Supporting Information
for

Double aza[4,5]helicenes with a common naphthalene core: synthesis, crystal structure and optical properties

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Experimental details, copies of NMR spectra, UV-vis spectra, X-ray crystallographic details

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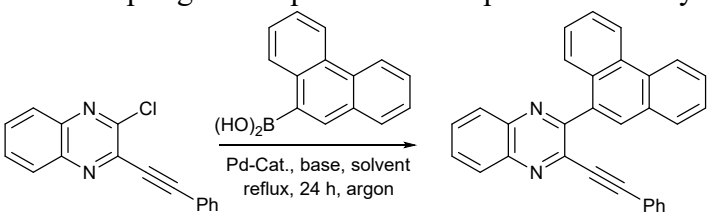
Experimental section

***General information*:**
Reactions were monitored by thin layer chromatography (silica gel 60 F_{254}) and visualized using UV. Flash column chromatography was performed using silica gel (230–400 mesh, grade 60). ^{1}H, ^{13}C NMR spectra were recorded on 250 MHz spectrometer. Chemical shifts were reported in ppm relative to Me_4Si. Electronic absorption spectra were recorded on an Agilent 8454 spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. The quantum yield of fluorescence was determined using quinine sulfate in 0.1 M H_2SO_4 water (Φ = 0.53 ± 0.023) as reference with optically matched samples having absorbances of 0.1 at λ_{ex} =365 nm; the experimental error in Φ_{FL} is ±20% [Adams M.J., Highfield J.G., Kirkbright G.F. *Anal. Chem.*, **1977**, *49*, 1850–1852]. The emission lifetimes were measured using a time-correlated single-photon-counting picosecond spectrophotometer FluoTime 200 (PicoQuant, Germany). The sample was excited by a 40 ps pulsed laser centered at 372 nm, and the emission signal was collected at the magic angle. The instrument response function (IRF) was recorded under described conditions by replacing the sample with a Ludox solution (Sigma-Aldrich). The time decay data were analyzed by nonlinear least squares fitting with deconvolution of the IRF using the FluoFit (PicoQuant, Germany) software package [Enderlein J., Erdmann R., Fast fitting of multi-exponential decay curves. *Opt. Commun.*, **1997**, *134*, 371-378]. Mass spectra were performed in electrospray ionization (ESI) modes (HR-ESI MS). Melting points were determined in glass capillaries and are uncorrected. Commercial *p*-tolylacetylene, phenanthren-9-ylboronic acid, Pd-catalysts, ICl, 2,3-dihaloazines, alkylamines, PPh_3, TFA, anhydrous DMSO, THF were used as received.

***Crystal Structure Determination*:** X-Ray measurements were conducted with diffractometer SyperNova, Dual, Cu at home/near, AtlasS2'. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2448317 (**5b**), CCDC 2448318 (**8a**), CCDC 2448319 (**8b**) and CCDC 2448320 (**8c**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

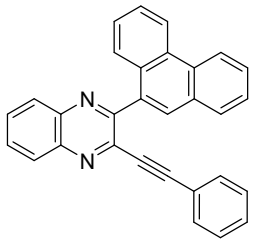
Table S1. Suzuki coupling of compound **1a** with phenanthren-9-ylboronic acid



1a **2a**

Entry	Pd-Cat.	Base	Solvent	Yield, %
1	5% Pd/C, PPh_3	K_2CO_3	Toluene, H_2O	40
2	$Pd(PPh_3)_4$	K_2CO_3	Toluene, H_2O, EtOH	30
3	$Pd(PPh_3)_4$	K_2CO_3	1,4-Dioxane, H_2O	31
4	**$Pd(PPh_3)_4$**	**K_2CO_3**	**THF, H_2O**	**58**
5	$Pd(PPh_3)_4$	K_3PO_4	THF	29

2-(Phenanthren-9-yl)-3-(phenylethynyl)quinoxaline (2a)

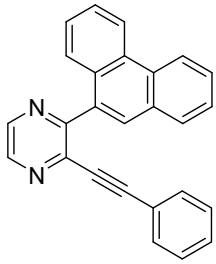


Method A. A mixture of 2-chloro-3-(phenylethynyl)quinoxaline **1a** (132 mg, 0.5 mmol), phenanthren-9-ylboronic acid (133 mg, 0.6 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), K_2CO_3 (346 mg, 2.5 mmol), THF (8 mL) and water (4 mL) was stirred and refluxed for 24 h under argon. The reaction mixture was then evaporated to dryness. The residue was treated with water (50 mL) and extracted with $CHCl_3$ (3 × 20 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (3.5 × 45 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.4 gave 118 mg (58%) of compound **2a**. The product was heated with EtOH (2 mL) for crystallization and filtered off.

Method B. A mixture of 2-chloro-3-(phenanthren-9-yl)quinoxaline **4a** (170 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (5 mg, 0.025 mmol), *i*-Pr_2NH (1 mL) and DMSO (5 mL) was refluxed under argon for 20 min. Then a solution of phenylacetylene (77 mg, 0.08 mL, 0.75 mmol) in *i*-Pr_2NH (2 mL) was added by portions for 2 h. The reaction mixture was refluxed for 22 h. Then it was evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (100 mL) and extracted with $CHCl_3$ (4 × 15 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (3.5 × 45 cm) with $CHCl_3$ as the eluent. The yellowish fraction with R_f 0.4 gave 154 mg (76%) of compound **2a**. The product was heated with EtOH (2 mL) for crystallization and filtered off.

Compound **2a** was obtained as a yellowish solid with mp 175–177 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.67-6.76 (m, 2 H), 7.12-7.23 (m, 2 H), 7.24-7.34 (m, 1 H), 7.60 (ddd, J = 8.1, 6.8, 1.0 Hz, 1 H), 7.67-7.88 (m, 4 H), 7.94-8.06 (m, 2 H), 8.13 (dd, J = 7.8, 1.4 Hz, 1 H), 8.17 (s, 1 H), 8.19-8.28 (m, 2 H), 8.99 (d, J = 8.3 Hz, 1 H), 9.04 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 87.8, 94.9, 120.3, 123.1, 123.4, 126.4, 127.1 (2C), 127.4, 128.0, 128.6(6), 128.7(2), 129.1, 129.2, 129.7(8), 129.8(2), 129.9(6), 130.1(2), 130.6, 131.1(7), 131.2(2), 131.4, 134.0, 139.2, 140.0, 141.0, 155.6 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 255 (4.74), 289 (4.39), 298 sh (4.32), 354 (4.18), 369 sh (4.13), end absorption up to 419 nm. HRMS (ESI): MH^+, found 407.1546. $C_{30}H_{19}N_2$ requires 407.1548.

2-(Phenanthren-9-yl)-3-(phenylethynyl)pyrazine (2b)

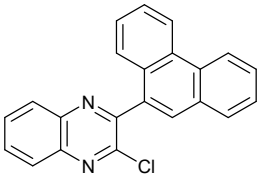


Method A. Compound **2b** was synthesized similarly to **2a** (*Method A*), using 2-chloro-3-(phenylethynyl)quinoxaline **1b** (107 mg, 0.5 mmol). Column chromatography was carried out on silica gel (2.5 × 25 cm) with hexane-ethyl acetate (3:1, v/v) as the eluent. The yellow fraction with R_f 0.3-0.4 gave 138 mg (77%) of compound **2b**.

Method B. Compound **2b** was synthesized similarly to **2a** (*Method B*), using 2-chloro-3-(phenanthren-9-yl)pyrazine **4b** (145 mg, 0.5 mmol). Column chromatography was carried out on silica gel (2.5 × 25 cm) with hexane-ethyl acetate (3:1, v/v) as the eluent. The yellow fraction with R_f 0.3-0.4 gave 142 mg (80%) of compound **2b**.

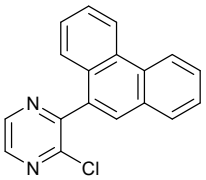
Compound **2b** was obtained as a beige solid with mp 112–114 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.84 (t, J = 1.7 Hz, 1 H), 6.87 (q, J = 1.7 Hz, 1 H), 7.05-7.14 (m, 2 H), 7.16-7.24 (m, 1 H), 7.57 (ddd, J = 8.2, 7.0, 1.2 Hz, 1 H), 7.61-7.80 (m, 4 H), 7.96 (dd, J = 7.8, 1.3 Hz, 1 H), 8.01 (s, 1 H), 8.70 (d, J = 2.5 Hz, 1 H), 8.72 (d, J = 2.5 Hz, 1 H), 8.78 (d, J = 8.3 Hz, 1 H), 8.83 (d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 86.9, 96.2, 121.5, 122.8, 123.1, 126.5, 126.9(2C), 127.1, 127.7, 128.2(2C), 129.2(7), 129.3(0), 129.7, 130.0, 130.6, 130.9, 131.1, 131.9(2C), 133.9, 140.3, 142.3, 143.2, 156.9 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 253 (4.77), 301 (4.42), end absorption up to 388 nm. HRMS (ESI): MH^+, found 357.1388. $C_{26}H_{17}N_2$ requires 357.1386.

2-Chloro-3-(phenanthren-9-yl)quinoxaline (4a)



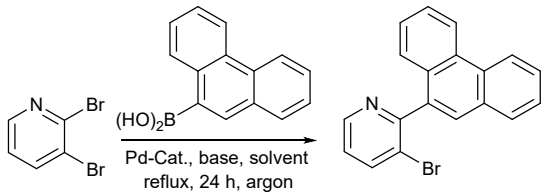
A stirred mixture of 2,3-dichloroquinoxaline (100 mg, 0.5 mmol), phenanthrene-9-boronic acid (133 mg, 0.6 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), K_2CO_3 (414 mg, 3 mmol), THF (6 mL) and water (6 mL) was refluxed for 24 h under argon. After evaporation of the reaction mixture the residue was diluted with water (100 mL) and extracted with $CHCl_3$ (3 × 20 mL). The extract was dried over Na_2SO_4. Flash column chromatography on silica gel (3.5 × 40 cm) was then carried out using $CHCl_3$ as the eluent. From the fraction with R_f 0.6 compound **4a** was isolated (83 mg, 49%). The raw product was crystallized from EtOH. The yellowish solid with mp 223-224 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.58 (m, 2 H), 7.45–7.60 (m, 2H), 7.63–7.80 (m, 3 H), 7.82–8.00 (m, 4 H), 8.15–8.25 (m, 2 H), 8.76–8.84 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 122.9, 123.4, 126.0, 127.1, 127.2, 127.3, 127.9, 128.5, 129.0, 129.4, 129.5, 130.1, 130.7, 130.8, 131.0, 131.1, 131.4, 133.6, 141.1, 141.7, 148.0, 153.7 ppm. HRMS (ESI): MH^+, found 341.0843. $C_{22}H_{14}ClN_2$ requires 341.0840.

2-Chloro-3-(phenanthren-9-yl)pyrazine (4b)



A stirred mixture of 2,3-dichloropyrazine (149 mg, 1.0 mmol), phenanthrene-9-boronic acid (244 mg, 1.1 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), K_2CO_3 (414 mg, 3 mmol), toluene (3 mL), EtOH (0.5 mL) and water (0.5 mL) was refluxed for 24 h under argon. After evaporation of the reaction mixture the residue was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4. Flash column chromatography on silica gel (3.5 × 35 cm) was then carried out using $CHCl_3$ as the eluent. From the fraction with R_f 0.3 compound **4b** was isolated (134 mg, 46%). The raw product was crystallized from hexane. The off-white solid with mp 105-107 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.46 (dd, J = 8.2, 0.9 Hz, 1 H), 7.57 (ddd, J = 8.2, 7.0, 1.2 Hz, 1 H), 7.62–7.78 (m, 3 H), 7.84 (s, 1 H), 7.95 (dd, J = 7.8, 1.3 Hz, 1 H), 8.53 (d, J = 2.5 Hz, 1 H), 8.73 (d, J = 2.5 Hz, 1 H), 8.74–8.85 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 122.8, 123.3, 125.8, 127.1, 127.2, 127.8, 129.0, 129.3, 129.7 (2C), 130.7, 130.9, 131.0, 133.0, 142.5, 143.1, 149.9, 154.2 ppm. HRMS (ESI): MH^+, found 291.0687. $C_{18}H_{12}ClN_2$ requires 291.0684.

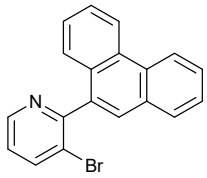
Table S2. Suzuki coupling of compound **3c** with phenanthren-9-ylboronic acid



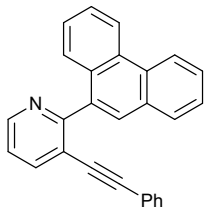
3c **4c**

Entry	Pd-Cat.	Base	Solvent	Yield, %
1	5% Pd/C, PPh_3	K_2CO_3	Toluene, H_2O	67
2	$Pd(PPh_3)_4$	K_2CO_3	Toluene, H_2O	65
3	$Pd(PPh_3)_4$	K_2CO_3	1,4-Dioxane, H_2O	45
4	$Pd(PPh_3)_4$	K_2CO_3	THF, H_2O	69-72
5	**$Pd(PPh_3)_4$**	**K_2CO_3 $KF{\cdot}2H_2O$**	**THF, H_2O**	**78**
5	$Pd(PPh_3)_4$	Na_2CO_3	MeCN, H_2O	64

3-Bromo-2-(phenanthren-9-yl)pyridine (4c)



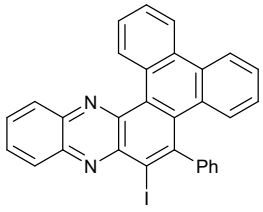
A stirred mixture of 2,3-dibromopyridine (119 mg, 0.5 mmol), phenanthrene-9-boronic acid (140 mg, 0.63 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), K_2CO_3 (414 mg, 3 mmol), $KF{\cdot}2H_2O$ (282 mg, 3 mmol), THF (5 mL) and water (5 mL) was refluxed for 24 h under argon. After evaporation of the reaction mixture the residue was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4. Flash column chromatography on silica gel (3.5 × 35 cm) was then carried out using CH_2Cl_2 as the eluent. From the fraction with R_f 0.5 compound **4c** was isolated (130 mg, 78%). The raw product was crystallized from EtOH. The pale yellow solid with mp 123-124 °C (EtOH). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 7.29 (d, J = 8.0 Hz, 1H), 7.45–7.60 (m, 2H), 7.62–7.78 (m, 3H), 7.80 (s, 1H), 8.03 (d, J = 7.0 Hz, 1H), 8.29 (dd, J = 8.1, 1.1 Hz, 1H), 8.73 (dd, J = 4.6, 1.1 Hz, 1H), 8.89 (pseudotriplet, J = 8.6 Hz, 2H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 122.3, 122.7, 123.1, 123.9, 126.2, 126.7, 126.8, 126.9, 127.2, 128.0, 129.1, 130.1, 130.5, 130.6, 131.2, 136.5, 140.8, 148.2, 158.6 ppm. HRMS (ESI): m/z calcd. for $C_{19}H_{13}BrN^+$ [M + H^+]: 334.0226 (^{79}Br), 336.0206 (^{81}Br), found 334.0226 (^{79}Br), 336.0207 (^{81}Br).



2-(Phenanthren-9-yl)-3-(phenylethynyl)pyridine (2c)

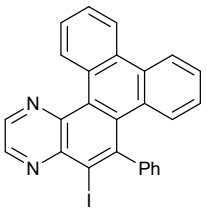
A mixture of 3-bromo-2-(phenanthren-9-yl)pyridine **4c** (167 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (5 mg, 0.025 mmol), i-Pr_2NH (1 mL) and DMSO (5 mL) was refluxed under argon for 20 min. Then a solution of phenylacetylene (77 mg, 0.08 mL, 0.75 mmol) in i-Pr_2NH (2 mL) was added by portions for 2 h. The reaction mixture was refluxed for 22 h. Then it was evaporated without heating to remove i-Pr_2NH, treated with H_2O (100 mL) and extracted with CH_2Cl_2 (4 × 15 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (3.5 × 40 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.6 and violet fluorescence under UV gave 160 mg (90%) of compound **2c** as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.82–6.85 (m, 2 H), 7.06–7.17 (m, 3 H), 7.39 (dd, J = 7.9, 4.9 Hz, 1 H), 7.58–7.73 (m, 4 H), 7.85 (dd, J = 8.1, 1.1 Hz, 1 H), 7.98 (dd, J = 7.8, 1.4 Hz, 1 H), 8.00–8.05 (m, 2 H), 8.78–8.85 (m, 3 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 86.8, 95.8, 120.8, 122.0, 122.4, 122.7, 122.9, 126.5, 126.6, 126.8, 126.9, 127.1, 128.1 (2C), 128.5, 128.9, 129.1, 130.4, 130.6, 130.7, 131.3 (2C), 131.4, 136.2, 139.8, 148.4, 160.8 ppm. HRMS (ESI): MH^+, found 356.1436. $C_{27}H_{18}N$ requires 356.1434.

6-Iodo-5-phenylphenanthro[9,10-*a*]phenazine (5a)



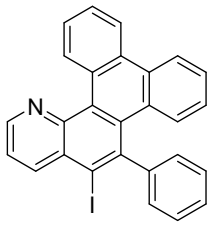
To a stirred suspension of 2-(phenanthren-9-yl)-3-(phenylethynyl)quinoxaline **2a** (81 mg, 0.2 mmol) in dry CH_3CN (7 mL), a solution of ICl (61 mg, 0.38 mmol) in dry CH_3CN (2 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark and then evaporated to dryness. The residue was shaken with $CHCl_3$ (50 mL) and saturated aq. $Na_2S_2O_3$ (5 mL). The organic layer was separated, dried over Na_2SO_4 and purified by flash column chromatography on silica gel (1.5 × 50 cm) with $CHCl_3$ as the eluent. The bright yellow fraction with R_f 0.8 gave 88 mg (83%) of compound **5a** as a yellow solid with mp 247–249 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.11 (ddd, J = 8.4, 7.1, 1.2 Hz, 1 H), 7.42–7.56 (m, 6 H), 7.70 (d, J = 8.5 Hz, 1 H), 7.76–7.84 (m, 2 H), 7.89–8.01 (m, 2 H), 8.42–8.51 (m, 2 H), 8.62 (d, J = 8.3 Hz, 1 H), 8.68–8.75 (m, 1 H), 10.00–10.09 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 109.6, 123.0, 123.2, 125.4, 127.5, 127.6, 127.8, 128.3, 128.4 (2C), 129.1(8), 129.2(3), 129.4, 129.6, 129.8, 130.7(7), 130.8(2), 131.4, 131.5 (2C), 131.8, 132.1, 132.3, 141.6, 142.4, 142.7, 147.0, 148.4 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 272 (4.65), 294 sh (4.52), 316 (4.52), 328 (4.60), 402 sh (3.99), 422 (4.05), end absorption up to 510 nm. HRMS (ESI): MH^+, found 533.0514. $C_{30}H_{17}IN_2$ requires 533.0509.

6-Iodo-5-phenylphenanthro[9,10-*f*]quinoxaline (5b)



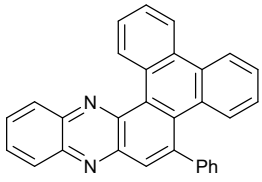
Compound **5b** was synthesized similarly to **5a** from 2-(phenanthren-9-yl)-3-(phenylethynyl)pyridine **2b** (72 mg, 0.2 mmol). Chromatographic purification was performed on a silica gel column (2 × 20 cm) using a $CHCl_3$-hexane mixture (2:1, v/v) as the eluent. The yellow fraction with R_f 0.4 gave 81 mg (84%) of compound **5b** as a yellow solid with mp 203–205 °C (MeCN). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.09 (ddd, *J* = 8.5, 7.0, 1.4 Hz, 1 H), 7.39–7.53 (m, 6 H), 7.69 (dd, *J* = 8.5, 0.9 Hz, 1 H), 7.71–7.80 (m, 2 H), 8.3 (d, *J* = 8.6 Hz, 1 H), 8.63–8.71 (m, 1 H), 8.99–9.07 (m, 2 H), 9.68–9.79 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 109.7, 123.1, 123.4, 125.6, 127.6, 127.7, 128.1, 128.4, 128.7(2C), 128.9, 129.1, 129.2, 130.0, 131.6, 131.7(2C), 131.8, 132.1, 132.4, 141.2, 142.6, 143.7, 144.7, 147.0, 147.4 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 263 (4.65), 282 sh (4.49), 310 (4.50), 360 sh (3.79), 379 (3.88), 395 (3.85), end absorption up to 438 nm. HRMS (ESI): MH^+, found 483.0349. $C_{26}H_{16}IN_2$ requires 483.0353.

6-Iodo-5-phenylphenanthro[9,10-*h*]quinoline (5c)



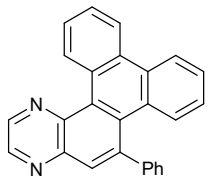
Compound **5b** was synthesized similarly to **5a** from 2-(phenanthren-9-yl)-3-(phenylethynyl)pyridine **2c** (71 mg, 0.2 mmol). Chromatographic purification was performed on a silica gel column (2.5 × 70 cm) using CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.8 gave 68 mg (70%) of compound **5c** as a yellow viscous oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.04–7.10 (m, 1 H), 7.37–7.50 (m, 6 H), 7.58–7.66 (m, 2 H), 7.70–7.77 (m, 2 H), 8.56 (d, *J* = 8.1 Hz, 1 H), 8.62–8.66 (m, 1 H), 8.82 (dd, *J* = 8.5, 1.5 Hz, 1 H), 9.05 (dd, *J* = 4.2, 1.5 Hz, 1 H), 9.75–9.82 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 106.2, 122.7, 122.9, 123.2, 125.3, 127.1, 127.2, 127.6, 128.1, 128.5, 129.4, 129.3, 129.4, 129.7, 130.1, 131.5, 131.6, 131.7, 131.9 (2C), 142.2, 143.7, 146.0, 147.6, 149.5 ppm. HRMS (ESI): MH^+, found 482.0397. $C_{27}H_{17}IN$ requires 482.0400.

5-Phenylphenanthro[9,10-*a*]phenazine (6a)



A stirred solution of compound **2a** (61 mg, 0.15 mmol) in CF_3COOH (8 mL) was heated at 60 °C for 24 h. The reaction mixture was evaporated to dryness, treated with saturated aq. K_2CO_3 (20 mL) and extracted with $CHCl_3$ (3 × 15 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (1.5 × 35 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.2 gave 53 mg (87%) of compound **6a** as a yellow solid with mp 247–248 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.16 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1 H), 7.35–7.62 (m, 6 H), 7.73–7.97 (m, 5 H), 8.25 (s, 1 H), 8.28–8.38 (m, 1 H), 8.40–8.51 (m, 1 H), 8.66 (d, *J* = 8.1 Hz, 1 H), 8.77 (dd, *J* = 7.8, 1.7 Hz, 1 H), 10.37 (dm, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 123.0, 123.3, 125.2, 127.5(6), 127.5(8), 127.6, 127.9, 128.4, 128.9, 129.0(6), 129.1(3), 129.1(6), 129.2(0), 129.8, 130.0(8), 130.1(0), 130.8, 131.2, 131.3, 131.7, 132.0, 141.7, 142.1, 142.5, 142.6, 142.8, 143.8, 144.2 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 270 (4.66), 280 sh (4.63), 313 (4.49), 324 (4.56), 408 sh (4.06), 425 (4.08), end absorption up to 485 nm. HRMS (ESI): MH^+, found 407.1545. $C_{30}H_{19}N_2$ requires 407.1543.

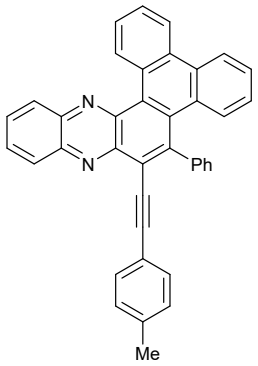
5-Phenylphenanthro[9,10-f]quinoxaline (6b)



Compound **6b** was synthesized similarly to **6a** from 2-(phenanthren-9-yl)-3-(phenylethynyl)pyridine **2b** (53 mg, 0.15 mmol). Chromatographic purification was performed on a silica gel column (2.5 × 25 cm) using a hexane - ethyl acetate mixture (3:1, v/v) as the eluent. The yellow fraction with R_f 0.7 gave 48 mg (90%) of compound **6b** as a yellow solid with mp 204–207 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.13 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1 H), 7.39–7.59 (m, 6

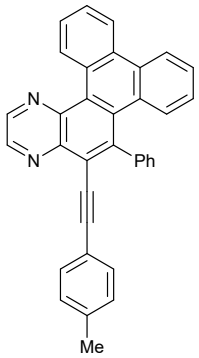
H), 7.71–7.82 (m, 3 H), 8.16 (s, 1 H), 8.11 (dm, *J* = 8.2 Hz, 1 H), 8.67–8.75 (m, 1 H), 8.93 (d, *J* = 1.9 Hz, 1 H), 9.04 (d, *J* = 1.9 Hz, 1 H), 10.03 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 123.0, 123.4, 125.2, 127.4, 127.5, 127.6, 127.7, 128.8, 129.1(2C), 129.3(2C), 129.6, 129.9, 130.2, 131.0, 131.2, 131.5, 131.8, 141.4, 142.4, 142.6, 142.9, 144.0(0), 144.0(2) ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 260 (4.66), 297 sh (4,47), 306 (4.48), 355 (3.79), 373 (3.80), 392 (3.72), end absorption up to 417 nm. HRMS (ESI): MH^+, found 357.1390. $C_{26}H_{17}N_2$ requires 357.1386.

5-Phenyl-6-(*p*-tolylethynyl)phenanthro[9,10-*a*]phenazine (7a)



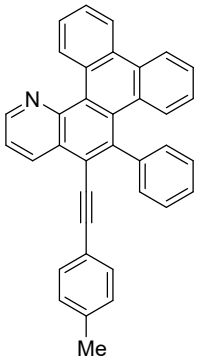
A mixture of iodide **5a** (53 mg, 0.1 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), piperidine (4 mL) was stirred and refluxed for 20 min under argon. A solution of *p*-tolylacetylene (35 mg, 0.3 mmol) in piperidine (2 mL) was then added by portions for 1.5 h. The reaction mixture was refluxed for 24 h and evaporated without heating to dryness. The residue was treated with H_2O (40 mL) and extracted with $CHCl_3$ (3 × 15 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (2.5 × 40 cm) using $CHCl_3$ as the eluent. The fluorescent orange fraction with R_f 0.4 gave compound **7a** (44 mg, 85%) as an orange solid with mp 218-219 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): 2.38 (s, 3 H), 7.09–7.19 (m, 3 H), 7.34–7.42 (m, 2 H), 7.44–7.59 (m, 4 H), 7.60–7.68 (m, 2 H), 7.70–7.88 (m, 3 H), 7.89–7.99 (m, 2 H), 8.39–8.53 (m, 2 H), 8.63 (d, *J* = 8.1 Hz, 1 H), 8.69–8.77 (m, 1 H), 10.16–10.25 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.8, 87.1, 100.5, 120.8, 121.7, 123.1, 123.4, 125.4, 127.5, 127.7, 127.9, 128.0, 128.4, 129.2 (2C), 129.5, 129.6, 129.9, 130.1, 130.3, 130.5(7), 130.5(9), 131.4, 131.5, 131.8(8), 131.9(4) (2C), 132.1, 132.3, 138.7, 142.1, 142.2, 142.3, 142.6, 143.1, 145.8 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 271 (4.52), 287 sh (4.50), 332 (4.60), 410 sh (3.89), 433 sh (4.00), 472 sh (3.82), end absorption up to 540 nm. HRMS (ESI): MH^+, found 521.2014. $C_{39}H_{24}N_2$ requires 521.2012.

5-Phenyl-6-(*p*-tolylethynyl)phenanthro[9,10-*f*]quinoxaline (7b)



Compound **7b** was synthesized similarly to **7a** from iodide **5b** (48 mg, 0.1 mmol). Chromatographic purification was performed on a silica gel column (4 × 32 cm) using $CHCl_3$ as the eluent. The fluorescent yellow fraction with R_f 0.35 gave 42 mg (89%) of compound **7b** as a yellow solid with mp 242-244 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.04–7.17 (m, 3 H), 7.22–7.35 (m, 2 H), 7.43–7.68 (m, 6 H), 7.71–7.83 (m, 3 H), 8.59 (d, *J* = 8.1, 1 H), 8.64–8.73 (m, 1 H), 9.08 (br s, 2 H), 9.80–9.90 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) 21.7, 86.7, 100.4, 120.5, 121.9, 123.1, 123.4, 125.5, 127.5, 128.0, 128.5 (2C), 128.6, 129.1(2C), 129.3, 129.4, 130.2, 131.4 (2C), 131.8, 131.9 (2C), 132.1, 138.7, 141.1, 142.5, 142.8, 143.3, 144.2, 144.9 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 268 (4.58), 292 sh (4.55), 313 (4.62), 323 sh (4.59), 404 (4.15), end absorption up to 465 nm. HRMS (ESI): MH^+, found 471.1859. $C_{35}H_{23}N_2$ requires 471.1856.

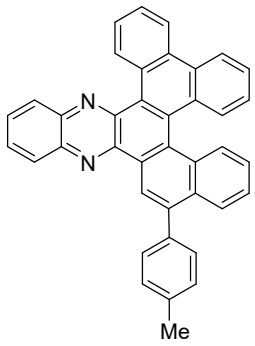
5-Phenyl-6-(*p*-tolylethynyl)phenanthro[9,10-*h*]quinoline (7c)



Compound **7c** was synthesized similarly to **7a** from iodide **5c** (48 mg, 0.1 mmol). Chromatographic purification was performed on a silica gel column (2.5 × 50 cm) using $CHCl_3$ as the eluent. The fluorescent yellowish fraction with R_f 0.6 gave 44 mg (93%) of compound **7c** as a yellowish solid with mp 197-198 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.06–7.17 (m, 3 H), 7.27–7.31 (m, 2 H), 7.46–7.52 (m, 4 H), 7.59–7.67 (m, 3 H), 7.72–7.80 (m, 3 H), 8.58 (d, *J* = 8.2 Hz, 1 H), 8.66 (dd, *J* = 8.8, 1.8 Hz, 1 H), 9.01 (dd, *J* = 8.0, 0.6 Hz, 1 H), 9.16 (d, *J* = 3.9 Hz, 1 H), 10.0 (dd, *J* = 9.1, 2.0 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.6, 86.8, 99.2, 119.9, 120.3, 121.6, 122.9,

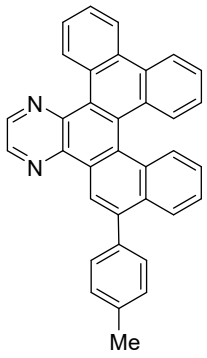
123.2, 125.2, 127.0, 127.2, 127.4, 127.5, 127.6, 128.3, 129.2, 129.6, 129.7, 130.0, 131.2, 131.4, 131.5, 131.6, 131.7, 131.8, 135.3, 138.8, 141.1, 142.8, 145.7, 149.1 ppm. HRMS (ESI): MH^+, found 470.1891. $C_{36}H_{24}N$ requires 470.1903.

9-(*p*-Tolyl)naphtho[2,1-*a*]phenanthro[9,10-*c*]phenazine (8a)



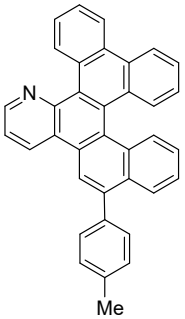
A stirred solution of alkyne **7a** (52 mg, 0.1 mmol) in CF_3COOH (5 mL) was heated at 60 °C for 24 h. The reaction mixture was evaporated to dryness, treated with saturated K_2CO_3 (15 mL) and extracted with $CHCl_3$ (3 × 15 mL). The organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2 × 25 cm) with $CHCl_3$ as the eluent. The fluorescent bright yellow fraction with R_f 0.8 gave cyclization product **7a** (40 mg, 77%) as a yellow orange solid with mp 309–311 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 7.19–7.36 (m, 2 H), 7.41–7.51 (m, 3 H), 7.60–7.73 (m, 3 H), 7.79–7.94 (m, 4 H), 8.02–8.16 (m, 3 H), 8.31–8.45 (m, 2 H), 8.68 (d, J = 8.1 Hz, 1 H), 8.81 (dd, J = 8.2, 1.3 Hz, 1 H), 9.48 (s, 1 H), 10.49 (dd, J = 8.3, 1.3 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 122.6, 123.0, 123.5, 124.9, 125.6, 126.7, 126.9, 127.1(6), 127.2(2), 127.4, 127.8, 128.2, 129.1, 129.2 (2C), 129.5, 129.7, 129.8, 130.0, 130.2 (2C), 130.4, 130.7, 130.7(8), 130.8(2), 131.4(1), 131.4(4), 133.0, 137.4, 137.7, 140.8 (2C), 142.0, 142.6, 143.7 ppm. HRMS (ESI): MH^+, found 520.2014. $C_{39}H_{24}N_2$ requires 520.2012.

10-(*p*-Tolyl)naphtho[2,1-*f*]phenanthro[9,10-*h*]quinoxaline (8b)



Compound **8b** was synthesized similarly to **8a** from alkyne **7b** (47 mg, 0.1 mmol). Chromatographic purification was performed on a silica gel column (2.5 × 20 cm) using $CHCl_3$ as the eluent. The fluorescent yellow fraction with R_f 0.6 gave 39 mg (82%) of compound **7b** as a yellow solid with mp 251–253 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.53 (s, 3 H), 7.21–7.34 (m, 2 H), 7.38–7.51 (m, 3 H), 7.58–7.69 (m, 3 H), 7.75–7.88 (m, 2 H), 8.09 (dd, J = 8.5, 0.8 Hz, 1 H), 8.14 (d, J = 8.2 Hz, 1 H), 8.27 (d, J = 8.5 Hz, 1 H), 8.65 (d, J = 8.2 Hz, 1 H), 8.73–8.83 (m, 1 H), 8.93 (d, J = 2.0 Hz, 1 H), 9.06 (d, J = 2.0 Hz, 1 H), 9.29 (s, 1 H), 10.05–10.13 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 121.8, 123.1, 123.7, 125.0, 125.7, 126.8, 127.0, 127.3, 127.5, 127.9, 128.9, 129.3(2C), 129.6, 130.2(2C), 130.3, 130.4, 130.5, 130.6(5), 130.7(5), 130.8, 131.4, 132.7, 137.5, 137.7, 140.9, 141.8, 142.4, 142.6, 143.1 ppm. HRMS (ESI): MH^+, found 471.1860. $C_{35}H_{23}N_2$ requires 471.1856.

10-(*p*-Tolyl)naphtho[2,1-*f*]phenanthro[9,10-*h*]quinoline (8c)



Compound **8c** was synthesized similarly to **8a** from alkyne **7c** (47 mg, 0.1 mmol). Chromatographic purification was performed on a silica gel column (2.5 × 45 cm) using $CHCl_3$ as the eluent. The fluorescent yellow fraction with R_f 0.7 gave 43 mg (92%) of compound **7c** as a yellowish solid with mp 243–244 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 7.20–7.30 (m, 2 H), 7.40–7.45 (m, 3 H), 7.56–7.65 (m, 4 H), 7.75–7.85 (m, 2 H), 8.01 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1 H), 8.26 (d, J = 8.5 Hz, 1 H), 8.58 (s, 1 H), 8.63 (d, J = 8.1 Hz, 1 H), 8.75 (dd, J = 7.1, 1.9 Hz, 1 H), 9.06 (d, J = 8.3 Hz, 1 H), 9.12 (d, J = 3.2 Hz, 1 H), 10.14 (dd, J = 9.0, 1.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 120.6, 121.0, 122.9, 123.5, 125.0, 125.2, 125.5, 125.7, 126.3, 126.4, 127.0, 127.1, 127.2, 127.3, 128.3, 129.3, 129.7, 130.1, 130.2, 130.3, 130.4, 131.0, 131.3, 131.3, 131.4, 1131.5, 131.6, 137.5, 137.7, 140.4, 147.2, 148.7 ppm. HRMS (ESI): MH^+, found 470.1904. $C_{36}H_{24}N$ requires 470.1903.

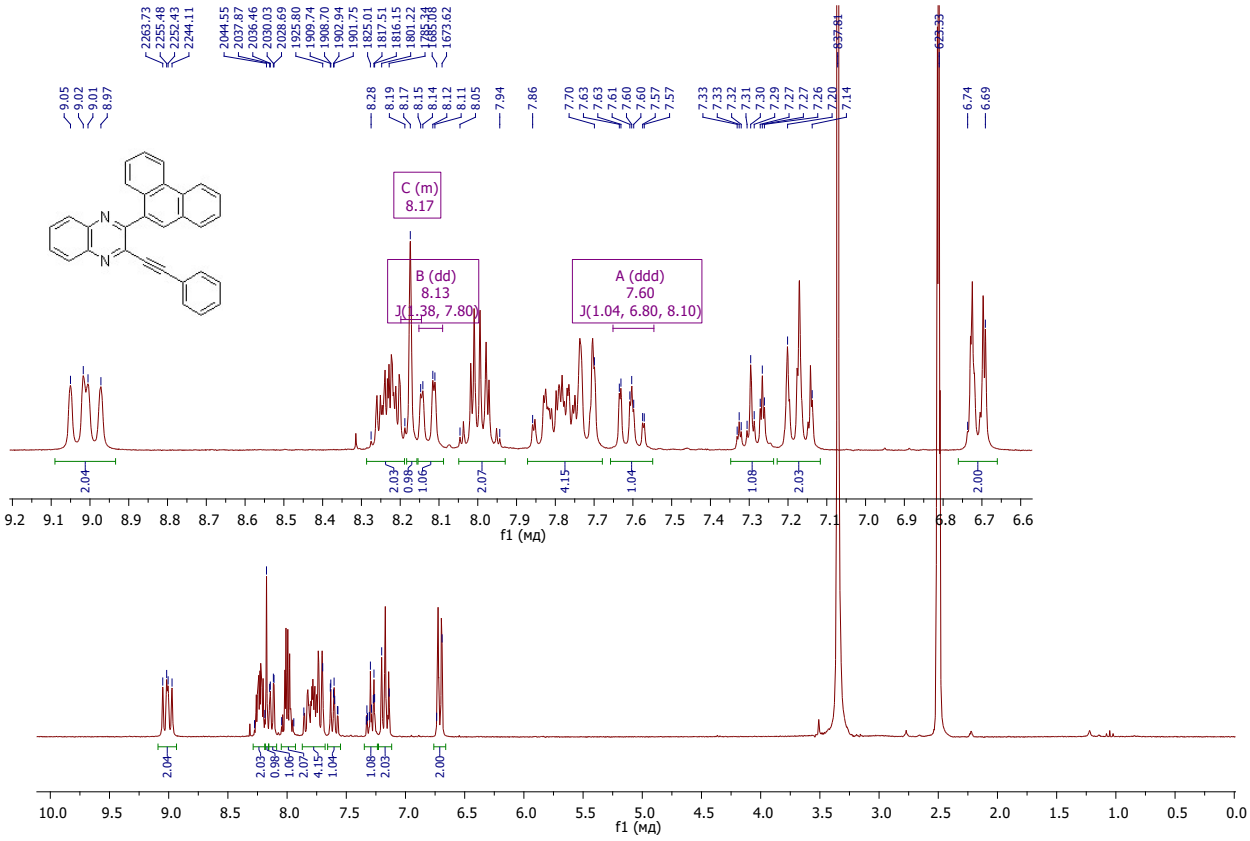


Fig. S1. ^{1}H NMR spectrum of compound **2a** (250 MHz, $CDCl_3$).

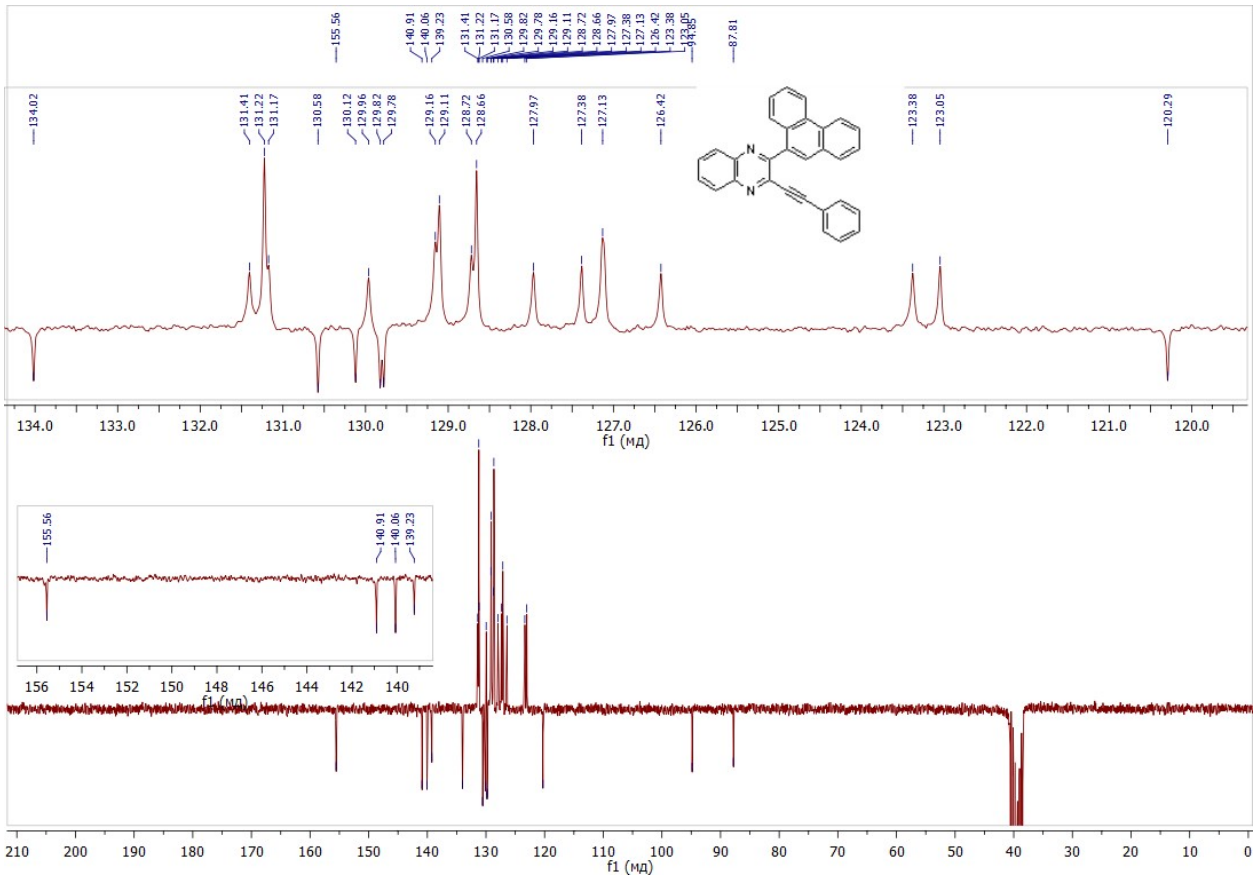


Fig. S2. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2a** (62.9 MHz, $CDCl_3$).

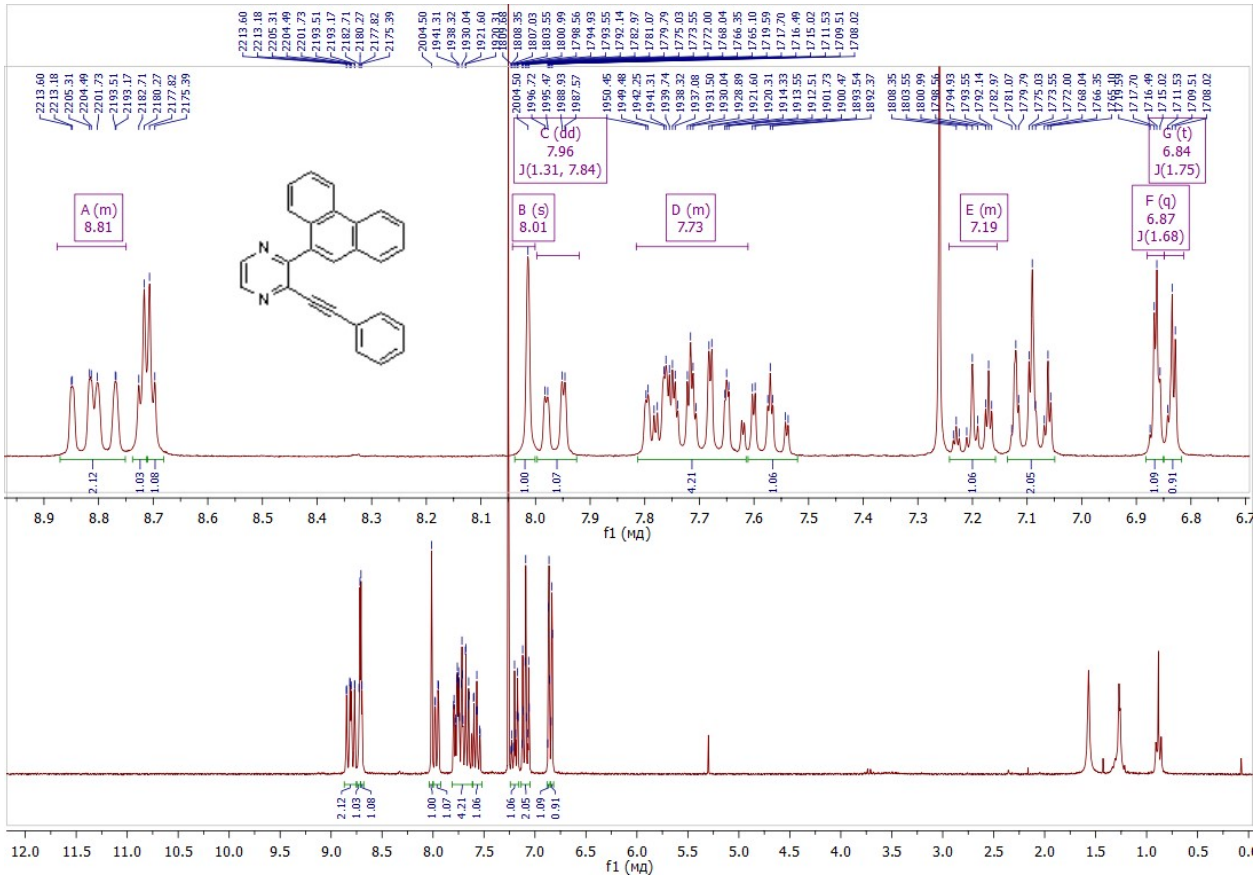


Fig. S3. ^{1}H NMR spectrum of compound **2b** (250 MHz, $CDCl_3$).

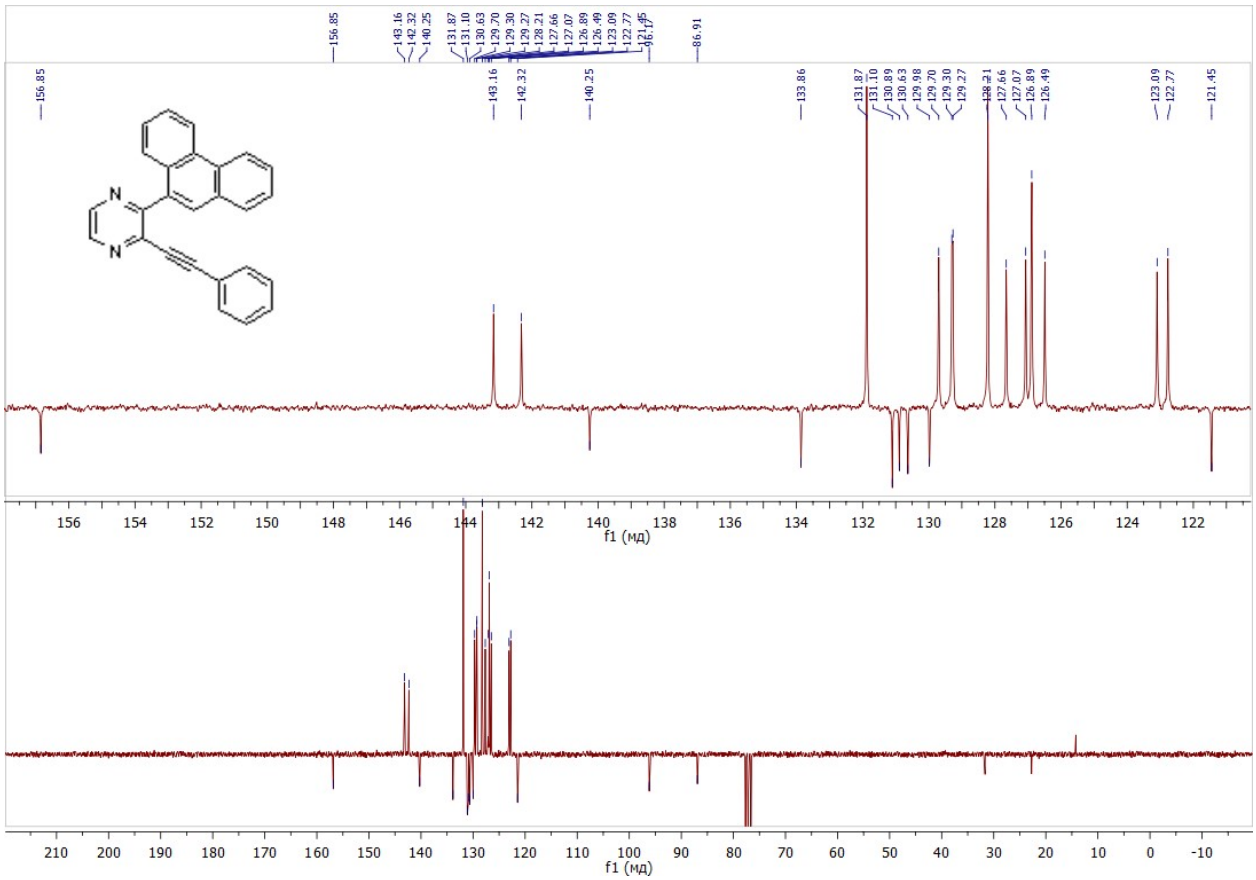


Fig. S4. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2b** (62.9 MHz, $CDCl_3$).

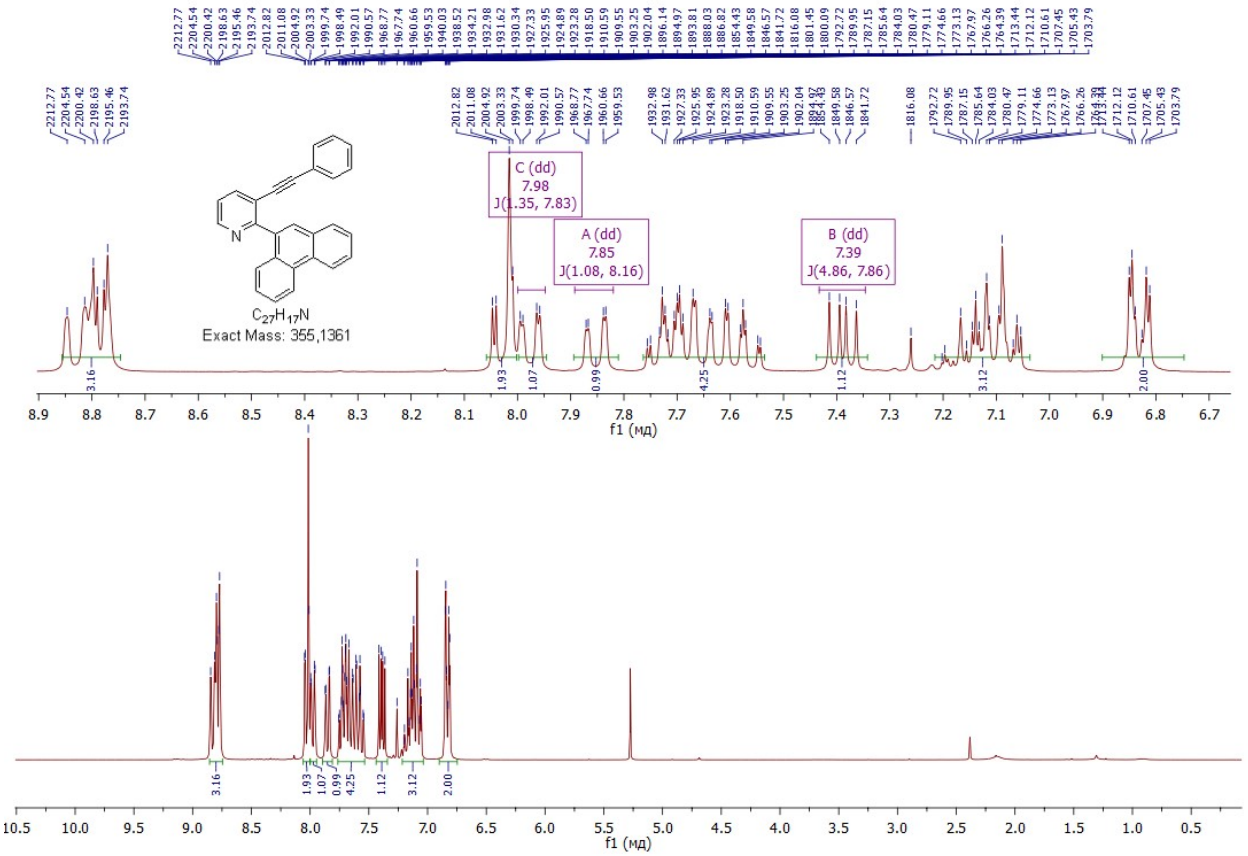


Fig. S5. ^{1}H NMR spectrum of compound **2c** (250 MHz, $CDCl_3$).

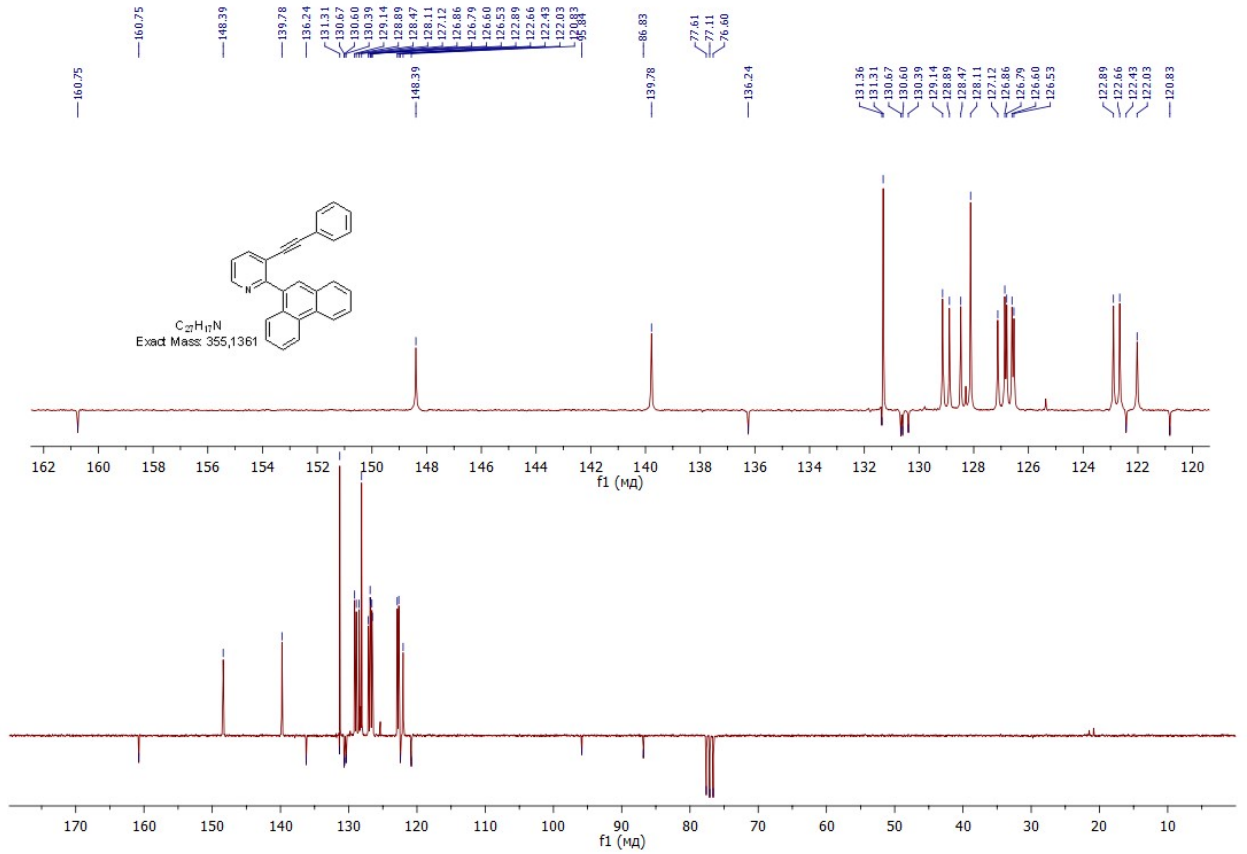


Fig. S6. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **2c** (62.9 MHz, $CDCl_3$).

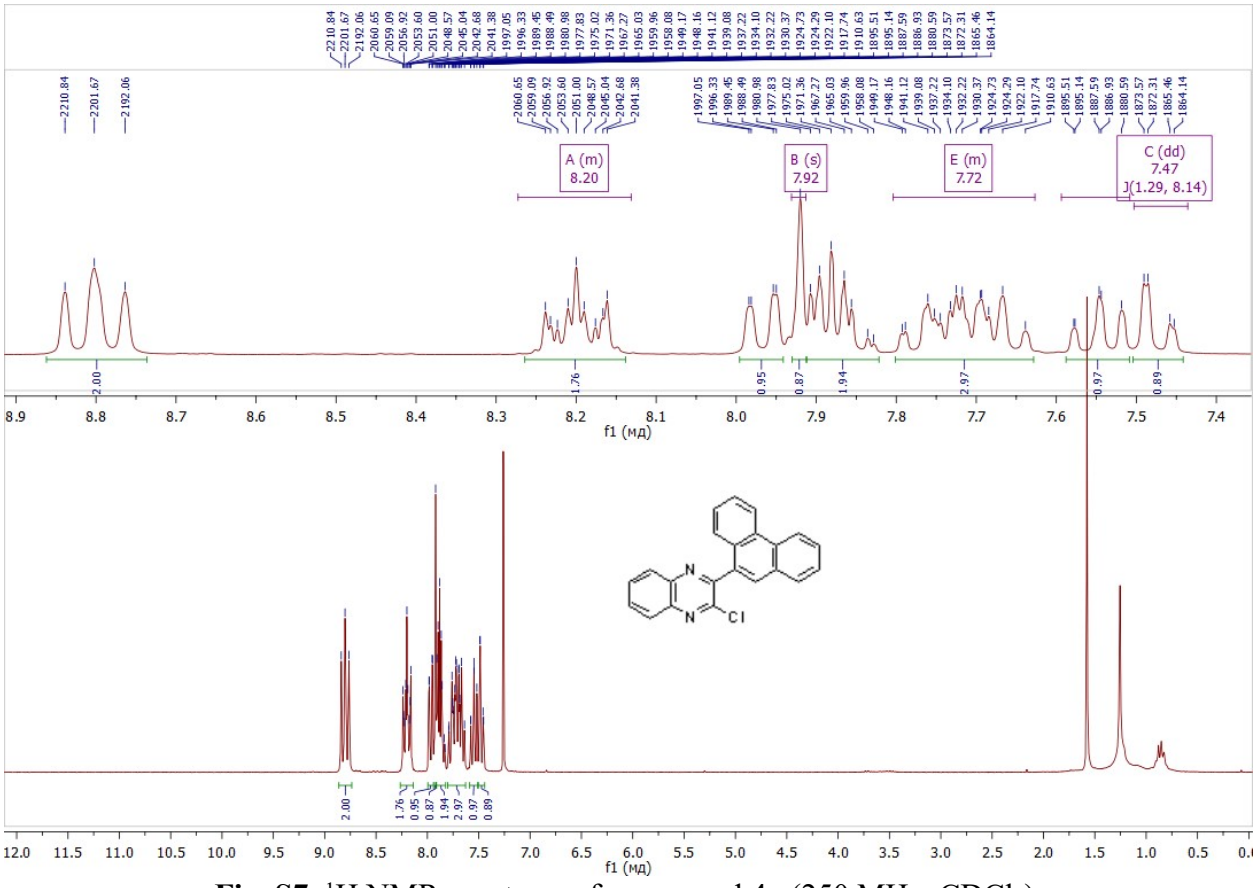


Fig. S7. ^{1}H NMR spectrum of compound **4a** (250 MHz, $CDCl_3$).

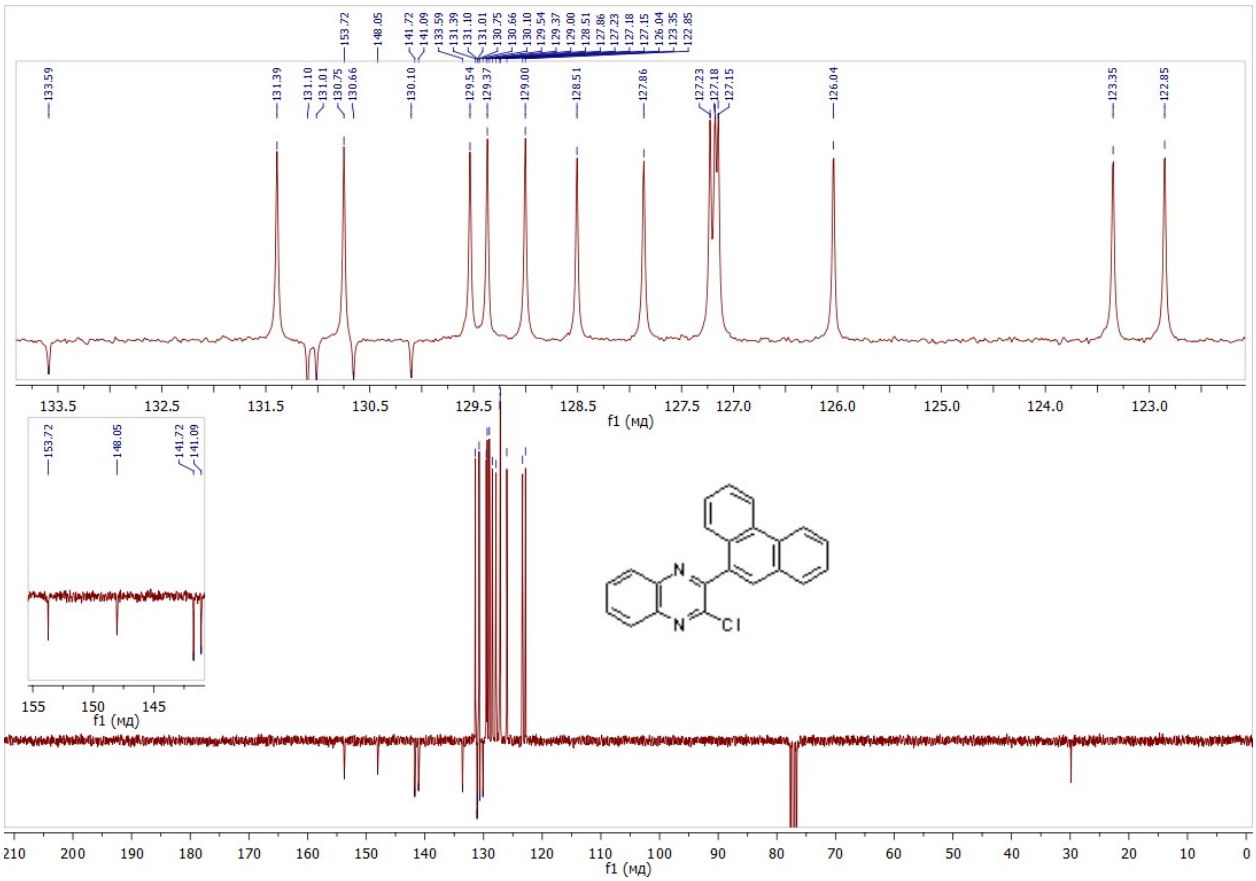


Fig. S8. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4a** (62.9 MHz, $CDCl_3$).

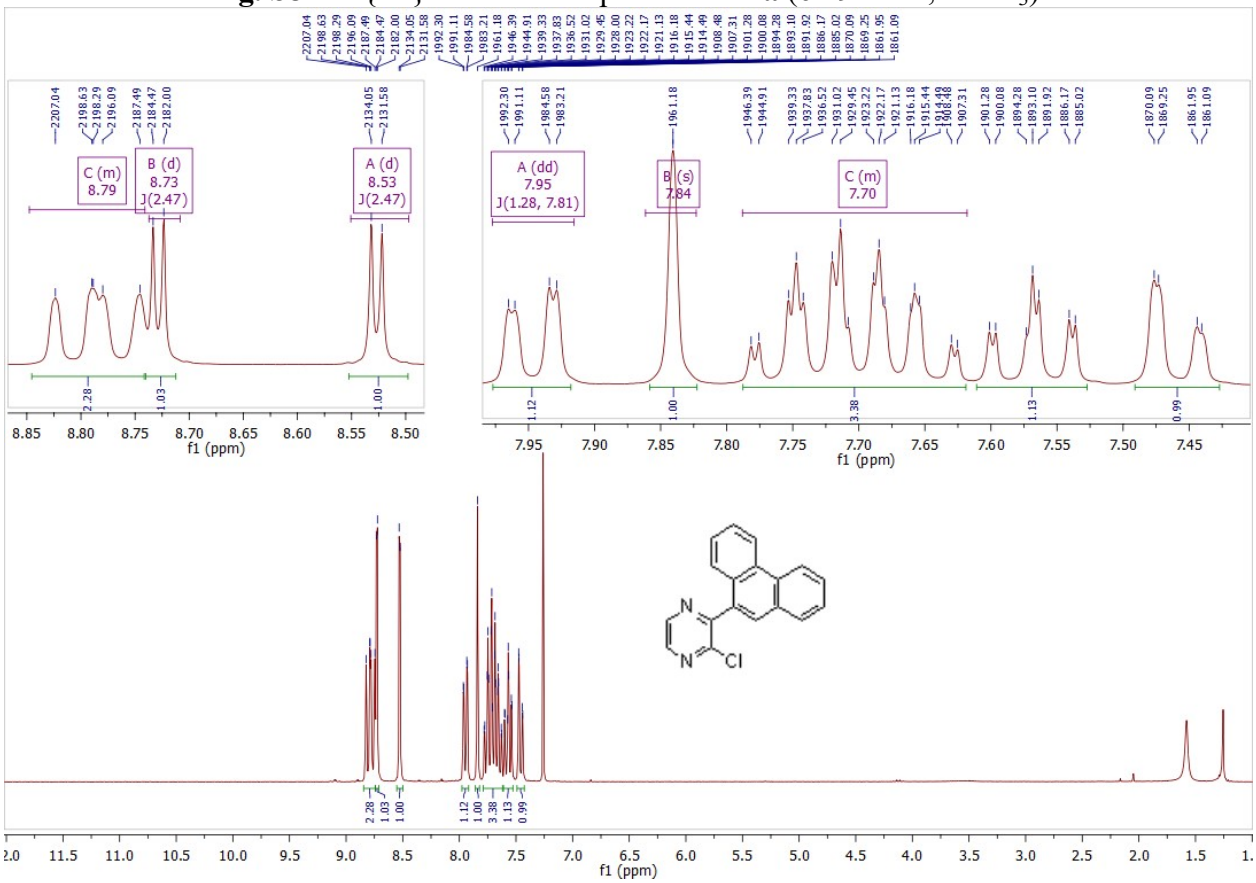


Fig. S9. ^{1}H NMR spectrum of compound **4b** (250 MHz, $CDCl_3$).

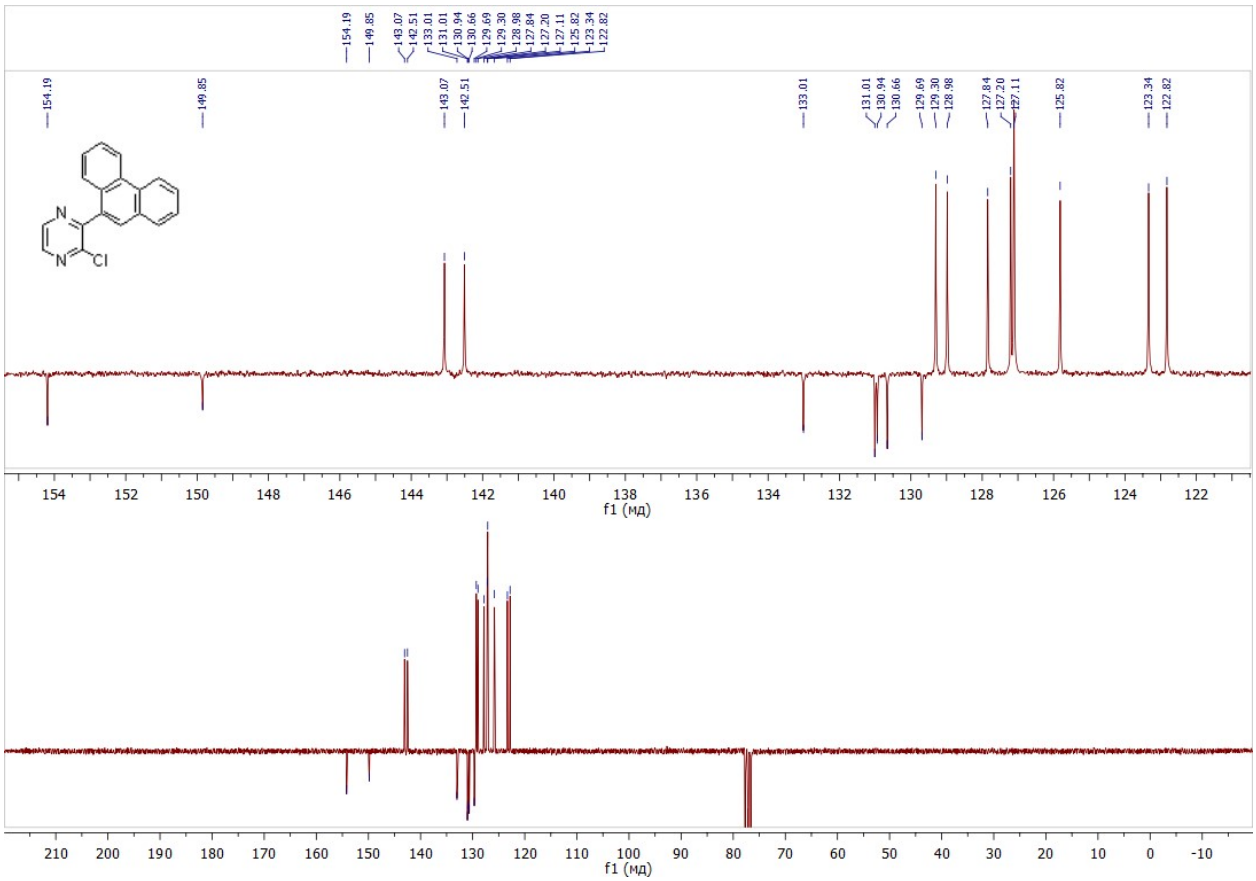


Fig. S10. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **4b** (62.9 MHz, $CDCl_3$).

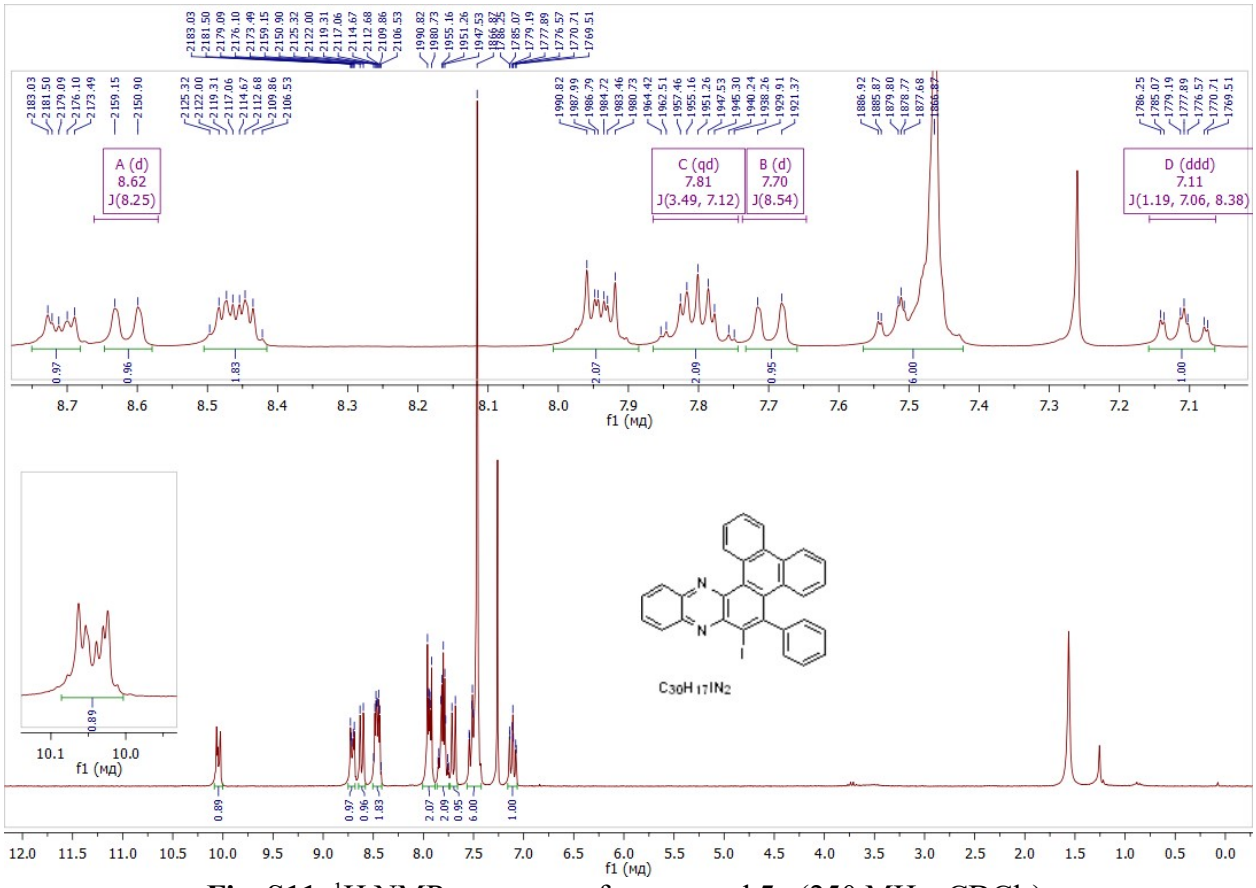


Fig. S11. ^{1}H NMR spectrum of compound **5a** (250 MHz, $CDCl_3$).

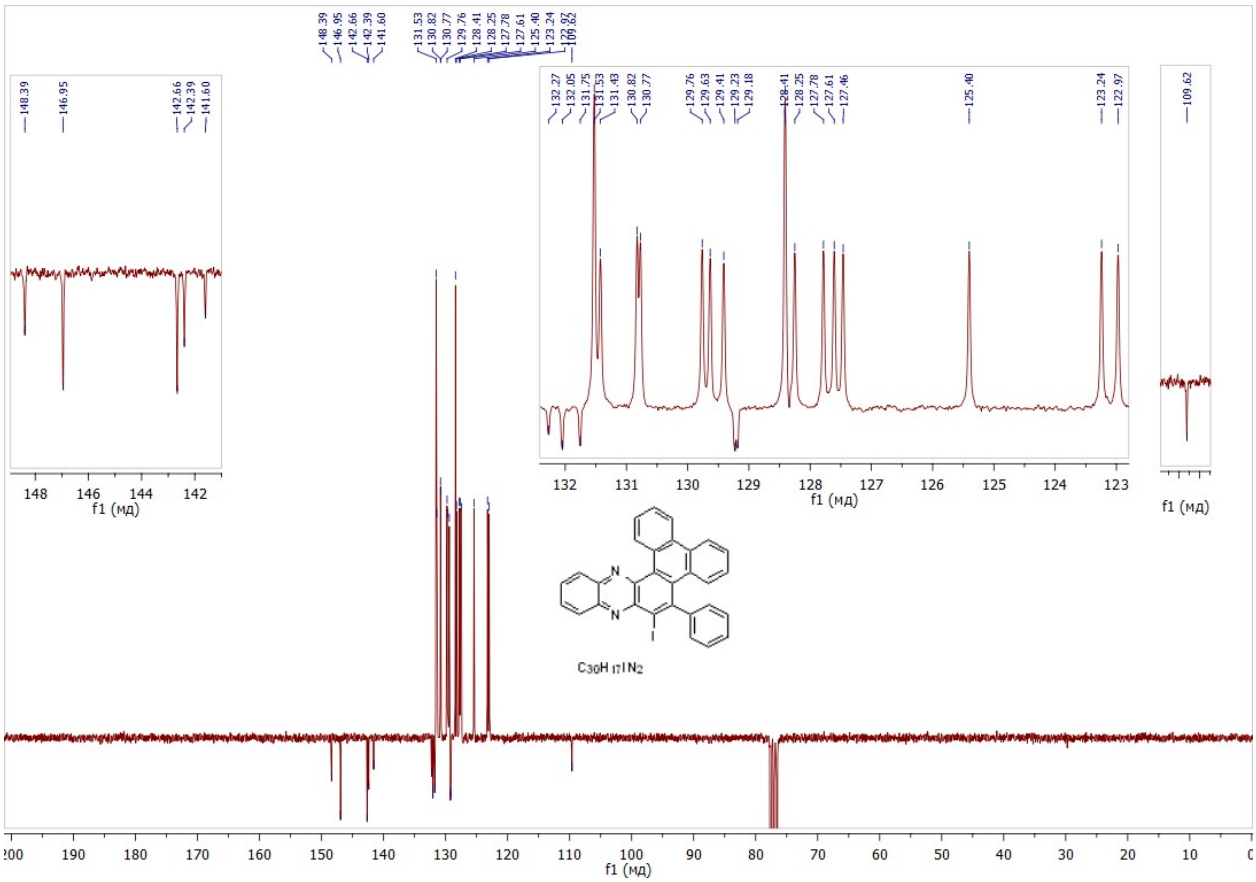


Fig. S12. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **5a** (62.9 MHz, $CDCl_3$).

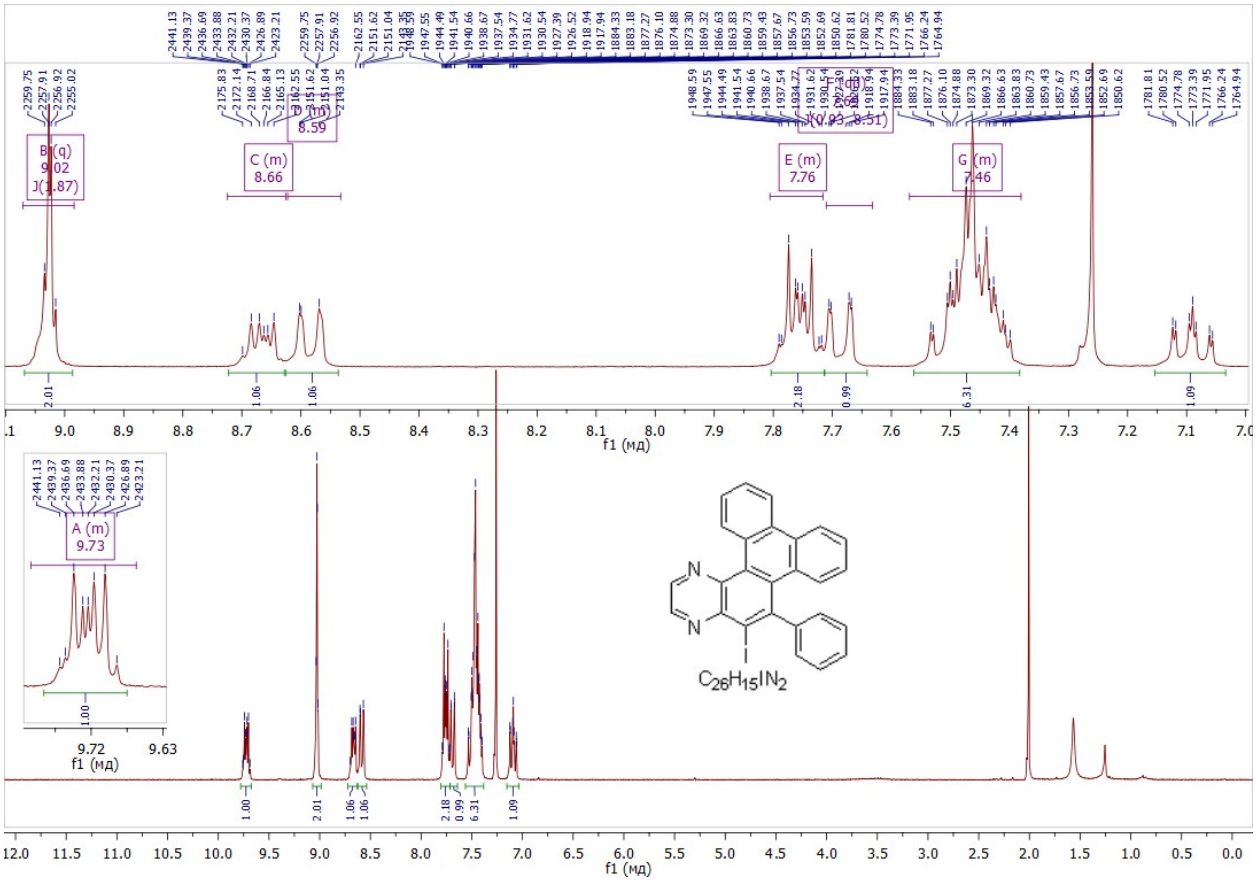


Fig. S13. ^{1}H NMR spectrum of compound **5b** (250 MHz, $CDCl_3$).

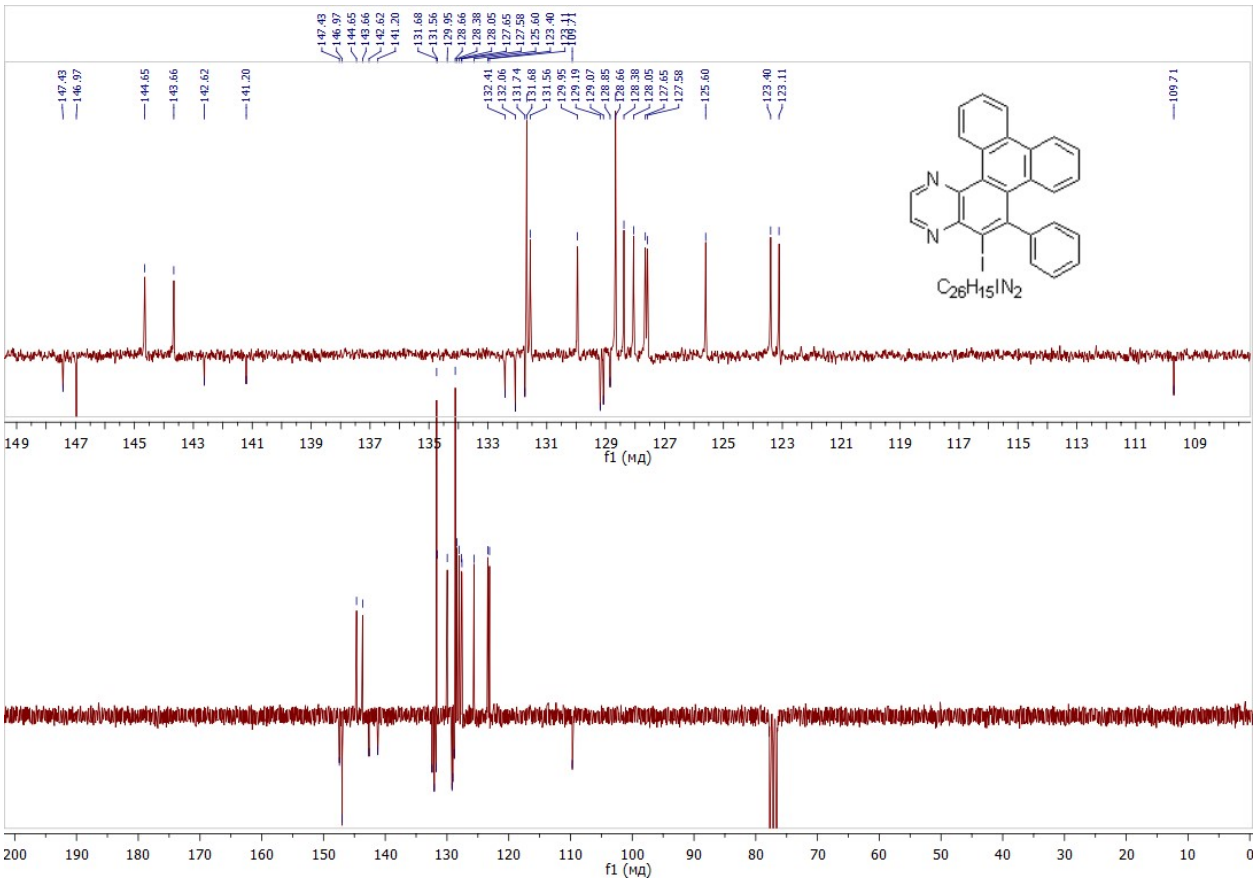


Fig. S14. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **5b** (62.9 MHz, $CDCl_3$).

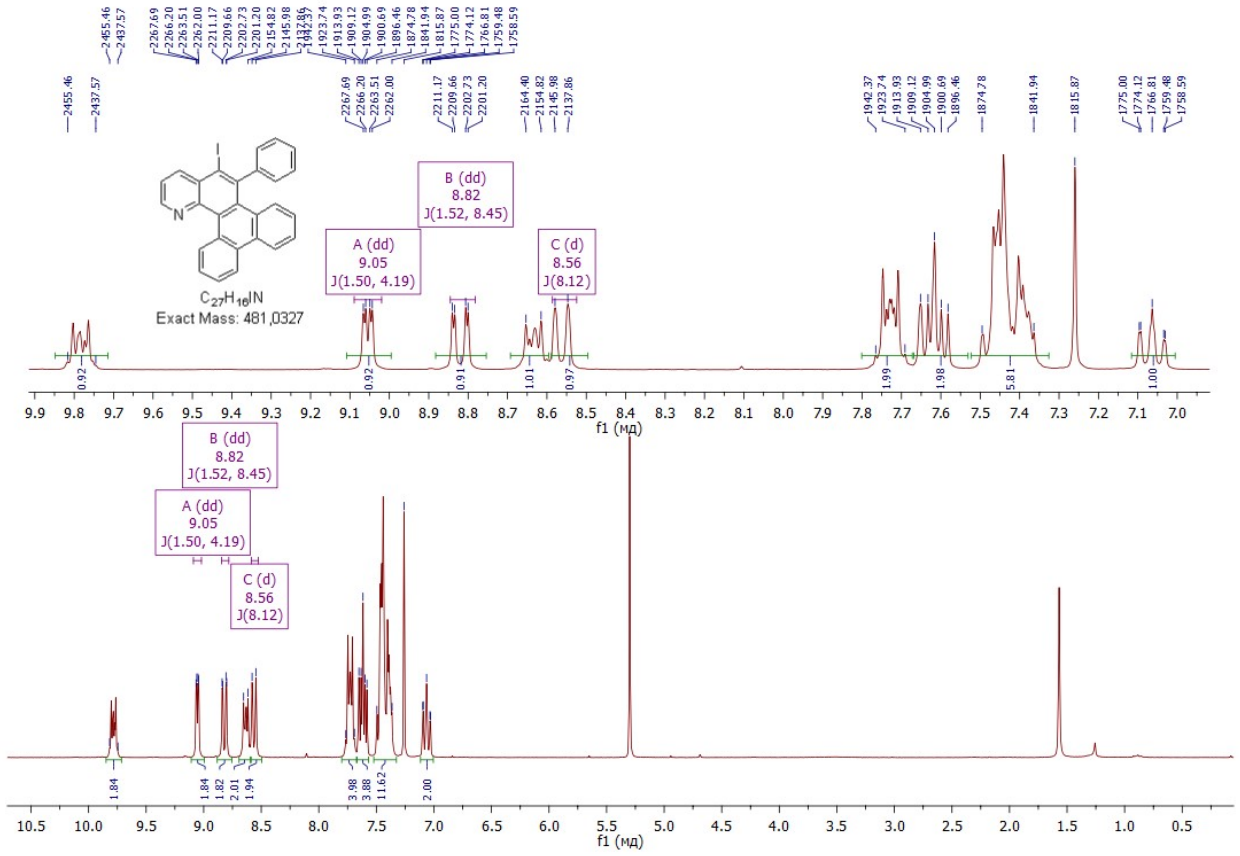


Fig. S15. ^{1}H NMR spectrum of compound **5c** (250 MHz, $CDCl_3$).

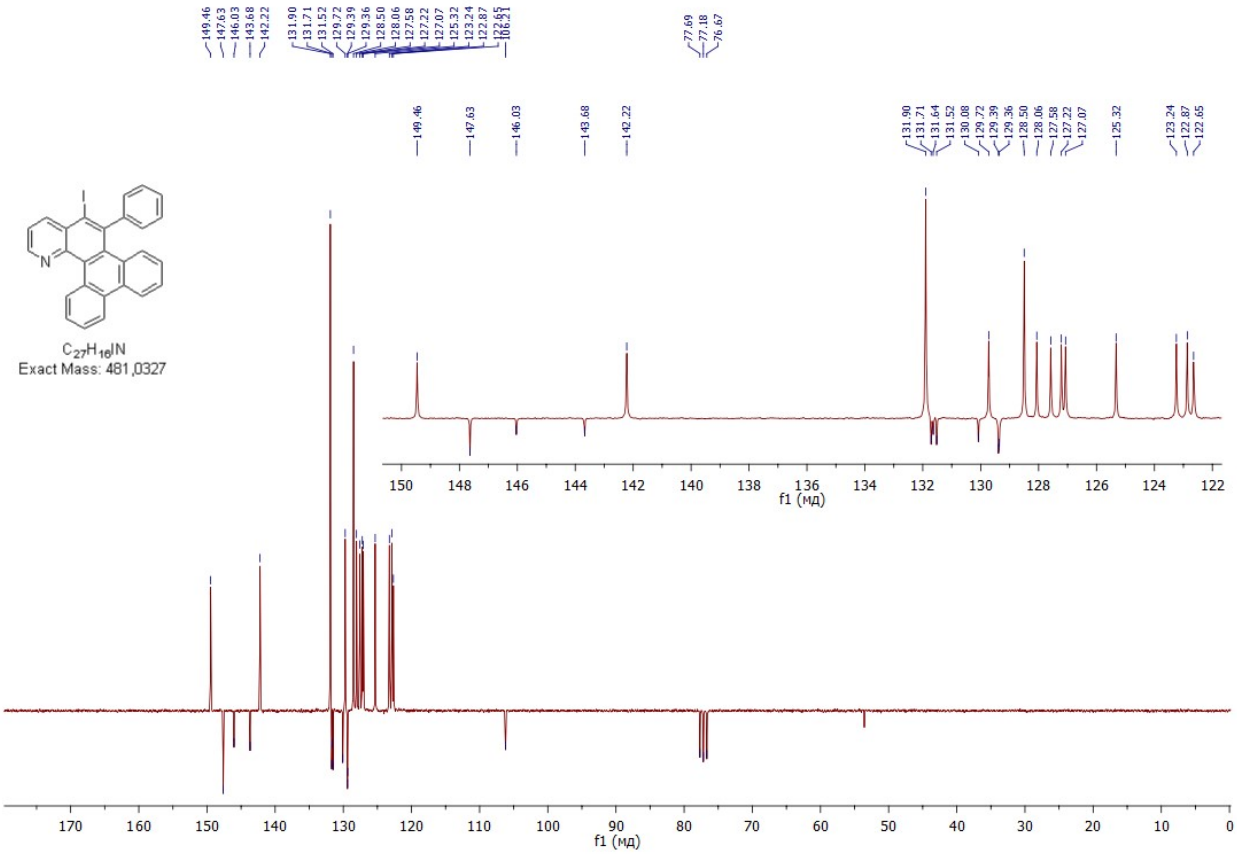


Fig. S16. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **5c** (62.9 MHz, $CDCl_3$).

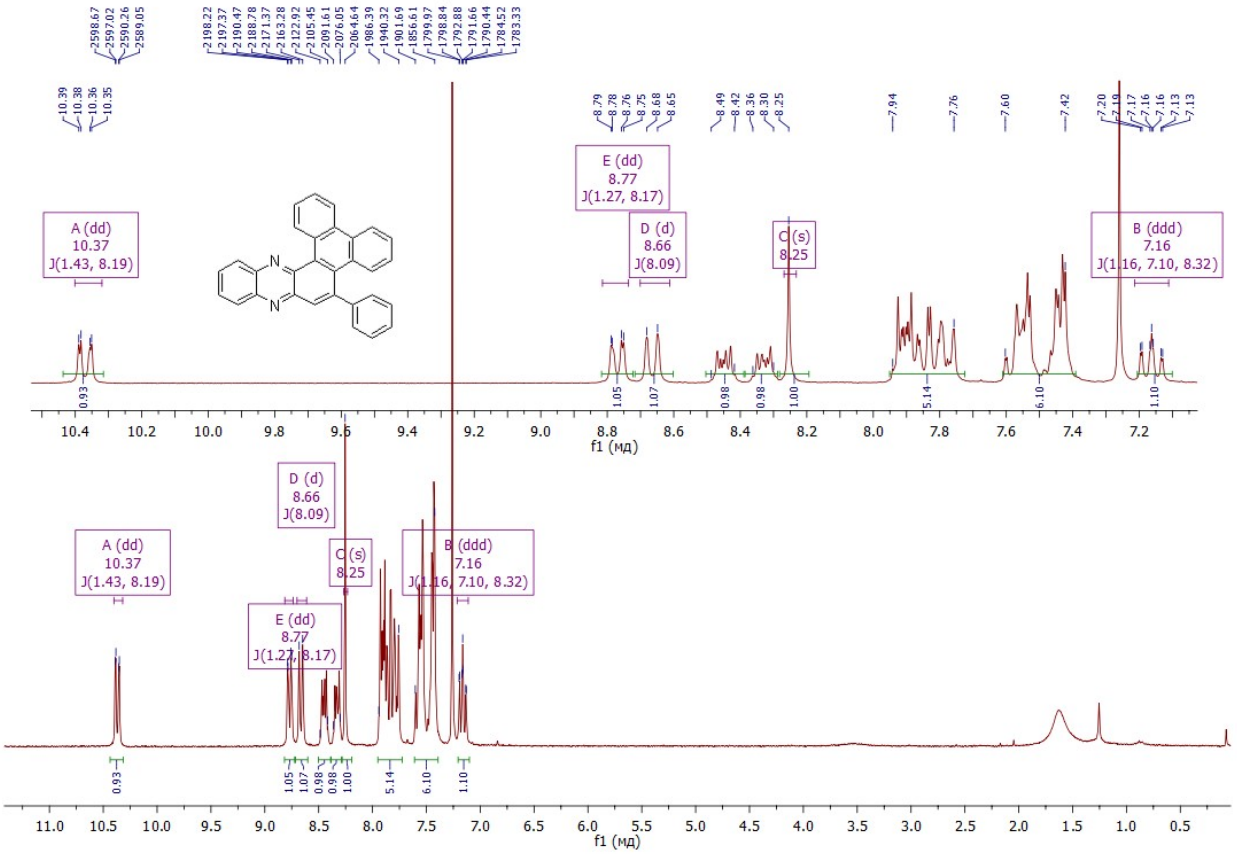


Fig. S17. ^{1}H NMR spectrum of compound **6a** (250 MHz, $CDCl_3$).

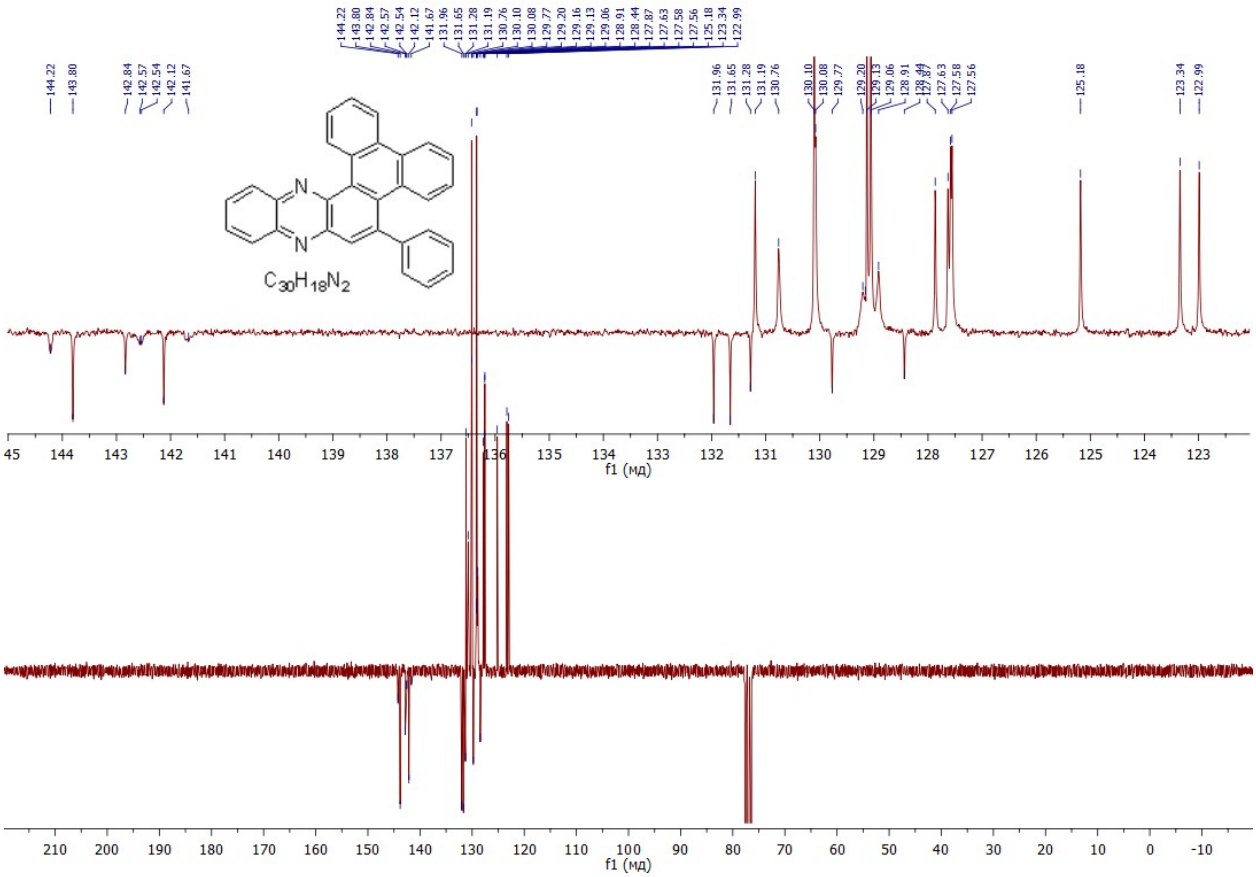


Fig. S18. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **6a** (62.9 MHz, $CDCl_3$).

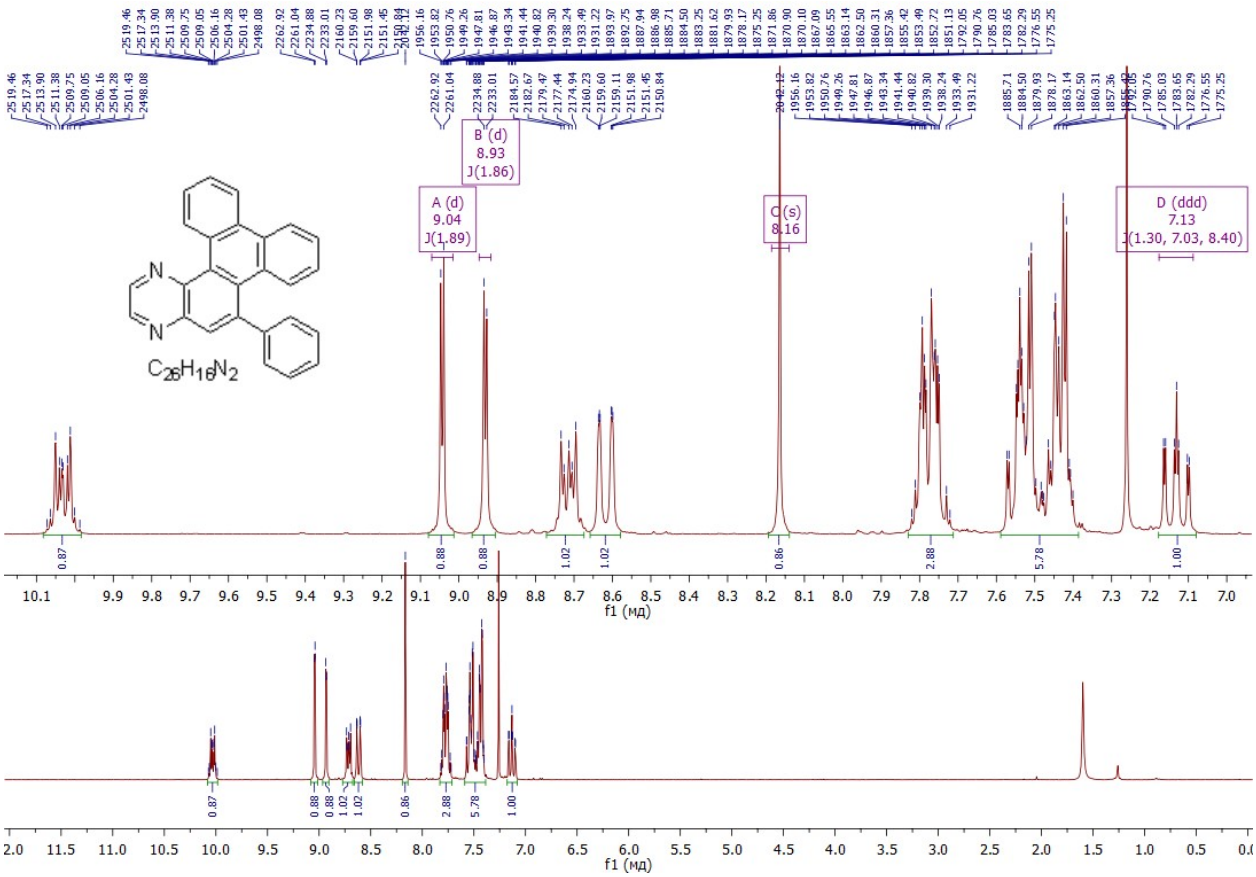


Fig. S19. ^{1}H NMR spectrum of compound **6b** (250 MHz, $CDCl_3$).

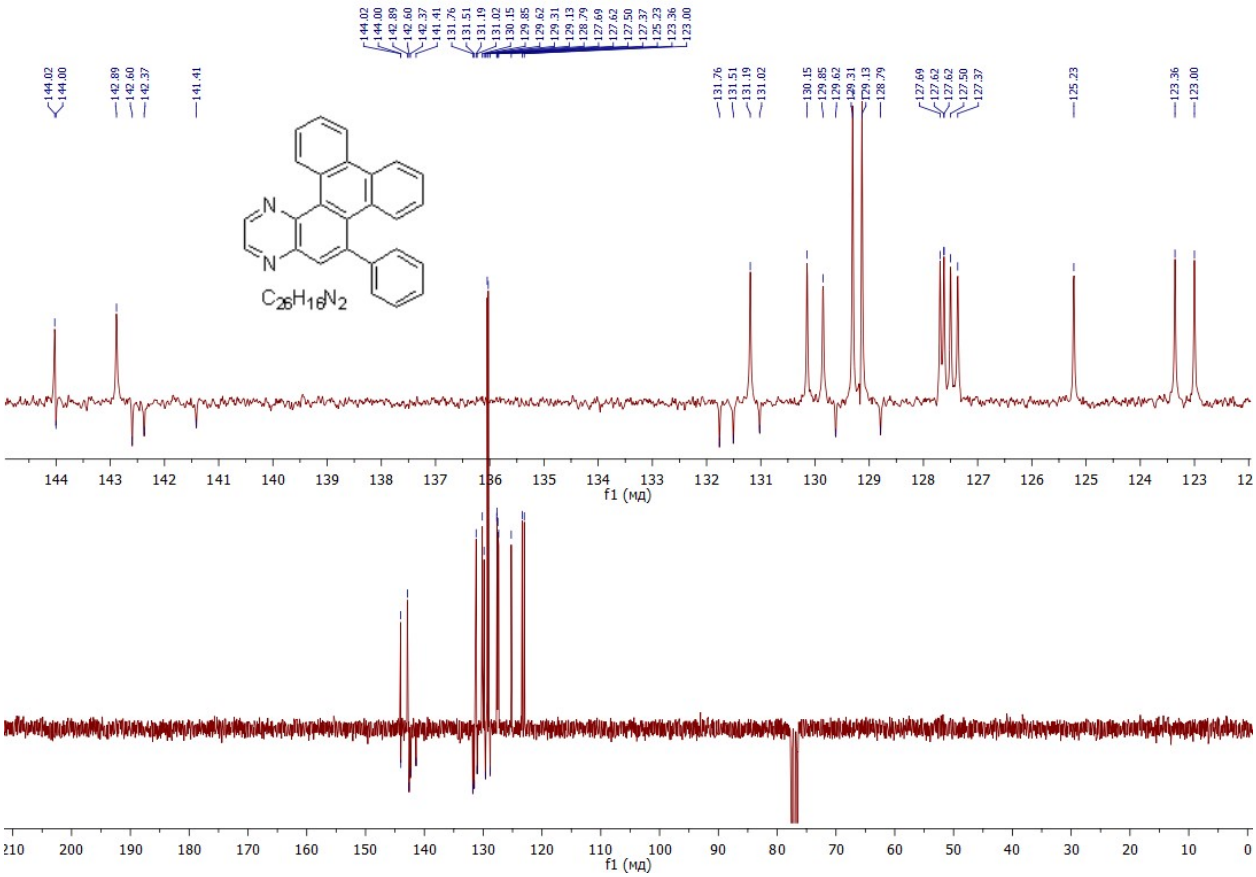


Fig. S20. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **6b** (62.9 MHz, $CDCl_3$).

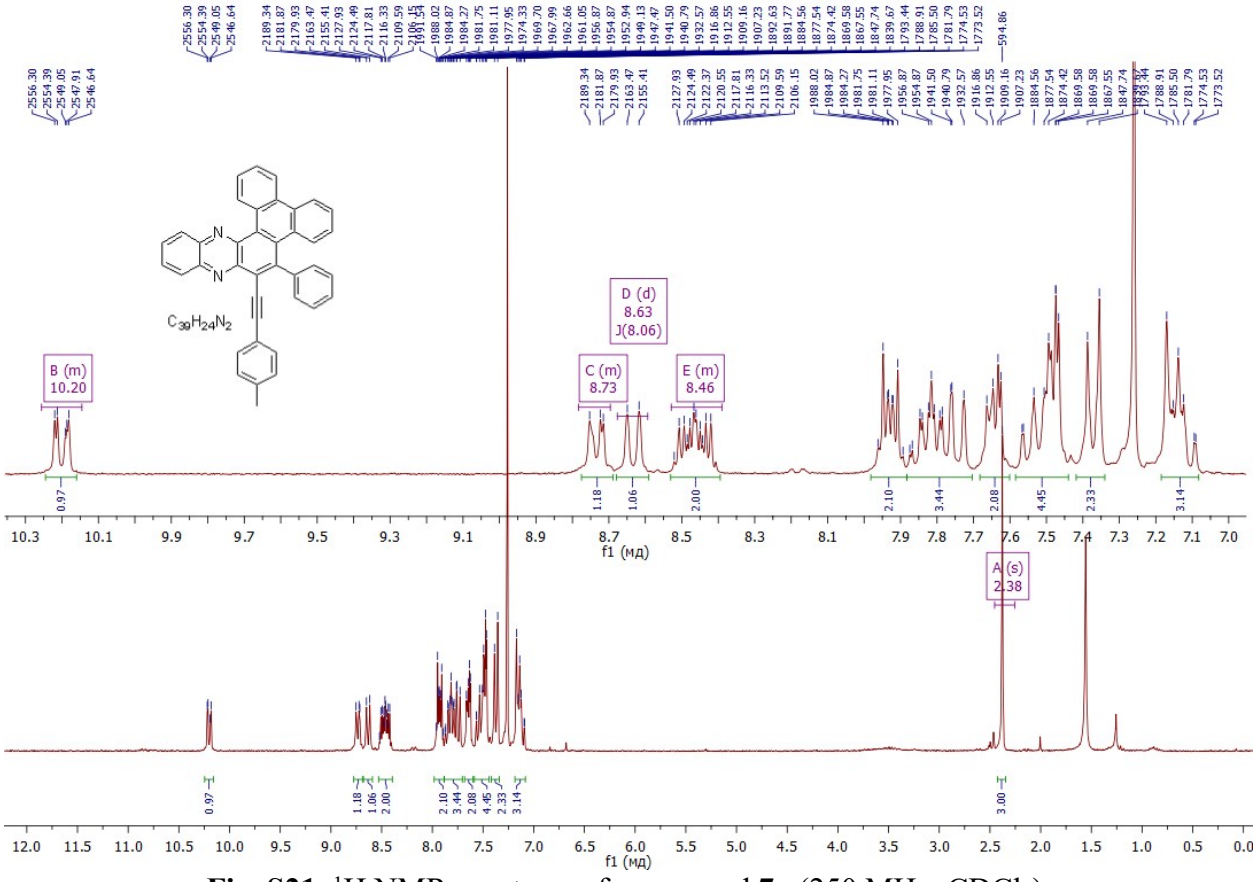


Fig. S21. ^{1}H NMR spectrum of compound **7a** (250 MHz, $CDCl_3$).

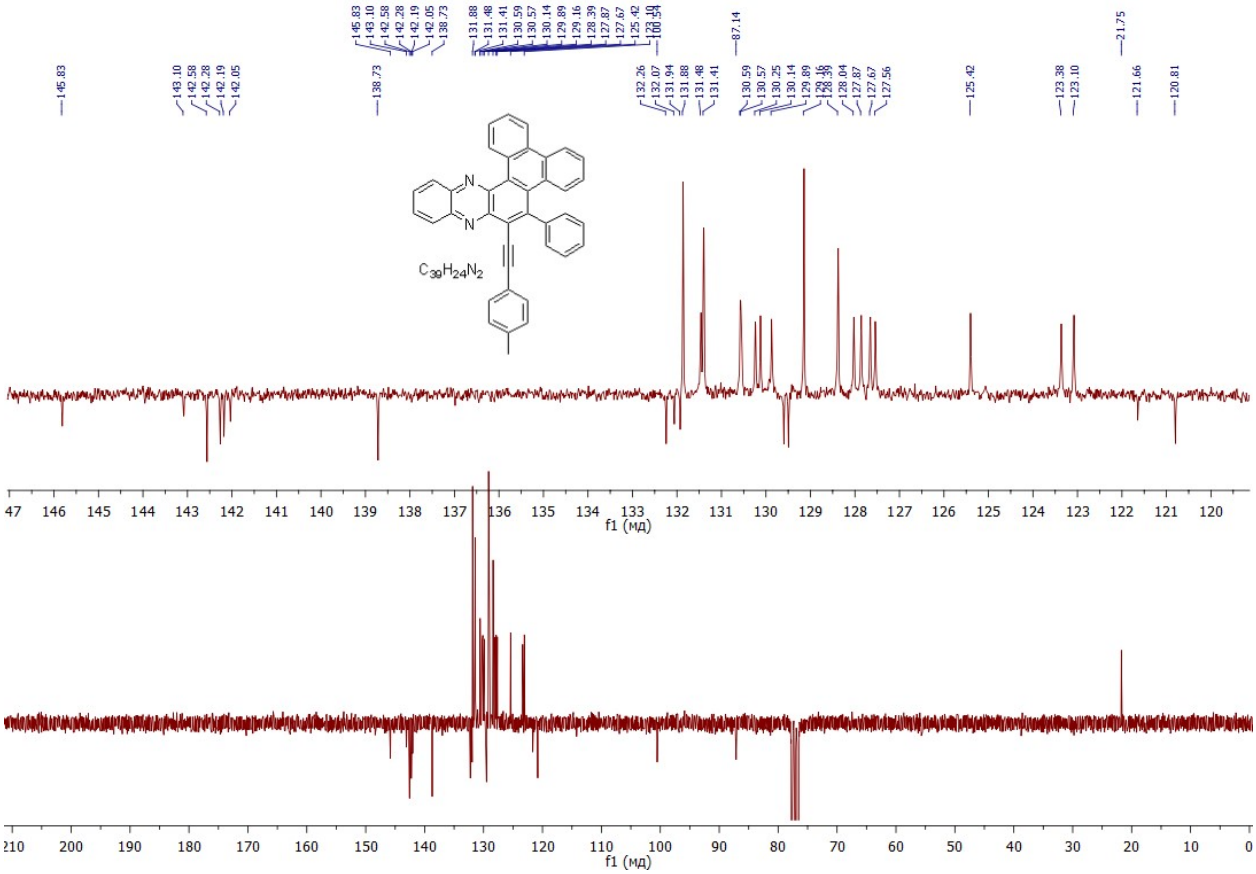


Fig. S22. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7a** (62.9 MHz, $CDCl_3$).

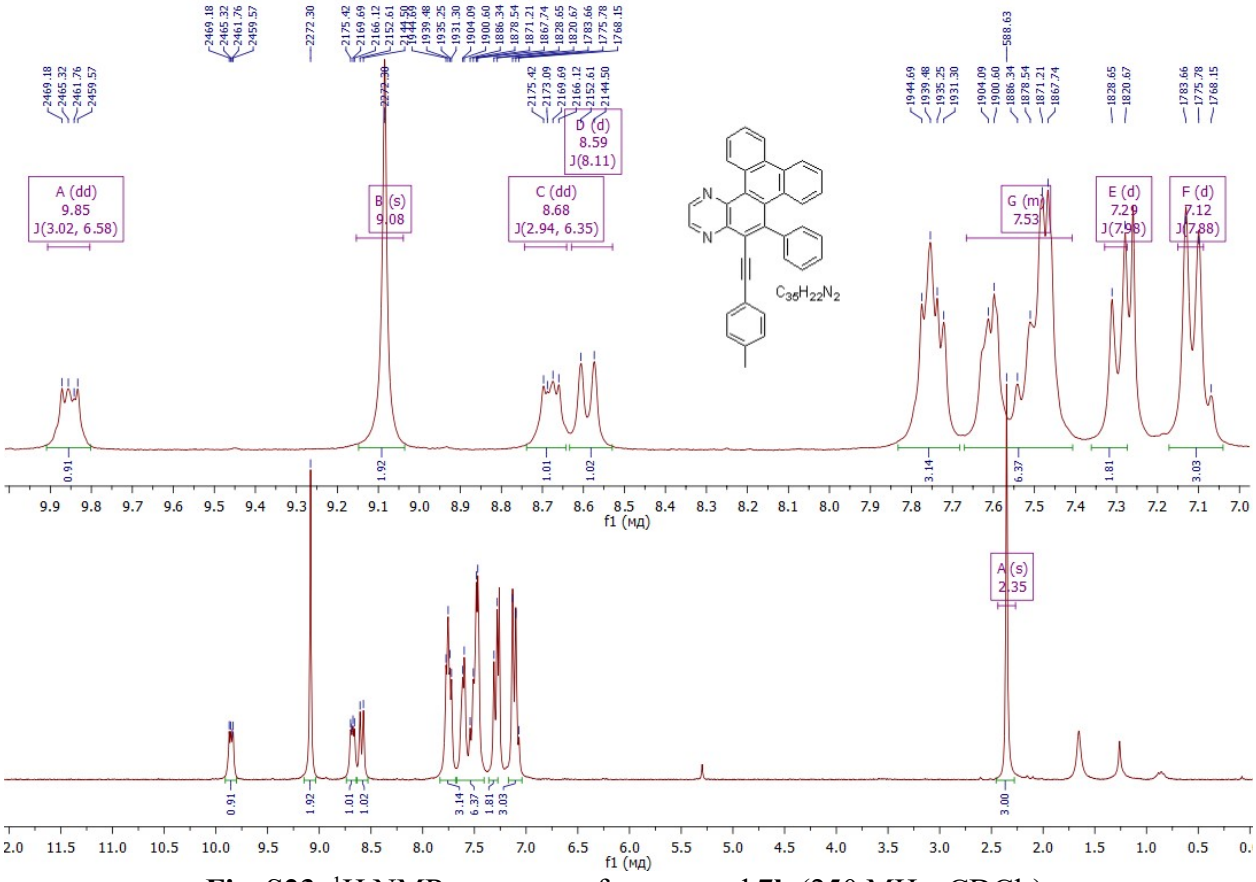


Fig. S23. ^{1}H NMR spectrum of compound **7b** (250 MHz, $CDCl_3$).

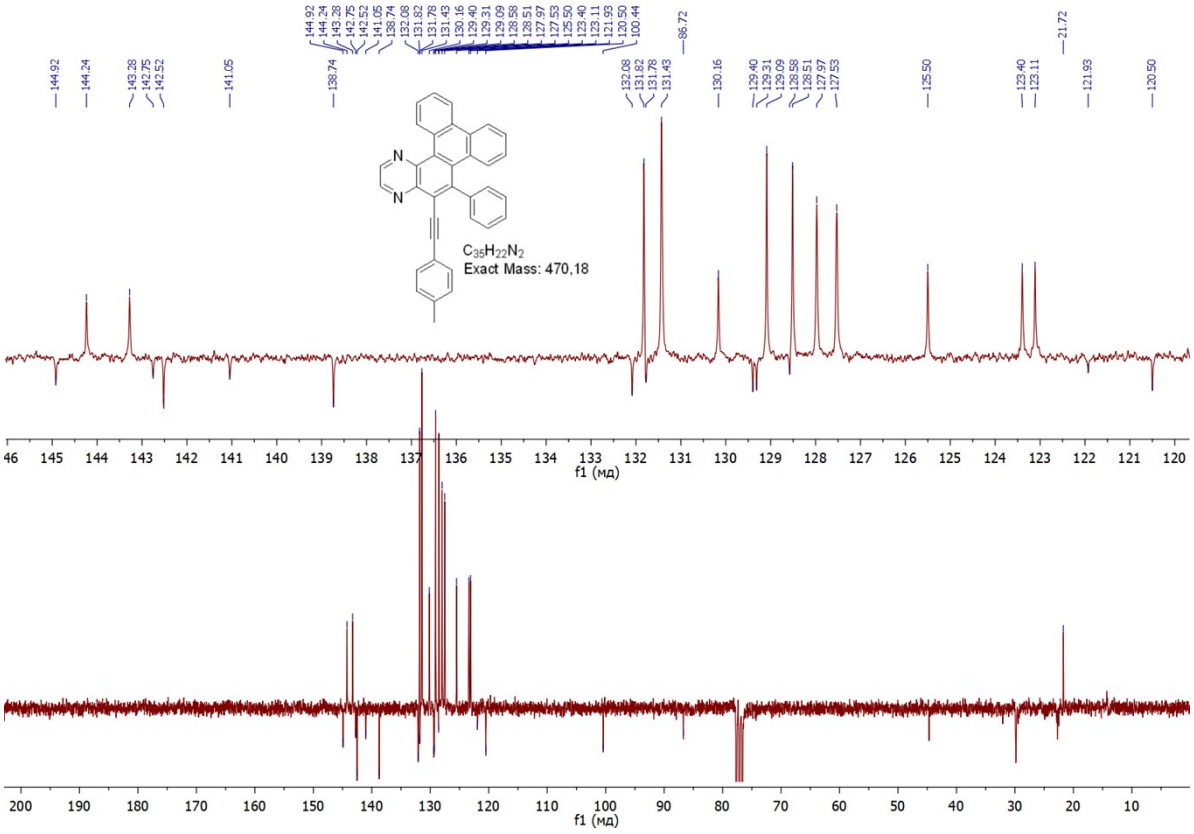


Fig. S24. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7b** (62.9 MHz, $CDCl_3$).

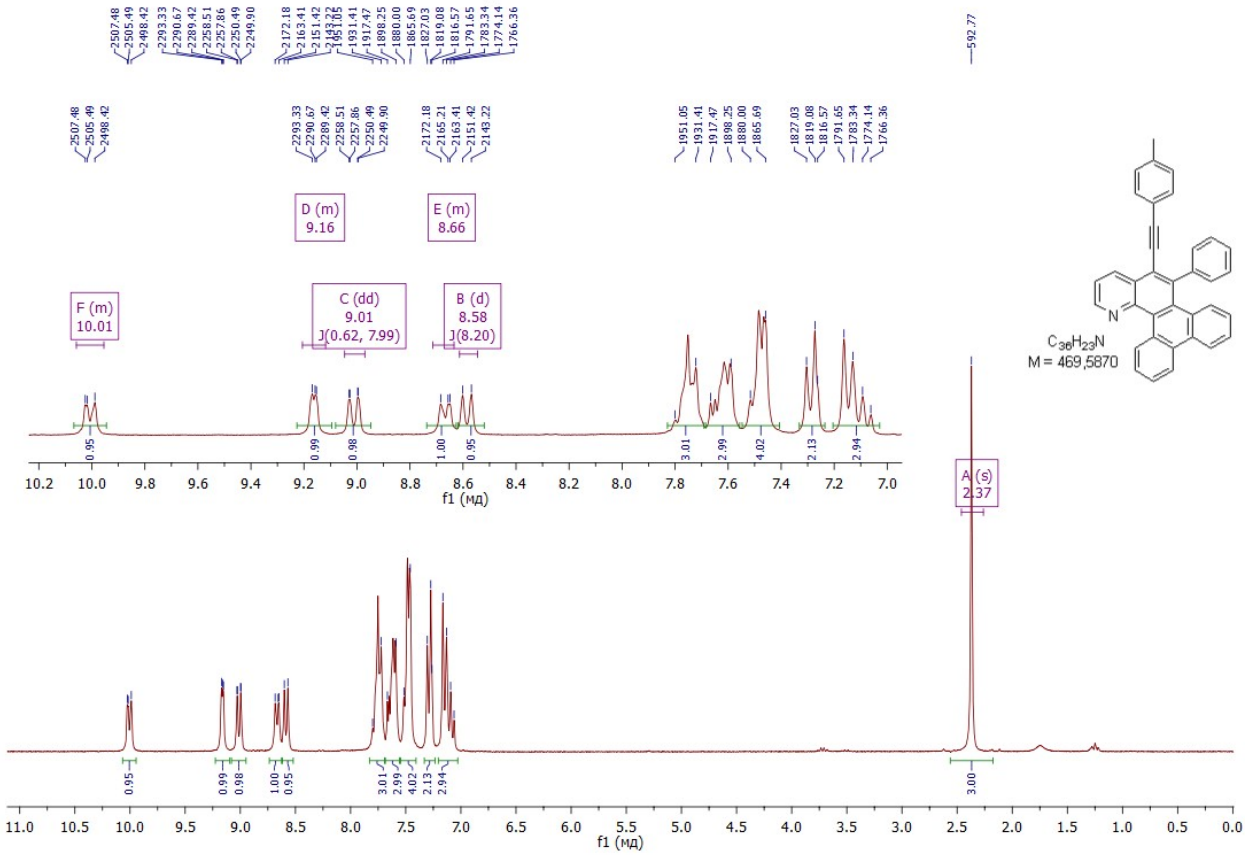


Fig. S25. ^{1}H NMR spectrum of compound **7c** (250 MHz, $CDCl_3$).

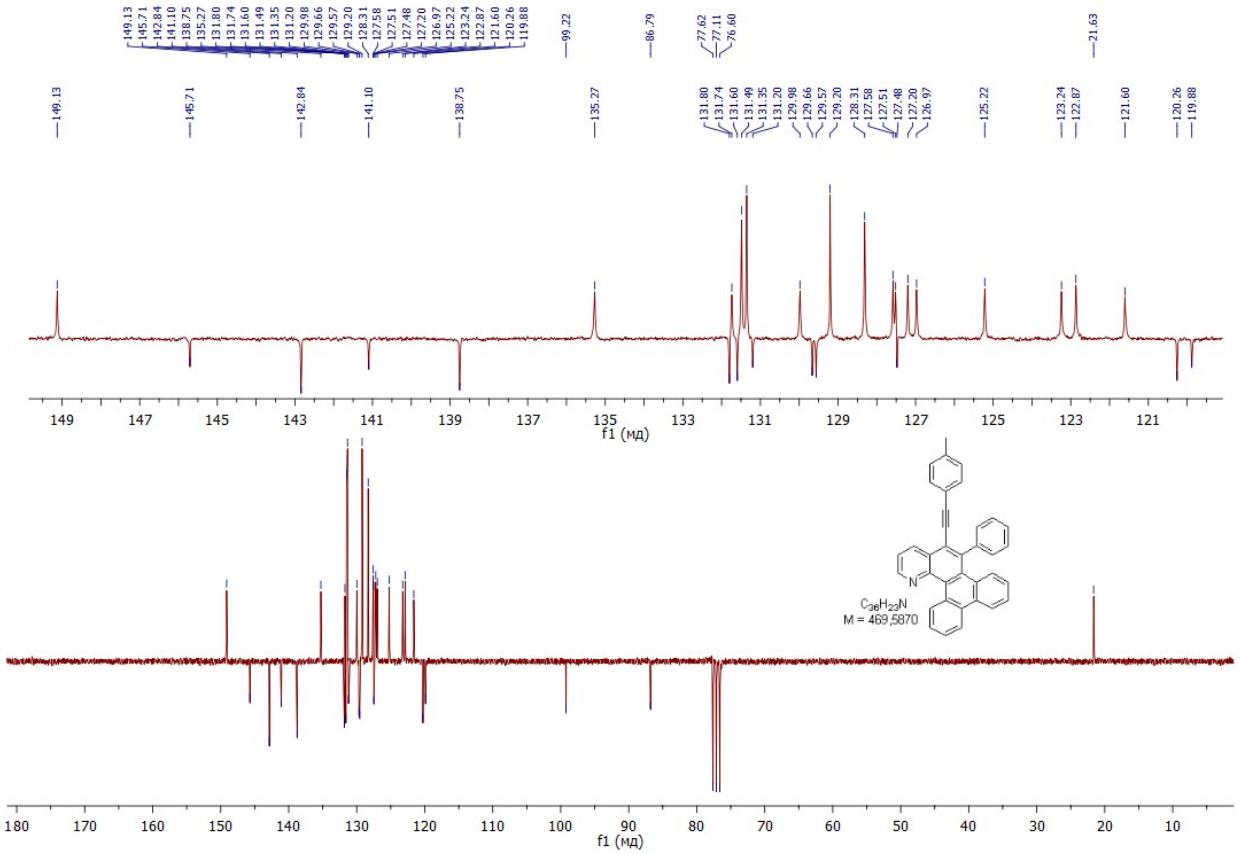


Fig. S26. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **7c** (62.9 MHz, $CDCl_3$).

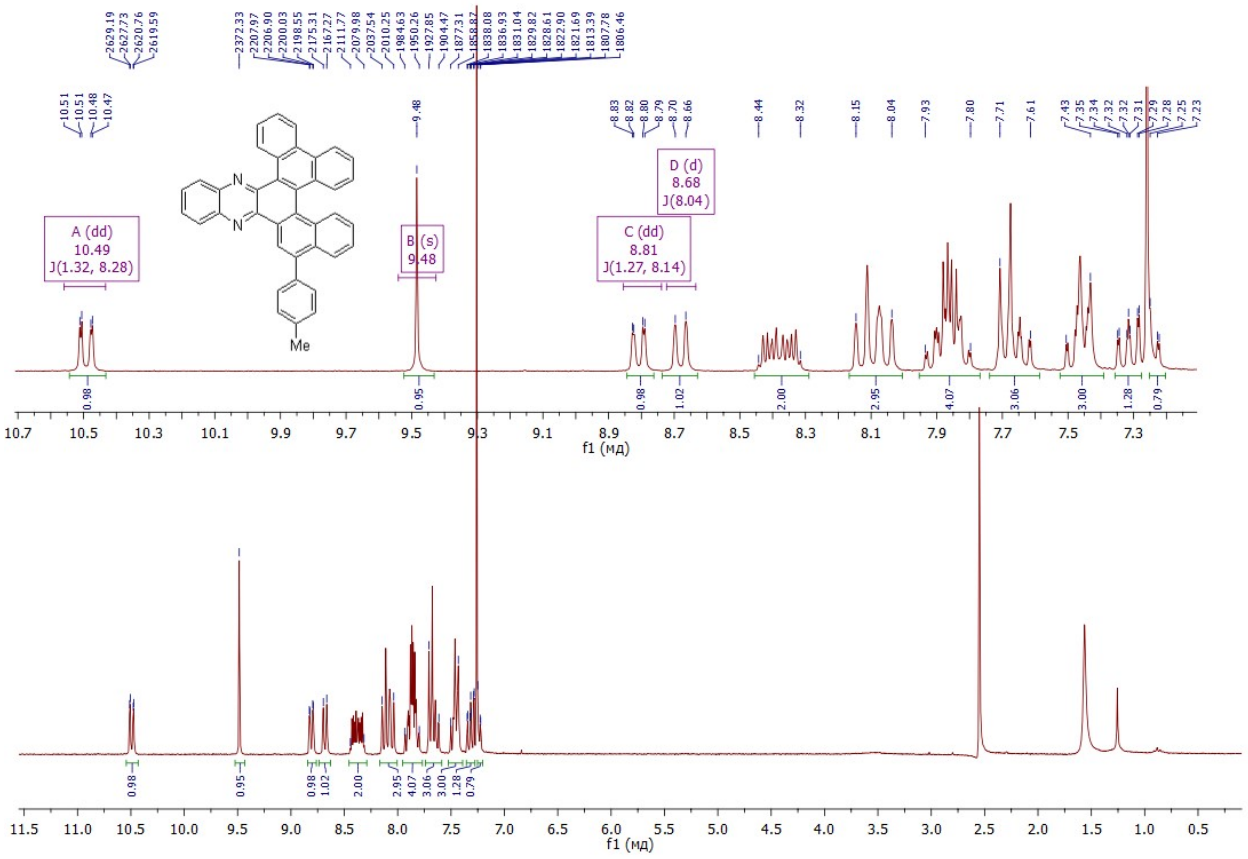


Fig. S27. ^{1}H NMR spectrum of compound **8a** at +30 °C (250 MHz, $CDCl_3$).

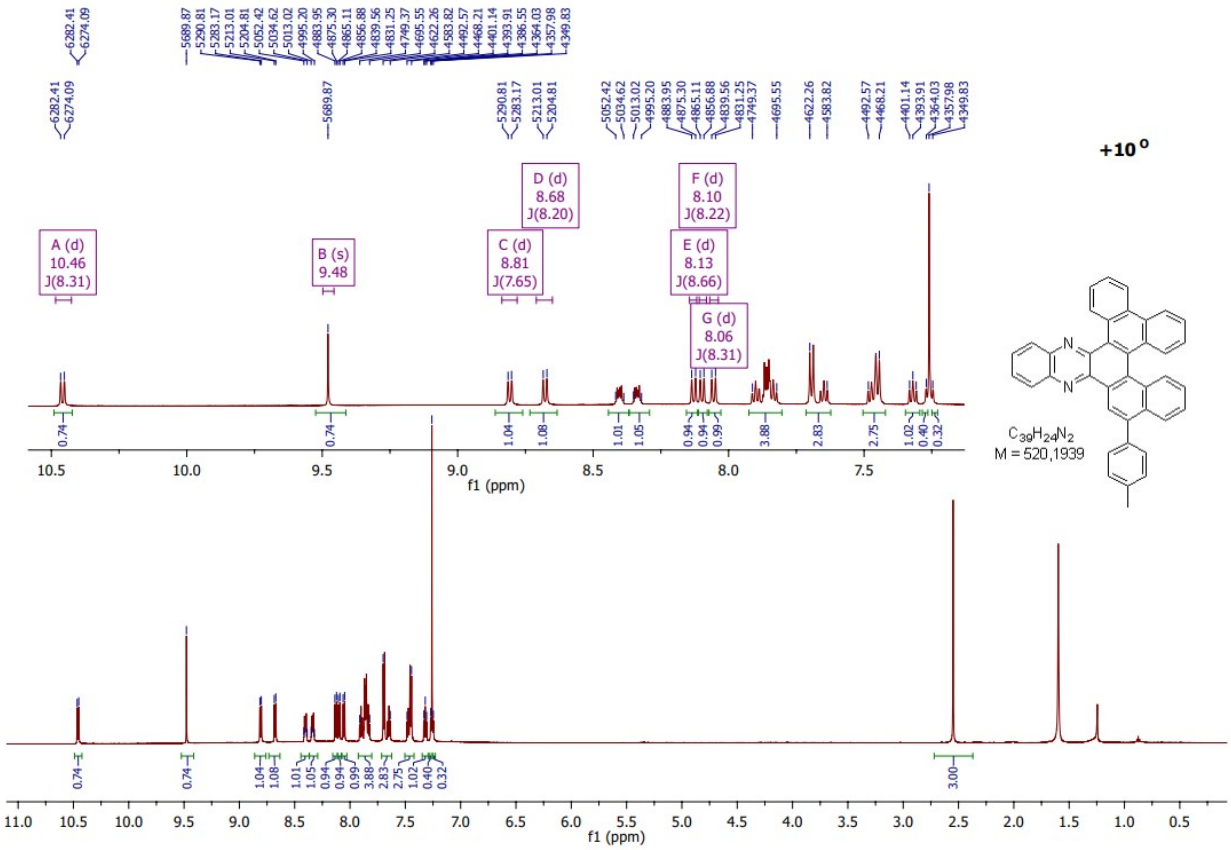


Fig. S27A. ^{1}H NMR spectrum of compound **8a** at +10 °C (600 MHz, $CDCl_3$).

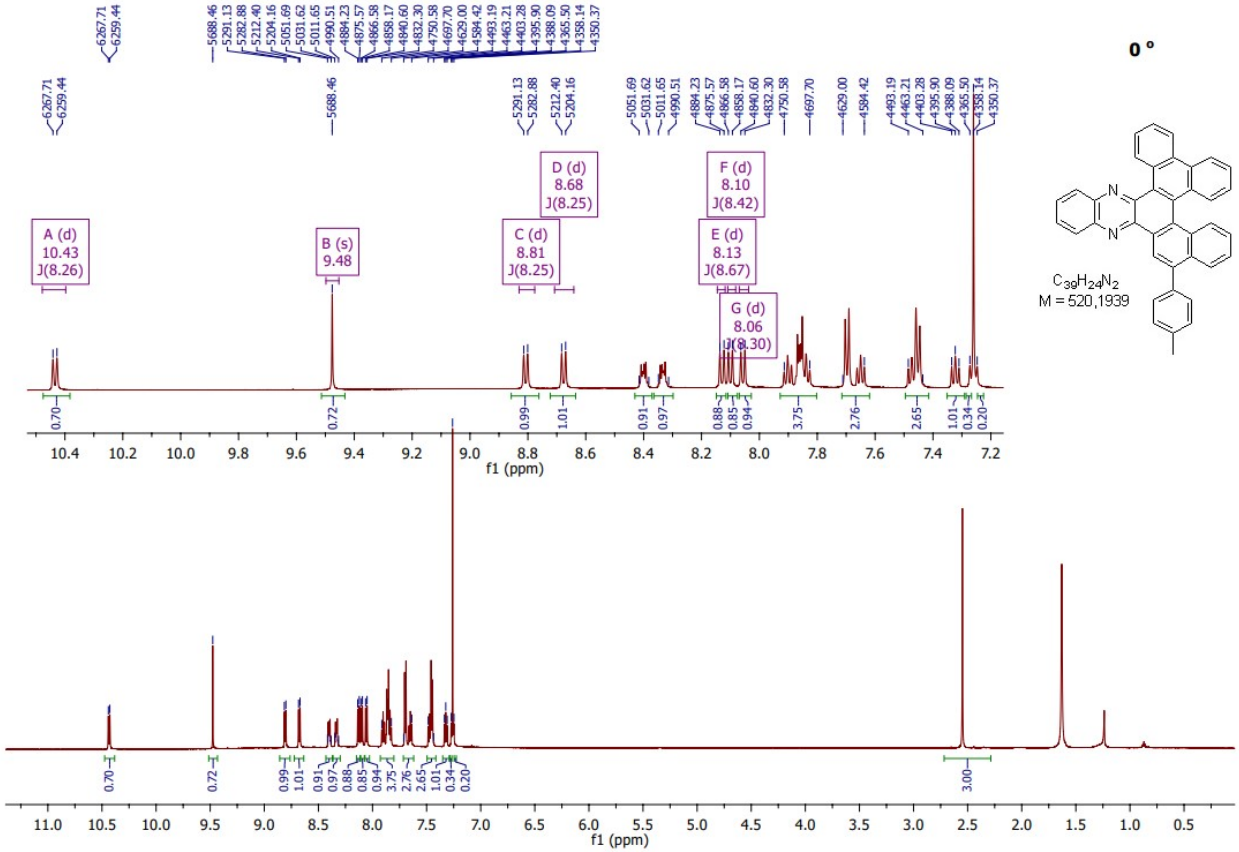


Fig. S27B. ^{1}H NMR spectrum of compound **8a** at 0 °C (600 MHz, $CDCl_3$).

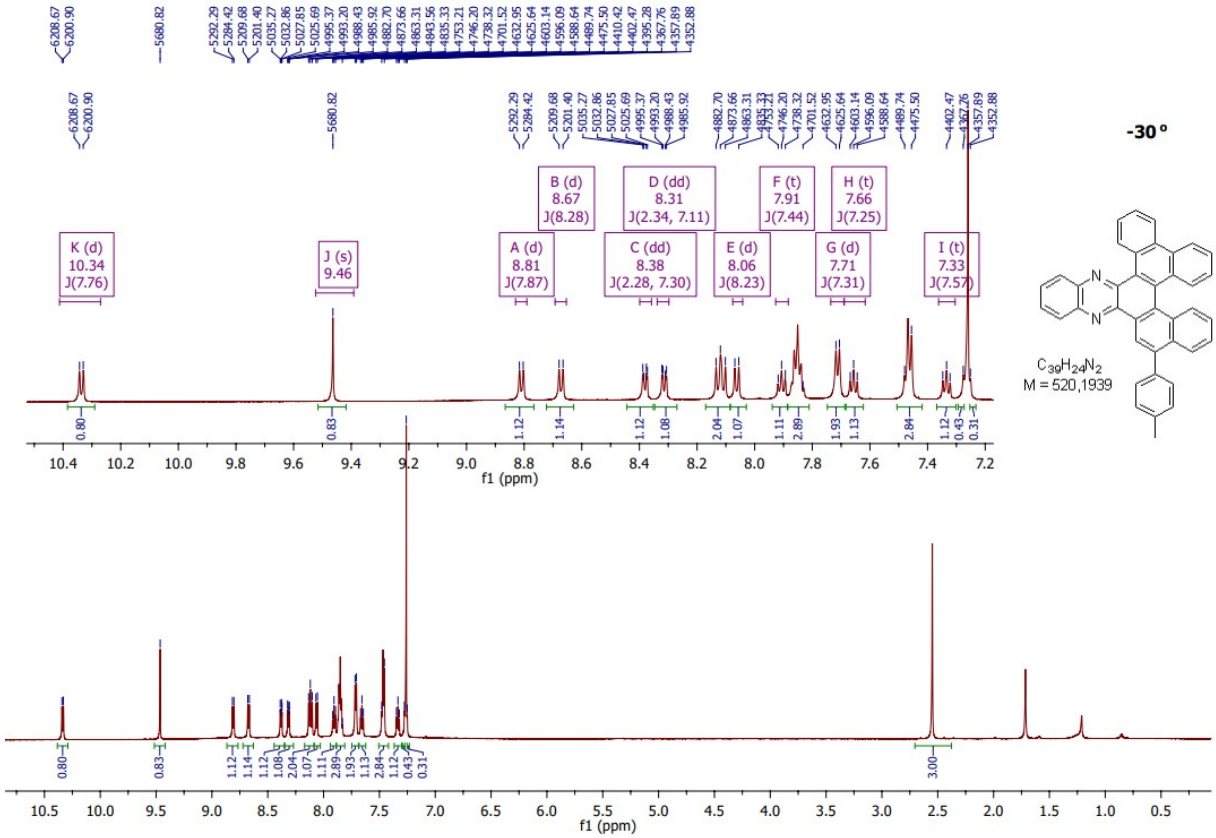


Fig. S27C. ^{1}H NMR spectrum of compound **8a** at -30 °C (600 MHz, $CDCl_3$).

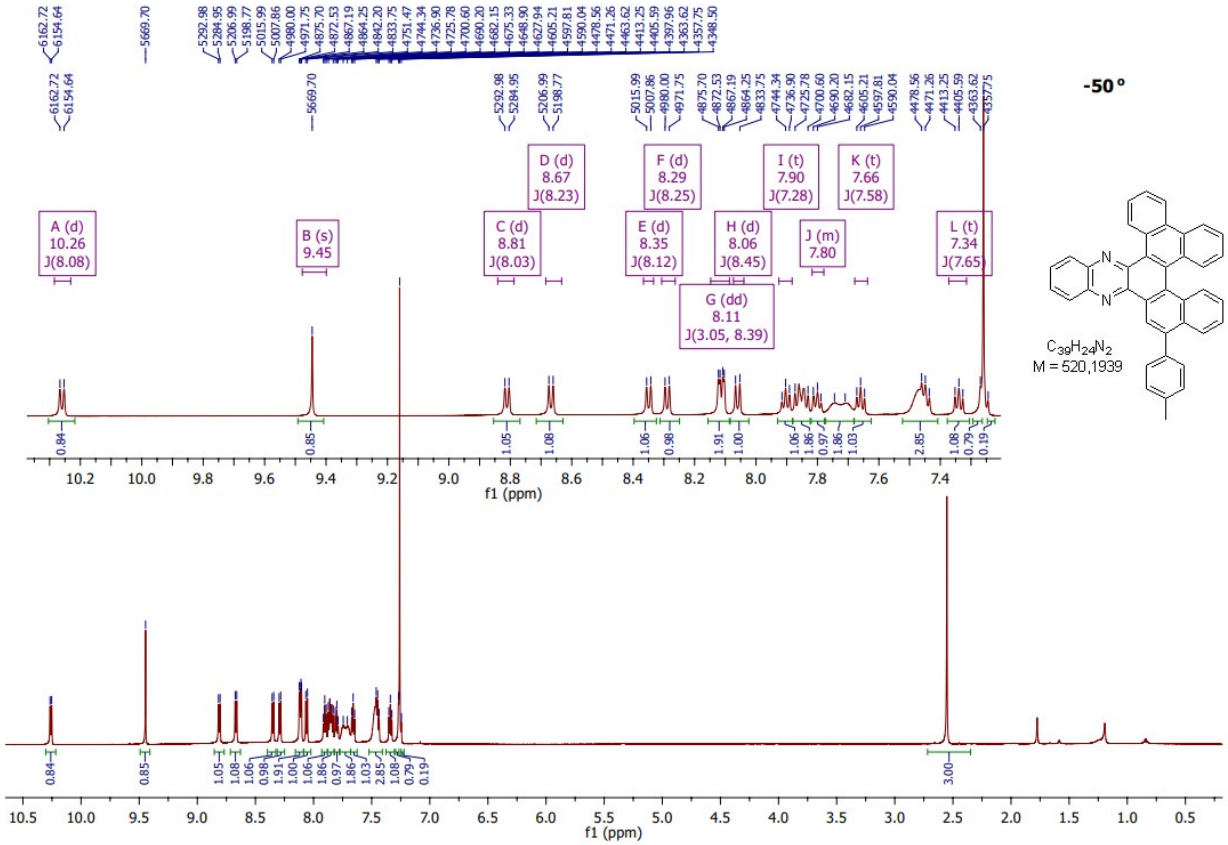


Fig. S27D. ^{1}H NMR spectrum of compound **8a** at -50 °C (600 MHz, $CDCl_3$).

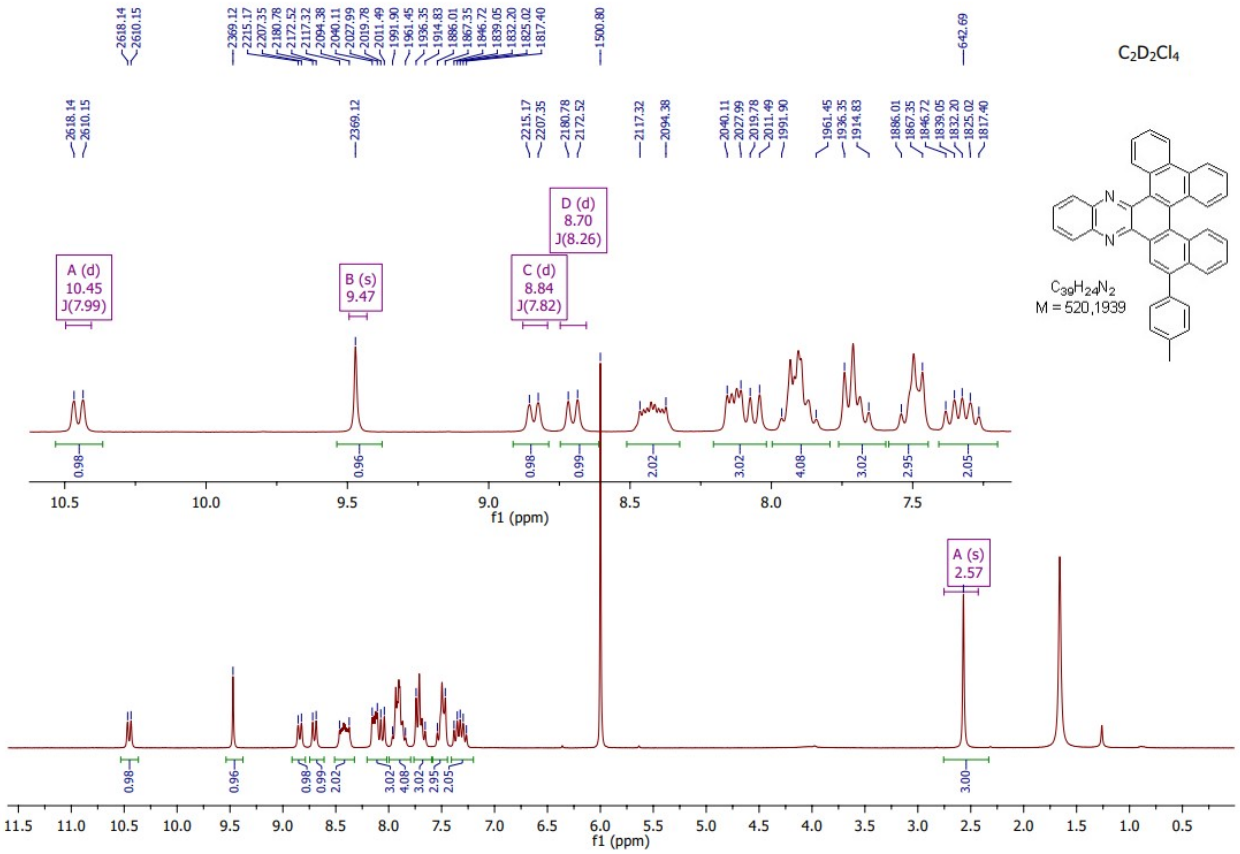


Fig. S27E. ^{1}H NMR spectrum of compound **8a** (250 MHz, 1,1,2,2-tetrachloroethane-d_2).

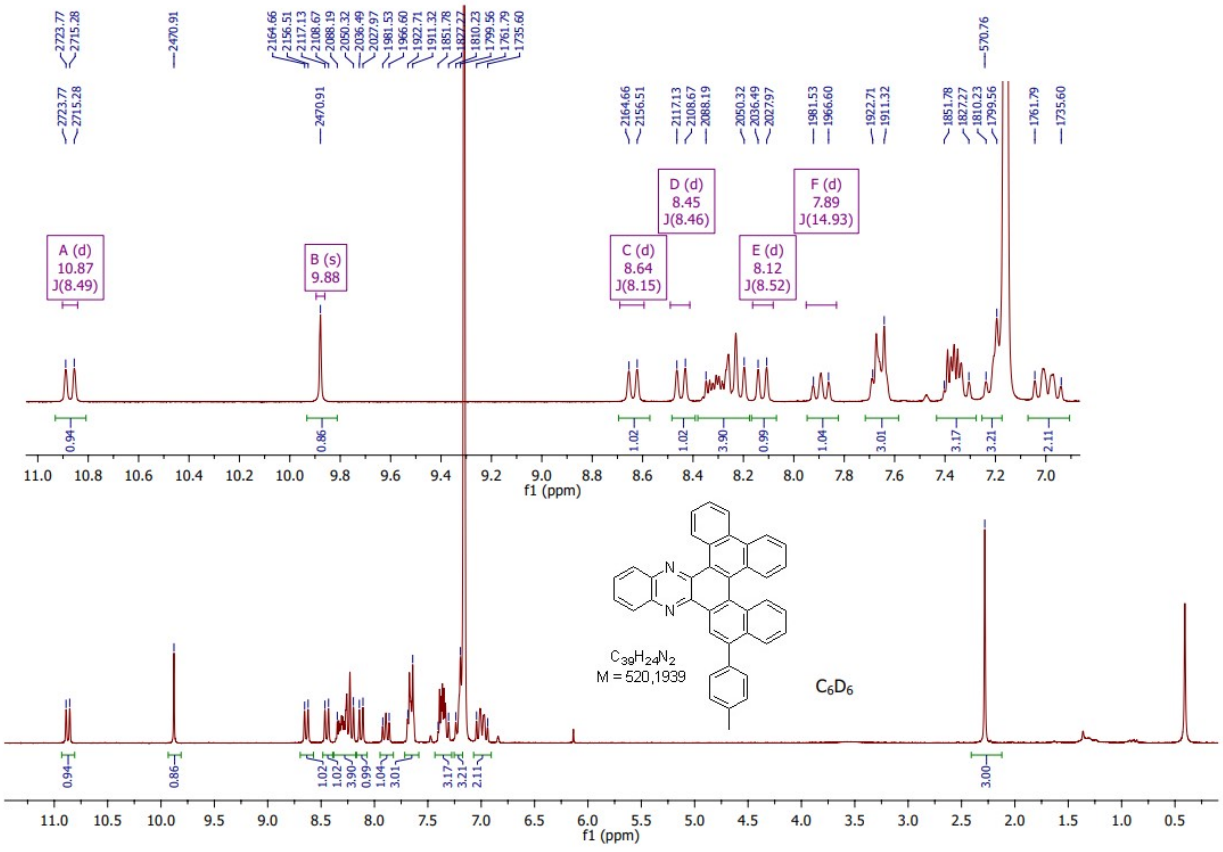


Fig. S27F. ^{1}H NMR spectrum of compound **8a** (250 MHz, benzene-d_6).

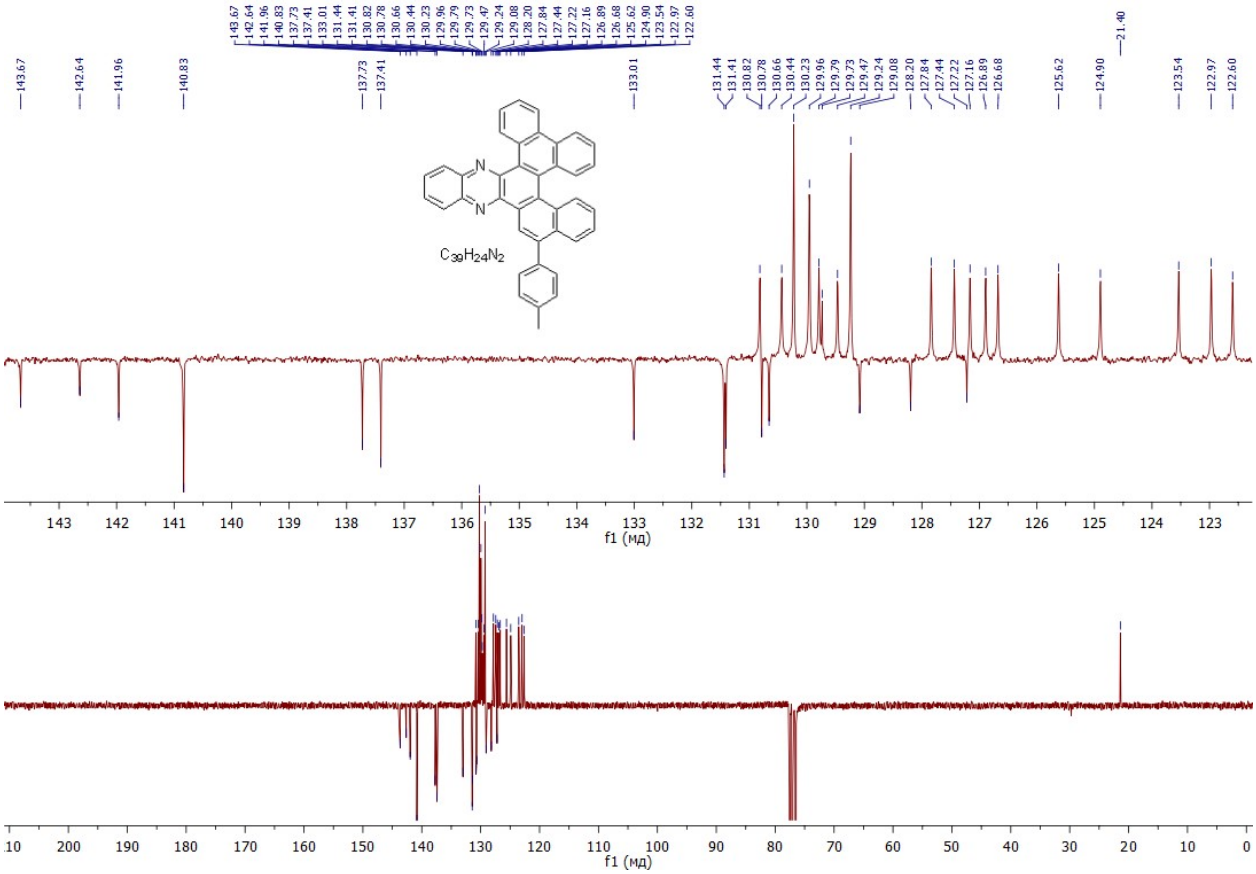


Fig. S28. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8a** (62.9 MHz, $CDCl_3$).

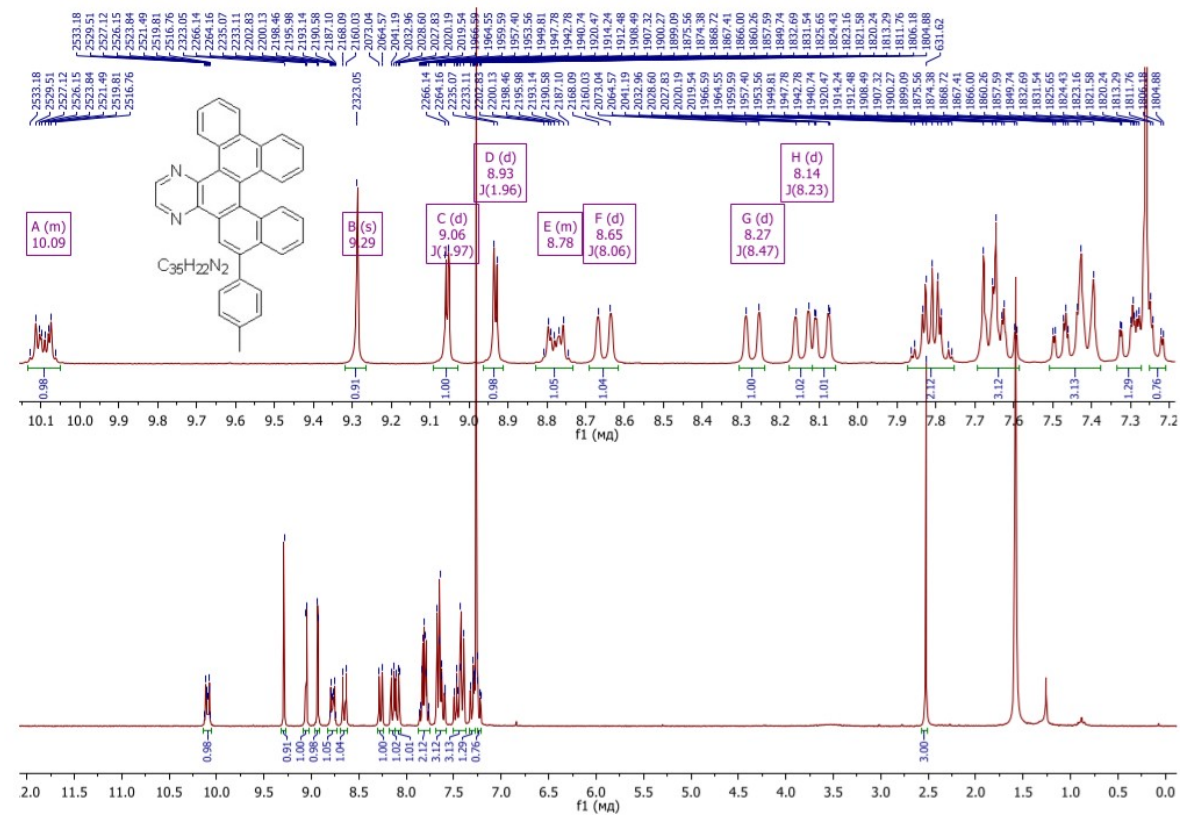


Fig. S29. ^{1}H NMR spectrum of compound **8b** (250 MHz, $CDCl_3$).

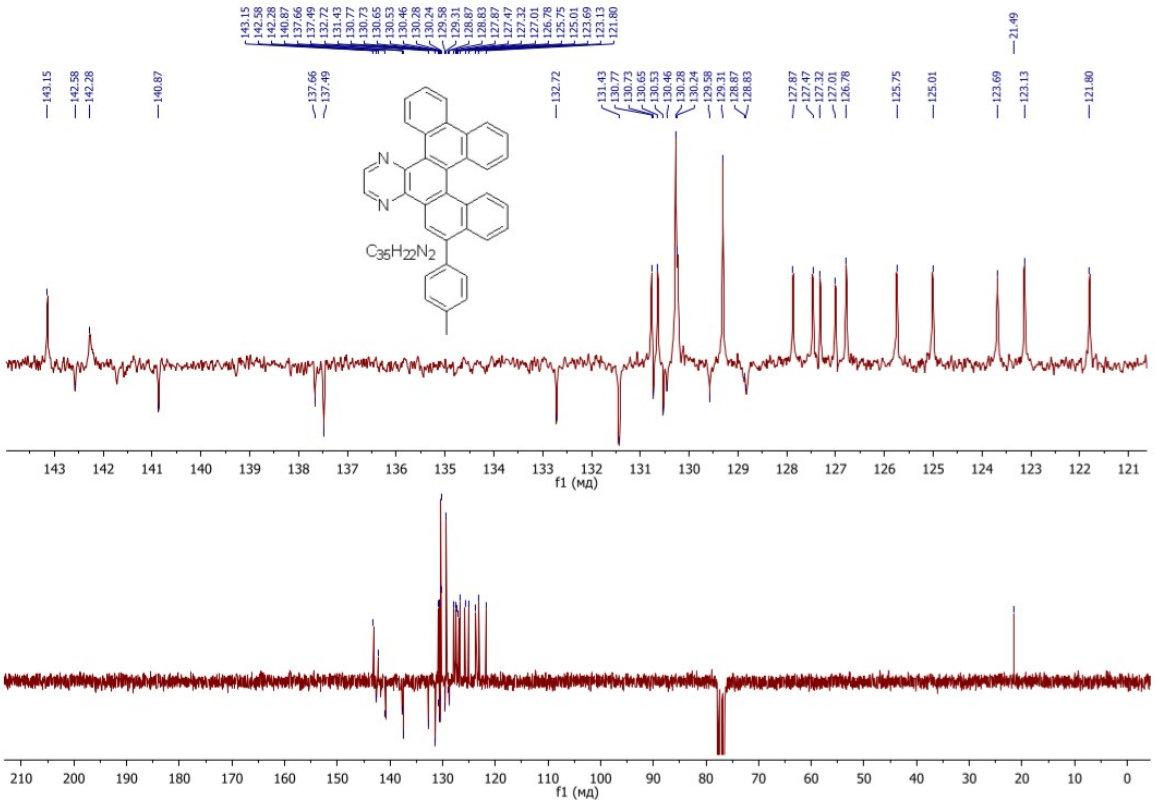


Fig. S30. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8b** (62.9 MHz, $CDCl_3$).

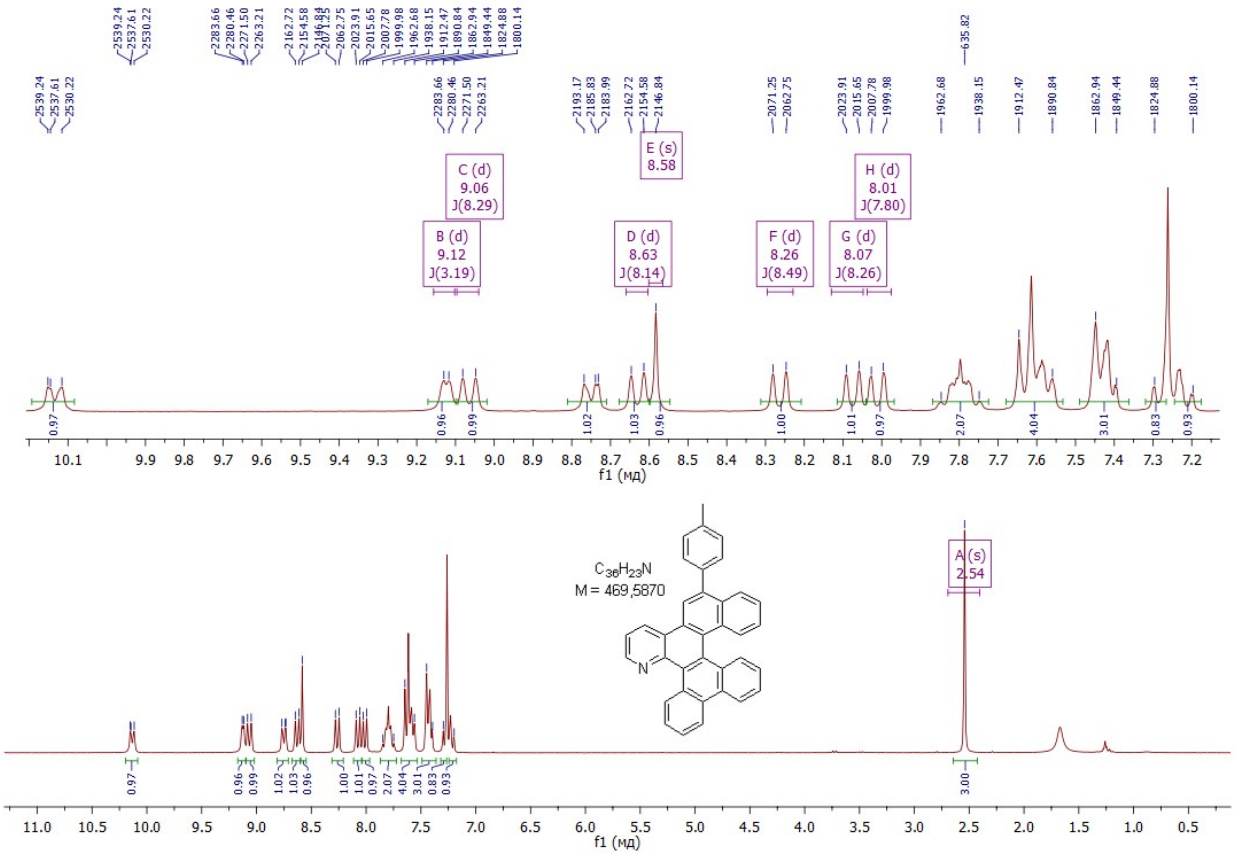


Fig. S31. ^{1}H NMR spectrum of compound **8c** (250 MHz, $CDCl_3$).

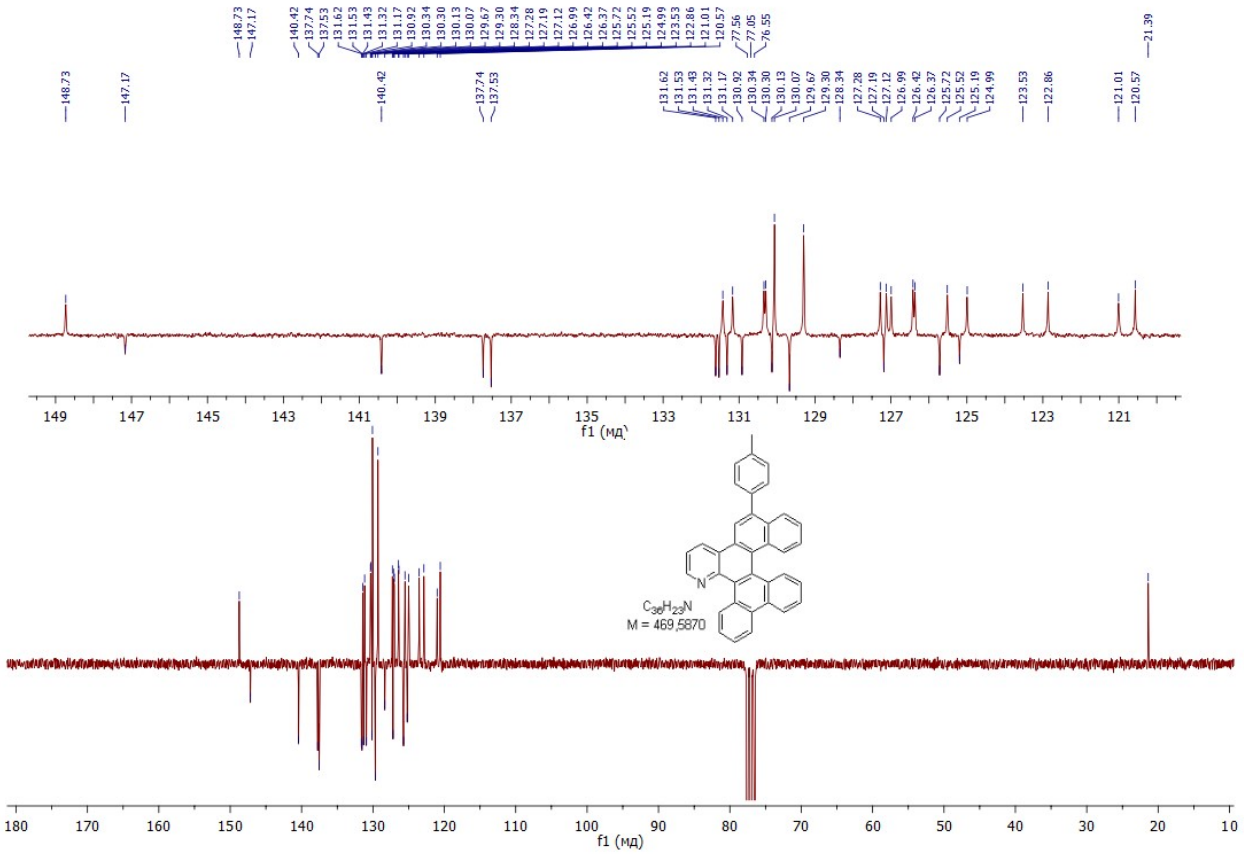


Fig. S32. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **8c** (62.9 MHz, $CDCl_3$).

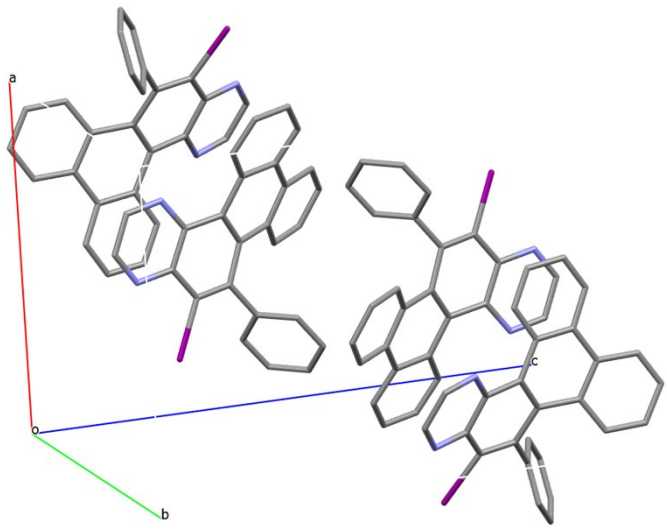


Fig. S33. Crystal unit cell of diaza[4]helicene **5b** (hydrogen atom are omitted).

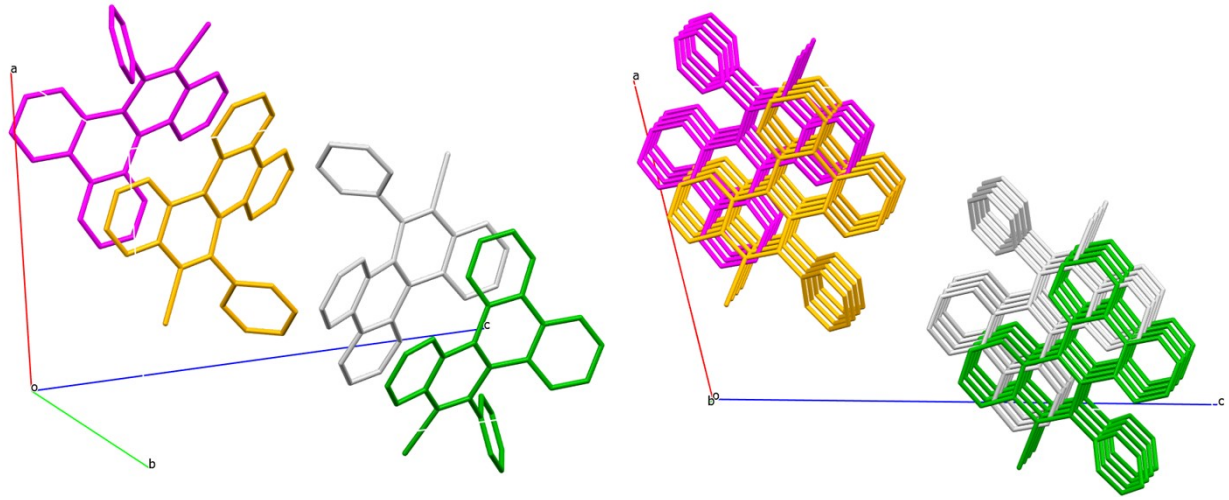


Fig. S34. Crystal unit cell and packing of **5b** (molecules are **c**olored by symmetry operation).

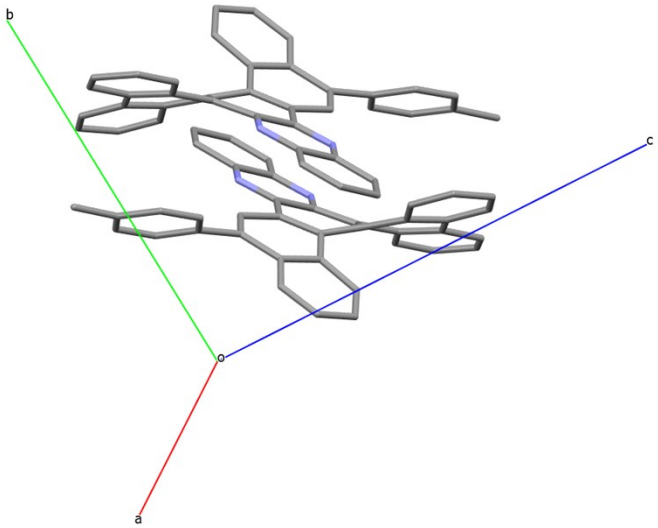


Fig. S35. Crystal unit cell of double [4,5]helicene **8a** (hydrogen atom are omitted).

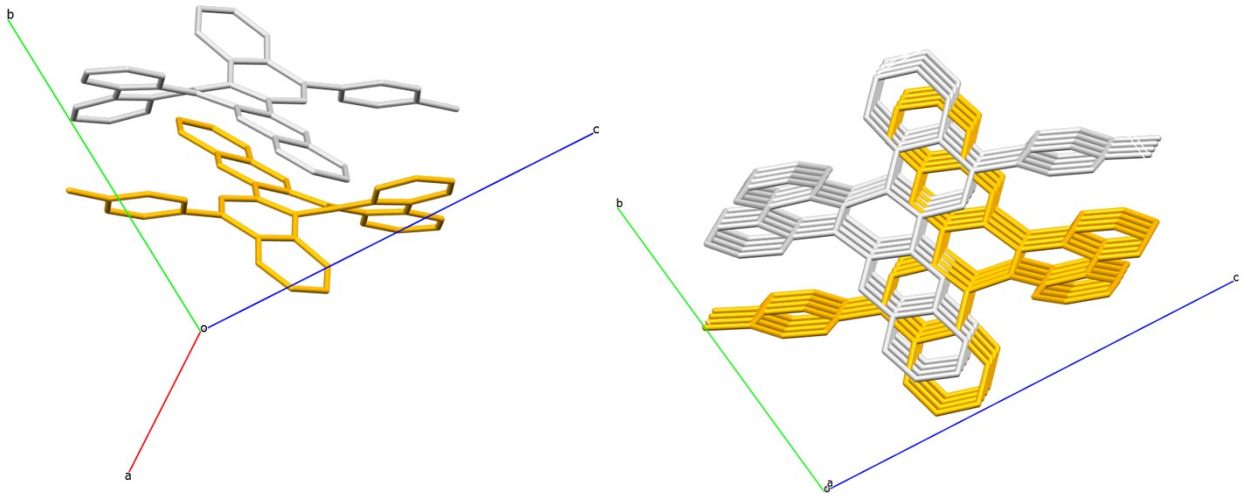


Fig. S36. Crystal unit cell and packing of **8a** (molecules are **c**olored by symmetry operation).

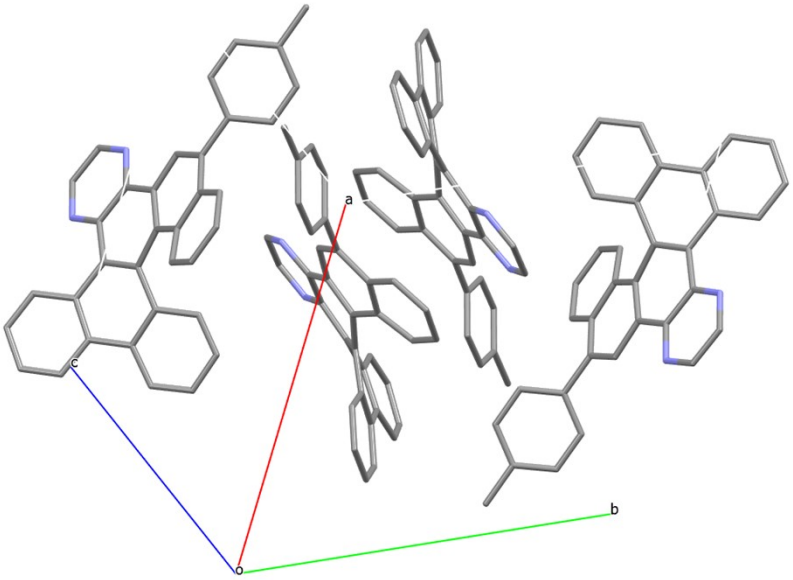


Fig. S37. Crystal unit cell of double [4,5]helicene **8b** (hydrogen atom are omitted).

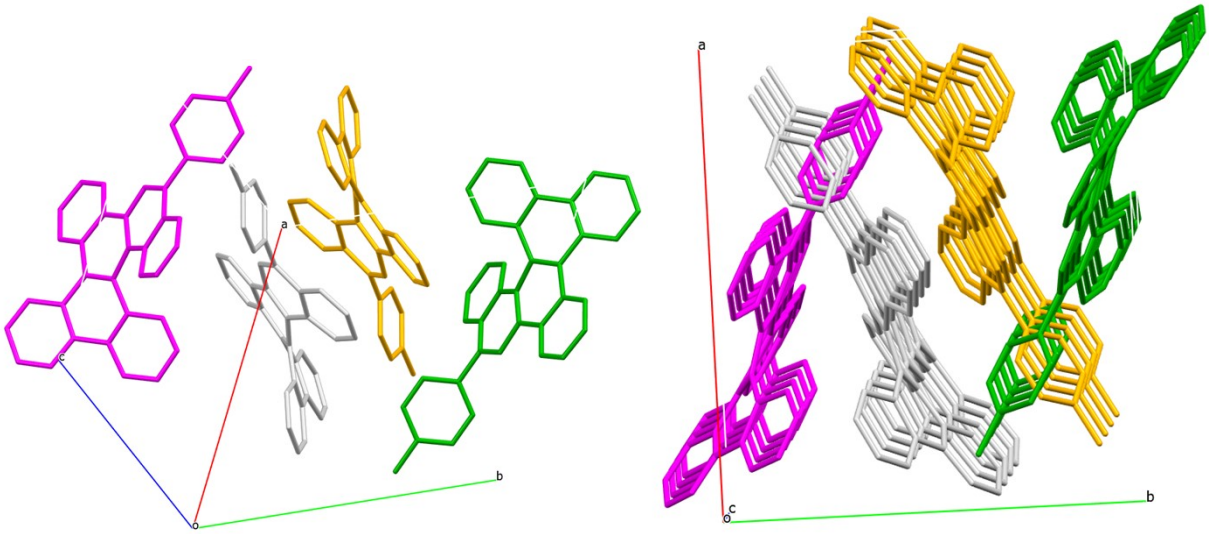


Fig. S38. Crystal unit cell and packing of **8b** (molecules are **c**olored by symmetry operation).

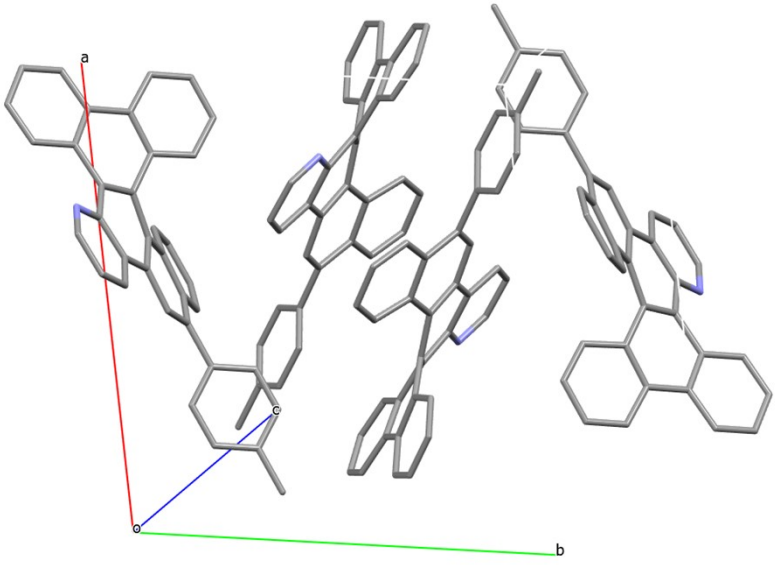


Fig. S39. Crystal unit cell of double [4,5]helicene **8c** (hydrogen atom are omitted).

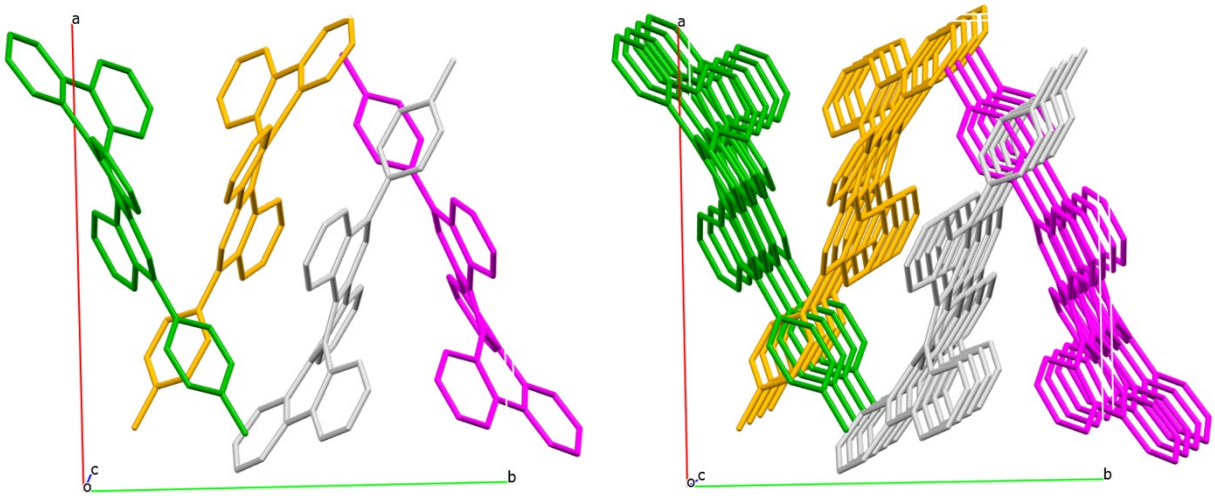


Fig. S40. Crystal unit cell and packing of **8c** (molecules are **c**olored by symmetry operation).

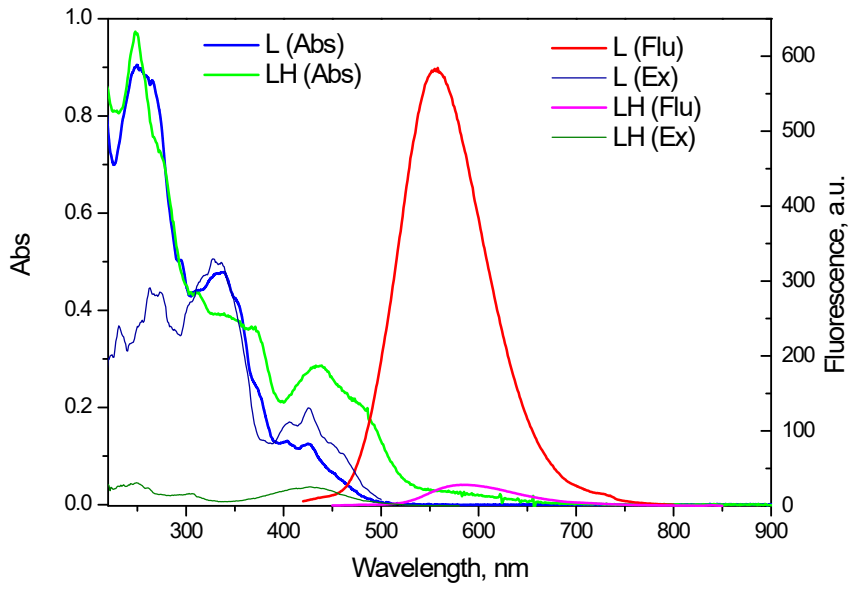


Fig. S41. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compound **8a** (L) in acetonitrile and (LH) in acidified acetonitrile (~0.02 M $HClO_4$).

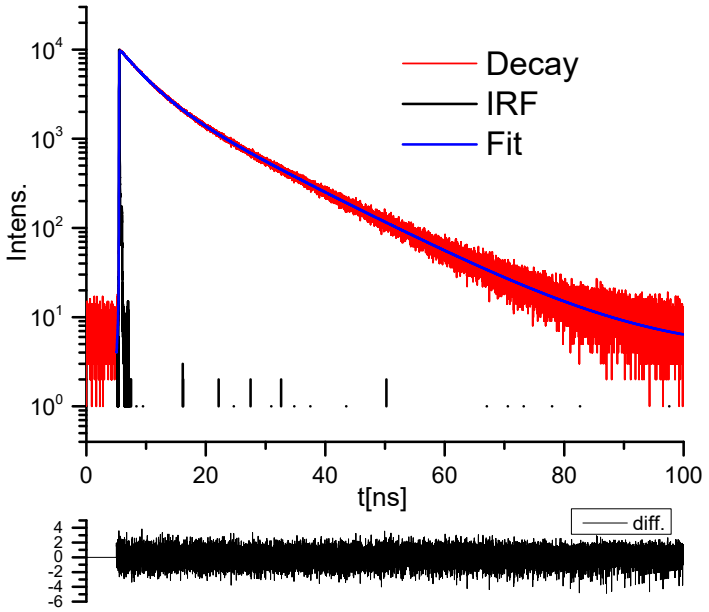


Fig. S42. Kinetics of fluorescence decay of compound **8a** (L) in acetonitrile (τ_1 = 12.92 ns, τ_2 = 4.075 ns).

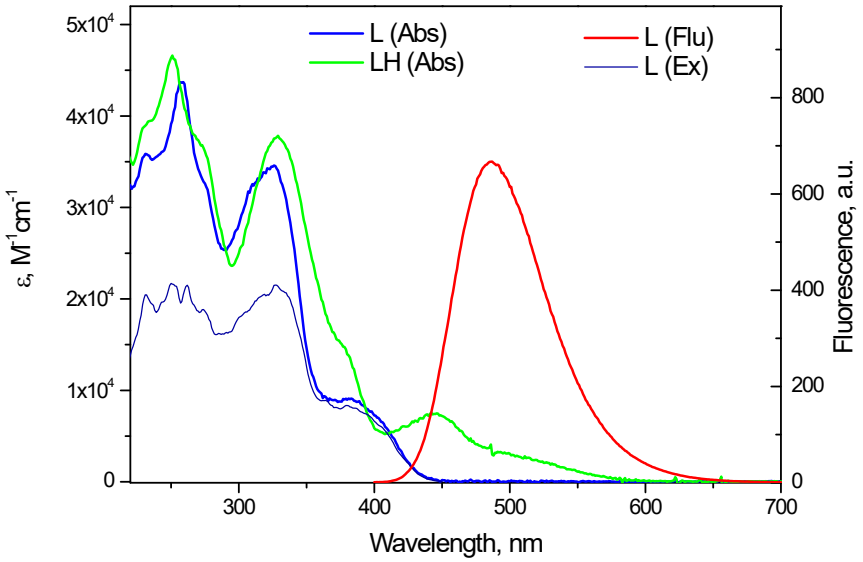


Fig. S43. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compound **8b** (L) in acetonitrile and (LH) in acidified acetonitrile (~0.02 M $HClO_4$).

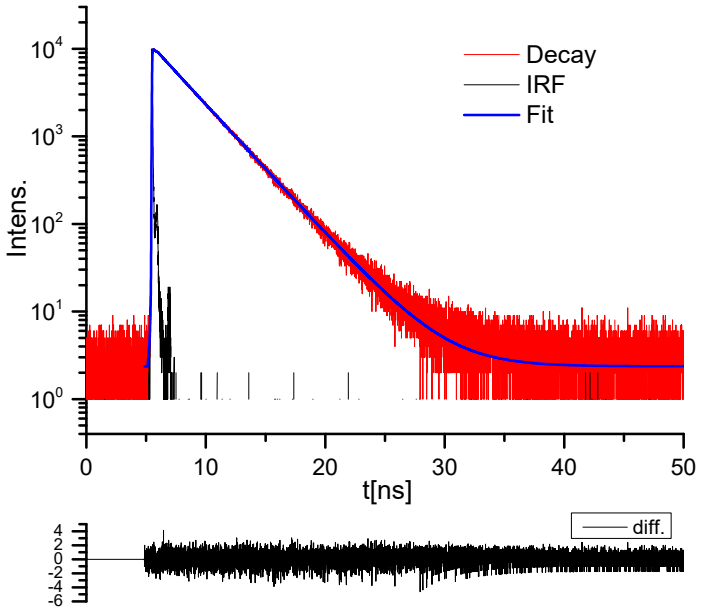


Fig. S44. Kinetics of fluorescence decay of compound **8b** (L) in acetonitrile (τ = 2.93 ns).

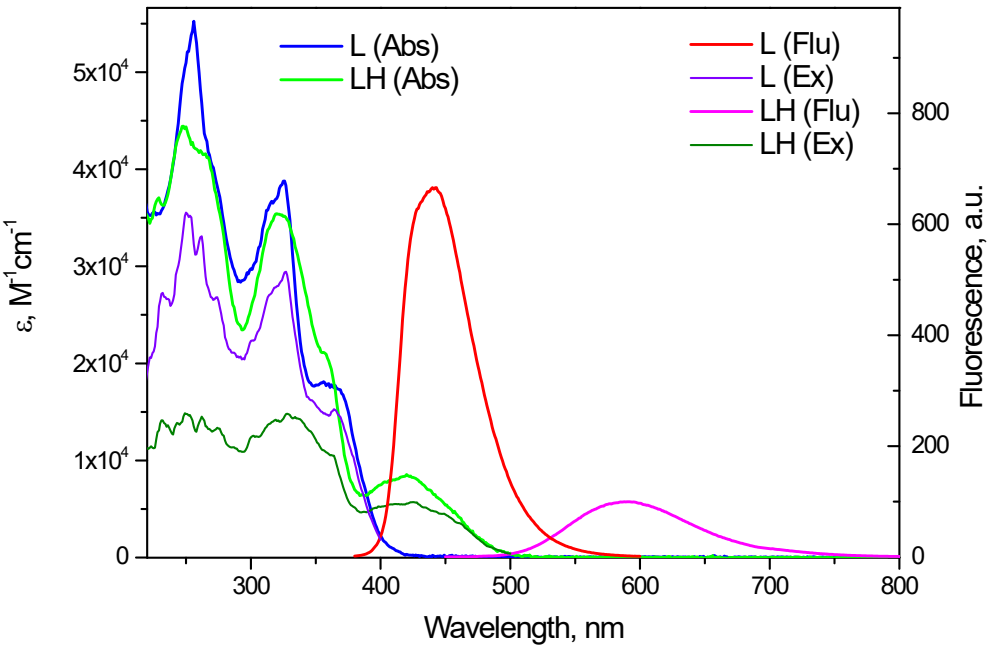


Fig. S45. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compound **8c** (L) in acetonitrile and (LH) in acidified acetonitrile (~0.02 M $HClO_4$).

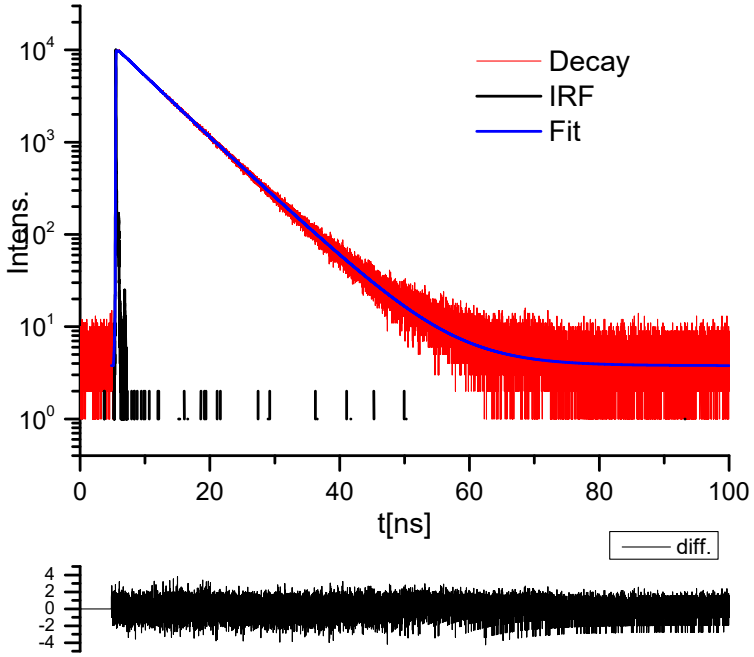


Fig. S46. Kinetics of fluorescence decay of compound **8c** (L) in acetonitrile (τ = 6.55 ns).

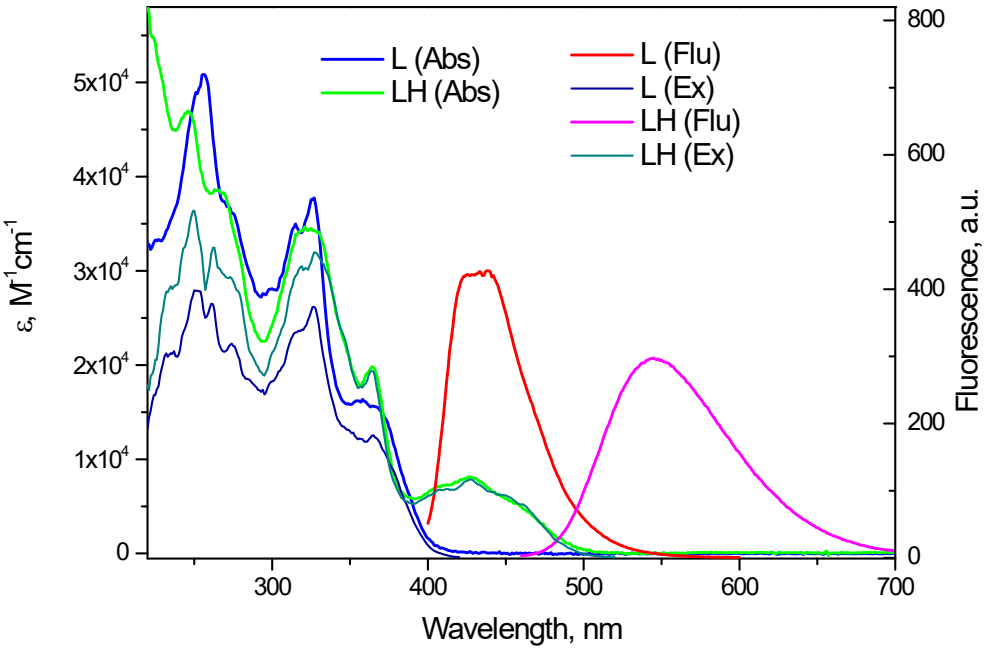


Fig. S47. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compound **8c** (L) in *n*-heptane and (LH) in acidified *n*-heptane (CF_3COOH).

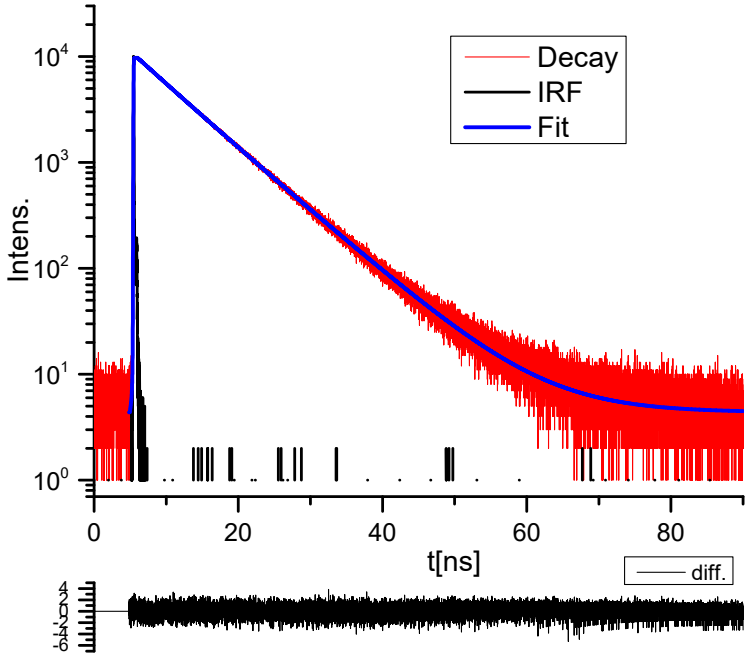


Fig. S48. Kinetics of fluorescence decay of compound **8c** (L) in *n*-heptane (τ = 7.25 ns).

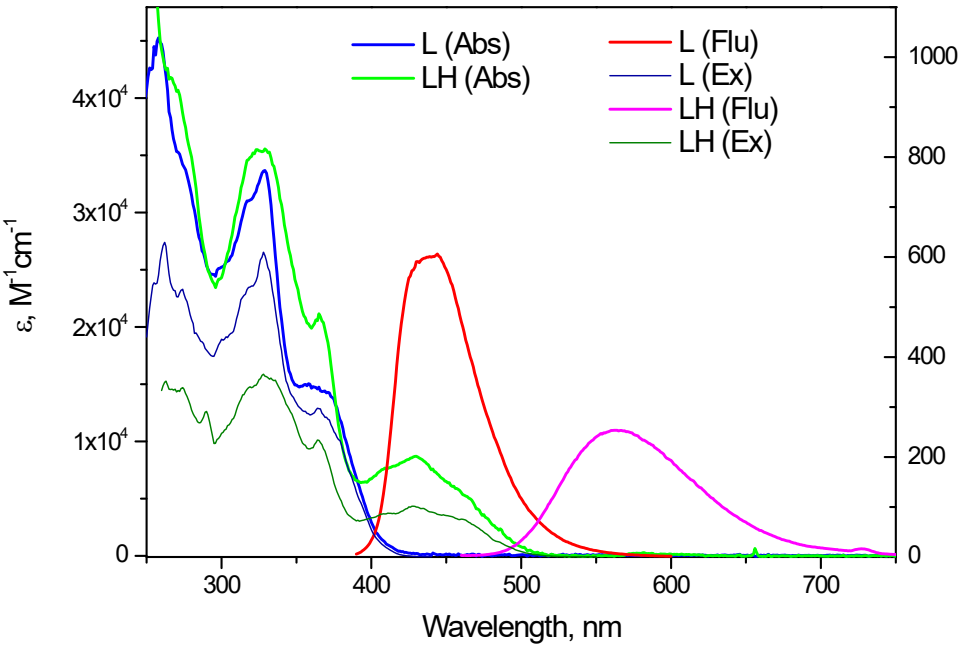


Fig. S49. Absorption (Abs), fluorescence (Flu) and fluorescence excitation (Ex) spectra of compound **8c** (L) in chloroform and (LH) in acidified chloroform (CF_3COOH).

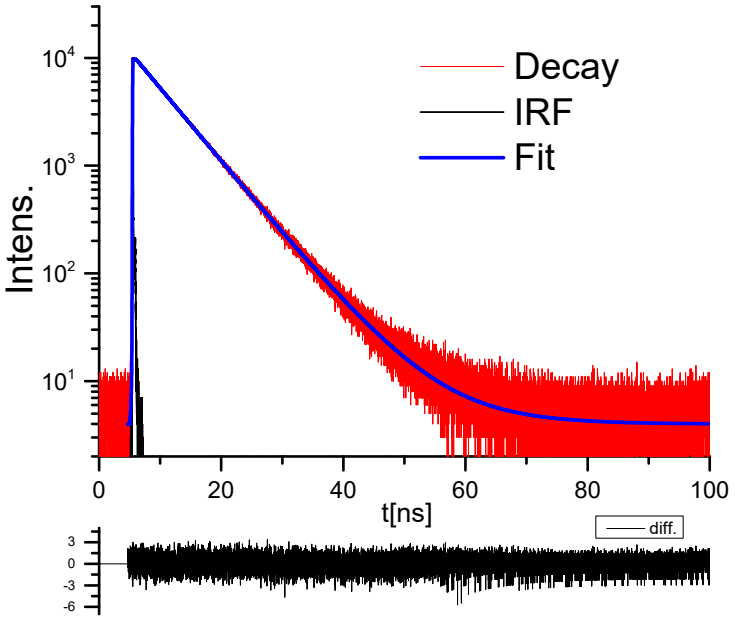


Fig. S50. Kinetics of fluorescence decay of compound **8c** (L) in chloroform (τ = 6.48 ns).

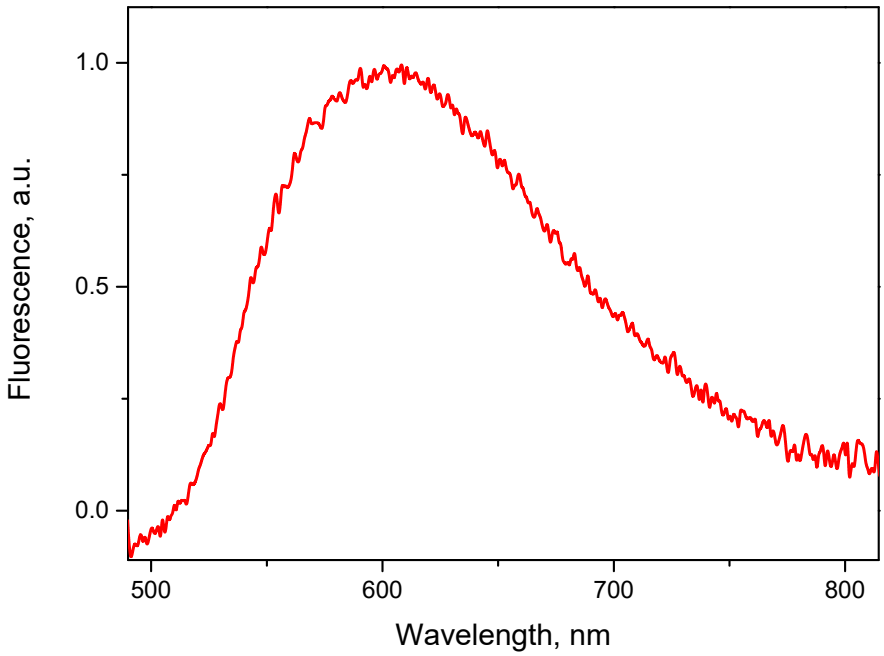


Fig. S51. Fluorescence spectrum of salt **8c-H**$^{+}$ $\mathbf{CF_3CO_2^-}$ in the solid phase

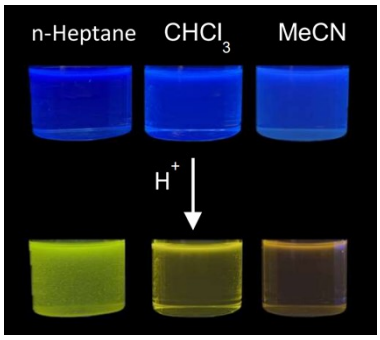


Fig S52. Solutions of helicene **8c** without acid (top) and with CF_3COOH (bottom) under UV irradiation (365 nm).