TIPS-Ethynylated Naphthodiquinoline and Naphthodiacridine: Novel Diazabisacenes

Lukas Ahrens, Steffen Maier, Erik Misselwitz, Thomas Oeser, Frank Rominger, Jan Freudenberg,* and Uwe H. F. Bunz*
Sections

S1. General remarks.................................................................S2
S2. Synthesis.................................................................S5
S3. Synthetic attempts towards tetraazabistetracene............................S15
S4. UV-Vis spectra.............................................................S17
S5. UV-Vis absorption stability study..............................................S18
S6. Electrochemistry/cyclovoltammetry...........................................S21
S7. Quantum-chemical calculations.................................................S23
S8. NMR spectra.................................................................S28
S9. X-ray single-crystal structure analysis.......................................S37
S1. General Remarks

Reagents and solvents for synthesis
All reagents were obtained from commercial suppliers and were used without further purification if not otherwise stated. Deuterated solvents were purchased from Merck KGaA (Darmstadt, Germany). All reactions requiring exclusion of oxygen and moisture were carried out in heat-gun dried glassware under a dry and oxygen free nitrogen or argon atmosphere using Schlenk and glovebox techniques.

Column chromatography
Column chromatography was performed using silica gel from Macherey, Nagel & Co. KG (Düren, Germany) (particle size: 0.040 - 0.063 mm). For TLC Polygram Sil G/UV 254 plates from Macherey, Nagel & Co. KG (Düren, Germany) were used and examined under UV-light irradiation (254 nm and 365 nm). Before column chromatography the crude product was mixed with Celite 545 and DCM to make a slurry. The solvent was removed by rotary evaporation to get a dry powder.

$^1$H-NMR spectra and $^{13}$C-NMR spectra
All spectra were recorded at room temperature on a Bruker Avance Neo 700 ($^1$H: 700 MHz, $^{13}$C: 176 MHz), Bruker Avance III 600 ($^1$H: 600 MHz, $^{13}$C: 151 MHz), Bruker Avance III 500 ($^1$H: 500 MHz, $^{13}$C: 125 MHz) or Bruker Avance III 400 ($^1$H: 400 MHz, $^{13}$C: 101 MHz). $^{13}$C-NMR spectra were measured proton decoupled if not stated otherwise. NMR spectra were integrated and processed using the Software TopSpin 3.5pl5 (Bruker). For calibration the residual solvent peaks were referenced. Chemical shifts $\delta$ are reported in ppm and coupling constants $J$ in Hz. The following abbreviations describe the observed multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

IR spectra
All spectra were recorded neat at room temperature on a Jasco FT/IR-4100. Signals are reported in wavenumbers [cm$^{-1}$].

Mass spectrometry
The mass spectra were recorded using the following instruments: Bruker ApexQe hybrid 9.4 T FT-ICR (MALDI, ESI); Bruker AutoFlex Speed time-of-flight (MALDI).
**Melting points**
Melting points were determined in open glass capillaries with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK).

**Cyclic voltammetry**
The cyclic voltammetry (CV) experiments were carried out using PGSTAT101 Potentiostat Galvanostat with a platinum working electrode (Metrohm 6.120.4190, diameter 1 mm), a platinum wire auxiliary electrode (Metrohm 3.109.0790), a silver wire reference electrode (Metrohm 6.1241.060), a 0.1 mol L⁻¹ NBu₄PF₆ solution in degassed, dry DCM, and ferrocene/ferrocenium as the reference redox system and internal standard (−5.1 eV) at room temperature and 0.2 V s⁻¹. To determine the reduction and oxidation potentials, the half-wave potentials were used.[⁵²]

**X-ray single-crystal structure analysis**
X-ray single-crystal structure analyses were measured on a Bruker Smart APEX-II Quazar Area Detector diffractometer by Dr. F. Rominger (Heidelberg University). Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F² with the full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL software package.

**Differential scanning calorimetry**
Differential scanning calorimetry measurements were carried out on a Mettler-Toledo TGA/DSC1 instrument with a TGA/DSC-Sensor 1100 equipped with a MX1 balance (Mettler-Toledo) and a GC100 gas control box for nitrogen supply.

**UV-Vis and fluorescence spectroscopy**
Absorption spectra were recorded on a Jasco UV-Vis V-670. Fluorescence spectra were recorded on a Jasco FP-6500.

**Quantum yields**
Quantum yields were determined by an Ulbricht sphere (6 inch) using a PTI QuantaMaster 40 equipped with a Hamamatsu R928P Photomultiplier.
Quantum lifetimes
Quantum lifetimes were determined on a Horiba FluoroCube-01-NL lifetime spectrofluorometer with emission monochromator (Seya-Namioka type, 200 nm to 800 nm) and diode excitation (Nano-LED N-375L, 375 ± 10 nm, < 200 ps).

Camera
The photos were taken by a Canon EOS 7D under daylight or UV-light irradiation (λ = 365 nm).

Computational studies
All calculations were performed using Gaussian 16.\textsuperscript{[S3]} TMS groups were used instead of TIPS groups to simplify calculations. First, the gas-phase ground-state equilibrium geometry of the molecules was optimized at the B3LYP/def2-SVP level of theory. Afterwards, the received geometries were refined using the B3LYP/def2-TZVP level of theory. FMO calculations were performed starting from the optimized geometries on the B3LYP/def2-TZVP level of theory. NICS(1)-values were calculated using the GIAO-method at the B3LYP/def2TZVP level of theory. ACID-plots were calculated using AICD-3.0.3 using the CSGT-method at the B3LYP/def2-TZVP IOP(10/93=1) level of theory; isovalue: 0.02; optimization limit: 0.02; maximal arrow length: 1; magnetic field vector is oriented out of plane.\textsuperscript{[S4]} The first fifty vertical singlet transition energies were calculated by time-dependant DFT (TD-DFT) at the CCAM-B3LYP/def2-SVP level of theory.
**S2. Synthesis**

$2,2'$-(Naphthalene-1,5-diy1)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**),[[55]](footnote) ethyl 2-bromoquinoline-3-carboxylate (**2b**),[[56]](footnote) ethyl 3-bromoquinoxaline-2-carboxylate (**S1**)[[57]](footnote) and benzo[g]quinoline-5,10-dione (**7**)[[58]](footnote) were synthesized according to literature procedures.

Diethyl $2,2'$-(naphthalene-1,5-diy1)di(pyridine-3-carboxylate) (**3a**)

In a heatgun dried Schlenk tube under an atmosphere of argon was added ethyl 2-bromopyridine-3-carboxylate (**2a**) (1.14 g, 4.97 mmol, 2.10 equiv.), $2,2'$-(naphthalene-1,5-diy1)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**1**)(900 mg, 2.37 mmol, 1.00 equiv.) and Pd(PPh$_3$)$_4$ (274 mg, 237 µmol, 0.10 equiv.). Then degassed THF (30 mL) and aqueous potassium carbonate solution (10 mL, 2.00 mol L$^{-1}$) were added, and the reaction mixture stirred at 80 °C for 72 h. The mixture was cooled to room temperature. The phases were separated, and the aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic phases were washed with brine (10 mL), dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/ethyl acetate 4:1 v/v -> 2:1 -> 1:1) the coupling product **3a** was isolated as colorless solid (290 mg, 1.85 µmol, 78%).

$R_f = 0.05$ (SiO$_2$; petroleum ether/ethyl acetate 2:1, v/v).

**M$\text{p}$:** 220 °C.

$^1$H NMR (CDCl$_3$, 600 MHz, rt): $\delta = 8.90$ (dd, $J = 4.94$ Hz, $J = 1.75$ Hz, 2H), 8.32 (dd, $J = 7.99$ Hz, $J = 1.75$ Hz, 2H), 7.60 (dd, $J = 7.33$ Hz, $J = 1.62$ Hz, 2H), 7.43 - 7.50 (m, 6H), 3.84 (bs, 4H), 0.70 (bs, 6H) ppm.

$^{13}$C{$^1$H} NMR (CDCl$_3$, 151 MHz, rt): $\delta = 166.9, 159.0, 151.9, 139.1, 138.2, 131.7, 128.9, 126.4, 125.7, 125.7, 122.3, 61.4, 13.5$ ppm.

IR (ATR): $\tilde{\nu} = 2978, 1702, 1699, 1302, 1138, 1016, 794, 778, 542$ cm$^{-1}$.

HRMS (El$^+$) m/z: [M+2H]$^+$: calcd. for [C$_{26}$H$_{22}$N$_2$O$_4$]$^+$: 426.1574; found 426.1561; correct isotope distribution.
Diethyl 2,2′-(naphthalene-1,5-diyl)di(quinoline-3-carboxylate) (3b)

\[
\begin{align*}
\text{O} & \quad \text{Et} \quad \text{Br} \\
2b & \quad \text{Bpin} \\
\text{Pd(PPh}_3\text{)}_4 & \quad \text{THF/H}_2\text{O} \\
\text{K}_2\text{CO}_3 & \quad \text{3b}
\end{align*}
\]

In a heatgun dried Schlenk tube under an atmosphere of argon was added ethyl 2-bromoquinoline-3-carboxylate (2b) (100 mg, 356 μmol, 2.20 equiv.), 2,2′-(naphthalene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1) (61.7 mg, 162 μmol, 1.00 equiv.) and Pd(PPh\(_3\))\(_4\) (18.7 mg, 16.2 μmol, 0.10 equiv.). Then degassed THF (10 mL) and aqueous potassium carbonate solution (6 mL, 2.00 mol L\(^{-1}\)) were added, and the reaction mixture stirred at 80 °C for 72 h. The mixture was cooled to room temperature. The phases were separated, and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (10 mL), dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite\(^\circledR\). After flash column chromatography (petroleum ether/ethyl acetate 6:1 v/v) the coupling product 3b was isolated as colorless solid (68.0 mg, 162 μmol, 80%).

\[R_f = 0.27 \quad \text{(SiO}_2; \text{petroleum ether/ethyl acetate 2:1, v/v).}\]

\[\text{Mp:} \geq 234 \degree\text{C (decomposition).}\]

\(^1\text{H NMR}\) (CDCl\(_3\), 600 MHz, rt): \(\delta = 8.88 \quad \text{(s, 2H)}, 8.24 \quad \text{(d, } J = 8.31 \text{ Hz, 2H}), 8.03 \quad \text{(d, } J = 8.15 \text{ Hz, 2H)}, 7.85 - 7.90 \quad \text{(m, 2H)}, 7.66 - 7.70 \quad \text{(m, 2H)}, 7.62 \quad \text{(d, } J = 8.51 \text{ Hz, 2H}), 7.56 \quad \text{(d, } J = 6.76 \text{ Hz, 2H)}, 7.47 \quad \text{(dd, } J = 8.51 \text{ Hz, } J = 6.76 \text{ Hz, 2H)}, 3.94 \quad \text{(bs, 4H)}, 0.84 \quad \text{(bs, 6H)} \text{ ppm.}\)

\(^{13}\text{C}\left(^{1}\text{H}\right) \text{NMR}\) (CDCl\(_3\), 151 MHz, rt): \(\delta = 166.8, 158.3, 148.8, 139.5, 139.5, 132.0, 131.9, 129.8, 128.6, 127.7, 126.7, 126.5, 126.4, 125.8, 125.7, 61.5, 13.7 \text{ ppm.}\)

\(\text{IR (ATR)}: \tilde{\nu} = 3058, 2925, 1694, 1588, 1370, 1317, 1252, 1240, 782, 759 \text{ cm}^{-1}\).

\(\text{HRMS \quad (MALDI):} \quad m/z: [M+H]^+: \text{ calcd. for } [\text{C}_{34}\text{H}_{27}\text{N}_{2}\text{O}_{4}]^+: 527.1971; \text{ found 527.1975; correct isotope distribution.}\)
Diethyl 3,3’-(naphthalene-1,5-diyl)di(quinoxaline-2-carboxylate) (S2)

In a heatgun dried Schlenk tube under an atmosphere of argon was added ethyl 3-bromoquinoxaline-2-carboxylate (S1) (1.63 g, 5.79 mmol, 2.20 equiv.), 2,2’-(naphthalene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1) (1.00 g, 2.63 mmol, 1.00 equiv.) and Pd(PPh₃)₄ (152 mg, 132 μmol, 0.05 equiv.). Then degassed THF (100 mL) and aqueous potassium carbonate solution (60 mL, 2.00 mol L⁻¹) were added, and the reaction mixture stirred at 80 °C for 24 h. The mixture was cooled to room temperature. THF was removed in vacuo, the aqueous residue was neutralized with 6 N HCl and extracted with DCM. The combined organic phases were dried over magnesium sulfate and filtrated. After flash column chromatography (petroleum ether/ethyl acetate 7:3 v/v -> 1:1) the coupling product S2 was isolated as beige solid (853 mg, 1.61 mmol, 61%).

Mp: 231 °C.

¹H NMR (CDCl₃, 500 MHz, rt): δ = 8.33 - 8.37 (m, 2H), 8.23 - 8.28 (m, 2H), 7.90 - 7.97 (m, 4H), 7.81 (d, J = 8.64 Hz, 2H), 7.65 (d, J = 6.81 Hz, 2H), 7.54 - 7.58 (m, 2H), 4.08 (q, J = 7.33 Hz, 4H), 0.93 (t, J = 7.33 Hz, 6H) ppm.

¹³C{¹H} NMR (CDCl₃, 125 MHz, rt): δ = 165.6, 152.8, 146.7, 142.6, 140.5, 136.5, 132.2, 131.9, 131.1, 130.1, 129.7, 127.8, 126.7, 126.2, 62.3, 13.8 ppm.

IR (ATR): v = 3437, 2981, 1730, 1548, 1480, 1466, 1369, 1321, 1264, 1224, 1182, 1171, 1159, 1132, 1105, 1068, 1049, 1037, 1026, 1012, 853, 798, 768, 722, 683, 678, 587, 574, 557, 542, 466, 458, 450, 436, 419 cm⁻¹.

HRMS (MALDI⁺) m/z: [M+H]⁺: calcd. for [C₃₂H₂₅N₄O₄]⁺: 529.1870; found 529.1881; correct isotope distribution.
2,2’-(Naphthalene-1,5-diyl)di(pyridine-3-carboxylic acid) (4a)

In a flask was dissolved 3a (200 g, 469 µmol, 1.00 equiv.) in 80 mL THF and 8 mL MeOH and potassium hydroxide (158 mg, 2.81 mmol, 6.00 equiv.) was added. After heating the reaction mixture to reflux for 4 h, the formed precipitate was filtered off and washed with methanol/tetrahydrofuran (1:1 v/v) to yield the product 4a (172 mg, 464 mmol, 99%) as a colorless solid which was used without further purification for the next step.

\[ \text{Mp: } \geq 350 \degree \text{C.} \]

\( ^1H \text{NMR} \) (DMSO-\( d_6 \), 700 MHz, rt): \( \delta = 8.52 \) (d, \( J = 4.12 \) Hz, 2H), 7.98 (d, \( J = 7.81 \) Hz, 2H), 7.49 (d, \( J = 8.24 \) Hz, 2H), 7.30 - 7.37 (m, 4H), 7.26 - 7.29 (m, 2H) ppm.

\( ^{13}C\{^1H\} \text{NMR} \) (DMSO-\( d_6 \), 176 MHz, rt): \( \delta = 169.3, 156.1, 146.9, 140.9, 139.8, 136.0, 131.0, 125.3, 125.1, 124.4, 121.8 \) ppm.

IR (ATR): \( \tilde{\nu} = 2995, 2946, 1726, 1563, 1273, 1077, 793, 735 \) cm\(^{-1} \).

HRMS (ESI\(^+\)) \( m/z \): [M-H]: calcd. for [C\(_{22}\)H\(_{13}\)N\(_2\)O\(_4\)]: 369.0881; found 369.0875; correct isotope distribution.

2,2’-(Naphthalene-1,5-diyl)di(quinoline-3-carboxylic acid) (4b)

In a flask was dissolved 3b (500 g, 950 µmol, 1.00 equiv.) in 100 mL THF and 10 mL MeOH and potassium hydroxide (320 mg, 5.70 mmol, 6.00 equiv.) was added. After heating the reaction mixture to reflux for 4 h, the formed precipitate was filtered off and washed with methanol/tetrahydrofuran (1:1 v/v) to yield the product 4b (435 mg, 925 mmol, 97%) as a grey solid which was used without further purification for the next step.

\[ \text{Mp: } \geq 350 \degree \text{C.} \]
$^1$H NMR (DMSO-d$_6$, 700 MHz, rt): $\delta$ = 8.52 (s, 2H), 8.07 (d, $J$ = 8.14 Hz, 2H), 7.98 (d, $J$ = 8.32 Hz, 2H), 7.73 (t, $J$ = 7.43 Hz, 2H), 7.61 (t, $J$ = 7.43 Hz, 2H), 7.56 (d, $J$ = 8.32 Hz, 2H), 7.33 - 7.41 (m, 4H) ppm.

$^{13}$C{$^1$H} NMR (DMSO-d$_6$, 176 MHz, rt): $\delta$ = 169.1, 158.6, 146.2, 141.2, 138.4, 134.6, 131.1, 129.0, 128.6, 128.0, 127.1, 126.2, 125.3, 125.2, 124.5 ppm.

IR (ATR): $\tilde{\nu}$ = 3038, 2993, 2947, 1724, 1438, 1266, 1226, 1198, 1118, 1053, 1029, 799, 761, 477 cm$^{-1}$.

HRMS (ESI$^-$) m/z: [M-H] - : calcd. for [C$_{30}$H$_{17}$N$_2$O$_4$]: 469.1194; found 469.1192; correct isotope distribution.

3,3’-(Naphthalene-1,5-diyl)di(quinoxaline-2-carboxylic acid) (S3)

In a flask was dissolved S2 (1.00 g, 1.89 mmol, 1.00 equiv.) in 150 mL THF and 30 mL MeOH and potassium hydroxide (2.00 g, 35.7 mmol, 18.8 equiv.) was added. After heating the reaction mixture to reflux for 4 h, the formed precipitate was filtered off and washed with methanol to yield the product S3 (886 mg, 1.88 mmol, 99%) as a yellow solid which was used without further purification for the next step.

Mp: >70 °C (decomposition).

$^1$H NMR (DMSO-d$_6$, 600 MHz, rt): $\delta$ = 13.80 (bs, 2H), 8.30 - 8.34 (m, 2H), 8.23 - 8.26 (m, 2H), 8.02-8.07 (m, 4H), 7.79 (d, $J$ = 8.66 Hz, 2H), 7.66 (dd, $J$ = 6.87 Hz, $J$ = 0.96 Hz, 2H), 7.60 (dd, $J$ = 8.66 Hz, $J$ = 6.87 Hz, 2H) ppm.

$^{13}$C{$^1$H} NMR (DMSO-d$_6$, 151 MHz, rt): $\delta$ = 166.7, 151.9, 147.5, 141.4, 139.6, 135.9, 132.1, 131.4, 131.2, 129.3, 129.2, 127.4, 126.7, 125.9 ppm.

IR (ATR): $\tilde{\nu}$ = 3057, 2921, 2852, 1725, 1543, 1466, 1338, 1214, 1187, 1115, 789, 759 cm$^{-1}$.

HRMS (ESI$^-$) m/z: [M-H] - : calcd. for [C$_{28}$H$_{15}$N$_4$O$_4$]: 471.1099; found 471.1103; correct isotope distribution.
Naphtho[1,8-\textit{gh}:5,4-\textit{h}']diquinoline-7,14-dione (5a)

![Chemical structure of Naphtho[1,8-\textit{gh}:5,4-\textit{h}']diquinoline-7,14-dione (5a)](image)

In a Schlenk tube under an atmosphere of argon was suspended 4a (170 mg, 459 \(\mu\)mol, 1.00 equiv.) in polyphosphoric acid (5 mL) and stirred at 170 °C for 18 h. Upon cooling to room temperature, the reaction mixture was quenched with an ice-water mixture and brought to pH 10 with an aqueous NaOH-solution (2M, 30 mL). The precipitate was filtered, washed with water (100 mL) and methanol (50 mL) to yield product 5a as a black solid (97.7 mg, 292 \(\mu\)mol, 64%), which was used without further purification for the next step.

\textbf{Mp:} ≥350 °C.

\textbf{HRMS (ESI\textsuperscript{+}) \(m/z\): [M+H]\textsuperscript{+}:} calcd. for \([C_{22}H_{11}N_{2}O_{2}]^{+}\): 335.0815; found 335.0812; correct isotope distribution.

Naphtho[1,8-\textit{bc}:5,4-\textit{b'}c']diacridine-8,17-dione (5b)

![Chemical structure of Naphtho[1,8-\textit{bc}:5,4-\textit{b'}c']diacridine-8,17-dione (5b)](image)

In a Schlenk tube under an atmosphere of argon was suspended 4b (200 mg, 425 mmol, 1.00 equiv.) in polyphosphoric acid (5 mL) and stirred at 140 °C for 3 d. Upon cooling to room temperature, the reaction mixture was quenched with an ice-water mixture and brought to pH 10 with an aqueous NaOH-solution (2M, 30 mL). The precipitate was filtered, washed with water (50 mL) and methanol (30 mL) to yield product 5b as a black solid (123 mg, 284 mmol, 67%), which was used without further purification for the next step.

\textbf{Mp:} ≥350 °C.

\textbf{HRMS (MALDI\textsuperscript{+}) \(m/z\): [M+H]\textsuperscript{+}:} calcd. for \([C_{30}H_{15}N_{2}O_{2}]^{+}\): 435.1128; found 435.1154; correct isotope distribution.
7,14-Bis[(trisopropylsilyl)ethynyl]naphtho[1,8-gh:5,4-h']diquinoline (6a)

In a heatgun dried Schlenk tube under an atmosphere of argon was added dropwise n-butyllithium (486 μL, 1.21 mmol, 5.80 equiv., 2.50 mol L⁻¹ in hexanes) to a solution of trisopropylsilylacetylene (282 μL, 1.26 mmol, 6.00 equiv.) in anhydrous THF (10 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Quinone 5a (70.0 mg, 209 μmol, 1.00 equiv.) was added and the mixture was stirred at room temperature for 16 h. SnCl₂·2H₂O (189 mg, 837 μmol, 4.00 equiv.) in aqueous HCl (454 μL, 1.36 mmol, 6.50 equiv., 3.00 mol L⁻¹) was added and the solution was stirred at room temperature for 3 h. The reaction was quenched with water (10 mL), neutralized with aqueous NaHCO₃ solution and extracted with dichloromethane (2x10 mL). The combined organic layers were dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/diethyl ether 250:1 -> 100:1 v/v) the product 6a was isolated as orange solid (6.30 mg, 9.47 μmol, 5%).

Rₚ = 0.65 (SiO₂; petroleum ether/ethyl acetate 5:1, v/v).

Mp: 296 °C.

¹H NMR (CDCl₃, 400 MHz, rt): δ = 9.75 (d, J = 9.4 Hz, 2H), 9.28 (dd, J = 4.1 Hz, J = 1.8 Hz, 2H), 9.18 (dd, J = 8.5 Hz, J = 1.8 Hz, 2H), 9.06 (d, J = 9.4 Hz, 2H), 7.80 (dd, J = 8.5 Hz, J = 4.0 Hz, 2H), 1.29 - 1.44 (m, 42H) ppm.

¹³C(¹H) NMR (CDCl₃, 101 MHz, rt): δ = 150.1, 142.2, 135.4, 132.9, 129.5, 127.8, 127.3, 125.5, 125.0, 122.5, 116.7, 105.1, 103.2, 19.1, 11.7 ppm.

IR (ATR): ν = 2924, 2864, 1463, 1259, 1016, 882, 798, 768, 675 cm⁻¹.

UV-Vis (n-hexane, rt): λₘₐₓ, abs = 509 nm, λₘₐₓ, em = 513 nm, ϕ = 77%.

HRMS (MALDI⁺) m/z: [M]⁺: calcd. for [C₄₄H₃₂N₂Si₂]: 664.3664; found 664.3660; correct isotope distribution.
**Crystal data**

Single crystalline specimen were obtained by slow diffusion of methanol into a dichloromethane solution of 6a:

Orange crystal (needle), dimensions 0.235 x 0.023 x 0.020 mm³, crystal system monoclinic, space group P2₁/c, Z = 2, a = 18.819(5) Å, b = 7.9626(15) Å, c = 14.043(4) Å, α = 90°, β = 108.58(2)°, γ = 90°, V = 1994.6(9) Å³, ρ = 1.107 g/cm³, T = 200(2) K, Θmax = 62.141°, 17283 reflections measured, 3041 unique (Rint = 0.0649), 1250 observed (I > 2σ(I)), µ = 1.03 mm⁻¹, Tmin = 0.71, Tmax = 1.69, 224 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 0.94 for observed reflections, final residual values R1(F) = 0.079, wR(F²) = 0.196 for observed reflections, residual electron density -0.29 to 0.32 eÅ⁻³.

8,17-Bis[(triisopropyl)silyl]ethynyl)naphtho[1,8-bc:5,4-b'c']diacridine (6b)

![Chemical structure of 6b](image)

In a heatgun dried Schlenk tube under an atmosphere of argon was added dropwise n-butyllithium (534 µL, 1.34 mmol, 5.80 equiv., 2.50 mol L⁻¹ in hexanes) to a solution of triisopropylsilylacetylene (310 µL, 1.38 mmol, 6.00 equiv.) in anhydrous THF (20 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Quinone 5b (100 mg, 230 µmol, 1.00 equiv.) was added and the mixture was stirred at room temperature for 16 h. SnCl₂·2H₂O (208 mg, 921 µmol, 4.00 equiv.) in aqueous HCl (499 µL, 1.50 mmol, 6.50 equiv., 3.00 mol L⁻¹) was added and the solution was stirred at room temperature for 3 h. The reaction was quenched with water (10 mL), neutralized with aqueous NaHCO₃ solution and extracted with dichloromethane (3x10 mL). The combined organic layers were dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/diethyl ether 500:1 -> 250:1 v/v) the product 6b was isolated as blue solid (36.8 mg, 48.1 µmol, 21%).

Rf = 0.55 (SiO₂; petroleum ether/dichloromethane 2:1, v/v).
Mp: ≥350 °C (decomposition).

$^1$H NMR (TCE-d$_2$, 600 MHz, 70 °C): $\delta = 9.96$ (d, $J = 9.32$ Hz, 2H), 9.74 (s, 2H), 9.07 (d, $J = 9.32$ Hz, 2H), 8.55 (d, $J = 8.68$ Hz, 2H), 8.15 (d, $J = 8.33$ Hz, 2H), 7.93 - 7.97 (m, 2H), 7.67 - 7.71 (m, 2H), 1.42 - 1.49 (m, 42H) ppm.

$^{13}$C($^1$H) NMR (TCE-d$_2$, 151 MHz, 70 °C): $\delta = 148.4$, 142.5, 135.1, 132.7, 129.7, 129.1, 128.2, 127.5, 126.7, 126.1, 125.3, 123.4, 120.1, 105.9, 103.4, 18.8, 11.5 ppm.

IR (ATR): $\nu = 2940$, 2863, 1461, 1068, 992, 881, 814, 785, 743, 676, 639, 595 cm$^{-1}$.

UV-Vis ($n$-hexane, rt): $\lambda_{\text{max, abs}} = 628$ nm, $\lambda_{\text{max, em}} = 634$ nm, $\Phi = 35\%$.

HRMS (MALDI$^+$) m/z: [M+H]$^+$: calcd. for [C$_{52}$H$_{57}$N$_2$Si$_2$]$^+$: 765.4055; found 765.4039; correct isotope distribution.

Crystal data

Single crystalline specimen were obtained by slow evaporation of a dichloromethane solution of 6b:

Blue crystal (needle), dimensions 0.193 x 0.018 x 0.017 mm$^3$, crystal system triclinic, space group P$\overline{1}$, $Z = 1$, $a = 9.0559(5)$ Å, $b = 9.0989(5)$ Å, $c = 16.8241(10)$ Å, $\alpha = 93.399(5)$ °, $\beta = 98.401(5)$ °, $\gamma = 107.252(5)$ °, $V = 1301.96(13)$ Å$^3$, $\rho = 1.280$ g/cm$^3$, $T = 200(2)$ K, $\Theta_{\text{max}} = 66.798$ °, 11274 reflections measured, 4400 unique ($R_{\text{int}} = 0.0486$), 2397 observed ($I > 2\sigma(I)$), $\mu = 3.73$ mm$^{-1}$, $T_{\text{min}} = 0.73$, $T_{\text{max}} = 1.43$, 383 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.00 for observed reflections, final residual values $R_1(F) = 0.054$, $wR(F^2) = 0.118$ for observed reflections, residual electron density -0.49 to 0.31 eÅ$^{-3}$.

In a heatgun dried Schlenk tube under an atmosphere of argon was added dropwise $n$-butyllithium (2.41 mL, 6.02 mmol, 9.00 equiv., 2.50 mol L$^{-1}$ in hexanes) to a solution of 7.2
triisopropylsilylacetylene (1.50 mL, 6.69 mmol, 10.0 equiv.) in anhydrous THF (40 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Quinone 7 (140 mg, 669 µmol, 1.00 equiv.) was added and the mixture was stirred at room temperature for 16 h. SnCl₂·2H₂O (2.11 g, 9.37 µmol, 14.0 equiv.) in aqueous HCl (15.0 mL, 6.00 mol L⁻¹) was added and the solution was stirred at room temperature for 5 h. The reaction was quenched with water (20 mL), neutralized with aqueous NaHCO₃ solution and extracted with dichloromethane (2x20 mL). The combined organic layers were dried over magnesium sulfate and filtrated. The solvent was removed under reduced pressure and the crude product was absorbed on Celite®. After flash column chromatography (petroleum ether/dichloromethane 4:1 v/v) the product 8 was isolated as yellow solid (186 mg, 344 µmol, 51%).

Rᶠ = 0.36 (SiO₂; petroleum ether/dichloromethane 2:1, v/v).

Mp: 166 °C.

¹H NMR (CDCl₃, 400 MHz, rt): δ = 9.08 (dd, J = 3.96 Hz, J = 1.76 Hz, 1H), 8.87 (dd, J = 8.76 Hz, J = 1.76 Hz, 1H), 8.73 - 8.79 (m, 1H), 8.60 - 8.66 (m, 1H), 7.62 - 7.69 (m, 2H), 7.47 (dd, J = 8.84 Hz, J = 3.86 Hz, 1H), 1.24 - 1.34 (m, 42H) ppm.

¹³C⁷{¹H} NMR (CDCl₃, 101 MHz, rt): δ = 152.3, 146.2, 135.3, 134.7, 132.7, 128.0, 127.8, 127.6, 127.5, 127.3, 121.8, 121.4, 119.0, 106.7, 105.4, 103.3, 102.5, 19.1, 19.0, 11.8, 11.6 ppm.

IR (ATR): ν = 2941, 2863, 1461, 1381, 1044, 881, 811, 677, 664, 651, 442 cm⁻¹.

UV-Vis (n-hexane, rt): λmax, abs = 443 nm, λmax, em = 452 nm, φ = 87%.

HRMS (MALDI⁺) m/z: [M+H]⁺: calcd. for [C₃₅H₅₀NSi₂]⁺: 540.3476; found 540.3474; correct isotope distribution.
S3. Synthetic attempts towards tetraazabistetracene

Carboxylic acid S3 was found to decompose under conditions utilized for ring closure. Instead of quinone S4, twofold decarboxylation yielded S5 as main product. S5 was identified by high-resolution mass spectrometry.

![Diagram of S3, S4, and S5 with conditions and reaction pathway]

Table S1: Conditions attempted for ring closure reaction from S3 to S4.

| catalyst | solvent | temperature | duration | commentary   |
|----------|---------|-------------|----------|--------------|
| PPA      | -       | 100 °C      | 4 h      | decarboxylation |
| AlCl₃    | THF     | reflux      | 4 h      | decarboxylation |
| H₂SO₄    | -       | 100 °C      | 4 h      | decarboxylation |
| TfOH     | MsOH    | 100 °C      | 4 h      | decarboxylation |
| AlCl₃    | THF     | 50 °C       | 12 h     | no reaction  |
| H₂SO₄    | -       | 70 °C       | 12 h     | no reaction  |
| TfOH     | MsOH    | 70 °C       | 12 h     | no reaction  |

Even without acid, decarboxylation takes place above 70 °C as evidenced by DSC decomposition studies performed under nitrogen and with a heat rate of 2 K min⁻¹. An exothermic heat flow occurs at T_onset = 70 °C attributed to decarboxylation of S3. For 4a,b no heat flow was observed under the same conditions.

![DSC spectrum graph showing heat flow vs. temperature for 4a, 4b, and S3]

Figure S1: DSC spectrum of 4a,b and S3 under nitrogen (2 K min⁻¹).
Further proof of decarboxylation is the disappearing peak attributed to carbonyl vibration modes in IR after reaction with PPA at 100 °C.

Figure S2: IR spectra before and after heating S3 in PPA at 100 °C for 4 h.

Figure S3: Crude $^1$H NMR spectrum (500 MHz) of S5 in D$_2$SO$_4$ taken directly after synthesis.
S4. UV-Vis spectra

Figure S4: Normalized absorption and emission spectra of 8 in n-hexane.
S5. UV-Vis absorption stability study

Figure S5: Change in absorption intensity of a solution of 6a (10^{-5}M, toluene) at ambient conditions.

Figure S6: Change in absorption intensity of a solution of 6a (10^{-5}M, chloroform) at ambient conditions.

Figure S7: Degree of degradation of a solution of 6a (10^{-5}M, chloroform) at ambient conditions.
Figure S8: Change in absorption intensity of a solution of 6b (10^{-5}M, toluene) at ambient conditions.

Figure S9: Change in absorption intensity of a solution of 6b (10^{-5}M, chloroform) at ambient conditions.

Figure S10: Degree of degradation of a solution of 6b (10^{-5}M, chloroform) at ambient conditions.
Figure S11: Change in absorption intensity of a solution of 8 (10^{-5}\text{M}, toluene) at ambient conditions.

Figure S12: Change in absorption intensity of a solution of 8 (10^{-5}\text{M}, chloroform) at ambient conditions.

Figure S13: Degree of degradation of a solution of 8 (10^{-5}\text{M}, chloroform) at ambient conditions.
S6. Electrochemistry/cyclovoltammetry

The cyclic voltammetry (CV) experiments were carried out using a platinum working electrode, a platinum wire auxiliary electrode, a silver wire reference electrode, a 0.1 mol L\(^{-1}\) NBu\(_4\)PF\(_6\) solution in degassed, dry DCM, and ferrocene/ferrocenium as the reference redox system and internal standard (−5.1 eV) at room temperature and 0.2 V s\(^{-1}\). To determine the first reduction potentials (E\(^{0/−}\)) of 6a, b and 8 and the first oxidation potential of ferrocene (Fc), the half-wave potentials were used.\(^{[S2]}\)

**Figure S14:** CV spectrum of 6a.

**Figure S15:** CV spectrum of 6b.
Figure S16: CV spectrum of 8.
S7. Quantum-chemical calculations

All calculations were performed using Gaussian 16.\textsuperscript{[S3]} TMS groups were used instead of TIPS groups to simplify calculations. First, the gas-phase ground-state equilibrium geometry of the molecules was optimized at the B3LYP/def2-SVP level of theory. Afterwards, the received geometries were refined using the B3LYP/def2-TZVP level of theory. FMO calculations were performed starting from the optimized geometries on the B3LYP/def2-TZVP level of theory. ACID-plots were calculated using AICD-3.0.3 using the CSGT-method at the B3LYP/def2-TZVP IOP(10/93=1) level of theory; isovalue: 0.02; optimization limit: 0.02; maximal arrow length: 1; magnetic field vector is oriented out of plane.\textsuperscript{[S4]} The first fifty vertical singlet transition energies were calculated by time-dependant DFT (TD-DFT) at the CAM-B3LYP/def2-SVP level of theory.

Figure S17: FMOs of 6a*, 6b*, and 8*. TMS groups were used instead of TIPS.

Figure S18: AICD plots of 6a*, 6b*, and 8*. TMS groups were used instead of TIPS.
Table S2: Calculated (gas-phase) FMO energies of Briseno’s nonazabistetracene, 6b* and hypothetical tetraazabistetracene. TMS groups were used instead of TIPS.

| catalyst | HOMO [eV] | LUMO [eV] | gap [eV] |
|----------|----------|-----------|----------|
| ![molecule](image1.png) | -4.91    | -2.99     | 1.92     |
| ![molecule](image2.png) | -5.11    | -3.17     | 1.94     |
| ![molecule](image3.png) | -5.33    | -3.51     | 1.82     |
**Figure S19:** Experimental absorption spectrum of 6a (blue line) with transitions energies and oscillator strengths for the lowest-lying excited states obtained from CAM-B3LYP/def2-SVP (green bars) calculations for 6a*. TMS groups were used instead of TIPS.

**Table S3:** TD-DFT singlet excitation energies, excitation wavelengths, oscillator strengths $f > 0.2$ and orbital contributions for 6a* at the optimized $S_0$ ground state. TMS groups were used instead of TIPS.

| entry | transition | wavelength [nm] | energy [eV] | oscillator strength [a. u.] |
|-------|------------|----------------|-------------|-----------------------------|
| 1     | $1_{31} \rightarrow 1_{32}$ (HOMO $\rightarrow$ LUMO) | 497 | 2.50 | 0.92 |
| 2     | $1_{30} \rightarrow 1_{32}$ | 300 | 4.14 | 1.57 |
|       | $1_{31} \rightarrow 1_{34}$ | | | |
| 3     | $1_{29} \rightarrow 1_{33}$ | 259 | 4.79 | 0.45 |
|       | $1_{29} \rightarrow 1_{35}$ | | | |
|       | $1_{30} \rightarrow 1_{32}$ | | | |
|       | $1_{31} \rightarrow 1_{36}$ | | | |
Figure S20: Experimental absorption spectrum of 6b (blue line) with transitions energies and oscillator strengths for the lowest-lying excited states obtained from CAM-B3LYP/def2-SVP (green bars) calculations for 6b*. TMS groups were used instead of TIPS.

Table S4: TD-DFT singlet excitation energies, excitation wavelengths, oscillator strengths f>0.2 and orbital contributions for 6b* at the optimized S0 ground state. TMS groups were used instead of TIPS.

| entry | transition | wavelength [nm] | energy [eV] | oscillator strength [a. u.] |
|-------|------------|-----------------|-------------|-----------------------------|
| 1     | 157 → 158  | 607             | 2.04        | 0.74                        |
|       | (HOMO → LUMO) |                 |             |                             |
| 2     | 154 → 158  | 331             | 3.75        | 1.56                        |
|       | 155 → 158  |                 |             |                             |
|       | 156 → 159  |                 |             |                             |
|       | 157 → 160  |                 |             |                             |
| 3     | 153 → 159  | 310             | 3.99        | 0.83                        |
|       | 154 → 158  |                 |             |                             |
|       | 156 → 159  |                 |             |                             |
|       | 157 → 160  |                 |             |                             |
| 4     | 155 → 158  | 287             | 4.32        | 1.03                        |
|       | 156 → 159  |                 |             |                             |
|       | 157 → 161  |                 |             |                             |
| 5     | 146 → 158  |                 |             |                             |
|       | 153 → 159  |                 |             |                             |
|       | 154 → 158  | 260             | 4.76        | 0.43                        |
|       | 155 → 160  |                 |             |                             |
|       | 156 → 159  |                 |             |                             |
|       | 157 → 161  |                 |             |                             |
Figure S21: Experimental absorption spectrum of 8 (blue line) with transitions energies and oscillator strengths for the lowest-lying excited states obtained from CAM-B3LYP/def2-SVP (green bars) calculations for 8*. TMS groups were used instead of TIPS.

Table S5: TD-DFT singlet excitation energies, excitation wavelengths, oscillator strengths f>0.2 and orbital contributions for 8* at the optimized S0 ground state. TMS groups were used instead of TIPS.

| entry | transition | wavelength [nm] | energy [eV] | oscillator strength [a. u.] |
|-------|------------|----------------|------------|---------------------------|
| 1     | 99 → 100 (HOMO → LUMO) | 430 | 2.88 | 0.54 |
| 2     | 99 → 132 | 261 | 4.75 | 0.27 |
| 3     | 98 → 100 | 254 | 4.88 | 1.50 |
|       | 99 → 101 | 254 | 4.88 | 1.50 |
|       | 99 → 102 | 254 | 4.88 | 1.50 |
S8. NMR spectra

Figure S22: $^1$H NMR spectrum (600 MHz) of 3a in CDCl$_3$.

Figure S23: $^{13}$C($^1$H) NMR spectrum (151 MHz) of 3a in CDCl$_3$. 

S28
Figure S24: $^1$H NMR spectrum (600 MHz) of 3b in CDCl$_3$.

Figure S25: $^{13}$C($^1$H) NMR spectrum (151 MHz) of 3b in CDCl$_3$. 
Figure S26: $^1$H NMR spectrum (500 MHz) of S2 in CDCl$_3$.

Figure S27: $^{13}$C($^1$H) NMR spectrum (101 MHz) of S2 in CDCl$_3$. 
Figure S28: $^1$H NMR spectrum (700 MHz) of crude 4a in DMSO-$d_6$.

Figure S29: $^{13}$C($^1$H) NMR spectrum (176 MHz) of crude 4a in DMSO-$d_6$. 
Figure S30: $^1$H NMR spectrum (700 MHz) of crude 4b in DMSO-$d_6$.

Figure S31: $^{13}$C($^1$H) NMR spectrum (176 MHz) of crude 4b in DMSO-$d_6$. 
Figure S32: $^1$H NMR spectrum (600 MHz) of crude S3 in DMSO-$d_6$.

Figure S33: $^{13}$C($^1$H) NMR spectrum (151 MHz) of crude S3 in DMSO-$d_6$. 
Figure S34: $^1$H NMR spectrum (400 MHz) of 6a in CDCl$_3$.

Figure S35: $^{13}$C($^1$H) NMR spectrum (101 MHz) of 6a in CDCl$_3$. 
Figure S36: $^1$H NMR spectrum (600 MHz) of 6b at 70 °C in TCE-d$_2$.

Figure S37: $^{13}$C($^1$H) NMR spectrum (151 MHz) of 6b at 70 °C in TCE-d$_2$. 
Figure S38: $^1$H NMR spectrum (400 MHz) of 8 in CDCl$_3$.

Figure S39: $^{13}$C($^1$H) NMR spectrum (101 MHz) of 8 in CDCl$_3$. 
S9.  X-ray single-crystal structure analysis

Table S6: Crystal data and structure refinement of 6a (CCDC 2068043).

| Property                              | Value                          |
|---------------------------------------|--------------------------------|
| Identification code                   | CCDC 2068043                   |
| Empirical formula                     | C₄₄H₅₂N₂Si₂                   |
| Formula weight                        | 665.05                         |
| Temperature                           | 200(2) K                       |
| Wavelength                            | 1.54178 Å                      |
| Crystal system                        | monoclinic                     |
| Space group                           | P2₁/c                          |
| Z                                      | 2                              |
| Unit cell dimensions                  | a = 18.819(5) Å, α = 90 deg.   |
|                                       | b = 7.9626(15) Å, β = 108.58(2) deg. |
|                                       | c = 14.043(4) Å, γ = 90 deg.   |
| Volume                                | 1994.6(9) Å³                   |
| Density (calculated)                  | 1.11 g/cm³                     |
| Absorption coefficient                | 1.03 mm⁻¹                      |
| Crystal shape                         | needle                         |
| Crystal size                          | 0.235 x 0.023 x 0.020 mm³      |
| Crystal colour                        | orange                         |
| Theta range for data collection       | 6.3 to 62.1 deg.               |
| Index ranges                          | -21≤h≤21, -4≤k≤8, -16≤l≤16      |
| Reflections collected                 | 17283                          |
| Independent reflections               | 3041 (R(int) = 0.0649)         |
| Observed reflections                  | 1250 (I > 2σ(I))               |
| Absorption correction                 | Semi-empirical from equivalents|
| Max. and min. transmission            | 1.69 and 0.71                  |
| Refinement method                     | Full-matrix least-squares on F²|
| Data/restraints/parameters            | 17283 / 42 / 224               |
| Goodness-of-fit on F²                 | 0.94                           |
| Final R indices (I>2sigma(I))         | R1 = 0.079, wR2 = 0.196        |
| Largest diff. peak and hole           | 0.32 and -0.29 eÅ⁻³            |
Table S7: Crystal data and structure refinement of 6b (CCDC 2068044).

| Property                                | Value                        |
|-----------------------------------------|------------------------------|
| Identification code                     | CCDC 2068044                 |
| Empirical formula                       | C_{54}H_{58}Cl_{6}N_{2}Si_{2} |
| Formula weight                          | 1003.90                      |
| Temperature                             | 200(2) K                     |
| Wavelength                              | 1.54178 Å                    |
| Crystal system                          | triclinic                    |
| Space group                             | P 1                          |
| Z                                       | 1                            |
| Unit cell dimensions                    | a = 9.0559(5) Å, \(\alpha = 93.399(5)\) deg. |
|                                          | b = 9.0989(5) Å, \(\beta = 98.401(5)\) deg. |
|                                          | c = 16.8241(10) Å, \(\gamma = 107.252(5)\) deg. |
| Volume                                  | 1301.96(13) Å^3              |
| Density (calculated)                    | 1.28 g/cm^3                  |
| Absorption coefficient                  | 3.73 mm^{-1}                 |
| Crystal shape                           | needle                       |
| Crystal size                            | 0.193 x 0.018 x 0.017 mm^3   |
| Crystal colour                          | blue                         |
| Theta range for data collection         | 2.7 to 66.8 deg.             |
| Index ranges                            | -10 \leq h \leq 6, -9 \leq k \leq 10, -19 \leq l \leq 19 |
| Reflections collected                   | 11274                        |
| Independent reflections                 | 4400 (R(int) = 0.0486)        |
| Observed reflections                    | 2397 (I > 2\sigma(I))        |
| Absorption correction                   | Semi-empirical from equivalents |
| Max. and min. transmission              | 1.43 and 0.73                |
| Refinement method                       | Full-matrix least-squares on F^2 |
| Data/restraints/parameters              | 4400 / 246 / 383             |
| Goodness-of-fit on F^2                  | 1.00                         |
| Final R indices (I > 2\sigma(I))        | R1 = 0.054, wR2 = 0.118       |
| Largest diff. peak and hole             | 0.31 and -0.49 eÅ^{-3}       |
Table S8: Crystal data and structure refinement of 8 (CCDC 2071304).

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | CCDC 2071304                               |
| Empirical formula               | C₃₅H₄₉NSi₂                                  |
| Formula weight                  | 539.93                                     |
| Temperature                     | 200(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Orthorhombic                               |
| Space group                     | Pbca                                       |
| Z                               | 8                                          |
| Unit cell dimensions            | a = 14.8914(10) Å, b = 14.2919(9) Å, c = 30.6055(19) Å |
|                                 | α = 90 deg., β = 90 deg., γ = 90 deg.      |
| Volume                          | 6513.7(7) Å³                               |
| Density (calculated)            | 1.10 g/cm³                                 |
| Absorption coefficient          | 0.13 mm⁻¹                                  |
| Crystal shape                   | brick                                      |
| Crystal size                    | 0.105 x 0.095 x 0.088 mm³                  |
| Crystal colour                  | yellow                                     |
| Theta range for data collection | 1.3 to 22.1 deg.                           |
| Index ranges                    | -15≤h≤15, -15≤k≤15, -32≤l≤31               |
| Reflections collected           | 29545                                      |
| Independent reflections         | 4015 (R(int) = 0.0784)                     |
| Observed reflections            | 2785 (I > 2σ(I))                           |
| Absorption correction           | Semi-empirical from equivalents            |
| Max. and min. transmission      | 0.74 and 0.70                              |
| Refinement method               | Full-matrix least-squares on F²            |
| Data/restraints/parameters      | 4015 / 1 / 359                             |
| Goodness-of-fit on F²           | 1.06                                       |
| Final R indices (I>2σ(I))       | R1 = 0.047, wR2 = 0.104                    |
| Largest diff. peak and hole     | 0.31 and -0.28 eÅ⁻³                        |
Figure S40: Solid-state structure of 6b with cocrystallized chloroform, closest contacts (C–N = 3.30 Å) and visualization of overlap and packing.

Figure S41: Solid-state structure of 8 (a, ellipsoids set to 50 % probability level) and visualization of packing (b). The nitrogen atom is distributed statistically among the four possible atom positions. Van-der-Waals contacts between the π-system and silyl groups of adjacent molecules in the crystal lattice of bis-TIPS-ethinyl-anthracene (c, CCDC 962668)\cite{99} and bis(TIPS)-ethinylmonoazaanthracene 8 (d).
G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, *Adv. Mater.* **2011**, *23*, 2367-2371.

*Gaussian 16, Revision C.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

a) D. Geuenich, R. Herges, *J. Phys. Chem. A* **2001**, *105*, 3214-3220; b) D. Geuenich, K. Hess, F. Koehler, R. Herges, *Chem. Rev.* **2005**, *105*, 3758-3772.

M. Más-Montoya, R. P. Ortiz, D. Curiel, A. Espinosa, M. Allain, A. Facchetti, T. J. Marks, *J. Mat. Chem. C* **2013**, *1*, 1959-1969.

a) D. Wang, Y. Wang, J. Zhao, L. Li, L. Miao, D. Wang, H. Sun, P. Yu, *Tetrahedron* **2016**, *72*, 5762-5768; b) N. Boudet, J. R. Lachs, P. Knochel, *Org. Lett.* **2007**, *9*, 5525-5528.

J. Yamamoto, K. Kinpara, Y. Fukuda, Y. Nakasato, K. Uchida, T. Nishikawa, Publication date 2011/08/04, PCT Int. Appl., Patent WO 2011093365.

K. T. Potts, D. Bhattacharjee, E. B. Walsh, *J. Org. Chem.* **1986**, *51*, 2011-2021.

J. E. Anthony, S. Parkin CCDC 962668: *Experimental Crystal Structure Determination*, **2016**, DOI: 10.5517/cc119qtw