Fluorescent Indolo[3,2-a]phenazines against *Toxoplasma gondii*: Concise Synthesis by Gold-Catalyzed Cycloisomerization with 1,2-Silyl Migration and *ipso*-Iodination Suzuki Sequence

Franziska K. Merkt, Flaminia Mazzone, Shabnam Shaneh Sazzadeh, Lorand Bonda, Larissa K. E. Hinz, Irina Gruber, Karin Buchholz, Christoph Janiak, Klaus Pfeffer, and Thomas J. J. Müller*
# Supporting Information

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1. General Considerations

Reagents, catalysts, and solvents were purchased in reagent grade and used without further purification. Anhydrous THF, CH\textsubscript{2}Cl\textsubscript{2}, and 1,4-dioxane was obtained from a drying system (MBraun system MB-SPS-800). Toluene was freshly distilled under nitrogen atmosphere over natrium/benzophenone. Triethylamine was stored over potassium hydroxide pellets. The reaction progress and the purification process were observed qualitatively by using TLC silica gel 60 F254 sheets obtained by Merck Serono KGaA. The spots were detected with UV light at 254 and 365 nm and with aqueous potassium permanganate solution. Column chromatography: silica gel 60, mesh 70–230. TLC: silica gel plates 60 F254. All products were purified with column chromatography on silica gel 60 (0.040–0.063 mm) by using flash technique under a pressure of 2 bar. The crude mixtures were absorbed on Celite\textsuperscript{\textregistered} 545 (0.02–0.10 mm) before chromatographic purification. Chemical shifts \( \delta \) in the \(^1\)H NMR and \(^{13}\)C NMR spectra are reported in ppm relative to CDCl\textsubscript{3}. The assignments of quaternary C, CH, CH\textsubscript{2}, and CH\textsubscript{3} signals were made by using DEPT-135 spectra. IR spectra were recorded with neat compounds under attenuated total reflection (ATR) and the intensities were characterized as strong (s), middle (m), and weak (w).

2. Synthesis of 1-Methyl-1\textsubscript{H}-indole-2-\textit{d} (4k)

\[
\text{C}_9\text{H}_8\text{DN} [132.18]
\]

1-Methyl-1\textsubscript{H}-indole-2-\textit{d} was prepared using a previously published method.\textsuperscript{1} 1-Methylindole (0.70g, 5.1mmol) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar. Anhydrous THF (20 mL) was added, and the reaction was allowed to stir until all the 1-methylindole is dissolved. The solution was cooled to 0 °C, and \( n \)-BuLi (1.6 M, 5.75 mL, 9.2mmol) was added drop wise. The mixture was allowed to warm to room temperature, and allowed to stir for an additional 60 minutes. Then 1.0 mL of D\textsubscript{2}O was slowly added drop wise. After the solution was fully quenched with D\textsubscript{2}O, it was extracted with ethyl acetate (2 \( \times \) 20mL) and petroleum ether boiling range 40-60 °C (1\( \times \)20mL). The resulting organic solution was dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed. The final product was filtered over a silica gel pad to afford the 1-methyl-1\textsubscript{H}-indole-2-\textit{d} (4k) as a yellowish oil with a 98% yield. According to the \textit{1}H NMR the compound contains 100% deuterium at position 2.
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 3.81 (s, 3 H), 6.50 (s, 1 H), 7.09-7.16 (m, 1 H), 7.21-7.28 (m, 1 H), 7.35 (dt, \(J = 8.2, 0.9\) Hz, 1 H), 7.65 (dd, \(J = 7.8, 1.2\) Hz, 1 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 32.9 (CH\(_3\)), 100.8 (CH), 109.3 (CH), 119.4 (CH), 121.0 (CH), 121.6 (CH), 128.4 (CH), 128.6 (C\(_{\text{quat}}\)), 136.8 (C\(_{\text{quat}}\)). MS (EI, \(m/z\) (%)): 132 ([M]+, 100), 131 ([M – H]+, 57). HR-MS (ESI) calcd. for (C\(_9\)H\(_8\)D\(_N\)+H): 133.0871. Found: 133.0870 (100%).

3. General Procedure GP1 for the Consecutive Four-component Synthesis of 2-Indolyl-3-[(trimethylsilyl)-ethynyl]quinoxalines 8

Indole 4 (1.0 equiv) in dry THF (2.5 mL/mmol) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and septum and degassed with nitrogen by syringe cannula for 5 min (for experimental details, see Table S1). After cooling to 0 °C (ice bath) oxalyl chloride (5) (1.0 equiv) was added dropwise to the solution. After stirring at room temp for 5 min the reaction mixture was stirred at 50 °C (oil bath) for 1 h. After cooling to room temp (water bath, 5 min) CuI (5 mol%), (trimethylsilyl)acetylene (6) (1.0 equiv) and NEt\(_3\) (2.1 equivs) were added to the reaction mixture and stirring at room temp was continued for 6 h. Then, MeOH, \(\alpha\)-phenylene diamine (7) (1.0 equiv), and acetic acid (2.0 equivs) were added and the reaction mixture was stirred at 50 °C for 1 h. After cooling to room temp deionized water (10 mL) was added and the aqueous layer was extracted with dichloromethane (3 x 20 mL), the combined organic phases were dried (anhydrous Na\(_2\)SO\(_4\)) and the crude reaction mixture was adsorbed on Celite\(^®\) and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 8.
Table S1. Experimental details of the synthesis of 3-(2-triethynyl)quinoxalines 8.

| Entry | Indole 4 mg (mmol) | Oxalylchloride mL (mmol) | NEt3 mL (mmol) | (Trimethylsilyl)-acetylene mL (mmol) | o-Phenylene diamine mmol | Acetic acid mL | 2-Indolyl-3-[(trimethylsilyl)-acetylenyl]quinoxalines 8 mg (yield) |
|-------|-------------------|--------------------------|---------------|-----------------------------------|-------------------------|---------------|---------------------------------------------------|
| 1     | 1340 (10.0)       | 0.90 (10.0)              | 5.90 (21.0)   | 1.40 (10.0)                       | 1080 (10.0)             | 1.20 (10.0)   | 2680 (80%) of 8a                                   |
| 2     | 363 (3.00)        | 0.27 (3.00)              | 1.77 (6.30)   | 0.44 (3.00)                       | 324 (3.00)              | 0.36 (3.00)   | 541 (49%) of 8b                                   |
| 3     | 478 (3.00)        | 0.27 (3.00)              | 1.77 (6.30)   | 0.44 (3.00)                       | 324 (3.00)              | 0.36 (3.00)   | 784 (68%) of 8c                                   |
| 4     | 314 (2.00)        | 0.18 (2.00)              | 1.18 (4.20)   | 0.28 (2.00)                       | 216 (2.00)              | 0.24 (2.00)   | 503 (66%) of 8d                                   |
| 5     | 604 (3.00)        | 0.27 (3.00)              | 1.77 (6.30)   | 0.28 (2.00)                       | 324 (3.00)              | 0.36 (3.00)   | 1104 (89%) of 8e                                  |
| 6     | 311 (1.00)        | 0.09 (1.00)              | 0.59 (2.10)   | 0.20 (1.00)                       | 108 (1.00)              | 0.12 (1.00)   | 376 (87%) of 8f                                   |
| 7     | 420 (2.00)        | 0.18 (2.00)              | 1.18 (4.20)   | 0.28 (2.00)                       | 216 (2.00)              | 0.24 (2.00)   | 661 (76%) of 8g                                   |
| 8     | 661 (4.00)        | 0.36 (4.00)              | 2.36 (8.40)   | 0.59 (4.00)                       | 432 (4.00)              | 0.48 (4.00)   | 1150 (74%) of 8h                                  |
| 9     | 322 (2.00)        | 0.18 (2.00)              | 1.18 (4.20)   | 0.28 (2.00)                       | 216 (2.00)              | 0.24 (2.00)   | 614 (80%) of 8i                                   |
| 10    | 704 (4.00)        | 0.36 (4.00)              | 2.36 (8.40)   | 0.59 (4.00)                       | 432 (4.00)              | 0.48 (4.00)   | 1070 (67%) of 8j                                  |
| 11    | 265 (2.00)        | 0.18 (2.00)              | 1.18 (4.20)   | 0.28 (2.00)                       | 216 (2.00)              | 0.24 (2.00)   | 272 (38%) of 8k                                   |

[a] For improving the solubility in the cyclocondensation step THF (2.0 mL) was added.
3.1. 2-(1-Methyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8a)²

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 7:1) compound 8a (2680 mg, 80%) was obtained as a yellow solid, Mp 162 °C (160 °C),² R\textsubscript{f} = 0.14 (petroleum ether/ethyl acetate 7:1).

¹H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.35 (s, 9 H), 3.92 (s, 3 H), 7.30-7.35 (m, 1 H), 7.35-7.40 (m, 1 H), 7.40-7.45 (m, 1 H), 7.66 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.05 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.16 (dd, J = 8.4 Hz, J = 1.5 Hz, 1 H), 8.59 (s, 1 H), 8.73-8.79 (m, 1 H).¹³C NMR (75 MHz, CDCl\textsubscript{3}): δ -0.3 (CH\textsubscript{3}), 33.5 (CH\textsubscript{3}), 101.1 (C\textsubscript{quat}), 104.4 (C\textsubscript{quat}), 109.5 (CH), 112.0 (C\textsubscript{quat}), 121.6 (CH), 123.1 (CH), 123.2 (CH), 127.6 (C\textsubscript{quat}), 128.6 (CH), 128.8 (CH), 128.9 (CH), 130.7 (CH), 133.0 (CH), 136.4 (C\textsubscript{quat}), 137.4 (C\textsubscript{quat}), 139.2 (C\textsubscript{quat}), 141.1 (C\textsubscript{quat}), 150.4 (C\textsubscript{quat}). MS (EI, m/z (%)): 356 (31), 355 ([M\textsuperscript{+}], 100), 354 ([M – H\textsuperscript{+}], 49), 341 (18), 340 ([M – CH\textsubscript{3}\textsuperscript{+}], 59), 310 ([M – 3 CH\textsubscript{3}\textsuperscript{+}], 11), 282 ([M – Si(CH\textsubscript{3})\textsubscript{3}\textsuperscript{+}], 14), 169 (25), 162 (13), 155 [C\textsubscript{10}H\textsubscript{5}N\textsubscript{2}\textsuperscript{+}], 15), 154 ([C\textsubscript{10}H\textsubscript{6}N\textsubscript{2}\textsuperscript{+}], 15), 148 (17).

3.2. 2-(1-Ethyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8b)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) compound 8b (541mg, 49%) was obtained as a yellow solid, Mp 116 °C, R\textsubscript{f} = 0.65 (petroleum ether/ethyl acetate 5:1).

¹H NMR (300 MHz, CDCl\textsubscript{3}): δ 0.37 (s, 9 H), 1.57 (t, J = 7.3 Hz, 3 H), 4.29 (q, J = 7.3 Hz, 2 H), 7.30-7.38 (m, 2 H), 7.40-7.46 (m, 1 H), 7.64 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.72 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.05 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.11 (ddd, J = 8.4 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.62 (s, 1 H), 8.77-8.83 (m, 1 H).¹³C
NMR (75 MHz, CDCl₃): δ -0.3 (CH₃), 15.6 (CH₃), 41.8 (CH₂), 100.8 (C₁₈quat), 104.6 (C₂quat), 109.6 (CH), 112.3 (C₂quat), 121.5 (CH), 123.0 (CH), 123.3 (CH), 127.8 (C₁₈quat), 128.75 (CH), 128.78 (CH), 128.8 (CH), 130.7 (CH), 131.4 (CH), 136.37 (C₁₈quat), 136.42 (C₂quat), 139.2 (C₂quat), 141.3 (C₂quat), 150.6 (C₂quat). MS (EI, m/z (%)): 370 (31), 369 ([M]⁺, 100), 368 ([M – H]⁺, 31), 355 ([M-CH₃]⁺, 12), 354 ([M-CH₃]⁺, 42), 340 ([M-(CH₃)₂]⁺, 20), 339 ([M-(CH₃)₂]⁺, 11), 296 ([C₁₈H₅N₃Si]⁺, 18), 231 (10), 155 ([C₁₀H₆N₂]⁺, 24). IR: ν [cm⁻¹] 2980 (m), 2961 (m), 2936 (m), 2901 (m), 1612 (w), 1537 (s), 1520 (m), 1506 (m), 1476 (m), 1456 (m), 1393 (m), 1379 (m), 1360 (m), 1341 (m), 1308 (m), 1288 (m), 1248 (m), 1229 (m), 1209 (m), 1196 (m), 1163 (m), 1146 (m), 1128 (m), 1119 (m), 1096 (m), 1084 (m), 1057 (m), 1015 (m), 959 (m), 926 (m), 910 (m), 837 (s), 820 (m), 756 (s), 741 (s), 723 (m), 704 (m), 648 (m), 633 (m), 613 (m). Anal calcd for C₂₃H₂₃N₃Si [369.5]: C 74.76, H 6.27, N 11.37; Found: C 74.68, H 6.30, N 11.37.

3.3. 2-(1-Propyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8c)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) compound 8c (784 mg, 68%) was obtained as a yellow solid, Mp 132 °C, Rᵣ = 0.36 (petroleum ether/ethyl acetate 20:1).

¹H NMR (600 MHz, CDCl₃): δ 0.37 (s, 9 H), 1.01 (t, J = 7.4 Hz, 3 H), 1.92-2.02 (m, 2 H), 4.19 (dd, J = 7.6 Hz, J = 6.6 Hz, 2 H), 7.30-7.37 (m, 2 H), 7.40-7.45 (m, 1 H), 7.64 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.72 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.04 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.12 (ddd, J = 8.3 Hz, J = 1.5 Hz, J = 0.6 Hz, 1 H), 8.63 (s, 1 H), 8.78-8.86 (m, 1 H). ¹³C NMR (150 MHz, CDCl₃): δ -0.3 (CH₃), 11.7 (CH₃), 23.7 (CH₂), 48.9 (CH₂), 100.9 (C₁₈quat), 104.6 (C₂quat), 109.8 (C₁₈quat), 112.1 (C₂quat), 121.5 (CH), 122.9 (CH), 123.3 (CH), 127.8 (C₁₈quat), 128.7 (CH), 128.8 (CH), 130.7 (CH), 132.1 (CH), 136.4 (C₂quat), 136.7 (C₂quat), 139.2 (C₂quat), 141.3 (C₂quat), 150.5 (C₂quat). MS (EI, m/z (%)): 384 (33), 383 ([M]⁺, 100), 382 ([M – H]⁺, 21), 369 (11), 368 ([M – CH₃]⁺, 30), 354 ([M – 2 CH₃]⁺, 13), 340 ([C₁₈H₁₈N₃Si]⁺, 17), 310 ([C₁₅H₁₂N₃Si]⁺, 17), 155 ([C₁₀H₆N₂]⁺, 22), 73 ([C₃H₃Si]⁺, 24). IR: ν [cm⁻¹] 2963 (w), 2926 (w), 2901 (w), 2874 (w), 1530 (m), 1520 (m), 1472 (m), 1447 (m), 1396 (m), 1383 (m), 1348 (m), 1337 (w), 1325 (w), 1285 (m), 1250 (m), 1207 (m), 1190 (m), 1163 (w), 1146 (w), 1130 (m), 1123 (m), 1099 (m), 1084 (w), 1072 (w), 1016 (w), 937 (m), 910 (w), 841 (s), 829.
(m), 818 (m), 797 (m), 772 (m), 760 (m), 739 (s), 698 (m), 646 (m), 615 (m). Anal calcd for C_{24}H_{25}N_{3}Si [383.6]: C 75.15, H 6.57, N 10.96; Found: C 74.89, H 6.48, N 10.85.

3.4. 2-(1-Allyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8d)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) compound 8d (503 mg, 66%) was obtained as a yellow solid, Mp 130 °C, R_f = 0.61 (petroleum ether/ethyl acetate 5:1).

^1^H NMR (600 MHz, CDCl_3): δ 0.34 (s, 9 H), 4.85 (dt, J = 5.3 Hz, J = 1.7 Hz, 2 H), 5.18 (dq, J = 17.1 Hz, J = 1.5 Hz, 1 H), 5.27-5.30 (m, 1 H), 5.31-5.35 (m, 2 H), 7.39-7.42 (m, 1 H), 7.66 (ddd, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, 1 H), 7.73, 7.74 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.04 (dd, J = 8.5 Hz, J = 1.4 Hz, 1 H), 8.12 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.58 (s, 1 H), 8.76-8.82 (m, 1 H). ^1^C NMR (75 MHz, CDCl_3): δ -0.3 (CH_3), 49.0 (CH_2), 100.5 (C_quat), 104.0 (C_quat), 109.6 (CH), 112.2 (C_quat), 117.5 (CH_2), 121.2 (CH), 122.7 (CH), 122.8 (CH), 127.3 (C_quat), 128.4 (CH), 128.5 (CH), 130.3 (CH), 131.6 (CH), 132.4 (CH), 136.0 (C_quat), 136.3 (C_quat), 138.8 (C_quat), 140.8 (C_quat), 150.1 (C_quat). MS (EI, m/z (%)): 382 (32), 381 ([M]^+ 100), 380 ([M – H]^+, 16), 340 ([C_{21}H_{18}N_{3}Si]^+, 29), 339 ([C_{21}H_{18}N_{3}Si]^+, 10), 325 ([C_{20}H_{14}N_{3}Si]^+, 20), 310 ([C_{21}H_{18}N_{3}Si]^+, 13), 309 ([C_{21}H_{18}N_{3}Si]^+, 17), 308 ([C_{21}H_{18}N_{3}Si]^+, 38), 190 (15), 169 (12), 108 (11), 73 ([C_{3}H_{5}Si]^+, 28), 41 ([C_{3}H_{5}]^+, 13). IR: " [cm⁻¹] 2955 (w), 1533 (m), 1518 (m), 1470 (m), 1452 (m), 1391 (m), 1350 (w), 1327 (w), 1285 (m), 1248 (m), 1202 (m), 1188 (m), 1123 (m), 1107 (w), 991 (w), 937 (m), 910 (w), 845 (s), 818 (m), 800 (w), 760 (m), 743 (s), 706 (w), 646 (m), 629 (m), 610 (m). Anal calcd for C_{24}H_{25}N_{3}Si [381.6]: C 75.15, H 6.57, N 10.96; Found: C 74.89, H 6.48, N 10.85.

3.5. 2-(1-Hexyl-1H-indol-3-yl)-3-((trimethylsilyl)ethyl)quinoxaline (8e)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) compound 8e (422 mg, 67%) was obtained as a yellow solid, Mp 130 °C, R_f = 0.61 (petroleum ether/ethyl acetate 5:1).

^1^H NMR (600 MHz, CDCl_3): δ 0.34 (s, 9 H), 1.30 (d, J = 6.6 Hz, 6 H), 1.38 (t, J = 7.2 Hz, 3 H), 1.40 (t, J = 7.2 Hz, 3 H), 1.51 (s, 9 H), 4.85 (dt, J = 5.3 Hz, J = 1.7 Hz, 2 H), 5.18 (dq, J = 17.1 Hz, J = 1.5 Hz, 1 H), 5.27-5.30 (m, 1 H), 5.27-5.30 (m, 1 H), 7.31-7.33 (m, 2 H), 7.39-7.42 (m, 1 H), 7.66 (ddd, J = 8.3 Hz, J = 6.8 Hz, J = 1.4 Hz, 1 H), 7.73 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.04 (dd, J = 8.5 Hz, J = 1.4 Hz, 1 H), 8.12 (dd, J = 8.3 Hz, J = 1.4 Hz, 1 H), 8.58 (s, 1 H), 8.76-8.82 (m, 1 H). ^1^C NMR (75 MHz, CDCl_3): δ -0.3 (CH_3), 49.0 (CH_2), 100.5 (C_quat), 104.0 (C_quat), 109.6 (CH), 112.2 (C_quat), 117.5 (CH_2), 121.2 (CH), 122.7 (CH), 122.8 (CH), 127.3 (C_quat), 128.4 (CH), 128.5 (CH), 130.3 (CH), 131.6 (CH), 132.4 (CH), 136.0 (C_quat), 136.3 (C_quat), 138.8 (C_quat), 140.8 (C_quat), 150.1 (C_quat). MS (EI, m/z (%)): 425.6 (100), 381 ([M]^+), 380 ([M – H]^+, 16), 340 ([C_{21}H_{18}N_{3}Si]^+, 29), 339 ([C_{21}H_{18}N_{3}Si]^+, 10), 325 ([C_{20}H_{14}N_{3}Si]^+, 20), 310 ([C_{21}H_{18}N_{3}Si]^+, 13), 309 ([C_{21}H_{18}N_{3}Si]^+, 17), 308 ([C_{21}H_{18}N_{3}Si]^+, 38), 190 (15), 169 (12), 108 (11), 73 ([C_{3}H_{5}Si]^+, 28), 41 ([C_{3}H_{5}]^+, 13). IR: " [cm⁻¹] 2955 (w), 1533 (m), 1518 (m), 1470 (m), 1452 (m), 1391 (m), 1350 (w), 1327 (w), 1285 (m), 1248 (m), 1202 (m), 1188 (m), 1123 (m), 1107 (w), 991 (w), 937 (m), 910 (w), 845 (s), 818 (m), 800 (w), 760 (m), 743 (s), 706 (w), 646 (m), 629 (m), 610 (m). Anal calcd for C_{27}H_{31}N_{3}Si [425.6]: C 75.15, H 6.57, N 10.96; Found: C 74.89, H 6.48, N 10.85.
According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1) compound 8e (1104 mg, 89%) was obtained as a yellow solid, Mp 98 °C, Rf = 0.30 (petroleum ether/ethyl acetate 15:1).

1H NMR (300 MHz, CDCl₃): δ 0.36 (s, 9 H), 0.81-0.92 (m, 3 H), 1.24-1.44 (m, 6 H), 1.83-2.01 (m, 2 H), 4.22 (t, J = 7.3 Hz, 2 H), 7.37-7.46 (m, 2 H), 7.28-7.37 (m, 2 H), 7.73 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.05 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.13 (ddd, J = 8.3 Hz, J = 1.5 Hz, J = 0.6 Hz, 1 H), 8.62 (s, 1 H), 8.77-8.83 (m, 1 H). 13C NMR (75 MHz, CDCl₃): δ 0.3 (CH₃), 14.1 (CH₃), 22.6 (CH₂), 26.8 (CH₂), 30.4 (CH₂), 31.6 (CH₂), 47.3 (CH₂), 101.1 (C quat), 104.5 (C quat), 109.8 (CH), 112.0 (C quat), 121.5 (CH), 123.0 (CH), 123.3 (CH), 127.7 (C quat), 128.7 (CH), 128.65 (CH), 128.76 (CH), 130.8 (CH), 132.1 (CH), 136.4 (C quat), 136.7 (C quat), 139.2 (C quat), 141.1 (C quat), 150.5 (C quat). MS (EI, m/z (%)): 426 (30), 425 ([M]+, 100), 410 ([M – CH₃]+, 26), 354 (23), 352 ([M – Me₃Si]+, 12), 340 ([M – C₆H₁₃]+, 19), 339 ([M – C₆H₁₄]+, 10), 325 (20), 310 (11), 296 (14), 282 (15), 73 (14), 43 (12). IR: v [cm⁻¹] 2153 (w), 1605 (w), 1526 (m), 1518 (m), 1472 (m), 1449 (m), 1391 (m), 1375 (m), 1346 (m), 1341 (m), 1285 (m), 1246 (m), 1211 (m), 1184 (m), 1144 (m), 1130 (m), 1121 (m), 1103 (w), 1009 (w), 932 (m), 910 (m), 843 (s), 816 (m), 800 (m), 754 (m), 746 (s), 706 (m), 644 (m), 633 (m), 608 (m). Anal calcd for C₂₇H₃₁N₃Si [425.7]: C 76.19, H 7.34, N 9.87; Found: C 76.26, H 7.22, N 9.74.

3.6. 2-(1-Benzyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8f)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 9:1) compound 8f (376 mg, 87%) was obtained as a yellow solid, Mp 191 °C, Rf = 0.44 (petroleum ether/ethyl acetate 9:1).

1H NMR (300 MHz, CDCl₃): δ 0.26 (s, 9 H), 5.46 (s, 2 H), 7.17 (ddt, J = 7.0 Hz, J = 1.6 Hz, J = 0.8 Hz, 2 H), 7.26-7.38 (m, 6 H), 7.67 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 7.75 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.06 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.15 (ddd, J = 8.3 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.67 (s, 1 H), 8.75-8.81 (m, 1 H). 13C NMR (75 MHz, CDCl₃): δ 0.1 (CH₃), 51.2 (CH₂), 101.5 (C quat), 104.7 (C quat), 110.6 (CH), 113.2 (C quat), 122.2 (CH), 123.6 (CH), 123.7 (CH), 126.9 (CH), 128.2 (C quat), 128.4 (CH), 129.1 (CH), 129.2 (CH), 129.40 (CH), 129.46 (CH), 131.1 (CH), 132.9 (CH), 136.9 (C quat), 137.2 (C quat), 137.4
(C\textsubscript{quat}), 139.7 (C\textsubscript{quat}), 141.6 (C\textsubscript{quat}), 150.9 (C\textsubscript{quat}). MS (EI, \textit{m/z} (%)): 432 (36), 431 ([M]+, 100), 430 ([M – H]+, 15), 416 ([M – CH\textsubscript{3}]+, 24), 358 ([M – Si(CH\textsubscript{3})\textsubscript{3}]+, 18), 341 ([C\textsubscript{2}H\textsubscript{18}N\textsubscript{5}Si]+, 14), 340 ([C\textsubscript{2}H\textsubscript{18}N\textsubscript{5}Si]+, 45), 239 ([C\textsubscript{2}H\textsubscript{18}N\textsubscript{5}Si]+, 12), 169 (10), 91 ([C\textsubscript{7}H\textsubscript{7}]+, 100), 73 ([C\textsubscript{3}H\textsubscript{5}Si]+, 11). IR: \textit{v} [\text{cm}^{-1}] 2924 (w), 2855 (w), 1589 (w), 1555 (m), 1516 (m), 1456 (m), 1393 (m), 1377 (w), 1354 (w), 1306 (w), 1287 (w), 1246 (m), 1219 (w), 1198 (w), 1180 (m), 1146 (w), 1130 (w), 1099 (w), 1069 (w), 1042 (w), 986 (w), 955 (w), 935 (m), 910 (w), 891 (w), 843 (m), 818 (w), 799 (w), 762 (m), 739 (s), 727 (m), 696 (m), 675 (w), 644 (m), 615 (m). Anal calcd for C\textsubscript{2}H\textsubscript{2}BrN\textsubscript{5}Si [431.6]: C 77.92, H 5.84, N 9.74; Found: C 77.75, H 5.95, N 9.44.

3.7. 2-(5-Bromo-1-methyl-1-indol-3-yl)-3-[(trimethylsilyl)ethynyl]quinoxaline (8g)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 8g (661 mg, 76%) was obtained as a yellow solid, Mp 154 °C, R\textsubscript{f} = 0.15 (petroleum ether/ethyl acetate 10:1).

$^{1}$H NMR (300 MHz, CDCl\textsubscript{3}): \textit{\delta} 0.37 (s, 9 H), 3.87 (s, 3 H), 7.23 (dd, \textit{J} = 8.7 Hz, \textit{J} = 0.5 Hz, 1 H), 7.41 (dd, \textit{J} = 8.7 Hz, \textit{J} = 2.0 Hz, 1 H), 7.66 (ddd, \textit{J} = 8.3 Hz, \textit{J} = 6.9, \textit{J} = 1.5 Hz, 1 H), 7.74 (ddd, \textit{J} = 8.4 Hz, \textit{J} = 6.9 Hz, \textit{J} = 1.6 Hz, 1 H), 8.03 (ddd, \textit{J} = 8.2 Hz, \textit{J} = 1.6 Hz, \textit{J} = 0.6 Hz, 1 H), 8.13 (ddd, \textit{J} = 8.3 Hz, \textit{J} = 1.5 Hz, \textit{J} = 0.6 Hz, 1 H), 8.55 (s, 1 H), 8.94 (dd, \textit{J} = 1.9 Hz, \textit{J} = 0.6 Hz, 1 H). $^{13}$C NMR (75 MHz, CDCl\textsubscript{3}): \textit{\delta} -0.3 (CH\textsubscript{3}), 33.7 (CH\textsubscript{3}), 101.3 (CH), 104.4 (C\textsubscript{quat}), 111.0 (CH), 111.8 (C\textsubscript{quat}), 115.2 (C\textsubscript{quat}), 125.86 (CH), 125.93 (CH), 128.79 (CH), 128.82 (CH), 129.1 (CH), 130.9 (CH), 133.7 (CH), 136.0 (C\textsubscript{quat}), 136.2 (C\textsubscript{quat}), 139.3 (C\textsubscript{quat}), 141.1 (C\textsubscript{quat}), 149.9 (C\textsubscript{quat}). MS (EI, \textit{m/z} (%)): 436 (27), 435 ([$^{18}$Br-M]+, 100), 434 (47), 433 ([$^{79}$Br-M]+, 94), 432 (19), 420 ([$^{18}$Br-M – CH\textsubscript{3}]+, 21), 418 ($^{79}$Br-M – CH\textsubscript{3}]+, 14), 340 ([C\textsubscript{2}H\textsubscript{18}N\textsubscript{5}Si]+, 10), 339 ([C\textsubscript{2}H\textsubscript{17}N\textsubscript{5}Si]+, 35), 338 ([C\textsubscript{2}H\textsubscript{17}N\textsubscript{5}Si]+, 16), 324 ([C\textsubscript{2}H\textsubscript{18}N\textsubscript{5}Si]+, 10), 177 (16), 169 (19), 161 (22), 155 ([C\textsubscript{10}H\textsubscript{5}N\textsubscript{2}]+, 12), 149 (26), 73 ([C\textsubscript{3}H\textsubscript{5}Si]+, 10). IR: \textit{v} [\text{cm}^{-1}] 2989 (w), 2967 (w), 2959 (w), 2920 (w), 2901 (w), 1530 (m), 1522 (m), 1474 (m), 1441 (m), 1422 (w), 1381 (m), 1366 (m), 1348 (w), 1323 (w), 1258 (m), 1250 (m), 1238 (m), 1219 (m), 1196 (w), 1132 (m), 1119 (m), 1088 (m), 1049 (m), 1028 (w), 1009 (w), 939 (m), 847 (s), 789 (m), 752 (s), 704 (w), 748 (m), 648 (m), 631 (m), 615 (m). Anal calcd for C\textsubscript{2}H\textsubscript{2}BrN\textsubscript{5}Si [434.4]: Ber.: C 60.83, H 4.64, N 9.67; Found: C 60.72, H 4.68, N 9.52.
3.8. 2-(5-Chloro-1-methyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8h)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) compound 8h (1150 mg, 74%) was obtained as a yellow solid, Mp 183 °C, Rf = 0.48 (petroleum ether/ethyl acetate 5:1).

\[^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3): \delta 0.31 \ (s, 9 \text{ H}), 3.85 \ (s, 3 \text{ H}), 7.23-7.28 \ (m, 2 \text{ H}), 7.70 \ (s, 1 \text{ H}), 7.99 \ (dd, J = 8.3 \text{ Hz, } J = 1.5 \text{ Hz, 1 H}), 8.09 \ (dd, J = 8.4 \text{ Hz, } J = 1.5 \text{ Hz, 1 H}), 8.54 \ (s, 1 \text{ H}), 8.72-8.75 \ (m, 1 \text{ H}). \]

\[^{13}\text{C} \text{ NMR} \ (75 \text{ MHz, CDCl}_3): \delta -0.3 \ (\text{CH}_3), 33.7 \ (\text{CH}_3), 101.2 \ (\text{C}_{\text{quat}}), 104.4 \ (\text{C}_{\text{quat}}), 110.5 \ (\text{CH}), 111.9 \ (\text{C}_{\text{quat}}), 122.8 \ (\text{CH}), 123.4 \ (\text{CH}), 127.5 \ (\text{C}_{\text{quat}}), 128.5 \ (\text{CH}), 128.8 \ (\text{CH}), 129.1 \ (\text{C}_{\text{quat}}), 130.9 \ (\text{CH}), 133.8 \ (\text{CH}), 135.8 \ (\text{C}_{\text{quat}}), 136.2 \ (\text{C}_{\text{quat}}), 141.1 \ (\text{C}_{\text{quat}}), 149.9 \ (\text{C}_{\text{quat}}).

\[\text{MS (EI, m/z (%))}: 391 ([37\text{Cl}-\text{M}]^+, 26), 390 (36), 389 ([35\text{Cl}-\text{M}]^+, 100), 388 ([35\text{Cl}-\text{M} - \text{H}]^+, 30), 376 ([37\text{Cl}-\text{M} - \text{CH}_3]^+, 14), 375 (14), 374 ([35\text{Cl}-\text{M} - \text{CH}_3]^+, 40), 373 (10), 359 (11), 354 (13), 339 (17), 338 (\text{CH}_3]^+, 11), 316 (11), 281 (12), 267 (10), 190 ([C_{10}H_{13}N_2]^+, 16), 189 ([C_{10}H_{13}N_2]^+, 13), 187 ([C_{10}H_{12}N_2]^+, 10), 169 (12), 167 (14), 155 (10), 149 (45), 148 (11), 97 ([C_7H_13]^+, 10), 85 ([C_7H_13]^+, 15), 84 (14), 73 ([C_7H_13]^+, 73, 71 (12), 57 ([C_4H_9]^+, 15), 55 ([C_4H_7]^+, 10). IR: \tilde{\nu} [(\text{cm}^{-1})]: 3057 (w), 2989 (w), 2959 (w), 2920 (w), 2900 (w), 1611 (w), 1530 (m), 1518 (m), 1474 (m), 1445 (w), 1424 (w), 1368 (m), 1348 (w), 1325 (w), 1283 (w), 1249 (m), 1236 (m), 1217 (m), 1209 (w), 1196 (w), 1150 (m), 1132 (m), 1121 (m), 1092 (m), 1051 (m), 1028 (w), 1011 (w), 943 (w), 912 (w), 847 (s), 835 (s), 789 (m), 752 (s), 737 (m), 706 (w), 652 (w), 627 (m). Anal. calcd for C_{22}H_{20}ClN_3Si [390.0]: C 67.76, H 5.17, N 10.78; Found: C 67.47, H 5.18, N 10.54.

3.9. 2-(5-Methoxy-1-methyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8i)
According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 6:1) compound 8i (614 mg, 80%) was obtained as a yellow solid, Mp 170 °C, Rf = 0.53 (petroleum ether/ethyl acetate 6:1).

1H NMR (300 MHz, CDCl3): δ 0.37 (s, 9 H), 3.88 (s, 3 H), 3.96 (s, 3 H), 7.01 (dd, J = 8.9 Hz, J = 2.5 Hz, 1 H), 7.29 (dd, J = 8.9 Hz, J = 0.5 Hz, 1 H), 7.64 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.72 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.04 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.09 (ddd, J = 8.3 Hz, J = 1.6 Hz, J = 0.6 Hz, 1 H), 8.36 (dd, J = 2.6 Hz, J = 0.5 Hz, 1 H), 8.58 (s, 1 H). 13C NMR (75 MHz, CDCl3): δ -0.3 (CH3), 33.7 (CH3), 56.0 (CH3), 101.1 (Cquat), 104.6 (Cquat), 105.0 (CH), 110.3 (CH), 111.5 (Cquat), 113.2 (CH), 128.2 (Cquat), 128.5 (CH), 128.75 (CH), 128.82 (CH), 130.8 (CH), 132.6 (Cquat), 133.4 (CH), 136.3 (Cquat), 139.1 (Cquat), 141.1 (Cquat), 150.6 (Cquat), 155.8 (Cquat). MS (El, m/z (%)): 386 (31), 385 ([M]+, 100), 384 ([M – H]+, 12), 370 ([M – CH3]+, 17), 355 ([M – OCH3]+, 11), 340 ([M – 3 CH3]+, 11), 312 ([M – SiMe3]+, 17), 170 (13), 169 (11), 148 (17). IR: ν [cm⁻¹] 2959 (w), 2901 (w), 1530 (m), 1487 (m), 1446 (m), 1421 (m), 1383 (m), 1371 (m), 1247 (m), 1209 (m), 1198 (m), 1132 (m), 1080 (s), 1057 (w), 874 (m), 845 (s), 814 (m), 791 (m), 756 (s), 739 (m), 704 (w). Anal calcd for C23H23N2SiO [385.57]: C 71.65, H 6.01, N 10.90; Found: C 71.36, H 6.01, N 10.63.

3.10. 2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8j)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 8j (1070 mg, 67%) was obtained as a yellow solid, Mp 132 °C, Rf = 0.29 (petroleum ether/ethyl acetate 10:1).

1H NMR (300 MHz, CDCl3): δ 0.37 (s, 9 H), 1.55 (t, J = 7.3 Hz, 3 H), 3.96 (s, 3 H), 4.25 (q, J = 7.3 Hz, 2 H), 7.00 (dd, J = 8.9 Hz, J = 2.5 Hz, 1 H), 7.24–7.36 (m, 1 H), 7.64 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.5 Hz, 1 H), 7.72 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1 H), 8.05 (ddd, J = 8.3 Hz, J = 1.5 Hz, J = 0.7 Hz, 2 H), 8.37 (d, J = 2.5 Hz, 1 H), 8.61 (s, 1 H). 13C NMR (75 MHz, CDCl3): δ -0.3 (CH3), 15.7 (CH3), 42.0 (CH3), 55.9 (CH3), 100.8 (Cquat), 104.6 (Cquat), 105.1 (CH), 110.4 (CH), 111.7 (Cquat), 113.1 (CH), 128.4 (Cquat), 128.6 (CH), 128.7 (CH), 128.8 (CH), 130.7 (CH), 131.6 (Cquat), 131.8 (CH), 136.3 (Cquat), 139.1 (Cquat), 141.2 (Cquat), 150.7 (Cquat), 155.7 (Cquat). MS (El, m/z (%)): 400 (29), 399 ([M]+, 100), 384 ([M – CH3]+, 15), 355 ([M – 3...
3.11. 2-(1-Methyl-1H-indol-3-yl-2-d)-3-((trimethylsilyl)ethynyl)quinoxaline (8k)

According to GP1 and flash chromatography on silica gel (petroleum ether/ethyl acetate 7:1) compound 8k (272 mg, 38%) was obtained as a yellow solid, Mp 163.5-165.8 °C, Rf = 0.41 (petroleum ether/ethyl acetate 7:1).

1H NMR (300 MHz, CDCl3): δ 0.35 (s, 9H), 3.92 (s, 3H), 7.29-7.35 (m, 1H), 7.35-7.37 (m, 1H), 7.38-7.44 (m, 1H), 7.65 (ddd, J = 8.3 Hz, J = 6.9 Hz, J = 1.6 Hz, 1H), 7.73 (ddd, J = 8.4 Hz, J = 6.9 Hz, J = 1.6 Hz, 1H), 8.04 (ddd, J = 8.2 Hz, J = 1.6 Hz, J = 0.7 Hz, 1H), 8.12 (ddd, J = 8.3 Hz, J = 1.6 Hz, J = 0.6 Hz 1H), 8.77-8.85 (m, 1H). 13C NMR (75 MHz, CDCl3): δ -0.3 (CH3), 33.5 (CH3), 101.0 (Cquat), 104.6 (Cquat), 109.6 (CH), 112.0 (Cquat), 121.6 (CH), 123.1 (CH), 123.2 (CH), 127.7 (Cquat), 128.8 (CH), 128.8 (CH), 130.7 (CH), 133.2 (CH), 136.5 (Cquat), 137.4 (Cquat), 139.2 (Cquat), 141.3 (Cquat), 150.6 (Cquat). MS (EI, m/z (%)): 357 (28), 356 ([M]+, 100), 355 ([M – H]+, 53), 342 (18), 341 ([M – CH3]+, 83), 326 (17), 311 ([M – 3 CH3]+, 14), 283 ([M – Si(CH3)3]+, 13), 232 (12), 191 (10), 171 (13), 157 (14), 156 (25), 155 (15), 149 (20), 111 (12), 109 (10), 97 (18), 95 (14), 85 (15), 83 (14), 81 (12), 73 (11), 71 (18), 69 (19), 57 (31), 55 (22). IR: ν [cm⁻¹] 2955 (w), 1510 (m), 1420 (m), 1248 (m), 1082 (m), 939 (m), 843 (s), 743 (s), 796 (m). HR-MS (ESI) calcd. for (C22H20D3Si+H)+: 357.1640. Found: 357.1642 (100%).

4. Optimization of the Cycloisomerization

Starting with the terminal alkyne 8l as a substrate screening of several carbophilic Lewis acids reveals that auric chloride (AuCl3) cycloisomerizes the alkyne to indolo[3,2-a]phenazine 9l in moderate yield (Table S2, entries 7-9), whereas indiumtrichloride, palladium dichloride and the
gold(I) complex (Ph₃P)₃AuCl prove to be inefficient (Table S2, entries 1-6). Likewise inefficient is NaAuCl₄ as a catalyst for compound 8l as a substrate in both toluene and THF (Table S2, entries 10 and 11). 3-[(Trimethylsilyl)ethynyl]quinoxaline 8a as a substrate contains an internal alkyne and first Kumar's and Pal's conditions, using trifluoroacetic acid as a catalyst in overstoichiometric amounts, are found to only lead to reisolation of compound 8a in 87% (Table S2, entry 12). Interestingly, NaAuCl₄ turns out to be the most efficient catalyst and toluene the solvent of choice for cycloisomerizing compound 8a to indolo[3,2-a]phenazine 9a (Table S2, entries 13-17). While cationic gold complex catalysts formed by in situ generation with silver(I) salts catalyze the cycloisomerization, however with lower efficiency (Table 1, entries 23-25 and 27), all attempts to achieve iodocyclization with iodine, hypervalent iodine compounds, and iodine monochloride (Table S2, entries 19-22) remained unsuccessful. Silver(I)nitrate is ineffective to achieve a cycloisomerization (Table S2, entry 26).

![Chemical structure](image)

Ethynyl quinoxaline 8 (0.50 mmol) and dry solvent (1.0 mL) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and solution was degassed with nitrogen by syringe cannula for 5 min (for experimental details, see Table S2). Then, the catalyst/additive was added under a stream of nitrogen. The mixture was then stirred at 80 °C (oil bath), except for Table S2, entry 22, for the time indicated. The reaction was monitored with TLC. In case of conversion, after cooling/warming to room temp dichloromethane was added and the crude reaction mixture was adsorbed on Celite® and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give the cycloisomerization product 9.

4.1. 8-Methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9a)
According to the conditions in Table S2, entry 15, and after flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 9a (134 mg, 75%) was obtained as a yellow solid; Mp 216 °C, Rf = 0.18 (petroleum ether/ethyl acetate 50:1).

^1H NMR (300 MHz, CDCl₃): δ 0.62 (s, 9 H), 4.06 (s, 3 H), 7.45-7.59 (m, 3 H), 7.76 (ddd, J = 8.2 Hz, J = 6.6 Hz, J = 1.5 Hz, 1 H), 7.85 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.6 Hz, 1 H), 8.13 (s, 1 H), 8.28 (ddd, J = 8.3 Hz, J = 1.6 Hz, J = 0.7 Hz, 1 H), 8.39 (ddd, J = 8.4 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.19-9.24 (m, 1 H). ^13C NMR (75 MHz, CDCl₃): δ 0.3 (CH₃), 29.7 (CH₃), 109.5 (CH), 115.1 (Cquat), 121.3 (CH), 123.7 (CH), 123.9 (CH), 124.2 (Cquat), 124.9 (CH), 127.8 (CH), 129.3 (CH), 129.7 (CH), 130.1 (CH), 139.6 (Cquat), 139.7 (Cquat), 140.5 (Cquat), 141.2 (Cquat), 142.1 (Cquat), 142.5 (Cquat), 145.3 (Cquat). MS (EI, m/z (%)): 356 (16), 355 ([M]+, 52), 354 ([M–H]+, 15), 340 ([M–CH₃]+, 29), 325 ([M–2CH₃]+, 32), 170 (38), 155 (24), 148 (10), 111 (12), 97 (14), 85 (11), 83 (11), 71 (15), 69 (11), 57 (22), 55 (12), 43 ([C₃H₇]+, 14). IR: ν [cm⁻¹] 3057 (w), 3021 (w), 2974 (w), 2941 (w), 2897 (w), 1612 (w), 1570 (w), 1551 (w), 1543 (w), 1518 (m), 1477 (w), 1466 (w), 1454 (m), 1437 (m), 1422 (m), 1412 (m), 1387 (m), 1339 (w), 1319 (w), 1308 (m), 1279 (w), 1236 (m), 1227 (m), 1211 (m), 1152 , 1123 (w), 1084 (m), 1018 (m), 999 (w), 937 (m), 918 (m), 895 (m), 870 (w), 833 (s), 793 (m), 764 (w), 743 (s), 731 (s), 673 (m), 638 (m), 606 (m). Anal calcd for C_{22}H_{21}N₃Si [355.5]: C 74.33, H 5.95, N 11.82; Found: C 74.06, H 6.16, N 11.75.

4.2. 8-Methyl-8H-indolo[3,2-a]phenazine (9i)

According to the conditions in Table S2, entry 8, and after flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 9i (100 mg, 28%) was obtained as a yellow-orange solid; Mp 192 °C, Rf = 0.35 (petroleum ether/ethyl acetate 50:1).

^1H NMR (600 MHz, CDCl₃): δ 4.08 (s, 3 H), 7.52 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 1.3 Hz, 1 H), 7.57 (ddd, J = 8.1 Hz, J = 6.8 Hz, J = 1.3 Hz, 1 H), 7.60 (dd, J = 8.1 Hz, J = 0.5 Hz, 1 H), 7.80 (ddd, J = 8.2 Hz, J = 6.6 Hz, J = 1.4 Hz, 1 H), 7.88 (ddd, J = 8.4 Hz, J = 6.6 Hz, J = 1.4 Hz, 1 H), 8.03 (d, J = 9.3 Hz, 1 H), 8.18 (d, J = 9.3 Hz, 1 H), 8.29 (dd, J = 8.5 Hz, J = 1.0 Hz, 1 H), 8.42 (dd, J = 8.6 Hz, J = 0.9 Hz, 1 H), 9.24 (d, J = 7.7 Hz, 1 H). ^13C NMR (75 MHz, CDCl₃): δ 29.6 (CH₃), 109.3 (CH), 114.1 (Cquat), 117.6 (CH), 121.3 (CH), 123.6 (CH), 123.9 (Cquat), 124.8 (CH), 127.5 (CH), 128.4 (CH), 129.4 (CH), 129.5 (CH), 129.8 (CH), 139.4 (Cquat), 139.5 (Cquat), 140.9 (Cquat), 141.1 (Cquat), 141.6 (Cquat), 142.9 (Cquat). MS (EI, m/z (%)): 284 (22), 283 ([M]+, 100), 282 ([M–H]+, 21), 268 ([M–CH₃]+, 10), 141 ([C₉H₅N₂]+, 21), 57 (13). IR: ν [cm⁻¹] 3048
(w), 2959 (w), 2926 (w), 2872 (w), 2857 (w), 1731 (m), 1614 (w), 1609 (w), 1585 (w), 1558 (m), 1516 (m), 1506 (m), 1483 (m), 1456 (m), 1445 (m), 1427 (m), 1387 (w), 1373 (w), 1329 (m), 1315 (m), 1287 (m), 1260 (m), 1231 (m), 1198 (w), 1138 (m), 1117 (m), 1078 (s), 1036 (m), 1011 (m), 984 (m), 935 (m), 903 (w), 856 (w), 822 (m), 797 (m), 775 (m), 750 (s), 737 (s), 661 (m), 611 (m). HRMS calcd for $[\text{C}_{19}\text{H}_{13}\text{N}_3\text{+H}]^+$: 284.1182; Found: 284.1186.
Table S2. Optimization of the cycloisomerization of 3-ethynylquinoxalines 8 to indolo[3,2-a]phenazines 9.

| Entry | Alkyne 8 | Catalyst/additive | T [°C] | t [h] | Solvent | Yield of compound 9<sup>[a]</sup> |
|-------|----------|-------------------|--------|-------|---------|-------------------------------|
| 1     | 142 mg (0.50 mmol) of 8k | 11 mg (49 μmol, 10 mol%) of InCl<sub>3</sub> | 80 | 5 | 1.0 mL of toluene | no conversion |
| 2     | 142 mg (0.50 mmol) of 8k | 22 mg (0.1 mmol, 20 mol%) of InCl<sub>3</sub> | 80 | 5 | 1.0 mL of toluene | no conversion |
| 3     | 142 mg (0.50 mmol) of 8k | 22 mg (0.1 mmol, 20 mol%) of InCl<sub>3</sub><sup>[b]</sup> | 80 | 24 | 1.0 mL of toluene | no conversion |
| 4     | 142 mg (0.50 mmol) of 8k | 33 mg (0.15 mmol, 30 mol%) of InCl<sub>3</sub> | 80 | 5 | 1.0 mL of toluene | no conversion |
| 5     | 142 mg (0.50 mmol) of 8k | 4.4 mg (25 μmol, 5 mol%) of PdCl<sub>2</sub> | 80 | 24 | 1.0 mL of toluene | no conversion |
| 6     | 142 mg (0.50 mmol) of 8k | 25 mg (50 μmol, 10 mol%) of (Ph₃P)₃AuCl | 80 | 24 | 1.0 mL of toluene | 16 mg (11%) of 9k<sup>[c]</sup> |
| 7     | 142 mg (0.50 mmol) of 8k | 50 mg (0.16 mmol, 33 mol%) of AuCl<sub>3</sub> | 80 | 24 | 1.0 mL of toluene | no conversion |
| 8     | 142 mg (0.50 mmol) of 8k | 61 mg (0.20 mmol, 40 mol%) of AuCl<sub>3</sub> | 80 | 24 | 1.0 mL of toluene | no conversion |
| 9     | 142 mg (0.50 mmol) of 8k | 45 mg (0.15 mmol, 30 mol%) of AuCl<sub>3</sub> | 80 | 24 | 1.0 mL of toluene | 20 mg (14%) of 9k |
| 10    | 142 mg (0.50 mmol) of 8k | 72 mg (0.2 mmol, 40 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of THF | no conversion |
| 11    | 142 mg (0.50 mmol) of 8k | 72 mg (0.2 mmol, 40 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of toluene | no conversion |
| 12    | 178 mg (0.50 mmol) of 8a | 2.0 mL (26 mmol) of CF₃CO₂H | 80 | 3 | - | no conversion<sup>[e]</sup> |
| 13    | 178 mg (0.50 mmol) of 8a | 72 mg (0.2 mmol, 40 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of toluene | 100 mg (56%) of 9a |
| 14    | 178 mg (0.50 mmol) of 8a | 18 mg (0.50 mmol, 10 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of toluene | 90 mg (50%) of 9a |
| 15    | 178 mg (0.50 mmol) of 8a | 3.6 mg (10 μmol, 2 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of toluene | 134 mg (75%) of 9a |
| 16    | 178 mg (0.50 mmol) of 8a | 1.8 mg (5.0 μmol, 1 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of toluene | 93 mg (52%) of 9a |
| 17    | 178 mg (0.50 mmol) of 8a | 3.6 mg (10 μmol, 2 mol%) of NaAuCl<sub>4</sub> | 80 | 48 | 1.0 mL of toluene | 123 mg (69%) of 9a |
| 18    | 178 mg (0.50 mmol) of 8a | 3.6 mg (10 μmol, 2 mol%) of NaAuCl<sub>4</sub> | 80 | 24 | 1.0 mL of CH₂Cl₂ | 39 mg (22%) of 9a |
| 19    | 178 mg (0.50 mmol) of 8a | 127 mg (0.50 mmol) of iodine | 80 | 24 | 1.0 mL of CH₂Cl₂ | no conversion |
| 20    | 46 mg (0.13 mmol) of 8a | 55 mg (0.17 mmol, 130 mol%) of PhI(OAc)<sub>2</sub> (PIDA) | 80 | 24 | 1.0 mL of 1,2-dichloroethane | no conversion |
| 21    | 46 mg (0.13 mmol) of 8a | 73 mg (0.17 mmol, 130 mol%) of PhI(OzCCF₃)<sub>2</sub> (PIFA) | 80 | 24 | 1.0 mL of 1,2-dichloroethane | no conversion |
| 22    | 89 mg (0.25 mmol) of 8a | 49 mg (0.3 mmol) of ICl | -78 | 24 | 1.0 mL of CH₂Cl₂ | no conversion |
| 23    | 178 mg (0.50 mmol) of 8a | 3.6 mg (10 μmol, 2 mol%) of NaAuCl<sub>4</sub>/0.2 mg (20 μmol, 4 mol%) of Ag₃SO₃ (4 mol%) | 80 | 24 | 1.0 mL of toluene | 64 mg (36%) of 9a |
| 24    | 178 mg (0.50 mmol) of 8a | 16 mg (10 μmol, 2 mol%) of [Ph₃PAu]NTf₂ · 0.5 toluene | 80 | 24 | 1.0 mL of toluene | 21 mg (12%) of 9a |
| 25    | 178 mg (0.50 mmol) of 8a | 16 mg (10 μmol, 2 mol%) of [Ph₃PAu]NTf₂ · 0.5 toluene/1.7 mg (10 μmol, 2 mol%) of AgNO₃ | 80 | 24 | 1.0 mL of toluene | 18 mg (10%) of 9a |
| 26    | 178 mg (0.50 mmol) of 8a | 1.7 mg (10 μmol, 2 mol%) of AgNO₃ | 80 | 24 | 1.0 mL of toluene | no conversion |
| 27    | 178 mg (0.50 mmol) of 8a | 16 mg (10 μmol, 2 mol%) of [Ph₃PAu]NTf₂ · 0.5 toluene/7.7 mg (30 μmol, 6 mol%) AgOTf | 80 | 24 | 1.0 mL of toluene | traces of 9a |

[a] Yield after isolation by column chromatography. [b] InCl<sub>3</sub> was dried in the Schlenk tube by heat gun. [c] Compound 8k (61 mg, 43%) was reisolated. [d] Compound 8k (50 mg, 35%) was reisolated. [e] Compound 8a (155 mg, 87%) was reisolated after column chromatography.
5. General Procedure GP2 for the Cycloisomerization-1,2-Silyl Shift Synthesis of Indolo[3,2-a]phenazines 9

![Chemical structure](image)

Ethynyl quinoxaline 8 (0.50 mmol, 1.0 equiv) in dry toluene (1.0 mL) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and degassed with nitrogen by syringe cannula for 5 min (for experimental details, see Table S3). Then NaAuCl₄ (4 mg, 5 µmol, 2 mol%) were added under a stream of nitrogen. The mixture was then stirred at 80 °C (oil bath) for 24 h. After cooling to room temp dichloromethane was added and the crude reaction mixture was adsorbed on Celite® and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 9.

Table S3. Experimental details of the synthesis of indolo[3,2-a]phenazines 9.

| Entry | 3-Ethynylquinoxaline 8 | Indolo[3,2-a]phenazine 9 (yield) |
|-------|------------------------|----------------------------------|
| 1[a]  | 178 mg (0.50 mmol) of 8a | 134 mg (75%) of 9a               |
| 2     | 178 mg (0.50 mmol) of 8b | 116 mg (63%) of 9b               |
| 3     | 192 mg (0.50 mmol) of 8c | 91 mg (48%) of 9c                |
| 4     | 191 mg (0.50 mmol) of 8d | 89 mg (47%) of 9d                |
| 5[b]  | 191 mg (0.50 mmol) of 8e | 32 mg (15%) of 9e                |
| 6     | 191 mg (0.50 mmol) of 8f | 20 mg (9%) of 9f                 |
| 7     | 191 mg (0.50 mmol) of 8g | 81 mg (37%) of 9g                |
| 8     | 191 mg (0.50 mmol) of 8h | 60 mg (30%) of 9h                |
| 9     | 193 mg (0.50 mmol) of 8i | 97 mg (50%) of 9i                |
| 10    | 200 mg (0.50 mmol) of 8j | 92 mg (46%) of 9j                |
| 11    | 125 mg (0.35 mmol) of 8k | 65 mg (53%) of 9k                |

[a]Compound 9a was also prepared on a 3.00 and 6.00 mmol scale with 64 and 61% yield, respectively. [b]4 mol% of NaAuCl₄ (8 mg, 10 µmol) as a catalyst was used.
5.1. 8-Methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9a)

![Chemical Structure]

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) compound 9a (134 mg, 75%) was obtained as a yellow solid, Mp 216 °C, Rf = 0.18 (petroleum ether/ethyl acetate 50:1). Likewise, starting from ethynyl quinoxaline 8a (2133 mg, 6.00 mmol) in toluene (12 mL) with NaAuCl₄ (48 mg, 58.8 μmol, 2 mol%) as a catalyst compound 9a (1300 mg, 61%) was obtained.

5.2. 8-Ethyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9b)

![Chemical Structure]

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1) compound 9b (116 mg, 63%) was obtained as a yellow solid, Mp 190 °C, Rf = 0.25 (petroleum ether/ethyl acetate 30:1).

1H NMR (300 MHz, CDCl₃): δ 0.62 (s, 9 H), 1.58 (t, J = 7.2 Hz, 3 H), 4.59 (q, J = 7.2 Hz, 2 H), 7.47-7.63 (m, 1 H), 7.76 (ddd, J = 8.2 Hz, J = 6.7 Hz, J = 1.5 Hz, 3 H), 7.85 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.6 Hz, 1 H), 8.15 (s, 1 H), 8.28 (ddd, J = 8.5 Hz, J = 1.6 Hz, J = 0.7 Hz, 1 H), 8.40 (ddd, J = 8.7 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.23-9.30 (m, 1 H).

13C NMR (75 MHz, CDCl₃): δ 0.3 (CH₃), 15.2 (CH₃), 38.1 (CH₂), 109.5 (CH), 115.3 (Cquat), 121.3 (CH), 123.7 (CH), 124.1 (CH), 124.4 (CH), 124.9 (Cquat), 127.8 (CH), 129.3 (CH), 129.7 (CH), 130.1 (CH), 138.6 (Cquat), 140.4 (Cquat), 141.3 (Cquat), 142.3 (Cquat), 142.5 (Cquat), 145.3 (Cquat). MS (EI, m/z (%)): 370 (18), 369 ([M]+, 58), 368 ([M – H]+, 16), 355 (30), 354 ([M – CH₃]+, 100), 325 ([C₂₀H₁₅N₃Si]+, 20), 170 (32), 155 ([C₁₁H₉N₂]+, 17), 149 (32), 71 (11), 57 ([C₄H₆]+, 15), 43 ([CH₃Si]+, 10). IR: ν [cm⁻¹] 2972 (w), 2955 (w), 2934 (w), 2893 (w), 1518 (w), 1470 (w), 1452 (m), 1431 (m), 1402 (w), 1387 (w), 1375 (m), 1356 (w), 1341 (w), 1310 (m), 1287 (w), 1238 (m), 1227 (m), 1211 (w), 1192 (m), 1144 (m), 1126 (m), 1107 (w), 1090 (m), 1078 (m), 1057 (w), 1030 (m), 1001 (w), 968 (w), 937 (m), 916 (w), 907 (m), 897 (w), 881 (w), 837 (s), 785 (m), 758 (s), 741 (s), 691 (m), 671 (m), 638 (m).
HRMS calcd for [C\textsubscript{23}H\textsubscript{23}N\textsubscript{3}Si+H]\textsuperscript{+}: 370.1734; Found: 370.1740.

5.3. 8-Propyl-6-(trimethylsilyl)-8\textit{H}-indolo[3,2-a]phenazine (9c)

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) compound 9c (91 mg, 48\%) was obtained as a yellow solid, Mp 156 °C, R\textsubscript{f} = 0.40 (petroleum ether/ethyl acetate 20:1).

\begin{align*}
\text{C}\textsubscript{24}H\textsubscript{25}N\textsubscript{3}Si
\end{align*}

[383.57]

\begin{align*}
\delta & \text{H NMR (300 MHz, CDCl}_3\text{): } \delta 0.62 (s, 9 H), 1.04 (t, J = 7.4 Hz, 3 H), 2.04 (q, J = 7.3 Hz, 2 H), 4.50 (t, J = 7.0 Hz, 2 H), 7.46-7.63 (m, 3 H), 7.76 (ddd, J = 8.2 Hz, J = 6.7 Hz, J = 1.5 Hz, 1 H), 7.85 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.6 Hz, 1 H), 8.15 (s, 1 H), 8.28 (ddd, J = 8.4 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 8.40 (ddd, J = 8.5 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.23-9.30 (m, 1 H).
\end{align*}

\begin{align*}
\delta & \text{C NMR (75 MHz, CDCl}_3\text{: } \delta -0.2 (\text{CH}_3), 11.6 (\text{CH}_3), 23.1 (\text{CH}_2), 44.6 (\text{CH}_2), 109.4 (\text{CH}), 114.7 (\text{C}_{\text{quat}}), 120.8 (\text{CH}), 123.6 (\text{C}_{\text{quat}}), 123.9 (\text{CH}), 124.4 (\text{CH}), 127.4 (\text{CH}), 128.9 (\text{CH}), 129.3 (\text{CH}), 129.7 (\text{CH}), 138.8 (\text{C}_{\text{quat}}), 138.9 (\text{C}_{\text{quat}}), 140.0 (\text{C}_{\text{quat}}), 140.7 (\text{C}_{\text{quat}}), 141.9 (\text{C}_{\text{quat}}), 142.1 (\text{C}_{\text{quat}}), 144.9 (\text{C}_{\text{quat}}). \text{MS (EI, } m/z (\%): 384 (20), 383 ([M]+, 62), 382 ([M – H]+, 16), 369 (31), 368 ([M – \text{CH}_3]+, 100), 338 ([M – (\text{CH}_3)\text{]+, 15), 325 ([C_{20}H_{15}N_3Si]+, 15), 170 (53), 155 ([C_{11}H_8N_2]+, 16).
\end{align*}

IR: ν [cm\textsuperscript{-1}]: 2951 (w), 2926 (w), 2895 (w), 2880 (w), 2853 (w), 1568 (m), 1516 (w), 1450 (w), 1431 (m), 1406 (w), 1389 (w), 1366 (w), 1341 (m), 1306 (w), 1277 (w), 1240 (m), 1225 (m), 1209 (m), 1192 (m), 1146 (m), 1128 (m), 1088 (m), 1038 (w), 1020 (m), 1001 (w), 951 (w), 922 (m), 891 (w), 872 (m), 864 (m), 831 (s), 797 (m), 772 (m), 748 (s), 735 (s), 692 (m), 671 (m), 644 (m), 623 (m). Anal calcd for C\textsubscript{24}H\textsubscript{25}N\textsubscript{3}Si [383.6]: C 75.15, H 6.57, N 10.96; Found: C 74.88, H 6.53, N 10.67.

5.4. 8-Allyl-6-(trimethylsilyl)-8\textit{H}-indolo[3,2-a]phenazine (9d)
According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1) compound 9d (89 mg, 47%) was obtained as a yellow solid, Mp 115 °C, Rf = 0.38 (petroleum ether/ethyl acetate 20:1).

1H NMR (300 MHz, CDCl3): δ 0.61 (s, 9 H), 5.07-5.16 (m, 3 H), 5.23-5.29 (m, 1 H), 6.05-6.19 (m, 1 H), 7.47-7.60 (m, 3 H), 7.77 (ddd, J = 8.3 Hz, J = 6.7 Hz, J = 1.5 Hz, 1 H), 7.86 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.6 Hz, 1 H), 8.11 (s, 1 H), 8.29 (ddd, J = 8.4 Hz, J = 1.6 Hz, J = 0.7 Hz, 1 H), 8.40 (ddd, J = 8.6 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.21-9.32 (m, 1 H). 13C NMR (75 MHz, CDCl3): δ 0.2 (CH3), 45.7 (CH3), 109.8 (CH), 115.4 (CH2), 117.5 (Cquat), 121.5 (CH), 123.9 (CH), 124.0 (CH), 124.4 (CH), 125.0 (Cquat), 127.9 (CH), 129.3 (CH), 129.7 (CH), 130.1 (CH), 132.6 (CH), 139.1 (Cquat), 139.2 (Cquat), 140.5 (Cquat), 141.3 (Cquat), 142.2 (Cquat), 142.5 (Cquat), 145.4 (Cquat). MS (EI, m/z (%)): 382 (21), 381 ([M]+, 16), 367 (33), 366 ([M – CH3]+, 100), 326 ([C29H15N3Si]+, 18), 325 ([C30H16N3Si]+, 61), 295 ([C26H14N3]+, 10), 182 (10). IR: ν [cm⁻¹] 2953 (w), 2930 (w), 2897 (w), 2853 (w), 2785 (w), 1566 (m), 1516 (m), 1186 (m), 1125 (m), 1088 (s), 1024 (m), 993 (m), 966 (m), 935 (m), 924 (m), 914 (m), 883 (m), 831 (s), 802 (m), 773 (m), 743 (s), 691 (m), 667 (m), 635 (m), 604 (m). Anal calcd for C23H25N3OSi [385.5]: C 75.55, H 6.08, N 11.01; Found: C 75.40, H 6.10, N 10.80.

5.5. 8-Hexyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9e)

![Chemical Structure of 8-Hexyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9e)](image)

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) compound 9e (32 mg, 15%) was obtained as a yellow solid, Rf = 0.25 (petroleum ether/ethyl acetate 50:1).

1H NMR (600 MHz, CDCl3): δ 0.60 (s, 9 H), 0.88 (t, J = 7.0 Hz, 3 H), 1.21-1.49 (m, 6 H), 1.99 (p, J = 7.3 Hz, 2 H), 4.53 (t, J = 7.2 Hz, 2 H), 7.46-7.63 (m, 3 H), 7.76 (ddd, J = 8.2 Hz, J = 6.7 Hz, J =1.5 Hz, 1 H), 7.85 (ddd, J = 8.5 Hz, 6.7, J = 1.6 Hz, 1 H), 8.15 (s, 1 H), 8.28 (ddd, J = 8.5 Hz, J =1.6 Hz, J = 0.7 Hz, 1 H), 8.39-8.44 (m, 1 H), 9.22-9.30 (m, 1 H). 13C NMR (75 MHz, CDCl3): δ 0.2 (CH3), 14.1 (CH2), 22.7 (CH2), 27.01 (CH2), 30.0 (CH2), 31.6 (CH2), 43.5 (CH2), 109.8 (CH), 114.93 (Cquat), 121.3 (CH), 124.1 (CH), 124.3 (Cquat), 124.9 (CH), 127.9 (CH), 129.1 (CH), 129.9 (CH), 130.1 (CH), 139.12 (Cquat), 139.38, 140.45 (Cquat), 141.19 (Cquat), 142.19 (Cquat), 145.42 (Cquat). MS (EI, m/z (%)): 426 (20), 425 ([M]+, 57), 424 ([M – H]+, 17), 411 ([M – CH3]+, 32), 410 (100), 339 ([M – C9H13]+, 32), 338 ([M – C9H14]+, 18), 326 (11), 325 S22
(20), 169 (39), 155 (14). IR: \( \tilde{\nu} [\text{cm}^{-1}] = 3055 (w), 3040 (w), 3017 (w), 2949 (w), 2924 (w), 2893 (w), 2857 (w), 1612 (w), 1566 (w), 1553 (w), 1516 (w), 1495 (w), 1466 (m), 1453 (m), 1431 (m), 1416 (w), 1377 (m), 1364 (m), 1339 (w), 1312 (w), 1229 (m), 1211 (m), 1199 (w), 1182 (m), 1144 (m), 1125 (m), 1090 (m), 1067 (w), 1059 (w), 1038 (w), 1019 (m), 999 (w), 953 (w), 937 (m), 918 (m), 907 (w), 878 (w), 835 (s), 817 (m), 806 (m), 789 (m), 7387 (s), 689 (m), 671 (m), 625 (m), 606 (m).

\[ \text{Anal calcd for } C_{27}H_{31}N_3Si [425.2]: \text{C} 76.19, \text{H} 7.34, \text{N} 9.87; \text{Found: C} 75.98, \text{H} 7.33, \text{N} 9.64. \]

5.6. 8-Benzyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9f)

![Diagram of 8-Benzyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9f)]

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 9f (20 mg, 9%) was obtained as a yellow solid, \( R_f = 0.25 \) (petroleum ether/ethyl acetate 10:1).

\(^1\text{H-NMR} \text{(600 MHz, CDCl}_3\): \( \delta \) 0.54 (s, 9 H), 7.26 (s, 2 H), 8.69-8.74 (m, 2 H), 8.81 (ddd, \( J = 14.2 \text{ Hz}, J = 8.0 \text{ Hz}, J = 6.3 \text{ Hz}, 3 \text{ H}), 8.99-9.03 (m, 2 H), 9.04-9.09 (m, 1 H), 9.28 (ddd, \( J = 8.0 \text{ Hz}, J = 6.5 \text{ Hz}, J = 1.4 \text{ Hz}, 1 \text{ H}), 9.37 (ddd, \( J = 8.3 \text{ Hz}, J = 6.6 \text{ Hz}, J = 1.4 \text{ Hz}, 1 \text{ H}), 9.62 (s, 1 H), 9.78 (dd, \( J = 8.5 \text{ Hz}, J = 1.4 \text{ Hz}, 1 \text{ H}), 9.92 (dd, \( J = 8.6 \text{ Hz}, J = 1.3 \text{ Hz}, 1 \text{ H}), 10.76-10.82 (m, 1 H). MS (El, \text{m/z} (%)): 432 (28), 431 ([M]+, 75), 430 ([M – H]+, 16), 417 (33), 416 ([M – CH\(_3\)]+), 100), 326 ([C\(_{20}\)H\(_{15}\)N\(_3\)Si]+, 23), 325 ([C\(_{20}\)H\(_{15}\)N\(_3\)Si]+, 83), 309 ([C\(_{19}\)H\(_{13}\)N\(_3\)Si]+, 11), 295 ([C\(_{18}\)H\(_{9}\)N\(_3\)Si]+, 13), 125 (14), 123 (10), 111 (23), 109 (14), 99 (10), 97 (31), 95 (20), 91 ([C\(_7\)H\(_7\)]+), 85 ([C\(_6\)H\(_2\)]+), 83 ([C\(_6\)H\(_2\)]+), 81 (16), 71 ([C\(_5\)H\(_10\)]+), 27), 69 ([C\(_5\)H\(_10\)]+), 22), 57 ([C\(_4\)H\(_8\)]+), 39), 55 ([C\(_4\)H\(_8\)]+), 22), 43 ([C\(_3\)H\(_3\)Si]+), 21).

5.7. 11-Bromo-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9g)

![Diagram of 11-Bromo-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9g)]

\[ \text{C}_{22}\text{H}_{20}\text{BrN}_3\text{Si} \]

[434.41]
According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) compound 9g (81 mg, 37%) was obtained as a yellow solid, Mp 288 °C, Rf = 0.30 (petroleum ether/ethyl acetate 50:1).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.60 (s, 9 H), 4.07 (s, 3 H), 7.43 (d, $J = 8.7$ Hz, 1 H), 7.61 (dd, $J = 8.7$ Hz, $J = 2.0$ Hz, 1 H), 7.77 (ddd, $J = 8.2$ Hz, $J = 6.6$ Hz, $J = 1.4$ Hz, 1 H), 7.87 (ddd, $J = 8.5$ Hz, $J = 6.7$ Hz, $J = 1.6$ Hz, 1 H), 8.12 (s, 1 H), 8.26 (ddd, $J = 8.5$ Hz, $J = 1.5$ Hz, $J = 0.6$ Hz, 1 H), 8.41 (ddd, $J = 8.5$ Hz, $J = 1.5$ Hz, $J = 0.6$ Hz, 1 H), 9.33 (dd, $J = 2.0$ Hz, $J = 0.5$ Hz, 1 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 0.2 (CH$_3$), 29.4 (CH$_3$), 110.5 (CH), 113.9 (C$_{quat}$), 114.1 (C$_{quat}$), 123.1 (CH), 125.1 (C$_{quat}$), 125.8 (CH), 127.2 (CH), 127.7 (CH), 128.9 (CH), 129.5 (CH), 129.6 (CH), 137.9 (C$_{quat}$), 139.6 (C$_{quat}$), 140.2 (C$_{quat}$), 141.4 (C$_{quat}$), 141.9 (C$_{quat}$), 142.0 (C$_{quat}$), 144.8 (C$_{quat}$). MS (EI, m/z (%)): 436 (14), 435 [81 Br$-$M]+, 49), 434 (28), 433 [79 Br$-$M]+, 45), 432 (15), 421 (27), 420 [37Br-M - CH$_3$]+, 100), 419 (28), 418 ([37Br-M - CH$_3$]+, 94), 405 (14), 403 (17), 308 (15), 210 (41), 209 (49), 170 (11), 169 (22), 162 (23), 155 (26), 154 (18). IR: $\tilde{\nu}$ [cm$^{-1}$] 2949 (w), 2895 (w), 2864 (w), 2820 (w), 1611 (w), 1557 (m), 1518 (w), 1454 (w), 1439 (m), 1414 (m), 1381 (w), 1354 (w), 1327 (w), 1308 (m), 1256 (w), 1240 (m), 1215 (m), 1138 (w), 1125 (m), 1088 (m), 1047 (m), 1015 (m), 1005 (m), 943 (m), 920 (m), 895 (m), 883 (m), 835 (s), 802 (m), 783 (s), 743 (s), 719 (m), 691 (m), 650 (m), 621 (m). Anal calcd for C$_{22}$H$_{20}$BrN$_3$Si [434.4]: C 60.83, H 4.64, N 9.67; Found: C 60.58, H 4.75, N 9.41.

5.8. 11-Chloro-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9h)

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 50:1) compound 9h (58 mg, 30%) was obtained as a yellow solid, Mp 272 °C, Rf = 0.24 (petroleum ether/ethyl acetate 50:1).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.60 (s, 9 H), 4.08 (s, 3 H), 7.48 (d, $J = 1.3$ Hz, 2 H), 7.78 (ddd, $J = 8.2$ Hz, $J = 6.7$ Hz, 1 H), 7.88 (ddd, $J = 8.5$ Hz, $J = 6.7$ Hz, $J = 1.6$ Hz, 1 H), 8.12 (s, 1 H), 8.23-8.31 (m, 1 H), 8.46 (d, $J = 8.6$ Hz, 1 H), 9.22 (s, 1 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 0.2 (CH$_3$), 29.8 (CH$_3$), 110.5 (CH), 114.3 (C$_{quat}$), 123.2 (CH), 123.6 (CH), 124.9 (C$_{quat}$), 125.0 (CH), 126.9 (C$_{quat}$), 128.1 (CH), 129.2 (CH), 130.0 (CH), 130.1 (CH), 138.0 (C$_{quat}$), 140.0 (C$_{quat}$), 140.6 (C$_{quat}$), 141.7 (C$_{quat}$), 142.3 (C$_{quat}$), 142.3 (C$_{quat}$), 145.2 (C$_{quat}$). MS (EI, m/z (%)): 391 ([37Cl-M]$^+$, 17), 390 (18), 389 ([37Cl-M]$^+$, 45), 376 ([37Cl-M - CH$_3$]$^+$, 46), 375 (31), 374
(\[^{37}\text{Cl-M-CH}_3\]^+, 100), 188 (30), 187 (77), 179 (13), 171 (18), 169 (12), 97 ([M-C\text{$_2$H}$_{13}$]$^+$, 12), 71 ([M-C$_3$H$_{15}$]$^+$, 11). IR: $\tilde{\nu} \text{[cm}^{-1}]$ 3057 (w), 2953 (w), 2889 (w), 2851 (w), 2818 (w), 1611 (w), 1572 (w), 1555 (w), 1456 (m), 1439 (m), 1416 (w), 1402 (w), 1379 (w), 1358 (w), 1327 (w), 1304 (m), 1238 (m), 1213 (m), 1179 (w), 1144 (m), 1132 (w), 1092 (m), 1055 (w), 1015 (m), 1003 (w), 951 (w), 922 (w), 897 (m), 887 (m), 837 (s), 808 (m), 789 (m), 746 (s), 727 (m), 691 (w), 658 (m), 621 (w). HRMS calcd for \([\text{C}_{22}\text{H}_{20}\text{ClN}_3\text{Si}^{35}\text{Cl}+\text{H}]^+\): 390.1188; Found: 390.1191.

5.9. 11-Methoxy-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9i)

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1) compound 9i (97 mg, 50%) was obtained as a orange solid, Mp 211 °C, $R_f = 0.31$ (petroleum ether/ethyl acetate 30:1).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 0.59 (s, 9 H), 4.08 (s, 3 H), 4.11 (s, 3 H), 7.20 (dd, $J$ = 8.8 Hz, $J$ = 2.6 Hz, 1 H), 7.49 (d, $J$ = 8.8 Hz, 1 H), 7.76 (ddd, $J$ = 8.2 Hz, $J$ = 6.6 Hz, $J$ = 1.4 Hz, 1 H), 7.84 (ddd, $J$ = 8.3 Hz, $J$ = 6.6 Hz, $J$ = 1.4 Hz, 1 H), 8.12 (s, 1 H), 8.24-8.31 (m, 1 H), 8.36-8.42 (m, 1 H), 8.74 (d, $J$ = 2.5 Hz, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 0.2 (CH$_3$), 29.8 (CH$_3$), 56.3 (CH$_3$), 100.5 (CH), 106.1 (CH), 110.3 (CH), 115.1 (CH), 124.1 (CH), 124.5 (C$_{\text{quat}}$), 127.8 (CH), 129.0 (C$_{\text{quat}}$), 129.8 (CH), 130.1 (CH), 130.5 (C$_{\text{quat}}$), 134.8 (C$_{\text{quat}}$), 140.0 (C$_{\text{quat}}$), 140.3 (C$_{\text{quat}}$), 141.0 (C$_{\text{quat}}$), 145.5 (C$_{\text{quat}}$), 156.6 (C$_{\text{quat}}$). MS (EI, $m/z$ (%)): 386 (22), 385 ([M]$^+$, 68), 384 ([M – H]$^+$, 14), 371 (30), 370 ([M – CH$_3$]$^+$, 100), 355 ([M-2 CH$_3$]$^+$, 10), 327 ([C$_{19}$H$_{12}$N$_2$OSi]$^+$, 13), 312 ([M-Si(CH$_3$)$_3$]$^+$, 18), 185 (18), 177 ([C$_{12}$H$_5$N$_3$]$^+$, 18), 163 ([C$_{12}$H$_4$N]$^+$, 38), 148 ([C$_9$H$_9$NO]$^+$, 11). IR: $\tilde{\nu} \text{[cm}^{-1}]$ 2949 (w), 2899 (w), 1626 (w), 1570 (w), 1557 (w), 1530 (w), 1518 (m), 1483 (w), 1470 (w), 1435 (m), 1418 (w), 1396 (w), 1314 (w), 1271 (w), 1254 (m), 1234 (m), 1213 (m), 1194 (m), 1169 (m), 1144 (w), 1130 (w), 1016 (m), 1005 (w), 987 (w), 966 (w), 924 (w), 899 (m), 831 (s), 795 (m), 743 (s), 696 (m), 675 (m), 665 (w), 640 (w), 633 (w). Anal calcd for C$_{23}$H$_{23}$N$_3$OSi [385.5]: C 71.65, H 6.01, N 10.90; Found: C 71.36, H 5.94, N 10.84.
5.10. 11-Methoxy-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9j)

\[ C_{24}H_{25}N_3O Si \]

[399.57]

According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1) and crystallization from pentane after sonication compound 9j (116 mg, 63%) was obtained as an orange solid, Mp 169 °C, Rf = 0.39 (petroleum ether/ethyl acetate 30:1).

\(^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 0.61 (s, 9H), 1.56 (t, J = 7.2 Hz, 3H), 4.11 (s, 3H), 4.56 (q, J = 7.2 Hz, 2H), 7.19 (dd, J = 8.9 Hz, J = 2.6 Hz, 1H), 7.46-7.51 (m, 1H), 7.75 (ddd, J = 8.3 Hz, J = 6.7 Hz, J = 1.5 Hz, 1H), 7.84 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.6 Hz, 1H), 8.10 (s, 1H), 8.28 (ddd, J = 8.5 Hz, J = 1.6 Hz, J = 0.7 Hz, 1H), 8.39 (ddd, J = 8.5 Hz, J = 1.5 Hz, J = 0.7 Hz, 1H), 8.75 (d, J = 2.6 Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl₃): \( \delta \) 0.2 (CH₃), 15.3 (CH₃), 38.2 (CH₂), 56.2 (CH₃), 105.7 (CH), 110.3 (CH), 114.7 (CH), 115.0 (C quat), 123.9 (CH), 124.9 (C quat), 127.7 (CH), 129.2 (CH), 129.6 (CH), 130.1 (CH), 133.7 (C quat), 139.0 (C quat), 140.3 (C quat), 140.9 (C quat), 142.4 (C quat), 142.5 (C quat), 145.4 (C quat), 155.4 (C quat). MS (EI, m/z (%)): 400 (28), 399 ([M]+, 84), 398 ([M – H]+, 14), 385 (33), 384 ([M – CH₃]+, 100), 340 ([M – 4 CH₃]+, 20), 312 ([C₂₀H₁₃N₃O]+, 19), 278 (21), 277 (56), 199 (17), 192 ([C₁₂H₇N₃]+, 20), 185 (30), 183 (10), 167 (15), 163 ([C₁₂H₄N]+, 13), 156 ([C₁₁H₈N₂]+, 15), 149 (48), 141 (10), 125 (10), 111 (16), 97 (23), 95 (14), 94 (11), 85 ([C₈H₁₂]+, 24), 83 ([C₈H₁₂]+, 22), 81 (11), 71 ([C₆H₁₀]+, 28), 57 ([C₄H₆Si]+, 43), 55 ([C₄H₄]+, 24), 43 ([C₃H₃Si]+, 39), 41 (18). IR: \( \tilde{\nu} [\text{cm}^{-1}] \) 2980 (m), 2949 (m), 2940 (m), 2830 (m), 1624 (m), 1582 (m), 1516 (m), 1503 (m), 1474 (m), 1470 (m), 1435 (m), 1408 (m), 1381 (m), 1356 (m), 1339 (m), 1317 (m), 1273 (m), 1240 (m), 1209 (m), 1192 (m), 1169 (m), 1144 (m), 1126 (m), 1082 (m), 1042 (m), 1024 (m), 1001 (m), 943 (m), 907 (m), 881 (m), 835 (s), 797 (s), 762 (s), 756 (s), 737 (m), 692 (m), 673 (m), 635 (m), 604 (m). Anal calcd for C₂₄H₂₅N₃O Si [399.6]: C 72.14, H 6.31, N 10.52; Found: C 71.92, H 6.21, N 10.44.

5.11. 8-Methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine-7-d (9k)

\[ C_{22}H_{20}D₃N₃Si \]

[356.52] S26
According to GP2 and flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1) compound 9k (65 mg, 53%) was obtained as a yellow solid; Mp 215.7-217.5 °C, Rf = 0.21 (petroleum ether/ethyl acetate 50:1). The integration of the singlet at δ8.15 reveals a degree of deuteration at position 7 of 70%.

1H NMR (300 MHz, CDCl₃): δ 0.61 (s, 9 H), 4.08 (s, 3 H), 7.44-7.61 (m, 3 H), 7.76 (ddd, J = 8.2 Hz, J = 6.7 Hz, J = 1.5 Hz, 1 H), 7.85 (ddd, J = 8.5 Hz, J = 6.6 Hz, J = 1.6 Hz, 1 H), 8.15 (s, 0.3 H), 8.23-8.32 (m, 1 H), 8.36-8.42 (m, 1 H), 9.20-9.25z (m, 1 H). 13C NMR (75 MHz, CDCl₃): δ 0.3 (CH₃), 28.8 (CH₃), 109.5 (CH), 115.2 (C quat), 121.4 (CH), 123.8 (CH), 123.9 (CH), 124.2 (C quat), 124.9 (CH), 127.9 (CH), 129.3 (CH), 130.1 (CH), 139.6 (C quat), 139.7 (C quat), 140.5 (C quat), 141.2 (C quat), 142.2 (C quat), 142.5 (C quat), 145.3 (C quat). MS (EI, m/z (%)): 357 (15), 356 ([M]+, 46), 355 ([M – H]+, 37), 342 (26), 341 ([M – CH₃]+, 100), 340 (44), 326 (23), 325 (13), 170 (38), 155 (17), 111 (12), 97 (15), 95 (14), 83 (11), 81 (11), 71 (11), 69 (14), 57 (23), 55 (15). IR: ν [cm⁻¹] 2941 (w), 1560 (m), 1518 (m), 1436 (m), 1422 (m), 1329 (m), 1236 (m), 1086 (m), 910 (m), 831 (s), 745 (s), 731 (s). HR-MS (ESI) calcd. for (C₂₂H₂₀DN₃Si+H)+ 357.1640. Found: 357.1638 (100%).

6. Optimization of the Synthesis of 6-Iodo-8-methyl-8H-indolo[3,2-a]phenazine (16)

The experimental procedure of the optimization was performed according to chapter 6 by variation of concentration of substrate 9a, equivs of ICl, reaction times (Table S4).

Table S4. Optimization of the iodination of indolo[3,2-a]phenazine 9a by ipso-substitution to give 6-iodo-8-methyl-indolo[3,2-a]phenazine (16).[a]

| Entry | c(9a) [M] | ICl [equivs] | t [min] | Yield of compound 16[b] |
|-------|-----------|-------------|--------|-------------------------|
| 1     | 0.10      | 1.00        | 30     | 64%                     |
| 2     | 0.10      | 1.00        | 60     | 64%                     |
| 3     | 0.17      | 1.00        | 30     | 61%                     |
| 4     | 0.17      | 1.70        | 30     | 76%                     |

[a] All reactions were performed on a 0.50 mmol scale with respect of indolo[3,2-a]phenazine 9a. [b]Yield after isolation by column chromatography.
7. Synthesis of 6-iodo-8-methyl-8H-indolo[3,2-a]phenazine (16)

Indolo[3,2-a]phenazine 9a (178 mg, 0.50 mmol) in dry dichloromethane (2.0 mL) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and cooled to -78 °C (dry ice/acetone). Then iodinemonochloride (138 mg, 0.85 mmol) was added by syringe. The syringe was rinsed with dichloromethane (1 mL), which was added to the reaction mixture. The cooling bath was removed and was allowed to come to room temp. The mixture was stirred at room temp for 30 min. Then, the reaction was stopped by addition of a 10 wt% aqueous solution of sodium thiosulfate pentahydrate (5 mL). The aqueous phase was extracted with dichloromethane (three times) and the combined organic layers were dried (anhdyrous magnesium sulfate). The crude reaction mixture was adsorbed on Celite® and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 16 (156 mg, 76%) as an orange solid, Mp 225 °C, Rf = 0.30 (petroleum ether/ethyl acetate 10:1).

C19H12IN3 [409.23]

1H NMR (600 MHz, CDCl3): δ 3.94 (s, 3 H), 7.46 (t, J = 7.4 Hz, 2 H), 7.51 (dd, J = 8.7 Hz, J = 6.4 Hz, 1 H), 7.81 (ddd, J = 8.0 Hz, J = 6.6 Hz, J = 1.3 Hz, 1 H), 7.85-7.92 (m, 1 H), 8.36 (dd, J = 8.6 Hz, J = 1.3 Hz, 2 H), 8.56 (s, 1 H), 9.07-9.13 (m, 1 H). 13C NMR (150 MHz, CDCl3): δ 29.8 (CH3), 100.2 (Cquat), 109.5 (CH), 115.4 (Cquat), 121.7 (CH), 123.8 (Cquat), 123.9 (CH), 125.5 (CH), 127.8 (CH), 128.8 (CH), 129.0 (CH), 130.0 (CH), 130.7 (CH), 139.3 (Cquat), 139.6 (Cquat), 139.9 (Cquat), 140.5 (Cquat), 141.7 (Cquat), 143.4 (Cquat). MS (EI, m/z (%)): 410 (21), 409 ([M]+, 100), 282 ([M – I]+, 41), 267 ([C18H12N3]+, 14), 205 (28), 140 (42), 127 (I+, 24). IR: ν [cm⁻¹] 2955 (w), 2922 (m), 2853 (w), 1570 (m), 1516 (m), 1466 (w), 1454 (m), 1439 (m), 1398 (w), 1385 (m), 1371 (w), 1333 (m), 1321 (m), 1308 (m), 1260 (m), 1207 (m), 1194 (m), 1121 (m), 1098 (m), 1080 (m), 1016 (m), 999 (m), 986 (w), 928 (w), 910 (w), 876 (w), 849 (m), 808 (m), 799
(m), 787 (m), 760 (m), 739 (s), 706 (m), 677 (m), 648 (w), 604 (m). Anal calcd for C_{19}H_{12}IN_{3} [409.2]: C 55.77, H 2.96, N 10.27; Found: C 55.66, H 2.94, N 10.17.

8. Optimization of the synthesis of compound 18a by Suzuki coupling of 6-iodo-indolo[3,2-a]phenazine 16

Table S5. Optimization of the Suzuki coupling of iodination of 6-iodo-8-methyl-indolo[3,2-a]phenazine (16) and p-methoxyphenylboronic acid (17a) to give 6-(p-anisyl)-8-methyl-indolo[3,2-a]phenazine (18a).

| Entry | c(16) [M] | base          | solvents                       | Yield of compound 18a^[a] |
|-------|--------|---------------|--------------------------------|--------------------------|
| 1     | 0.17   | Na$_2$CO$_3$  | 1,4-dioxane/MeOH (2:1)         | 42%                      |
| 2     | 0.17   | Na$_2$CO$_3$  | DMF/H$_2$O (2:1)               | 66%                      |
| 3^[b] | 0.10   | K$_2$CO$_3$   | DMF/H$_2$O (2:1)               | 75% (75%)^[c]            |

^[a] Yields were determined by $^1$H NMR spectroscopy in the crude reaction mixture with 1,3,5-trimethoxybenzene as a standard (integration of the methoxy proton resonances). [b] After 1 h 2 mL of DMF were added to the reaction mixture (2 mL). [c] Yield after isolation by column chromatography.

6-Iodo-indolo[3,2-a]phenazine 16 (205 mg, 0.50 mmol, 1.00 equiv), DMF (2.0 mL), and water (1.0 mL) were placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and degassed with nitrogen by syringe cannula for 5 min. Then, Pd[(PPh)$_3$)$_4$ (58 mg, 50 µmol, 10 mol%), 4-methoxybenzylboronic acid (17a) (84 mg, 0.55 mmol, 1.10 equivs) and K$_2$CO$_3$ (173 mg, 1.25 mmol, 2.50 equivs) were successively added to the reaction mixture. The mixture was placed into an oil bath (100 °C) and heated for 17 h. After cooling to room temp (water bath) a 10% aqueous sodium thiosulfate pentahydrate solution (10 mL) was added to the reaction mixture, which was extracted with dichloromethane (controlled by TLC), the combined organic phases were dried (anhydrous Na$_2$SO$_4$) and the crude product was adsorbed on Celite® and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 18a (146 mg, 75%) as an orange solid, Mp 224 °C, R$_f$ = 0.23 (petroleum ether/ethyl acetate 10:1) (for analytical data see chapter 9.1).
9. Optimization of the one-pot ipso-iodination-Suzuki synthesis of compound 18a

The optimization was performed on a 0.50 mmol scale with respect to substrate 9a as described in GP3 (chapter 9) with varying the solvents and additives. The optimal solvent mixture again is DMF/water (2:1) (Table S6, entries 2-10). Interestingly, potassium carbonate as a base is clearly superior over cesium fluoride, which was expected to activate the carbon-silicon bond for transmetalation, but which gave considerably lower yield (Table S6, entries 4 and 5). Furthermore, a slight excess of iodine monochloride appears to give similar yield (Table S6, entries 3 and 9), however, in combination with increasing the amount of base the optimal conditions were identified, which could be directly transposed to yield after isolation (Table S6, entry 10).

Table S6. Optimization of the one-pot ipso-iodination-Suzuki coupling sequence of 6-(trimethylsilyl)indolo[3,2-a]phenazine 9a and p-methoxyphenylboronic acid (17a) to give 6-(p-anisyl)-8-methyl-indolo[3,2-a]phenazine (18a).[a]

| Entry | ICl [equivs] | solvents | base ([equivs]) | Yield of compound 18a[b] |
|-------|-------------|----------|----------------|-------------------------|
| 1     | 1.00        | 1,4-dioxane/MeOH (2:1) | K₂CO₃ (2.50) | 40%                     |
| 2     | 1.00        | DMF/H₂O (2:1) | K₂CO₃ (2.50) | 71%                     |
| 3     | 1.20        | DMF/H₂O (2:1) | K₂CO₃ (2.50) | 66%                     |
| 4     | 1.20        | DMF/H₂O (2:1) | CsF (2.50) | 26%                     |
| 5     | 1.30        | DMF/H₂O (2:1) | CsF (2.50) | 33%                     |
| 6     | 1.30        | DMF/H₂O (2:1) | K₂CO₃ (2.50) | 57%                     |
| 7     | 1.30        | DMF/H₂O (2:1) | Na₂CO₃ (2.50) | 58%                     |
| 8     | 2.00        | DMF/H₂O (2:1) | K₂CO₃ (2.50) | 7%                      |
| 9     | 1.50        | DMF/H₂O (2:1) | K₂CO₃ (5.00) | 68%                     |
| 10    | 1.70        | DMF/H₂O (2:1) | K₂CO₃ (5.00) | 75% (72%[c])           |

[a] The optimizations were performed on a 0.50 mmol scale with respect to indolo[3,2-a]phenazine (9a) at [9a] = 0.17 M. [b] Yields were determined by ¹H NMR spectroscopy in the crude reaction mixture with 1,3,5-trimethoxybenzene as a standard (integration of the methoxy proton resonances). [c] Yield after isolation by column chromatography on silica gel.
10. **General Procedure GP3 for the Iodination-Suzuki Synthesis of 6-Aryl-indolo[3,2-a]phenazines 18**

Indolo[3,2-a]phenazine 9a (356 mg, 1.00 mmol, 1.00 equiv) in dry dichloromethane (2.0 mL) was placed under nitrogen atmosphere in a sintered screw-cap Schlenk tube with a magnetic stir bar and degassed with nitrogen by syringe cannula for 5 min. The solution was then cooled to -78 °C (dry ice/acetone bath) and stirred for 5 min. Then, iodine(I) chloride (276 mg, 1.70 mmol) was quickly added and the syringe was rinsed with dichloromethane (2 mL). Then, the cooling bath was removed and reaction mixture was stirred at room temp for 30 min. Then, deionized water (2 mL), K$_2$CO$_3$ (692 mg, 5.00 mmol), aryl boronic acid/boronate 17 (1.10 mmol, 1.1 equivs) (for experimental details, see Table S7), Pd[(PPh)$_3$]$_4$ (116 mg, 0.1 mmol, 10 mol%), and DMF (4 mL) were successively added to the reaction mixture. The mixture was placed into an oil bath (100 °C) and heated for 17 h. After cooling to room temp (water bath) a 10% aqueous sodium thiosulfate pentahydrate solution (10 mL) was added to the reaction mixture, which was extracted with dichloromethane (controlled by TLC), the combined organic phases were dried (anhydrous Na$_2$SO$_4$) and the crude product was adsorbed on Celite® and subjected to flash chromatography on silica gel (petroleum ether boiling range 40-60 °C/ethyl acetate) to give compound 18.
Table S7. Experimental details of the synthesis of 6-aryl-indolo[3,2-a]phenazines 18.

| Entry | Aryl boronic acid/boronate 17 | 6-Aryl-indolo[3,2-a]phenazines 18 |
|-------|-------------------------------|-----------------------------------|
| 1[a]  | 168 mg (1.10 mmol) of p-OMeC₆H₄B(OH)₂ (17a) | 284 mg (72%) of 18a |
| 2[a]  | 75 mg (0.55 mmol) of p-MeC₆H₄B(OH)₂ (17b) | 104 mg (56%) of 18b |
| 3     | 134 mg (1.10 mmol) of PhB(OH)₂ (17c) | (167 mg (47%) of 18c |
| 4     | 262 mg (1.10 mmol) of p-ClC₆H₄Bpin (17d) | 293 mg (74%) of 18d |
| 5     | 134 mg (1.10 mmol) of p-NCC₆H₄B(OH)₂ (17e) | 133 mg (35%) of 18e |
| 6[b]  | 132 mg (0.61 mmol) of p-PrOC₆H₄Br | (132 mg, 63%) of 18f |
| 7[c]  | 146 mg (0.60 mmol) of p-NpentylOC₆H₄Br | (118 mg, 53%) of 18g |

[a] Performed on a 0.5 mmol scale.  
[b] Performed by one-generation of boronate 17f from 1-bromo-4-isopropoxybenzene in THF (3.6 mL) with n-BuLi (0.42 mL, 0.67 mmol) in hexanes at -78 °C for 15 min followed by addition of trimethyl borate (0.08 mL, 0.71 mmol) and warming to RT; the boronate was transferred to the reaction mixture of the 6-iodo indolo[3,2-a]phenazine 16 via syringe.  
[c] Performed by one-generation of boronate 17g from 1-bromo-4-pentoxybenzene in THF (3.6 mL) with n-BuLi (0.42 mL, 0.67 mmol) in hexanes at -78 °C for 15 min followed by addition of trimethyl borate (0.08 mL, 0.71 mmol) and warming to RT; the boronate was transferred to the reaction mixture of the 6-iodo indolo[3,2-a]phenazine 16 via syringe.

10.1. 6-(4-Methoxyphenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18a)

![Chemical structure](https://example.com/structure.png)

**C₂₆H₁₉N₃O**  
[389.46]

According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 18a (284 mg, 72%) was obtained as an orange solid, Mp 224 °C, Rf = 0.23 (petroleum ether/ethyl acetate 10:1). ¹H NMR (300 MHz, CDCl₃): δ 3.95 (s, 3 H), 4.08 (s, 3 H), 7.12 (d, J = 2.1 Hz, 1 H), 7.14 (d, J = 2.1 Hz, 1 H), 7.55 (m, 3 H), 7.74 (ddd, J = 8.3 Hz, J = 6.6 Hz, J = 1.4 Hz, 1 H), 7.87 (m, 3 H), 8.00 (s, 1 H), 8.24 (ddd, J = 8.6 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 8.40 (ddd, J = 8.5 Hz, J = 1.4 Hz, J = 0.7 Hz, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 29.7 (CH₃), 55.6 (CH₂), 109.4 (CH), 113.5 (C₉), 113.7 (CH), 116.9 (CH), 121.4 (CH), 123.7 (CH), 124.3 (C₉), 124.7 (CH), 128.0 (CH), 129.2 (CH), 130.1 (CH), 130.5 (CH), 131.8 (C₉), 132.4 (CH), 138.8 (C₉), 139.5 (C₉), 139.9 (C₉), 140.0 (C₉), 140.8 (C₉), 141.9 (C₉), 142.5 (C₉), 159.5 (C₉). MS (EI, m/z (%)): 390 (31), 389 ([M⁺], 100), 388 ([M – H⁺], 26), 374 ([M –
10.2. 8-Methyl-6-(p-tolyl)-8H-indolo[3,2-a]phenazine (18b)

\[
\text{\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Me} \\
\end{array}}
\]

\[
\text{C}_{26}\text{H}_{19}\text{N}_3
\]

[373.46]

According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 18b (104 mg, 56%) was obtained as an orange solid, Mp 233 °C, R_f = 0.23 (petroleum ether/ethyl acetate 10:1). ^1H NMR (300 MHz, CDCl_3): δ 2.52 (s, 3 H), 4.07 (d, J = 0.9 Hz, 3 H), 7.37-7.44 (m, 2 H), 7.47-7.62 (m, 3 H), 7.73 (ddd, J = 8.3 Hz, J = 6.6 Hz, J = 1.5 Hz, 1 H), 7.78-7.90 (m, 3 H), 8.02 (d, J = 0.8 Hz, 1 H), 8.18-8.27 (m, 1 H), 8.40 (ddd, J = 8.7 Hz, J = 1.4 Hz, J = 0.7 Hz, 1 H), 9.23-9.29 (m, 1 H). ^13C NMR (75 MHz, CDCl_3): δ 21.5 (CH_3), 29.7 (CH_3), 109.4 (CH), 113.6 (C_quat), 117.2 (CH), 121.4 (CH), 123.8 (CH), 124.3 (C_quat), 124.8 (CH), 128.0 (CH), 128.9 (CH), 129.2 (CH), 130.1 (CH), 130.5 (CH), 131.2 (CH), 136.5 (C_quat), 137.6 (C_quat), 139.2 (C_quat), 139.5 (C_quat), 139.9 (C_quat), 140.0 (C_quat), 140.8 (C_quat), 141.9 (C_quat), 142.6 (C_quat). MS (El, m/z (%)): 374 (32), 373 ([M]^+), 100, 372 ([M – H]^+), 21, 359 (15), 358 ([M – CH_3]^+), 31, 357 ([M – CH_4]^+), 22, 356 (22), 343 ([M – CH_2]^+), 13, 342 ([M – CH_2]^+), 11, 341 (11), 295 (11), 293 (11), 281 ([M – CH_3]^+), 25, 221 (28), 207 (14), 186 (12), 179 ([C_12H_6N_2]^+), 16, 178 ([C_12H_6N_2]^+), 40, 177 ([C_12H_6N_2]^+), 17, 167 (22), 165 (18), 155 (11), 153 (15), 149 (52), 147 (22), 139 (18), 137 (16), 127 (20), 125 (30). IR: ν [cm\(^{-1}\)] 3915 (w), 3998 (w), 3836 (w), 1614 (w), 1585 (w), 1516 (m), 1479 (w), 1445 (w), 1385 (w), 1339 (w), 1314 (w), 1279 (w), 1254 (w), 1221 (w), 1202 (w), 1169 (w), 1125 (w), 115 (w), 1076 (w), 1016 (w), 1007 (w), 935 (m), 912 (w), 885 (w), 862 (w), 813 (m), 785 (w), 734 (s), 706 (w), 678 (m), 648 (w), 619 (m). Anal calcd for C_{26}H_{19}N_3 [373.5]: C 83.62, H 5.13, N 11.25; Found: C 83.34, H 5.13, N 11.11.
10.3. 8-Methyl-6-phenyl-8H-indolo[3,2-a]phenazine (18c)

\[
\text{C}_{25}\text{H}_{17}\text{N}_3
\]

[359.43]

According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 18c (167 mg, 47%) was obtained as an orange solid, Mp 240 °C, Rf = 0.14 (petroleum ether/ethyl acetate 10:1). ¹H NMR (300 MHz, CDCl₃): δ 4.06 (s, 3 H), 7.47-7.64 (m, 5 H), 7.73 (ddd, J = 8.3 Hz, J = 6.7 Hz, J = 1.4 Hz, 1 H), 7.86 (ddd, J = 8.5 Hz, J = 6.7 Hz, J = 1.5 Hz, 1 H), 7.89-7.95 (m, 2 H), 8.02 (s, 1 H), 8.22 (ddd, J = 8.6 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 8.40 (ddd, J = 8.6, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.23-9.28 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 29.7 (CH₃), 109.4 (CH), 113.8 (Cₘᵢₜₘᵢₜ), 117.6 (CH), 121.5 (CH), 123.8 (CH), 124.3 (Cₘᵢₜₘᵢₜ), 124.9 (CH), 127.8 (CH), 128.1 (CH), 128.2 (CH), 129.3 (CH), 130.2 (CH), 130.5 (CH), 131.3 (CH), 139.2 (Cₘᵢₜₘᵢₜ), 139.4 (Cₘᵢₜₘᵢₜ), 139.4 (Cₘᵢₜₘᵢₜ), 139.9 (Cₘᵢₜₘᵢₜ), 140.0 (Cₘᵢₜₘᵢₜ), 140.9 (Cₘᵢₜₘᵢₜ), 141.9 (Cₘᵢₜₘᵢₜ), 142.6 (Cₘᵢₜₘᵢₜ). MS (EI, m/z (%)): 360 (25), 359 ([M⁺], 100), 358 ([M – H⁺], 75), 344 ([M – CH₃⁺], 16), 343 ([M – CH₄⁺], 32), 342 (13), 179 (19), 178 ([C₁₂H₈N₂⁺], 32), 172 (28). IR: \(\tilde{\nu} [\text{cm}^{-1}] \) 3057 (w), 3021 (w), 2974 (w), 2941 (w), 2897 (w), 1622 (w), 1584 (w), 1574 (w), 1558 (w), 1520 (w), 1495 (w), 1460 (m), 1439 (m), 1423 (w), 1387 (w), 1366 (w), 1341 (w), 1312 (w), 1258 (w), 1221 (w), 1204 (w), 1171 (w), 1157 (w), 1119 (w), 1078 (w), 1032 (w), 1015 (w), 1005 (w), 935 (w), 910 (w), 883 (w), 760 (s), 741 (s), 702 (s), 681 (m), 664 (w), 635 (m). Anal calcd for C₂₅H₁₇N₃ [359.4]: C 83.54, H 4.77, N 11.69; Found: C 83.29, H 4.78, N 11.47

10.4. 6-(4-Chlorophenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18d)

\[
\text{C}_{25}\text{H}_{16}\text{ClN}_3
\]

[393.87]
According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 18d (293 mg, 74%) was obtained as an orange solid, Mp 276 °C, R<sub>r</sub> = 0.23 (petroleum ether/ethyl acetate 10:1). 1H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.08 (s, 3 H), 7.43-7.64 (m, 5 H), 7.75 (ddd, J = 8.3 Hz, J = 6.7 Hz, J = 1.4 Hz, 1 H), 7.80-7.93 (m, 3 H), 8.00 (s, 1 H), 8.20 (ddd, J = 8.6 Hz, J = 1.4 Hz, J = 0.6 Hz, 1 H), 8.41 (ddd, J = 8.6 Hz, J = 1.4 Hz, J = 0.7 Hz, 1 H), 9.19-9.31 (m, 1 H). 13C NMR (75 MHz, CDCl<sub>3</sub>): δ 29.8 (CH<sub>3</sub>), 109.5 (CH), 114.1 (C<sub>quat</sub>), 117.4 (CH), 121.6 (CH), 123.9 (CH), 124.2 (C<sub>quat</sub>), 128.29 (CH), 128.36 (CH), 129.3 (CH), 130.37 (CH), 130.40 (CH), 132.6 (CH), 133.9 (C<sub>quat</sub>), 137.8 (C<sub>quat</sub>), 137.8 (C<sub>quat</sub>), 139.2 (C<sub>quat</sub>), 139.6 (C<sub>quat</sub>), 140.0 (C<sub>quat</sub>), 140.8 (C<sub>quat</sub>), 141.8 (C<sub>quat</sub>), 142.7 (C<sub>quat</sub>). MS (EI, m/z (%)): 395 ([37Cl-M]<sup>+</sup>, 33), 393 ([35Cl-M]<sup>+</sup>, 100), 380 ([37Cl-M - CH<sub>3</sub>]<sup>+</sup>, 14), 378 ([35Cl-M - CH<sub>3</sub>]<sup>+</sup>, 43), 358 ([M - Cl]<sup>+</sup>, 11), 343 (15), 179 (27), 178 (68), 177 (18), 171 (15), 165 (12), 164 (14). IR: ν [cm<sup>-1</sup>] 3049 (w), 3015 (w), 2968 (w), 2932 (w), 2876 (w), 1614 (w), 1582 (m), 1553 (w), 1520 (w), 1489 (m), 1456 (m), 1445 (m), 1423 (w), 1396 (w), 1385 (w), 1366 (w), 1339 (m), 1314 (m), 1254 (w), 1225 (w), 1207 (w), 1171 (m), 1119 (m), 1105 (w), 1078 (m), 1003 (w), 935 (m), 883 (w), 864 (w), 851 (w), 833 (m), 814 (m), 797 (w), 760 (m), 741 (s), 729 (m), 718 (w), 702 (w), 692 (w), 681 (w). Anal calcd for C<sub>25</sub>H<sub>16</sub>ClN<sub>3</sub> [393.9]: C 76.24, H 4.09, N 10.67; Found: C 75.99, H 4.36, N 10.75.

10.5. 4-(8-Methyl-8H-indolo[3,2-a]phenazin-6-yl)benzonitrile (18e)

According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) compound 18e (133 mg, 35%) was obtained as a red solid, Mp 298 °C, R<sub>r</sub> = 0.18 (petroleum ether/ethyl acetate 10:1). 1H NMR (300 MHz, CDCl<sub>3</sub>): δ 4.05 (s, 3 H), 7.49-7.60 (m, 3 H), 7.71-7.80 (m, 1 H), 7.80-7.92 (m, 4 H), 7.94-8.04 (m, 2 H), 7.97 (s, 1H), 8.15 (ddd, J = 8.6 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 8.38 (ddd, J = 8.6 Hz, J = 1.5 Hz, J = 0.7 Hz, 1 H), 9.23 (dt, J = 7.4 Hz, J = 1.2 Hz, 1 H). 13C NMR (75 MHz, CDCl<sub>3</sub>): δ 29.8 (CH<sub>3</sub>), 109.6 (CH), 111.3 (C<sub>quat</sub>), 114.7 (C<sub>quat</sub>), 117.9 (CH), 119.4 (C<sub>quat</sub>), 121.7 (CH), 124.0 (CH), 125.5 (CH), 128.6 (CH), 129.3 (CH), 130.2 (CH), 130.5 (CH), 131.8 (CH), 132.0 (CH), 136.8 (C<sub>quat</sub>), 138.8 (C<sub>quat</sub>), 139.1 (C<sub>quat</sub>), 140.1 (C<sub>quat</sub>), 140.8 (C<sub>quat</sub>), 141.6 (C<sub>quat</sub>), 142.8 (C<sub>quat</sub>), 144.1 (C<sub>quat</sub>). MS (EI, m/z (%)): 385 (27), 384 ([M]<sup>+</sup>, 100), 383 ([M – H]<sup>+</sup>, 71), 369 ([M – CH<sub>3</sub>]<sup>+</sup>, 15), 368 ([M – CH<sub>3</sub>]<sup>+</sup>, 29), 367 ([M – H]<sup>+</sup>, 12), [384.44]
283 ([M – C₇H₄N⁺], 18), 192 (18), 191 (32), 184 (28), 177 ([C₁₂H₆N₂⁺], 11). IR: ̃ν [cm⁻¹] 3048 (w), 2965 (w), 2922 (w), 2218 (w), 1622 (w), 1603 (m), 1585 (m), 1578 (m), 1551 (m), 1460 (m), 1445 (m), 1423 (m), 1406 (m), 1387 (m), 1371 (m), 1341 (m), 1323 (m), 1314 (m), 1285 (m), 1259 (m), 1236 (m), 1223 (m), 1206 (m), 1171 (m), 1155 (m), 1123 (m), 1078 (m), 1045 (m), 1013 (m), 980 (m), 960 (m), 935 (m), 879 (m), 862 (m), 841 (m), 808 (m), 795 (m), 758 (s), 741 (s), 698 (m), 681 (m), 633 (m), 617 (m). Anal calcd for C₂₆H₁₆N₄ [359.4]: C 81.23, H 4.20, N 14.57; Found: C 80.98, H 4.11, N 14.54.

10.6. 6-(4-Isopropoxyphenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18f)

According to GP3 and flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) compound 18f (132 mg, 63%) was obtained as an orange solid, Mp 222.1–222.6 °C, Rᵣ = 0.21 (petroleum ether/ethyl acetate 10:1). ¹H NMR (300 MHz, CDCl₃): δ 1.45 (d, J = 6.0 Hz, 6 H), 4.08 (s, 3 H), 4.71 (quin, J = 6.0 Hz, 1 H), 7.10 (d, J = 8.2 Hz, 2 H), 7.62–7.47 (m, 3 H), 7.75 (ddd, J = 8.3 Hz, 6.6 Hz, 1.3 Hz, 1 H), 7.87 (dd, J = 8.3 Hz, 6.6 Hz, 3 H), 8.01 (s, 1 H), 8.25 (dd, J = 8.6 Hz, 1.4 Hz, 1 H), 8.48 (dd, J = 8.6 Hz, 1.3 Hz, 1 H), 9.32–9.25 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): δ 22.4 (CH₃), 27.1 (CH₃), 70.1 (CH), 109.5 (CH), 113.2 (C₉), 115.5 (CH), 117.0 (CH), 121.6 (CH), 123.8 (CH), 124.2 (C₉), 124.9 (CH), 128.0 (CH), 128.9 (CH), 130.4 (CH), 130.5 (CH), 131.4 (C₉), 132.5 (CH), 139.0 (C₉), 139.9 (C₉), 140.0 (C₉), 140.2 (C₉), 140.8 (C₉), 141.2 (C₉), 142.0 (C₉), 158.0 (C₉). MS (EI, m/z (%)): 418 (23), 417 (M⁺, 84), 409 (13), 376 (21), 375 ([M – C₃H₆⁺], 92), 374 ([M – C₃H₇]+, 100), 360 (16), 359 (31), 358 (43), 346 (15), 345 (12), 343 (10), 331 (22), 330 (27), 187 (21), 180 (16), 149 (10). IR: ̃ν [cm⁻¹] 2978 (w), 1510 (m), 1460 (w), 1244 (m), 1114 (m), 1103 (m), 1078 (m), 827 (m), 761 (m), 744 (s). Anal calcd for C₂₆H₂₃N₃O [417.5]: C 80.55, H 5.55, N 10.06; Found: C 80.34, H 5.54, N 9.85.
10.7. 8-Methyl-6-(4-(pentyloxy)phenyl)-8H-indolo[3,2-a]phenazine (18g)

![Chemical structure of 8-Methyl-6-(4-(pentyloxy)phenyl)-8H-indolo[3,2-a]phenazine](image)

C$_{30}$H$_{27}$N$_3$O  [445.57]

According to GP3 and flash chromatography on silica gel (petroleum ether/acetone 50:1) compound 18g (118 mg, 53%) was obtained as a yellow solid, Mp 210.9–211.7 °C, $R_f = 0.05$ (petroleum ether/acetone 50:1). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.98 (t, $J$ = 7.0 Hz, 3 H), 1.38–1.59 (m, 4 H), 1.87 (dt, $J$ = 7.9 Hz, 6.5 Hz, 2 H), 4.05 (s, 3 H), 4.10 (t, 2 H), 7.11 (d, $J$ = 8.3 Hz, 2 H), 7.48–7.58 (m, 3 H), 7.74 (ddd, $J$ = 8.1 Hz, 6.5 Hz, 1.3 Hz, 1 H), 7.80-7.89 (m, 3 H), 7.98 (s, 1 H), 8.25 (dd, $J$ = 8.5 Hz, 1.4 Hz, 1 H), 8.48 (dd, $J$ = 8.9 Hz, 1.3 Hz, 1 H), 9.20–9.31 (m, 1 H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.2 (CH$_3$), 22.7 (CH$_2$), 28.4 (CH$_2$), 29.2 (CH$_2$), 29.8 (CH$_3$), 68.3 (CH$_2$), 109.4 (CH), 113.4 (C$_{quat}$), 114.3 (CH), 117.0 (CH), 121.5 (CH), 123.8 (CH), 124.3 (C$_{quat}$), 124.8 (CH), 128.0 (CH), 129.1 (CH), 130.2 (CH), 130.5 (CH), 131.5 (C$_{quat}$), 132.4 (CH), 139.0 (C$_{quat}$), 139.7 (C$_{quat}$), 140.0 (C$_{quat}$), 140.1 (C$_{quat}$), 140.8 (C$_{quat}$), 141.8 (C$_{quat}$), 142.4 (C$_{quat}$), 159.2 (C$_{quat}$). MS (EI, $m/z$ (%)): 446 (26), 445 ([M]$^+$, 100), 375 ([M – C$_5$H$_{10}$]$^+$, 32), 374 ([M – C$_9$H$_{11}$]$^+$, 66), 360 (11), 359 (31), 358 (48), 346 (30), 345 (17), 331 (22), 330 (32). IR: $\tilde{\nu}$ [cm$^{-1}$] 2936 (w), 1512 (m), 1456 (m), 1242 (m), 1171 (m), 1022 (m), 831 (m), 741 (s). Anal calcd for C$_{30}$H$_{27}$N$_3$O [445.6]: C 80.87, H 6.11, N 9.43; Found: C 80.63, H 6.12, N 9.18.
11.  $^1$H and $^{13}$C NMR Spectra of Compounds 4k, 8, 9, 13, and 18

11.1. 1-Methyl-$^1$H-indole-$2$-$d$ (4k)

Figure S1. $^1$H NMR spectrum of (4k) recorded in CDCl$_3$ at 298 K (300 MHz).

Figure S2. $^{13}$C NMR spectrum of (4k) recorded in CDCl$_3$ at 298 K (75 MHz).
11.2. 2-(1-Ethyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8b)

**Figure S3.** $^1$H NMR spectrum of (8b) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

**Figure S4.** $^{13}$C NMR spectrum of (8b) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.3. 2-(1-Propyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8c)

Figure S5. $^1$H NMR spectrum of (8c) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S6. $^{13}$C NMR spectrum of (8c) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.4. 2-(1-Allyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8d)

Figure S7. $^1$H NMR spectrum of (8d) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S8. $^{13}$C NMR spectrum of (8d) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.5. 2-(1-Benzyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8e)

Figure S9. $^1$H NMR spectrum of (8e) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S10. $^{13}$C NMR spectrum of (8e) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.6. 2-(1-Hexyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8f)

Figure S11. $^1$H NMR spectrum of (8f) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S12. $^{13}$C NMR spectrum of (8f) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.7. 2-(5-Bromo-1-methyl-1-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8g)

Figure S13. $^1$H NMR spectrum of (8g) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S14. $^{13}$C NMR spectrum of (8g) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.8. 2-(5-Chloro-1-methyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8h)

Figure S15. $^1$H NMR spectrum of (8h) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S16. $^{13}$C NMR spectrum of (8h) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.9. 2-(5-Methoxy-1-methyl-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8i)

Figure S17. $^1$H-NMR spectrum of (8i) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S18. $^{13}$C NMR spectrum of (8i) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.10. 2-(1-Ethyl-5-methoxy-1H-indol-3-yl)-3-((trimethylsilyl)ethynyl)quinoxaline (8j)

Figure S19. $^1$H-NMR spectrum of (8j) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S20. $^{13}$C NMR spectrum of (18j) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.11. 2-(1-Methyl-1H-indol-3-yl-2-d)-3-((trimethylsilyl)ethynyl)quinoxaline (8k)

Figure S21. $^1$H NMR spectrum of (8k) recorded in CDCl$_3$ at 298 K (300 MHz).

Figure S22. $^{13}$C NMR spectrum of (8k) recorded in CDCl$_3$ at 298 K (75 MHz).
11.12. 8-Methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9a)

Figure S23. $^1$H NMR spectrum of (9a) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S24. $^{13}$C- NMR spectrum of (9a) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.13. 8-Ethyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9b)

Figure S25. $^1$H NMR spectrum of (9b) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S26. $^{13}$C NMR spectrum of (9b) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.14. 8-Propyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9c)

Figure S27. $^1$H NMR spectrum of (9c) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S28. $^{13}$C NMR spectrum of (9c) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.15. 8-Allyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9d)

Figure S29. $^1$H NMR spectrum of (9d) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S30. $^{13}$C- NMR spectrum of (9d) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.16. 8-Hexyl-6-(trimethylsilyl)-8\textit{H}-indolo[3,2-\textit{a}]phenazine (9e)

Figure S31. $^1$H NMR spectrum of (9e) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S32. $^{13}$C NMR spectrum of (9e) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.17. 8-Benzyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9f)

Figure S33. $^1$H NMR spectrum of (9f) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.
11.18. 11-Bromo-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9g)

Figure S34. $^1$H NMR spectrum of (9g) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S35. $^{13}$C NMR spectrum of (9g) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.19. 11-Chloro-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9h)

Figure S36. $^1$H NMR spectrum of (9h) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S37. $^{13}$C NMR spectrum of (9h) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.20. 11-Methoxy-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9i)

Figure S38. $^1$H NMR spectrum of (9i) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S39. $^{13}$C NMR spectrum of (9i) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.21. 11-Methoxy-8-methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine (9j)

Figure S40. $^1$H NMR spectrum of (9j) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S41. $^{13}$C NMR spectrum of (9j) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.22. 8-Methyl-6-(trimethylsilyl)-8H-indolo[3,2-a]phenazine-7-d (9k)

Figure S42. $^1$H NMR spectrum of (9k) recorded in CDCl$_3$ at 298 K (300 MHz). *Minor impurities.

Figure S43. $^{13}$C NMR spectrum of (9k) recorded in CDCl$_3$ at 298 K (75 MHz). *Minor impurities.
11.23. 8-Methyl-8H-indolo[3,2-a]phenazine (9l)

Figure S44. $^1$H NMR spectrum of (9l) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S45. $^{13}$C NMR spectrum of (9l) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.24. 6-iodo-8-methyl-8H-indolo[3,2-a]phenazine (13)

Figure S46. $^1$H-NMR spectrum of (13) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S47. $^{13}$C NMR spectrum of (13) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.25. 6-(4-Methoxyphenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18a)

Figure S48. $^1$H NMR spectrum of (18a) recorded in CDCl$_3$ at 298 K (600 MHz). * Minor impurities.

Figure S49. $^{13}$C NMR spectrum of (18a) recorded in CDCl$_3$ at 298 K (150 MHz). * Minor impurities.
11.26. 8-Methyl-6-(p-tolyl)-8H-indolo[3,2-a]phenazine (18b)

Figure S50. $^1$H NMR spectrum of (18b) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S51. $^{13}$C NMR spectrum of (18b) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.27. 8-Methyl-6-phenyl-8H-indolo[3,2-a]phenazine (18c)

Figure S52. $^1$H-NMR spectrum of (18c) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S53. $^{13}$C NMR spectrum of (18c) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.28. 6-(4-Chlorophenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18d)

Figure S54. $^1$H NMR spectrum of (18d) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S55. $^{13}$C NMR spectrum of (18d) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.29. 4-(8-Methyl-8H-indolo[3,2-a]phenazin-6-yl)benzonitrile (18e)

Figure S56. $^1$H NMR spectrum of (18e) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S57. $^{13}$C NMR spectrum of (18e) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.30. 6-(4-Isopropoxyphenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18f)

Figure S58. $^1$H NMR spectrum of (18f) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S59. $^{13}$C NMR spectrum of (18f) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
11.31. 8-Methyl-6-(4-pentoxyphenyl)-8H-indolo[3,2-a]phenazine (18g)

Figure S60. $^1$H NMR spectrum of (18g) recorded in CDCl$_3$ at 298 K (300 MHz). * Minor impurities.

Figure S61. $^{13}$C NMR spectrum of (18g) recorded in CDCl$_3$ at 298 K (75 MHz). * Minor impurities.
12. Absorption and Emission Characteristics of Compounds 9 and 18

12.1. Absorption and Emission Characteristics of Compounds 9

While variation of the N-indolyl substituent expectedly did not reveal any marked differences, substitution on position 11 in the indolyl part showed some differences. Therefore, we recorded absorption and emission spectra of compounds 9a (R^2 = H), 9g (R^2 = Br), and 9i (R^2 = OMe) (Table S8, Figure S56). The longest wavelength absorption maxima of compounds 9a and 9g are identical and appear at 406 nm, whereas the methoxy derivative is redshifted and is found at 438 nm. The molar extinction coefficients of these bands are in a narrow range between 11000 bis 14300 L·mol^{-1}·cm^{-1}. The substituent effect in the emission spectra is more distinct and correlate with the electronic nature of the substituent with respect to the wavelength of the emission band. The weakly electron-withdrawing bromine substituent causes a blueshift of the emission band of 9g to 504 nm with respect to the electroneutral hydrogen substituent of 9a (510 nm). The electron-releasing methoxy substituent of 9i causes a significant redshift to 561 nm. The same tendency is also found for the fluorescence quantum yields \( \Phi_f \) which increase from electron-deficient 9g (less than 1%) over electroneutral 9a (9%) to electron-rich 9i (28%).

All three compounds show significant Stokes shifts between 4800 bis 5000 cm^{-1}.

Table S8. Selected absorptions and emission maxima, extinction coefficients, fluorescence quantum yields \( \Phi_f \), and Stokes shifts \( \Delta \bar{\nu} \) of compounds 9a, 9g und 9i.

| compound | \( \lambda_{\text{max,abs}}[^{\text{nm}}] (\epsilon [\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}])^{[a]} \) | \( \lambda_{\text{max,em}}[^{\text{nm}}] \) (\( \Phi_f \)\(^{[b,c]} \)) | Stokes shift \( \Delta \bar{\nu} \) [cm^{-1}]\(^{[d]} \) |
|----------|-------------------------------------------------|------------------|-----------------|
| 9a       | 270 (41000), 308 (27000), 406 (11000)             | 510 (0.09)       | 5000            |
| 9g       | 272 (46600), 309 (33900), 406 (14300)             | 504 (>0.01)      | 4800            |
| 9i       | 271 (46700), 297 (32900), 438 (14100)             | 561 (0.28)       | 5000            |

[a] Recorded in CH₂Cl₂, \( T = 293 \) K, \( c(9) = 10^{-5} \) M. [b] Recorded in CH₂Cl₂, \( T = 293 \) K, \( c(9) = 10^{-7} \) M; \( \lambda_{\text{exc}} = 420 \) nm. [c] Fluorescence quantum yields determined with coumarin 153 (\( \Phi_f = 0.45 \)) as a standard in methanol. [d] \( \Delta \bar{\nu} = 1/\lambda_{\text{max,abs}} - 1/\lambda_{\text{max,em}} \).
Figure S62. Normalized longest wavelength absorption bands (solid lines) and emission bands (dashed lines) of compounds 9a (green), 9g (blue), and 9i (orange) (absorption spectra recorded in CH$_2$Cl$_2$, $T = 293$ K, $c(9) = 10^{-5}$ M; emission spectra recorded in CH$_2$Cl$_2$, $T = 293$ K, $c(9) = 10^{-7}$ M, $\lambda_{\text{exc}} = 420$ nm).

Upon titration of indolo[3,2-a]phenazine 9a with trifluoroacetic acid (TFA) the spectral characteristics were followed with UV/VIS (Figure S57A) and fluorescence spectroscopy (Figure 4B). Assuming complete dissociation of TFA in dichloromethane the pH value was varied between 5.12 and 6.37. With increasing protonation the longest absorption maximum of 9a is continuously redshifted from 406 nm to 480 nm as well as the shorter wavelength maximum at 270 nm, which is bathochromically shifted to 284 nm (Figure S57A). The distinct appearance of isosbestic points supports the presence of an associative equilibrium between nonprotonated 9a and protonated 9a-H$^+$ without intermediates. From the isosbestic points and the corresponding difference spectra of nonprotonated and protonated species the chromophore’s $pK_a$ was determined to 5.60 (Figure S58). Therefore, indolo[3,2-a]phenazine 9a by more than four orders of magnitude less acidic than simple phenazine ($pK_a = 1.2$).[7] Upon protonation of indolo[3,2-a]phenazine 9a the fluorescence is quenched and species 9a-H$^+$ clearly is nonfluorescent (Figure S57B).
Figure S63. (A) UV/Vis titration of 9a with trifluoroacetic acid (TFA) (recorded in CH₂Cl₂, T = 293 K, c(9a) = 10⁻⁵ M). (B) Fluorescence titration of 9a with trifluoroacetic acid (recorded in CH₂Cl₂, T = 293 K, c(9a) = 10⁻⁵ M).
Figure S64. (A) Intensity (absorbance) ratios at 404.0nm/505.0nm of 9a/9a-H+ vs. the amount of TFA (recorded in CH2Cl2, T = 293 K, c(9a) = 10⁻⁵ M). (B) Intensity (absorbance) ratios at 404.0nm/505.0nm of 9a/9a-H+ vs. pH (recorded in CH2Cl2, T = 293 K, c(9a) = 10⁻⁵ M).

12.2. Absorption and Emission Characteristics of Compounds 18

As seen upon eyesight 6-arylindolo[3,2-a]phenazines 18 in dichloromethane solution and in the solid state intensively luminesce under the handheld UV-lamp. Therefore, absorption and emission spectra of the consanguineous series bearing electron-releasing, electroneutral, and electron-deficient substituents were recorded in dichloromethane solution (Table S9, Figure S59). The longest wavelength absorption maxima appear in a very narrow range between 416 to 420 nm with molar extinction coefficients between 14200 and 17900 L·mol⁻¹·cm⁻¹. This
indicates that the remote electronic substituent effect in the para-position of aryl unit is only very weak in the electronic ground state. In addition, the higher energy absorption bands are found at similar wavelength for all representatives. The emission energies more strongly depend on the remote substituent effect of \( R^3 \) and ranges from 575 nm (\( R^3 = \text{OMe} \)) to 540 nm (\( R^3 = \text{CN} \)). In addition, an electronic effect can be seen for the Stokes shifts \( \Delta \nu \), which decreases from strong donors to strong acceptors from trend 6500 to 5500 cm\(^{-1}\). Finally, also the relative fluorescence quantum yields \( \phi_f \) decrease in the same order from 52\% (\( R^3 = \text{OMe} \)) to 16\% (\( R^3 = \text{CN} \)).

Table S9. Selected absorptions and emission maxima, extinction coefficients, fluorescence quantum yields \( \phi_f \), and Stokes shifts \( \Delta \nu \) of selected compounds 18.

| Compound | \( \lambda_{\text{max.abs}} \) [nm] \( (\epsilon [\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}])^{[a]} \) | \( \lambda_{\text{max.em}} \) [nm] \( (\phi_f)^{[b,c]} \) | Stokes shift \( \Delta \nu \) [cm\(^{-1}\)]\(^{[d]} \) |
|----------|-------------------------------------------------|---------------|-----------------|
| 18a      | 273 (52900), 303 (36700), 310 (29400), 420 (14400) | 575 (0.52)    | 6500            |
| 18b      | 273 (57000), 301 (37200), 313 (33900), 418 (15200) | 558 (0.38)    | 6000            |
| 18c      | 272 (75600), 300 (sh, 48200), 311 (55000), 417 (17900) | 551 (0.30)    | 5800            |
| 18d      | 273 (53200), 302 (sh, 33200), 312 (33900), 417 (14200) | 549 (0.25)    | 5800            |
| 18e      | 275 (50600), 312 (30200), 416 (15100)            | 540 (0.16)    | 5500            |

\(^{[a]}\) Recorded in CH\(_2\)Cl\(_2\), \( T = 293 \) K, \( c(18) = 10^{-5} \) M. \(^{[b]}\) Recorded in CH\(_2\)Cl\(_2\), \( T = 293 \) K, \( c(18) = 10^{-7} \) M; \( \lambda_{\text{exc}} = 420 \) nm. \(^{[c]}\) Fluorescence quantum yields determined with coumarin 153 (\( \phi_f = 0.45 \)) as a standard in methanol. \(^{[d]}\) \( \Delta \nu = 1/\lambda_{\text{max.abs}} - 1/\lambda_{\text{max.em}} \).
Figure S65. Normalized longest wavelength absorption bands (solid lines) and emission bands (dashed lines) of compounds 18a (green), 18b (blue), 18c (black), 18d (orange), and 18e (red) (absorption spectra recorded in CH$_2$Cl$_2$, $T = 293$ K, $c(18) = 10^{-5}$ M; emission spectra recorded in CH$_2$Cl$_2$, $T = 293$ K, $c(18) = 10^{-7}$ M, $\lambda_{exc} = 420$ nm).

These systematic, electronic effects prompted us to perform physical organic correlation studies of the data and to seek for structure-property correlations using free energy linear relationships (LFER) with Hammett $\sigma$ parameters ($\sigma_p$, $\sigma_{p+}$, $\sigma_R$, and $\sigma_l$). Interestingly, best correlations with correlation coefficients $R^2 \geq 95\%$ were unanimously found for absorption maxima $\lambda_{max,abs}$, emission maxima $\lambda_{max,em}$, Stokes shifts $\Delta \tilde{\nu}$ (Figure S60A), and relative fluorescence quantum yields $\Phi_f$ (Figure S60B) and $\sigma_{p+}$ parameters. However, the slopes of the linear correlation equations ($\lambda_{max,abs} = 140 \sigma_{p+} + 24000$ [cm$^{-1}$], $R^2 = 0.95$; $\lambda_{max,em} = 780 \sigma_{p+} + 18500$ [cm$^{-1}$], $R^2 = 0.95$; $\Delta \tilde{\nu} = 640 \sigma_{p+} + 5900$ [cm$^{-1}$], $R^2 = 0.95$; $\Phi_f = -0.253 \sigma_{p+} + 0.306$ [cm$^{-1}$], $R^2 = 0.98$) indicate different extents of the electronic substituent effects. The absorption correlation gives the smallest slope, indicating an only minor polarity of the electronic ground state. In contrast, all effects reflecting the excited state ($\lambda_{max,em}$, $\Delta \tilde{\nu}$, $\Phi_f$) are strongly depended on stabilization of positive partial charges as supported by the $\sigma_{p+}$ substituent parameter.
Figure S66. Linear correlations of absorption (blue triangles), emission maxima (green squares), and Stokes shifts (red dots) (energies in cm$^{-1}$) of 6-aryl-8H-indolo[3,2-a]phenazines 18 and Hammett $\sigma_{p+}$-parameters (A). Linear correlations of relative fluorescence quantum yields $\Phi_f$ of 6-aryl-8H-indolo[3,2-a]phenazines 18a (green), 18b (blue), 18c (black), 18d (orange), and 18e (red) and Hammett $\sigma_{p+}$-parameters (B).
Electronic structure by DFT and TDDFT calculations

A deeper understanding of the electronic transitions in the absorption spectra of selected 6-aryl-8H-indolo[3,2-a]phenazines 18a, 18c, and 18e was sought by calculating UV/Vis absorption spectra on the DFT level of theory, with a special focus on comparison to the remote substituent R¹ and on the origin of the longest wavelength absorption maxima of each structure. The geometries of the electronic ground-state structures were optimized using Gaussian09 with CAM-B3LYP as a functional and the Pople 6-311+G(d,p) basis set. Since the absorption spectra were recorded in dichloromethane solutions, the polarizable continuum model (PCM) with dichloromethane as a solvent was applied. All minimum structures were unambiguously assigned by analytical frequency analysis.

13.1. Computed xyz-coordinates of TD-DFT calculated structures 18a, 18c, and 18e

13.1.1. xyz-Coordinates for 6-(4-Methoxyphenyl)-8-methyl-8H-indolo[3,2-a]phenazine (18a)

|   | C   | C   | C   | C   | N   | C   | C   | O   | H   | H  |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 0 | -0.090217 | -1.765133 | 0.058807 |
| 0 | -1.327584 | -1.690245 | 0.023777 |
| 0 | 0.170888 | 0.664932 | 0.015019 |
| 0 | 0.838978 | 0.626754 | 0.060426 |
| 0 | -2.010592 | -0.480396 | 0.008434 |
| 0 | -1.274383 | 0.736874 | -0.001504 |
| 0 | 0.264670 | 2.949351 | -0.075546 |
| 0 | -1.158092 | 3.018037 | -0.067296 |
| 0 | 1.115318 | 3.414333 | 0.004341 |
| 0 | -1.787335 | 4.293926 | -0.103613 |
| 0 | 1.214133 | 5.426912 | -0.149844 |
| 0 | 0.867020 | 5.357653 | -0.163386 |
| 0 | 1.020927 | 4.153629 | -0.128070 |
| 0 | 2.319025 | 0.720908 | 0.095963 |
| 0 | -2.226300 | -2.728941 | 0.019054 |
| 0 | 3.502896 | -2.198004 | 0.017871 |
| 0 | -3.414333 | -0.788145 | 0.004341 |
| 0 | -4.729184 | -2.859616 | 0.027783 |
| 0 | -5.874764 | -2.036353 | 0.016463 |
| 0 | -5.806068 | -0.682878 | -0.002379 |
| 0 | 1.020927 | 4.153629 | -0.128070 |
| 0 | 2.319025 | -0.720908 | 0.095963 |
| 0 | -2.226300 | -2.728941 | 0.019054 |
| 0 | 3.502896 | -2.198004 | 0.017871 |
| 0 | -3.414333 | -0.788145 | 0.004341 |
| 0 | -4.729184 | -2.859616 | 0.027783 |
| 0 | -5.874764 | -2.036353 | 0.016463 |
| 0 | -5.806068 | -0.682878 | -0.002379 |
| 0 | -4.587571 | 0.028407 | -0.008196 |
| 0 | 1.926143 | -4.145242 | 0.073295 |
| 0 | 3.081822 | -0.024614 | 1.041128 |
| 0 | 4.452188 | -0.171998 | 1.099240 |
| 0 | 5.109486 | -1.015124 | 0.201059 |
| 0 | 4.372642 | -1.710396 | -0.749666 |
| 0 | 2.989394 | -1.557245 | -0.789205 |
| 0 | 6.459777 | -1.089177 | 0.331609 |
| 0 | 7.179014 | -1.929411 | -0.558017 |
| 0 | 0.585100 | -2.725962 | 0.111740 |
| 0 | -2.869711 | 4.328518 | -0.095393 |
| 0 | -1.515432 | 6.396824 | -0.178273 |
H 0  0.961775  6.274817  -0.202160
H 0  2.101153  4.075534  -0.136988
H 0  -4.790106  -3.940396  0.047606
H 0  -6.843524  -2.568692  0.024167
H 0  -6.723925  -0.17487  -0.010758
H 0  -6.843524  -2.568692  0.024167
H 0  -4.532416  1.051584  -0.020602
H 0  -2.558934  -4.683118  -0.632743
H 0  -0.889886  -4.313255  -0.208722
H 0  -2.089492  -4.545749  1.076335
H 0  2.590806  0.633982  1.744991
H 0  5.038607  0.360236  1.838120
H 0  4.852764  -2.363843  -1.464204
H 0  2.427552  -2.096241  -1.543178
H 0  8.225572  -1.836753  -0.278422
H 0  6.867160  -2.972173  -0.455966
H 0  7.050633  -1.608405  -1.594991

SCF Done:  E(RCAM-B3LYP) = -1241.35137658  A.U. after 17 cycles

Sum of electronic and zero-point Energies= -1240.960595
Sum of electronic and thermal Energies= -1240.937610
Sum of electronic and thermal Enthalpies= -1240.936666
Sum of electronic and thermal Free Energies= -1241.013965

13.1.2. xyz-Coordinates for 8-Methyl-6-phenyl-8H-indolo[3,2-a]phenazine (18c)

C 0  -0.042706  -2.020930  0.001260
C 0  -1.340885  -1.444815  -0.004349
C 0  -1.546918  -0.070857  0.007724
C 0  -0.425465  0.804647  -0.003751
C 0  0.898759  0.222067  -0.013969
C 0  1.060746  -1.222622  0.005045
N 0  -0.597075  2.120913  -0.014895
C 0  0.496130  2.894702  -0.048211
C 0  1.800745  2.322960  -0.082879
N 0  1.971582  0.993943  -0.064836
C 0  0.363182  4.311595  -0.059279
C 0  1.470820  5.101792  -0.106619
C 0  2.773145  4.530395  -0.146662
C 0  2.936124  3.179195  -0.135957
N 0  -2.550789  -2.094603  -0.004388
C 0  -3.553597  -1.143302  0.026070
C 0  -2.967785  0.142207  0.027229
C 0  -4.935261  -1.323259  0.052894
C 0  -5.727578  -0.189263  0.073836
C 0  -5.163155  1.095051  0.070325
C 0  -3.791688  1.271209  0.047678
C 0  -2.772351  -3.525990  0.030519
C 0  2.411928  -1.838943  0.021270
C 0  3.358588  -1.492874  0.987422
C 0  4.594106  -2.121359  1.021633
SCF Done:  E(RCAM-B3LYP) = -1126.83944184  A.U. after  17 cycles

Sum of electronic and zero-point Energies=  -1125.903254
Sum of electronic and thermal Energies=  -1125.882697
Sum of electronic and thermal Enthalpies=  -1125.881753
Sum of electronic and thermal Free Energies=  -1125.953190

13.1.3. xyz-Coordinates for 4-(8-Methyl-8H-indolo[3,2-a]phenazin-6-yl)benzonitrile (18e)

C 0  0.086249  -1.834394  -0.011413
C 0  -1.322602  -1.661452  -0.003436
C 0  -1.917976  -0.405363  0.009086
C 0  -1.099708  0.758929  -0.005488
C 0  0.335393  0.587487  -0.020227
C 0  0.907301  -0.747578  -0.009957
N 0  -1.645965  1.968703  -0.014243
C 0  -0.824790  3.026445  -0.047792
C 0  0.590209  2.858858  -0.083708
N 0  1.139187  1.636835  -0.069494
C 0  -1.363983  4.343496  -0.056758
C 0  -0.533865  5.421326  -0.102512
C 0  0.878424  5.253291  -0.142852
C 0  1.427751  4.008219  -0.134544
N 0  -2.292755  -2.633657  0.006284
C 0  -3.526793  -2.012879  0.036005
C 0  -3.339046  -0.613040  0.033576
C 0  2.377914  -0.943972  -0.002394
C 0  -2.099337  -4.069533  0.032629
C 0  -4.796580  -2.586884  0.065157
The DFT calculated torsional angle of 52° of the p-cyanophenyl substituent (compound 15e) with respect to the indolo[3,2-a]phenazine mean plane is good agreement with the value of 54.3° determined by X-rays structure analysis (vide supra).

13.2. Computed UV/Vis spectra of TD-DFT calculated structures for the 6-aryl-indolo[3,2-a]phenazines 18a, 18c, and 18e

The optimized structures of 18a, 18c, and 18e were submitted to TD-DFT calculations to study the absorption characteristics in more detail again applying PCM with dichloromethane as a solvent (Table S10). The experimentally determined longest wavelength absorption bands are reasonably well reproduced by the TD-DFT calculations. As expected, the longest wavelength absorption bands of all three calculated 6-aryl-8H-indolo[3,2-a]phenazines originate from
dominant contributions of HOMO–LUMO based transitions. The relevant oscillator strengths additionally indicate permitted electronic transitions. In the HOMO of structures 18 the coefficient density is predominantly localized on the carbazole moiety of the indolo[3,2-a]phenazine, while the coefficient density in the LUMO almost exclusively is localized on the phenazine part (Figure S61). This is in agreement with an angular charge transfer transition from donor (carbazole moiety) to acceptor (phenazine moiety). This charge transfer character is enhanced by placing an additional donor (18a, R1 = OMe) at position 6 in the indolo[3,2-a]phenazine. This design principle of chromophores 18 might be further extended by placing further donor substituents at position 11 (R2) and acceptor substituents at positions 2 and 3 in the indolo[3,2-a]phenazine scaffold to create redshifted emissions with high fluorescence quantum yields.

Table S10. Experimental and TD-DFT calculated (CAM-B3LYP/6-311++G(d,p)) absorption maxima of selected 6-aryl-indolo[3,2-a]phenazines 18 using PCM with dichloromethane as a solvent.

| structure | λ_{max(abs)} [nm] | λ_{max,calcd} [nm] | Most dominant contributions | Oscillator strength |
|-----------|-------------------|-------------------|-----------------------------|-------------------|
| 18a       | 420 (14400)       | 404               | HOMO→LUMO (95 %)            | 0.148             |
|           | 310 (29400)       | 341               | HOMO-1→LUMO (77 %)          | 0.278             |
|           | 303 (36700sh)     |                   | HOMO-5→LUMO (4 %)           |                   |
|           |                   |                   | HOMO→LUMO+1 (4 %)           |                   |
|           |                   |                   | HOMO→LUMO+5 (3 %)           |                   |
|           | 273 (52900)       | 266               | HOMO→LUMO+1 (77 %)          | 0.780             |
|           |                   |                   | HOMO-3→LUMO+1 (6 %)         |                   |
|           |                   |                   | HOMO-1→LUMO+1 (2 %)         |                   |
| 18c       | 417 (17900)       | 398               | HOMO→LUMO (95 %)            | 0.126             |
|           | 311 (55000)       | 341               | HOMO-1→LUMO (79 %)          | 0.288             |
|           | 300 (48200sh)     |                   | HOMO-5→LUMO (7 %)           |                   |
|           |                   |                   | HOMO→LUMO+2 (4 %)           |                   |
|           |                   |                   | HOMO→LUMO+3 (4 %)           |                   |
|           | 272 (75600)       | 265               | HOMO→LUMO+1 (79 %)          | 0.772             |
|           |                   |                   | HOMO-2→LUMO+1 (5 %)         |                   |
|           |                   |                   | HOMO-1→LUMO (3 %)           |                   |
| 18e       | 416 (15100)       | 399               | HOMO→LUMO (95 %)            | 0.155             |
|           | 312 (30200)       | 344               | HOMO-1→LUMO (79 %)          | 0.302             |
|           |                   |                   | HOMO-4→LUMO (6 %)           |                   |
|           |                   |                   | HOMO→LUMO+2 (6 %)           |                   |
|           | 275 (50600)       | 273               | HOMO→LUMO+1 (58 %)          | 0.612             |
|           |                   |                   | HOMO-2→LUMO (10 %)          |                   |
|           |                   |                   | HOMO-4→LUMO (6 %)           |                   |
|           |                   |                   | HOMO→LUMO+2 (6 %)           |                   |

[a] Recorded in CH$_2$Cl$_2$, $T = 293$ K, $c(18) = 10^{-5}$ M.
Figure S67. Selected DFT-computed (CAM-B3LYP/6–311++G(d,p)) Kohn–Sham frontier molecular orbitals of 6-aryl-indolo[3,2-a]phenazines 18a, 18c, and 18e.
14. **Crystal structures of compounds 9a and 18e**

Single crystals of compound 9a and 18e were mounted on a loop under a polarizing microscope. *Data collection:* Compound 1: diffractometer (with microfocus tube), Mo–Kα radiation (λ = 0.71073 Å) at 100 ± 2 K, multilayer mirror, ω- and ϕ-scan; data collection with Apex2,[12] cell refinement and data reduction with SAINT,[12] experimental absorption correction with SADABS.[13] *Structure Analysis and Refinement:* Both structures were solved by direct methods using SHELXS-97; refinement was done by full-matrix least squares on F² using the SHELXL-97 program suite.[14] All non-hydrogen positions were refined with anisotropic displacement parameters. Hydrogen atoms on carbon were positioned geometrically (with C–H = 0.95 Å for aromatic CH and C–H = 0.98 Å for CH₃) and refined using riding models (AFIX 43 and 137, respectively) with Uiso(H) = 1.2 Ueq and Uiso(H) = 1.5 Ueq.

In the structure of 9a the H atoms of the CH₃ group on N3 were refined using PART commands with two sets of half-occupied positions rotated by 60° with respect to each other. The first set with H22a-c was calculated with AFIX 137 or eventually AFIX 33 and Uiso(H) = 1.5Ueq(C). The second set with H22d-f was found from the residual electron density and refined freely with Uiso(H) = 1.5Ueq(C).
14.1. Crystal structure of compound 9a

| Identification code | FM263 |
|---------------------|-------|
| Empirical formula   | C_{22}H_{21}N_{3}Si |
| Formula weight      | 355.51 g·mol^{-1} |
| Temperature         | 100 (2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Monoclinic |
| Space group         | P2_1/c |
| Unit cell dimensions| a = 15.4788 (14) Å, α = 90° |
|                     | b = 16.7597 (15) Å, β = 93.977 (4)° |
|                     | c = 7.1711 (7) Å, γ = 90° |
| Volume              | 1855.8 (3) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.272 Mg·m⁻³ |
| Absorption coefficient| 0.137 mm⁻¹ |
| F(000)              | 752 |
| Crystal size        | 0.05 × 0.05 × 0.03 mm³ |
| Theta range for data collection | 4.861 to 59.376° |
| Index ranges        | -19<=h<=19, -20<=k<=20, -7<=l<=8 |
| Reflections collected | 30690 |
| Independent reflections | 3704 [R_{int} = 0.0506] |
| Completeness to theta | 59.376° |
| 99.9 % |
| Absorption correction | multi-scan (SADABS; Sheldrick, 1996) |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 3704 / 0 / 247 |
| Goodness-of-fit on F² | 1.044 |
| Final R indices [I>2sigma(I)] | R1 = 0.0373, wR2 = 0.0960 |
| R indices (all data) | R1 = 0.0502, wR2 = 0.1029 |
| Largest diff. peak and hole (max and min) | 0.276 e·Å⁻³ and -0.288 e·Å⁻³ |
Selected bond lengths [Å] and angles [°] for compound 9a.

| Bond/Angle | Length/Angle |
|------------|--------------|
| Si—C15     | 1.8675 (18)  |
| Si—C13     | 1.8681 (18)  |
| Si—C14     | 1.8684 (19)  |
| Si—C12     | 1.8817 (16)  |
| N1—C7      | 1.337 (2)    |
| N1—C4      | 1.350 (2)    |
| N2—C8      | 1.335 (2)    |
| N2—C5      | 1.350 (2)    |
| N3—C10     | 1.377 (2)    |
| N3—C16     | 1.382 (2)    |
| N3—C22     | 1.450 (2)    |
| C1—C6      | 1.358 (2)    |
| C1—C2      | 1.413 (3)    |
| C2—C3      | 1.361 (2)    |
| C3—C4      | 1.419 (2)    |
| C4—C5      | 1.426 (2)    |
| C5—C6      | 1.420 (2)    |
| C7—C9      | 1.425 (2)    |
| C15—Si—C13 | 108.42 (9)   |
| C15—Si—C14 | 111.60 (9)   |
| C13—Si—C14 | 108.05 (9)   |
| C15—Si—C12 | 111.75 (8)   |
| C13—Si—C12 | 108.07 (8)   |
| C14—Si—C12 | 108.82 (8)   |
| C7—N1—C4   | 116.22 (14)  |
| C8—N2—C5   | 117.12 (14)  |
| C10—N3—C16 | 108.35 (13)  |
| C10—N3—C22 | 125.83 (14)  |
| C16—N3—C22 | 125.82 (14)  |
| C6—C1—C2   | 120.60 (16)  |
| C3—C2—C1   | 120.66 (16)  |
| C2—C3—C4   | 120.45 (17)  |
| N1—C4—C3   | 119.39 (15)  |
| N1—C4—C5   | 121.80 (15)  |
| C3—C4—C5   | 118.81 (15)  |
| N2—C5—C6   | 119.45 (16)  |
| N2—C5—C4   | 121.55 (15)  |
| C6—C5—C4   | 118.99 (15)  |
| C1—C6—C5   | 120.43 (17)  |
| N1—C7—C9   | 120.30 (14)  |
| N1—C7—C8   | 122.33 (14)  |
| C9—C7—C8   | 117.36 (14)  |
Packing analysis of compound 9a

Significant significant \( \pi \)-stacking show rather short centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles (\( \beta \), \( \gamma \) <25°) and vertical displacements (slippage <1.5 Å) which translate into a sizable overlap of the aryl-plane areas.\(^{[15]}\) (see Scheme S62 below).

Significant intermolecular C-H···\( \pi \) contacts are less than 2.7 Å for the (C-)H···ring centroid distances with H-perp below 2.6-2.7 Å and C-H···Cg > 145°.\(^{[16]}\)

The molecules of 9a are stacked on top of each other with sizeable \( \pi \)-\( \pi \) stacking\(^{[15]}\) along the c-direction (see Table) and arranged in undulated layers parallel to the ab-plane.
Table S11. Packing Analysis for 9a for possible π-π interactions.\(^8\)

| Cg(I) | Res(I) | Cg(J) | ARU(J) | Cg-Cg | Alpha | Beta | Gamma | Cg\(_{\text{Perp}}\) | Cg\(_{\text{Perp}}\) | Slippage |
|-------|--------|-------|--------|-------|-------|------|-------|----------------|----------------|----------|
| Cg(1) | 1 \rightarrow Cg(1) | [3666.01] | 3.5300(10) | 0.00(9) | 15.8 | 15.8 | -3.3964(6) | -3.3964(6) | 0.962 |
| Cg(1) | 1 \rightarrow Cg(1) | [3667.01] | 4.3968(10) | 0.00(9) | 39.6 | 39.6 | 3.3871(6) | 3.3871(6) | 2.804 |
| Cg(1) | 1 \rightarrow Cg(4) | [3666.01] | 4.1766(10) | 1.55(8) | 34.8 | 36.0 | -3.3782(6) | -3.4311(6) | 2.382 |
| Cg(1) | 1 \rightarrow Cg(5) | [3666.01] | 4.4240(11) | 1.94(9) | 39.2 | 40.3 | -3.3717(6) | -3.4270(8) | 2.798 |
| Cg(1) | 1 \rightarrow Cg(5) | [3667.01] | 4.4687(11) | 1.94(9) | 41.3 | 41.8 | 3.3316(6) | 3.3565(8) | 2.950 |
| Cg(2) | 1 \rightarrow Cg(2) | [4564.01] | 4.9490(10) | 8.92(7) | 50.4 | 41.9 | 3.6860(6) | 3.6859(6) | 3.303 |
| Cg(2) | 1 \rightarrow Cg(2) | [4565.01] | 4.9490(10) | 8.92(7) | 41.9 | 50.4 | -3.1552(6) | 3.4270(8) | 2.967 |
| Cg(2) | 1 \rightarrow Cg(3) | [4564.01] | 4.5330(11) | 6.75(8) | 40.9 | 38.0 | 3.5706(6) | 3.4142(8) | 1.256 |
| Cg(2) | 1 \rightarrow Cg(3) | [4565.01] | 3.6380(11) | 6.75(8) | 20.2 | 26.6 | -3.2535(6) | 3.4142(8) | 1.628 |
| Cg(3) | 1 \rightarrow Cg(2) | [4564.01] | 3.6380(11) | 6.75(8) | 26.6 | 20.2 | 3.4142(8) | -3.5236(6) | 2.856 |
| Cg(3) | 1 \rightarrow Cg(2) | [4565.01] | 4.5330(11) | 6.75(8) | 38.0 | 40.9 | -3.4270(8) | 3.5705(6) | 2.793 |
| Cg(3) | 1 \rightarrow Cg(3) | [4564.01] | 3.6142(12) | 4.46(9) | 18.4 | 20.1 | 3.3944(8) | -3.4297(8) | 1.140 |
| Cg(3) | 1 \rightarrow Cg(3) | [4565.01] | 3.6143(12) | 4.46(9) | 20.1 | 18.4 | -3.4297(8) | 3.3944(8) | 1.241 |
| Cg(3) | 1 \rightarrow Cg(4) | [4564.01] | 4.9245(11) | 8.40(8) | 52.2 | 45.3 | 3.4648(8) | -3.0151(6) | 3.894 |
| Cg(4) | 1 \rightarrow Cg(1) | [3666.01] | 4.1766(10) | 1.55(8) | 36.0 | 34.8 | -3.4311(6) | -3.3782(6) | 2.456 |
| Cg(4) | 1 \rightarrow Cg(3) | [4565.01] | 4.9247(11) | 8.40(8) | 45.3 | 52.2 | -3.0152(6) | 3.4649(8) | 3.500 |
| Cg(4) | 1 \rightarrow Cg(5) | [3666.01] | 4.0814(11) | 3.44(8) | 31.9 | 31.5 | -3.4796(6) | -3.4635(8) | 2.159 |
| Cg(5) | 1 \rightarrow Cg(1) | [3666.01] | 4.4240(11) | 1.94(9) | 40.3 | 39.2 | -3.4270(8) | -3.3717(6) | 2.864 |
| Cg(5) | 1 \rightarrow Cg(1) | [3667.01] | 4.4687(11) | 1.94(9) | 41.8 | 41.3 | 3.3655(8) | 3.3316(6) | 2.978 |
| Cg(5) | 1 \rightarrow Cg(4) | [3666.01] | 4.0814(11) | 3.44(8) | 31.5 | 31.9 | -3.4635(8) | -3.4797(6) | 2.133 |

| Min or Max | 3.530 | 0.0 | 15.8 | 60.1 | -3.567 | -3.567 |

\(^8\) The Table presents a selection of the Cg-Cg distances calculated by PLATON,\(^{[17]}\) here chosen according to the criteria of centroid-centroid contacts (<3.8 Å), near parallel ring planes (alpha < 10° to ~0° or even exactly 0° by symmetry), small slip angles (\(\beta, \gamma < 25°\)) (Scheme S1).

Interactions highlighted in yellow are the unique interactions to symmetry-related neighboring molecules on one side of the molecule of origin. The highlighted interactions are depicted in Figure I in the main text.

The Cg(I) refer to the Ring Centre-of-Gravity numbers with atoms:

- Cg(1) = N3-C9-C10-C16-C17
- Cg(2) = N1-N2-C4-C5-C7-C8
- Cg(3) = C1-C2-C3-C4-C5-C6
- Cg(4) = C7-C8-C9-C10-C11-C12
- Cg(5) = C16-C17-C18-C19-C20-C21
14.2. Crystal structure of compound 18e

| Identification code     | FM_LBO482  |
|-------------------------|------------|
| Empirical formula       | \( \text{C}_{26}\text{H}_{16}\text{N}_{4} \) |
| Formula weight          | 384.43 g·mol\(^{-1}\) |
| Temperature             | 100 (2) K |
| Wavelength              | 0.71073 Å |
| Crystal system          | Triclinic |
| Space group             | \( P\bar{1} \) |
| Unit cell dimensions    | \( a = 9.7229 \) (15) Å, \( \alpha = 78.70 \) (1)° |
|                         | \( b = 9.9068 \) (16) Å, \( \beta = 83.316 \) (10)° |
|                         | \( c = 10.2683 \) (17) Å, \( \gamma = 75.00 \) (1)° |
| Volume                  | 934.6 (3) Å\(^3\) |
| Z                       | 2 |
| Density (calculated)    | 1.366 Mg·m\(^{-3}\) |
| Absorption coefficient  | 0.08 mm\(^{-1}\) |
| F(000)                  | 400 |
| Crystal size            | 0.08 × 0.03 × 0.03 mm\(^3\) |
| Theta range for data collection | 2.0 - 32.2° |
| Index ranges            | -14≤h≤14, -13≤k≤14, -15≤l≤15 |
| Reflections collected   | 24692 |
| Independent reflections | 6550 [R\(_{int}\) =0.094] |
| Completeness to theta   | 32.2° 98.9 % |
| Absorption correction   | multi-scan (SADABS; Sheldrick, 1996) |
| Refinement method       | Full-matrix least-squares on \( F^2 \) |
| Data / restraints / parameters | 6550/ 0/ 272 |
| Goodness-of-fit on \( F^2 \) | 1.014 |
| Final R indices [I>2\sigma(I)] | R1 = 0.0564, wR2 = 0.1502 |
| R indices (all data)    | R1 = 0.1170, wR2 = 0.1275 |
| Largest diff. peak and hole (max and min) | 0.366 e·Å\(^{-3}\) and -0.298 e·Å\(^{-3}\) |
Selected bond lengths [Å] and angles [°] for compound 9a.

| Bond             | Length [Å] (E) | Angle [°] (E) |
|------------------|---------------|--------------|
| N1—C7            | 1.3240 (19)   | C9—C10      | 1.4194 (19)   |
| N1—C3            | 1.3533 (17)   | C10—C11     | 1.3957 (19)   |
| N2—C12           | 1.3420 (17)   | C11—C12     | 1.411 (2)     |
| N2—C4            | 1.3443 (19)   | C11—C21     | 1.440 (2)     |
| N3—C19           | 1.1412 (19)   | C13—C14     | 1.395 (2)     |
| N4—C10           | 1.3600 (19)   | C13—C18     | 1.3985 (18)   |
| N4—C22           | 1.3895 (17)   | C14—C15     | 1.384 (2)     |
| N4—C20           | 1.4544 (19)   | C15—C16     | 1.397 (2)     |
| C1—C2            | 1.3613 (19)   | C16—C17     | 1.392 (2)     |
| C1—C6            | 1.420 (2)     | C16—C19     | 1.444 (2)     |
| C2—C3            | 1.410 (2)     | C17—C18     | 1.3798 (19)   |
| C3—C4            | 1.428 (2)     | C21—C26     | 1.4011 (19)   |
| C4—C5            | 1.4228 (19)   | C21—C22     | 1.411 (2)     |
| C5—C6            | 1.359 (2)     | C22—C23     | 1.391 (2)     |
| C7—C8            | 1.4503 (18)   | C23—C24     | 1.377 (2)     |
| C7—C12           | 1.4531 (19)   | C24—C25     | 1.401 (2)     |
| C8—C9            | 1.357 (2)     | C25—C26     | 1.375 (2)     |
| C8—C13           | 1.4778 (19)   |             |              |

| Bond             | Length [Å] (E) | Angle [°] (E) |
|------------------|---------------|--------------|
| C7—N1—C3         | 117.29 (12)   | C10—C11—C21 | 106.39 (13)   |
| C12—N2—C4        | 116.87 (12)   | C12—C11—C21 | 134.24 (13)   |
| C10—N4—C22       | 108.36 (11)   | N2—C12—C11  | 120.73 (12)   |
| C10—N4—C20       | 126.66 (12)   | N2—C12—C7   | 121.04 (13)   |
| C22—N4—C20       | 124.96 (13)   | C11—C12—C7  | 118.22 (12)   |
| C2—C1—C6         | 120.24 (15)   | C14—C13—C18 | 119.02 (13)   |
| C1—C2—C3         | 120.47 (13)   | C14—C13—C8  | 121.48 (12)   |
| N1—C3—C2         | 119.40 (13)   | C18—C13—C8  | 119.33 (13)   |
| N1—C3—C4         | 121.12 (14)   | C15—C14—C13 | 120.74 (13)   |
| C2—C3—C4         | 119.48 (12)   | C14—C15—C16 | 119.35 (14)   |
| N2—C4—C5         | 119.61 (13)   | C17—C16—C15 | 120.54 (13)   |
| N2—C4—C3         | 121.89 (12)   | C17—C16—C19 | 119.11 (13)   |
| C5—C4—C3         | 118.50 (14)   | C15—C16—C19 | 120.34 (14)   |
| C6—C5—C4         | 120.32 (14)   | C18—C17—C16 | 119.46 (13)   |
| C5—C6—C1         | 120.84 (13)   | C17—C18—C13 | 120.83 (14)   |
| N1—C7—C8         | 118.66 (12)   | N3—C19—C16  | 178.52 (17)   |
| N1—C7—C12        | 121.57 (12)   | C26—C21—C22 | 118.74 (14)   |
| C8—C7—C12        | 119.76 (13)   | C26—C21—C11 | 134.96 (15)   |
| C9—C8—C7         | 120.19 (12)   | C22—C21—C11 | 106.28 (12)   |
| C9—C8—C13        | 118.91 (12)   | N4—C22—C23  | 129.04 (14)   |
| C7—C8—C13        | 120.90 (13)   | N4—C22—C21  | 108.69 (13)   |
| C8—C9—C10        | 119.51 (12)   | C23—C22—C21 | 122.26 (13)   |
| N4—C10—C11       | 110.26 (12)   | C24—C23—C22 | 117.45 (15)   |
| N4—C10—C9        | 127.00 (12)   | C23—C24—C25 | 121.32 (15)   |
| C11—C10—C9       | 122.71 (14)   | C26—C25—C24 | 121.16 (14)   |
| C10—C11—C12      | 119.36 (13)   | C25—C26—C21 | 119.04 (15)   |
Packing analysis of compound 18e

See also the general remarks and the Figure 62 for π–π interactions above for compound 9a. For packing analysis see Table S12.

Table S12. Packing Analysis for 18e for possible π–π interactions. a

| Cg(I) Res(I) | Cg(J) | ARU(J) | Cg-Cg | Alpha | Beta | Gamma | Cgl_Perp | Cgl_Perp | Slippage |
|--------------|-------|--------|-------|-------|------|-------|----------|----------|----------|
| Cg(1) 1 -> Cg(1) 2656.01 | 3.3808(10) | 0.00(8) | 14.1 | 14.1 | -3.2793(6) | -3.2793(6) | 0.822 |
| Cg(1) 1 -> Cg(2) 2666.01 | 4.5867(11) | 7.327 | 40.6 | 43.7 | 3.3173(6) | 3.4819(5) | 2.986 |
| Cg(1) 1 -> Cg(3) 2666.01 | 3.7412(11) | 10.948(8) | 20.8 | 31.4 | 3.1916(6) | 3.4975(6) | 1.328 |
| Cg(1) 1 -> Cg(4) 2666.01 | 4.3716(11) | 3.867(7) | 40.0 | 43.9 | -3.1518(6) | -3.3485(6) | 2.810 |
| Cg(1) 1 -> Cg(5) 2666.01 | 3.5901(10) | 2.03(8) | 22.5 | 24.4 | -3.2682(6) | -3.3170(6) | 1.373 |
| Cg(2) 1 -> Cg(1) 2666.01 | 4.5867(11) | 7.327(7) | 43.7 | 40.6 | 3.4819(5) | 3.3174(6) | 3.168 |
| Cg(2) 1 -> Cg(2) 2666.01 | 3.5466(9) | 0.00(6) | 14.2 | 14.2 | 3.4387(5) | 3.4387(5) | 0.868 |
| Cg(2) 1 -> Cg(3) 2666.01 | 4.7097(11) | 3.657(7) | 43.2 | 43.0 | 3.4448(5) | 3.4305(6) | 3.227 |
| Cg(2) 1 -> Cg(4) 2666.01 | 3.7831(10) | 4.10(6) | 23.5 | 25.8 | 3.4056(5) | 3.4703(6) | 1.506 |
| Cg(2) 1 -> Cg(5) 2666.01 | 4.7334(11) | 54.907(7) | 24.1 | 36.4 | 3.8084(5) | 4.3206(6) | 1.206 |
| Cg(2) 1 -> Cg(6) 2666.01 | 4.7698(12) | 9.15(7) | 45.6 | 43.7 | -3.4493(5) | -3.3392(6) | 3.406 |
| Cg(3) 1 -> Cg(1) 2666.01 | 3.7411(11) | 10.948(8) | 31.4 | 20.8 | 3.4975(6) | 3.1917(6) | 1.952 |
| Cg(3) 1 -> Cg(2) 2666.01 | 4.7097(11) | 3.657(7) | 43.0 | 43.2 | 3.4305(6) | 3.4448(5) | 3.212 |
| Cg(3) 1 -> Cg(4) 2666.01 | 3.568810 | 7.46(7) | 13.7 | 13.2 | 3.4739(6) | 3.4666(6) | 0.848 |
| Cg(3) 1 -> Cg(5) 2666.01 | 4.5753(11) | 54.337(7) | 16.3 | 65.6 | 1.8905(6) | -4.3929(6) | 3.168 |
| Cg(3) 1 -> Cg(6) 2666.01 | 4.8948(12) | 12.80(7) | 55.9 | 43.1 | 3.5738(6) | 2.7448(6) | 4.053 |
| Cg(4) 1 -> Cg(1) 2666.01 | 4.3716(11) | 3.867(7) | 43.9 | 40.0 | -3.3486(6) | -3.3158(6) | 3.029 |
| Cg(4) 1 -> Cg(2) 2666.01 | 3.7830(10) | 4.10(6) | 25.8 | 23.5 | 3.4703(6) | 3.4056(5) | 1.647 |
| Cg(4) 1 -> Cg(3) 2666.01 | 3.568810 | 7.46(7) | 13.2 | 13.7 | 3.4665(6) | 3.4739(6) | 0.818 |
| Cg(4) 1 -> Cg(4) 2666.01 | 3.5523(10) | 5.88(7) | 20.5 | 16.1 | -3.4136(6) | -3.3268(6) | 1.245 |
| Cg(4) 1 -> Cg(5) 2666.01 | 4.7333(11) | 54.907(7) | 36.4 | 24.1 | -4.3206(6) | 3.8083(5) | 1.245 |
| Cg(4) 1 -> Cg(6) 2666.01 | 4.6240(11) | 54.337(7) | 10.7 | 62.6 | -2.1311(6) | -4.5434(6) | 1.486 |
| Cg(5) 1 -> Cg(1) 2666.01 | 3.5900(10) | 2.03(8) | 24.4 | 22.5 | -3.3170(6) | -3.2682(6) | 1.486 |
| Cg(5) 1 -> Cg(2) 2666.01 | 4.7698(12) | 9.15(7) | 43.7 | 45.6 | -3.3392(6) | -3.4493(5) | 3.294 |
| Cg(5) 1 -> Cg(3) 2666.01 | 4.8948(12) | 12.80(7) | 43.1 | 55.9 | 2.7448(6) | 3.5738(6) | 3.345 |
| Cg(5) 1 -> Cg(4) 2666.01 | 3.5522(10) | 5.88(7) | 16.1 | 20.5 | -3.3268(6) | -3.4135(6) | 0.983 |
| Cg(5) 1 -> Cg(6) 2666.01 | 4.8664(12) | 0.02(7) | 48.3 | 48.3 | -3.2361(6) | -3.3261(6) | 3.634 |
| Cg(6) 1 -> Cg(6) 2756.01 | 4.9005(12) | 0.02(7) | 40.7 | 40.7 | 3.7153(6) | 3.7153(6) | 3.196 |

Min or Max 3.381 0.0 10.7 83.3 -4.329 -4.543

[ 2656] = 1-X,Y,1-Z
[ 2666] = 1-X,1-Y,1-Z
[ 2566] = -X,1-Y,1-Z

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\[ [1554] = X, Y, -1 + Z \]
\[ [1465] = -1 + X, 1 + Y, Z \]
\[ [2756] = 2 - X, -Y, 1 - Z \]

\(^a\) The Table presents a selection of the Cg-Cg distances calculated by PLATON,\(^b\) here chosen according to the criteria of centroid-centroid contacts (< 3.8 Å), near parallel ring planes (alpha < 10° to 0° or even exactly 0° by symmetry), small slip angles (β, γ < 25°) (Scheme S1).
Interactions highlighted in yellow are the unique interactions to symmetry-related neighboring molecules on one side of the molecule of origin. The highlighted interactions are depicted in Figure 2 in the main text.

The Cg(I) refer to the Ring Centre-of-Gravity numbers with atoms#

Cg(1) = N4-C10-C11-C21-C22
Cg(2) = N1-N2-C3-C4-C7-C12
Cg(3) = C1-C2-C3-C4-C5-C6
Cg(4) = C7-C8-C9-C10-C11-C12
Cg(5) = C13-C14-C15-C16-C17-C18
Cg(6) = C21-C22-C23-C24-C25-C26
15. Biological testing

15.1. Compounds

The selected synthetic indolo[3,2-a]phenazines 9a and 18 and berberine hemisulfate (Figure S62) were dissolved in DMSO as 10 mM stocks and stored at 4 °C. They were diluted into culture medium immediately prior to use.

Figure S69. Structures of the selected synthetic indolo[3,2-a]phenazines 9a and 18 and of berberine hemisulfate used for testing of inhibitory activity on Toxoplasma proliferation and for cell toxicity in a MTT assay

15.2. Parasite propagation

The ME49 strain of T. gondii, obtained from ATTC (Wesel, Germany), was grown in Hs27 human foreskin fibroblast, as host cells in the tachyzoite stage. Hs27 cells were grown in
Iscove's Modified Dulbecco's medium (Gibco-Thermo Fisher Scientific, Braunschweig, Germany) plus 10 % fetal bovine serum (Invitrogen, Karlsruhe, Germany) and 500 µL 2-mercaptoethanol 50 mM (Gibco-Thermo Fisher Scientific, Braunschweig, Germany). For toxoplasma propagation, 25 cm² cell culture flasks, containing a confluent monolayer of Hs27 cells, were infected with 5x10⁶ T. gondii tachyzoites after medium change. After three days, T. gondii tachyzoites were harvested from the infected cultures. Accordingly, the entire contents of the cell culture flask were transferred to a 15 mL centrifuge tube and centrifuged at 700 rpm for 5 min. Toxoplasma parasites are found in the supernatant.

15.3. Proliferation assay

96-well microtiter plates with a final volume of 200 µL per well were used for the assay. Hs27 fibroblasts were used in a number of 2x10⁴ per well and infected with T. gondii (2x10⁴) (moi 1:1) for 48 h at 37 °C. The compounds, dissolved in DMSO, were used in a dilution of 1:250 with culture medium, corresponding to a concentration of 40 µM. Subsequently, the compounds were transferred to the individual wells and titrated on the microtiter plate in a ratio of 1:2 unto 0.15 µM. Cells pre-stimulated for 24 hours with IFNγ (300 U/ml) and only T. gondii infected cells were used as controls in this assay. 48 hours later, proliferating toxoplasmas were radioactively labelled with tritiated uracil (5mCi, diluted 1:30, 10 µL per 200 µL total culture volume per well) in order to determine parasite proliferation. In the subsequent step, the assay was frozen at -20 °C after 28-30 h. To evaluate the assay, the microtiter plates were thawed at room temperature and the amount of incorporation of tritiated uracil into the RNA by T. gondii was quantified using a beta-counter device (Betaplate Liquid Scintillation Counter 1205, LKB-WALLAK, Australia). After thawing the microtiter plates, the cells were transferred to glass-fiber filters (Printed Filtermat A 102x258 mm, PerkinElmer, Waltham, USA) using a cell harvester (Basic96 Harvester, Zinsser Analytic, Skatron Instruments, USA). The filters were dried for 20 min at 130 °C in a drying cabinet, afterwards they were soaked in 10 mL of scintillation fluid (Betaplate Scint, PerkinElmer, Waltham, USA) and shrink-wrapped in plastic covers (Sample Bag for Betaplate, PerkinElmer, Waltham, USA). The filters were then clamped in cassettes and evaluated in the beta-counter to measure the Cherenkov radiation. IC₅₀ values, the concentration of inhibitors necessary to inhibit the growth of tachyzoites by 50%, were determined for each experiment with the use of Prism GraphPad version 5.0 software to fit the concentration-response data to a sigmoidal curve (Figure S63).

15.4. Cell viability assay

The 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide (MTT) test was used to assess cell viability of the tested compounds against Hs27 cells. The MTT assay is a
colorimetric reaction based on the enzymatic reduction of MTT to MTT-formazan that is catalyzed by mitochondrial succinate dehydrogenase.

Hs27 cells were plated in duplicates in 96-well plates, and grown to confluence prior incubation at 37 °C with synthetic indolo[3,2-a]phenazines 9a and 18 at the same concentration range as used for the *Toxoplasma gondii* proliferation assays. After 24 h, the medium of the culture was removed and replaced with 100 μL of FluoroBrite DMEM medium (Gibco-Thermo Fisher Scientific, Braunschweig, Germany) plus 10 % fetal bovine serum (Invitrogen, Karlsruhe, Germany), and 500 μL 2-mercaptoethanol 50 mM (Gibco-Thermo Fisher Scientific, Braunschweig, Germany). Then, 10 μL of the 12 mM MTT stock solution (Vybrant MTT Cell Proliferation Assay Kit, Thermo Fisher Scientific, Braunschweig, Germany), was added for each well. The plates containing Hs27 cells plus / minus Indolo[3,2-a]phenazine compounds 9a and 18 or controls were incubated for 4 h at 37 °C. Then, 100 μL of SDS solution (1 gr of SDS in 10 mL 0.01 M HCl), was added to each well and mixed thoroughly using a pipette. The 96-well plates were incubated again for 4 h at 37 °C to dissolve the formazan salt. Finally, the absorbance was measured at 570 nm by spectrophotometer (TECAN Sunrise, Männedorf, Switzerland). Stauroporine (STR) in a concentration range from 5.00 μM to 0.0375 μM, DMSO (20 μM) and the natural product berberine hemisulfate were used as controls. The relative cell viability (%) of each compound in different concentrations was calculated as the mean absorbance of the compound minus the absorbance of the blank at 570 nm divided by the mean absorbance of the DMSO control minus the absorbance of the blank at 570 nm multiplied per 100. All the results were normalized to the 100% DMSO control. All data were analyzed using Prism GraphPad version 5.0 software.
Toxoplasma proliferation assay. Typical data from 1 out of 3 experiments are shown.

Toxoplasma proliferation assays were performed to investigate the activity of the selected synthetic indolo[3,2-a]phenazines against *T. gondii* ME49 strain. Hs27 cells in a monolayer were cultured in 96-well plates and infected with *T. gondii* (2x10^4). Cultures were treated with indolo[3,2-a]phenazines and berberine hemisulfate at the concentration range of 0.15–20.00 µM for 48 hours at 37 °C. Afterwards, the cultures were labelled with ^3^H-U (5mCi, diluted 1:30) for 28-30 hours at 37 °C. Based on the incorporation of ^3^H-U into the parasite nucleic acid, the parasite growth was quantified. As a positive control, uninfected Hs27 cells without treatment (pink), IFNγ pre-stimulated infected Hs27 cells (green) and only *T. gondii* infected Hs27 cells (red) as a negative control were used. Three independent assays, in duplicates, were performed. Mean ± SD of IC50 values of each compound of one typical experiment are shown.

| Compound                  | IC50 Value (µM) |
|---------------------------|-----------------|
| Berberine hemisulfate     | 1.55            |
| 18c                       | 0.36            |
| 9a                        | 0.59            |
| 18d                       | 1.75            |
| 18a                       | 0.80            |
| 18f                       | 1.70            |
| 18b                       | 0.70            |
| 18g                       | 1.38            |

Figure S63. Toxoplasma proliferation assay. Typical data from 1 out of 3 experiments are shown.
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