$ (s, 2H, OCH₂O), 6.88 (d, $J = 3.5$ Hz, 1H, 4-H), 7.46 (t, $J = 7.7$ Hz, 1H, 2-H), 7.65 (s, 1H, 11-H), 7.74 (d, $J = 7.7$ Hz, 1H, 3-H), 7.91 (d, $J = 7.7$ Hz, 1H, 1-H), 7.97 (s, 1H, 8-H), 8.03 (d, $J = 3.5$ Hz, 1H, 5-H).

¹³C-NMR (75 MHz, CDCl₃): $\delta = 101.9, 102.5, 108.2, 110.9, 116.9, 118.6, 121.3, 122.6, 122.7, 123.6, 124.1, 128.6, 131.8, 148.7, 152.8, 158.3$.

MS (EI, 70 eV): m/z (%) = 263 (100) [M]⁺, 207 (18), 183 (39), 108 (13).

HRMS: calcd for C₁₆H₉NO₃: 263.0582, found: 263.0587.

C₁₆H₉NO₃ (263.25).

⁵ (a) Ghosal, S.; Rao, P. H.; Jaiswal, D. K.; Kumar, Y.; Frahm, A. W. *Phytochemistry* **1981**, 20, 2003. (b) Ali, A. A.; Mesbah, M. K.; Frahm, A. W. *Planta Med.* **1981**, 43, 407. (c) Chattopadhyay, S.; Chattopadhyay, U.; Marthur, P. P.; Saini, K. S.; Ghosal, S. *Planta Med.* **1983**, 49, 252. (d) Harrowven, D. C.; Lai, D.; Lucas, M. C. *Synthesis* **1999**, 1300-1302. (e) Hutchings, R. H.; Meyers, A. I. *J. Org. Chem.* **1996**, 61, 1004.

Preparation of 7-(2-Diethylcarbamoyl-4,5-dimethoxy-phenyl)-indole-1-carboxylic acid diethylamide (16a)

Following the General Procedure IV, a solution of 7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (100 mg, 241 μ mol), 1.2 equiv 2-bromo-*N,N*-diethyl-4,5-dimethoxy-benzamide⁶ (92 mg, 290 μ mol), 10 mol% Pd(PPh₃)₄ (28 mg, 24 μ mol) and 3 equiv K₃PO₄ (153 mg, 0.72 mmol) in 3 ml DMF was stirred at 80 °C for 40 h. Column chromatography on silica gel (hexanes / EtOAc = 5:1 $\rightarrow$ 1:1), gave the pure title compound as a slightly yellow foam.

Isol. yield: 40%.

¹H-NMR (300 MHz, CDCl₃): δ = 0.70-1.30 (m, 12H, NCH₂CH₃), 2.90-3.50 (m, 8H, N(CH₂CH₃)₂), 3.87 (s, 6H, OCH₃), 6.59 (d, *J* = 3.3 Hz, 1H, 3-H), 6.77-7.00 (m, 2H, 6-H, 6'-H), 7.03-7.12 (m, 1H, 5-H), 7.17 (d, *J* = 3.3 Hz, 1H, 2-H), 7.53 (d, *J* = 8.9 Hz, 1H, 4-H), 7.99 (s, 1H, 3'-H).

MS (EI, 70 eV): *m/z* (%) = 451 (100) [M]⁺, 378 (55), 335 (8), 281 (11), 236 (7), 207 (24), 100 (70) [CONEt₂]⁺, 72 (30) [NEt₂]⁺.

C₂₆H₃₃N₃O₄ (451.56).

Preparation of 9,10-Dimethoxy-pyrrolo[3,2,1-*de*]phenanthridin-7-one (pratosine)⁷ (2a)

In the reaction described for 7-(2-diethylcarbamoyl-4,5-dimethoxy-phenyl)-indole-1-carboxylic acid diethylamide the title compound was isolated as a side product (colourless solid) after column chromatography on silica gel (hexanes / EtOAc = 5:1 $\rightarrow$ 1:1).

Isol. yield: 18%.

mp.: 232 °C (CH₂Cl₂) [Lit. 3: 238-239 °C (CH₃CN); Lit 5e: 234-235 °C].

¹H-NMR (300 MHz, CDCl₃): δ = 4.02 (s, 3H, OCH₃), 4.08 (s, 3H, OCH₃), 6.86 (d, *J* = 3.4 Hz, 1H, 4-H), 7.44 (t, *J* = 7.7 Hz, 1H, 2-H), 7.58 (s, 1H, 11-H), 7.70 (d, *J* = 7.7 Hz, 1H, 3-H), 7.90 (d, *J* = 7.7 Hz, 1H, 1-H), 7.94 (s, 1H, 8-H), 8.01 (d, *J* = 3.4 Hz, 1H, 5-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 56.4, 56.5, 103.9, 110.2, 110.9, 116.8, 118.4, 120.9, 122.6, 123.7, 124.1, 128.7, 129.6, 131.3, 149.9, 153.9, 158.6.

⁶ 2-Bromo-*N,N*-diethyl-4,5-dimethoxy-benzamide was synthesized from 2-Bromo-4,5-dimethoxybenzoic acid via acid chloride formation and conversion with diethylamine (93%: 1. SOCl₂ / reflux; 2. excess HNEt₂ / rt).

⁷ (a) Ghosal, S.; Saini, K. S.; Frahm, A. W. *Phytochemistry* **1983**, 22, 2305. (b) Martin, S. F. In *The Alkaloids: The Amaryllidaceae Alkaloids*, Vol. 30; Brossi, A., Ed.; Academic Press: San Diego, 1987; p. 251-376. (c) Grundon, M. F. *Natural Products Reports* **1989**, 6, 79. (d) Miki, Y.; Shirokoshi, H.; Matsushita, K.-i. *Tetrahedron Lett.* **1999**, 40, 4347.

MS (EI, 70 eV): m/z (%) = 279 (100) $[M]^+$, 264 (32) $[M - CH_3]$, 236 (50), 221 (12), 207 (15), 193 (15), 165 (10).

HRMS: calcd for $C_{17}H_{13}NO_3$: 279.0895, found: 279.0892.

$C_{17}H_{13}NO_3$ (279.29).

Preparation of 7-Pyridin-3-yl-indole-1-carboxylic acid diethylamide (14g)

Following the General Procedure IV, a solution of 7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2-trimethylsilyl-indole-1-carboxylic acid diethylamide (51 mg, 123 μ mol), 2.4 equiv 3-bromopyridine (47 mg, 295 μ mol), 5 mol% $Pd(PPh_3)_4$ (7 mg, 6 μ mol) and 3 equiv K_3PO_4 (78 mg, 369 μ mol) in 2 ml DMF was stirred at 80 °C for 16 h. Column chromatography on silica gel (hexanes / EtOAc = 2:1), gave the pure title compound as a colorless oil.

Isol. yield: 89%.

1H -NMR (300 MHz, $CDCl_3$): δ = 0.91 (s_{br} , 6H, CH_3), 3.02 (s_{br} , 4H, CH_2), 6.66 (d, J = 3.5 Hz, 1H, 3-H), 7.11 (dd, J = 7.3 & 1.0 Hz, 1H, 6-H), 7.19 (d, J = 3.5 Hz, 1H, 2-H), 7.25 (dd, J = 7.9 & 7.3 Hz, 1H, 5-H), 7.34 (dd, J = 7.8 & 4.8 Hz, 1H, 5'-H), 7.64 (dd, J = 7.9 & 1.0 Hz, 1H, 4-H), 7.75 (dt, J = 7.8 & 1.8 Hz, 1H, 6'-H), 8.55 (dd, J = 4.8 & 1.8 Hz, 1H, 4'-H), 8.63 (d, J = 1.8 Hz, 1H, 2'-H),.

^{13}C -NMR (75 MHz, $CDCl_3$): δ = 13.2, 42.3, 105.4, 121.3, 121.9, 123.5, 124.3, 125.8, 127.4, 130.6, 133.3, 136.1, 136.1, 148.5, 148.9, 153.6.

MS (EI, 70 eV): m/z (%) = 293 (100) $[M]^+$, 262 (19), 193 (21), 166 (7), 139 (8), 100 (80) $[CONEt_2]^+$, 72 (46) $[NEt_2]^+$.

HRMS: calcd for $C_{18}H_{19}N_3O$: 293.1528, found: 293.1530.

$C_{18}H_{19}N_3O$ (293.36).

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-1*H*-indole (4)

To a solution of indole (586 mg, 5.0 mmol) in 10 ml anhydrous THF at 0 °C was added a solution of *n*-BuLi (solution in hexanes, 6.0 mmol) dropwise. After stirring for 15 min, chloro-di-*tert*-butylphosphine (1.14 ml, 6.0 mmol) was added dropwise. The mixture was allowed to stir and warm to room temperature over several hours. After addition of 2 ml MeOH, most of the solvent was removed under reduced pressure and the residue was suspended in 30 ml MeOH and cooled to 0 °C. Slow addition of excess H_2O_2 (1 ml of 30% solution, approx. 8 mmol) caused the suspended material to dissolve over a 30 min period resulting in a light yellow solution. After adding 8 ml Na_2SO_3 (2 M solution) dropwise, the solution was stirred for 2 h, allowed to warm to room temperature, treated with 12 ml HCl (10% solution), and stirred for another hour. Most of the MeOH was removed under reduced pressure, and the remaining residue was poured into 40 ml H_2O and extracted with CH_2Cl_2 (3 x 50 ml). The combined organics were dried (Na_2SO_4) and evaporated to give an orange solid.

Purification by flash chromatography (1% MeOH / CH₂Cl₂) provided the title compound as a white solid.

Isol. yield: 78%.

mp.: 166-167 °C.

¹H-NMR (200 MHz, CDCl₃): δ = 1.31 (d, *J* = 14.7 Hz, 18H, CH₃), 6.67 (t, *J* = 2.4 Hz, 1H; 3-H), 7.57 (d, *J* = 7.4 Hz, 1H, 4-H), 7.1-7.3 (m, 3H, 2-H, 5-H, 6-H), 8.53 (d, *J* = 7.8 Hz, 1H, 7-H).

¹³C-NMR (50 MHz, CDCl₃): δ = 26.5, 38.4 (d, *J* = 69.2 Hz), 106.9 (d, *J* = 4.9 Hz), 116.1, 120.0, 121.3, 123.2, 126.2 (d, *J* = 4.8 Hz), 129.0 (d, *J* = 5.4 Hz), 141.4.

³¹P-NMR (81 MHz, CDCl₃): δ = 63.0.

IR (KBr) ν_{max} = 2973, 1475, 1445, 1266, 1175, 1133, 994, 749, 657 cm⁻¹.

MS (CI, isobutane): *m/z* (%) = 277 (57) [M]⁺, 165 (18), 164 (18), 117 (11), 116 (10), 89 (12), 57 (100).

HRMS: calcd for C₁₆H₂₄NOP: 277.1596, found: 277.1577.

Elemental Analysis: calcd for C₁₆H₂₄NOP: C, 69.29; H, 8.72; N, 5.05. found: C, 69.41; H, 8.77; N, 5.08.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-7-trimethylsilyl-1*H*-indole (5a)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (100 mg, 0.36 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 0.79 mmol). After 2 h, TMSCl (0.11 ml, 0.90 mmol) was added. Purification by column chromatography (CH₂Cl₂) provided the product as a white solid.

Isol. yield: 72%.

mp.: 127-128 °C.

¹H-NMR (500 MHz, {³¹P}, CDCl₃): δ = 0.47 (s, 9H, SiMe₃), 1.25 (s, 18H, CH₃), 6.72 (d, *J* = 3.6 Hz, 1H, 3-H), 7.18 (t, *J* = 7.5 Hz, 1H, 5-H), 7.28 (d, *J* = 3.6 Hz, 1H, 2-H), 7.59 (dd, *J* = 7.5 & 1.3 Hz, 1H, 6-H), 7.64 (dd, *J* = 7.5 & 1.3 Hz, 1H, 4-H).

¹³C-NMR (50 MHz, CDCl₃): δ = 4.3, 27.8, 39.5 (d, *J* = 6.7 Hz), 108.5 (d, *J* = 5.8 Hz), 121.5, 121.8, 127.3 (d, *J* = 5.7 Hz), 128.2, 130.3 (d, *J* = 5.2 Hz), 133.5, 145.7.

³¹P-NMR (203 MHz, CDCl₃): δ = 61.8.

IR (KBr) ν_{max} = 2953, 2901, 1477, 1392, 1259, 1235, 1183, 1144, 1128, 841, 727, 658 cm⁻¹.

MS (EI, 70 eV): *m/z* (%) = 349 (1) [M]⁺, 224 (100), 278 (46), 236 (26), 222 (41), 220 (47), 190 (21), 174 (12).

HRMS: calcd for C₁₉H₃₂NOPSi: 349.1991, found: 349.1988.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-7-methyl-1*H*-indole (5b)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (140 mg, 0.50 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 1.1 mmol). After 2 h, MeI (70 μ l, 1.1 mmol) was added. Purification by column chromatography (1% MeOH / CH₂Cl₂) provided the product as a white solid.

Isol. yield: 93%.

mp.: 52-53 °C.

¹H-NMR (200 MHz, CDCl₃): δ = 1.33 (d, J = 14.7 Hz, 18H, CH₃), 2.88 (s, 3H, 7-CH₃), 6.70 (dd, J = 3.5 & 1.5 Hz, 1H, 3-H), 7.08-7.14 (m, 2H, 5-H, 6-H), 7.30-7.38 (m, 1H, 2-H), 7.37-7.48 (m, 1H, 4-H).

¹³C-NMR (75 MHz, CDCl₃): δ = 23.9, 27.2, 39.6 (d, J = 69.5 Hz), 107.8 (d, J = 6.3 Hz), 118.2, 121.9, 126.4, 127.5, 127.8 (d, J = 6.3 Hz), 131.3 (d, J = 5.3 Hz), 140.4.

³¹P-NMR (81 MHz, CDCl₃): δ = 62.1.

IR (KBr) ν_{max} = 2964, 1477, 1448, 1402, 1262, 1232, 1205, 1125, 1092, 985, 815, 788, 680, 657 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 291 (42) [M]⁺, 235 (17), 179 (55), 178 (77), 130 (39), 105 (21), 77 (13), 57 (100).

HRMS: calcd for C₁₇H₂₆NOP: 291.1752; found: 291.1757.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-7-(3-methyl-but-2-enyl)-1*H*-indole (5c)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (277 mg, 1.0 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 2.1 mmol). After 2 h, 1-bromo-3-methylbut-2-ene (0.24 ml, 2.1 mmol) was added. Purification by column chromatography (CH₂Cl₂) provided the product as a white crystalline solid.

Isol. yield: 87%.

mp.: 98-99 °C (hexanes).

¹H-NMR (200 MHz, CDCl₃): δ = 1.32 (d, J = 15.0 Hz, 18H, CH₃), 1.78 (s, 6H, CH=C(CH₃)₂), 4.19 (d, J = 10.1 Hz, 2H, CH₂), 5.38 (m, 1H, CH), 6.73 (dd, J = 4.8 & 2.0 Hz, 1H, 3-H), 7.10-7.22 (m, 2H, 5-H, 6-H), 7.32-7.37 (m, 1H, 2-H), 7.43 (m, 1H, 4-H).

¹³C-NMR (50 MHz, CDCl₃): δ = 17.9, 25.8, 27.1, 33.2, 39.7 (d, J = 6.8 Hz), 108.0 (d, J = 6.0 Hz), 118.2, 122.1, 125.0, 126.0, 128.0 (d, J = 5.8 Hz), 130.2, 130.7, 131.4 (d, J = 4.2 Hz), 140.0.

³¹P-NMR (81 MHz, CDCl₃): δ = 62.5.

IR (KBr) ν_{max} = 2968, 2908, 2869, 1477, 1448, 1408, 1369, 1259, 1225, 1203, 1178, 1127, 1089, 983 cm⁻¹.

MS (CI, isobutane): m/z (%) = 345 (8) $[M]^+$, 232 (12), 184 (17), 176 (14), 168 (14), 105 (10), 63 (10), 57 (100).

HRMS: calcd for $C_{21}H_{32}NOP$: 345.2222, found: 345.2207.

X-ray analysis, see Appendix.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-1*H*-indole-7-carbaldehyde (5d)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (140 mg, 0.5 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 1.1 mmol). After 2 h, anhydrous DMF (90 μ l, 1.1 mmol) was added. Purification by column chromatography (2% MeOH / CH_2Cl_2) provided the product as a white solid.

Isol. yield: 53%.

mp.: 105-107 °C.

1H -NMR (250 MHz, $CDCl_3$): δ = 1.30 (d, J = 14.9 Hz, 18H, CH_3), 6.90 (d, J = 3.4 Hz, 1H, 3-H), 7.31 (dd, J = 7.3 & 7.7 Hz, 1H, 5-H), 7.40 (dd, J = 3.2 & 1.9 Hz, 1H, 2-H), 7.75 (d, J = 7.3 Hz, 1H, 6-H), 7.80 (d, J = 7.7 Hz, 1H, 4-H), 10.56 (s, 1H, CHO).

^{31}P -NMR (81 MHz, $CDCl_3$): δ = 63.3.

IR (KBr) ν_{max} = 2969, 2902, 2872, 1683, 1478, 1415, 1400, 1263, 1248, 1167, 1129, 1094, 663 cm^{-1} .

MS (CI, isobutane): m/z (%) = 306 (100) $[M + H]^+$, 277 (85), 221 (30), 165 (59), 161 (11), 117 (14), 57 (37).

$C_{17}H_{24}NO_2P$ (305.35).

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-7-diphenylphosphanyl-1*H*-indole (5e)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (140 mg, 0.5 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 1.1 mmol). After 2 h, chlorodiphenylphosphine (0.20 ml, 1.1 mmol) was added. Purification by column chromatography (CH_2Cl_2) provided the product as a white solid.

Isol. yield: 44%.

mp.: 161-165 °C.

1H -NMR (250 MHz, $CDCl_3$): δ = 1.19 (d, J = 14.6 Hz, 18H, CH_3), 6.91-7.13 (m, 2H), 7.20-7.42 (m, 11H), 7.54 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 3.7 Hz, 1H).

^{13}C -NMR (63 MHz, $CDCl_3$): δ = 27.2, 39.5 (d, J = 66.8 Hz), 108.2 (d, J = 5.7 Hz), 121.6 (d, J = 51.5 Hz), 125.8 (d, J = 30.5 Hz), 127.3, 127.8 (d, J = 7.6 Hz), 128.3 (d, J = 3.8 Hz), 131.0-131.5 (m, 2C), 133.3, 133.8 (d, J = 21.0 Hz), 141.9 (d, J = 17.2 Hz), 144.4 (d, J = 24.8 Hz).

³¹P-NMR (81 MHz, CDCl₃): δ = 62.2 (d, *J* = 8.7 Hz), -4.8 (d, *J* = 8.7 Hz).

IR (KBr) ν_{max} = 2964, 1477, 1435, 1255, 1235, 1208, 1180, 1119, 1075, 693 cm⁻¹.

MS (EI, 70 eV): *m/z* (%) = 461 (6) [M]⁺, 420 (21), 404 (100), 364 (18), 347 (69), 258 (15), 222 (85), 183 (33), 154 (16), 107 (22), 77 (30), 57 (56).

HRMS: calcd for C₂₈H₃₃NOP₂: 461.2037; found: 461.2030.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-7-iodo-1*H*-indole (5f)

According to the General Procedure II, a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (140 mg, 0.5 mmol) in 10 ml anhydrous THF at -40 °C was treated with *n*-BuLi (solution in hexanes, 1.1 mmol). After 2 h, a solution of I₂ (279 mg, 1.1 mmol) was added and the solution was allowed to warm to room temperature. 25 ml aqueous Na₂S₂O₃ (2 M solution) was added and the mixture was extracted with CH₂Cl₂ (3 x 20 ml). The combined organics were dried (Na₂SO₄) and evaporated to provide a light yellow oil. Purification by column chromatography (1% MeOH / CH₂Cl₂) provided the title product as a colourless oil which crystallized on standing.

Isol. yield: 78%.

mp.: 122-123 °C (hexanes).

¹H-NMR (300 MHz, CDCl₃): δ = 1.34 (d, *J* = 14.7 Hz, 18H, CH₃), 6.70 (d, *J* = 3.6 Hz, 1H, 3-H), 6.85 (t, *J* = 7.6 Hz, 1H, 5-H), 7.35 (t, *J* = 3.1 Hz, 1H, 2-H), 7.55 (d, *J* = 7.6 Hz, 1H, 6-H), 7.98 (dd, *J* = 7.5 & 0.7 Hz, 1H, 4-H).

¹³C-NMR (50 MHz, CDCl₃): δ = 27.2, 40.3 (d, *J* = 65.6 Hz), 77.2, 109.0 (d, *J* = 6.1 Hz), 120.7, 123.6, 129.0, 133.3 (d, *J* = 3.1 Hz), 139.2, 143.6.

³¹P-NMR (81 MHz, CDCl₃): δ = 66.6.

IR (KBr) ν_{max} = 2990, 2970, 1476, 1393, 1360, 1255, 1234, 1180, 1124, 973, 798, 657 cm⁻¹.

MS (EI, 70 eV): *m/z* (%) = 403 (62) [M]⁺, 291 (33), 276 (84), 243 (15), 220 (31), 164 (90), 163 (90), 128 (12), 116 (42), 105 (49), 89 (22), 57 (100).

HRMS: calcd for C₁₆H₂₃INOP: 403.0562; found: 403.0559.

Preparation of 1-(Di-*tert*-butyl-phosphinoyl)-2-trimethylsilyl-1*H*-indole

To a solution of 1-(di-*tert*-butyl-phosphinoyl)-1*H*-indole (277 mg, 1.0 mmol) in 20 ml anhydrous THF at 0 °C was added freshly prepared LDA (2.1 ml, 2.1 mmol, 1.0 M solution prepared by adding *n*-BuLi to a cooled solution of freshly distilled diisopropylamine in anhydrous THF). After stirring for 15 min while maintaining the temperature at 0 °C, TMSCl (0.32 ml, 2.5 mmol) was added and the solution was gradually warmed to room temperature. Aqueous NH₄Cl (10 ml, saturated solution) was added and the

mixture was extracted with CH₂Cl₂ (3 x 30 ml). The combined organics were dried (Na₂SO₄) and evaporated to provide a slightly yellow solid. Purification by column chromatography (CH₂Cl₂) provided the title product as a colourless solid.

Isol. yield: 82%.

mp.: 208-210 °C.

¹H-NMR (500 MHz, CDCl₃): δ = 0.36 (s, 9H, SiMe₃), 1.30 (d, *J* = 15.0 Hz, 18H, CH₃), 7.01 (s, 1H, 3-H), 7.13 (t, *J* = 7.2 Hz, 1H, 5-H), 7.17 (t, *J* = 7.6 Hz, 1H, 6-H), 7.57 (d, *J* = 7.2 Hz, 1H, 4-H), 7.67 (d, *J* = 8.3 Hz, 1H, 7-H).

¹³C-NMR (63 MHz, CDCl₃): δ = 2.6, 27.6, 39.8 (d, *J* = 65.5 Hz), 119.8 (d, *J* = 6.7 Hz), 120.9, 121.0, 122.2, 132.2 (d, *J* = 5.8 Hz), 139.5 (d, *J* = 5.4 Hz), 148.2 (d, *J* = 5.9 Hz).

³¹P-NMR (81 MHz, CDCl₃): δ = 67.0.

IR (KBr) ν_{max} = 2990, 2958, 2897, 1479, 1467, 1239, 1222, 1199, 1171, 1132, 1096, 1028, 843 cm⁻¹.

MS (EI, 70 eV): *m/z* (%) = 349 (3) [M]⁺, 334 (100), 278 (49), 236 (35), 222 (40), 220 (56), 190 (12), 174 (13), 146 (14).

HRMS: calcd for C₁₉H₃₂NOPSi: 349.1991, found: 349.1994.

Elemental Analysis: calcd for C₁₉H₃₂NOPSi: C, 65.29; H, 9.23; N, 4.01. found: C, 65.09; H, 9.26; N, 3.94.

Preparation of 7-(3-Methyl-but-2-enyl)-1*H*-indole (1)

To a solution of 1-(di-*tert*-butyl-phosphinoyl)-7-(3-methyl-but-2-enyl)-1*H*-indole (250 mg, 0.70 mmol) in 15 ml anhydrous toluene was added an excess of LiAlH₄ (133 mg, 3.5 mmol). The mixture was heated to reflux and reaction progress was monitored by GC over several hours. After 1 h the reaction was incomplete, and after 3 h no further progress had been noted so a second portion of LiAlH₄ (95 mg, 2.5 mmol) was added. After another 2 h the reaction mixture was cooled to room temperature and then to 0 °C in an ice bath. Excess LiAlH₄ was quenched by the careful addition of H₂O (5 ml) over several minutes. When all effervescence had ceased, the mixture was transferred to a separatory funnel containing H₂O (50 ml) and extracted with EtOAc (3 x 40 ml). The combined organics were dried (Na₂SO₄) and evaporated to provide a light yellow solid. Purification by flash column (5% EtOAc / hexane) provided the title product as a light yellow solid. The product was characterized by comparison with the literature.⁸

Isol. yield: 44%.

mp.: 35-38 °C (lit.⁸ 43-44 °C).

¹H-NMR (250 MHz, CDCl₃): δ = 1.80 (s, 6H, CH₃), 3.53 (d, *J* = 7.2 Hz, CH₂), 5.40 (m, 1H, CH), 6.56 (dd, *J* = 3.2 & 2.2 Hz, 1H, 3-H), 7.00-7.13 (m, 2H), 7.18 (dd, *J* = 3.2 & 2.5 Hz, 1H), 7.41-7.54 (m, 1H), 8.11 (s, 1H, NH).

(8) Achenbach, H.; Renner, C. *Heterocycles* **1985**, 23, 2075-2081.

Appendix. X-Ray Structure of **5c** (CCDC 207794)

Crystal data for **5c**: $C_{21}H_{32}NOP$, $M_r = 345.4$, monoclinic, $P2_1/c$, $a = 12.4082(11)$, $b = 14.5597(9)$, $c = 11.4867(9)$ Å, $\beta = 107.924(6)^\circ$, $V = 1974.5(3)$ Å³, $Z = 4$, $F(000) = 752$, $D_c = 1.162$ g/cm³, $T = 160$ K. Data were collected on a Siemens P4 Diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). A total of 3868 independent reflections were measured. The structure was solved using direct methods (SHELXTL IRIS) and refined by full-matrix least-squares on F^2 (346 parameters) resulting in R , wR , and GoF values of 3.58 [for 3294 data with $F > 2\sigma(F)$], 8.56, and 2.629 respectively.

Figure 1. Single Crystal X-Ray Structure of **5c** (CCDC 207794)

Table 1. Bond lengths (Å)

N(1)-C(2)	1.405(2)	N(1)-C(7A)	1.432(2)
N(1)-P(8)	1.731(1)	C(2)-C(3)	1.340(3)
C(3)-C(3A)	1.424(2)	C(3A)-C(4)	1.399(2)
C(3A)-C(7A)	1.420(2)	C(4)-C(5)	1.372(3)
C(5)-C(6)	1.388(3)	C(6)-C(7)	1.391(2)
C(7)-C(7A)	1.410(2)	C(7)-C(18)	1.520(2)
P(8)-O(9)	1.476(1)	P(8)-C(10)	1.844(2)
P(8)-C(14)	1.863(2)	C(10)-C(11)	1.537(3)
C(10)-C(12)	1.539(2)	C(10)-C(13)	1.532(3)
C(14)-C(15)	1.532(3)	C(14)-C(16)	1.537(3)
C(14)-C(17)	1.548(3)	C(18)-C(19)	1.498(3)
C(19)-C(20)	1.330(3)	C(20)-C(21)	1.498(3)
C(20)-C(22)	1.497(4)		

Table 2. Bond angles (°)

C(2)-N(1)-C(7A)	106.0(1)	C(2)-N(1)-P(8)	119.0(1)
C(7A)-N(1)-P(8)	134.0(1)	N(1)-C(2)-C(3)	112.1(2)
C(2)-C(3)-C(3A)	107.1(2)	C(3)-C(3A)-C(4)	130.2(2)
C(3)-C(3A)-C(7A)	108.3(1)	C(4)-C(3A)-C(7A)	121.5(2)
C(3A)-C(4)-C(5)	118.3(2)	C(4)-C(5)-C(6)	119.8(2)
C(5)-C(6)-C(7)	124.4(2)	C(6)-C(7)-C(7A)	115.8(2)
C(6)-C(7)-C(18)	116.0(1)	C(7A)-C(7)-C(18)	128.2(1)
N(1)-C(7A)-C(3A)	106.6(1)	N(1)-C(7A)-C(7)	133.2(1)
C(3A)-C(7A)-C(7)	120.1(1)	N(1)-P(8)-O(9)	112.2(1)
N(1)-P(8)-C(10)	104.1(1)	O(9)-P(8)-C(10)	110.7(1)
N(1)-P(8)-C(14)	106.0(1)	O(9)-P(8)-C(14)	108.0(1)
C(10)-P(8)-C(14)	115.8(1)	P(8)-C(10)-C(11)	114.8(1)
P(8)-C(10)-C(12)	105.1(1)	C(11)-C(10)-C(12)	109.1(2)
P(8)-C(10)-C(13)	109.4(1)	C(11)-C(10)-C(13)	109.5(2)
C(12)-C(10)-C(13)	108.8(2)	P(8)-C(14)-C(15)	107.1(1)
P(8)-C(14)-C(16)	119.2(1)	C(15)-C(14)-C(16)	111.1(1)
P(8)-C(14)-C(17)	105.0(1)	C(15)-C(14)-C(17)	108.0(2)
C(16)-C(14)-C(17)	105.9(1)	C(7)-C(18)-C(19)	109.9(1)
C(18)-C(19)-C(20)	127.2(2)	C(19)-C(20)-C(21)	123.8(2)
C(19)-C(20)-C(22)	121.0(2)	C(21)-C(20)-C(22)	115.2(2)