Supporting Information

for

Synthesis, crystal structures and properties of carbazole-based [6]helicenes fused with an azine ring

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Experimental procedures and analytical data, copies of $^1$H and $^{13}$C NMR spectra of all new compounds, X-ray data for 9c and 10a–c, HPLC spectra of helicenes 10a–c, UV–vis and fluorescence spectra of 10a–c
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Experimental section

General information: $^1$H and $^{13}$C NMR spectra were recorded on a 250 MHz spectrometer (Bruker DPX-250). Chemical shifts were reported in ppm relative to Me$_4$Si. The UV-vis spectra were recorded on a Varian Cary 50 Probe spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source. Melting points were determined on a Stuart SMP30 instrument in glass capillaries and are uncorrected. Flash column chromatography was performed on silica gel (70–230 mesh, Aldrich). Reactions were monitored by thin layer chromatography (silica gel 60 F$_{254}$) and visualized using UV. Commercial alkynes, 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, catalysts, ICl, 2,3-dihaloazines, diisopropylamine, triethylamine, PPh$_3$, TFA, triflic acid, anhydrous DMSO, THF were used as received.

9-Ethyl-3-(3-(phenylethynyl)quinoxalin-2-yl)-9H-carbazole (2a): A stirred mixture of 2-chloro-3-(phenylethynyl)quinoxaline 1a [1] (132 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (161 mg, 0.5 mmol), Pd(PPh$_3$)$_4$ (58 mg, 0.05 mmol), K$_2$CO$_3$ (345 mg, 2.5 mmol), 1,4-dioxane (8 mL) and water (4 mL) was heated at 100 °C for 17 h under argon. After evaporation of the reaction mixture the residue was diluted with water (50 mL) and extracted with CH$_2$Cl$_2$ (3 × 15 mL). The extract was dried over Na$_2$SO$_4$. Flash column chromatography was carried out on silica gel (3.5 × 50 cm) using CH$_2$Cl$_2$ as the eluent. The yellow fraction with $R_f$ 0.45 gave compound 2a (203 mg, 96%). Compound 2a was obtained as lemon yellow needles with mp 158–160 °C (EtOH). $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.47 (t, $J = 7.1$ Hz, 3 H), 4.42 (q, $J = 7.1$ Hz, 2 H), 7.21–7.35 (m, 4 H), 7.43–7.57 (m, 5 H), 7.70–7.78 (m, 2 H), 8.12–8.18 (m, 3 H), 8.29 (dd, $J = 8.6$, 1.4 Hz, 1 H), 9.03 (d, $J = 1.0$ Hz, 1 H) ppm. $^{13}$C NMR (62.9 MHz, CDCl$_3$) δ 13.9, 37.8, 89.3, 94.9, 108.4, 108.8, 119.4, 120.8, 121.9, 122.4, 122.7, 123.2, 126.1, 127.9, 128.2, 128.5, 128.8, 129.2, 129.5, 129.8, 130.6, 132.3, 138.3, 140.6, 140.7, 140.9, 141.1, 155.5 ppm. HRMS (ESI): MH$^+$, found 424.1815. C$_{30}$H$_{22}$N$_3$ requires 424.1808. M+Na$^+$, found 446.1633. C$_{30}$H$_{21}$N$_3$Na requires 446.1628.

Another catalytic systems, e.g. Pd(PPh$_3$)$_4$/K$_3$PO$_4$/THF (80 °C, 24 h, 36% yield) and Pd(PPh$_3$)$_4$/K$_3$PO$_4$/1,4-dioxane (100 °C, 24 h, 44% yield), were less effective.
9-Ethyl-3-(3-(phenylethynyl)pyrazin-2-yl)-9H-carbazole (2b): Synthesis of compound 2b was carried out similarly to 2a from 2-chloro-3-(phenylethynyl)pyrazine 1b [1] (108 mg, 0.5 mmol). Flash column chromatography was performed on silica gel (2 × 20 cm) using ethylacetate-petroleum ether (1:3, v/v) as the eluent. From the yellow fraction with $R_f$ 0.2–0.3 compound 2b was isolated (153 mg, 82%). Compound 2b was obtained as yellowish solid with mp 133–135 °C (CH$_3$CN). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.52 (t, $J$ = 7.2 Hz, 3 H), 4.47 (q, $J$ = 7.2 Hz, 2 H), 7.26–7.40 (m, 4 H), 7.48–7.59 (m, 5 H), 8.14 (d, $J$ = 7.7 Hz, 1 H), 8.28 (dd, $J$ = 8.6, 1.7 Hz, 1 H), 8.54 (d, $J$ = 2.3 Hz, 1 H), 8.64 (d, $J$ = 2.3 Hz, 1 H), 9.02 (d, $J$ = 1.6 Hz, 1 H) ppm. $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 11.1, 35.0, 85.5, 91.5, 105.4, 106.0, 116.6, 117.8, 119.1, 119.2, 119.9, 120.4, 123.2, 124.5, 124.7, 125.6, 126.5, 129.2, 134.2, 137.7, 138.1, 138.6, 139.5, 153.3 ppm. HRMS (ESI): MH$^+$, found 374.1666. C$_{26}$H$_{20}$N$_3$ requires 374.1652. M+Na$^+$, found 396.1484. C$_{26}$H$_{19}$N$_3$Na requires 396.1471.

3-(3-Chloroquinoxalin-2-yl)-9-ethyl-9H-carbazole (4a) was synthesized in a similar manner as described in [1]. A stirred mixture of 2,3-dichloroquinoxaline 3a (100 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (193 mg, 0.6 mmol), 5% Pd/C (32 mg, 0.015 mmol), PPh$_3$ (16 mg, 0.06 mmol), 2M aqueous solution K$_2$CO$_3$ (2 mL) and toluene (1 mL) was heated at 100 °C for 24 h under argon. The reaction mixture was then extracted with CHCl$_3$ (3 × 20 mL). The extract was dried over Na$_2$SO$_4$ and purified by flash column chromatography on silica gel (3.5 × 45 cm) with CHCl$_3$ as the eluent. The first and second fractions were recovered starting materials: 43 mg (43%) of 3a and 142 mg (73%) of the boronic acid. The fraction with $R_f$ 0.6 gave compound 4a (28 mg, 15%). Compound 4a was obtained as lemon yellow crystals with mp 120–122 °C (EtOH). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.51 (t, $J$ = 7.2 Hz, 3 H), 4.47 (q, $J$ = 7.2 Hz, 2 H), 7.31–7.34 (m, 1 H), 7.47–7.59 (m, 3 H), 7.78–7.85 (m, 2 H), 8.04–8.12 (m, 2 H), 8.19–8.22 (m, 2 H), 8.70 (d, $J$ = 1.2 Hz, 1 H) ppm. $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 13.9, 37.8, 108.3, 108.8, 119.5, 120.8, 122.5, 122.9, 123.1, 126.2, 126.4, 127.3, 127.5, 128.1, 129.2, 130.4 (2C), 140.6, 140.7, 140.8, 141.3, 153.8 ppm. HRMS (ESI): MH$^+$, found 358.1107 ($^{35}$Cl); 360.1081 ($^{37}$Cl). C$_{22}$H$_{17}$ClN$_3$ requires 358.1106 ($^{35}$Cl); 360.1078 ($^{37}$Cl). M+Na$^+$, found 380.0924 ($^{35}$Cl); 382.0902 ($^{37}$Cl). C$_{22}$H$_{16}$ClN$_3$Na requires 380.0925 ($^{35}$Cl); 382.0897 ($^{37}$Cl).

3-(3-Bromopyridin-2-yl)-9-ethyl-9H-carbazole (4b) and 3,3’-(pyridine-2,3-diyl)bis(9-ethyl-9H-carbazole) (5b). A stirred mixture of 2,3-dibromopyridine 3b (119 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (161 mg, 0.5 mmol), Pd(PPh$_3$)$_4$ (58
mg, 0.05 mmol), K₂CO₃ (345 mg, 2.5 mmol), 1,4-dioxane (8 mL) and water (4 mL) was heated at 100 °C for 17 h under argon. After evaporation of the reaction mixture the residue was diluted with water (100 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The extract was dried over Na₂SO₄. Flash column chromatography on silica gel (3.5 × 55 cm) was then carried out using CH₂Cl₂ as the eluent. From the colorless fraction with Rf 0.3 compound 4b was isolated (142 mg, 80%). The yellowish fraction with Rf 0.2 gave compound 5b (20 mg, 8%).

3-(3-Bromopyridin-2-yl)-9-ethyl-9H-carbazole (4b). Yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ = 1.52 (t, J = 7.1 Hz, 3 H), 4.46 (q, J = 7.1 Hz, 2 H), 7.17 (dd, J = 8.0, 4.6 Hz, 1 H), 7.28–7.34 (m, 1 H), 7.47–7.58 (m, 3 H), 7.91 (d, J = 8.5 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 8.20 (d, J = 7.7 Hz, 1 H), 8.55 (s, 1 H), 8.72 (d, J = 4.6 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.9, 37.7, 107.9, 108.7, 119.2, 120.1, 120.7, 121.9, 122.6, 122.7, 123.3, 125.9, 127.3, 130.4, 140.2, 140.5, 141.4, 148.1, 159.0 ppm. HRMS (ESI): MH⁺ (⁸¹Br), found 353.0476; MH⁺ (⁷⁹Br), found 351.0497. C₁₀H₁₆BrN₂ requires 353.0472 (⁸¹Br), 351.0491 (⁷⁹Br).

3,3’-(Pyridine-2,3-diyl)bis(9-ethyl-9H-carbazole) (5b). Yellowish oil. ¹H NMR (250 MHz, CDCl₃): δ = 1.38 (t, J = 7.2 Hz, 3 H), 1.41 (t, J = 7.2 Hz, 3 H), 4.29 (q, J = 7.2 Hz, 2 H), 4.33 (q, J = 7.2 Hz, 2 H), 7.12–7.27 (m, 5 H), 7.34–7.52 (m, 6 H), 7.90 (dd, J = 7.7, 1.6 Hz, 1 H), 7.97 (d, J = 7.7 Hz, 1 H), 8.05 (d, J = 7.7 Hz, 1 H), 8.12 (br s, 1 H), 8.38 (d, J = 1.3 Hz, 1 H), 8.77 (dd, J = 4.7, 1.6 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.7(8), 13.8(0), 37.5(8), 37.6(2), 107.6, 108.2, 108.4, 108.6, 118.8, 118.9, 120.5, 120.6, 121.2, 121.5, 122.3, 122.9, 123.0, 123.2, 123.4, 125.5, 125.8, 127.8, 128.2, 131.4, 131.5, 136.7, 139.1, 139.2, 139.6, 140.3, 147.9, 158.1 ppm. HRMS (ESI): MH⁺, found 466.2287. C₃₃H₂₈N₃ requires 466.2278.

9-Ethyl-3-(3-phenylethynyl)pyridin-2-yl)-9H-carbazole (6) was synthesized in a similar manner as described in [1]. A stirred mixture of 3-(3-bromopyridin-2-yl)-9-ethyl-9H-carbazole 4b (92 mg, 0.25 mmol), Pd(PPh₃)₂Cl₂ (18 mg, 0.025 mmol), CuI (2 mg, 0.01 mmol), i-Pr₂NH (0.5 mL) and DMSO (2.5 mL) was heated at 80 °C for 20 min under argon. A solution of phenylacetylene (93 mg, 0.1 mL, 0.75 mmol) in i-Pr₂NH (1 mL) was then added by portions for 1 h. The reaction mixture was stirred at 80 °C for 24 h, evaporated without heating to remove i-Pr₂NH, treated with H₂O (50 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The extract was dried over Na₂SO₄ and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 30 cm) with CH₂Cl₂ as the eluent. The fraction with Rf 0.2 and violet fluorescence gave compound 6 (69 mg, 74%). Compound 6 was obtained as a yellow brown oil. ¹H NMR (250 MHz, CDCl₃): δ = 1.55 (t, J = 7.2 Hz, 3 H), 4.50 (q, J = 7.2 Hz, 2 H), 7.27–7.37
1-Ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-a]phenazine (7a) was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)quinoxalin-2-yl)-9H-carbazole 2a (85 mg, 0.2 mmol) in dry CH₃CN (17 mL) a solution of ICl (33 mg, 0.2 mmol) in dry CH₃CN (2 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark. The yellow orange needles precipitate of 7a (48 mg) was filtered off and washed on the filter with CH₃CN (2 mL). The filtrate was then evaporated to dryness. The residue was extracted with CH₂Cl₂ (15 mL) and saturated Na₂S₂O₃ solution (5 mL). The organic layer was separated and dried over Na₂SO₄ and purified by flash column chromatography on silica gel (2.5 × 55 cm) with CH₂Cl₂ as the eluent. The bright yellow orange fraction with Rf 0.85 gave 24 mg of cyclization product 7a. Total yield was 72 mg (65%). 1-Ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-a]phenazine 7a was obtained as yellow orange needles with mp 248–250 °C (EtOH). ¹H NMR (250 MHz, CDCl₃): δ = 1.50 (t, J = 7.2 Hz, 3 H), 4.52 (q, J = 7.2 Hz, 2 H), 6.29 (d, J = 8.4 Hz, 1 H), 6.63 (ddd, J = 8.2, 7.0, 1.2 Hz, 1 H), 7.27–7.30 (m, 1 H), 7.37 (d, J = 7.9 Hz, 1 H), 7.43–7.52 (m, 3 H), 7.63–7.66 (m, 2 H), 7.82–7.92 (m, 2 H), 7.95 (d, J = 9.0 Hz, 1 H), 8.38–8.47 (m, 2 H), 9.81 (d, J = 9.0 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃) δ 13.8, 37.8, 107.9, 110.8, 112.2, 118.0, 118.8, 123.3, 124.4, 124.8, 125.4, 128.5, 128.8, 128.9, 129.6, 129.9, 130.6, 132.5, 139.5, 141.5, 141.6, 142.5, 142.6, 143.0 (2C), 146.4, 149.0 ppm. HRMS (ESI): MH⁺, found 550.0785. C₃₀H₂₁N₅ requires 550.0775. M+Na⁺, found 572.0584. C₃₀H₂₀N₃Na requires 550.0594.

When using a 1.5-fold excess of ICl, a hardly separable mixture of 7a and its 4-iodo derivative 8a in a 7.7:1 ratio was obtained.

7-Ethyl-13-iodo-12-phenyl-7H-quinoxalino[5,6-c]carbazole (7b) was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)pyrazin-2-yl)-9H-carbazole 2b (59 mg, 0.16 mmol) in dry CH₃CN (2 mL) a solution of ICl (15 mg, 0.09 mmol) in dry CH₃CN (1.5 mL) was added. After 1 h, the next portion of the solution of ICl (5 mg, 0.03 mmol) in dry CH₃CN (1.5 mL) was added. The stirred
reaction mixture was kept at room temperature for 20 h in the dark and then evaporated to dryness. The residue was extracted with CH₂Cl₂ (30 mL) and saturated Na₂S₂O₃ solution (5 mL). The organic layer was separated and dried over Na₂SO₄. The extract was purified by flash column chromatography on silica gel (2 × 25 cm) with ethyl acetate - petroleum ether (1:3, v/v) as the eluent. The yellow fraction with Rf 0.45 gave 46 mg (75%) of cyclization product 7b. 7-Ethyl-13-iodo-12-phenyl-7H-quinoxalino[5,6-c]carbazole 7b was obtained as yellow needles with mp 217–219 °C (EtOH). ¹H NMR (250 MHz, CDCl₃): δ = 1.49 (t, J = 7.2 Hz, 3 H), 4.51 (q, J = 7.2 Hz, 2 H), 6.20 (d, J = 8.5 Hz, 1 H), 6.67 (ddd, J = 8.3, 7.0, 1.2 Hz, 1 H), 7.31 (ddd, J = 8.0, 7.0, 1 H), 7.42 (m, 5 H), 7.67 (ddd, J = 8.0, 7.0, 0.9 Hz, 1 H), 7.48–7.65 (m, 5 H), 7.98 (d, J = 9.0 Hz, 1 H), 8.90 (d, J = 1.8 Hz, 1 H), 8.97 (d, J = 1.8 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.9, 37.7, 107.9, 111.3, 111.7, 116.8, 118.8, 123.4, 123.6, 124.5, 125.3, 126.0, 128.6, 128.8, 130.0, 132.5, 139.1, 140.4, 141.3, 141.7, 143.9, 144.0, 146.7, 147.4 ppm. HRMS (ESI): MH⁺, found 500.0625. C₂₆H₁₉IN₃ requires 500.0618.

When using equimolar amount of ICl, a hardly separable mixture of 7b and its 4-iodo derivative 8b in a 10:1 ratio (69% total yield) was obtained.

7-Ethyl-10,13-diiodo-12-phenyl-7H-quinoxalino[5,6-c]carbazole (8b): To a suspension of 7-ethyl-13-iodo-12-phenyl-7H-quinoxalino[5,6-c]carbazole 7b (25 mg, 0.05 mmol) in dry CH₃CN (4 mL), a solution of ICl (24 mg, 0.15 mmol) in dry CH₃CN (2 mL) was added. The reaction mixture was stirred at room temperature for 24 h in the dark. After evaporation in air without heating the residue was extracted with CH₂Cl₂ (30 mL) and saturated Na₂S₂O₃ solution (5 mL). The extract dried over Na₂SO₄ and purified by flash column chromatography on silica gel (2 × 25 cm) using a mixture of ethyl acetate - petroleum ether (1:3, v/v) as the eluent. The cyclization product 8b (30 mg, 97%) was isolated from the yellow fraction with Rf 0.5. Compound 8b was obtained as a yellow solid with mp 254–255 °C (EtOH). ¹H NMR (250 MHz, CDCl₃): δ = 1.51 (t, J = 7.2 Hz, 3 H), 4.53 (q, J = 7.2 Hz, 2 H), 6.44 (d, J = 1.4 Hz, 1 H), 7.18 (d, J = 8.7 Hz, 1 H), 7.55–7.62 (m, 5 H), 7.66–7.75 (m, 1 H), 7.97 (d, J = 9.0 Hz, 1 H), 8.92 (d, J = 1.8 Hz, 1 H), 8.99 (d, J = 1.8 Hz, 1 H), 9.66 (d, J = 9.0 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.8, 37.8, 83.0, 109.9, 111.3, 111.9, 115.8, 124.4, 125.1, 126.4, 128.9, 129.9, 130.0, 132.1, 133.1, 133.5, 138.2, 140.4, 141.1, 141.6, 144.0, 144.2, 145.9, 147.2 ppm. HRMS (ESI): MH⁺, found 625.9576. C₂₆H₁₉I₂N₃ requires 625.9585.
7-Ethyl-13-iodo-12-phenyl-7H-quinolino[8,7-c]carbazole (7c) was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)pyridin-2-yl)-9H-carbazole 6 (74 mg, 0.2 mmol) in dry CH$_3$CN (6 mL) a solution of ICl (52 mg, 0.3 mmol) in dry CH$_3$CN (3 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark. The yellow orange needles precipitate of 7c (51 mg) was filtered off and washed on the filter with CH$_3$CN (2 mL). The filtrate was then evaporated to dryness. The residue was extracted with CH$_2$Cl$_2$ (20 mL) and saturated Na$_2$SO$_4$ and purified by flash column chromatography on silica gel (2.5 x 25 cm) with CH$_2$Cl$_2$ as the eluent. The yellow fraction with $R_f$ 0.7 gave 11 mg of cyclization product 7c. Total yield of 7c was 62 mg (62%). Compound 7c was obtained as yellow needles with mp 196–197 °C. $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.55 (t, $J$ = 7.0 Hz, 3 H), 4.58 (q, $J$ = 7.0 Hz, 2 H), 6.25 (d, $J$ = 8.4 Hz, 1 H), 6.68 (t, $J$ = 7.6 Hz, 1 H), 7.28–7.34 (m, 1 H), 7.44 (d, $J$ = 8.0 Hz, 1 H), 7.52–7.65 (m, 6 H), 7.99 (d, $J$ = 9.0 Hz, 1 H), 8.81 (d, $J$ = 8.2 Hz, 1 H), 9.01 (d, $J$ = 3.4 Hz, 1 H), 9.78 (d, $J$ = 9.0 Hz, 1 H) ppm. $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ = 13.9, 37.7, 107.8, 108.6, 110.9, 116.5, 118.5, 122.0, 123.6, 124.0, 124.1, 125.2, 126.8, 127.3, 128.5, 128.6, 129.9, 132.8, 139.0, 141.4, 142.8, 143.7, 146.4, 147.7, 149.4 ppm. HRMS (ESI): MH$^+$, found 499.0681. C$_{27}$H$_{19}$N$_2$ requires 499.0666.

1-Ethyl-6-phenyl-7-(p-tolylethynyl)-1H-carbazolo[3,4-a]phenazine (9a): A stirred mixture of 1-ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-a]phenazine 7a (110 mg, 0.2 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (14 mg, 0.02 mmol), CuI (2 mg, 0.01 mmol), Et$_3$N (3 mL) and dry THF (5 mL) was heated at 85 °C for 20 min under argon. A solution of p-tolylacetylene (35 mg, 0.3 mmol) and Et$_3$N (2 mL) in dry THF (2 mL) was then added by portions for 3 h. The reaction mixture was stirred for total 24 h at 85 °C. After subsequent evaporation, the residue was treated with H$_2$O (100 mL) and extracted with CH$_2$Cl$_2$ (2 x 20 mL). The extract was dried over Na$_2$SO$_4$ and concentrated. Flash column chromatography on silica gel (3.5 x 55 cm) was then carried out using CH$_2$Cl$_2$ as the eluent. The yellow orange fraction with $R_f$ 0.6 (yellow fluorescence under UV 356 nm) gave 90 mg (84%) of compound 9a. The product was then heated with hexane (3 mL) for crystallization and filtered off. 1-Ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-a]phenazine 9a was obtained as orange needles with orange fluorescence in the solid state under UV (356 nm) and mp 214–217 °C (ethyl acetate - petroleum ether, 1:3, v/v). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.54 (t, $J$ = 7.1 Hz, 3 H), 2.41 (s, 3 H), 4.56 (q, $J$ = 7.1 Hz, 2 H), 6.42 (d, $J$ = 8.4 Hz, 1 H), 6.70 (ddd, $J$ = 8.0, 6.7, 1.0 Hz, 1 H), 7.19 (d, $J$ = 7.9 Hz, 2 H), 7.27–7.34 (m, 1 H), 7.36–7.45 (m, 3 H), 7.46–7.55 (m, 3 H), 7.82–8.00 (m, 5 H), 8.39–8.44 (m, 1 H),
8.46–8.50 (m, 1 H), 9.81 (d, J = 8.9 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 13.8, 21.7, 37.7, 87.8, 100.1, 107.9, 110.7, 118.5, 118.8, 120.9, 121.6, 123.4, 123.9, 124.7, 125.5, 125.6, 128.2, 128.4, 129.0, 129.2, 129.3, 129.6, 130.0, 130.1, 131.7, 131.9, 138.4, 139.5, 141.5, 141.8, 142.2, 142.4, 142.5, 142.6, 146.3 ppm. HRMS (ESI): MH⁺, found 538.2265. C₃₀H₂₈N₃ requires 538.2278.

7-Ethyl-12-phenyl-13-(p-tolylethynyl)-7H-quinoxalino[5,6-c]carbazole (9b): A stirred mixture of 7-ethyl-13-iodo-12-phenyl-7H-quinoxalino[5,6-c]carbazole 7b (50 mg, 0.1 mmol), PdCl₂(PPh₃)₂ (7 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), Et₃N (3 mL) was heated at 85 °C for 20 min under argon. A solution of p-tolylacetylene (23 mg, 0.2 mmol) in Et₃N (1.6 mL) was then dropped for 3 h. The reaction mixture was stirred at 85 °C for total 24 h followed by evaporation. The residue was then diluted with H₂O (50 mL) and extracted with CHCl₃ (3 × 10 mL). The extract was dried over Na₂SO₄. Flash column chromatography on silica gel (2 × 20 cm) was carried out using a mixture of ethyl acetate - petroleum ether (1:3, v/v) as the eluent. Compound 9b (40 mg, 82%) was isolated from the yellow fraction with Rf 0.3 (yellow-green fluorescence under UV 356 nm). Compound 9b was synthesized as yellow plates with green fluorescence in the solid state under UV (356 nm) and mp 152–154 °C (hexane). ¹H NMR (250 MHz, CDCl₃): δ = 1.54 (t, J = 7.2 Hz, 3 H), 2.38 (s, 3 H), 4.57 (q, J = 7.2 Hz, 2 H), 6.28 (d, J = 8.5 Hz, 1 H), 6.69 (ddd, J = 8.1, 7.3, 0.8 Hz, 1 H), 7.14 (d, J = 7.9 Hz, 2 H), 7.28–7.36 (m, 3 H), 7.42–7.53 (m, 4 H), 7.78–7.82 (m, 2 H), 7.99 (d, J = 9.0 Hz, 1 H), 9.03 (dd, J = 4.1, 1.9 Hz, 2 H), 9.59 (d, J = 9.0 Hz, 1 H) ppm. ¹³C NMR (62.9 MHz, CDCl₃): δ = 14.0, 21.6, 37.8, 88.5, 101.2, 108.0, 111.6, 117.3, 118.9, 120.3, 121.4, 123.1, 123.3, 124.6, 125.4, 125.7, 128.4, 128.6, 129.0, 129.6, 131.9, 132.0, 138.9, 139.2, 140.6, 141.4, 141.6, 141.9, 143.4, 144.0, 145.6 ppm. HRMS (ESI): MH⁺, found 488.2099. C₃₅H₂₆N₃ requires 488.2121. M+Na⁺, found 510.1916. C₃₅H₂₅N₃Na requires 510.1946.

7-Ethyl-12-phenyl-13-(p-tolylethynyl)-7H-quinolino[8,7-c]carbazole (9c): Compound 9c was obtained similarly to 9a starting from 7c (50 mg, 0.1 mmol). The reaction was carried out at 80–82 °C. Flash column chromatography was carried out on silica gel (3.5 × 45 cm) with CH₂Cl₂ as the eluent. The yellow fraction with Rf 0.6 and light blue fluorescence under UV (356 nm) gave compound 9c (43 mg, 88%) as yellow prisms (CH₂Cl₂) with mp 210–212 °C (EtOH). ¹H NMR (250 MHz, CDCl₃): δ = 1.53 (t, J = 7.2 Hz, 3 H), 2.40 (s, 3 H), 4.56 (q, J = 7.2 Hz, 2 H), 6.36 (d, J = 8.3 Hz, 1 H), 6.68
(ddd, J = 8.3, 7.0, 1.1 Hz, 1 H), 7.18 (d, J = 7.9 Hz, 2 H), 7.25–7.35 (m, 3 H), 7.42 (d, J = 8.1 Hz, 1 H), 7.46–7.52 (m, 3 H), 7.63 (dd, J = 8.2, 4.4 Hz, 1 H), 7.77–7.81 (m, 2 H), 7.96 (d, J = 9.1 Hz, 1 H), 9.10 (dd, J = 4.4, 1.7 Hz, 1 H), 9.74 (d, J = 9.1 Hz, 1 H) ppm. 

$^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ = 13.9, 21.6, 37.7, 87.6, 99.1, 107.9, 111.0, 117.1, 118.6, 119.8, 120.4, 121.0, 123.5, 123.6, 124.1, 124.5 (2C), 125.4, 128.0, 128.2, 129.2, 131.3, 132.1, 135.6, 138.6 (2C), 139.2, 141.3, 141.4, 142.2, 148.7 ppm. HRMS (ESI): MH$^+$, found 487.2180. C$_{36}$H$_{27}$N$_2$ requires 487.2174.

8-Ethyl-17-$p$-tolyl-8$H$-carbazolo[3,4-a]naphtho[1,2-c]phenazine (10a) was synthesized in a similar manner as described in [1, compound 14c]. To a solution of compound 9a (54 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 mL) CF$_3$SO$_3$H (0.1 mL) was added. The dark red reaction mixture was kept at room temperature for 24 h in the dark. Then it was mixed with saturated aqueous K$_2$CO$_3$ (50 mL) and separated in a separating funnel. The yellow CH$_2$Cl$_2$ phase was dried over Na$_2$SO$_4$ and purified by flash column chromatography on silica gel (2 $\times$ 50 cm) with CH$_2$Cl$_2$ as the eluent. The bright yellow fraction with $R_f$ 0.9 gave the cyclization product (50 mg, 92%). Compound 10a was obtained as a yellow orange solid with mp 294–295 °C. 

$^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.61 (t, J = 7.2 Hz, 3 H), 2.58 (s, 3 H), 4.62 (q, J = 7.2 Hz, 2 H), 6.71 (d, J = 8.1 Hz, 1 H), 6.81 (t, J = 7.4 Hz, 1 H), 7.18 (d, J = 7.8 Hz, 1 H), 7.39 (d, J = 7.6 Hz, 1 H), 7.46–7.52 (m, 4 H), 7.77 (d, J = 7.8 Hz, 2 H), 7.81–7.90 (m, 2 H), 7.94 (d, J = 8.9 Hz, 1 H), 8.20 (d, J = 8.3 Hz, 1 H), 8.32–8.39 (m, 3 H), 9.48 (s, 1 H), 9.66 (d, J = 8.9 Hz, 1 H) ppm. $^{13}$C NMR (62.9 MHz, CDCl$_3$): $\delta$ = 14.0, 21.4, 37.9, 108.2, 109.6, 118.0, 120.2, 122.7, 123.4, 123.8, 124.9, 125.3, 125.4, 125.7, 126.4, 126.9, 127.1, 128.8, 129.0, 129.1, 129.2 (2C), 129.4, 129.5, 129.6, 130.3, 130.7, 132.4, 137.3, 137.8, 140.0, 140.7, 141.7, 141.8, 141.9, 142.2, 143.8 ppm. UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ nm (lg $\varepsilon$): 264 (4.75), 303 (4.72), sh 324 (4.59), 357 (4.36), 374 (4.46), 433 (4.23), end absorption up to 507 nm. HRMS (ESI): MH$^+$, found 538.2285. C$_{39}$H$_{28}$N$_3$ requires 538.2278.

7-Ethyl-16-$p$-tolyl-7$H$-naphtho[1',2';7,8]quinoxalino[5,6-c]carbazole (10b): Compound 10b was obtained similarly to 10a starting from 7-ethyl-12-phenyl-13-(p-tolylethynyl)-7$H$-quinoxalino[5,6-c]carbazole 9b (49 mg, 0.1 mmol). Flash column chromatography was carried out on silica gel (2 $\times$ 40 cm) with CH$_2$Cl$_2$ as the eluent. The yellow fraction with $R_f$ 0.3 gave the cyclization product 10b (40 mg, 82%) as a yellow orange solid with mp 225–227 °C (hexane). 

$^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.61 (t, J = 7.2 Hz, 3 H), 2.56 (s, 3 H), 4.63 (q, J = 7.2 Hz, 2 H), 6.73 (d, J = 7.9 Hz, 1 H), 6.80–
6.86 (m, 1 H), 7.18 (dd, J = 8.1, 7.2, 0.9 Hz, 1 H), 7.37–7.55 (m, 5 H), 7.76 (d, J = 7.9 Hz, 2 H), 7.98 (d, J = 8.9 Hz, 1 H), 8.21 (d, J = 8.2 Hz, 1 H), 8.37 (d, J = 8.4 Hz, 1 H), 8.90 (d, J = 2.0 Hz, 1 H), 8.94 (d, J = 2.0 Hz, 1 H), 9.30 (s, 1 H), 9.50 (d, J = 8.9 Hz, 1 H) ppm. \(^{13}\)C NMR (62.9 MHz, CDCl\(_3\)): \(\delta = 14.0, 21.4, 37.9, 108.3, 110.1, 118.0, 119.5, 122.8, 123.4, 124.6, 125.1, 125.4, 125.7, 126.2, 126.4, 126.7, 127.6, 128.9, 129.0, 129.1, 130.3, 130.7, 131.2, 137.2, 137.7, 139.2, 140.1, 140.6, 141.3, 142.1, 142.7, 143.2 ppm.

UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{\text{max}}\) (lg \(\varepsilon\)): 294 (4.57), 323 (4.54), 359 (4.35), 397 (4.03), 418 nm (3.96). HRMS (ESI): MH\(^+\), found 488.2120. C\(_{35}\)H\(_{26}\)N\(_3\) requires 488.2121. M+Na\(^+\), found 510.1929. C\(_{35}\)H\(_{25}\)N\(_3\)Na requires 510.1946.

7-Ethyl-16-p-tolyl-7H-naphtho[2',1';5,6]quinolino[8,7-c]carbazole (10c) was synthesized in a similar manner as described in [1, compound 14a]. A dark solution of 7-ethyl-12-phenyl-13-(p-tolylethynyl)-7H-quinolino[8,7-c]carbazole 9c (49 mg, 0.1 mmol) in CF\(_3\)COOH (3 mL) was heated at 85 °C for 24 h. The reaction mixture was evaporated to dryness, treated with saturated K\(_2\)CO\(_3\) (2 mL) and CH\(_2\)Cl\(_2\) (20 mL), extracted in a separating funnel and separated. The organic phase was dried over Na\(_2\)SO\(_4\) and purified by flash column chromatography on silica gel (2.5 × 30 cm) with CH\(_2\)Cl\(_2\) as the eluent. The yellow fraction with \(R_f\) 0.5 gave cyclization product 10c (46 mg, 94 %). Compound 10c was obtained as a yellow orange solid with mp 223–225 °C (EtOH). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 1.60 (t, J = 7.2 Hz, 3 H), 2.57 (s, 3 H), 4.62 (q, J = 7.2 Hz, 2 H), 6.68 (d, J = 7.9 Hz, 1 H), 6.80 (ddd, J = 7.9, 7.0, 0.8 Hz, 1 H), 7.16 (ddd, J = 8.2, 7.1, 1.1 Hz, 1 H), 7.38 (ddd, J = 8.0, 7.0, 1.1 Hz, 1 H), 7.46–7.58 (m, 5 H), 7.73 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.9 Hz, 1 H), 8.14 (d, J = 8.0 Hz, 1 H), 8.37 (d, J = 8.2 Hz, 1 H), 8.61 (s, 1 H), 8.96 (dd, J = 8.4, 1.4 Hz, 1 H), 9.03 (dd, J = 4.4, 1.5 Hz, 1 H), 9.61 (d, J = 8.9 Hz, 1 H) ppm. \(^{13}\)C NMR (62.9 MHz, CDCl\(_3\)): \(\delta = 14.1, 21.4, 37.9, 108.2, 109.8, 117.7, 119.3, 120.7, 120.8, 123.0, 123.3, 123.5, 124.7, 125.1, 125.7, 125.8, 125.9, 126.0, 126.1, 126.2, 127.4, 129.2, 129.3, 130.2, 130.7, 130.9, 131.1, 137.4, 137.9, 139.6, 140.2, 140.8, 147.7, 148.8 ppm. UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{\text{max}}\) (lg \(\varepsilon\)): 265 (4.63), 285 (4.53), sh 306 (4.48), 324 (4.56), 371 (4.08), sh 388 (3.96), 411 nm (3.79). HRMS (ESI): MH\(^+\) found 487.2175. C\(_{36}\)H\(_{27}\)N\(_2\) requires 487.2169.
Figure S1. $^1$H NMR spectrum of 2a (CDCl$_3$, 250 MHz)
Figure S2. $^{13}$C NMR APT spectrum of 2a (CDCl$_3$, 62.9 MHz)
Figure S3. $^1$H NMR spectrum of 2b (CDCl$_3$, 250 MHz)
Figure S4. $^{13}$C NMR APT spectrum of 2b (CDCl$_3$, 62.9 MHz)
Figure S5. $^1$H NMR spectrum of 4a (CDCl$_3$, 250 MHz)
Figure S6. $^{13}$C NMR APT spectrum of 4a (CDCl$_3$, 62.9 MHz)
Figure S7. $^1$H NMR spectrum of 4b (CDCl$_3$, 250 MHz)
Figure S8. $^{13}$C NMR APT spectrum of 4b (CDCl$_3$, 62.9 MHz)
Figure S9. $^1$H NMR spectrum of 5b (CDCl$_3$, 250 MHz)
Figure S10. $^{13}$C NMR APT spectrum of 5b (CDCl$_3$, 62.9 MHz)
Figure S11. $^1$H NMR spectrum of 6 (CDCl$_3$, 250 MHz)
Figure S12. $^{13}$C NMR APT spectrum of 6 (CDCl$_3$, 62.9 MHz)
Figure S13. $^1$H NMR spectrum of the mixture 7a and 8a (CDCl$_3$, 250 MHz)
Figure S14. \(^1\)H NMR spectrum of 7a (CDCl\(_3\), 250 MHz)
Figure S15. $^{13}$C NMR APT spectrum of 7a (CDCl$_3$, 62.9 MHz)
Figure S16. $^1$H NMR spectrum of 7b (CDCl$_3$, 250 MHz)
Figure S17. $^{13}$C NMR APT spectrum of 7b (CDCl$_3$, 62.9 MHz)
Figure S18. $^1$H NMR spectrum of 7c (CDCl$_3$, 250 MHz)
Figure S19. $^{13}$C NMR APT spectrum of 7c (CDCl$_3$, 62.9 MHz)
Figure S20. $^1$H NMR spectrum of 8b (CDCl$_3$, 250 MHz)
Figure S21. $^{13}$C NMR APT spectrum of 8b (CDCl$_3$, 62.9 MHz)
Figure S22. $^1$H NMR spectrum of 9a (CDCl$_3$, 250 MHz)
Figure S23. $^{13}$C NMR APT spectrum of 9a (CDCl$_3$, 62.9 MHz)
Figure S24. $^1$H NMR spectrum of 9b (CDCl$_3$, 250 MHz)
Figure S25. $^{13}$C NMR APT spectrum of 9b (CDCl$_3$, 62.9 MHz)
Figure S26. $^1$H NMR spectrum of 9c (CDCl$_3$, 250 MHz)
Figure S27. $^{13}$C NMR APT spectrum of 9c (CDCl$_3$, 62.9 MHz)
Figure S28. $^1$H NMR spectrum of 10a (CDCl$_3$, 250 MHz)
Figure S29. $^{13}$C NMR APT spectrum of 10a (CDCl$_3$, 62.9 MHz)
Figure S30. $^1$H NMR spectrum of 10b (CDCl$_3$, 250 MHz)
Figure S31. $^{13}$C NMR APT spectrum of 10b (CDCl$_3$, 62.9 MHz)
Figure S32. $^1$H NMR spectrum of 10c (CDCl$_3$, 250 MHz)
Figure S33. $^{13}$C NMR APT spectrum of 10c (CDCl$_3$, 62.9 MHz)
Crystal structure determination: X-ray measurements were conducted with Bruker APEX II CCD diffractometer and four-circle diffractometer SuperNova, Single source at offset/far, HyPix3000. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2034941 (9c), CCDC 2034943 (10a), CCDC 2034944 (10b), and CCDC 2034945 (10c). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S34. Molecular structure of compound 9c showing 50% probability amplitude displacement ellipsoids.

Figure S35. Molecular structure of compound 10a showing 50% probability amplitude displacement ellipsoids.
Figure S36. Molecular structure of compound 10b showing 50% probability amplitude displacement ellipsoids (one of two independent molecules).

Figure S37. Molecular structure of compound 10c showing 50% probability amplitude displacement ellipsoids (one of two independent molecules).
### Table S1. Crystal data and structure refinement for compounds 9c and 10a-c

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The HPLC separations were performed at 25 °C using Agilent 1200 equipment on the column Kromasil 5-Cellucoat (4.6 mm × 250 mm, particle size 5 µm), photodiode array detector; mobile phase is CH$_3$CN of HPLC grade; injection of 5 µL of analyte solution in CH$_3$CN; nominal flow rate is 0.8 mL min$^{-1}$; UV detection at fixed wavelength 300 nm (for 10a) and 320 nm (for 10b,c).
Figure S38. Chromatogram (UV-detection) of $(P,M)$-10a on Kromasil 5-Cellucoat
(mobile phase CH$_3$CN)
**Figure S39.** Chromatogram (UV-detection) of (P,M)-10b on Kromasil 5-Cellucoat (mobile phase CH₃CN)
Figure S40. Chromatogram (UV-detection) of (P,M)-10c on Kromasil 5-Cellucoat
(mobile phase CH$_3$CN)
**Figure S41:** UV–vis spectra of [6]helicene 10b in different solvents.

**Figure S42:** Solutions of [6]helicenes 10 in different solvents under UV irradiation (365 nm).
Figure S43: Normalized absorption and fluorescence spectra of 10a in acetonitrile.

Figure S44: Normalized absorption and fluorescence spectra of 10b in acetonitrile.

Figure S45: Normalized absorption and fluorescence spectra of 10c in acetonitrile.
References