Supporting Information

Pyrene-bridged acenaphthenes: synthesis and properties of a diacenaphtho[1,2-e:1',2'-l]pyrene and its symmetrical nitrogen analogue

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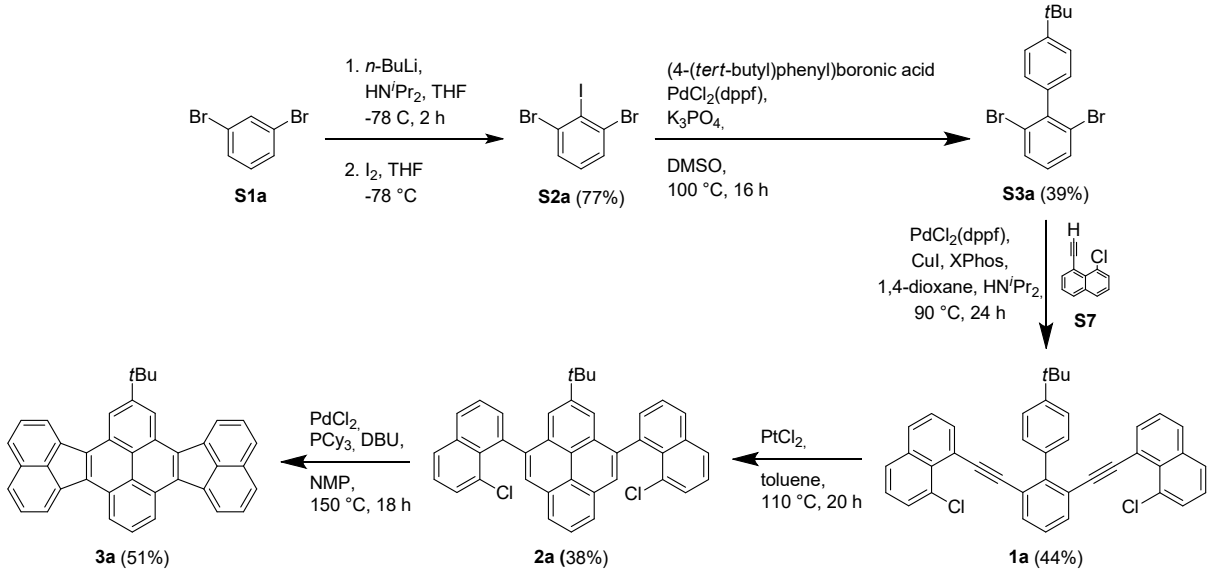
General information

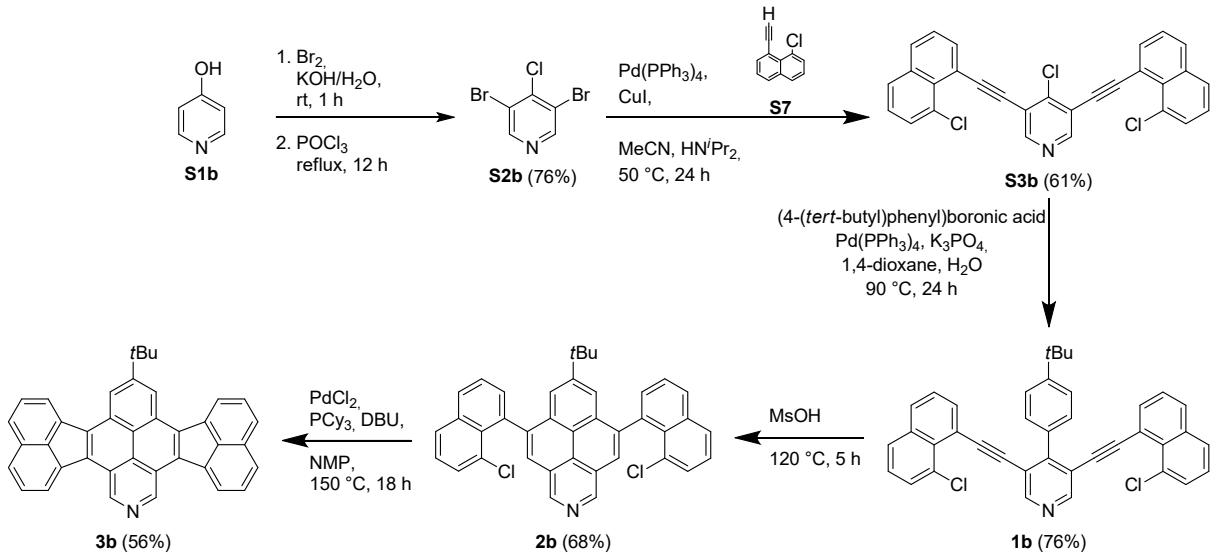
The nuclear magnetic resonance spectra ($^{1}H/^{13}C$) were recorded on a Bruker AVANCE 300 III, 250 II, or 500. The analyzed chemical shifts δ are referenced to residual solvents signals of the deuterated solvents $CDCl_3$ (δ = 7.26 ppm/77.0 ppm) and DMSO-d_6 (δ = 2.50 ppm/39.5 ppm). Multiplicities due to spin−spin correlation are reported as follows, s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, and further described through their coupling constants *J*. Infrared spectra (IR) were measured as attenuated total reflection (ATR) experiments with a Nicolet 380 FT-IR spectrometer. The signals have been characterized through their wave numbers ṽ and their corresponding absorption as very strong (vs), strong (s), medium (m) or weak (w). UV/Vis spectra were recorded on a Cary 60 UV−vis spectrophotometer and emission spectra with an Agilent Cary Eclipse fluorescence spectrophotometer. Cyclic voltammograms *were m*easured at room temperature in DCM ($c = 10^{-4}$ M*)* with 0.1 M n-Bu_4NPF_6 as a supporting electrolyte, glassy carbon working electrode, ANE2 ($Ag/AgNO_3$ *0.01 M in* CH_3CN) as reference electrode and Pt counter-electrode *(0.5 mm diameter platinum wire)* with ferrocene *(*$c = 10^{-3}$ M*, in* CH_3CN*)* as *an external* standard at a scan rate of 100 mV/*s.* The potentiostat used was a Parstat 4000 from Ametek. The working electrode is a 3 mm diameter (length 80, 6.35 mm outer diameter) glassy carbon disk electrode in a KeI-F coating that was polished on a polishing pad in aqueous alumina slurry (0.03 µm aluminapowder). The solvents were deoxygenated by purging with argon. The potential is given vs Fc/Fc+. The direction of scan is reductive with a starting potential of 1.5 V and a switching potential of -1.8 V. CVs are plotted using the IUPAC convention and shown in the range between −2.0 and 2.0 V. Basic and high-resolution mass spectra (MS/HRMS) were measured on instruments which are paired with a preceding gas chromatograph (GC) or liquid chromatograph (LC). The samples have been ionized through electron impact ionization (EI) on an Agilent 6890/5973 or Agilent 7890/5977 GC-MS equipped with a HP-5 capillary column using helium carrier gas or by applying electron spray ionization (ESI) on an Agilent 1200/6210 Time-of-Flight (TOF) LC−MS. Melting points (mp) were determined by a Micro-Hot-Stage GalenTM III Cambridge Instruments and are not corrected. X-ray single-crystal structure analysis was performed on a Bruker Apex Kappa-II CCD diffractometer.

Synthesis

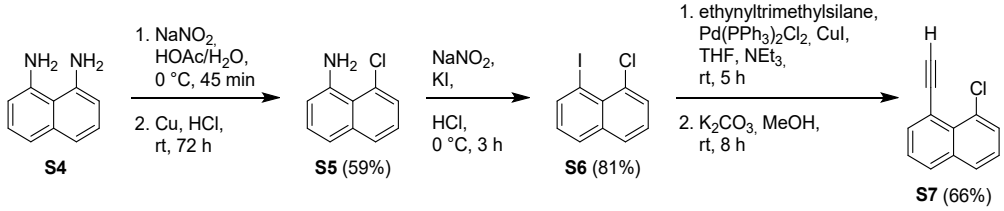
Reaction schemes



*Scheme S1: Synthesis of 8-(tert-butyl)diacenaphtho[1,2-e:1',2'-l]pyrene (**3a**)*



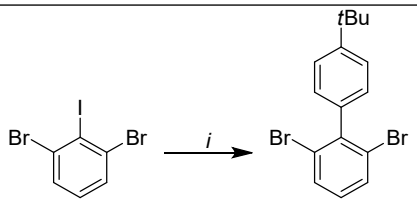
*Scheme S2: Synthesis of 17-(*tert*-butyl)acenaphtho[1',2':3,4]naphtho[2,1,8-*def*]acenaphtho[1,2-h]isoquinoline (**3b**)*



*Scheme S3: Synthesis of 1-chloro-8-ethynylnaphthalene (**S7**)*

Optimization tables

*Table S1: Optimization of suzuki reaction for **S3a**; i: (4-(tert-butyl)phenyl)boronic acid (1.5 eq.), [Pd] (0.05 eq.), base (2 eq.), solvent, T, t.*

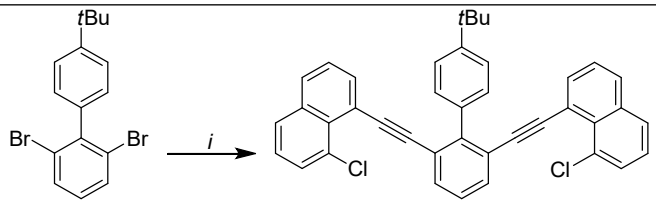


S2a **S3a**

Nr.	[Pd]	base	solvent	*T* [°C]	*t* [h]	yield[a] [%]
1	$Pd(dppf)Cl_2$	K_3PO_4	DMSO	100	24	39
2	$Pd(dppf)Cl_2$	K_3PO_4	DMSO	60	24	16
3	$Pd(PPh_3)_4$	K_3PO_4	THF/H_2O	80	24	34

[a] isolated yield

*Table S2: Optimization of sonogashira reaction for **1a**; i: [Pd] (0.05 eq.), **S7**, ligand (0.1 eq.), CuI (0.05 eq), solvent, T, t.*

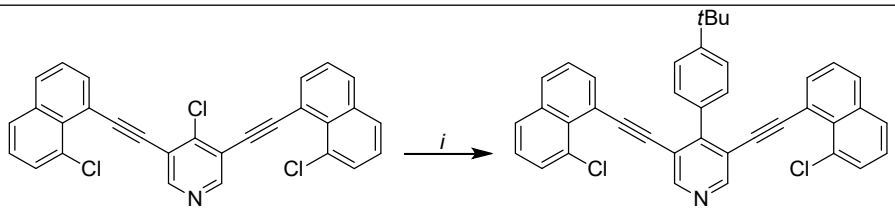


S3a **1a**

Nr.	[Pd]	eq. S7	ligand	solvent	*T* [°C]	*t* [h]	yield[a] [%]
1	$Pd(OAc)_2$	3	XPhos	1,4-dioxane/HN^iPr_2	90	24	36
2	$Pd(OAc)_2$	3	XPhos	toluene/HN^iPr_2	100	24	44

[a] isolated yield

*Table S3: Optimization of suzuki reaction for **1b**; i: (4-(tert-butyl)phenyl)boronic acid, [Pd] (0.05 eq.), base (2 eq.), solvent, T, t.*



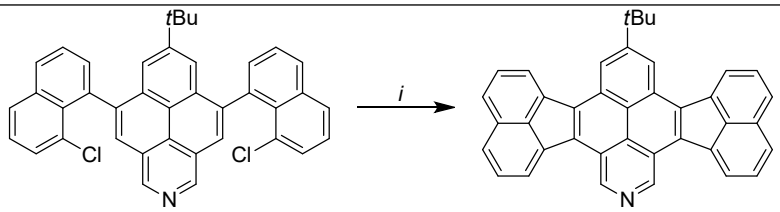
S3b **1b**

Nr.	[Pd]	eq. boronic acid	base	solvent	*T* [°C]	*t* [h]	yield[a] [%]
1[1]	$Pd(PPh_3)_4$	2	K_3PO_4	1,4-dioxane/H_2O	90	24	42

2	$Pd(PPh_3)_4$	1.2	K_3PO_4	1,4-dioxane/H_2O	90	24	76

[a] isolated yield

*Table S4: Optimization of CH activation for **3b**; i: [Pd], ligand, additive, base, solvent, T, t.*



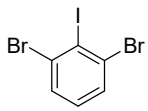
2b **3b**

Nr.	**[Pd] (eq.)**	**ligand (eq.)**	**additive (eq.)**	**base (eq.)**	**solvent**	***T* [°C]**	***t* [h]**	**yield [%][a]**
1[2]	$PdCl_2(PhCN)_2$ (0.1)	PCy_3 (0.2)	PivOH (0.4)	Cs_2CO_3 (2)	DMA	150	18	-
2[3]	$Pd(OAc)_2$ (1)	PCy_3HBF_4 (0.2)	-	K_2CO_3 (6)	DMA	130	48	-
3	$Pd_2(dba)_3$ (0.2)	-	-	K_3PO_4 (10)	DMF	140	18	-
4[4]	$PdCl_2$ (0.4)	PCy_3 (0.8)	-	DBU (6)	NMP	150	18	56

[a] isolated yield,

Reaction conditions and analytical data

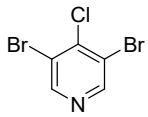
1,3-dibromo-2-iodobenzene (**S2a**)



According to literature-known procedure **S2a** was synthesized starting from 1,3-dibromobenzene (**S1a**).[5] In a 250 ml Schlenk-flask 40 ml THF were cooled to -78 °C and 1 eq. HN^iPr_2 (21.2 mmol, 3 ml) and 1.025 eq. *n*-BuLi in hexane (2.5 M, 21.7 mmol, 8.7 ml) was added to generate LDA *in-situ*. The mixture was stirred for 30 min. and 1 eq. (21.2 mmol, 5 g) 1,3-dibromobenzen was slowly added. The mixture was stirred for 2 h at -78 °C and quenched with 1.05 eq. iodine (22.25 mmol, 5.65 g) dissolved in 15 ml THF. The solution was washed with sat. $Na_2S_2O_3$-solution to remove excess of iodine and extracted with EtOAc. The organic phase was dried over Na_2SO_4 The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane to give colorless **S2a** in yield of 91% (6.97 g, 19.3 mmol). The spectral data are in accordance with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 131.3 (C), 131.1, 130.3 (CH), 109.3 (C).

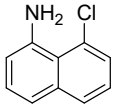
3,5-dibromo-4-chloropyridine (**S2b**)



According to literature-known procedure **S2b** was synthesized starting from pyridin-4-ol (**S1b**).[1] 5.14 g (54.0 mmol) of **S1b** and 2 eq. (108.0 mmol, 6.1 g) KOH were dissolved in 100 ml H_2O and cooled to 0 °C, then 2 eq. (108.0 mmol, 17.3 g, 5.6 ml) bromine was added dropwise. The mixture was stirred for 30 min, the precipitate was filtered off, washed with H_2O and dried in *vacuo*. The precipitate was dissolved in 50 ml $POCl_3$ and stirred in an oil bath under reflux for 12 h. The mixture was quenched with ice, neutralized with sat. $NaHCO_3$-solution and extracted with DCM. The organic phases were dried over Na_2SO_4. The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (10:1, $\mathbf{R_f}$ = 0.44) to give **S2b** as a colorless solid in 76% (11.12 g, 41.0 mmol) yield. The spectral data are in accordance with the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.65 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 150.8 (CH), 144.1 (C), 121.8 (C).

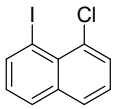
8-chloronaphthalen-1-amine (**S5**)



According to literature-known procedures **S5** was synthesized starting from 1,8-diaminonaphtalene (**S4**).[6,7] 20 g (126.0 mmol) of **S4** was dissolved in a mixture of 240 ml HOAc and 175 ml H_2O, 1.05 eq. (132.8 mmol, 9.16 g) $NaNO_2$ in 53 ml H_2O was added to the solution. The mixture was diluted with 40 ml H_2O and stirred at 0 °C for 45 min. The brown precipitate was filtered off, washed with H_2O, dried and used directly for the next reaction.[6] The brown powder and 0.1 eq. (12.6 mmol, 800 mg) Cu-powder was added slowly to 300 ml ice-cooled conc. hydrochloric acid. The mixture was stirred for 72 h at room temperature, then ice was added, and the solution was treated with ammonia until the pH was about 11. The mixture was extracted with DCM and dried over Na_2SO_4. The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (5:1, $\mathbf{R_f}$ = 0.37) to give **S5** as a colorless solid in 59% (13.16 g, 74.0 mmol) yield.[7] The spectral data are in accordance with the literature[8]:

^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 8.2 Hz, *J* = 1.4 Hz, 1H), 7.42 (dd, *J* = 7.4 Hz, *J* = 1.4 Hz, 1H), 7.35 – 7.27 (m, 3H), 6.76 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 1H), 5.06 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 143.7, 137.4, 129.5 (C), 128.4, 127.5, 127.1, 125.2 (CH), 120.1 (C), 118.8, 112.2 (CH).

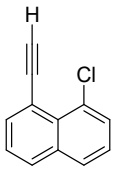
1-chloro-8-iodonaphthalene (**S6)**



According to literature-known procedure **S6** was synthesized.[9] 3 g (16.9 mmol) of **S5** was suspended in 57 ml HCl (2 M) and 1.5 eq. (25.4 mmol, 1.75 g) $NaNO_2$ in 17 ml H_2O was slowly added at 0 °C. After stirring for 30 min, 4 eq. (67.6 mmol, 11.2 g) KI in 17 ml H_2O was added. The mixture was stirred 3 h at room temperature and was quenched with sat. $NaHCO_3$- and sat. $Na_2S_2O_3$-solution. The mixture was extracted with DCM and dried over Na_2SO_4, the solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane ($\mathbf{R_f}$ = 0.54) to give **S6** as a yellow solid in 59% (3.95 g, 13.7 mmol) yield. The spectral data are in accordance with the literature[9]:

^{1}H NMR (300 MHz, $CDCl_3$) δ =8.38 (dd, *J* = 7.4 Hz, *J* = 1.3 Hz, 1H), 7.82 (ddd, *J* = 8.1 Hz, *J* = 1.3 Hz, *J* = 0.5 Hz, 1H), 7.77 (ddd, *J* = 8.1 Hz, *J* = 1.4 Hz, *J* = 0.5 Hz, 1H), 7.66 (dd, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.36 (dd, *J* = 8.2 Hz, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 8.1 Hz, *J* = 7.4 Hz, 1H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ = 144.1 (CH), 136.4, 131.6 (C), 130.4, 130.2 (CH), 129.5 (C), 129.3, 127.1, 125.8 (CH), 88.3 (C).

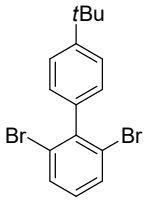
1-chloro-8-ethynylnaphthalene (**S7**)



According to literature-known procedure **S7** was synthesized.[9] Under an Ar-atmosphere **S6** (3.9 g 13.5 mmol), 0.05 eq. (0.67 mmol, 471 mg) $PdCl_2(PPh_3)_2$ and 0.05 eq. (0.67 mmol, 128 mg) CuI were dissolved in 10 ml NEt_3 and 30 ml THF, then 1.5 eq. (20.1 mmol, 1.98 g, 2.78 ml) ethynyltrimethylsilane was added. The solution was stirred 5 h at room temperature. The mixture was quenched with H_2O, extracted with DCM and dried over Na_2SO_4, the solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane ($\mathbf{R_f}$ = 0.45) to give a pale-yellow oil. The oil was dissolved in 45 ml MeOH and 1 eq. (13.5 mmol, 1.87 g) K_2CO_3 was added. The solution was stirred 8 h at room temperature. The mixture was quenched with H_2O, extracted with DCM and dried over Na_2SO_4, the solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane ($\mathbf{R_f}$ = 0.43) to give **S7** as a brown solid in 66% (1.66 g, 8.9 mmol) yield. The spectral data are in accordance with the literature[9]:

^{1}H NMR (250 MHz, $CDCl_3$) δ = 7.89 – 7.81 (m, 2H), 7.75 (ddd, *J* = 8.2 Hz, *J* = 1.4 Hz, *J* = 0.5 Hz, 1H), 7.59 (dd, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.46 – 7.32 (m, 2H), 3.53 (s, 1H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ = 136.9 (CH), 135.5, 131.7 (C), 130.2 (CH), 130.1 (C), 129.6, 128.3, 126.1, 125.6 (CH), 118.5 (C), 84.6, 84.2 (C≡C).

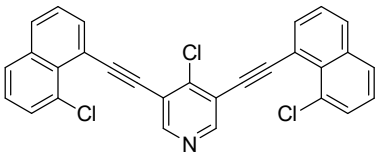
2,6-dibromo-4'-(*tert*-butyl)-1,1'-biphenyl (**S3a**)



In a pressure tube, 500 mg (1.382 mmol) of **S2a**, 0.05 eq. (0.069 mmol, 51 mg) $Pd(dppf)Cl_2$, 2 eq. (2.764 mmol, 594 mg) K_3PO_4 and 1.5 eq. (2.073 mmol, 374 mg) (4-(*tert*-butyl)phenyl)boronic acid were dissolved in 6 mL of DMSO under argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 24 h at 100 °C in a heating block. The reaction mixture was cooled to room temperature and quenched with H_2O, extracted with DCM and dried over Na_2SO_4, the solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane ($\mathbf{R_f}$ = 0.66) to give **S3a** as a colorless oil in 39% (200.1 mg, 0.544 mmol) yield. The spectral data are in accordance with the literature.[10]

1H NMR (500 MHz, $CDCl_3$) δ = 7.64 (d, ^3J = 8.0 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.19 – 7.16 (m, 2H), 7.05 (t, ^3J = 8.0 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.8, 143.1, 138.1 (C), 131.8, 129.6, 128.7, 125.0 (CH), 124.8, 34.6 (C), 31.4 (CH_3).

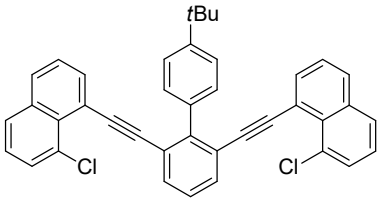
4-chloro-3,5-*bis*((8-chloronaphthalen-1-yl)ethynyl)pyridine (**S3b**)



According to a modified literature procedure unknown **S3b** was synthesized.[1] In a pressure tube, 200 mg (0.74 mmol) of **S2b**, 0.05 eq. (0.037 mmol, 43 mg) $Pd(PPh_3)_4$, 0.05 eq. (0.037 mmol, 7 mg) CuI and 2.2 eq. (1.62 mmol, 303 mg) **S7** were dissolved in 2 mL of HN^iPr_2 and 4 mL of MeCN under argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 24 h at 50 °C in a heating block. The reaction mixture was cooled to room temperature and quenched with H_2O, the precipitate was filtered off and washed several times with water, heptane, ethyl acetate and a little DCM. After drying *in vacuo*, **S3b** was isolated as a colorless solid in a yield of 61% (217.8 mg, 0.45 mmol).

mp. 186-189 °C. **^{1}H NMR** (250 MHz, DMSO, 100 °C) δ = 8.79 (s, 2H), 8.16 – 7.96 (m, 6H), 7.80 – 7.51 (m, 6H). **^{13}C NMR** (63 MHz, DMSO, 100 °C) δ = 150.7, 136.1 (CH), 134.9 (C), 130.7 (CH), 129.8 (C), 129.4, 128.3, 126.3, 125.6 (CH), 120.2, 116.8 (C), 98.0, 88.9 (C≡C). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1418 (m), 1401 (m), 1197 (m), 816 (vs), 785 (m), 752 (vs), 729 (m), 622 (m), 548 (m). **MS** (EI, 70 eV): m/z (%) = 481 (36, M^+), 348 (52), 242 (91), 241 (93), 240 (51), 192 (62), 188 (58), 187 (91), 174 (100), 173 (96), 182 (58). **HRMS** (ESI-TOF): calculated for $C_{29}H_{15}Cl_3N$ ($[M+H]^+$) 482.0270, found 482.0280.

8,8'-((4'-(*tert*-butyl)-[1,1'-biphenyl]-2,6-diyl)*bis*(ethyne-2,1-diyl))*bis*(1-chloronaphthalene) (**1a**)

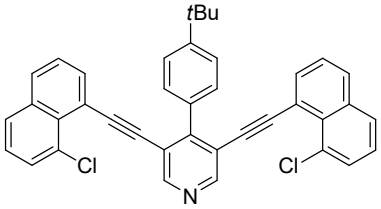


In a pressure tube, 100 mg (0.272 mmol) of **S3a**, 0.05 eq. (0.014 mmol, 3 mg) $Pd(OAc)_2$, 0.05 eq. (0.014 mmol, 3 mg) CuI, 0.1 eq. (0.027 mmol, 13 mg) XPhos and 3 eq. (0.816 mmol, 152 mg) **S7** were dissolved in 1 mL of HN^iPr_2 and 2 mL of toluene under an argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 24 h at 100 °C in a heating block. The reaction mixture was cooled to room temperature and quenched with H_2O, extracted with DCM and dried over Na_2SO_4. The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (20:1, $\mathbf{R_f}$ = 0.33) to give **1a** as a colorless solid in 44% (68.9 mg, 0.119 mmol) yield.

mp. 129-131 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.73 – 7.69 (m, 3H), 7.68 – 7.64 (m, 3H), 7.62 – 7.58 (m, 2H), 7.55 – 7.49 (m, 4H), 7.38 – 7.27 (m, 6H), 7.24 (d, *J* = 2.2 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 150.3, 146.1, 136.7 (C), 135.7 (CH), 135.5, 131.9 (C), 131.4, 130.3 (CH), 129.5 (C), 129.3, 129.3, 128.1, 127.0, 125.9, 125.5, 124.5 (CH), 124.1, 119.9 (C), 95.8, 93.9 (C≡C), 34.7 (C), 31.5 (CH_3). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1362 (m), 1197 (m), 832 (m), 816 (s), 804 (m), 752 (vs), 732 (m), 604 (m), 587 (m). **MS** (EI, 70 eV): m/z (%) = 578

(35, M^+), 523 (66), 522 (66), 486 (68), 452 (68), 451 (71), 450 (73), 225 (100), 224 (79). **HRMS** (EI): calculated for $C_{40}H_{28}Cl_2$ ($[M]^+$) 578.15626, found 578.15545; calculated for $C_{40}H_{28}Cl_1{}^{37}Cl_1$ ($[M]^+$) 580.15331, found 580.15411.

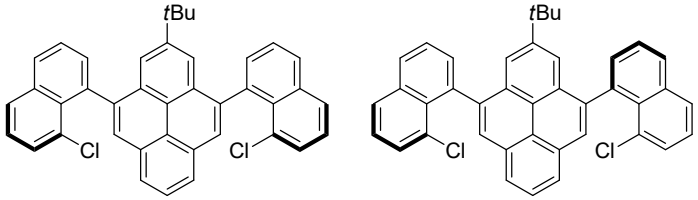
4-(4-(*tert*-butyl)phenyl)-3,5-*bis*((8-chloronaphthalen-1-yl)ethynyl)pyridine (**1b**)



In a pressure tube, 100 mg (0.207 mmol) of **S3b**, 0.05 eq. (0.01 mmol, 12 mg) $Pd(PPh_3)_4$, 2 eq. (0.414 mmol, 88 mg) K_3PO_4 and 1.2 eq. (0.248 mmol, 44 mg) (4-(*tert*-butyl)phenyl)boronic acid were dissolved in 3 mL of 1.4-dioxane and 1 mL of H_2O under an argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 24 h at 90 °C in a heating block. The reaction mixture was cooled to room temperature and quenched with H_2O, extracted with DCM and dried over Na_2SO_4. The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (4:1, $\mathbf{R_f}$ = 0.27) to give **1b** as a colorless solid in 76% (91.5 mg, 0.158 mmol) yield.

mp. 192-195 °C.**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.87 (s, 2H), 7.78 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 2H), 7.74 – 7.66 (m, 4H), 7.59 – 7.52 (m, 4H), 7.46 (dd, *J* = 7.3 Hz, *J* = 1.3 Hz, 2H), 7.35 (td, *J* = 7.8 Hz, *J* = 2.2 Hz, 4H), 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 151.7 (C), 136.0 (CH), 135.4, 133.8, 131.8 (C), 130.0, 129.6 (CH), 129.5 (C), 129.5, 128.2, 126.1, 125.5, 124.8 (CH), 119.1 (C), 96.5, 92.5 (C≡C), 34.8 (C), 31.4 (CH_3). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1397 (m), 1362 (m), 1197 (m), 835 (m), 814 (s), 752 (vs), 699 (m), 581 (m), 546 (m). **MS** (EI, 70 eV): m/z (%) = 579 (17, M^+), 527 (14), 526 (24), 525 (69), 524 (43), 523 (100), 589 (12), 488 (25), 452 (27), 451 (26). **HRMS** (ESI-TOF): calculated for $C_{39}H_{28}Cl_2N$ ($[M+H]^+$) 580.1599, found 580.1606.

2-(*tert*-butyl)-4,10-bis(8-chloronaphthalen-1-yl)pyrene (**2a**)

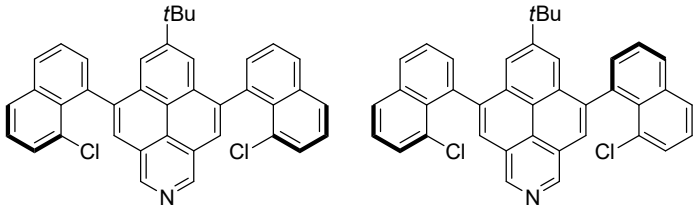


According to modified literature-known procedure unknown **2a** was synthesized.[11] In a pressure tube, 100 mg (0.173 mmol) of **1a** and 1 eq. $PtCl_2$ (0.173 mmol, 45 mg) were dissolved in 3 mL of toluene under an argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 20 h at 110 °C in a heating block. The reaction mixture was cooled to room temperature, quenched with H_2O, extracted with DCM and dried over Na_2SO_4. The solvent was distilled off in *vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (20:1, $\mathbf{R_f}$ = 0.40) to give **2a** as a yellow solid, as mixture of two atropisomers, in 38% (38.0 mg, 0.066 mmol) yield.

mp. 125-128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.18, 8.17 (2 s, 4H), 8.06 – 8.00 (m, 10H), 7.96 – 7.93 (m, 4H), 7.78 – 7.74 (m, 2H), 7.71 – 7.64 (m, 6H), 7.61 – 7.58 (m, 4H), 7.47 – 7.39 (m, 8H), 0.99, 0.98 (2 s,18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 148.4, 148.2, 141.1,

141.1, 137.7, 137.7, 135.9, 132.5, 132.4 (C), 131.9 (CH), 131.7 (C), 131.7 (CH), 130.6, 130.6, 130.2 (C), 129.2, 129.2, 129.1, 128.2, 128.2, 127.2, 127.2, 125.9, 125.8, 125.8, 125.7, 125.6, 124.6 (CH), 124.0, 124.0, 122.1, 122.0 (C), 121.1, 121.0 (CH), 34.9, 34.9 (C), 31.4, 31.3 (CH_3). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1195 (m), 905 (m), 888 (m), 822 (s), 812 (m), 779 (m), 762 (vs), 729 (s), 707 (m). **MS** (EI, 70 eV): m/z (%) = 578 (71, M^+), 489 (50), 488 (56), 487 (66), 486 (57), 452 (67), 451 (68), 450 (65), 238 (53), 237 (77), 231 (77), 225 (100), 44 (58). **HRMS** (EI): calculated for $C_{40}H_{28}Cl_2$ ([M]$^+$) 578.15626, found 578.15566; calculated for $C_{40}H_{28}Cl_1{}^{37}Cl_1$ ([M]$^+$) 580.15331, found 580.15497.

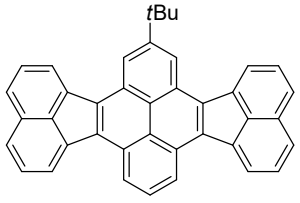
7-(*tert*-butyl)-5,9-*bis*(8-chloronaphthalen-1-yl)naphtho[2,1,8-*def*]isoquinoline (**2b**)



According to literature-known procedure unknown **2b** was synthesized.[1] In a pressure tube, 100 mg (0.172 mmol) of **1b** were dissolved in 60 eq. (10.32 mmol, 993 mg, 670 µl) MsOH. The pressure tube was sealed with a Teflon cap and the solution was stirred for 5 h at 120 °C in a heating block. The reaction mixture was cooled to room temperature, neutralized with sat. $NaHCO_3$-solution and extracted with DCM. The combined organic phases were dried over Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (1:1, $\mathbf{R_f}$ = 0.45) to give **2b** as a yellow solid, as mixture of two atropisomers, in a yield of 68% (67.8 mg, 0,117 mmol).

mp. 132-135 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.43 (s, 4H), 8.09 – 8.05 (m, 8H), 7.97 – 7.94 (m, 4H), 7.76 – 7.74 (m, 2H), 7.70 – 7.66 (m, 8H), 7.65 (s, 2H), 7.48 – 7.41 (m, 8H), 0.99, 0.98 (2 s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 151.1, 151.0 (C), 143.9 (CH), 142.9, 142.9, 136.8, 136.7, 135.9, 135.9, 133.5, 133.4 (C), 131.9, 131.6 (CH), 131.4, 131.3, 130.0 (C), 129.6, 129.6, 129.3, 129.2, 128.4, 128.3 (CH), 127.0, 126.9 (C), 125.9, 125.8 (CH), 124.9 (C), 124.6, 124.5, 121.8, 121.7 (CH), 120.5, 120.5 (C), 35.2, 35.2 (C), 31.3, 31.2(CH_3). **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1362 (m), 1197 (m), 903 (m), 820 (s), 812 (s), 779 (m), 762 (vs), 740 (s), 682 (m). **MS** (EI, 70 eV): m/z (%) = 579 (100, M^+), 490 (14), 489 (14), 488 (48), 452 (20), 451 (22), 239 (16), 238 (18), 233 (11), 232 (19), 226 (13). **HRMS** (ESI-TOF): calculated for $C_{39}H_{28}Cl_2N$ ([M+H]$^+$) 580.1599, found 580.1597.

8-(*tert*-butyl)diacenaphtho[1,2-*e*:1',2'-l]pyrene (**1a**)

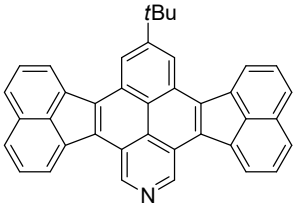


In a pressure tube, 50 mg (0.086 mmol) of **1a**, 0.4 eq. (0.035 mmol, 6 mg) $PdCl_2$, 0.8 eq. (0.069 mmol, 19 mg) PCy_3 and 6 eq. (0.516 mmol, 8 mg, 77 µl) DBU were dissolved in 3 mL of NMP

under an argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 18 h at 150 °C in a heating block. The reaction mixture was cooled to room temperature, quenched with H_2O and extracted with DCM. The combined organic phases were dried over Na_2SO_4. The solvent was distilled off *in vacuo* and the residue was purified by column chromatography with heptane/ethyl acetate (5:1, $\mathbf{R_f}$ = 0.48) to give **3a** as a red solid in a yield of 51% (22.3 mg, 0.044 mmol).

mp. 343-346 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.18 (s, 2H), 8.98 (d, *J* = 7.8 Hz, 2H), 8.59 (d, *J* = 7.0 Hz, 2H), 8.55 (d, *J* = 7.0 Hz, 2H), 8.07 (t, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.74 (dd, *J* = 8.1 Hz, *J* = 6.9 Hz, 2H), 7.68 (dd, *J* = 8.1 Hz, *J* = 6.9 Hz, 2H), 1.82 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.2, 138.1, 138.0, 134.5, 134.3, 132.2, 129.3, 129.1 (C), 127.9, 127.9, 127.6, 127.5, 126.1 (CH), 125.0 (C), 124.9, 124.9 (CH), 123.4 (C), 121.9, 119.4 (CH), 35.7 (C), 32.2 (CH_3). **IR** (ATR, cm^{-1}): ṽ = 1451 (m), 1420 (m), 830 (m), 814 (m), 756 (vs), 721 (m), 705 (m), 699 (m), 641 (m). **MS** (EI, 70 eV): m/z (%) = 509 (60, M^+), 491 (57), 461 (42), 451 (52), 450 (57), 448 (42), 253 (53), 237 (46), 232 (51), 231 (100), 230 (57). **HRMS** (EI): calculated for $C_{40}H_{26}$ ($[M]^+$) 506.20290, found 506.20281.

17-(*tert*-butyl)acenaphtho[1',2':3,4]naphtho[2,1,8-*def*]acenaphtho[1,2-*h*]isoquinoline (**3b**)



In a pressure tube, 100 mg (0.172 mmol) of **1b**, 0.4 eq. (0.069, 12 mg) $PdCl_2$, 0.8 eq. (0.138 mmol, 39 mg) PCy_3 and 6 eq. (1.032 mmol, 157 mg, 154 µl) DBU were dissolved in 3 mL of NMP under an argon counter current. The pressure tube was sealed with a Teflon cap and the solution was stirred for 18 h at 150 °C in a heating block. The reaction mixture was cooled to room temperature and quenched with H_2O, the precipitate was filtered off and washed several times with water, heptane and ethyl acetate. The residue was solved in DCM and the solvent was distilled off in *vacuo* to give **3b** as a red solid in a yield of 56% (49 mg, 0.097 mmol). Due to the poor solubility it was not possible to record a ^{13}C-NMR spectrum.

mp. > 350 °C. **^{1}H NMR** (500 MHz, CS_2/$CDCl_3$) δ = 10.27 (s, 2H), 9.23 (s, 2H), 8.68 – 8.62 (m, 4H), 7.95 – 7.91 (m, 4H), 7.80 – 7.76 (m, 4H), 1.87 (s, 9H). **IR** (ATR, cm^{-1}): ṽ = 1420 (m), 1154 (m), 853 (m), 816 (m), 760 (vs), 721 (m), 645 (m), 620 (m), 556 (m). **MS** (EI, 70 eV): m/z (%) = 507 (100, M^+), 233 (65), 232 (41), 169 (29), 113 (28), 83 (34), 71 (32) 69 (74), 57 (49), 55 (49), 43 (62), 41 (53). **HRMS** (ESI-TOF): calculated for $C_{39}H_{26}N$ ($[M+H]^+$) 508.2065, found 508.2062.

X-Ray data

*Table S5: X-Ray data of 8-(tert-butyl)diacenaphtho[1,2-e:1',2'-l]pyrene (**3a**)*

Chem. Formula	$C_{40}H_{26}$
Form. Wght [g mol^{-1}]	506.61
colour	red
Crsyt. system	monoclinic
Space group (Hall group)	P 21/n (--P 2yn)
a [Å]	5.1374(2)
b [Å]	19.8255(7)
c [Å]	12.6832(4)
α [°]	90
β [°]	92.011(1)
γ [°]	90
V [Å^3]	1291.01(8)
Z	2
N_{ref}	2819
θ_{max} [°]	27.000
h,k,l_{max}	6,25,16
ρ_x[g cm^{-3}]	1.303
μ [mm^{-1}]	0.074
$\lambda_{MoK\alpha}$ [A]	0.71073
T [K]	123
F(000)	532.0
N_{par}	219
R	0.0493(2221)
wR_2	0.1370(2819)
S	1.042

Measurements

Absorption and Emission spectra

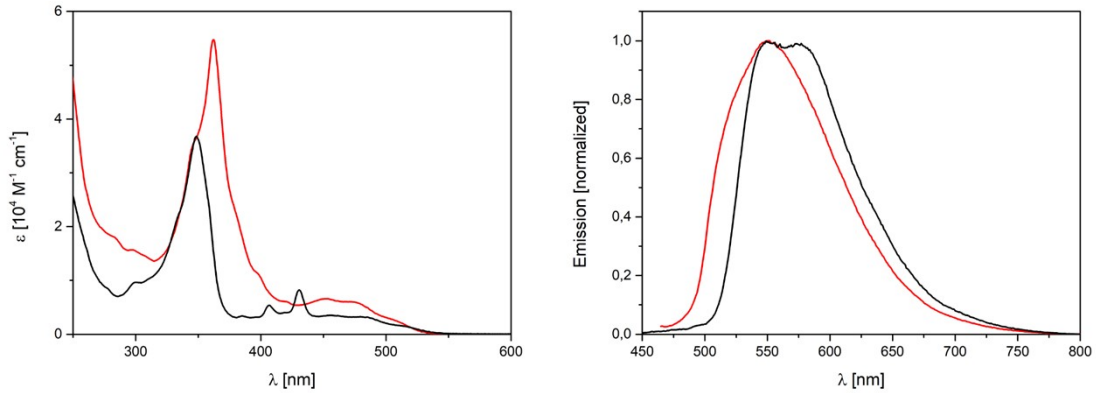


*Figure S1: Absorption (left) and Emission (right, λ_{ex} = 430 nm (**3a**), λ_{ex} = 450 nm (**3b**)) spectra of **3a** (black) and **3b** (red) in DCM (c = 10^{-5} M) at 20 °C.*

*Table S6: Spectroscopic Data (absorption) of **3a** and **3b**, DCM (c = 10^{-5} M) at 20 °C.*

	$\lambda_{1,abs}$ [nm]	ε_1[a]	$\lambda_{2,abs}$ [nm]	ε_2[a]	$\lambda_{3,abs}$ [nm]	ε_3[a]	$\lambda_{4,abs}$ [nm]	ε_4[a]	$\lambda_{5,abs}$ [nm]	ε_5[a]	$\lambda_{6,abs}$ [nm]	ε_6[a]	$\lambda_{7,abs}$ [nm]	ε_7[a]
3a	512[b]	0.16	486[b]	0.31	455	0.35	431	0.82	407	0.54	385	0.34	348	3.68
3b	505[b]	0.23	475[b]	0.60	452	0.66	397[b]	1.2	362	5.47				
[a] [10^4 M^{-1} cm^{-1}]; [b] indicated as shoulder														

*Table S7: Spectroscopic Data (emission) of **3a** and **3b**, DCM (c = 10^{-5} M) at 20 °C.*

	$\lambda_{1,emi}$ [nm]	$\lambda_{2,emi}$ [nm]	Φ [%]
3a	550	577	2[a]
3b	550		3[a]
[a] Fluorescence standard: coumarine 153 in EtOH (φ = 0.38[12], λ_{exc} = 430 nm (**3a**); λ_{exc} = 450 nm (**3b**))			

Cyclic and differential pulse voltammetry

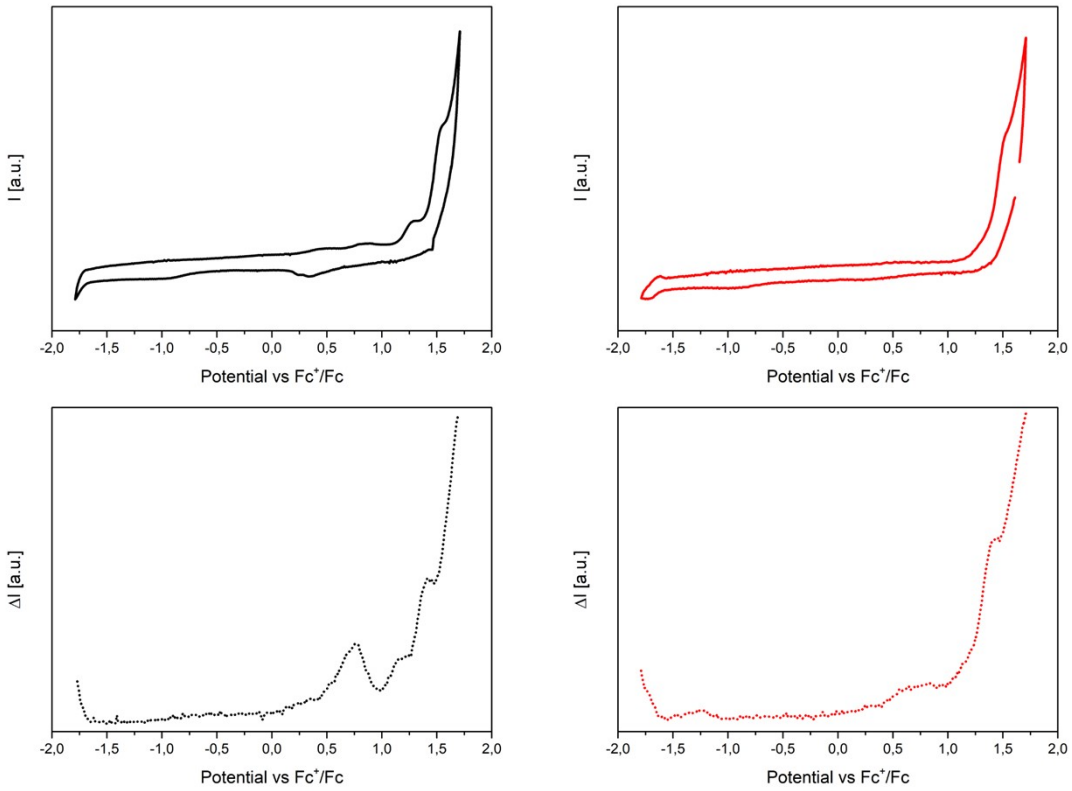


*Figure S2: Cyclic voltammograms (top) of **3a** (left, black) and **3b** (right, red) and differential pulse voltammograms (bottom) of **3a** (left, black) and **3b** (right, red). Measured in concentration of $1 \cdot 10^{-4}$ in DCM with 0.25 M n-Bu_4NPF_6 as a supporting electrolyte, glassy carbon working electrode, and Pt counter-electrode with ferrocene as standard at a scan rate of 100 mV/s.*

Table S8: data of cyclic and differential pulse voltammetry and DFT calculations

	Ox_1 [V][a]	$Ox_{1,on}$ [V][a]	Ox_2 [V][a]	$Ox_{2,on}$ [V][a]	Ox_3 [V][a]	$Ox_{1,on}$ [V][a]	E_{HOMO} [eV]	$E_{HOMO/DFT}$ [eV]	$E_{HOMO/DFT}$ [eV]	$E_{gap/DFT}$ [eV]
3a	0.85	0.75	1.29	1.18	1.54	1.43	-5.55[a]	-5.17	-2.39	2.78
3b	0.94[b]	0.84	1.54	1.43			-5.64[a]	-5.31	-2.50	2.81
[a] V vs. Fc^+/FC [b] estimated with DPV [c] determined the HOMO level of ferrocene is considered to be 4.80 eV below the vacuum level: $E_{HOMO} = -e[(E_{Ox,on} \text{ vs } Fc^+/FC)+4.8]$										

DFT Calculations

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed with Gaussian09.[13] The ground and excited state structures were optimized using the B3LYP, functional and the 6-31G(d,p) basis set. The solvent effects have been considered by using the integral equation formalism variant (IEFPCM) model. NICS2BC were calculated with the B3LYP functional coupled with Grimme's D3empirical dispersion correction and 6-311G(d,p) basis set. Nucleus independent chemical shifts (NICS) were calculated using the gauge including atomic orbitals (GIAO) method at the same level of theory. The bond current maps were generated using the BC-Wizard.[14]

Cartesian coordinates of the optimized ground-states (S_0) and excited states (S_1)

*Table S9: **S_o:** 8-(tert-butyl)diacenaphtho[1,2-e:1',2'-l]pyrene (**3a**)*

E = -1540.0609 Hartree

Symbol	X	Y	Z
C	0.022035	-4.217914	-0.019989
C	-1.187840	-3.533087	-0.012587
C	-1.226723	-2.128839	-0.001527
C	0.012757	-1.400306	-0.003887
C	1.256785	-2.120641	-0.000498
C	1.226782	-3.526189	-0.011415
C	-2.458229	-1.383729	0.001681
C	0.008451	0.030980	-0.007049
C	-1.228822	0.759546	-0.008858
C	-2.460330	0.013086	-0.018591
C	-1.193685	2.160954	0.010377
H	-2.127408	2.702105	0.026338
C	0.001544	2.888867	0.026309
C	1.198096	2.172525	0.013156
C	1.238654	0.766552	-0.007398
C	2.474432	0.029793	-0.017061
C	2.482372	-1.367975	0.003164
H	0.025183	-5.303624	-0.034149
H	-2.106728	-4.100483	-0.026774
H	2.149389	-4.087534	-0.024637
H	2.129868	2.712731	0.032824
C	3.877998	0.509292	-0.040036

C	-3.866752	0.483151	-0.040912
C	-4.667424	-0.689126	-0.013238
C	4.686524	-0.657604	-0.012142
C	-4.526633	1.700933	-0.089927
H	-4.007733	2.650436	-0.128549
C	-5.948927	1.728970	-0.098910
H	-6.442764	2.695279	-0.136881
C	-6.712707	0.578115	-0.061062
H	-7.797380	0.637798	-0.067473
C	-6.070964	-0.691749	-0.016803
C	-5.940469	-3.112176	0.064384
H	-6.430944	-4.080323	0.099028
C	-4.518211	-3.078929	0.061961
H	-3.995541	-4.026331	0.101046
C	-3.863102	-1.858573	0.017625
C	6.090159	-0.650773	-0.016552
C	6.723243	0.623346	-0.061884
H	7.807487	0.690332	-0.068877
C	5.951689	1.768960	-0.100333
H	6.438978	2.738551	-0.139441
C	4.529601	1.731481	-0.090707
H	4.004696	2.677579	-0.130625
C	4.553899	-3.048563	0.062863
H	4.037674	-3.999510	0.101846
C	3.890396	-1.832699	0.018966
C	-6.708214	-1.964066	0.023883
H	-7.792680	-2.027668	0.025070
C	5.976300	-3.072033	0.064808
H	6.473466	-4.036776	0.099189
C	6.736124	-1.918656	0.023994
H	7.821011	-1.974770	0.024653
C	-0.044728	4.428775	0.061434
C	-0.797988	4.949325	-1.185885
H	-0.289061	4.644424	-2.106178
H	-1.824479	4.573723	-1.230473
H	-0.844684	6.043754	-1.170142
C	1.360696	5.059616	0.069163

H	1.939671	4.757433	0.948096
H	1.931717	4.795922	-0.827299
H	1.270965	6.150096	0.093154
C	-0.786256	4.890502	1.338738
H	-0.834021	5.984426	1.374026
H	-1.811844	4.511560	1.375816
H	-0.268042	4.544003	2.238889

Table S10: ***S_o:*** *17-(tert-butyl)acenaphtho[1',2':3,4]naphtho[2,1,8-def]acenaphtho[1,2-h]isoquinoline (**3b**)*

E = -1556.0979 Hartree

Symbol	X	Y	Z
C	-1.125946	-3.512485	0.101016
C	-1.213611	-2.111607	0.053336
C	0.012688	-1.375569	0.037604
C	1.243621	-2.103333	0.054269
C	1.164755	-3.505913	0.101120
C	-2.452394	-1.382901	0.022256
C	0.008349	0.051217	0.017969
C	-1.232167	0.771158	0.015094
C	-2.460341	0.015279	0.000726
C	-1.196549	2.172133	0.031108
H	-2.129170	2.715478	0.045160
C	0.001550	2.897637	0.044307
C	1.200840	2.183751	0.031938
C	1.241870	0.778150	0.014699
C	2.474446	0.032062	-0.000204
C	2.476642	-1.367094	0.023925
H	-2.025273	-4.115980	0.126420
H	2.068225	-4.103333	0.125365
H	2.131467	2.726307	0.048616
C	3.880458	0.501334	-0.040297
C	-3.869229	0.475086	-0.037260
C	-4.661646	-0.702933	-0.030171
C	4.680897	-0.671246	-0.029580
C	-4.536408	1.688837	-0.087080
H	-4.023104	2.642055	-0.109468

C	-5.958389	1.706186	-0.118541
H	-6.459021	2.668928	-0.155508
C	-6.714256	0.549052	-0.106472
H	-7.798967	0.601585	-0.132837
C	-6.064514	-0.716704	-0.064193
C	-5.914703	-3.138759	-0.028538
H	-6.398308	-4.110843	-0.028076
C	-4.493331	-3.094463	-0.000358
H	-3.958927	-4.036409	0.014168
C	-3.850933	-1.866936	0.002697
C	6.083942	-0.675481	-0.063674
C	6.724887	0.594530	-0.111031
H	7.809199	0.654406	-0.137866
C	5.961052	1.746324	-0.127853
H	6.455016	2.712335	-0.169204
C	4.539219	1.719436	-0.095813
H	4.019671	2.669061	-0.123142
C	4.529525	-3.063954	0.008598
H	4.001688	-4.009539	0.027083
C	3.878500	-1.840942	0.006620
C	-6.690742	-1.995230	-0.058862
H	-7.774341	-2.068063	-0.081261
C	5.951114	-3.098376	-0.018892
H	6.441577	-4.067013	-0.014457
C	6.719098	-1.949515	-0.053510
H	7.803201	-2.014774	-0.075448
C	-0.044735	4.437701	0.074666
C	-0.799280	4.953238	-1.174122
H	-0.291122	4.645256	-2.093755
H	-1.826041	4.578207	-1.216582
H	-0.845342	6.047606	-1.161647
C	1.360423	5.069137	0.079352
H	1.940174	4.770841	0.959088
H	1.931043	4.803303	-0.816696
H	1.269415	6.159480	0.099779
C	-0.785518	4.902284	1.351459
H	-0.832813	5.996207	1.383176

H	-1.811217	4.523983	1.390508
H	-0.266527	4.558569	2.252179
N	0.022058	-4.196316	0.126651

Table S11: ***S_o:*** *diacenaphtho[1,2-e:1',2'-l]pyrene (**3a'**)*

E = -1383.1092 Hartree

Symbol	X	Y	Z
C	0.000041	-3.525007	0.268057
C	-1.204484	-2.839526	0.216158
C	-1.238456	-1.439838	0.127936
C	-0.000002	-0.715115	0.110113
C	1.238458	-1.439810	0.127861
C	1.204538	-2.839505	0.216170
C	-2.464286	-0.696746	0.064537
C	0.000002	0.715113	0.110121
C	-1.238459	1.439839	0.127873
C	-2.464279	0.696729	0.064380
C	-1.204520	2.839512	0.216258
H	-2.125600	3.397244	0.271673
C	-0.000015	3.525018	0.268236
C	1.204488	2.839526	0.216311
C	1.238453	1.439842	0.127976
C	2.464289	0.696759	0.064531
C	2.464271	-0.696720	0.064386
H	0.000042	-4.606011	0.351826
H	-2.125542	-3.397302	0.271428
H	2.125632	-3.397215	0.271594
H	2.125556	3.397279	0.271702
C	3.865749	1.168893	-0.014853
C	-3.865724	1.168878	-0.015148
C	-4.666732	-0.000001	-0.049956
C	4.666716	-0.000010	-0.050055
C	-4.516267	2.385845	-0.089966
H	-3.988234	3.328791	-0.101166
C	-5.934427	2.417610	-0.173876

H	-6.424193	3.383595	-0.225773
C	-6.698541	1.270393	-0.198422
H	-7.779345	1.331322	-0.266913
C	-6.063026	0.000016	-0.145534
C	-5.934545	-2.417584	-0.172785
H	-6.424342	-3.383581	-0.224190
C	-4.516375	-2.385850	-0.088958
H	-3.988448	-3.328862	-0.099667
C	-3.865749	-1.168891	-0.014769
C	6.063011	-0.000026	-0.145582
C	6.698604	1.270335	-0.197914
H	7.779413	1.331222	-0.266342
C	5.934545	2.417579	-0.172878
H	6.424348	3.383571	-0.224296
C	4.516379	2.385850	-0.089052
H	3.988435	3.328854	-0.099801
C	4.516266	-2.385846	-0.089836
H	3.988273	-3.328820	-0.100943
C	3.865702	-1.168882	-0.015176
C	-6.698613	-1.270349	-0.197856
H	-7.779420	-1.331260	-0.266300
C	5.934431	-2.417616	-0.173713
H	6.424178	-3.383618	-0.225491
C	6.698545	-1.270400	-0.198352
H	7.779351	-1.331317	-0.266805
H	-0.000020	4.606013	0.352115

Table S12: ***S_o:*** *acenaphtho[1',2':3,4]naphtho[2,1,8-def]acenaphtho[1,2-h]isoquinoline (**3b'**)*

E = -1399.1487 Hartree

Symbol	X	Y	Z
C	-1.141412	-2.822589	-0.000182
C	-1.225095	-1.421663	-0.000095
C	0.000005	-0.688357	-0.000257
C	1.225099	-1.421648	-0.000386
C	1.141424	-2.822590	-0.000133
C	-2.459821	-0.693826	0.000033

C	-0.000002	0.737998	-0.000394
C	-1.242342	1.454289	-0.000632
C	-2.466598	0.701232	-0.000377
C	-1.207106	2.856542	-0.001115
H	-2.125947	3.420309	-0.001282
C	-0.000007	3.540762	-0.001514
C	1.207100	2.856544	-0.001189
C	1.242347	1.454296	-0.000428
C	2.466600	0.701240	0.000024
C	2.459822	-0.693820	-0.000457
H	-2.040250	-3.423149	-0.000361
H	2.040287	-3.423120	0.000176
H	2.125928	3.420332	-0.001876
C	3.874043	1.162661	0.000743
C	-3.874044	1.162657	-0.000373
C	-4.666716	-0.012550	0.000162
C	4.666714	-0.012547	0.000120
C	-4.538401	2.374613	-0.000723
H	-4.021237	3.323563	-0.001153
C	-5.959088	2.394314	-0.000519
H	-6.459070	3.356377	-0.000811
C	-6.713958	1.240494	0.000054
H	-7.797333	1.292824	0.000221
C	-6.066116	-0.024514	0.000441
C	-5.919082	-2.442516	0.001554
H	-6.403421	-3.412464	0.002139
C	-4.499102	-2.399471	0.001267
H	-3.962055	-3.337451	0.001735
C	-3.857783	-1.175535	0.000493
C	6.066114	-0.024514	0.000415
C	6.713956	1.240493	0.001655
H	7.797331	1.292822	0.001944
C	5.959087	2.394315	0.002610
H	6.459073	3.356375	0.003725
C	4.538401	2.374617	0.002215
H	4.021234	3.323565	0.003320
C	4.499094	-2.399469	-0.001627

H	3.962041	-3.337447	-0.002546
C	3.857780	-1.175530	-0.000685
C	-6.692277	-1.300643	0.001134
H	-7.774666	-1.370737	0.001368
C	5.919073	-2.442517	-0.001532
H	6.403410	-3.412465	-0.002284
C	6.692271	-1.300645	-0.000484
H	7.774660	-1.370743	-0.000357
N	0.000018	-3.508054	-0.000107
H	-0.000001	4.625041	-0.002114

TD-DFT calculations

*Table S13: Calculated TD-DFT transitions of compound **3a** at B3LYP/6-31+G(d,p) level (IEFPCM).*

S_n	E (eV)	λ (nm)	*f*	Configuration	CI coefficent
S_1	2.3758	521.87	0.1339	HOMO → LUMO	0.69450
S_2	2.4895	498.04	0.0003	HOMO-2 → LUMO	0.11417
				HOMO → LUMO+1	0.69364
S_3	2.9490	420.43	0.3802	HOMO-1 → LUMO	0.68175
				HOMO → LUMO+2	-0.16082
S_4	3.0002	413.25	0.0000	HOMO-2 → LUMO	0.69062
				HOMO → LUMO+2	-0.11803

*Table S14: Calculated TD-DFT transitions of compound **3b** at B3LYP/6-31+G(d,p) level (IEFPCM).*

S_n	E (eV)	λ (nm)	*f*	Configuration	CI coefficent
S_1	2.4183	512.70	0.1342	HOMO → LUMO	0.69355
S_2	2.5477	486.66	0.0019	HOMO-2 → LUMO	-0.11298
				HOMO → LUMO+1	0.68969
S_3	2.9958	413.86	0.0000	HOMO-2 → LUMO	0.63832
				HOMO-1 → LUMO	-0.25522
				HOMO → LUMO+1	0.13521
S_4	3.0538	406.00	0.2972	HOMO-2 → LUMO	0.24843
				HOMO-1 → LUMO	0.60960
				HOMO → LUMO+2	0.22241

1H-, 13C- and NOESY-NMR Spectra of unknown compounds

4-chloro-3,5-*bis*((8-chloronaphthalen-1-yl)ethynyl)pyridine (**S3b**)

	Parameter	Value
1	Solvent	DMSO
2	Temperature	373.5
3	Pulse Sequence	zg30
4	Number of Scans	16
5	Receiver Gain	912.0
6	Relaxation Delay	1.0000
7	Pulse Width	10.0000
8	Acquisition Time	6.3439
9	Spectrometer Frequency	250.13
10	Spectral Width	5165.3
11	Lowest Frequency	-1036.5
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

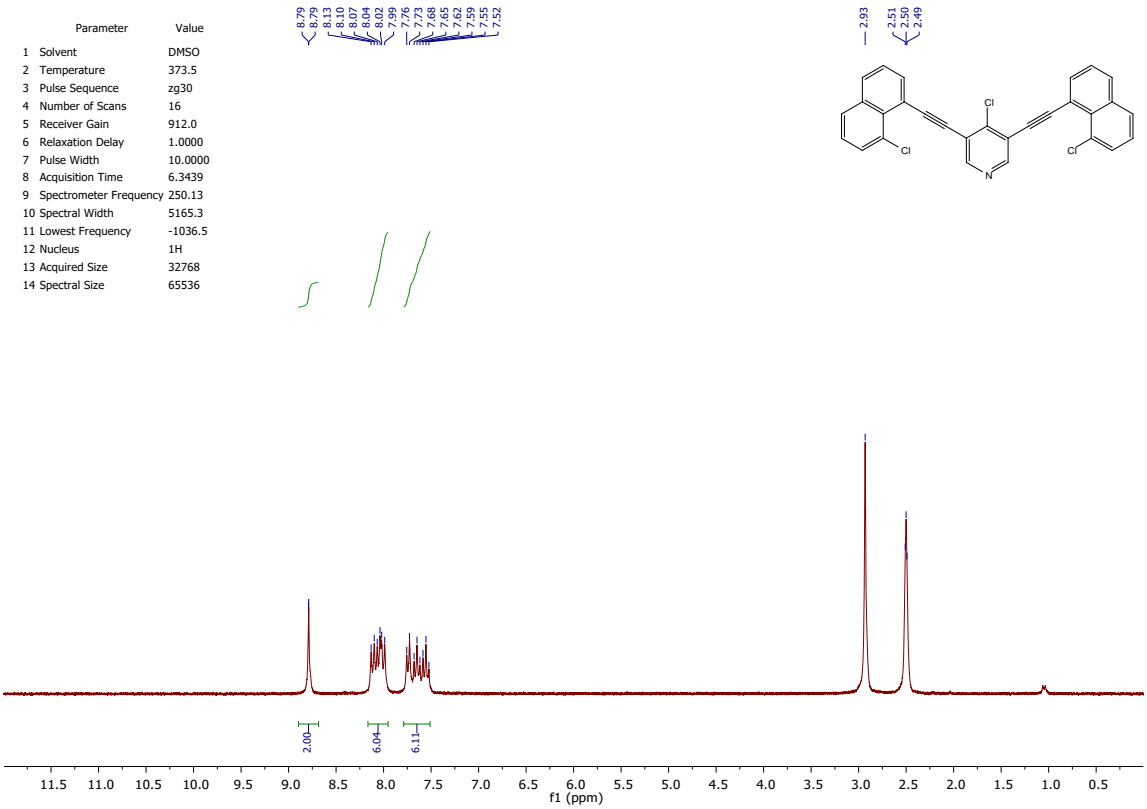


*Figure S3: [1]H-NMR of **S3b***

	Parameter	Value
1	Solvent	DMSO
2	Temperature	373.2
3	Pulse Sequence	zgpg30
4	Number of Scans	2048
5	Receiver Gain	2050.0
6	Relaxation Delay	2.0000
7	Pulse Width	10.0000
8	Acquisition Time	2.1846
9	Spectrometer Frequency	62.90
10	Spectral Width	15000.0
11	Lowest Frequency	-1273.8
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

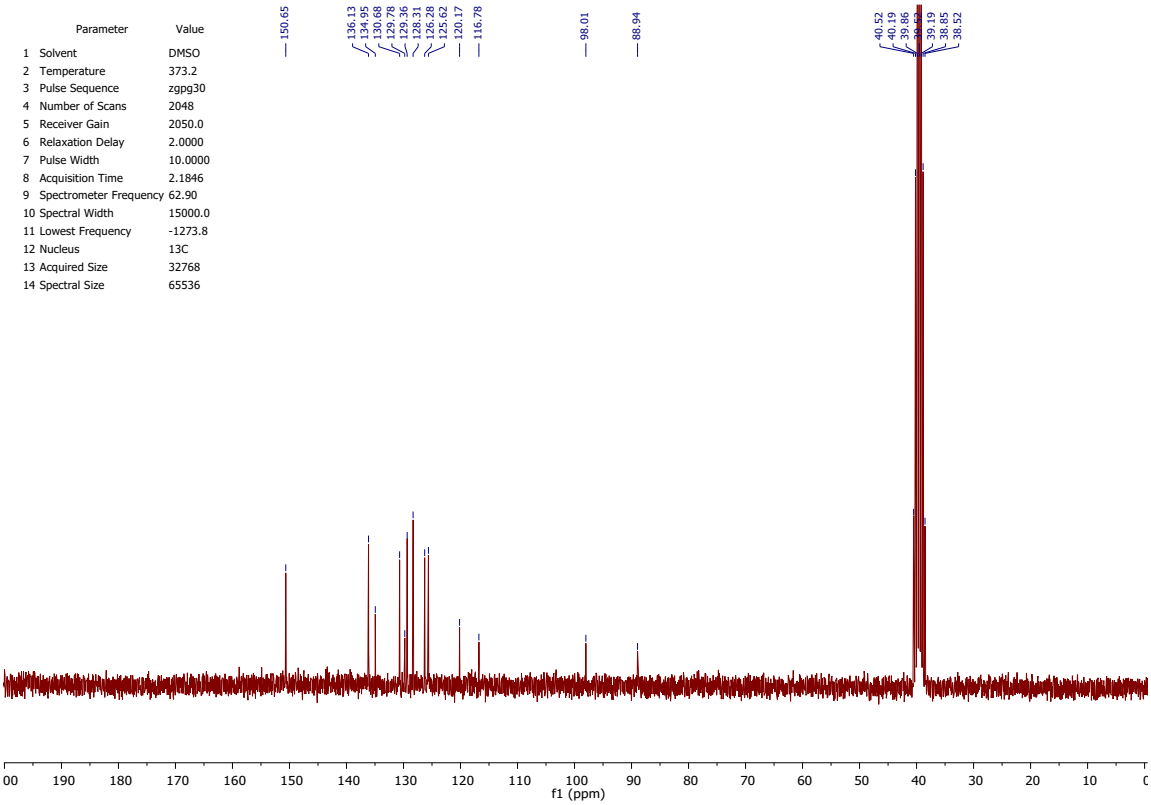


*Figure S4: [13]C-NMR of **S3b***

8,8'-((4'-(*tert*-butyl)-[1,1'-biphenyl]-2,6-diyl)*bis*(ethyne-2,1-diyl))*bis*(1-chloronaphthalene) (**1a**)

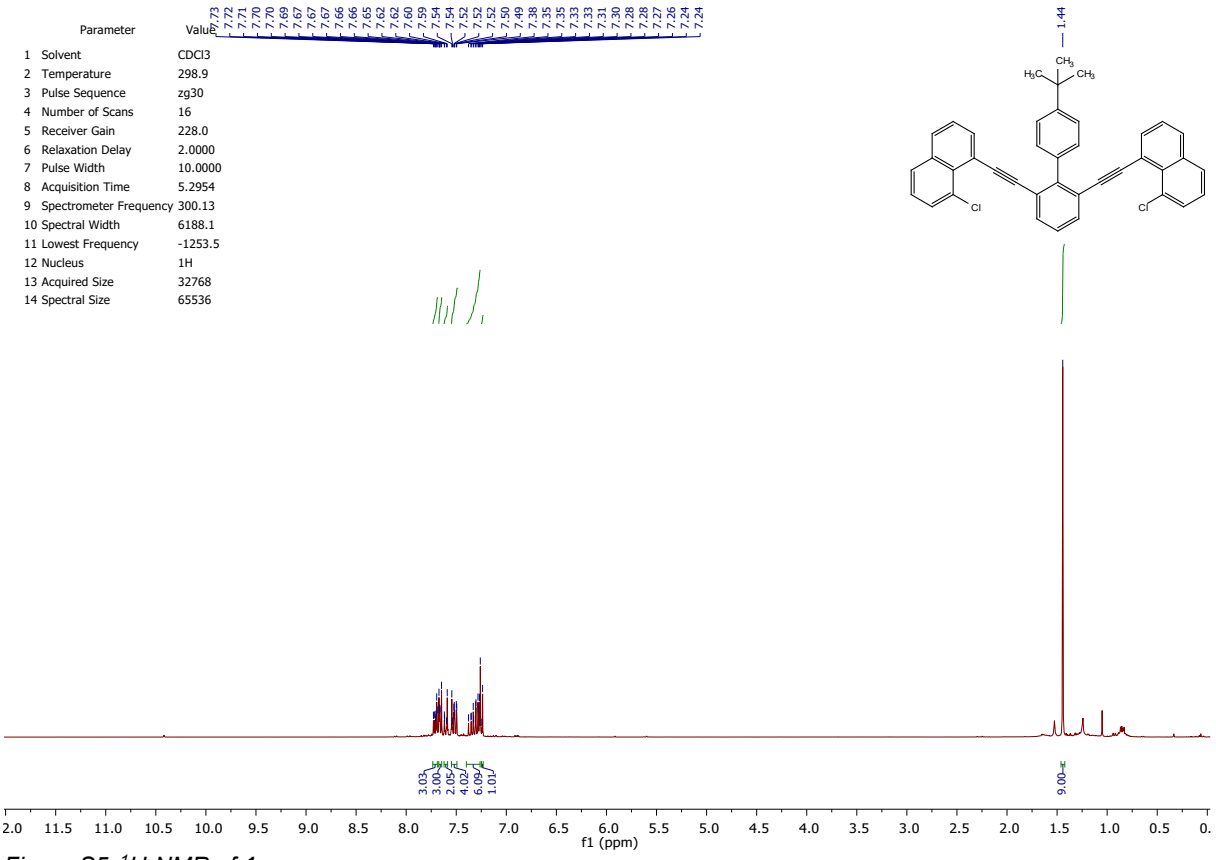


*Figure S5: [1]H-NMR of **1a***

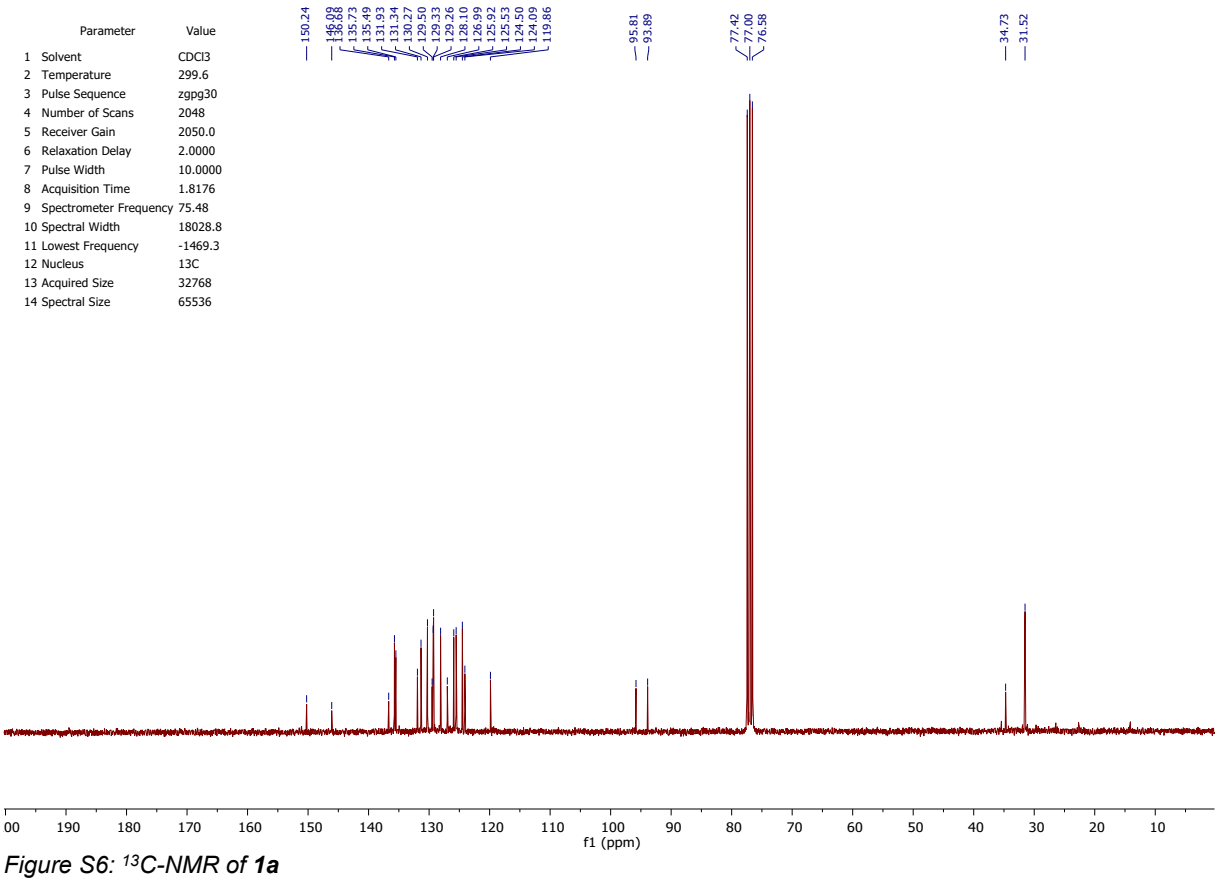


*Figure S6: [13]C-NMR of **1a***

4-(4-(*tert*-butyl)phenyl)-3,5-*bis*((8-chloronaphthalen-1-yl)ethynyl)pyridine (**1b**)

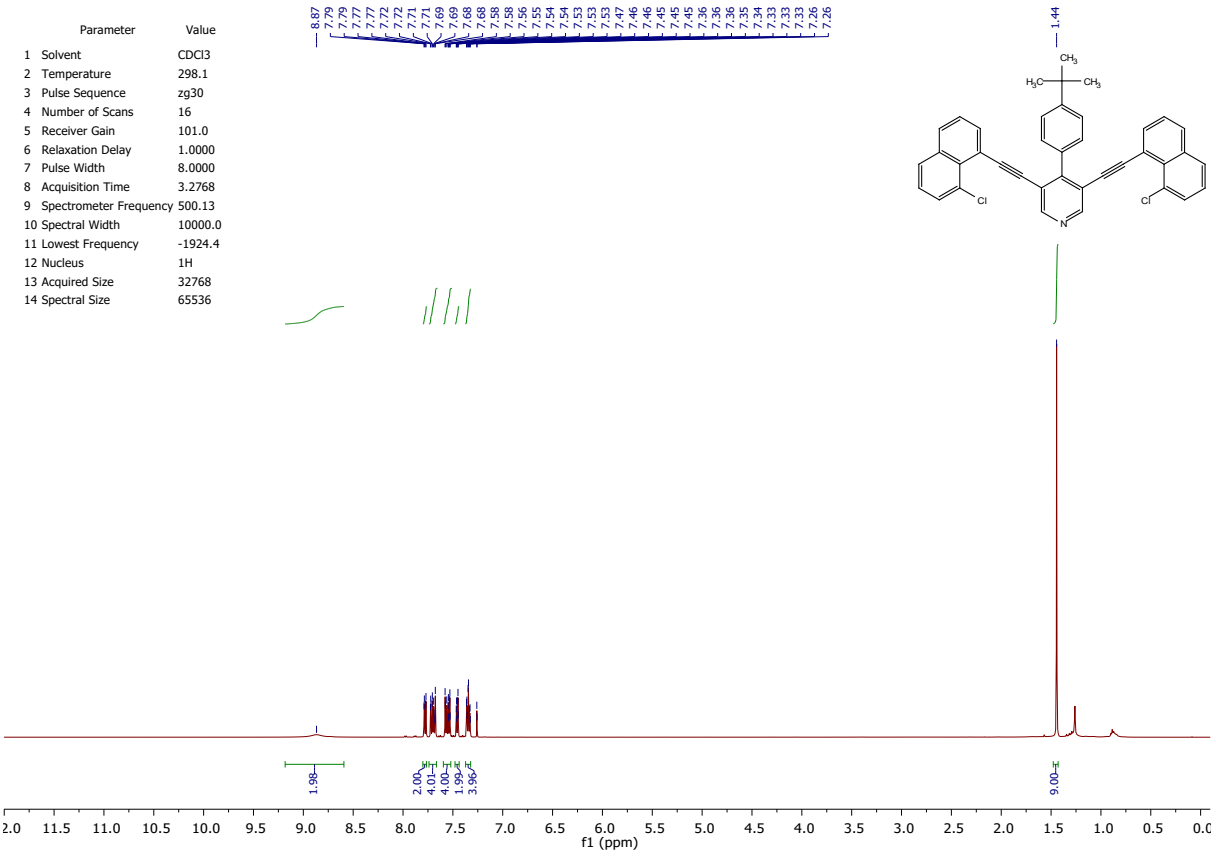


*Figure S7: [1]H-NMR of **1b***

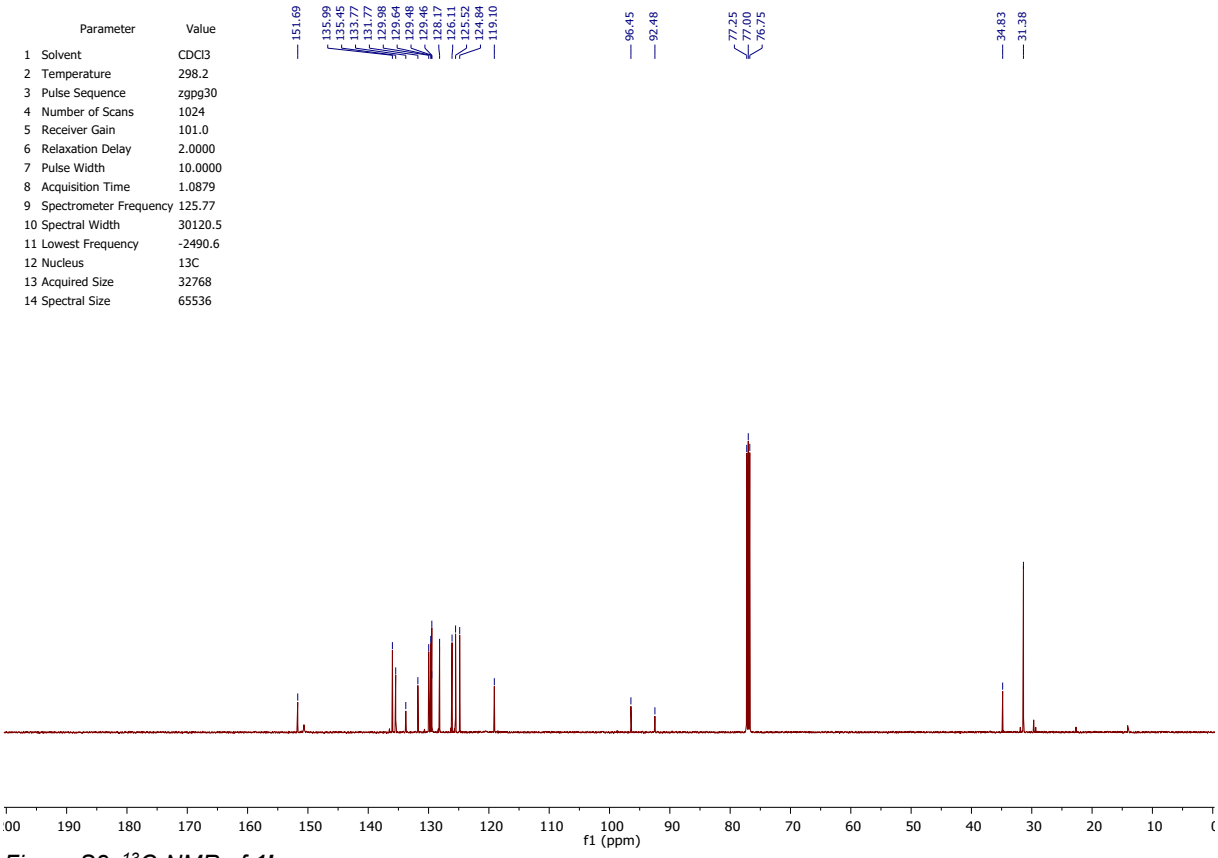


*Figure S8: [13]C-NMR of **1b***

2-(tert-butyl)-4,10-bis(8-chloronaphthalen-1-yl)pyrene (**2a**)

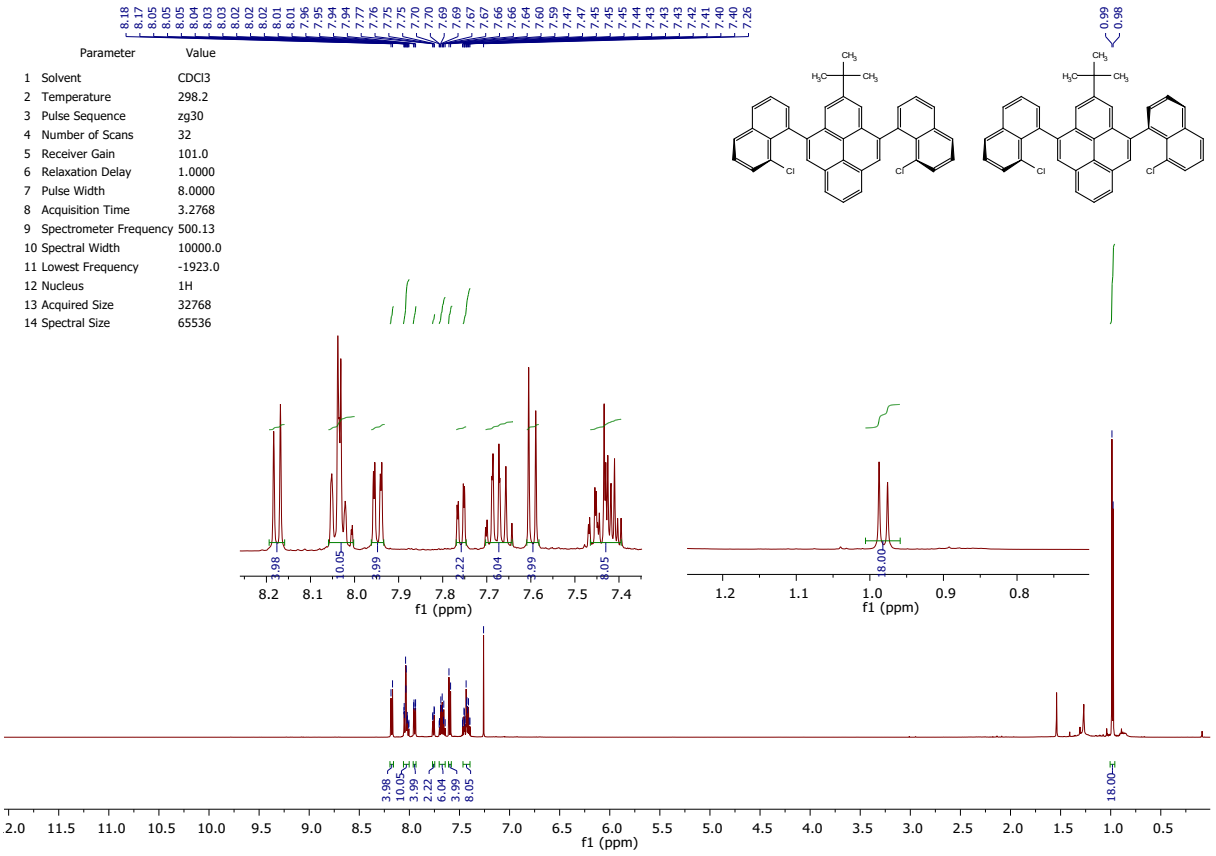


*Figure S9: [1]H-NMR of **2a***

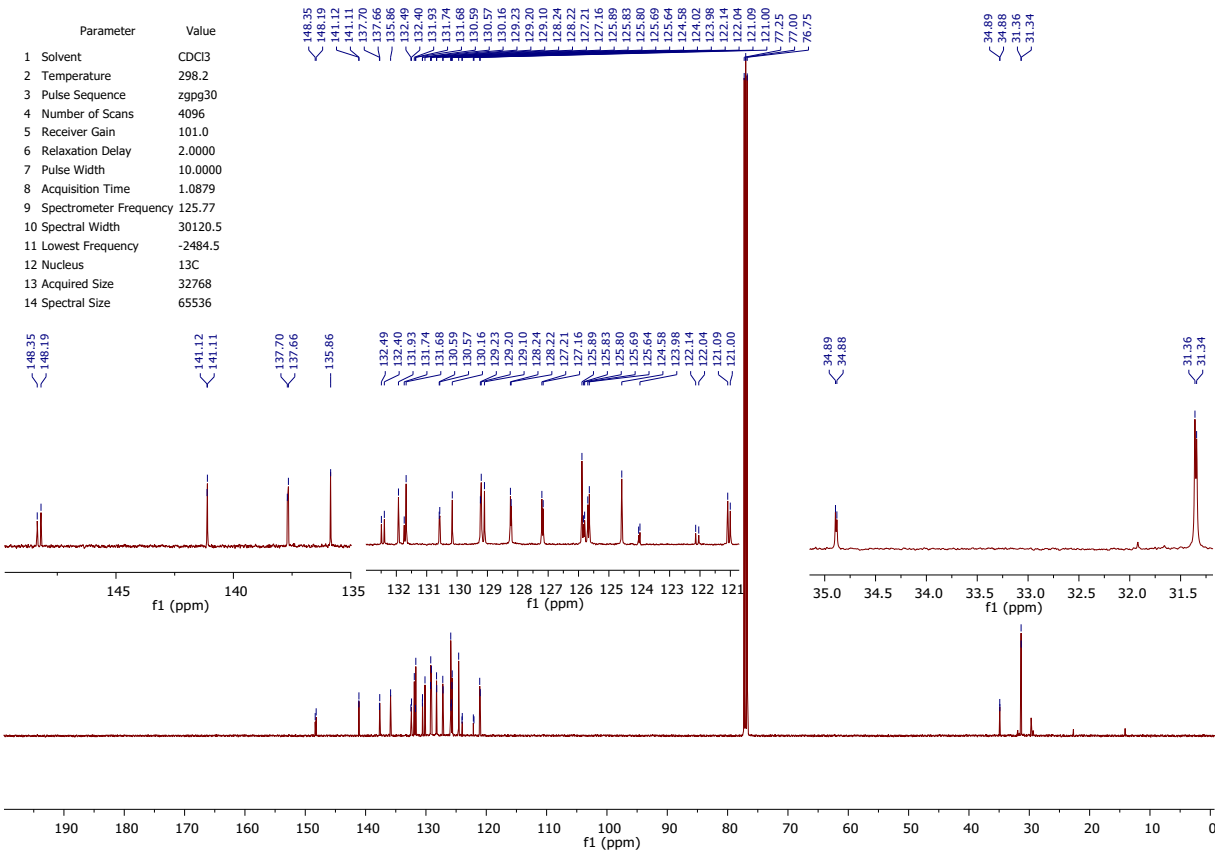


*Figure S10: [13]C-NMR of **2a***

7-(*tert*-butyl)-5,9-*bis*(8-chloronaphthalen-1-yl)naphtho[2,1,8-*def*]isoquinoline (**2b**)

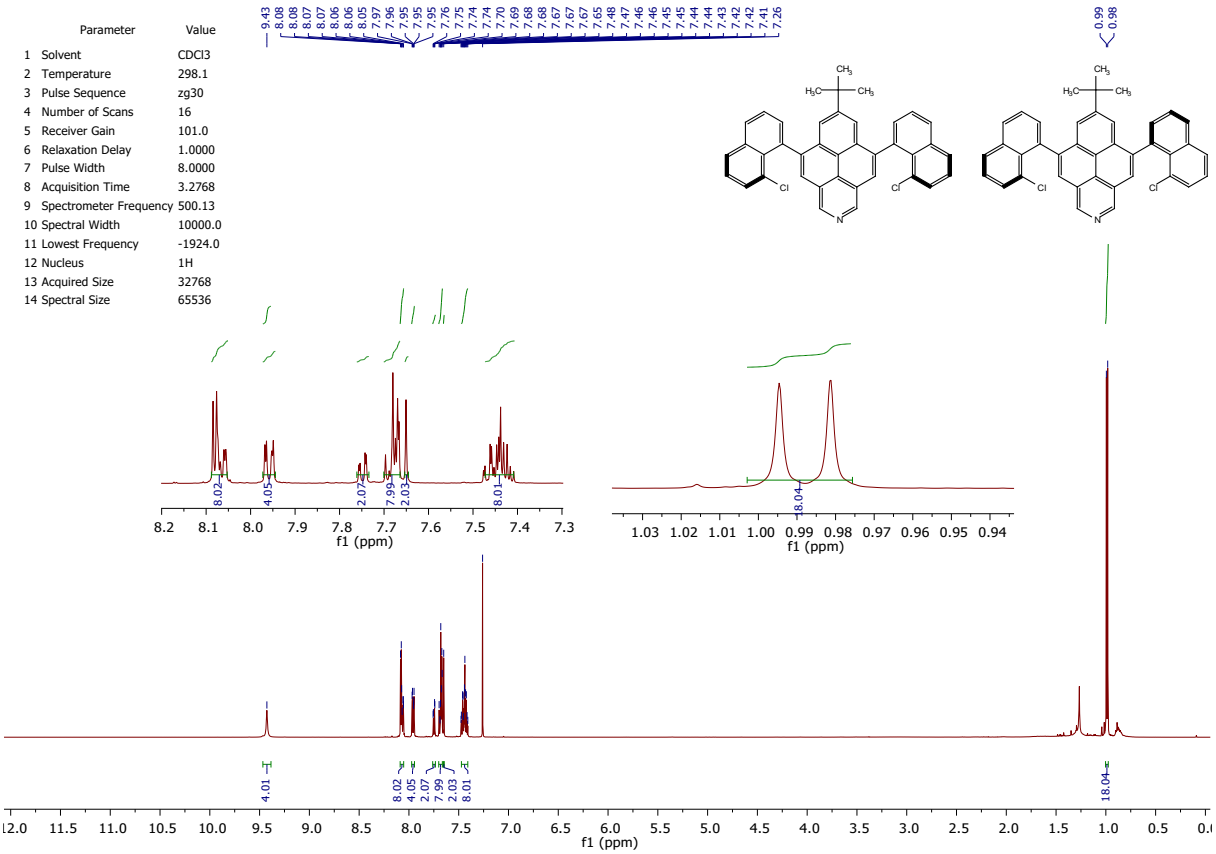


*Figure S11: [1]H-NMR of **2b***

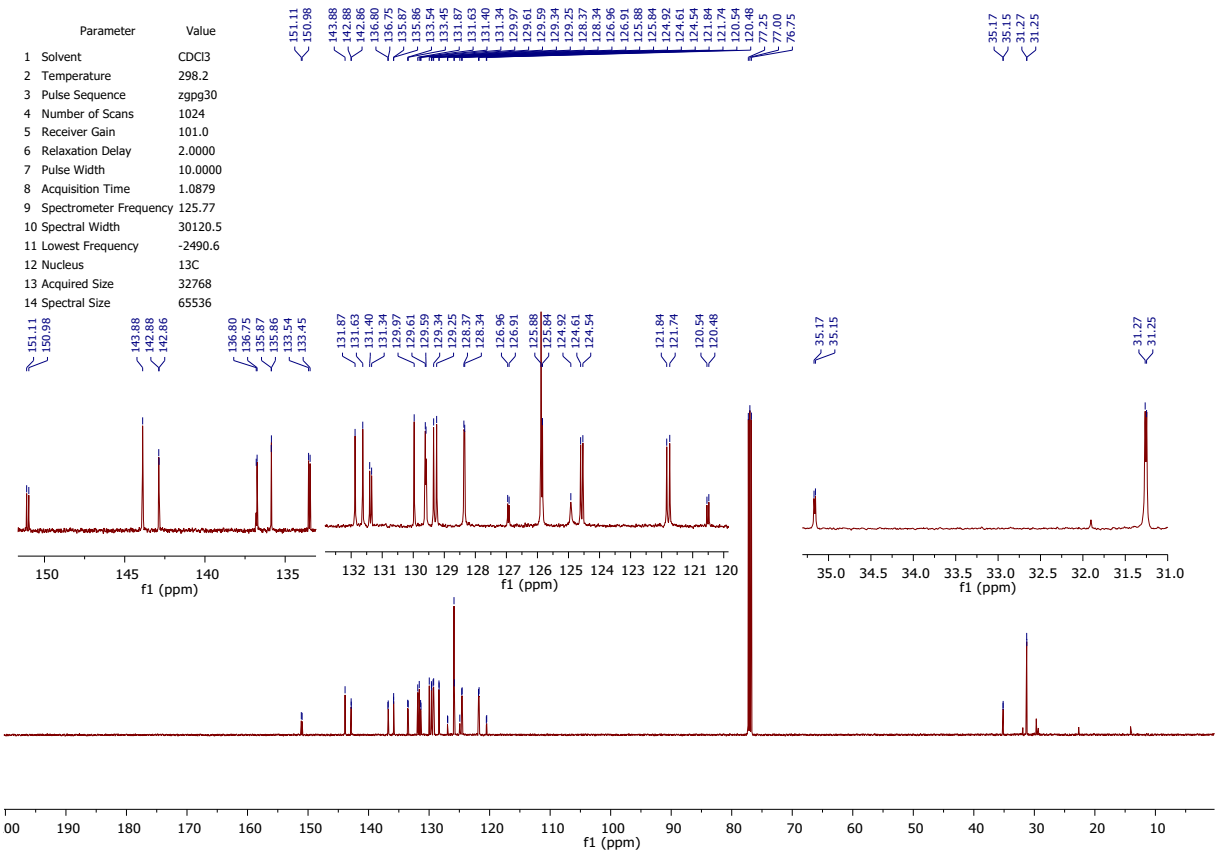


*Figure S12: [13]C-NMR of **2b***

8-(*tert*-butyl)diacenaphtho[1,2-*e*:1',2'-*l*]pyrene (**3a**)

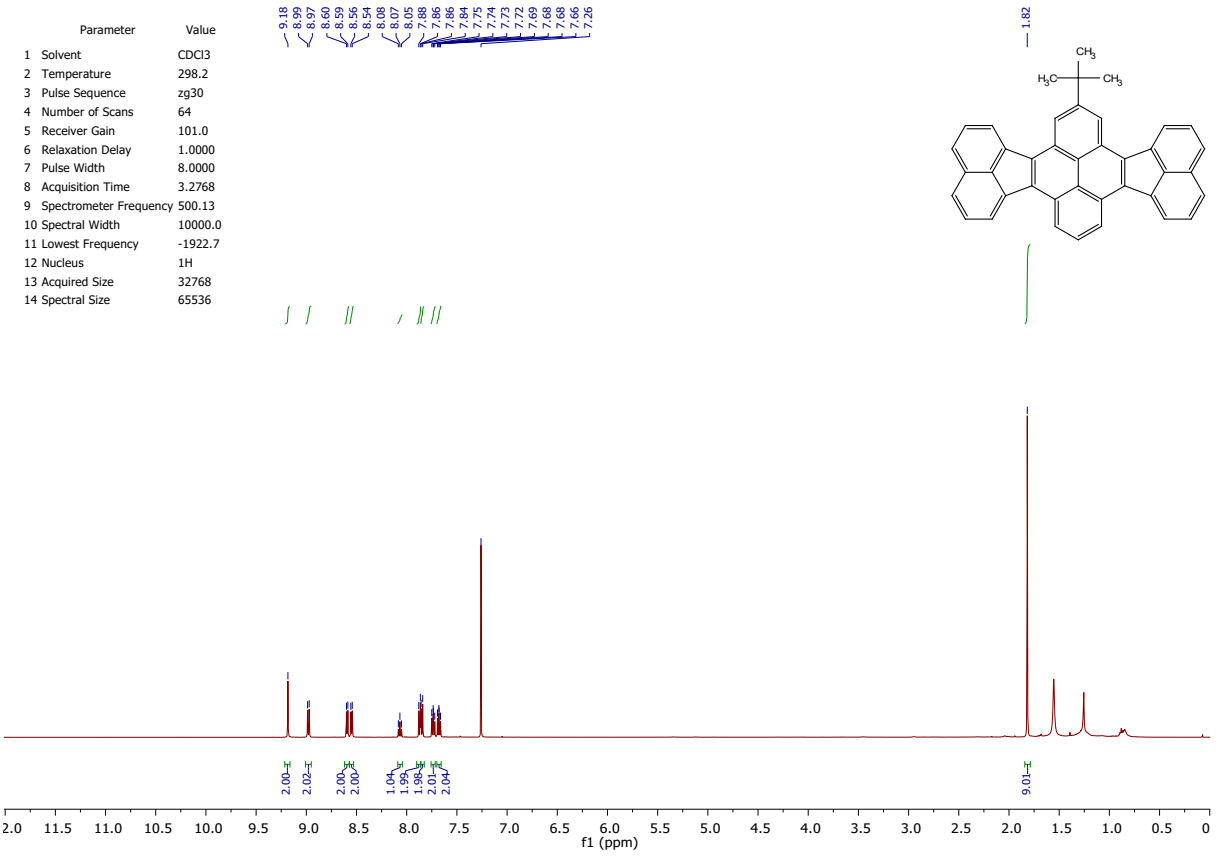


*Figure S13: [1]H-NMR of **3a***

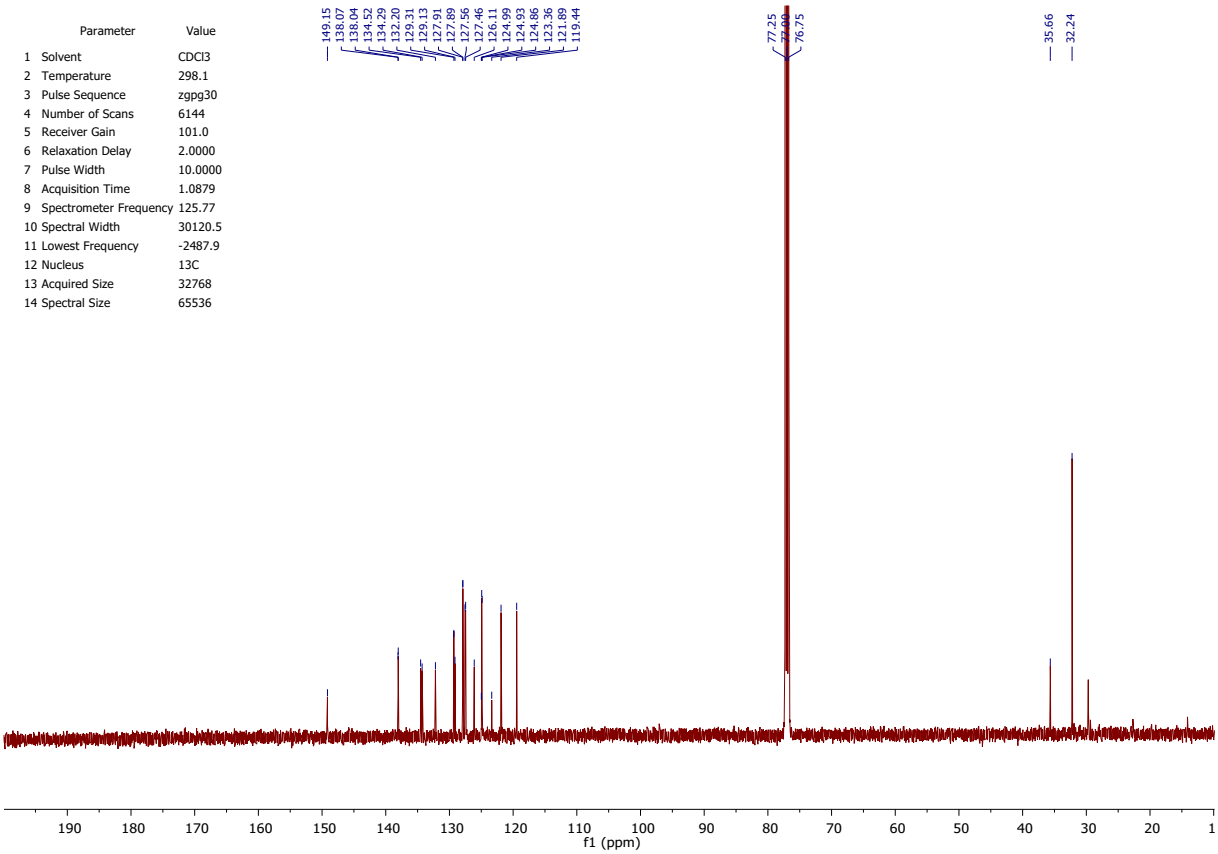


*Figure S14: [13]C-NMR of **3a***

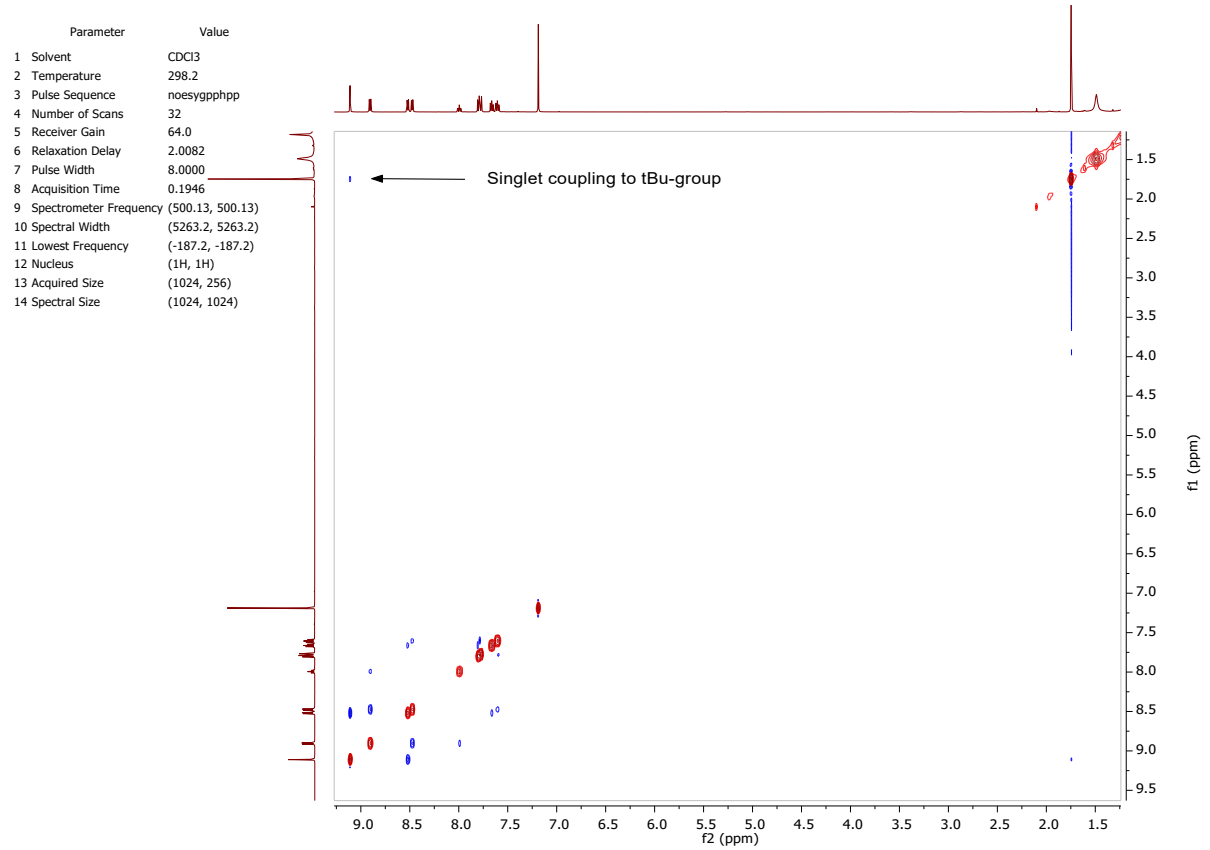


*Figure S15: NOESY-NMR of **3a***

17-(*tert*-butyl)acenaphtho[1',2':3,4]naphtho[2,1,8-*def*]acenaphtho[1,2-*h*]isoquinoline (**3b**)

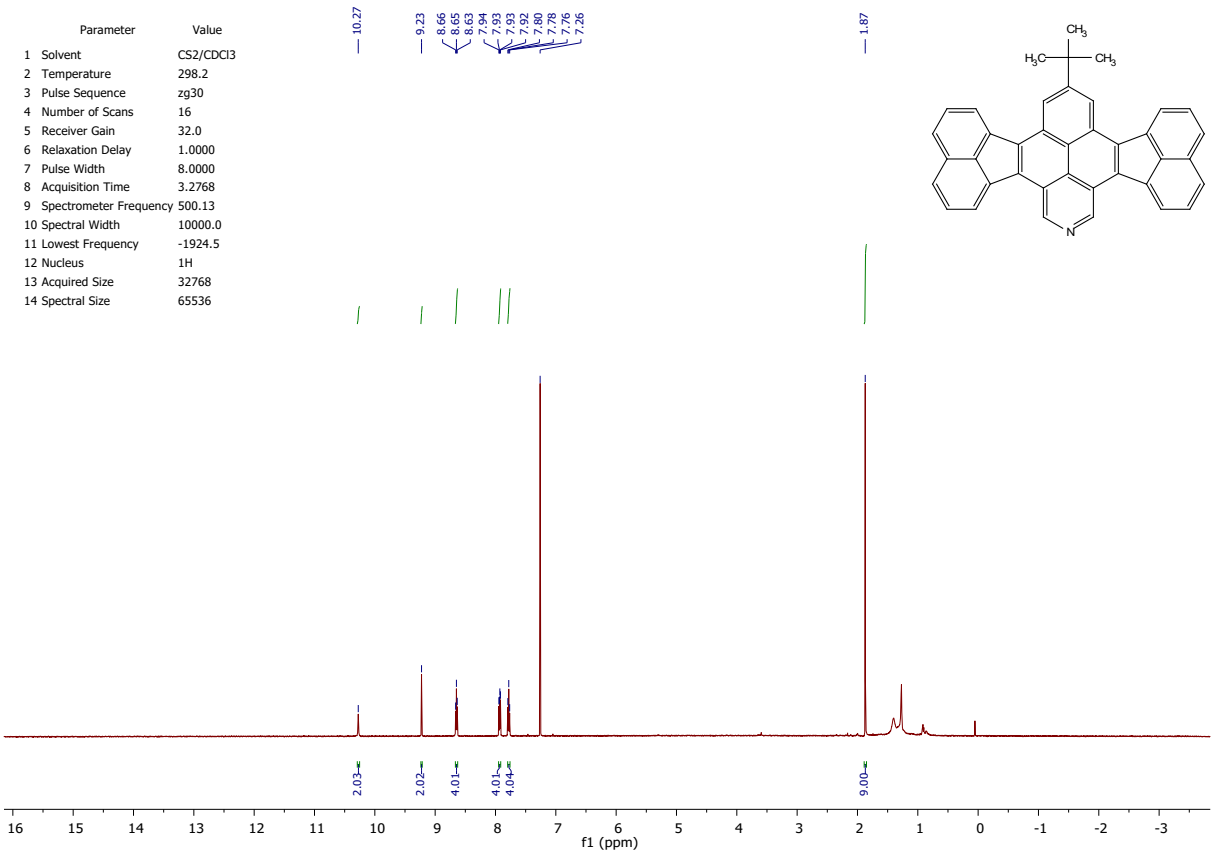


*Figure S16: ^{1}H-NMR of **3b***

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