Supporting Information:

A Persistent Diazaheptacene-Derivative

Jens U. Engelhart, Olena Tverskoy, Uwe H. F. Bunz

Organisch-Chemisches Institut; Ruprecht-Karls-Universität Heidelberg; Im Neuenheimer Feld 270, 69120 Heidelberg, Germany; Fax: (+) 49 (0) 6221 54 8404

E-mail: uwe.bunz@oci.uni-heidelberg.de

Contents

S1. General methods

All reagents and solvents were obtained from Fisher Scientific, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. All of the other absolute solvents were dried by a MB SPS-800 using drying columns. Preparation of air- and moisture-sensitive materials was carried out in oven dried flasks under an atmosphere of nitrogen using Schlenk-techniques. The reactions under microwave conditions were carried out in the microwave reactor Monowave 300 from Anton Paar. For thin layer chromatography 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). Column chromatography was performed on silica gel from Macherey, Nagel & Co. KG, Düren (Germany) (particle size: 0.04-0.063 mm) using mixtures of dichloromethane and petrol ether or ethyl acetate and petrol ether. Melting points were determined with a Melting Point Apparatus MEL-TEMP (Electrothermal, Rochford, UK) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 500 (500 MHz) or Bruker Avance 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$ or accordingly CD_2Cl_2 in the corresponding deuterated solvent.[1] All NMR spectra were integrated and processed using TopSpin 3.0 (Bruker). MS spectra were recorded on a Vakuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. Crystal structure analysis was accomplished on Bruker Smart CCD or Bruker APEX diffractometers. Infrared (IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded on a Jasco FT/IR-4100 spectrometer. Absorption spectra were recorded on a Jasco UV-VIS V-660 or Jasco UV-VIS V-670. Emission spectra were recorded on a Jasco FP-6500. Elemental Analysis was performed by the Microanalytical Laboratory of the University of Heidelberg using an Elementar Vario EL machine. Cyclic voltammetry was performed on the potentiostat VersaSTAT3 from Princton Appied Research using VersaStudio v2 software for the evaluation. Nomenclature of all compounds described in the supporting information was determined according to IUPAC-rules using the program ACD/Labs 7.0.

S2. Stability of the synthesized dihydroazaacenes

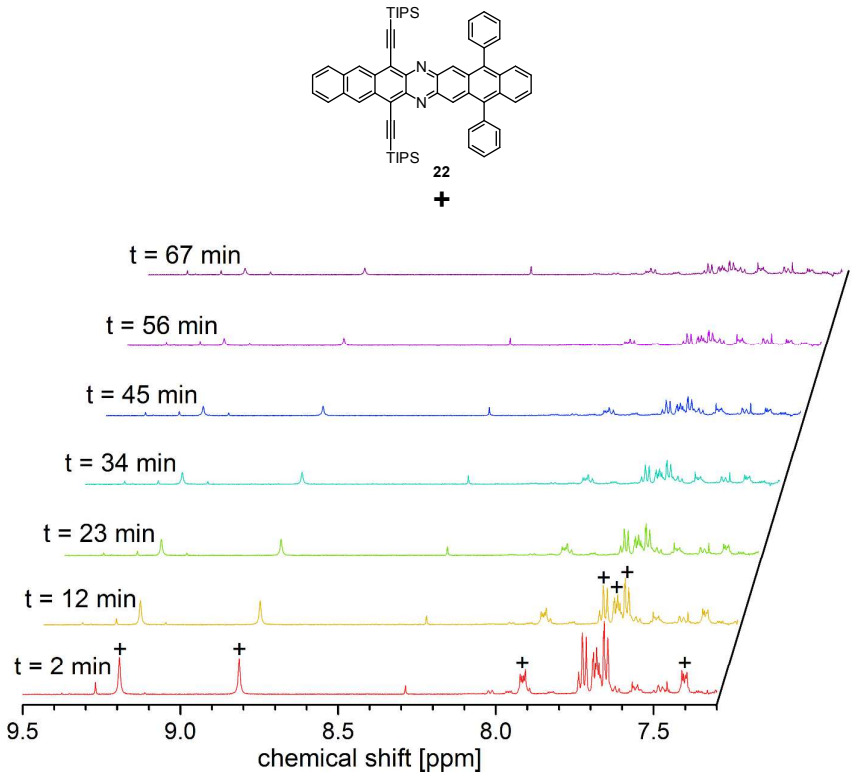


Figure S 1: Fast decomposition of 22 observed *via* ^{1}H NMR.

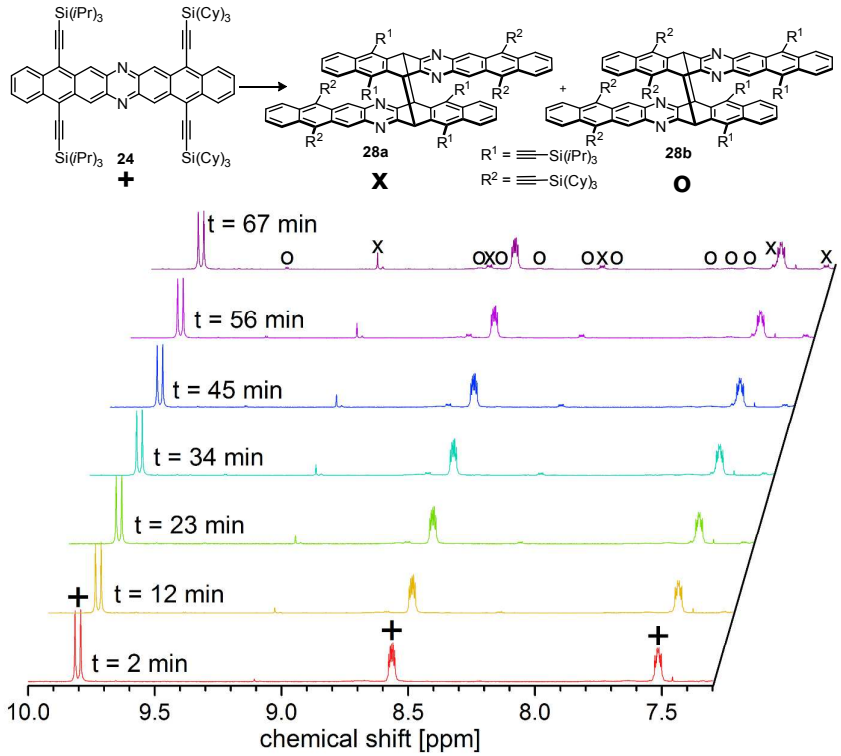


Figure S 2: Slow decomposition of 24 observed *via* ^{1}H NMR.

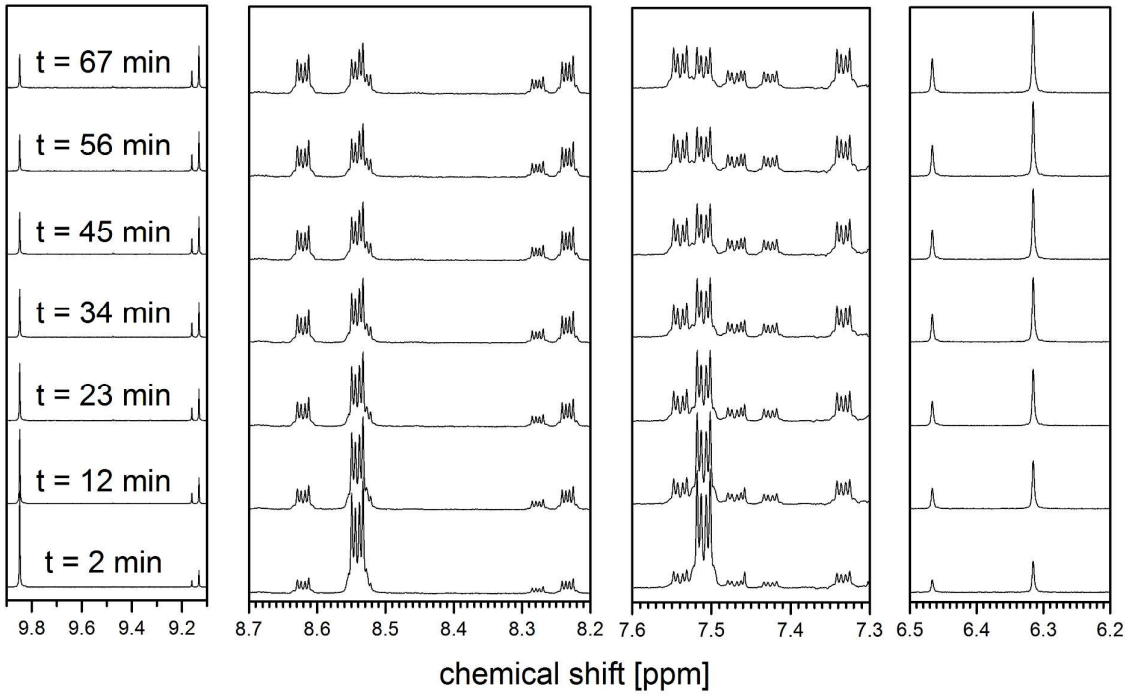


Figure S 3: Dimerization process of 2 magnifying all signals in the aromatic region.

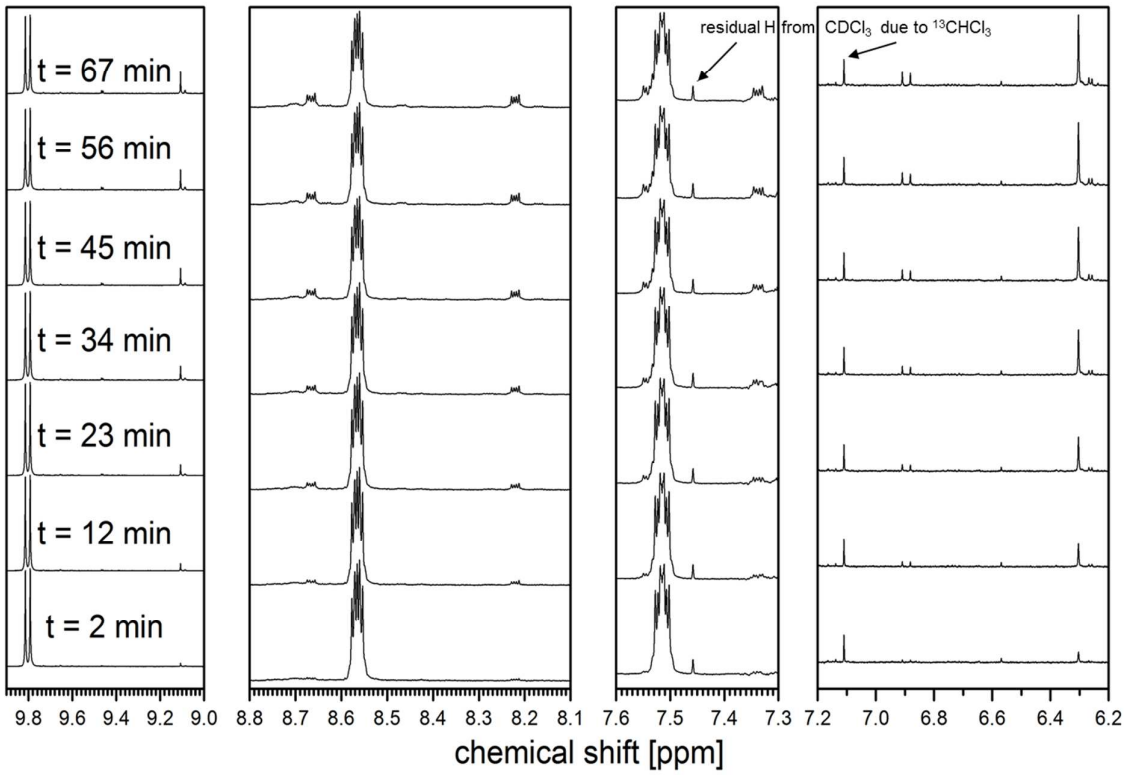


Figure S 4: Dimerization process of 24 magnifying all signals in the aromatic region.

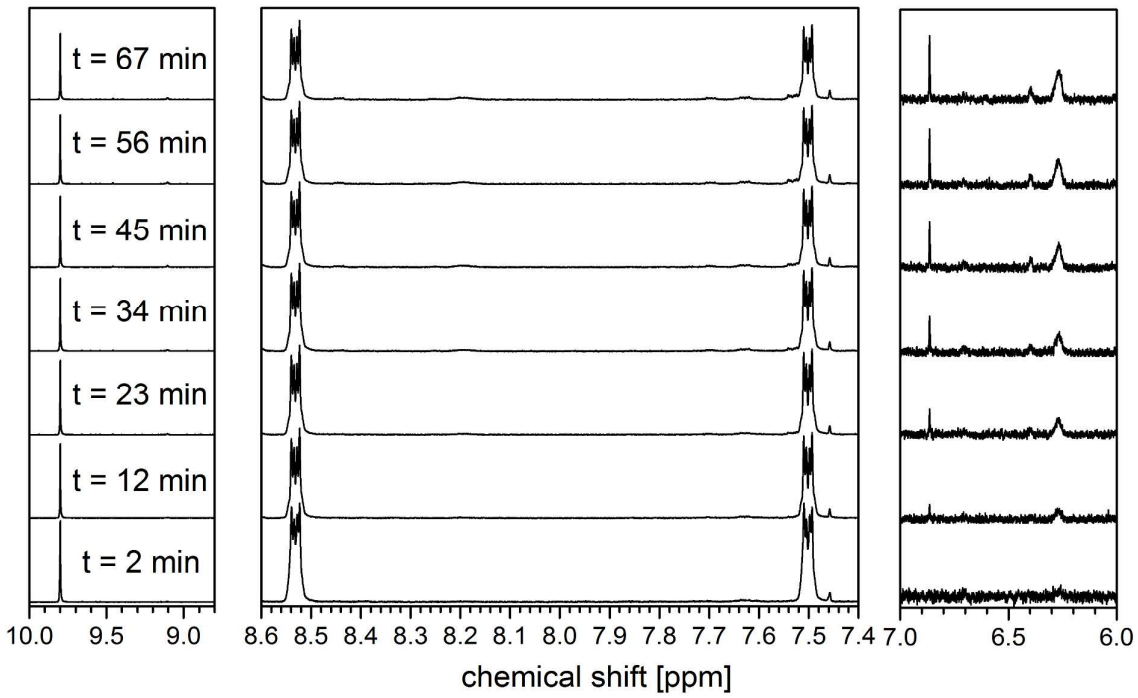


Figure S 5: Dimerization process of 25 magnifying all signals in the aromatic region.

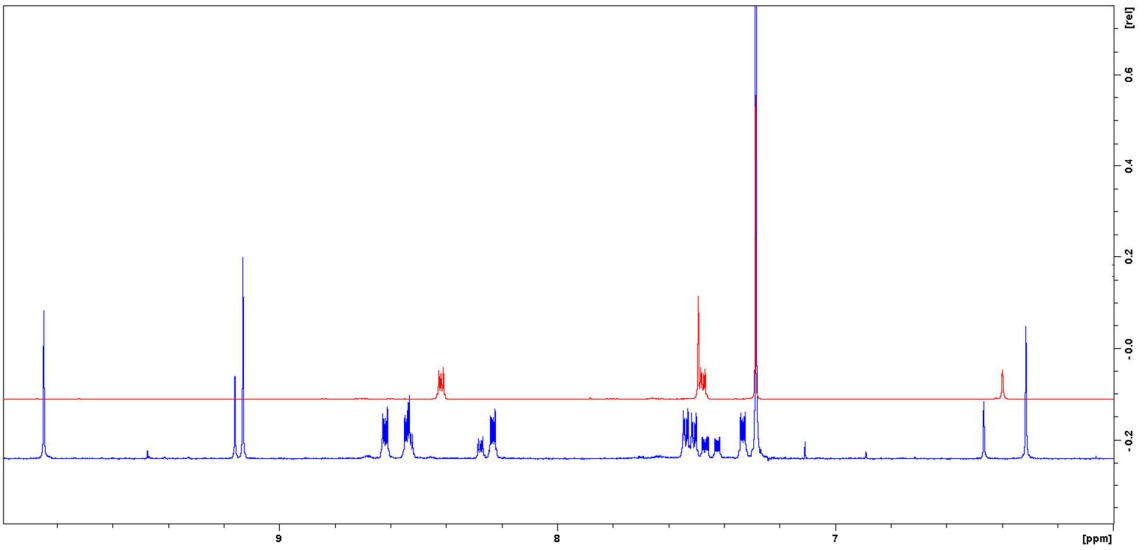


Figure S 6: Comparison of dihydroazaacene 19 with dimerizing 23 after 70 minutes indicates that 19 is not reformed as degradation product from 23.

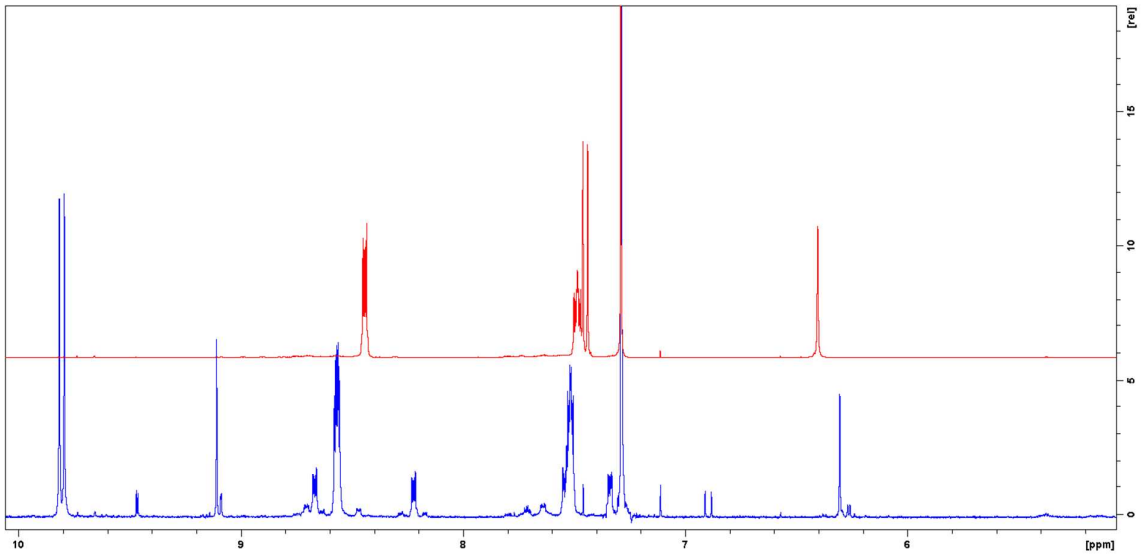


Figure S 7: Comparison of dihydroazaacene 20 with dimerizing 24 after 6.5 hours indicates that 20 is not reformed as degradation product from 24.

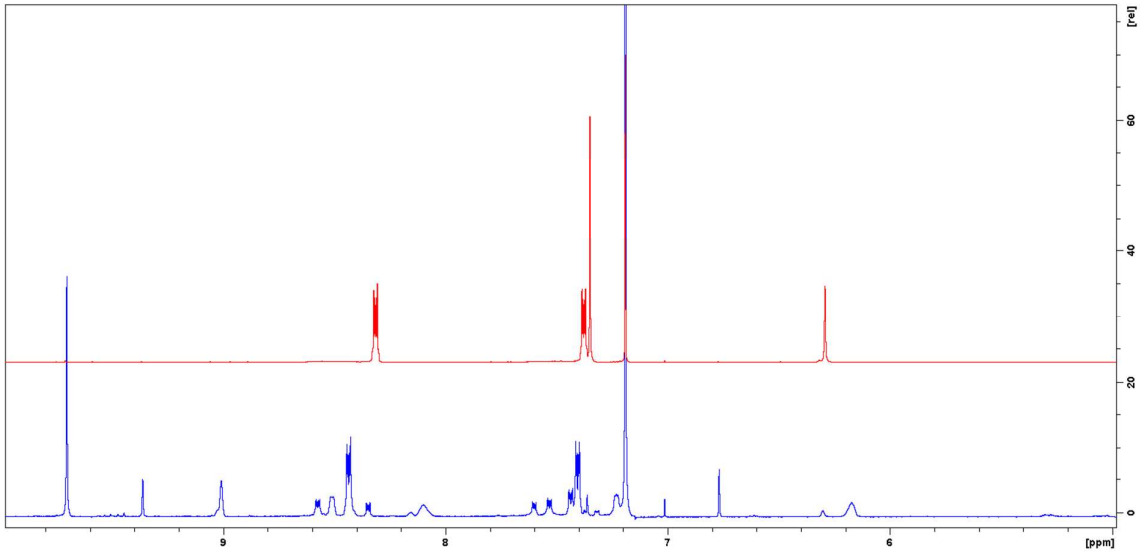


Figure S 8: Comparison of dihydroazaacene 21 with dimerizing 25 after 7.5 hours indicates that 21 is not reformed as degradation product from 25.

S3. Kinetic examination of the dimerization process

For the kinetic studies of the dimerization the intensities of the low field aromatic signals were examined with respect to the time. All values are normalized to the initial intensity of the azaheptacene signal. The obtained values are estimations, as T_1-values could not be determined and the intensities of degradations products are affected by noise. The decrease of the heptacene signal was fitted to a second order rate law with respect to the heptacene. The rate constant k was extracted according to the equation (1).

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \qquad (1)$$

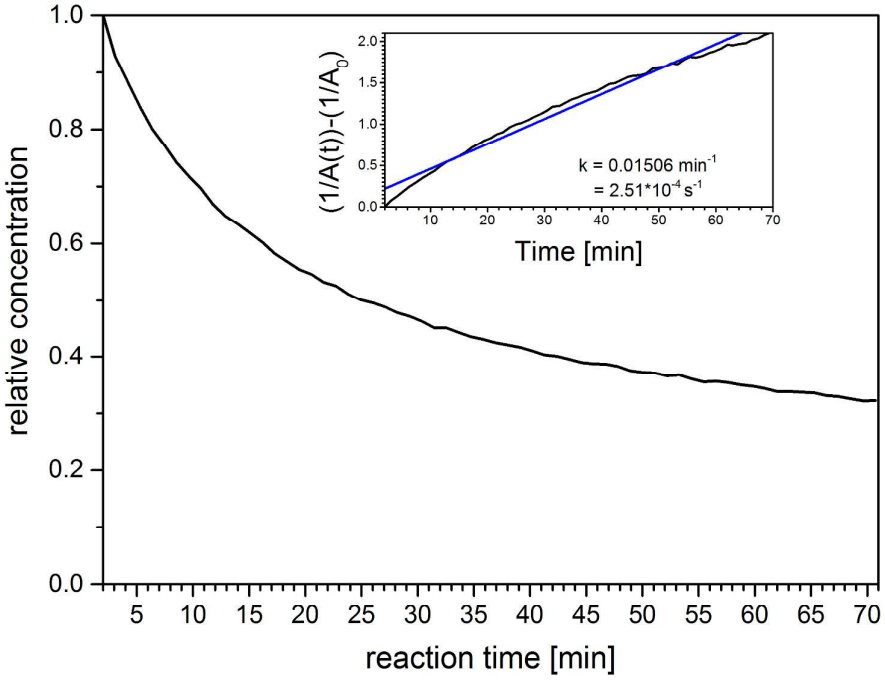


Figure S 9: The degradation of compound 22 fulfilled hardly the second order rate law that belongs to the dimerization process. TLC showed a complex mixture of degradation products.

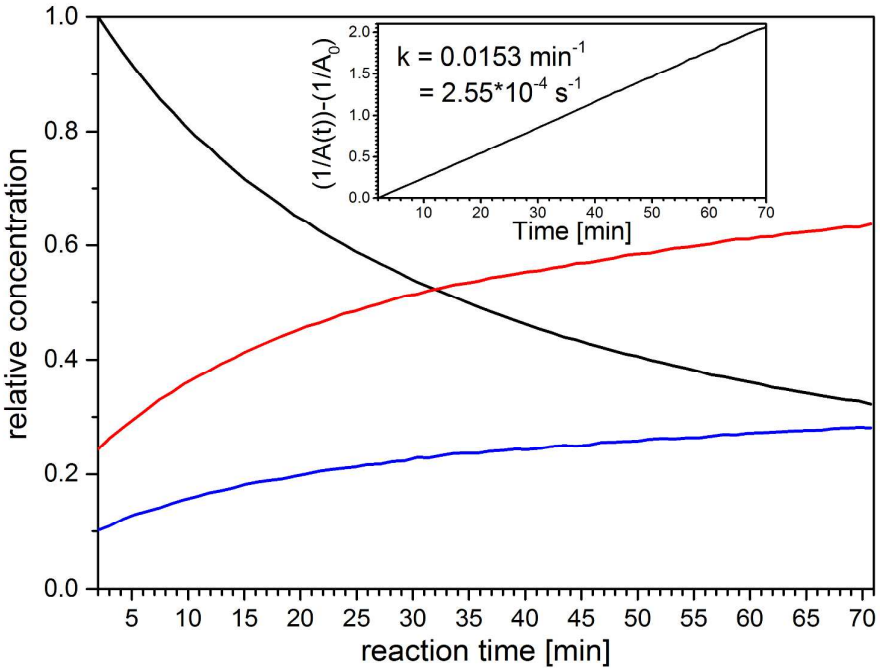


Figure S 10: The dimerization process of 23 clearly corresponds to a second order rate law. The formation of the products of this degradation is shown by the red and blue graph.

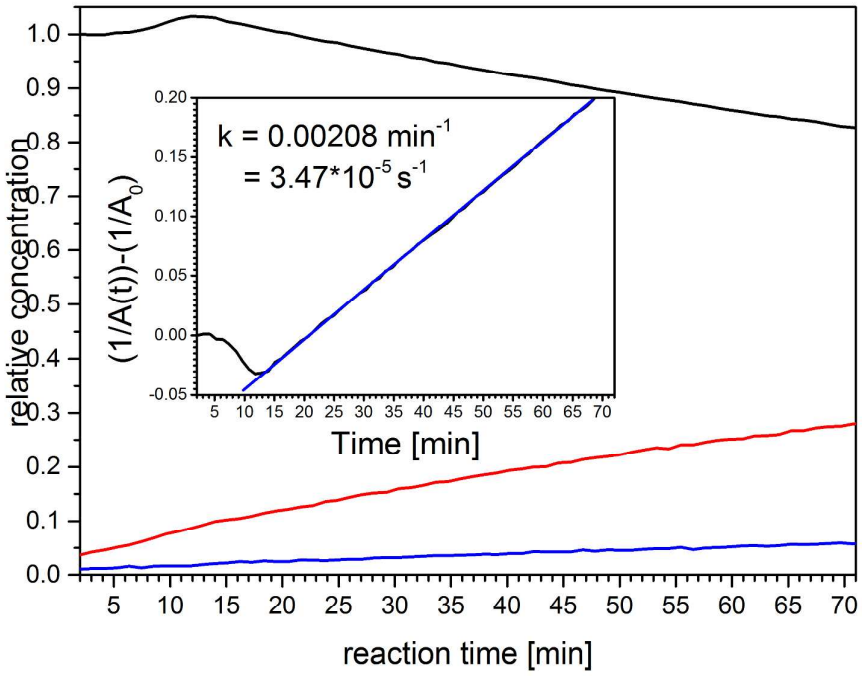


Figure S 11: The dimerization process of 24 corresponds to a second order rate law after a short period of 11 min. The formation of the products of this degradation is shown by the red and blue graph.

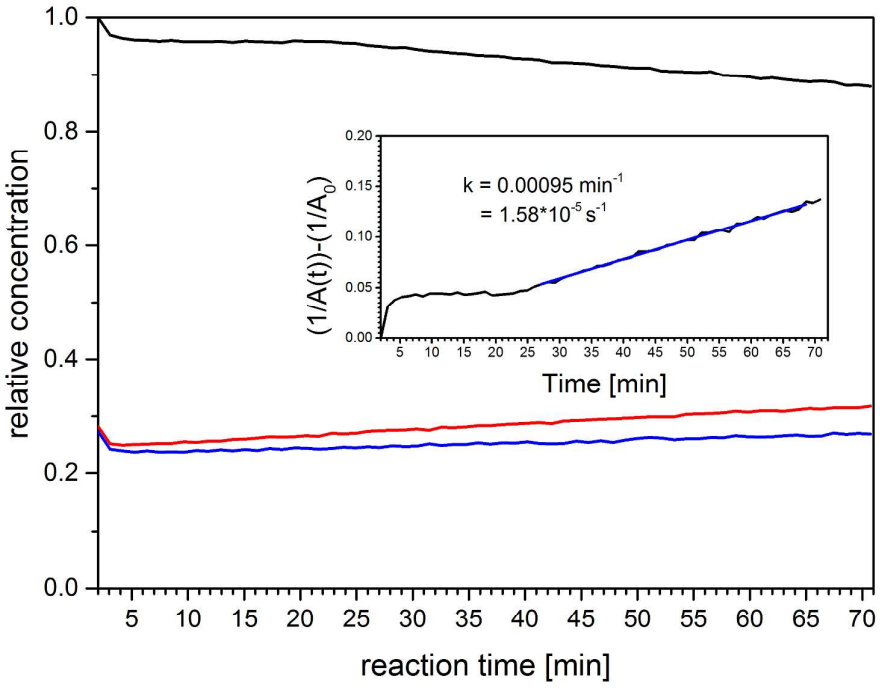


Figure S 12: The dimerization process of 25 corresponds to a second order rate law after a period of 23 min. The formation of the products of this degradation is shown by the red and blue graph.

S4. Additional structure proofs for diazaheptacene 24

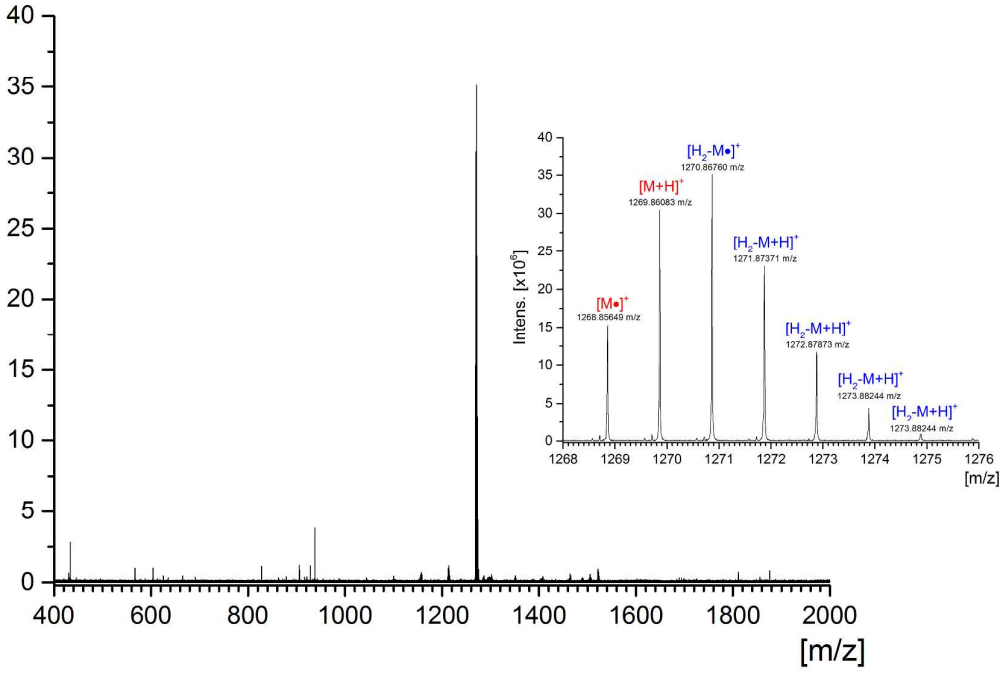


Figure S 13: Mass spectra shows the product 25 ([M]) and formation of a significant amount of 21 ([H_2-M]). Reduction during mass spectra methods is a common feature of azaacenes.

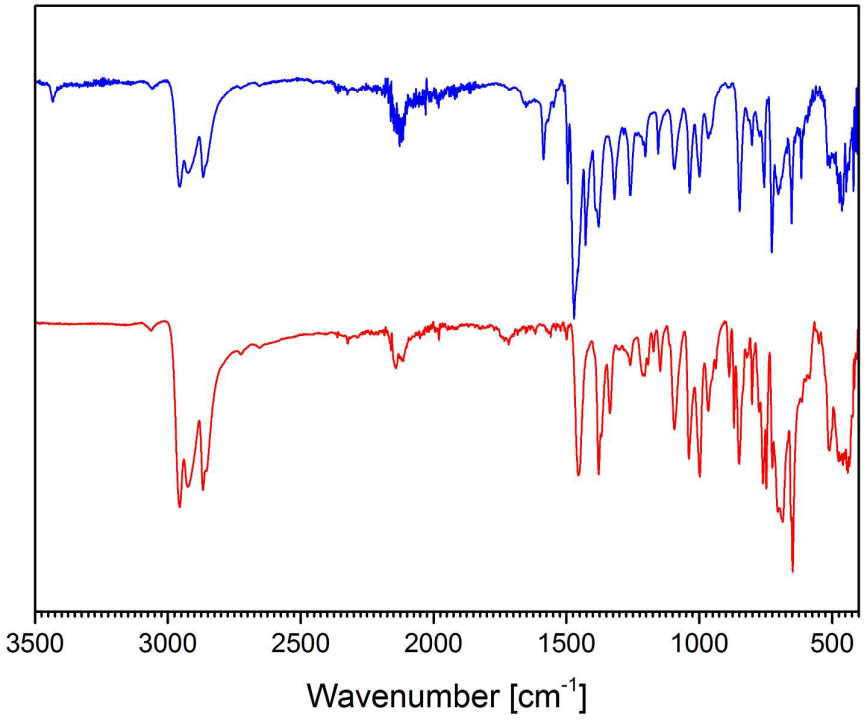


Figure S 14: Comparison of IR spectra of 21 (blue) and 25 (red). The lack of the vibration mode of the NH bond at 3450 cm^{-1} for 24 (red) indicates the existence of the oxidized azaacene 25.

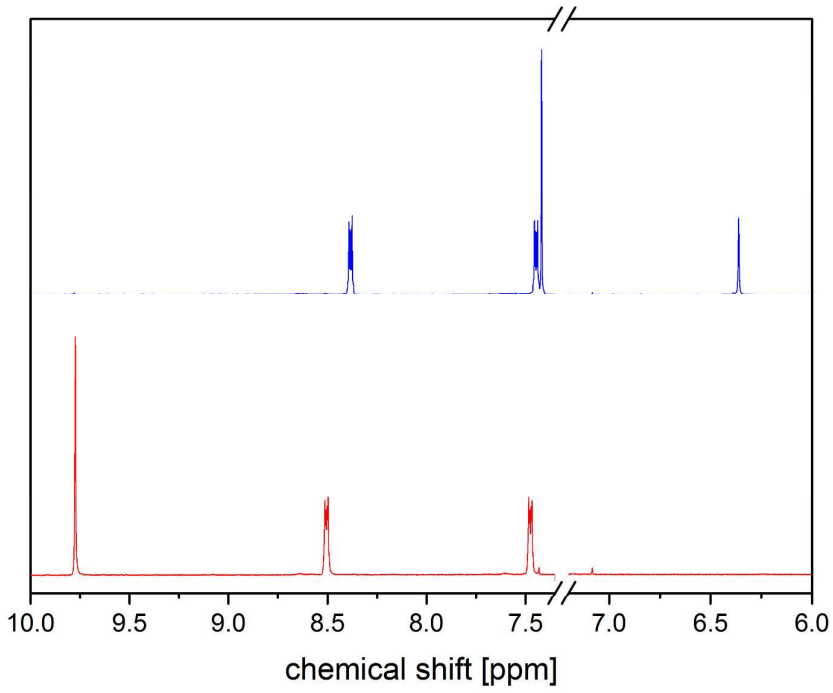


Figure S 15: Comparison of 1H NMR spectra of 21 (blue) and 25 (red). Upon oxidation the NH proton signal disappears and the protons next to the nitrogen are shifted 2.25 ppm to low field.

S5. Synthesis and analytical data

S5.1 General Procedures (GP)

Starting materials **6**[2], **10**[3], **17**[4] and the alkynes[5] were synthesized according to literature procedures.

S5.1.1 *GP1*: Alkinylation of dibromoanthracendion

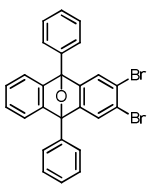
The tri-alkylsilyl acetylene was dissolved in dry THF at 0°C and treated with *n*-BuLi in hexane. After stirring for 1.5 h at room temperature the dibromoanthracendione was added portionwise to form a light brown solution, which was stirred for 20 h. The reaction was quenched with aqueous ammonium chloride, followed by extraction with diethyl ether. The combined organic layer was washed with water and brine and dried over Na_2SO_4. Evaporation under reduced pressure gave the crude diol which was filtered through a plug of silica using petroleum ether and diethyl ether subsequently to separate excessive acetylene. After evaporation the intermediate diole was diluted in THF (20.0 mL) and a saturated solution of $SnCl_2$ in conc. hydrochloric acid (7 mL) was added to form a reddish brown reaction mixture, which was stirred for 2.5 h. At this point the product was extracted with diethyl ether (3 x 50.0 mL) and the combined organic layer was washed with water (30.0 mL), 1M aqueous sodium hydroxide (30.0 mL) and brine (30.0 mL). After drying over Na_2SO_4, the solvent was evaporated under reduced pressure. Flash column chromatography gave the pure product.

S5.1.2 *GP2*: Palladium-Catalyzed amination in dioxane

In an oven dried microwave vial under an atmosphere of argon, the *ortho*-diamino compound (1.00 equiv), the *ortho*-dihalogen compound (1.50 equiv), and the precatalyst **Cat** (5 mol%) were dissolved in dry dioxane. Degassing the resulting mixture for 10 min by bubbling of argon, was followed by the addition of Cs_2CO_3 (4.00 equiv). The microwave vial was sealed and the reaction mixture was stirred for 16 h at 120°C in the microwave reactor. Subsequently it was diluted with saturated, aqueous solution of ammonium chloride (2 mL). The phases were separated and the aqueous phase was extracted with diethyl ether (2 x10 mL). The combined organic layer was washed with brine (20 mL) and dried over sodium sulfate. Flash column chromatography gave the clean *N*,*N*`-Dihydrodiazaacene.

S5.2 Products

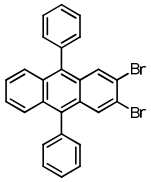
S5.2.1 2,3-Dibromo-9,10-diphenyl-9,10-epoxyanthracene (**4**)



In an heat-gun dried flask 1,3-diphenylisobenzofuran (2.00 g, 11.0 mmol, 1.00 equiv.) and 1,2,4,5-tetrabromobenzene (4.37 g, 11.0 mmol, 1.00 equiv.) were dissolved in toluene (120 mL) at -78°C under an atmosphere of argon. *n*-BuLi (7.70 mL ,1.60 M, 12.3 mmol, 1.05 equiv) was added dropwise over a period of 20 min. The mixture remained stirring at this temperature for 3 h, before it was allowed to warm slowly to room temperature over night. The reaction mixture was quenched with water (10 mL). The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the pure product (**4**) was obtained as a colorless solid (2.06 g, 4.08 mmol, 37%) after flash column chromatography (silica gel, petroleum ether/dichloromethane).

R_f = 0.56 (PE/EE = 9:1); m.p. 207 °C; ^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C): δ = 7.08-7.14 (m, 2H), 7.36-7.43 (m, 2H), 7.50-7.60 (m, 4H), 7.60-7.67 (m, 4H), 7.86-7.92 (m, 4H); ^{13}C {^{1}H} NMR (100.63 MHz, $CDCl_3$, 25 °C): δ = 90.4, 120.8, 121.9, 125.8, 126.5, 126.7, 128.8, 129.1, 134.1, 149.3, 151.8; IR: ν = 3060, 3032, 1733, 1448, 1422, 1346; UV-Vis λ_{max} (hexane): 296 nm; ε(296 nm) = 14514 L·mol^{-1}·cm^{-1}; HR-MS (Electron impact ionization, EI): *m/z* calcd. for $C_{26}H_{16}Br_2O$: $[M]^+$ 501.9562, found: 501.9588, correct isotope distribution; Elemental analysis: calcd. for $C_{26}H_{16}Br_2O$ C 61.93, H 3.20, found: C 61.56, H 3.40.

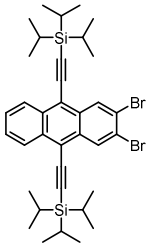
S5.2.2 2,3-Dibromo-9,10-diphenylanthracene (**5**)



Under an inert atmosphere **4** (1.63 g, 3.20 mmol, 1.00 equiv.) and sodium iodide (1.40 g, 9.60 mmol, 3.00 equiv) were suspended in acetonitrile (90 mL) and dichloromethane (10.0 mL) at room temperature. Upon addition of trimethylsilyl chloride (1.20 mL, 1.08 g, 9.69 mmol, 3.00 equiv.) the mixture changed color to brown. TLC monitoring showed full consumption of **4** after 1 h. The reaction was diluted with water an extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Flash column chromatography gave the pure **5** product as yellow solid (1.03 g, 2.12 mmol, 66 %).

R_f = 0.64 (PE/EE = 9:1); m.p. 188-191 °C; ^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C): δ = 7.34-7.40 (m, 2H), 7.43-7.48 (m, 4H), 7.58-7.70 (m, 8H), 8.00 (m, 2H); ^{13}C {^{1}H} NMR (100.63 MHz, $CDCl_3$, 25 °C): δ = 121.8, 126.1, 127.2, 128.2, 128.8, 129.5, 130.7, 131.3, 131.4, 136.8, 138.0; IR: ν = 3055, 1495, 1439, 408, 1389; UV-Vis λ_{max} (hexane): 404 nm; ε(404 nm) = 20975 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max} (hexane): 418 nm; HR-MS (Electron impact ionization, EI): *m/z* calcd. for $C_{26}H_{16}Br_2$: $[M]^+$ 485.9613, found: 485.9617, correct isotope distribution.

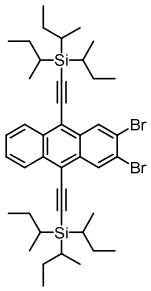
S5.2.3 [(2,3-Dibromoanthracene-9,10-diyl)diethyne-2,1-diyl]bis(tripropan-2-ylsilane) (**7**)



GP1 was carried out with tri-*iso*-propylsilyl acetylene (1.50 g, 8.19 mmol), *n*-BuLi (5.00 mL, 1.6 M in hexane, 8.19 mmol) and **6** (1.00 g, 2.73 mmol) in dry THF (30 mL). Finally flash column chromatography gave the pure product (**7**) as bright yellow solid (745 mg, 1.07 mmol, 38 %).

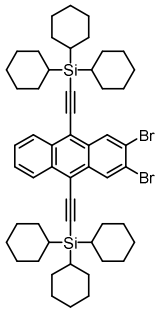
R_f = 0.84 (PE/EE = 9:1); m.p. 205 °C; ^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.23-1.30 (m, 42H), 7.62-7.66 (m, 2H), 8.55-8.60 (m, 2H), 8.97 (s, 2H); ^{13}C {^{1}H} NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 11.6, 19.0, 102.4, 106.3, 118.0, 123.8, 127.5, 127.8, 131.8, 132.0, 132.8; IR: ν = 3061, 2938, 2889, 2862, 2126, 1459, 1378; UV-Vis λ_{max} (hexane): 448 nm; ε(448 nm) = 41972 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max} (hexane): 453 nm; HR-MS (Electron impact ionization, EI): *m/z* calcd. for $C_{36}H_{48}Br_2Si_2$: $[M]^+$ 696.1635, found: 696.1643, correct isotope distribution.

S5.2.4 [(2,3-Dibromoanthracene-9,10-diyl)diethyne-2,1-diyl]bis(tripropan-2-ylsilane) (**8**)



GP1 was carried out with tri-*sec*-butylsilyl acetylene (368 mg, 1.64 mmol), *n*-BuLi (938 µL, 1.6 M in hexane, 1.50 mmol) and **6** (192 mg, 526 µmol) in dry THF (15 mL). After flash column chromatography the product (**8**) could not be obtained analytically pure. The crude product (40.8 mg, 52.4 µmol, 10%) was used in the next step without further purification.

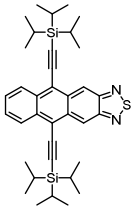
S5.2.5 [(2,3-Dibromoanthracene-9,10-diyl)diethyne-2,1-diyl]bis(tricyclohexylsilane) (**9**)



GP1 was carried out with tri-*cyclo*-hexylsilyl acetylene (350 mg, 1.15 mmol), *n*-BuLi (400 µL, 2.5 M in hexane, 1.00 mmol) and **6** (140 mg, 380 µmol) in dry THF (30.0 mL). Finally flash column chromatography gave the pure product (**9**) as bright yellow solid (140 mg, 150 µmol, 39 %).

R_f = 0.24 (petroleum ether); m.p. 237 °C; ^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C): δ = 1.10 (tt, 6H, *J* = 12.4 Hz, *J* = 12.4 Hz), 1.26-1.37 (m, 18H), 1.42-1.53 (m, 12H), 1.73-1.86 (m, 18H), 1.92-2.01 (m, 12H),7.61-7.66 (m, 2H), 8.53-8.59 (m, 2H), 8.98 (s, 2H); ^{13}C {^{1}H} NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 23.5, 27.2, 28.5, 29.0, 102.8, 107.0, 118.2, 123.7, 127.6, 127.7, 131.9, 132-1, 132.9; IR: ν = 3057, 2915, 2844, 2124, 1444, 1411, 1378; UV-Vis λ_{max} (hexane): 450 nm; ε(450 nm)= 43144 $L \cdot mol^{-1} \cdot cm^{-1}$; Fluorescence λ_{max} (hexane): 455 nm; HR-MS (Direct Analysis in Real Time, DART): *m/z* calcd. for $C_{54}H_{73}{}^{79}Br^{81}BrSi_2$: $[M+H]^+$ 937.35916, found: 937.35735, correct isotope distribution.

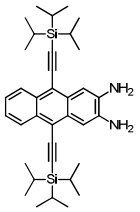
S5.2.6 5,10-Bis[(tripropan-2-ylsilyl)ethynyl]anthra[2,3-c][1,2,5]thiadiazole (**11**)



Tri-*iso*-propylsilyl acetylene (4.20 mL, 3.42 g, 18.8 mmol) was dissolved in dry THF (20 mL) at 0°C and treated with *n*-BuLi (4.20 mL, 2.5 M in hexane, 11.3 mmol). After stirring for 1.5 h at room temperature, **10** (1.00 g, 3.76 mmol) was added portionwise to form a light brown solution, which was stirred for 20 h. The reaction was quenched with aqueous ammonium chloride (10.0 mL), followed by extraction with diethyl ether (3 x 70.0 ml). The solvent was reduced and the intermediate diol was filtered through a plug of silica gel, eluated with petroleum ether to re-isolate the alkyne and ethyl acetate to isolate the intermediate product. The solvent was removed and the intermediate product was dissolved in dichloromethane (20.0 mL) and a saturated solution of $SnCl_2$ in conc. hydrochloric acid (7.00 mL). A dark blue solution was formed, which was stirred for 20 min. At this point the product was extracted with diethyl ether (3 x 50.0 mL) and the combined organic phase was washed with water (50.0 mL), 1M aqueous sodium hydroxide (50.0 mL) and brine (50.0 mL). After drying over Na_2SO_4, the solvent was evaporated under reduced pressure. Flash column chromatography (silica gel, petroleum ether) gave the pure product **11** as dark blue solid (1.08 g, 1.80 mmol, 48 %), which is sensitive towards light.

R_f = 0.71 (PE/EE = 9:1); m.p. > 134 °C decomp.; ^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.26-1.33 (m, 42H), 7.48-7.52 (m, 2H), 8.51-8.55 (m, 2H), 9.57 (s, 2H); ^{13}C {^{1}H}NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 11.6, 19.1, 103.4, 107.6, 118.8, 119.7, 127.6, 127.8, 132.5, 133.9, 152.61; IR: ν = 3064, 2940, 2888, 2863, 2142, 2113, 1459, 1278; UV-Vis λ_{max} (hexane): 630 nm; ε(630 nm) = 16135 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max} (hexane): 637 nm; HR-MS (Electrospray ionization, ESI): *m/z* calcd. for $C_{36}H_{49}N_2SSi_2$: $[M+H]^+$ 597.31495, found: 597.31566, correct isotope distribution; Elemental analysis: calcd. for $C_{36}H_{48}N_2SSi_2$ C 72.43, H 8.10, N 4.69, found: C 72.27, H 8.05, N 4.45.

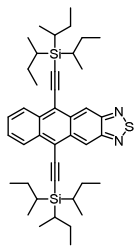
S5.2.7 9,10-Bis[(tripropan-2-ylsilyl)ethynyl]anthracene-2,3-diamine (**14**)



Compound **11** (988 mg, 1.66 mmol) was dissolved in THF (35.0 mL) at 0°C under an inert atmosphere. LAH (327 mg, 8.62 mmol) was added slowly and the reaction mixture was warmed to ambient temperature. After 1 h the reaction was quenched with aqueous NH_4Cl (15 mL). After extraction with diethyl ether (200 mL) the combined organic phase was washed with aqueous ammonium chloride (30.0 mL), water (30.0 mL) and brine (30.0 mL). After drying over Na_2SO_4, evaporation of the solvent under reduced pressure gave the crude product, which was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate). The clean product **14** is a yellowish brown solid (599 mg, 1.05 mmol, 64 %).

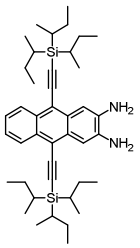
R_f = 0.27 (PE/EE = 4:1); m.p. >123 °C decomp.; ^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.24-1.30 (m, 42H), 3.82-3.93 (brs, 4H, NH), 7.45-7.49 (m, 2H), 7.79 (s, 2H), 8.48-8.52 (m, 2H); ^{13}C {^{1}H}NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 11.7, 19.1, 103.1, 104.4, 109.1, 115.2, 125.6, 126.9, 130.5, 131.2, 138.4; IR: ν = 3376, 3348, 3057, 2938, 2889, 2862, 2116, 1627, 1498, 1461 ; UV-Vis λ_{max} (hexane): 458 nm; ε(458 nm) = 22941 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max} (hexane): 503 nm; HR-MS (Electrospray ionization, ESI): *m/z* calcd. for $C_{36}H_{53}N_2Si_2$: $[M+H]^+$ 569.37418, found: 569.37363, correct isotope distribution; Elemental analysis: calcd. for $C_{36}H_{52}N_2Si_2$ C 75.99, H 9.21, N 4.92, found: C 75.50, H 9.10, N 4.91.

S5.2.8 5,10-Bis[(tributan-2-ylsilyl)ethynyl]anthra[2,3-*c*][1,2,5]thiadiazole (**12**)



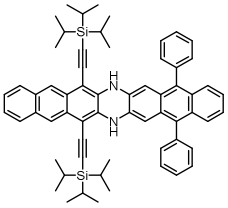
In a heat-gun dried Schlenk flask under an atmosphere of argon the tri-*sec*-butyl-silylacetylene (911 mg, 4.06 mmol) was dissolved in dry THF (27.0 mL). Under ice bath cooling a solution of *n*-BuLi in hexane (2.19 mL ,1.60 M, 3.50 mmol) was added. The ice bath was removed and the mixture was stirred for 1.5 h at room temperature. The anthra[2,3-*c*][1,2,5]thiadiazole-5,10-dione (**10**) (360 mg, 1.35 mmol) was added slowly, forming a brown solution, which was stirred at room temperature for 18 h. After quenching with water and extraction with diethyl ether, the combined organic layer was washed with aqueous NH_4Cl, water and brine. The solvent was removed and the resulting intermediate product was dissolved in acetic acid (15 mL). Potassium iodide (1.12 g, 6.75 mmol) and sodium hypophosphite (594 mg, 6.75 mmol) was added and the mixture was heated to 100°C for 1 h, forming a dark blue solution. After cooling to ambient temperature the reaction mixture was poured onto water and extraction with petroleum ether gave the crude product after evaporation of the solvent. The product **12** (147 mg, 216 µmol, 16%) was used for the next step after a facile flash chromatography without characterization due to instability.

S5.2.9 9,10-Bis[(tributan-2-ylsilyl)ethynyl]anthracene-2,3-diamine (**15**)



Under an atmosphere of nitrogen **12** (147 mg, 216 µmol) was dissolved in 15 mL of dry THF. Under ice bath cooling LAH (37 mg, 0.972 mmol) was added portionwise, which vanished the blue color to form a brown suspension. After 2 h the reaction was quenched with water (10 mL) and extracted with diethyl ether (50 mL). The combined organic layer was washed with aqueous ammonium chloride (20 mL), water (20 mL) and brine (20 mL). Drying over Mg_2SO_4 and evaporation o the solvent under reduced pressure gave the crude product **15** (20.1 mg, 30.6 µmol, 14%), which was used for the next step after a facile flash chromatography without characterization due to instability.

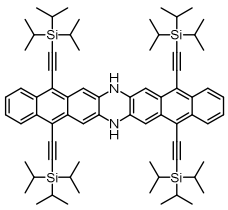
S5.2.10 5,18-Diphenyl-8,15-bis[(tripropan-2-ylsilyl)ethynyl]-7,16-dihydrodinaphtho[2,3-b:2',3'-i] phenazine (**18**)



GP2 was applied to diamino compound **17** (100 mg, 176 µmol) and dibromo arene **5** (104 mg, 212 µmol) in dioxane (3.00 mL). The reaction mixture was diluted in dichloromethane and washed aqueous ammonium chloride (10.0 mL), water (10.0 mL) and brine (10.0 mL). After re-extraction the combined organic layer were dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave the crude product, which was purified by flash column chromatography (silica gel, petroleum ether/ dichloromethane). The product **18** (94 mg, 105 µmol, 60%) was obtained as brown solid.

R_f = 0.60 (PE/DCM = 5:1); m.p. >250 °C decomp.; ^{1}H NMR (400.17 MHz, $CDCl_3$, 25 °C): δ = 1.12-1.22 (m, 42H), 6.49 (s, 2H), 7.13-7.17 (brs, 2H), 7.19-7.24 (m, 2H), 7.31-7.36 (m, 2H), 7.44-7.49 (m, 4H), 7.52-7.57 (m, 4H), 7.58-7.64 (m, 4H), 7.79-7.84 (m, 2H); ^{13}C {^{1}H}NMR (100.63 MHz, $CDCl_3$, 25 °C): δ = 11.5, 19.0, 97.6, 100.9, 104.5, 105.4, 122.8, 124.4, 125.1, 126.6, 127.5, 127.9, 127.9, 128.6, 128.7, 129.4, 129.6, 131.4, 131.6, 134.2, 134.4, 139.4; IR: ν = 3375, 3054, 2939, 2861, 2142, 1582, 1455; UV-Vis λ_{max} (hexane): 497 nm; ε(497 nm) = 78164 L·mol^{-1}·cm^{-1}; Fluorescence λ_{max} (hexane): 501 nm; HR-MS (Electrospray ionization, ESI): *m/z* calcd. for $C_{62}H_{63}N_2Si_2$: $[M+H]^+$ 895.48373, found: 895.48420, correct isotope distribution.

S5.2.11 5,9,14,18-Tetrakis[(tripropan-2-ylsilyl)ethynyl]-7,16-dihydrodinaphtho[2,3-b:2',3'-i]phenazine (**19**)

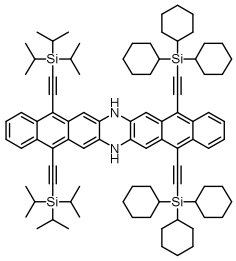


GP2 was applied to diamino compound **14** (93.0 mg, 163 µmol) and dibromo arene **7** (113.0 mg, 163 µmol) in dioxane (5.50 mL). The reaction mixture was diluted in dichloromethane and washed aqueous ammonium chloride (10.0 mL), water (10.0 mL) and brine (10.0 mL). After re-extraction the combined organic layer were dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave the crude product, which was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane). The product **19** (83 %, 184 mg, 135 µmol) was obtained as brown solid.

R_f = 0.45 (PE/DCM = 4:1); m.p. >250 °C decomp.; ^{1}H NMR (300.51 MHz, $CDCl_3$, 25 °C): δ = 1.25-1.33 (m, 84H), 6.32-6.39 (brs, 2H), 7.42-7.50 (m, 8H), 8.36-8.43 (m, 4H); ^{13}C {^{1}H}NMR (75.47 MHz, $C_2D_2Cl_4$, 25 °C): δ = 11.6, 18.7, 103.6, 104.0, 105.4, 115.2, 125.8, 126.5, 131.3, 131.5, 131.8; IR: ν = 3436, 3054,

2939, 2861, 2126, 1586, 1475; UV-Vis λ_{max} (hexane): 525 nm; ε(525 nm) = 63109 $L \cdot mol^{-1} \cdot cm^{-1}$; Fluorescence λ_{max} (hexane): 530 nm; HR-MS (Matrix-assisted laser desorption/ionization, MALDI): *m/z* calcd. for $C_{72}H_{98}N_2Si_4$: $[M]^+$ 1102.68016, found: 1102.68016, correct isotope distribution.

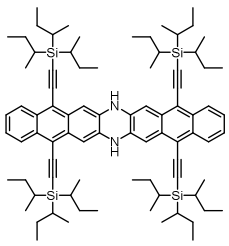
S5.2.14 5,18-bis[(tricyclohexylsilyl)ethynyl]-9,14-bis[(tripropan-2-ylsilyl)ethynyl]-7,16-dihydrodinaphtho[2,3-*b*:2',3'-*i*]phenazine (**20**)



GP3 was applied to diamino compound **14** (25.0 mg, 43.5 µmol) and dibromoarene **9** (34.0 mg, 36.3 µmol) in dioxane (2.00 mL). The reaction mixture was diluted in dichloromethane and washed aqueous ammonium chloride (10.0 mL), water (10.0 mL) and brine (10.0 mL). After re-extraction the combined organic layer were dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave the crude product, which was purified by flash column chromatography, silica gel, petroleum ether/dichloromethane). The product **20** (34 %, 20.1 mg, 15.0 µmol) was obtained as brown solid (m.p. >250 °C decomp.).

^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.11 (tt, 6H, *J* = 12.82 Hz, *J* = 2.76 Hz), 1.26-1.34 (m, 60H), 1.47-1.54 (m, 12H), 1.77-1.86 (m, 18H), 1.97-2.01 (m, 12H), 6.36-6.38 (brs, 2H), 7.41 (s, 2H), 7.43 (s, 2H), 7.44-7.49 (m, 4H), 8.36-8.38 (m, 4H); ^{13}C {^{1}H}NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 11.7, 19.1, 23.5, 27.2, 28.6, 29.0, 103.5, 104.0, 104.0, 104.2, 105.3, 105.5, 115.2, 115.3, 126.0, 126.0, 126.8, 126.9, 131.3, 131.8, 131.9, 131.9; IR: ν = 3431, 2917, 2845, 2120, 1585, 1471, 1428; UV-Vis λ_{max} (hexane): 524 nm; ε(524 nm) = 44495 $L \cdot mol^{-1} \cdot cm^{-1}$; Fluorescence λ_{max} (hexane): 530 nm; HR-MS (Electrospray ionization, ESI): *m/z* calcd. for $C_{90}H_{123}N_2Si_4$: $[M+H]^+$ 1343.87578, found: 1343.87646.

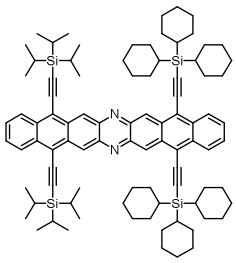
S5.2.12 5,9,14,18-Tetrakis[(tributan-2-ylsilyl)ethynyl]-7,16-dihydrodinaphtho[2,3-*b*:2',3'-*i*]phenazine (**21**)



GP3 was applied to diamino compound **15** (20.0 mg, 30.6 µmol) and dibromo arene **7** (30.0 mg, 38.5 µmol) in dioxane (2.00 mL). The reaction mixture was diluted in dichloromethane and washed aqueous ammonium chloride (10.0 mL), water (10.0 mL) and brine (10.0 mL). After re-extraction the combined organic layer were dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave the crude product, which was purified by flash column chromatography (silica gel, petroleum ether/dichloromethane). The product **21** (18 %, 7.10 mg, 5.50 µmol) was obtained as brown solid.

R_f = 0.58 (PE/DCM = 4:1); m.p. >250 °C decomp.; ^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.07-1.11 (m, 48H), 1.23-1.26 (m, 36H), 1.40-1.47 (m, 12H), 1.88-1.95 (m, 12H), 6.34-6.38 (brs, 2H), 7.42-7.47 (m, 8H), 8.36-8.40 (m, 4H); ^{13}C {^{1}H}NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 14.0, 14.0, 14.83, 19.3, 25.7, 104.1, 104.4, 105.4, 115.2, 126.0, 126.8, 131.4, 131.8, 131.9; IR: ν = 3433, 3060, 2955, 2924, 2897, 2128, 1586, 1471, 1428, 1378; UV-Vis λ_{max} (hexane): 524 nm; ε(524 nm)= 60609 $L \cdot mol^{-1} \cdot cm^{-1}$; Fluorescence λ_{max} (hexane): 530 nm; HR-MS (Matrix-assisted laser desorption/ionization, MALDI): *m/z* calcd. for $C_{84}H_{123}N_2Si_4$: $[M+H]^+$ 127.87578, found: 1271.87371, correct isotope distribution.

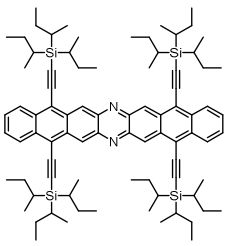
S5.2.14 5,18-Bis[(tricyclohexylsilyl)ethynyl]-9,14-bis[(tripropan-2-ylsilyl)ethynyl]dinaphtho[2,3-*b*:2',3'-*i*]phenazine (**24**)



The dihydrodiazaheptacene **20** (2.70 mg, 1.90 µmol) was dissolved in 600 µL of deuterated chloroform (for NMR studies) or dichloromethane (for optical and electronic investigations). 40.0 mg of MnO_2 was added and the mixture was stirred for exactly 40 s. At this point the mixture was filtered through a silica plug in a pipette into a NMR tube or glas vail to give a pure solution of **24**. Afterwards the solvent was evaporated as fast as possible under reduces pressure to obtain a solid sample of **24** and the dimers **28** as black solid with a red shine.

^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.21 (tt, 6H, *J* = 12.82 Hz, *J* = 2.76 Hz), 1.34-1.43 (m, 60H), 1.56-1.64 (m, 12H), 1.79-1.90 (m, 18H), 2.05-2.10 (m, 12H), 7.46-7.51 (m, 4H), 8.51-8.56 (m, 4H), 9.77 (s, 2H), 9.79 (s, 2H); ^{13}C {^{1}H} NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 11.7, 19.1, 23.5, 27.2, 28.6, 29.0, 103.6, 103.9, 108.0, 108.7, 119.5, 119.6, 127.9, 127.9, 127.9, 128.0, 129.2, 129.3, 133.4, 133.5, 134.4, 134.4, 142.3; IR: ν = 3064, 2918, 2846, 2141, 2118, 1445, 1379, 996; UV-Vis λ_{max} (hexane): 865 nm.

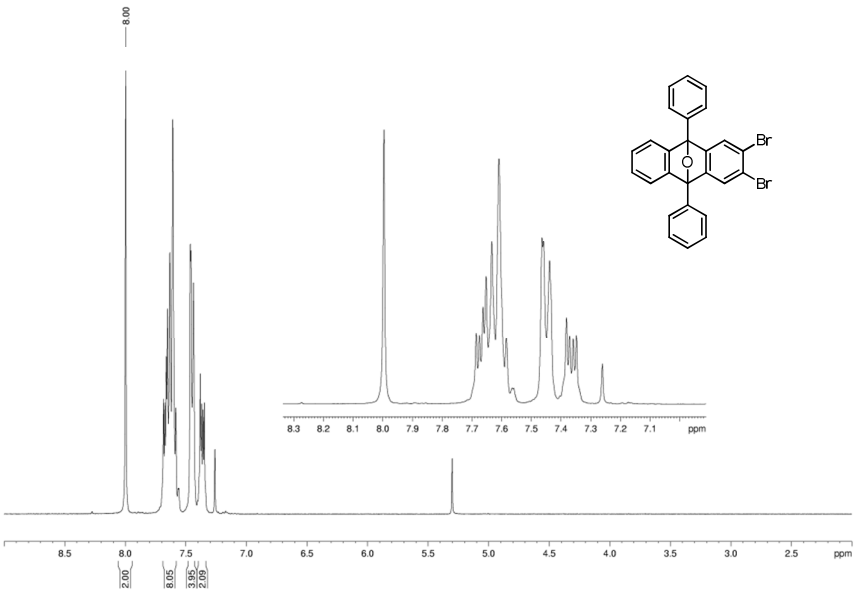
S5.2.13 5,9,14,18-tetrakis[(tributan-2-ylsilyl)ethynyl]dinaphtho[2,3-*b*:2',3'-*i*]phenazine (**25**)



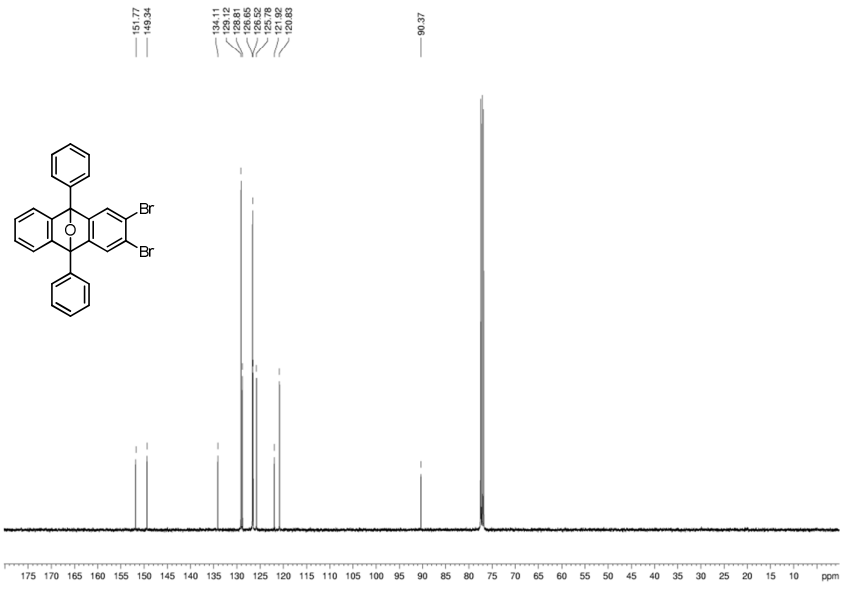
The dihydrodiazaheptacene **21** (2.4 mg, 1.90 µmol) was dissolved in 600 µL of deuterated chloroform. 40.0 mg of MnO_2 was added and the mixture was stirred for exactly 40 s. At this point the mixture was filtered through a silica plug in a pipette into a NMR tube or glas vail. NMRs were recorded over a period of 1 h. Afterwards the solvent was evaporated as fast as possible under reduces pressure to obtain a solid sample of **25** and the dimers **27** as black solid with a red shine..

^{1}H NMR (600.24 MHz, $CDCl_3$, 25 °C): δ = 1.08-1.16 (m, 34H), 1.16-1.22 (m, 12H), 1.24-1.27 (m, 4H), 1.30-1.36 (m, 32H), 1.47-1.56 (m, 12H), 1.94-2.03 (m, 12H), 7.44-7.50 (m, 8H), 8.47-8.53 (m, 4H), 9.77 (s, 4H); ^{13}C {^{1}H}NMR (150.93 MHz, $CDCl_3$, 25 °C): δ = 14.0, 14.0, 14.0, 14.9, 19.4, 25.8, 103.7, 109.0, 119.6, 127.9, 127.9, 129.3, 133.5, 134.3, 142.3; IR: ν = 3064, 2956, 2925, 2869, 2143, 1455, 1378, 1337, 1093, 1039, 998, 851, 760, 747, 704, 685, 648; UV-Vis λ_{max} (hexane): 859 nm; HR-MS (Matrix-assisted laser desorption/ionization, MALDI): *m/z* calcd. for $C_{84}H_{120}N_2Si_4$: $[M\cdot]^+$ 1268.85231, found: 1268.85649, *m/z* calcd. for $C_{84}H_{121}N_2Si_4$: $[M+H]^+$ 1269.86013, found: 1269.86083.

S7. ^{1}H and ^{13}C NMR spectra



FigureS 16: ^{1}H NMR of compound **4** in CD_2Cl_3.



FigureS 17: $^{13}C\{^{1}H\}$ NMR of compound **4** in CD_2Cl_2

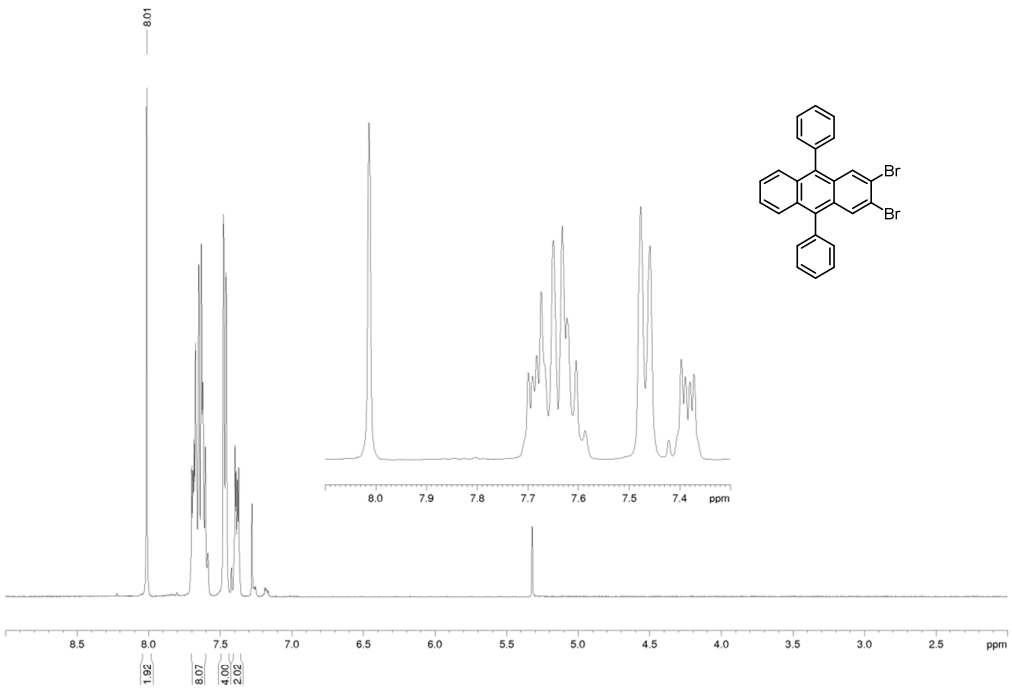


Figure S 18: ^{1}H NMR of compound **5** in $CDCl_3$.

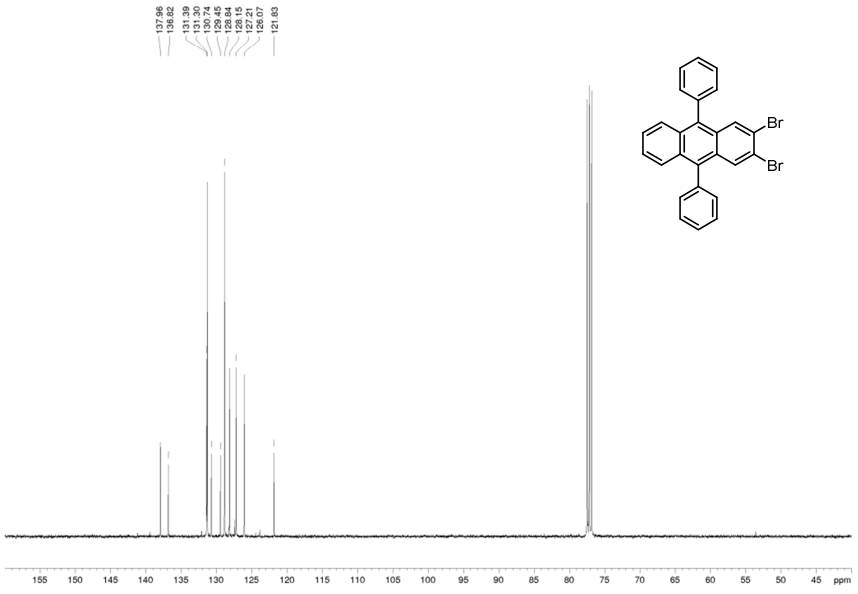


Figure S 19: ^{13}C $\{^{1}H\}$ NMR of compound **5** in $CDCl_3$

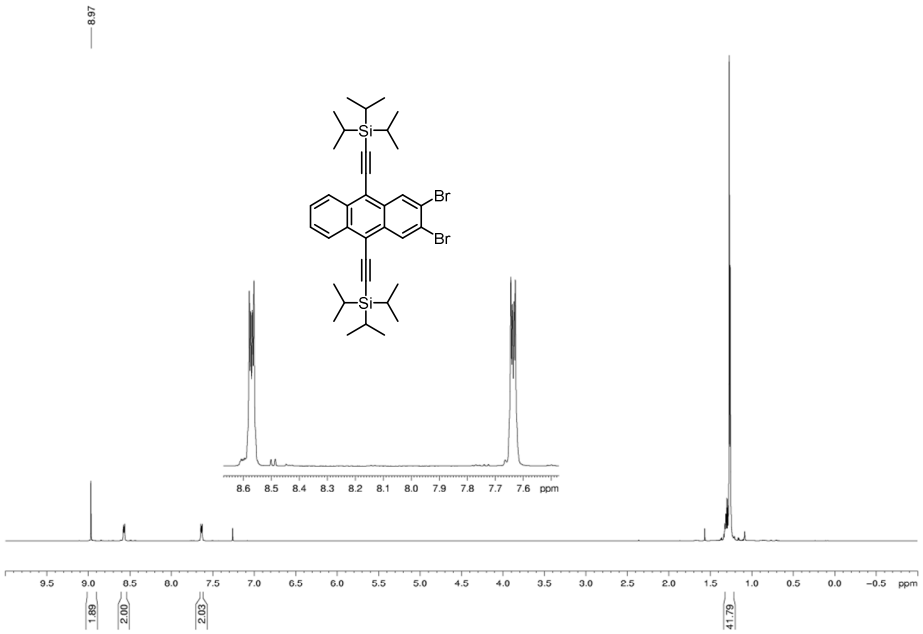


Figure S 20: ^{1}H NMR of compound **7** in $CDCl_3$.

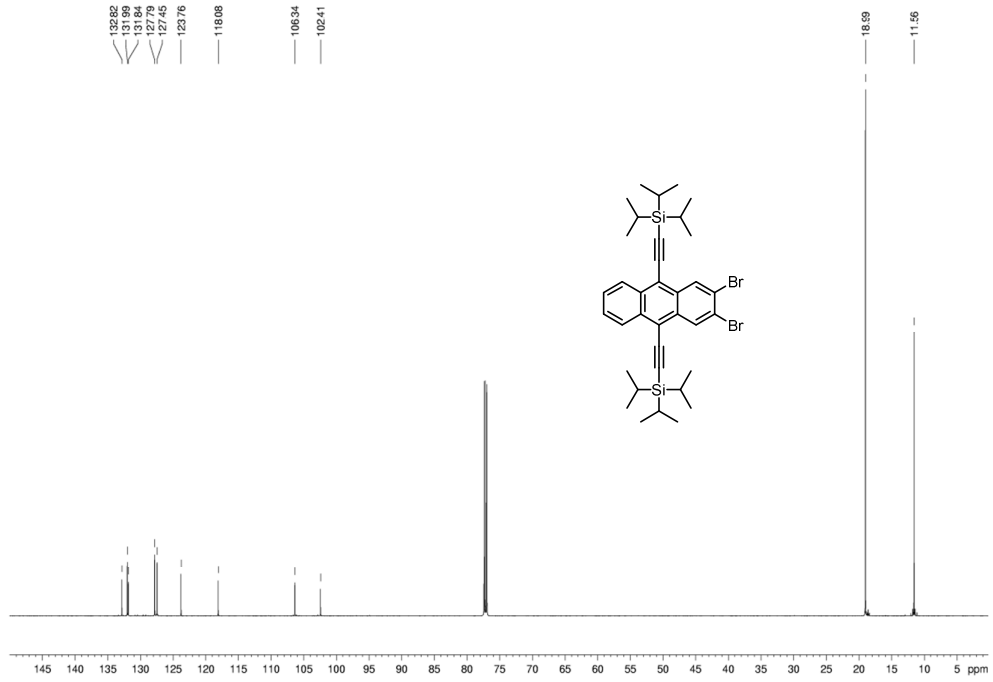


Figure S 21: ^{13}C {^{1}H} NMR of compound **7** in $CDCl_3$.

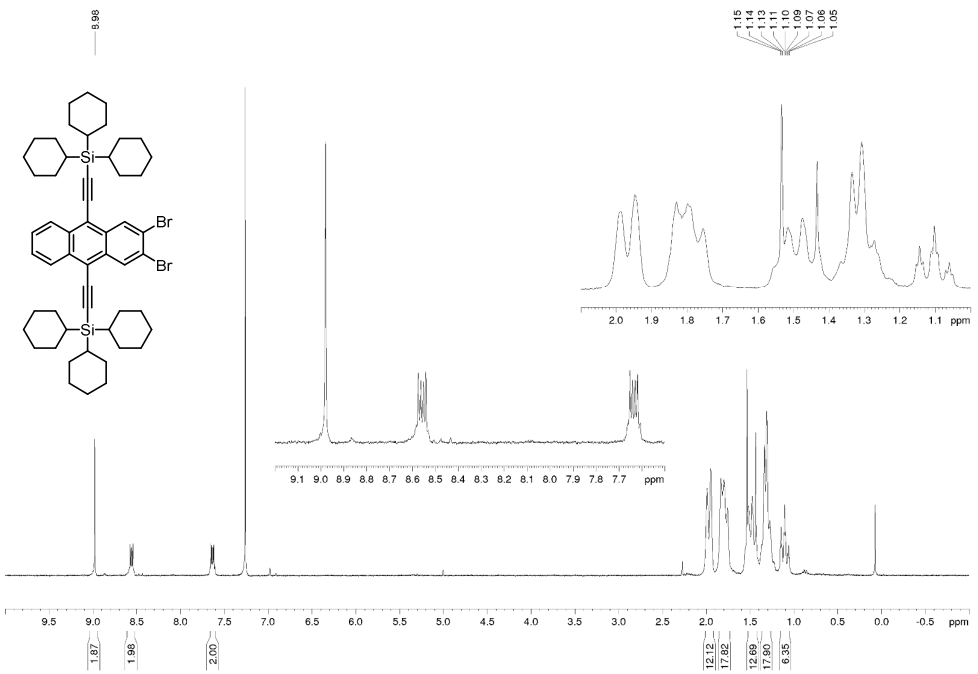


Figure S 22: ^{1}H NMR of compound **9** in $CDCl_3$.

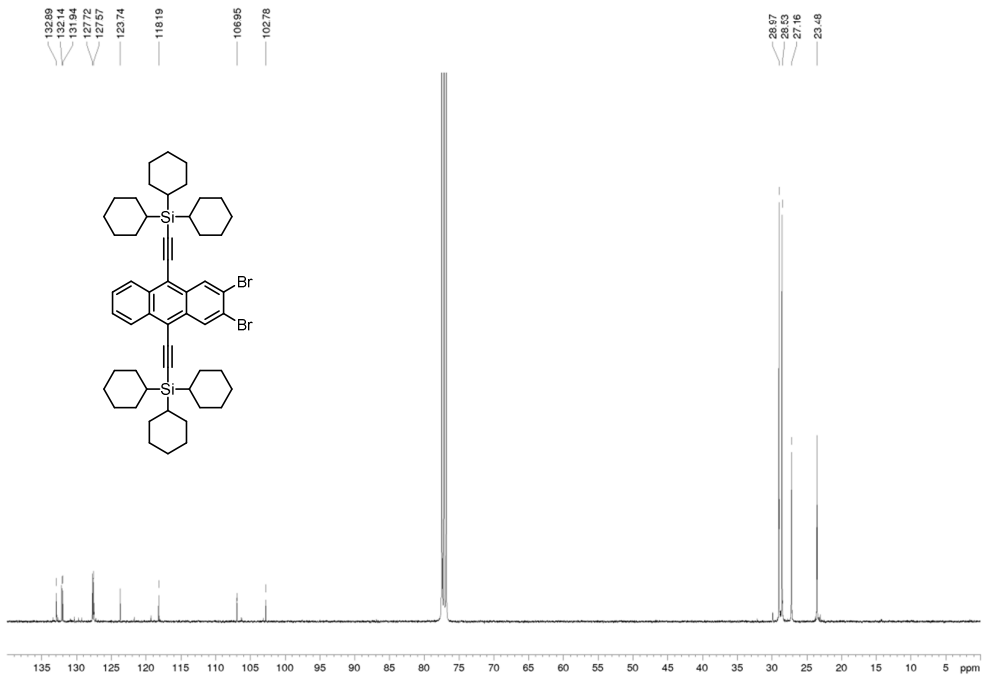


Figure S 23: ^{13}C {^{1}H} NMR of compound **9** in $CDCl_3$.

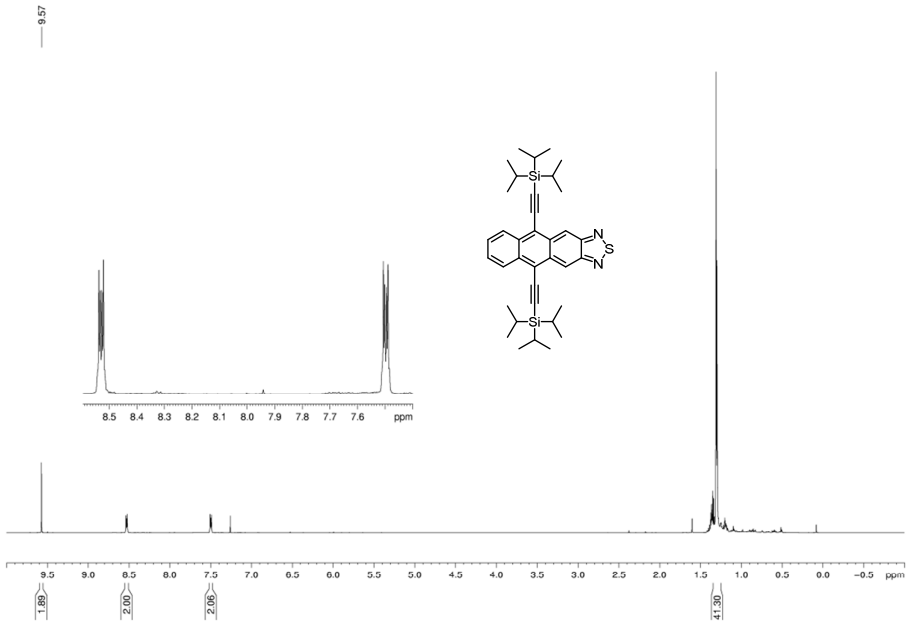


Figure S 24: ^{1}H NMR of compound **11** in $CDCl_3$.

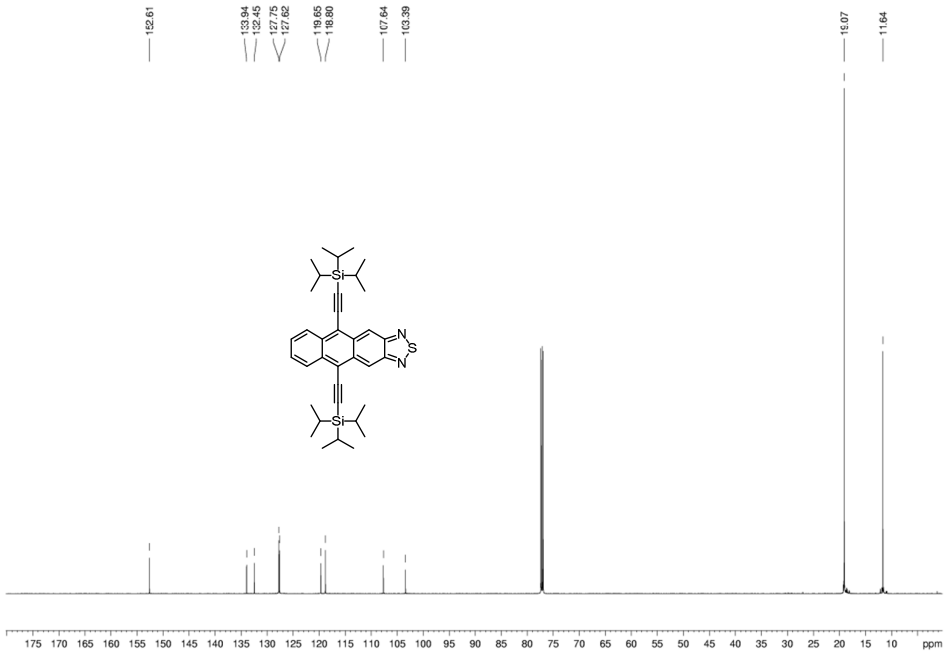


Figure S 25: ^{13}C $\{^{1}H\}$ NMR of compound **11** in $CDCl_3$.

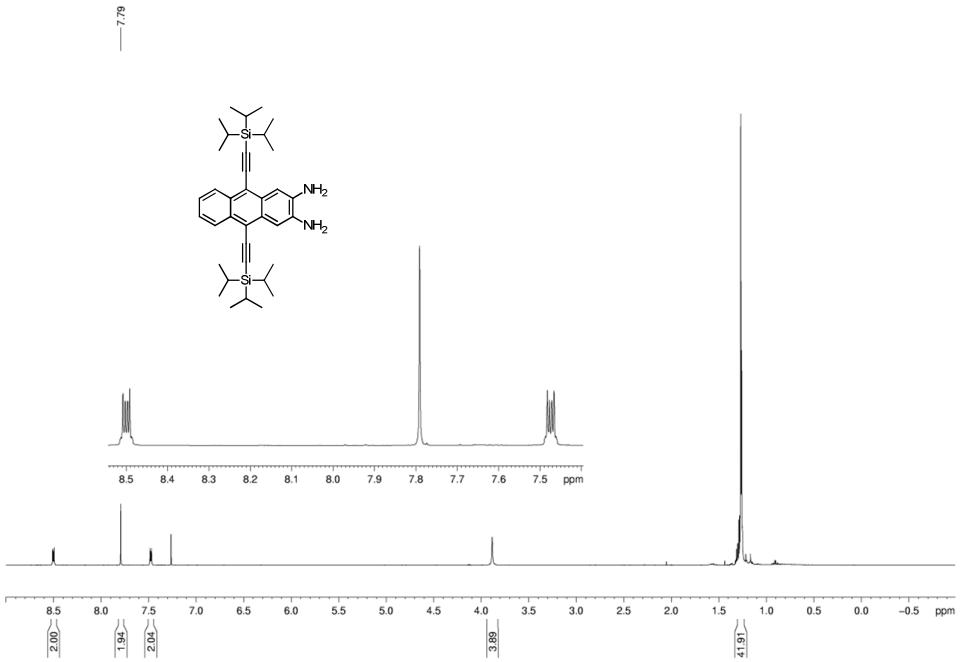


Figure S 26: ^{1}H NMR of compound **14** in $CDCl_3$.

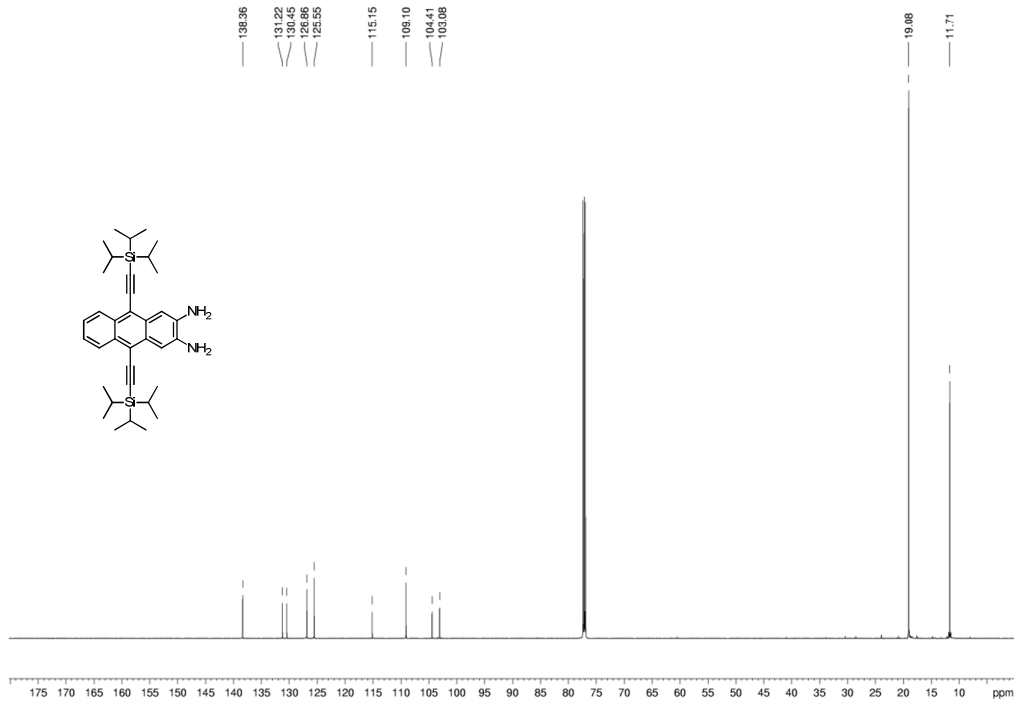


Figure S 27: $^{13}C\ \{^{1}H\}$ NMR of compound **14** in $CDCl_3$.

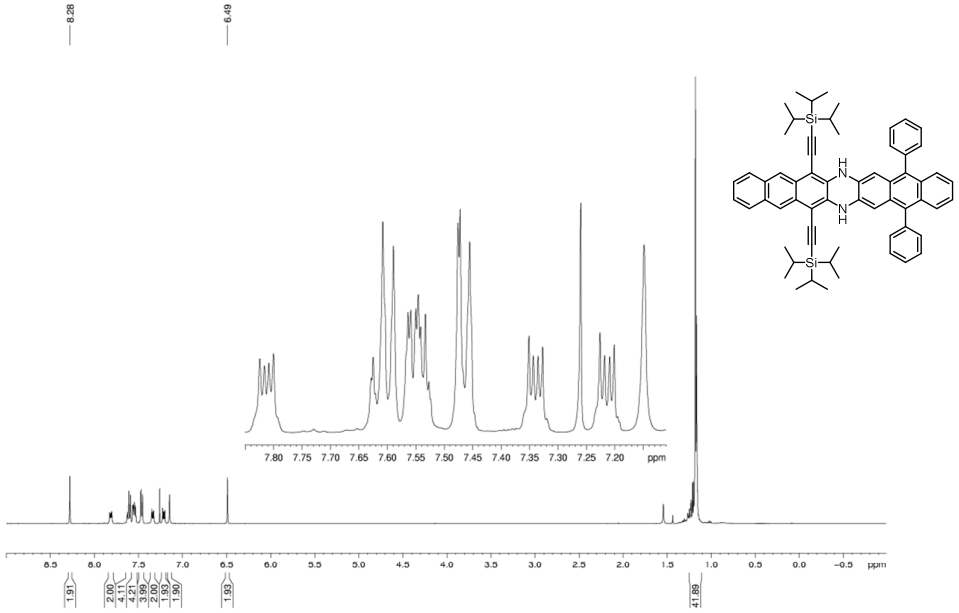


Figure S 28: ^{1}H NMR of compound **18** in $CDCl_3$.

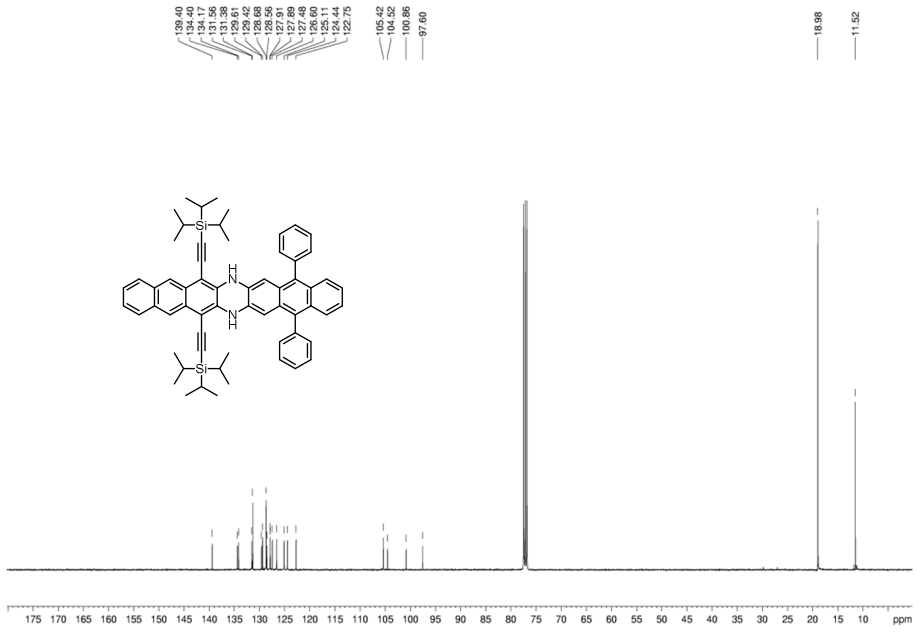


Figure S 29: ^{13}C $\{^{1}$H$\}$ NMR of compound **18** in $CDCl_3$.

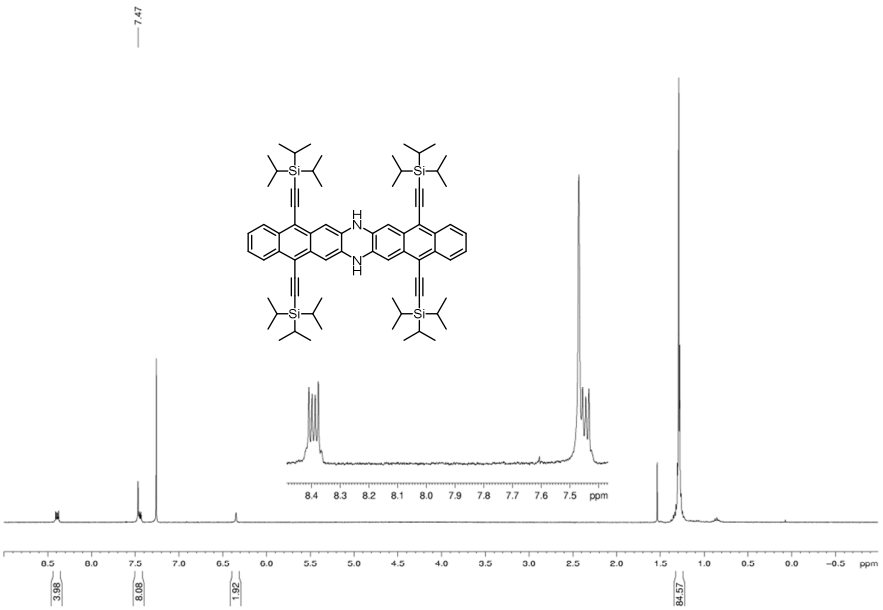


Figure S 30: ^{1}H NMR of compound **19** in $CDCl_3$.

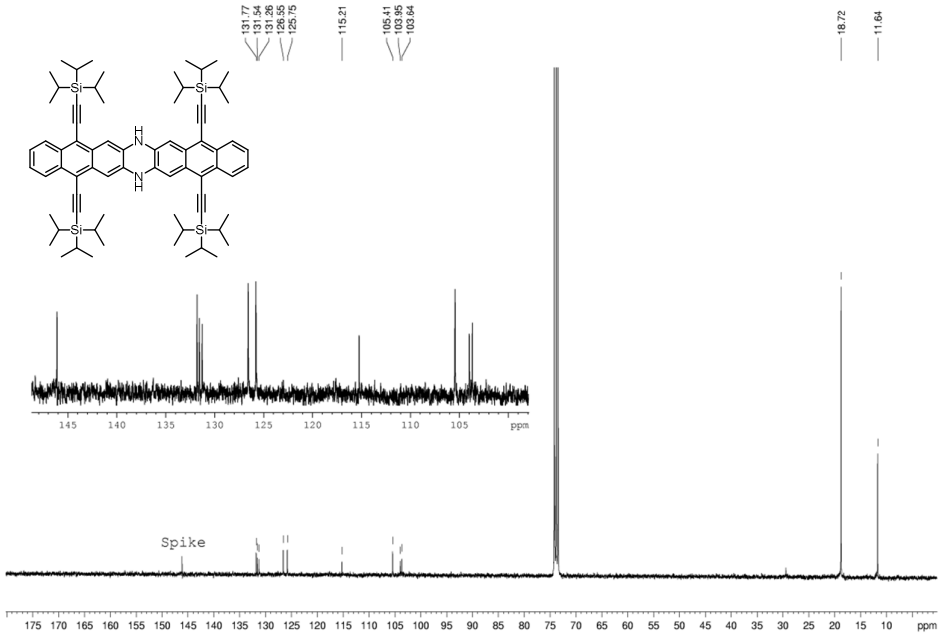


Figure S 31: ^{13}C $\{^{1}$H$\}$ NMR of compound **19** in $CDCl_3$.

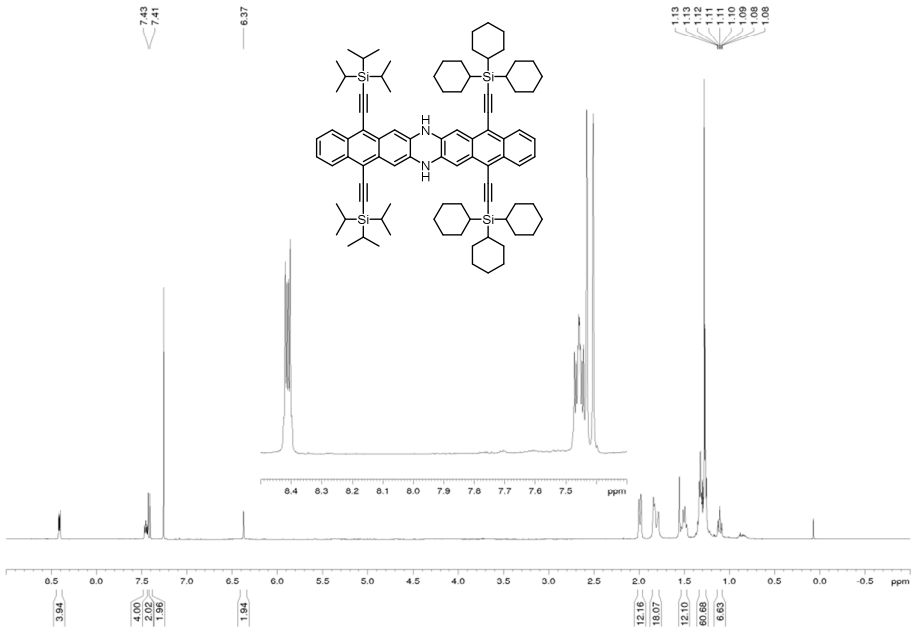


Figure S 32: ^{1}H NMR of compound **20** in $CDCl_3$.

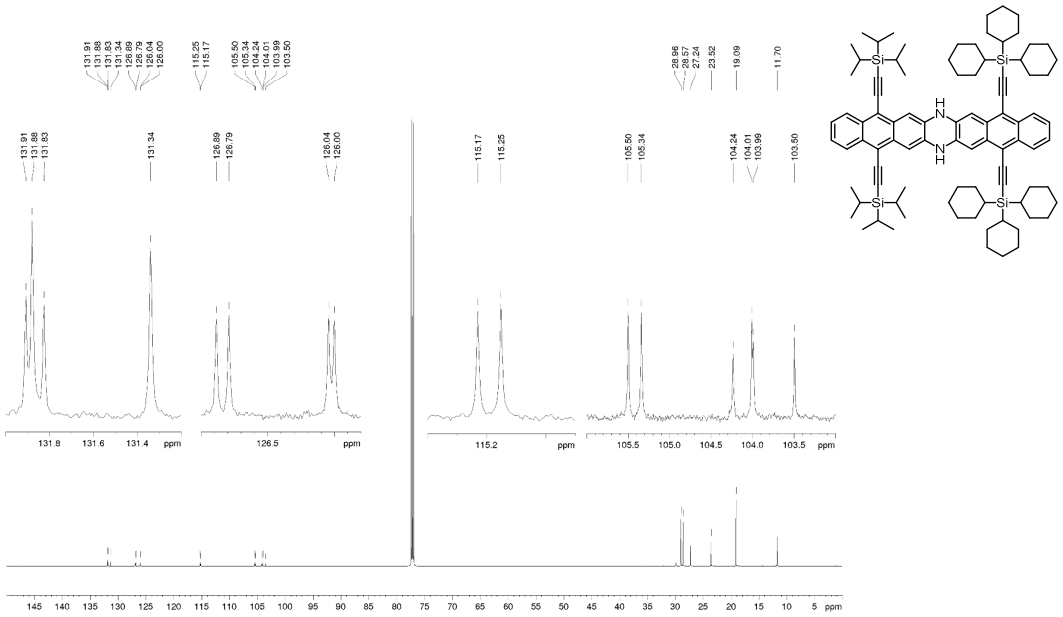


Figure S 33: ^{13}C $\{^{1}$H$\}$ NMR of compound **20** in $CDCl_3$.

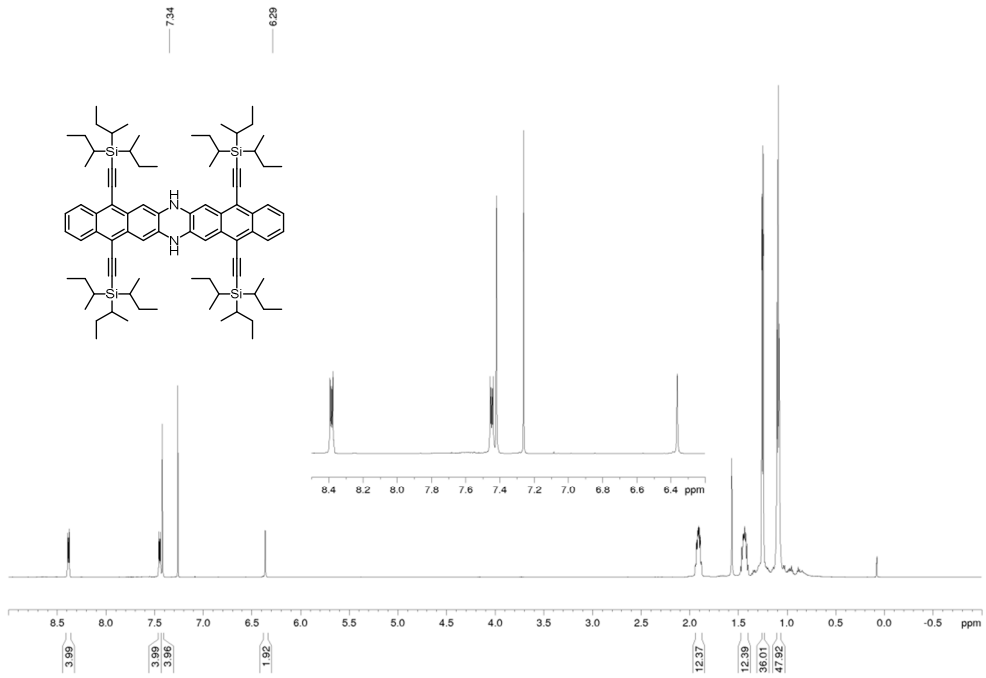


Figure S 34: ^{1}H NMR of compound **21** in $CDCl_3$.

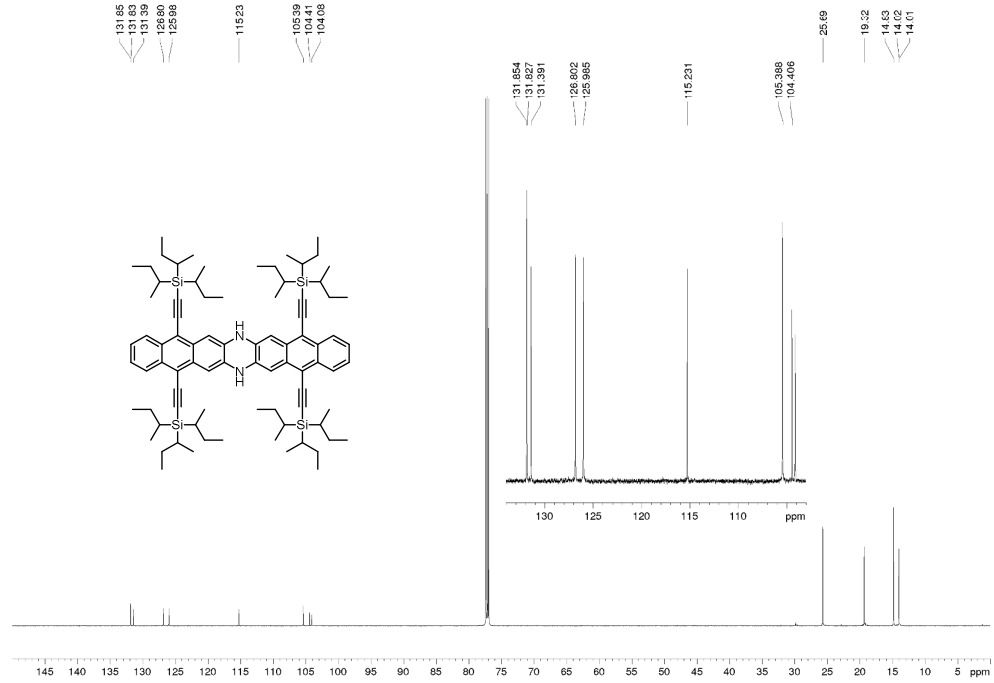


Figure S 35: ^{13}C $\{^{1}H\}$ NMR of compound **21** in $CDCl_3$.

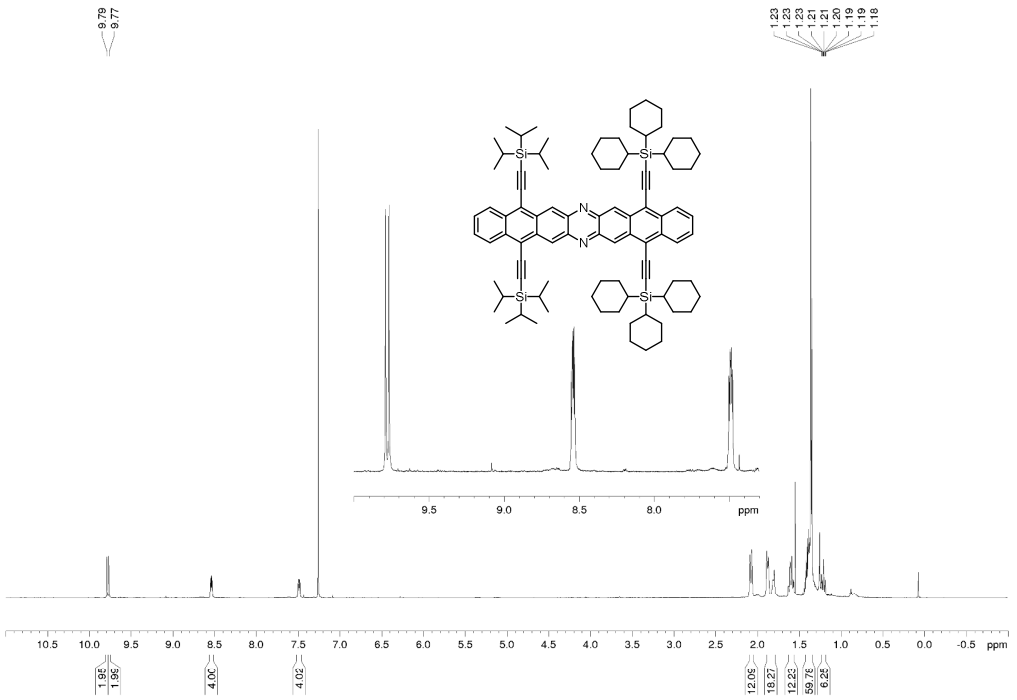


Figure S 36: ^{1}H NMR of compound **24** in $CDCl_3$.

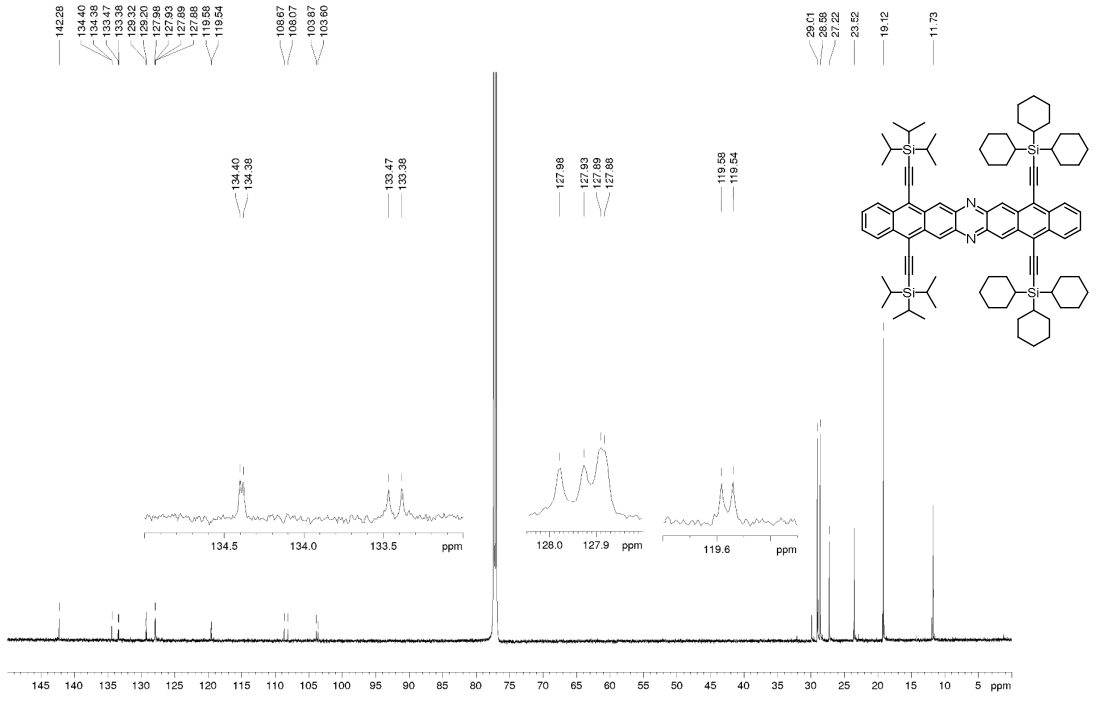


Figure S 37: ^{13}C $\{^{1}H\}$ NMR of compound **24** in $CDCl_3$

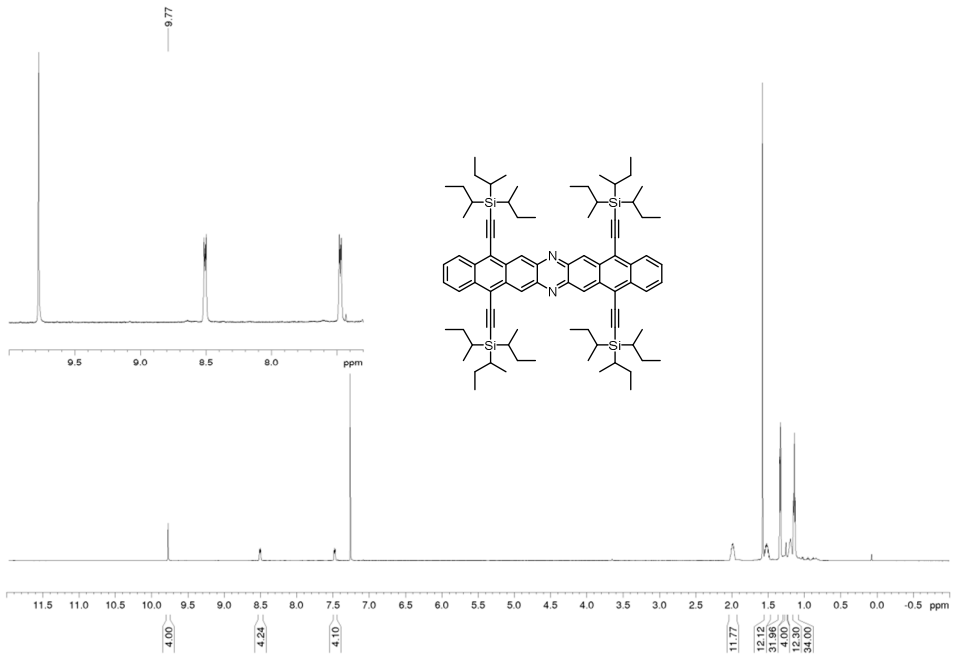


Figure S 38: ^{1}H NMR of compound **25** in $CDCl_3$.

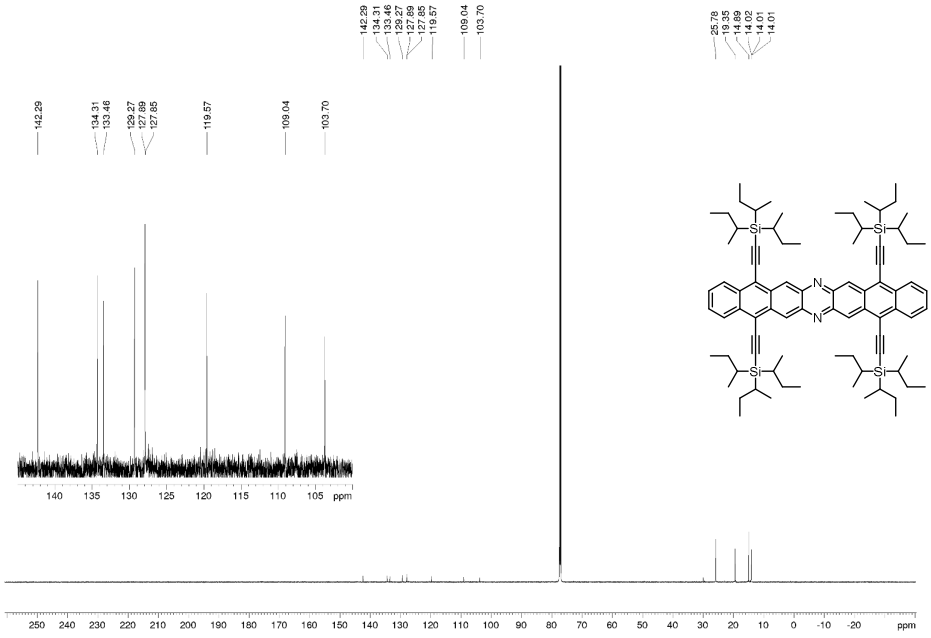


Figure S 39: ^{13}C {^{1}H} NMR of compound **25** in $CDCl_3$.

S8. References

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010,** *29*, 2176.

2. Bailey, D.; Williams, V. E. An efficient synthesis of substituted anthraquinones and naphthoquinones *Tetrahedron Lett.* 2004, *45*, 2511-2513

3. (a) Scholl, R.; Kačer, F. Chem. *Ber.* **1904**, *37*, 4531-4534. (b) Scholl, R. Chem. *Ber.* **1904**, *37*, 4427-4448. (c) Gorelik, M. V.; Lomzakova, V. I., Anthra[2,3-c][1,2,5]oxa-, -thio-, and -selenadiazole-5,10-diones and their amination *Khimiya Geterotsiklicheskikh Soedinenii* **1974**, *9*, 1275.

4. Appleton, A. L.; Miao, S.; Brombosz, S. M.; Berger, N. J.; Barlow, S.; Marder, S. R.; Lawrence, B. M.; Hardcastle, K. I.; Bunz, U. H. F., Alkynylated Aceno[2,1,3]thiadiazoles. *Org. Let.* **2009,** *11*, 5222.

5. Lim, Y.-F.; Shu, Y.; Parkin, S. R.; Anthony, J. E.; Malliaras, G. G., Soluble n-type pentacene derivatives as novel acceptors for organic solar cells *J. Mater. Chem.* **2009**, *19*, 3049-3056.