Supporting Information

for

Synthesis and crystal structure of pH-sensitive fluorescent pyrene-based double aza- and diaza[4]helicenes

Daria I. Tonkoglazova, Lyubov M. Oryabinskaya, Aleksandr A. Shcherbatykh, Anna V. Gulevskaya*

Department of Chemistry, Southern Federal University, Zorge str., 7, Rostov-on-Don 344090, Russian Federation

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

Table of contents

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). Commercial *p*-tolylacetylene, pyrene-1-boronic acid, catalysts, ICl, 2,3-dihaloazines, alkylamines, PPh_3, TFA, triflic acid, anhydrous DMSO, THF were used as received. ^1H, ^{13}C NMR spectra were recorded on 250 and 600 MHz spectrometers. Chemical shifts were reported in ppm relative to Me_4Si. The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source. Melting points were determined on a Stuart SMP30 instrument in glass capillaries and are uncorrected. The UV-vis spectra were recorded on a Varian Cary 50 Probe spectrophotometer. Fluorescence emission spectra were collected using a Cary Eclipse Varian spectrofluorimeter. Emission quantum yields were determined by relative method with a solution of anthracene in degassed EtOH as a standard ($\Phi = 0.28$)[1] and solutions of studied compounds in MeCN using equation 1[2]:

$$\Phi_x = \Phi_{st}\frac{I_x}{I_{st}}\cdot\frac{f_{st}(\lambda_{ex})}{f_x(\lambda_{ex})}\cdot\frac{n_x^2(\lambda_{em})}{n_{st}^2(\lambda_{em})} = \Phi_{st}\frac{I_x}{I_{st}}\cdot\frac{(1-10^{-A_{st}(\lambda_{ex})})}{(1-10^{-A_x(\lambda_{ex})})}\cdot\frac{n_x^2(\lambda_{em})}{n_{st}^2(\lambda_{em})} \qquad \text{(eq.1)}$$

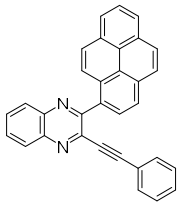
Where I_x and I_{st} are the integrated emission intensities of the studied compounds and standard compound, respectively; f_x and f_{st} are their respective absorption factors from the measured absorbances (A) at the excitation wavelength; n_x and n_{st} are the corresponding refractive indexes of the solvents used.

Protolytic equilibrium constant of helicene **9c** was estimated in MeCN – H_2O solution (1:1, v/v) by *direct* fluorimetric titration as a function of pH using the fluorescence emission spectra. To adjust the pH of the solutions, 0.1 M solution of HCl and 0.1 M solution of disodium citrate were used. To measure the pH values a pH-150M potentiometer with an indicator glass electrode and a silver–silver chloride reference electrode was applied. The electrode was calibrated before each measurement. The acidity constant pK_a was calculated according to linear eq. 2[3]:

$$pK_a = pH + lg\frac{F_{max}-F_i}{F_i-F_{min}} \qquad \text{(eq.2)}$$

Where F is a function of pH resulting in pK_a values and F_{max} and F_{min} are the signals at maximal and minimal [H^+], respectively.

2-(Phenylethynyl)-3-(pyren-1-yl)quinoxaline (2a)



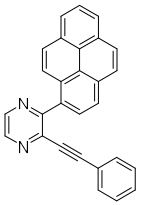
Method A. A mixture of 2-chloro-3-(phenylethynyl)quinoxaline **1a**[4] (132 mg, 0.5 mmol), pyrene-1-boronic acid (148 mg, 0.6 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), K_3PO_4 (212 mg, 1.0 mmol) and dry THF (8 mL) was stirred and refluxed under argon for 24 h. The reaction mixture was then evaporated 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 × 36 cm) with $CHCl_3$ as the eluent. The fraction with R_f 0.7 was the recovered starting compound (20%). The next yellowish fraction with R_f 0.35 gave 101 mg (47%) of compound **2a**.

Method B. A mixture of 2-chloro-3-(phenylethynyl)quinoxaline **1a** (132 mg, 0.5 mmol), pyrene-1-boronic acid (135 mg, 0.55 mmol), 5% Pd/C (32 mg, 0.015 mmol Pd), PPh_3 (16 mg, 0.06 mmol), toluene (3 mL) and a solution of K_2CO_3 (276 mg, 2 mmol) in water (3 mL) was stirred at 100 °C for 18 h under argon. The reaction mixture was then diluted 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 × 40 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.35 gave 95 mg (44%) of compound **2a**.

Method C. A mixture of 2-chloro-3-(phenylethynyl)quinoxaline **1a** (132 mg, 0.5 mmol), pyrene-1-boronic acid (148 mg, 0.6 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), K_2CO_3 (345 mg, 2.5 mmol), 1,4-dioxane (8 mL) and water (4 mL) was stirred and heated at 100 °C for 20 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 × 70 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.35 gave 160 mg (74%) of compound **2a**. The product was heated with EtOH (2 mL) for crystallization and filtered off.

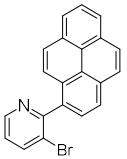
Compound **2a** was obtained as a yellow solid with mp 207–209 °C (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.80 (d, J = 7.7 Hz, 2 H), 6.99 (t, J = 7.7 Hz, 2 H), 7.14 (t, J = 7.6 Hz, 1 H), 7.86–7.92 (m, 2 H), 8.06–8.10 (m, 3 H), 8.20–8.22 (m, 3 H), 8.26–8.30 (m, 3 H), 8.36 (q, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 88.1, 96.1, 121.2, 124.4, 124.7, 124.8, 124.9, 125.5, 125.6, 126.2, 127.4, 127.9, 128.0, 128.2, 128.4, 129.0, 129.3, 129.5, 129.6, 130.6, 130.8, 130.9, 131.3, 131.9, 132.1, 132.5, 140.3, 140.6, 141.3, 156.4 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 267 sh (4.61), 277 (4.67), 344 (4.50), 401 (3.83), end absorption up to 469 nm. HRMS (ESI): MH^+, found 431.1530. $C_{32}H_{19}N_2$ requires 431.1543. $M+Na^+$, found 453.1366. $C_{32}H_{18}N_2Na$ requires 453.1362.

2-(Phenylethynyl)-3-(pyren-1-yl)pyrazine (2b)



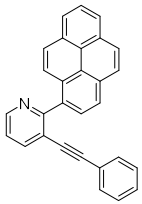
Compound **2b** was synthesized similarly to **2a** (*Method C*) starting from 2-chloro-3-(phenylethynyl)pyrazine **1b**[4] (107 mg, 0.5 mmol). Flash column chromatography was carried out on silica gel (3.5 × 50 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.3 and violet fluorescence under UV gave 142 mg (75%) of compound **2b** as a beige solid with mp 131–132 °C (AcOEt). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.88 (d, J = 8.3 Hz, 2 H), 7.03 (t, J = 7.7 Hz, 2 H), 7.17 (ddd, J = 8.6, 7.6, 1.2 Hz, 1H), 8.06–8.09 (m, 2 H), 8.11 (d, J = 9.2 Hz, 1 H), 8.18 (d, J = 8.9 Hz, 1 H), 8.20 (d, J = 8.9 Hz, 1 H), 8.22 (d, J = 7.5 Hz, 1 H), 8.27 (d, J = 7.6 Hz, 1 H), 8.29 (d, J = 7.8 Hz, 1 H), 8.34 (d, J = 7.8 Hz, 1 H), 8.74 (d, J = 2.3 Hz, 1 H), 8.78 (d, J = 2.3 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 87.1, 95.7, 121.4, 124.3, 124.6(5), 124.6(7), 124.8, 125.5, 125.6, 126.1, 127.4, 127.9, 128.1, 128.2, 128.3, 129.1, 129.2, 130.8, 131.3, 131.7, 132.0, 132.1, 140.2, 142.2, 142.9, 157.2 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 279 (4.55), 329 (4.33), 349 (4.33), end absorption up to 423 nm. HRMS (ESI): MH^+, found 381.1378. $C_{28}H_{17}N_2$ requires 381.1386. $M+Na^+$, found 403.1200. $C_{28}H_{16}N_2Na$ requires 403.1206.

3-Bromo-2-(pyren-1-yl)pyridine (4)



A mixture of 2,3-dibromopyridine **3** (238 mg, 1.0 mmol), pyrene-1-boronic acid (296 mg, 1.2 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), K_2CO_3 (690 mg, 5.0 mmol), 1,4-dioxane (12 mL) and water (6 mL) was stirred and refluxed for 24 h under argon. The reaction mixture was then evaporated to dryness. The residue was treated with water (100 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (3.5 × 35 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.3 gave 305 mg (85%) of compound **4** as a light yellow solid with mp 149–151 °C (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (dd, J = 8.2, 4.7 Hz, 1 H), 7.77 (d, J = 9.1 Hz, 1 H), 8.04–8.09 (m, 3 H), 8.14 (dd, J = 8.2, 1.5 Hz, 1 H), 8.16 (s, 2 H), 8.22 (d, J = 7.5 Hz, 1 H), 8.25 (d, J = 7.6 Hz, 1 H), 8.31 (d, J = 7.8 Hz, 1 H), 8.81 (dd, J = 4.7, 1.5 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 122.4, 123.7, 124.5, 124.6, 124.7, 125.3, 125.4, 126.0, 126.9, 127.4, 127.9, 128.0, 128.6, 130.9, 131.3, 131.6, 134.8, 140.7, 148.1, 159.0 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 269 (4.48), 279 (4.63), 315 (4.04), 329 (4.36), 345 (4.52), end absorption up to 389 nm. HRMS (ESI): MH^+ (^{79}Br), found 358.0227; MH^+ (^{81}Br), found 360.0206. $C_{21}H_{13}BrN$ requires 358.0226 (^{79}Br), 360.0206 (^{81}Br). $M+Na^+$ (^{79}Br) found 380.0043, M^+Na^+ (^{81}Br) found 382.0025. $C_{21}H_{12}BrNNa$ requires 380.0045 (^{79}Br), 382.0026 (^{81}Br).

3-(Phenylethynyl)-2-(pyren-1-yl)pyridine (2c)

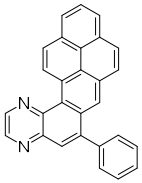


A mixture of 3-bromo-2-(pyren-1-yl)pyridine **4** (179 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol), CuI (4 mg, 0.21 mmol), *i*-Pr_2NH (1 mL) and DMSO (5 mL) was stirred at 80 °C under argon for 20 min. Then a solution of phenylacetylene (153 mg, 0.165 mL, 1.5 mmol) in *i*-Pr_2NH (2 mL) was added by portions for 2 h. The reaction mixture was stirred at 100 °C for 24 h. Then it was evaporated without heating to remove *i*-Pr_2NH, treated with H_2O (50 mL) and extracted with CH_2Cl_2 (4 × 10 mL). The extract was dried over Na_2SO_4, concentrated and purified by flash column chromatography on silica gel (3.5 × 30 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.25 and violet fluorescence under UV gave 176 mg (92%) of compound **2c** as a beige solid with mp 58–60 °C (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.77–6.78 (m, 1 H), 6.79–6.80 (m, 1 H), 6.96–7.00 (m, 2 H), 7.07–7.10 (m, 1 H), 7.40 (dd, J = 7.9, 4.9 Hz, 1 H), 8.00 (t, J = 7.6 Hz, 1 H), 8.03–8.08 (m, 3 H), 8.13 (br s, 2 H), 8.16 (dd, J = 7.6, 1.1 Hz, 1 H), 8.21 (dd, J = 7.6, 1.1 Hz, 1 H), 8.23 (d, J = 7.8 Hz, 1 H), 8.28 (d, J = 7.8 Hz, 1 H), 8.79 (dd, J = 4.9, 1.8 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 87.0, 95.4, 120.9, 121.8, 122.4, 124.3, 124.8, 124.9, 125.1, 125.2(7), 125.3(3), 125.9, 127.5, 127.6, 127.8(4), 127.8(5), 128.0, 128.3, 129.0, 130.9, 131.2, 131.3, 131.6, 134.8, 139.8, 148.4, 161.1 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 267 sh (4.60), 279 (4.71), 304 (4.41), 332 (4.31), 347 (4.44), end absorption up to 410 nm. HRMS (ESI): MH^+, found 380.1436. $C_{29}H_{18}N$ requires 380.1434.

Synthesis of 7-phenylpyreno[1,2-*f*]quinoxaline (5b) and 12-phenylpyreno[2,1-*f*]quinoxaline (6b)

A stirred solution of alkyne **2b** (38 mg, 0.1 mmol) in CF_3COOH (2 mL) was heated at 60 °C for 22 h. The reaction mixture was evaporated to dryness, treated with saturated aq. K_2CO_3 (50 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (1.0 × 25 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.4 gave 8 mg (21%) of compound **5b**. The next fraction with R_f 0.3 gave 5 mg (13%) of compound **6b**.

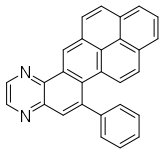
7-Phenylpyreno[1,2-f]quinoxaline **5b**, yellow needles (yellow-green fluorescence under UV) with mp 236–237 °C (ethylacetate – hexane, 1:3 v/v). ^{1}H



NMR (250 MHz, $CDCl_3$): δ = 7.60–7.73 (m, 5 H), 8.00 (d, J = 9.0 Hz, 1 H), 8.06–8.13 (m, 3 H), 8.20 (dd, J = 7.5, 0.7 Hz, 1 H), 8.34 (dd, J = 7.5, 0.7 Hz, 1 H), 8.47 (d, J = 9.7 Hz, 1 H), 8.63 (s, 1 H), 8.98 (d, J = 2.0 Hz, 1 H), 9.18 (d, J = 2.0 Hz, 1 H), 11.26 (d, J = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 123.8, 124.1, 124.5, 124.9, 125.7, 125.8, 126.6, 128.2, 128.3, 128.8(0) (2C), 128.8(3), 128.8(5), 129.2, 130.3, 130.5, 131.0, 131.6(3), 131.6(6), 131.8, 140.5, 141.7, 143.0, 143.1, 144.3, 145.0 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 258

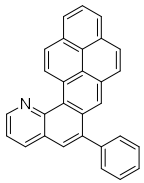
sh (4.63), 284 (4.67), 305 sh (4.42), 335 sh (4.25), 345 (4.26), 372 (4.23), 391 (4.45), 421 (3.99), 446 (4.05), end absorption up to 482 nm. HRMS (ESI): MH^+, found 381.1384. $C_{28}H_{17}N_2$ requires 381.1386.

12-Phenylpyreno[2,1-f]quinoxaline **6b**, a yellow solid (yellow fluorescence under UV) with mp 238–240 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ =



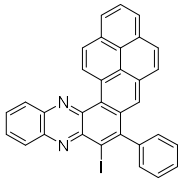
7.51–7.56 (m, 5 H), 7.80 (d, J = 9.5 Hz, 1 H), 7.99–8.20 (m, 6 H), 8.31 (d, J = 9.0 Hz, 1 H), 9.02 (d, J = 2.0 Hz, 1 H), 9.06 (d, J = 2.0 Hz, 1 H), 10.14 (s, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 121.4, 124.7, 125.6, 125.7, 125.8, 126.2, 126.6, 126.8, 127.3, 127.9(6), 128.0(1), 128.5, 128.9 (2C), 129.3, 130.0, 130.9, 131.1, 131.8, 141.6, 141.8, 143.3, 144.3, 144.6, 144.8(0), 144.8(3) ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 283 (4.50), 344 sh (3.93), 375 (3.90), 396 (4.03), 422 sh (3.70), 443 (3.68), end absorption up to 475 nm. HRMS (ESI): MH^+, found 381.1394. $C_{28}H_{17}N_2$ requires 381.1386.

7-Phenylpyreno[2,1-*h*]quinoline (5c)



Compound **5c** was synthesized similarly to **5b** using alkyne **2c** (38 mg, 0.1 mmol) and CF_3COOH (3 mL). Flash column chromatography was carried out on silica gel (1.0 × 25 cm) with $CHCl_3$ as the eluent. The yellowish fraction with R_f 0.7 gave cyclization product **5c** (26 mg, 69%). Compound **5c** was obtained as a yellow solid with mp 215–217 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.57–7.71 (m, 6 H), 7.86 (s, 1 H), 7.97–8.10 (m, 3 H), 8.19 (dd, J = 7.3, 0.7 Hz, 1 H), 8.33–8.36 (m, 2 H), 8.49 (d, J = 9.6 Hz, 1 H), 8.62 (s, 1 H), 9.30 (dd, J = 4.3, 1.9 Hz, 1 H), 11.54 (d, J = 9.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 121.1, 123.8, 124.6 (2C), 124.7, 125.1, 125.4, 126.2, 127.0, 127.2, 127.8, 128.0(8), 128.1(0), 128.6, 129.5(4), 129.5(6), 130.1, 130.4, 130.9(4), 130.9(7), 131.6, 131.9, 136.2, 140.6, 141.1, 147.8, 148.7 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 281 (4.63), 304 (4.58), 314 sh (4.56), 329 sh (4.38), 350 (3.96), 372 (4.32), 391 (4.47), 407 (4.11), 430 (3.99), end absorption up to 458 nm. HRMS (ESI): MH^+, found 380.1440. $C_{29}H_{18}N$ requires 380.1439.

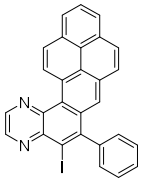
8-Iodo-7-phenylpyreno[1,2-*a*]phenazine (7a)



To a stirred suspension of compound **2a** (86 mg, 0.2 mmol) in dry CH_3CN (15 mL), a solution of ICl (55 mg, 0.34 mmol) in dry CH_3CN (5 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

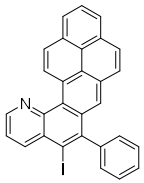
by flash column chromatography on silica gel (2.5 × 55 cm) with $CHCl_3$ as the eluent. The orange fraction with R_f 0.8 gave 107 mg (95%) of compound **7a** as an orange solid with mp 254–257 ºC (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48–7.50 (m, 2 H), 7.66–7.73 (m, 3 H), 7.82 (d, J = 8.9 Hz, 1 H), 7.88–7.92 (m, 2 H), 7.98–8.01 (m, 2 H), 8.07 (s, 1 H), 8.11 (d, J = 7.3 Hz, 1 H), 8.22 (d, J = 7.5 Hz, 1 H), 8.38 (d, J = 7.8 Hz, 1 H), 8.39–8.41 (m, 1 H), 8.46–8.49 (m, 1 H), 11.25 (d, J = 9.5 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 109.3, 122.5, 123.9, 124.8, 125.6(9), 125.7(4), 125.8, 126.5, 127.8, 128.3, 128.5, 128.7, 128.9, 129.2, 129.3, 129.8, 130.1, 130.2, 130.4(6), 130.5(0), 131.2, 131.9, 132.8, 141.2, 141.3, 142.0, 144.2, 144.7, 151.7 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 278 (4.76), 293 sh (4.64), 304 (4.65), 332 sh (4.42), 350 (4.57), 359 sh (4.54), 373 (4.58), 401 sh (4.16), 435 (3.85), 463 (4.14), 492 (4.25), end absorption up to 535 nm. HRMS (ESI): MH^+, found 557.0503. $C_{32}H_{18}IN_2$ requires 557.0509.

8-Iodo-7-phenylpyreno[1,2-*f*]quinoxaline (7b)



Compound **7b** was synthesized similarly to **7a** using a solution of 2-(phenylethynyl)-3-(pyren-1-yl)pyrazine **2b** (76 mg, 0.2 mmol) in dry CH_3CN (4 mL) and a solution of ICl (55 mg, 0.34 mmol) in dry CH_3CN (1.5 mL). Flash column chromatography was carried out on silica gel (2 × 40 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.9 gave **7b** in near quantitative yield (99 mg, 98%). Compound **7b** was obtained as yellow needles with mp 268–269 ºC (AcOEt – hexane, 1:3 v/v). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.49 (m, 2 H), 7.64–7.76 (m, 3 H), 7.91 (d, J = 9.2 Hz, 1 H), 8.05–8.14 (m, 2 H), 8.21–8.23 (m, 2 H), 8.35 (d, J = 7.4 Hz, 1 H), 8.46 (d, J = 9.6 Hz, 1 H), 9.06 (d, J = 1.9 Hz, 1 H), 9.14 (d, J = 1.9 Hz, 1 H), 11.11 (d, J = 9.6 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 108.2, 123.0, 124.1, 124.9, 125.2, 125.7, 125.8, 126.6, 127.9, 128.3, 128.6, 128.8, 128.9, 129.2, 129.9, 130.8, 131.4, 131.8, 132.7, 134.2, 141.9, 142.1, 143.0, 144.1, 144.6, 150.7 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 261 sh (4.68), 286 (4.65), 315 (4.46), 347 (4.45), 374 (4.28), 394 (4.46), 427 (3.97), 451 (4.02), end absorption up to 487 nm. HRMS (ESI): MH^+, found 507.0338. $C_{28}H_{16}IN_2$ requires 507.0353.

8-Iodo-7-phenylpyreno[2,1-*h*]quinoline (7c)



Compound **7c** was synthesized similarly to **7a** using a solution of 2-(phenylethynyl)-3-(pyren-1-yl)pyridine **2c** (50 mg, 0.131 mmol) in dry CH_3CN (2 mL) and a solution of ICl (15 mg, 0.092 mmol) in dry CH_3CN (2 mL). Flash column chromatography was carried out on silica gel (1.5 × 52 cm) with $CHCl_3$ as the eluent. The yellow fraction with R_f 0.7 gave 19 mg (41%) of compound **7c** as a yellow needles with mp 248–251 ºC (EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40–7.42 (m, 2 H), 7.60–7.66 (m, 4 H), 7.85 (d, J = 8.9 Hz, 1 H), 7.99 (d, J = 8.9 Hz, 1 H), 8.04 (t, J = 7.5 Hz, 1 H), 8.12 (s, 1 H), 8.14 (d, J = 7.3 Hz, 1 H), 8.29 (d, J = 7.4 Hz, 1 H), 8.42 (d, J = 9.6 Hz, 1 H), 8.87 (dd, J = 8.2, 1.7 Hz, 1 H), 9.18 (dd, J = 4.2, 1.7 Hz, 1 H), 11.28 (d, J = 9.6 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 105.1, 122.1, 124.1, 124.3, 125.0, 125.2, 125.3, 125.5, 126.4, 128.0, 128.2, 128.3, 128.6, 128.7(2), 128.7(8), 129.5(1), 129.5(4), 130.2, 130.9, 131.2, 131.5, 132.7, 142.2, 145.6, 146.7, 148.2, 148.7 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 279 (4.62), 320 (4.67), 333 sh (4.57), 355 (4.06), 374 (4.35), 393 (4.49), 410 (4.03), 434 (3.90), end absorption up to 473 nm. HRMS (ESI): MH^+, found 506.0404. $C_{29}H_{17}IN$ requires 506.0400.

Synthesis of 7-phenyl-8-(*p*-tolylethynyl)pyreno[1,2-*a*]phenazine (8a) and 7-phenylpyreno[1,2-*a*]phenazine (5a)

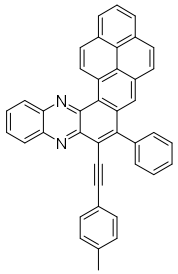
Method A. A mixture of iodide **7a** (56 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (1 mg, 0.005 mmol) and Et_3N (1 mL) was stirred at 80 ºC for 20 min under argon. A solution of *p*-tolylacetylene (18 mg, 0.15 mmol) in Et_3N (1 mL) was then added by portions for 2.5 h to the reaction mixture heated to 80 ºC. The reaction mixture was stirred at 80 ºC for 24 h and then evaporated. The residue was treated with H_2O (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 × 65 cm) using $CHCl_3$ as the eluent. The yellow fraction with R_f 0.5 gave compound **8a** (6 mg, 11%).

Method B. A mixture of iodide **7a** (56 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 0.007 mmol), CuI (1 mg, 0.005 mmol), *i*-Pr_2NH (1 mL) and DMSO (3 mL) was stirred at 80 ºC under argon for 20 min and then heated to 80 ºC. A solution of *p*-tolylacetylene (18 mg, 0.15 mmol) in *i*-Pr_2NH (1 mL) was then added by portions for 2.5 h. The reaction mixture was stirred at 80 ºC for 24 h and then evaporated without heating to remove *i*-Pr_2NH. The residue was treated with H_2O (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 × 65 cm) using $CHCl_3$ as the eluent. The yellow fraction with R_f 0.5 gave compound **8a** (15 mg, 27%). The yellow fraction with R_f 0.3 and yellow fluorescence under UV gave compound **5a** (10 mg, 18%).

Method C. A mixture of iodide **7a** (56 mg, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), *i*-Pr_2NH (1 mL) and toluene (6 mL) was stirred at 80 °C for 20 min under argon. A solution of *p*-tolylacetylene (45 mg, 0.39 mmol) in *i*-Pr_2NH (1 mL) was then added by portions for 2.5 h. The reaction mixture was stirred at 80 °C for 24 h and evaporated without heating to remove *i*-Pr_2NH. The residue was treated with H_2O (100 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 (1.5 × 50 cm) using $CHCl_3$ as the eluent. The yellow fraction with R_f 0.5 gave compound **8a** (30 mg, 55%).

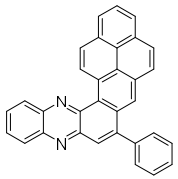
Method D. A mixture of iodide **7a** (56 mg, 0.1 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01mmol), piperidine (3 mL) was stirred at 105 °C for 20 min under argon and then heated to 105 °C. A solution of *p*-tolylacetylene (35 mg, 0.3 mmol) in piperidine (2 mL) was then added by portions for 1.5 h. The reaction mixture was stirred at 105 °C for 24 h and evaporated without heating to dryness. The residue was treated with H_2O (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 (2.5 × 50 cm) using a mixture of $CHCl_3$ – hexane (2:1, v/v) as the eluent. The yellow fraction with R_f 0.5 gave compound **8a** (53 mg, 97%)

7-Phenyl-8-(p-tolylethynyl)pyreno[1,2-a]phenazine **8a** was obtained as an orange solid with mp 254–256 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ =



2.37 (s, 3 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 7.24 (d, *J* = 7.9 Hz, 2 H), 7.63–7.75 (m, 5 H), 7.89–7.99 (m, 3 H), 8.03–8.13 (m, 2 H), 8.20 (d, *J* = 7.1 Hz, 1 H), 8.30–8.38 (m, 2 H), 8.44–8.60 (m, 3 H), 11.49 (d, *J* = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7, 86.7, 100.4, 120.8, 121.7, 122.8, 124.4, 125.2, 125.3, 125.9(6), 126.0(3), 126.7, 128.2, 128.6, 128.8, 129.1(2C), 129.4, 129.5(6), 129.5(7), 129.9, 130.1, 130.2, 130.8, 131.0(2C), 131.6, 131.9, 132.1, 132.6, 138.6, 139.8, 141.1, 141.2, 143.2, 144.8, 149.3 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 278 (4.76), 297 sh (4.64), 351 (4.62), 375 (4.62), 387 sh (4.58), 439 (3.92), 469 (4.07), 500 (4.19), end absorption up to 541 nm. HRMS (ESI): MH^+, found 545.2012. $C_{41}H_{25}N_2$ requires 545.2012.

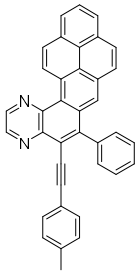
7-Phenylpyreno[1,2-a]phenazine **5a** was obtained as a yellow orange solid with mp 269–271 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): *δ* = 7.58–7.74



(m, 5 H), 7.86–7.96 (m, 2 H), 7.99–8.12 (m, 4 H), 8.21 (dd, *J* = 7.6, 1.0 Hz, 1 H), 8.27–8.35 (m, 2 H), 8.51 (d, *J* = 9.7 Hz, 1 H), 8.55–8.60 (m, 2 H), 11.55 (d, *J* = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$) *δ* 123.4, 124.4, 124.6, 125.0, 125.9, 126.0, 126.7, 128.1, 128.4, 128.6, 128.8(4), 128.8(7), 129.0, 129.4, 129.5, 129.8, 129.9, 130.1(8), 130.2(1), 130.9, 131.3, 131.6, 132.1(1), 132.1(2), 140.5, 141.2, 141.4, 144.1, 145.5, 146.3 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 278 (4.71), 293 sh (4.62), 300 sh (4.60), 333 sh (4.39), 348 (4.50), 367

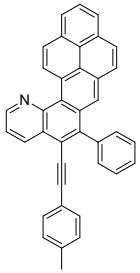
(4.42), 395 sh (4.13), 430 sh (3.82), 461 (4.09), 488 (4.21), end absorption up to 532 nm. HRMS (ESI): MH^+, found 431.1545. $C_{32}H_{18}IN_2$ requires 431.1543.

7-Phenyl-8-(*p*-tolylethynyl)pyreno[1,2-*f*]quinoxaline (8b)



Compound **8b** was synthesized similarly to **8a** (*Method D*) starting from iodide **7b** (51 mg, 0.1 mmol). A solution of *p*-tolylacetylene (35 mg, 0.3 mmol) in piperidine (2 mL) was added by portions for 1.5 h was added by portions for 5 h. Flash column chromatography was carried out on silica gel (2.0 × 50 cm) using CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.7 and green fluorescence gave compound **8b** (48 mg, 98%) as yellow needles (yellow fluorescence under UV) with mp 242–244 ºC (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.63–7.73 (m, 5 H), 7.93 (d, *J* = 9.1 Hz, 1 H), 8.00–8.11 (m, 2 H), 8.18 (d, *J* = 7.3, 1 H), 8.32 (d, *J* = 7.5 Hz, 1 H), 8.37 (s, 1 H), 8.44 (d, *J* = 9.7 Hz, 1 H), 9.12 (d, *J* = 1.8 Hz, 1 H), 9.20 (d, *J* = 1.8 Hz, 1 H), 11.17 (d, *J* = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7, 86.5, 100.3, 120.4, 121.4, 123.1, 124.4, 124.6, 125.1, 125.8, 125.9, 126.7, 128.1, 128.2, 128.6, 128.7, 128.9, 129.0, 129.2, 130.2, 130.8, 131.0, 131.6, 131.8, 131.9, 132.1, 138.6, 139.8, 141.9, 142.6, 143.0, 144.0, 148.3 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 280 (4.68), 310 (4.52), 327 (4.59), 356 (4.68), 374 sh (4.58), 394 (4.44), 437 (3.92), 464 (3.99), end absorption up to 494 nm. HRMS (ESI): MH^+, found 495.1856. $C_{37}H_{23}N_2$ requires 495.1856.

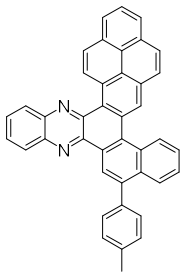
7-Phenyl-8-(*p*-tolylethynyl)pyreno[2,1-*h*]quinoline (8c)



Compound **8c** was synthesized similarly to **8a** (*Method D*) starting from iodide **7c**. Flash column chromatography was carried out on silica gel (1.5 × 55 cm) using a mixture of $CHCl_3$ – hexane (2:1, v/v) as the eluent. The yellow fraction with R_f 0.5 gave compound **8c** (43 mg, 85%) as yellowish needles with mp 204–206 ºC (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 3 H), 7.09–7.22 (m, 4 H), 7.61–7.69 (m, 5 H), 7.73 (dd, *J* = 8.2, 4.3 Hz, 1 H), 7.94 (d, *J* = 9.0 Hz, 1 H), 7.99–8.10 (m, 2 H), 8.17 (br d, *J* = 6.7 Hz, 1 H), 8.32 (br d, *J* = 7.5 Hz, 1 H), 8.39 (s, 1 H), 8.47 (d, *J* = 9.7 Hz, 1 H), 9.06 (dd, *J* = 8.2, 1.8 Hz, 1 H), 9.31 (dd, *J* = 4.3, 1.8 Hz, 1 H), 11.44 (d, *J* = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.7, 86.4, 99.4, 119.2, 120.3, 121.4, 124.3, 124.5, 124.6, 125.1, 125.4, 125.6, 126.5, 126.7, 127.9, 128.2, 128.3, 128.5, 128.8, 129.3, 129.6, 129.9, 131.1(0), 131.1(4), 131.2, 131.5, 131.7, 132.2, 135.2, 138.8, 140.3, 144.2, 148.1, 148.5 ppm. UV-vis ($CHCl_3$),

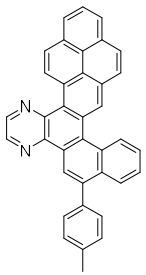
λ_{max} nm (lg ε): 276 (4.62), 330 sh (4.70), 346 (4.87), 363 sh (4.67), 373 sh (4.53), 393 (4.42), 423 (3.76), 449 (3.76), end absorption up to 470 nm. HRMS (ESI): MH^+, found 494.1903. $C_{38}H_{24}N$ requires 494.1903.

11-(*p*-Tolyl)naphtho[2,1-*a*]pyreno[2,1-*c*]phenazine (9a)



A stirred solution of alkyne **8a** (25 mg, 0.046 mmol) in CF_3COOH (3 mL) was heated at 80 ºC for 4 h. The reaction mixture was evaporated to dryness, treated with saturated K_2CO_3 (5 mL) and extracted with $CHCl_3$ (3 × 15 mL). The organic layer was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.5 × 25 cm) with $CHCl_3$ as the eluent. The yellow orange fraction with R_f 0.8 and greenish-yellow fluorescence gave cyclization product **9a** (24 mg, 96%). Compound **9a** was obtained as a yellow-orange solid (orange fluorescence under UV) with mp 300–302 ºC (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 7.45 (d, *J* = 7.8 Hz, 2 H), 7.60–7.75 (m, 4 H), 7.85–7.95 (m, 2 H), 8.10 (t, *J* = 7.6 Hz, 1 H), 8.17–8.20 (m, 3 H), 8.27 (dd, *J* = 7.6, 0.9 Hz, 1 H), 8.32–8.37 (m, 2 H), 8.48–8.57 (m, 2 H), 9.10 (d, *J* = 8.4 Hz, 1 H), 9.41 (s, 1 H), 9.48 (s, 1H), 11.42 (d, *J* = 9.7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 122.9, 123.2, 124.5, 124.6, 125.9, 126.0, 126.5, 126.6, 126.7, 127.1, 127.2, 128.0, 128.5(6), 128.6, 128.7, 129.2, 129.3(5), 129.4(3), 129.4(4), 129.6, 129.8, 129.9, 130.3, 130.7(0), 130.7(7), 130.8(3), 130.9, 131.5, 131.6, 134.4, 137.5, 137.9, 140.8, 140.9, 141.2, 142.9, 145.3 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 284 (4.94), 341 (4.82), 370 (4.60), 389 (4.62), 427 (4.21), 453 (4.24), 483 (4.25), end absorption up to 527 nm. HRMS (ESI): MH^+, found 545.2011. $C_{41}H_{25}N_2$ requires 545.2012.

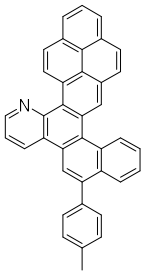
5-(*p*-Tolyl)naphtho[2,1-*f*]pyreno[2,1-*h*]quinoxaline (9b)



A stirred solution of alkyne **8b** (25 mg, 0.05 mmol) in CF_3COOH (4 mL) was heated at 60 ºC for 5 h. The reaction mixture was evaporated to dryness, treated with saturated K_2CO_3 (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (2.0 × 22 cm) with CH_2Cl_2 as the eluent. The yellow fraction with R_f 0.8 and greenish-blue fluorescence gave cyclization product **9b** (23 mg, 92%). Compound **9b** was obtained as a yellow solid (bright yellow fluorescence under UV) with mp 228–230 ºC (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): *δ* = 2.53 (s, 3 H), 7.41 (d, *J* = 7.8 Hz, 2 H), 7.61–7.68 (m, 3 H), 7.72 (ddd, *J* = 8.3, 6.7, 1.5 Hz, 1H), 8.10 (t, *J* = 7.6 Hz, 1 H), 8.17–8.28 (m, 4 H), 8.35 (dd, *J* = 7.6, 0.9 Hz, 1 H), 8.45 (d, *J* = 9.6 Hz, 1 H), 8.95 (d, *J* = 2.0

Hz, 1 H), 9.10–9.17 (m, 2 H), 9.25 (s, 1 H), 9.59 (s, 1 H), 11.09 (d, J = 9.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 122.2, 123.1, 124.3(8), 124.4(3), 125.7, 126.1, 126.4(2), 126.4(4), 126.9, 127.1, 127.9, 128.1, 128.5, 128.6, 128.7, 129.1(6), 129.2(1) (2C), 129.4, 129.8, 129.9, 130.2, 130.7, 130.8, 130.9, 131.5, 133.9, 137.4, 137.7, 140.7, 141.7(5), 141.8(1), 141.8(5), 144.1 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 265 (4.69), 279 (4.72), 291 (4.73), 338 (4.66), 377 (4.49), 398 (4.43), 427 (3.96), 453 (3.96), end absorption up to 476 nm. HRMS (ESI): MH^+, found 495.1856. $C_{37}H_{23}N_2$ requires 495.1856.

5-(*p*-Tolyl)naphtho[2,1-*f*]pyreno[2,1-*h*]quinoline (9c)



Method A. The stirred solution of alkyne **8c** (25 mg, 0.05 mmol) in CF_3COOH (2 mL) was heated at 60 °C for 22 h. The reaction mixture was evaporated to dryness, treated with saturated K_2CO_3 (50 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The organic phase was dried over Na_2SO_4 and purified by flash column chromatography on silica gel (1.5 × 34 cm) with CH_2Cl_2 as the eluent. The yellowish fraction with R_f 0.9 gave cyclization product **9c** (21 mg, 84%). Compound **9c** was obtained as a yellow solid (green fluorescence under UV) with mp 245–247 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 7.42 (d, J = 7.8 Hz, 2 H), 7.57–7.64 (m, 4 H), 7.69 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 8.03–8.17 (m, 4 H), 8.22 (dd, J = 7.5, 0.9 Hz, 1 H), 8.33 (dd, J = 7.7, 0.7 Hz, 1 H), 8.44 (d, J = 9.6 Hz, 1 H), 8.49 (s, 1 H), 8.98 (dd, J = 8.1, 0.7 Hz, 1 H), 9.10 (d, J = 8.6 Hz, 1 H), 9.21 (dd, J = 4.2, 1.2 Hz 1 H), 9.53 (s, 1 H), 11.24 (d, J = 9.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4, 120.6, 121.1, 124.4(2), 124.4(8), 124.5, 125.2, 125.3, 125.5, 126.1, 126.2, 126.3(5), 126.3(7), 126.4, 126.7, 127.4, 127.8(6), 127.9(2), 128.7, 129.0, 129.3, 129.3(7), 129.4(0), 129.6, 130.0, 130.3, 130.9(2), 130.9(7), 131.3, 131.6, 132.8, 137.5, 137.8, 140.3, 147.6, 148.8 ppm. UV-vis ($CHCl_3$), λ_{max} nm (lg ε): 276 (4.93), 346 (4.71), 377 sh (4.39), 397 (4.38), 420 sh (3.83), 440 (3.70), end absorption up to 470 nm. HRMS (ESI): MH^+, found 494.1903. $C_{38}H_{24}N$ requires 494.1903.

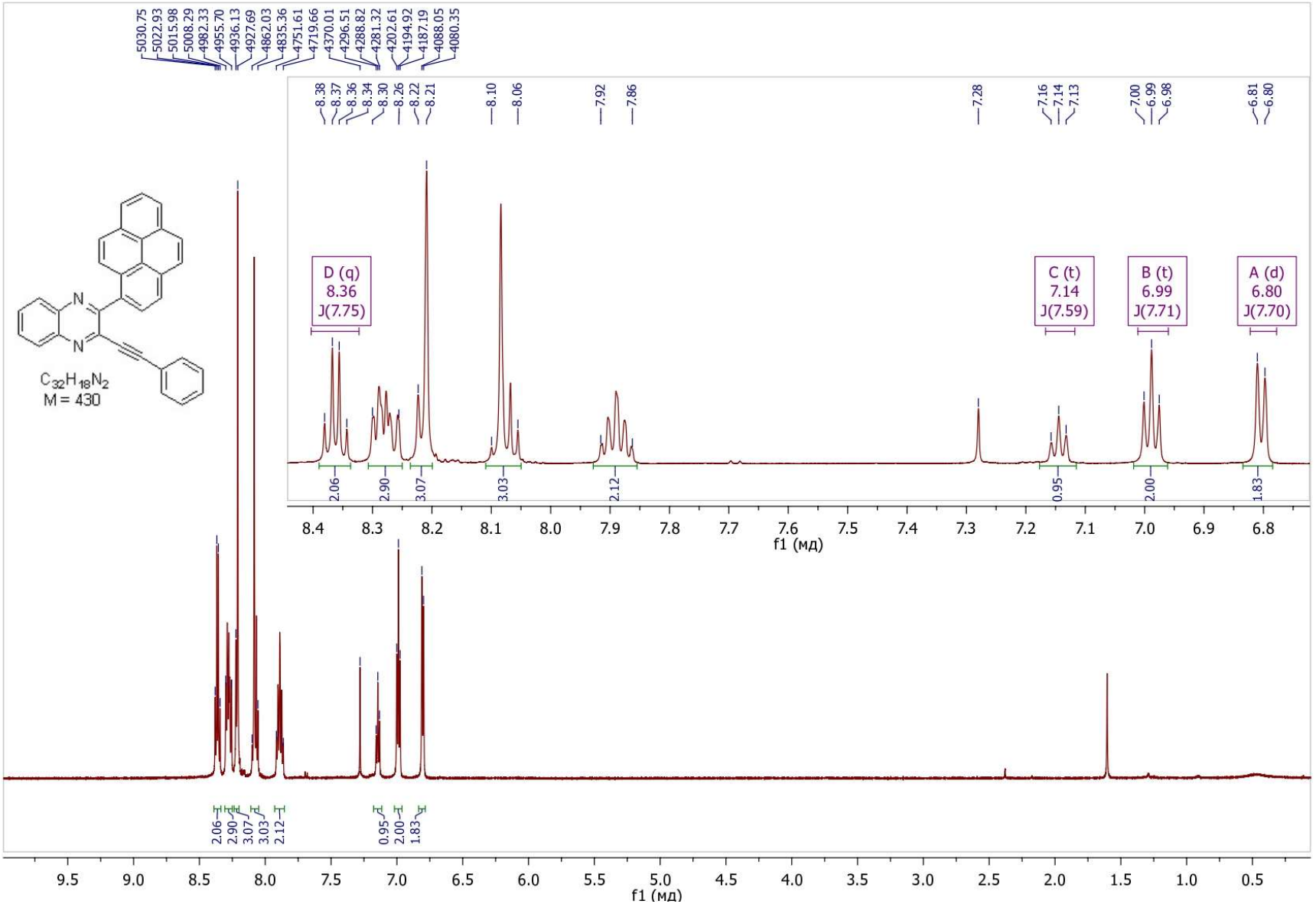


Figure S1. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 600 MHz)

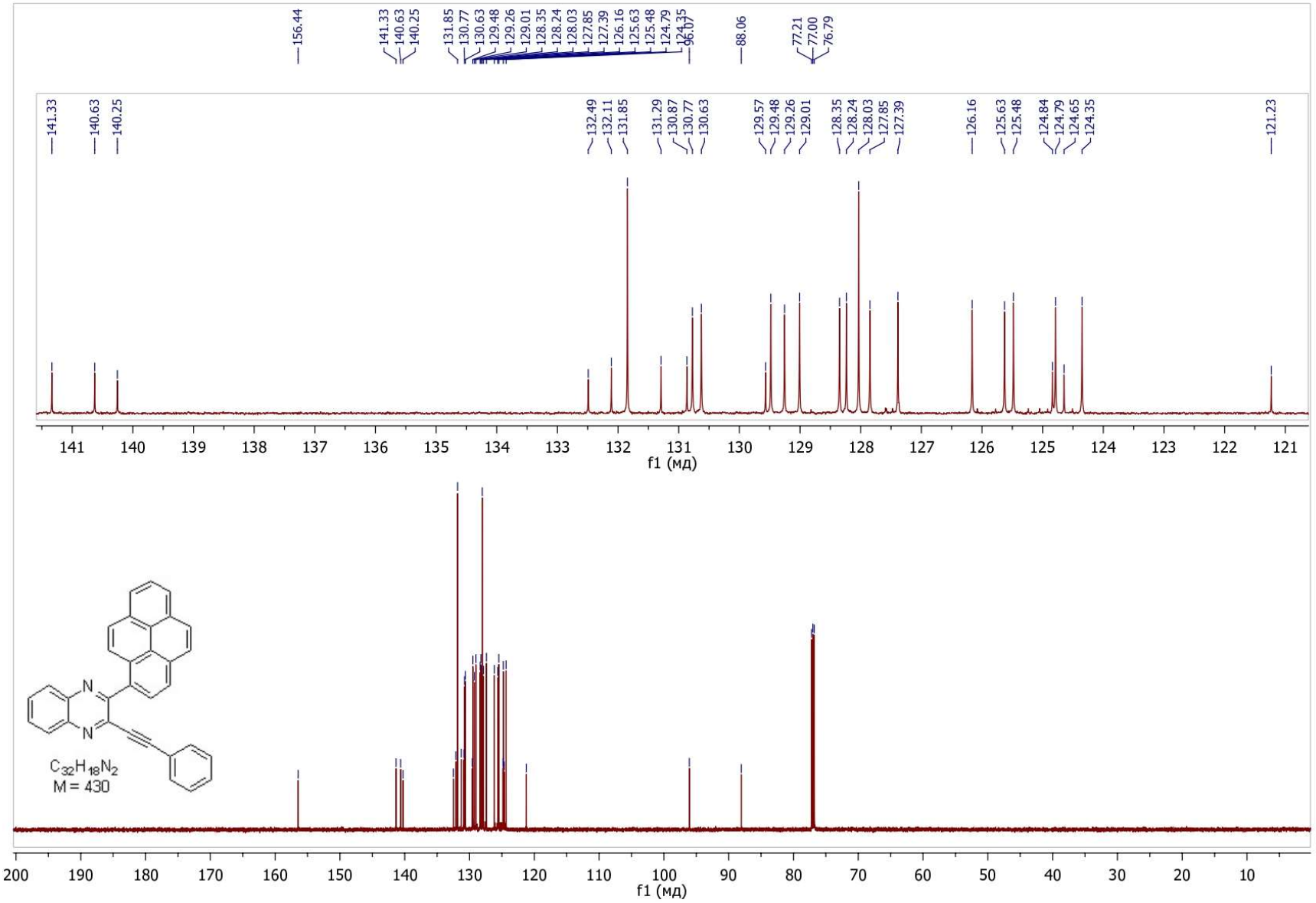


Figure S2. ^{13}C NMR spectrum of **2a** ($CDCl_3$, 150 MHz)

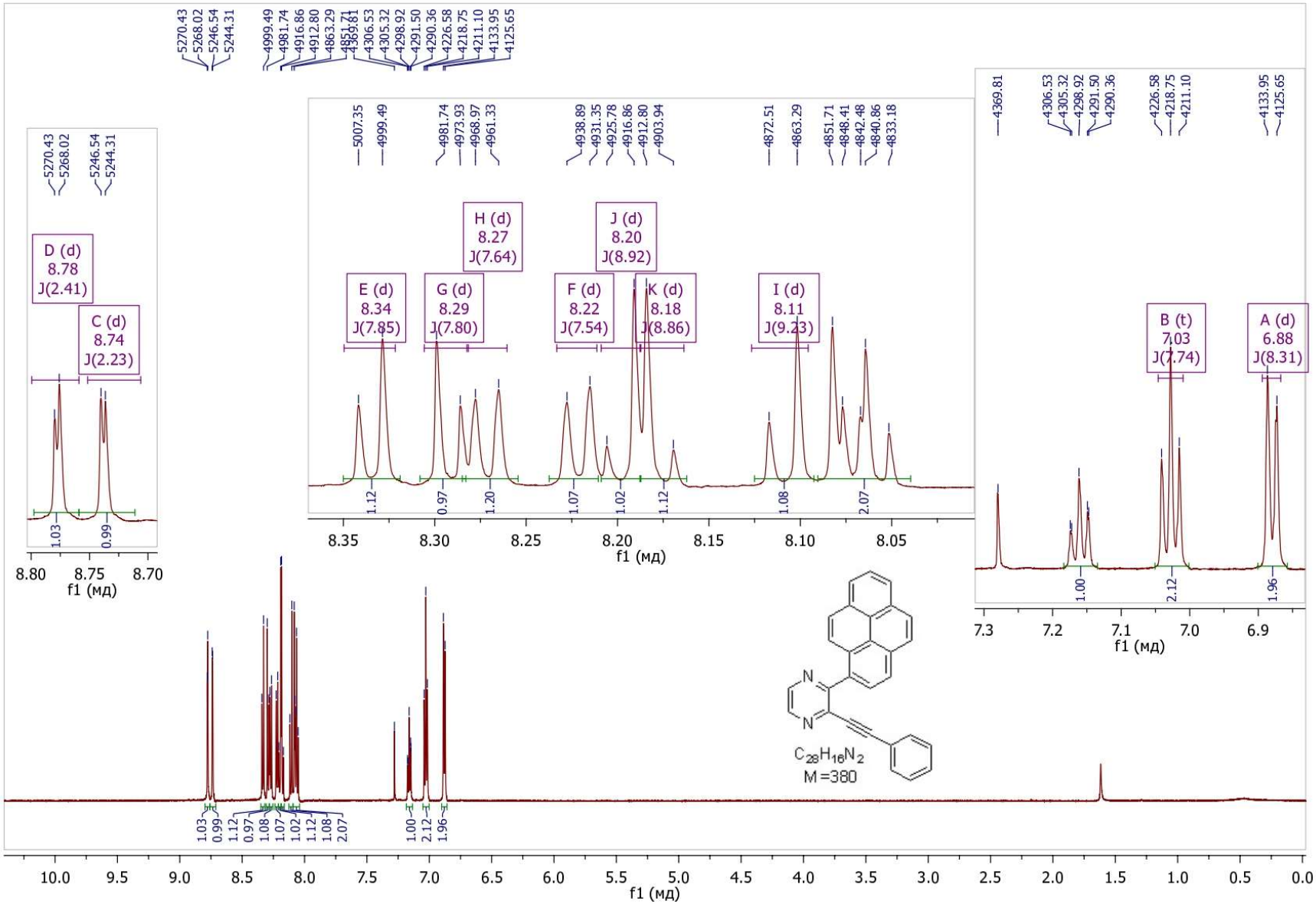


Figure S3. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 600 MHz)

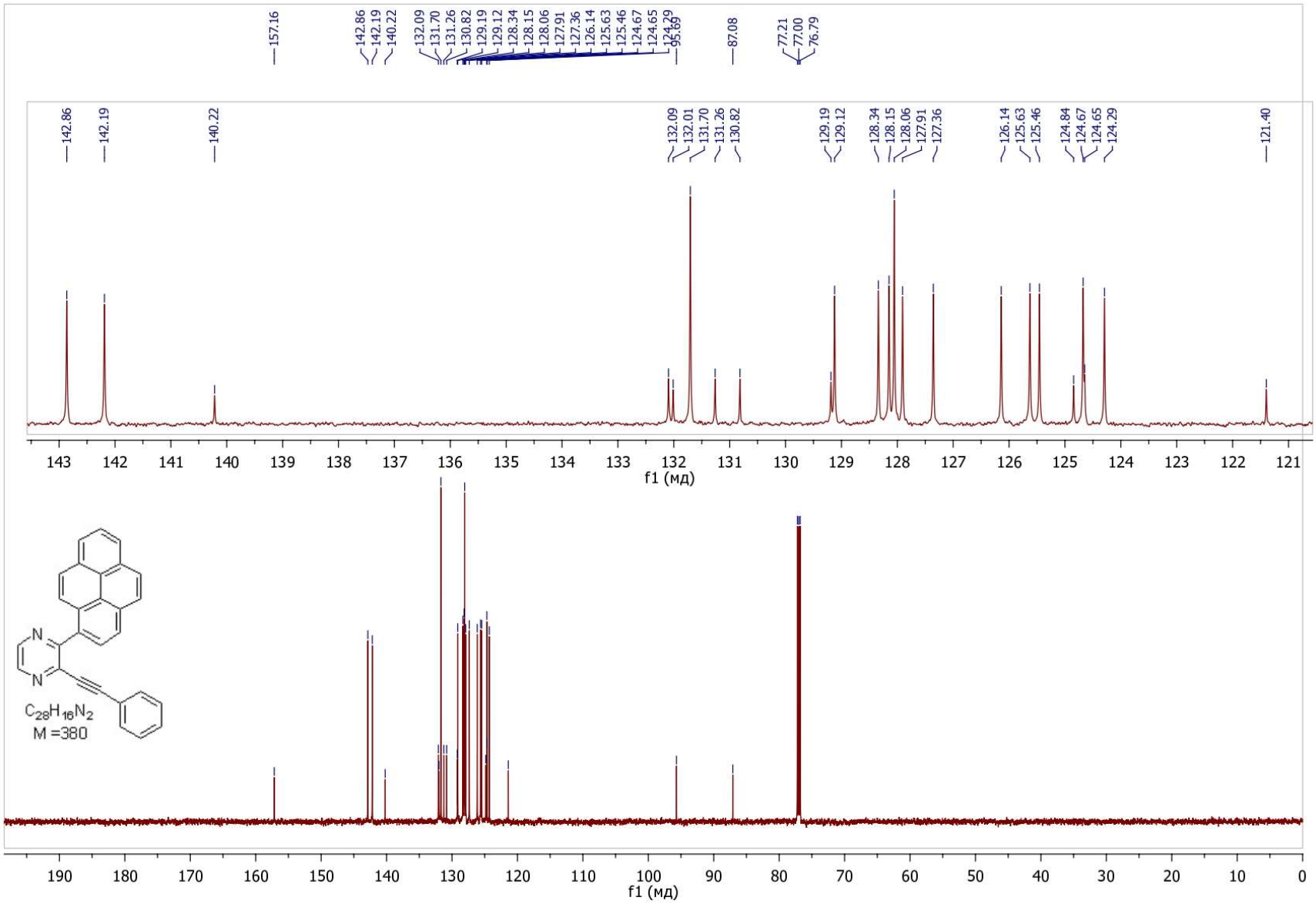


Figure S4. ^{13}C NMR spectrum of **2b** ($CDCl_3$, 150 MHz)

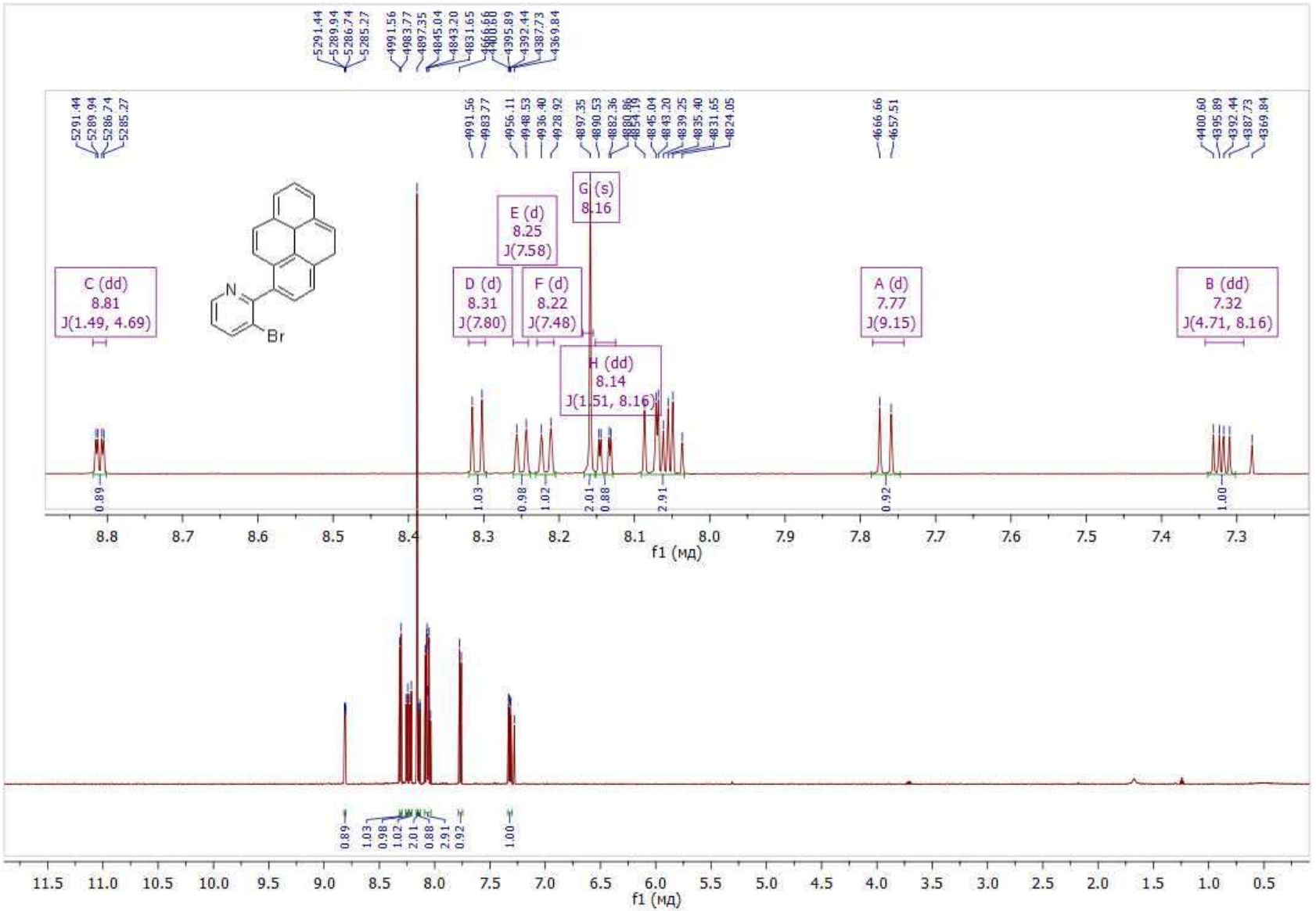


Figure S5. ^{1}H NMR spectrum of **4** ($CDCl_3$, 600 MHz)

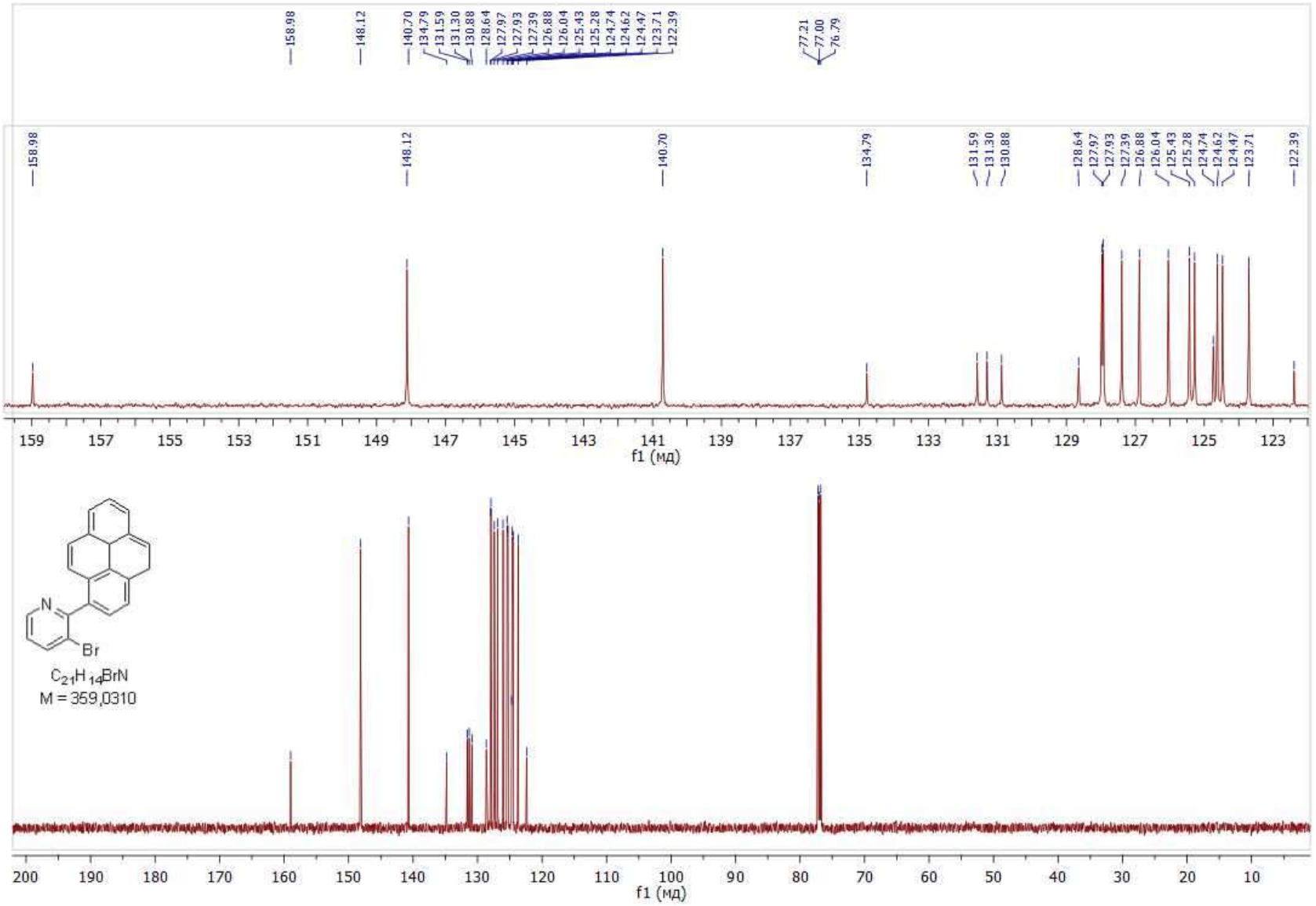


Figure S6. ^{13}C NMR spectrum of **5** ($CDCl_3$, 150 MHz)

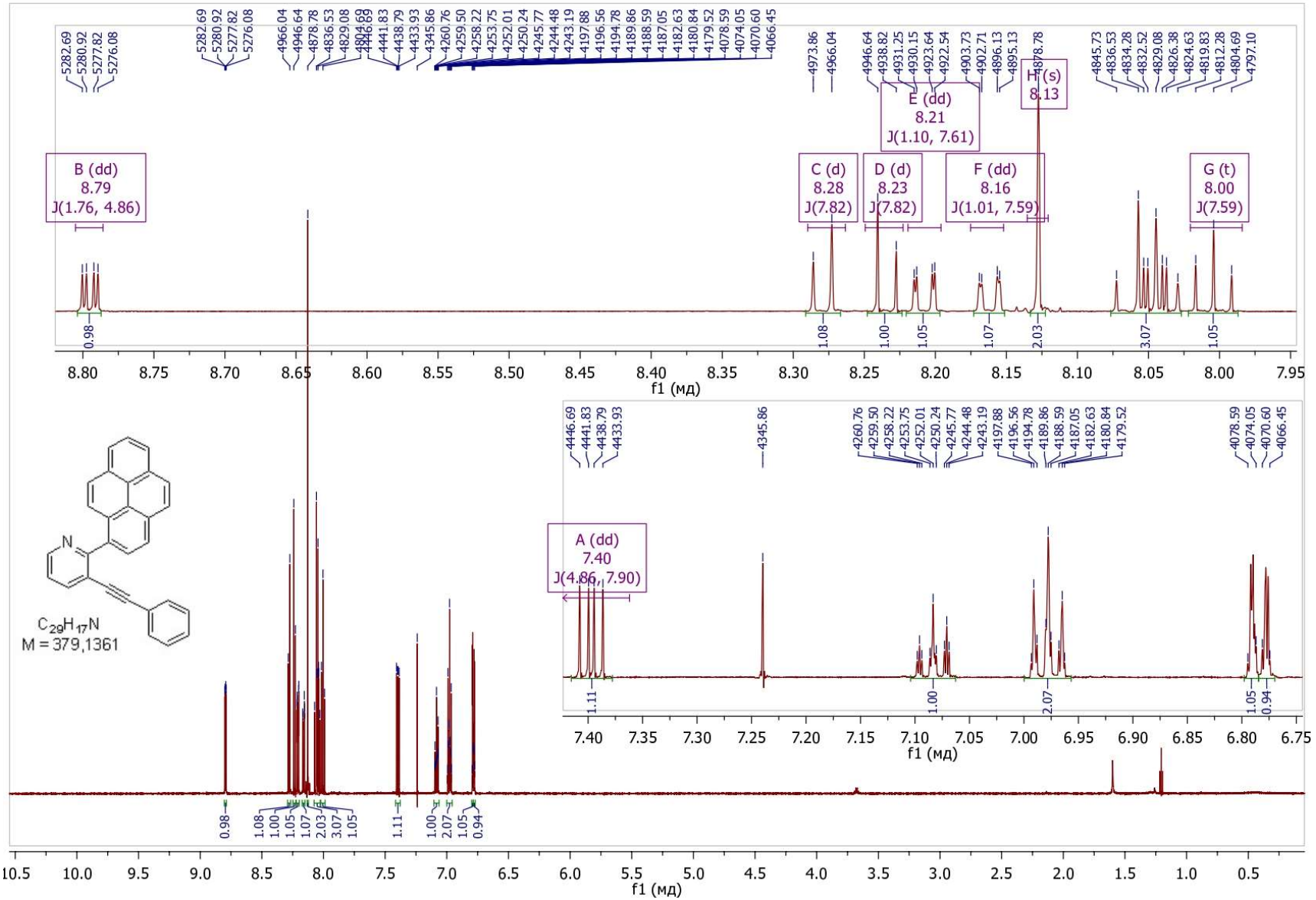


Figure S7. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 600 MHz)

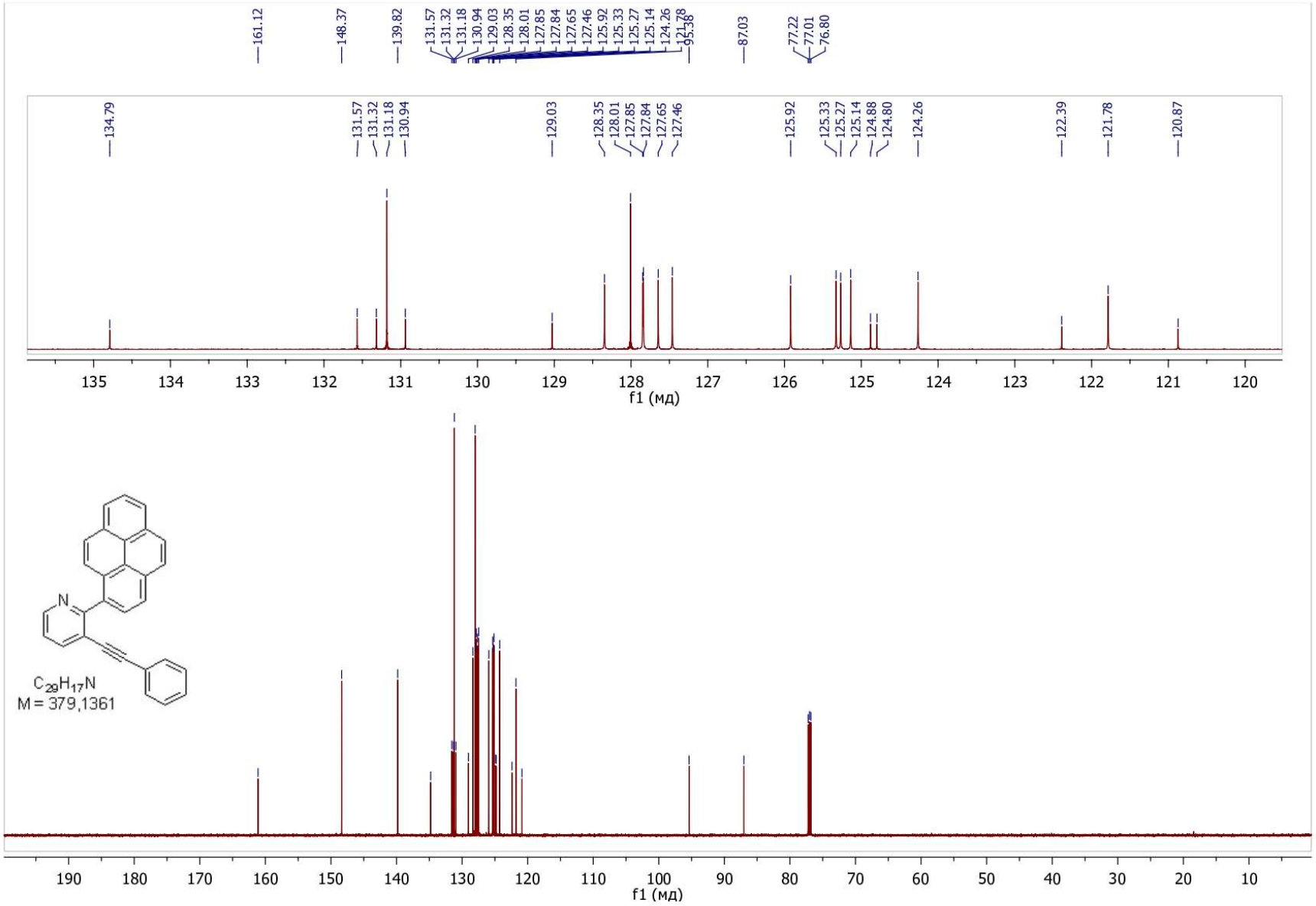


Figure S8. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 150 MHz)

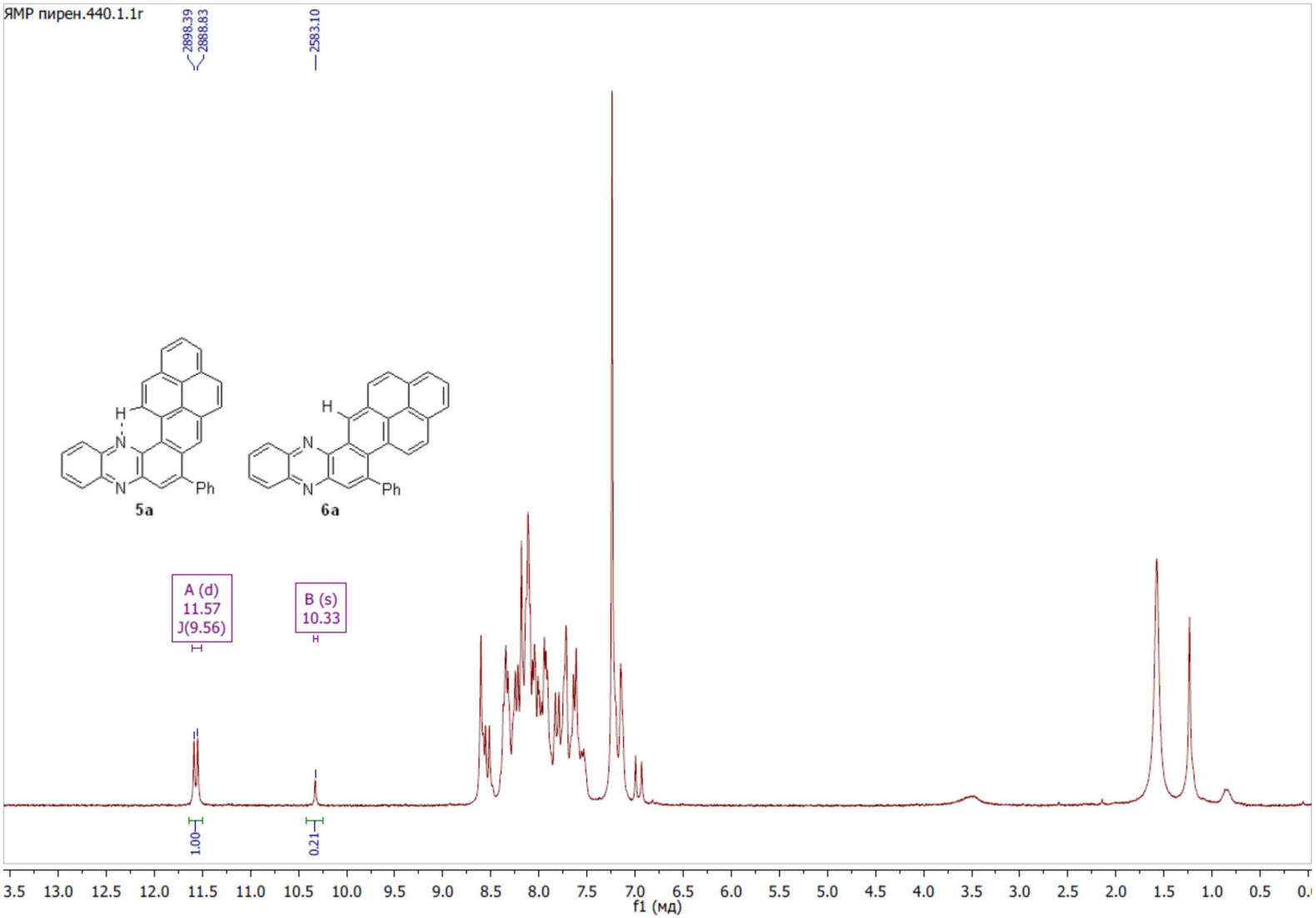


Figure S9. ^{1}H NMR spectrum of a mixture of compounds **5a** and **6a** ($CDCl_3$, 250 MHz)

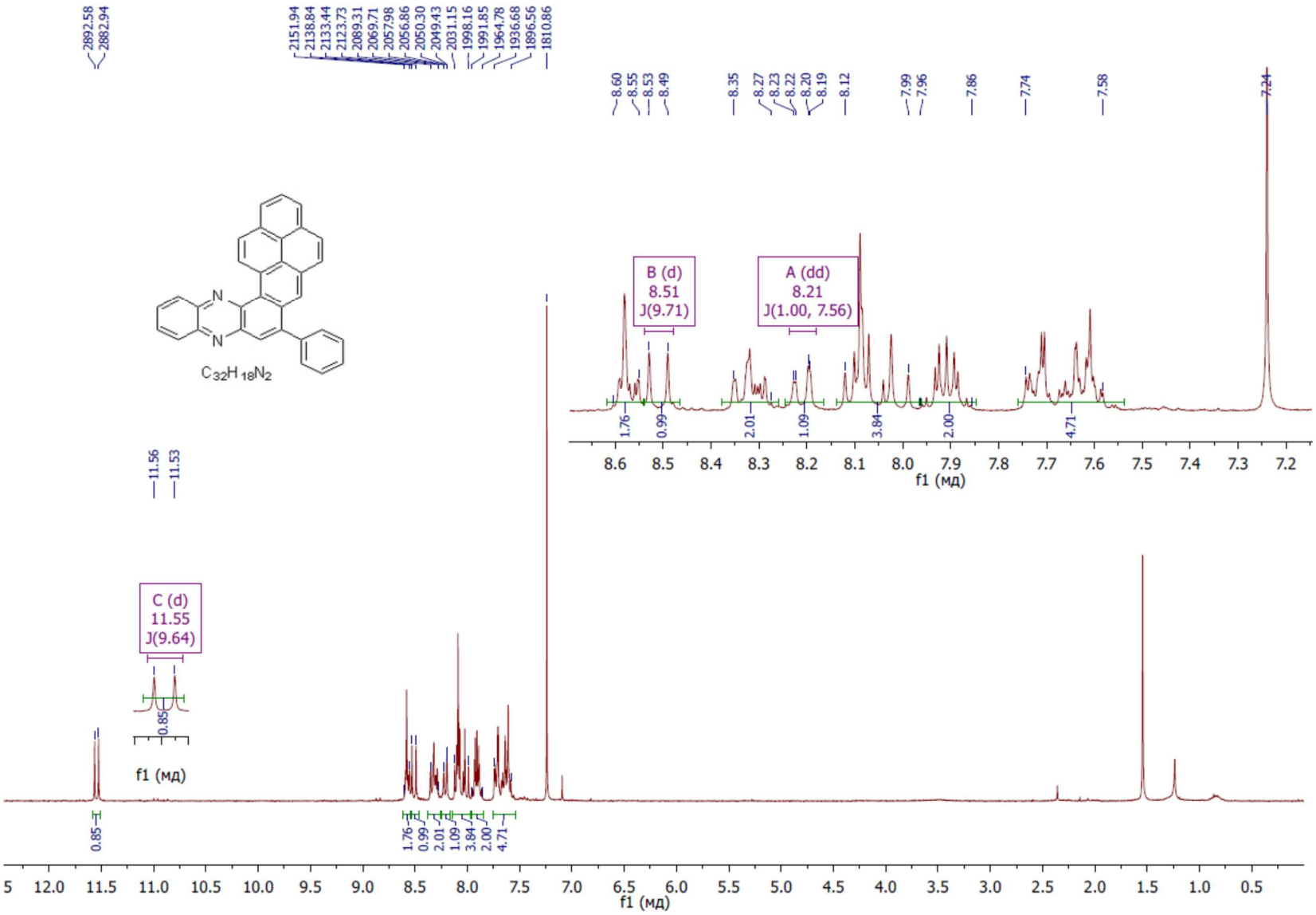


Figure S10. ^{1}H NMR spectrum of **5a** ($CDCl_3$, 250 MHz)

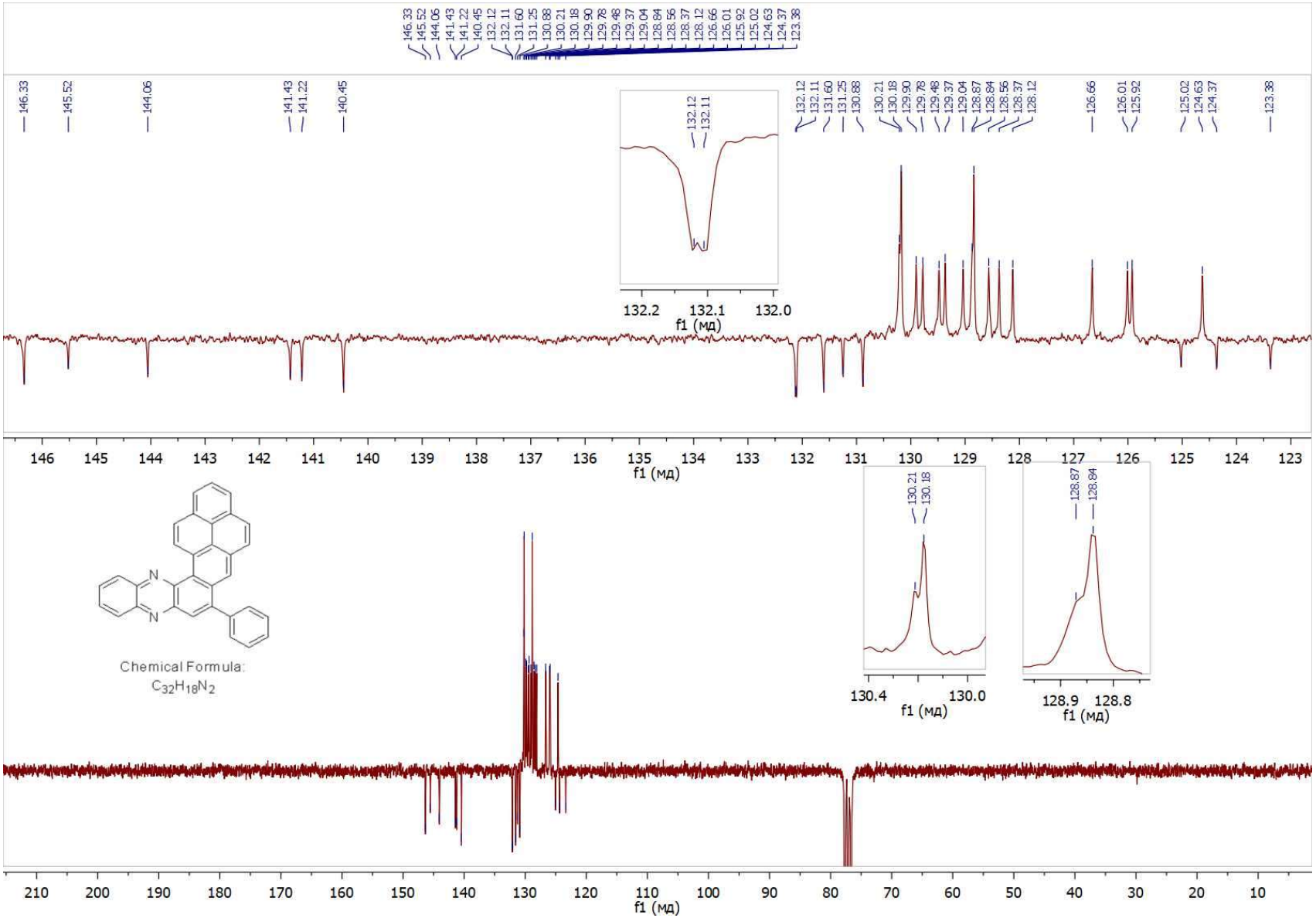


Figure S11. ^{13}C NMR APT spectrum of **5a** ($CDCl_3$, 62.9 MHz)

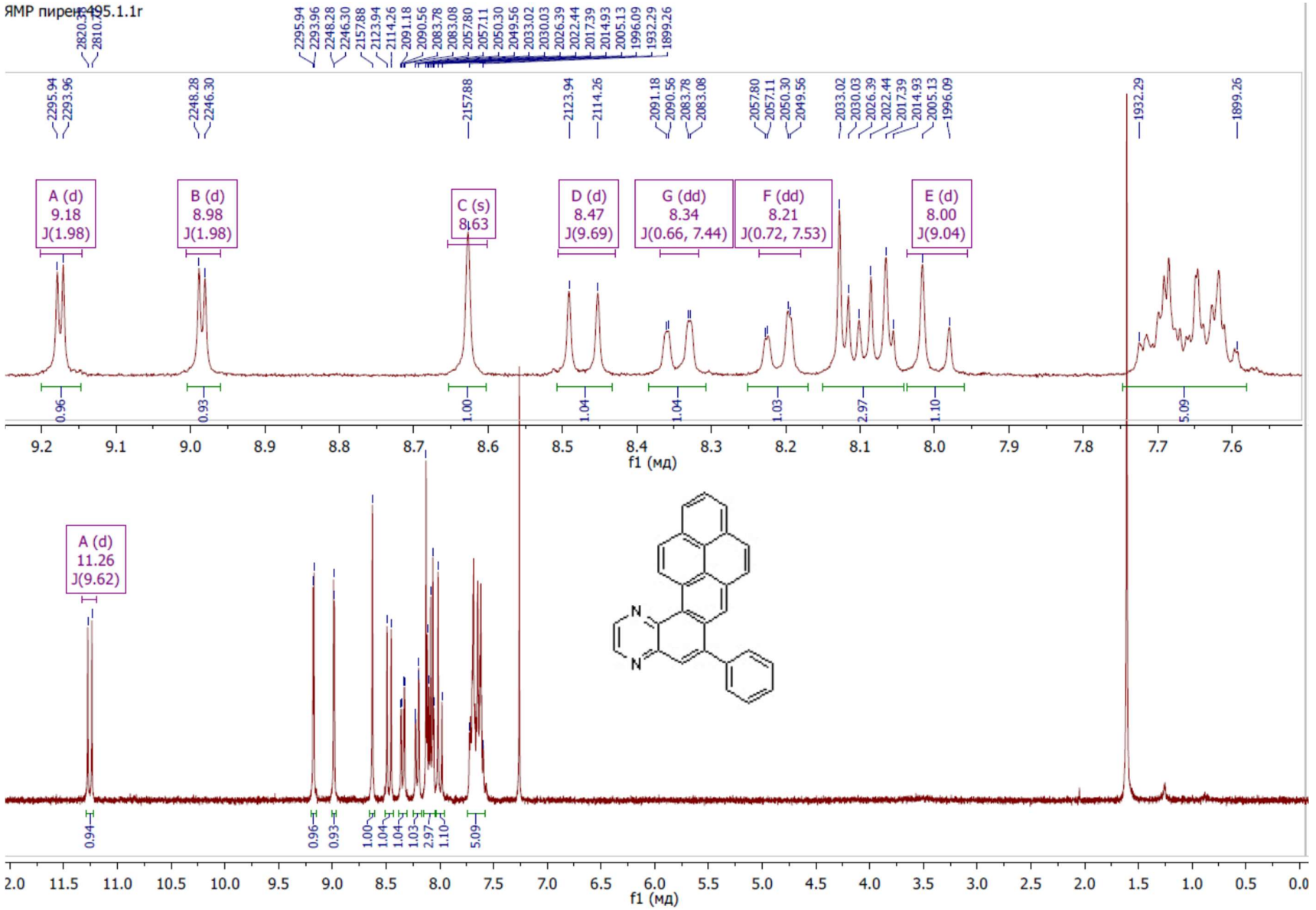


Figure S12. ^{1}H NMR spectrum of **5b** ($CDCl_3$, 250 MHz)

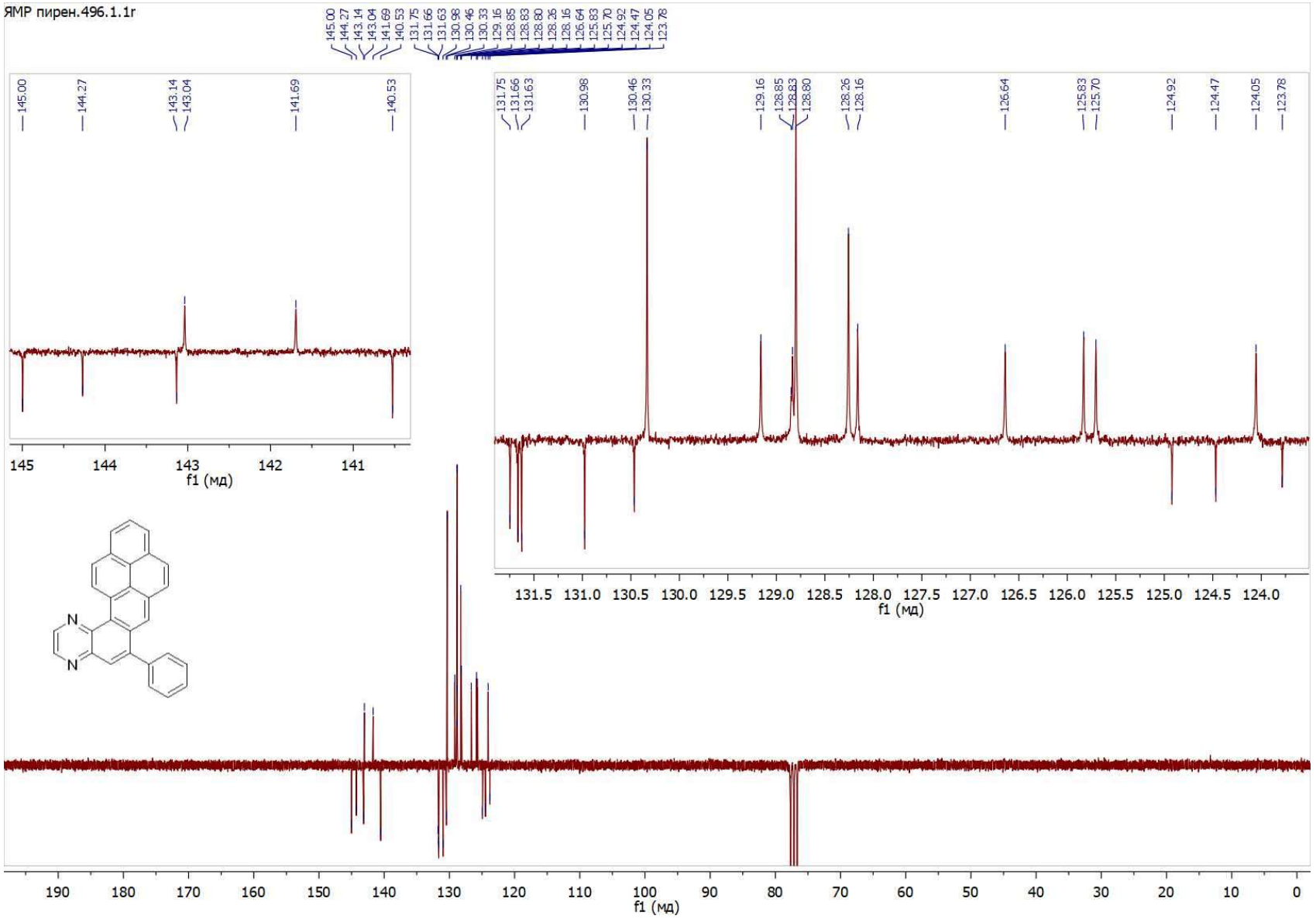


Figure S13. ^{13}C NMR APT spectrum of **5b** ($CDCl_3$, 62.9 MHz)

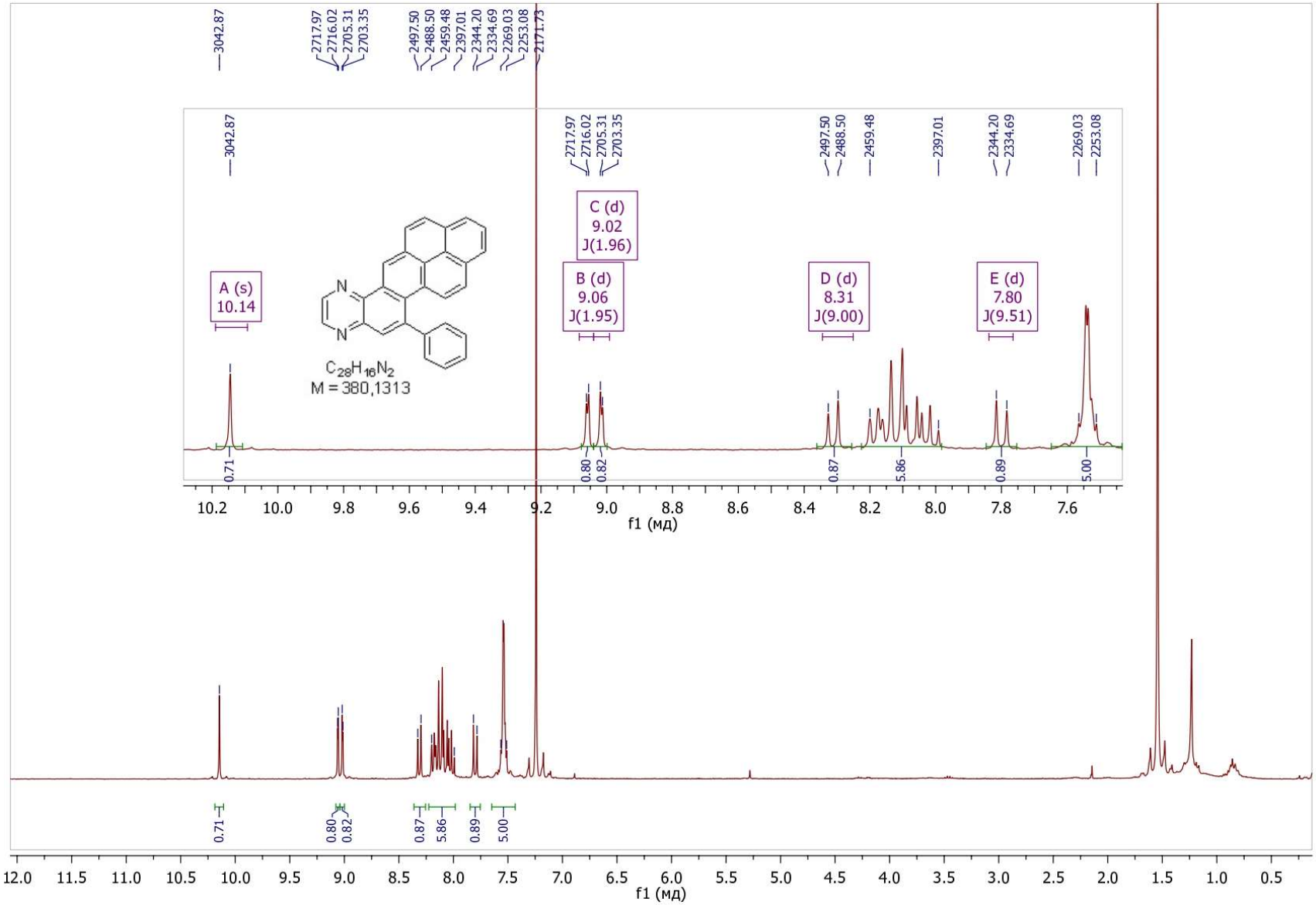


Figure S14. ^{1}H NMR spectrum of **6b** ($CDCl_3$, 300 MHz)

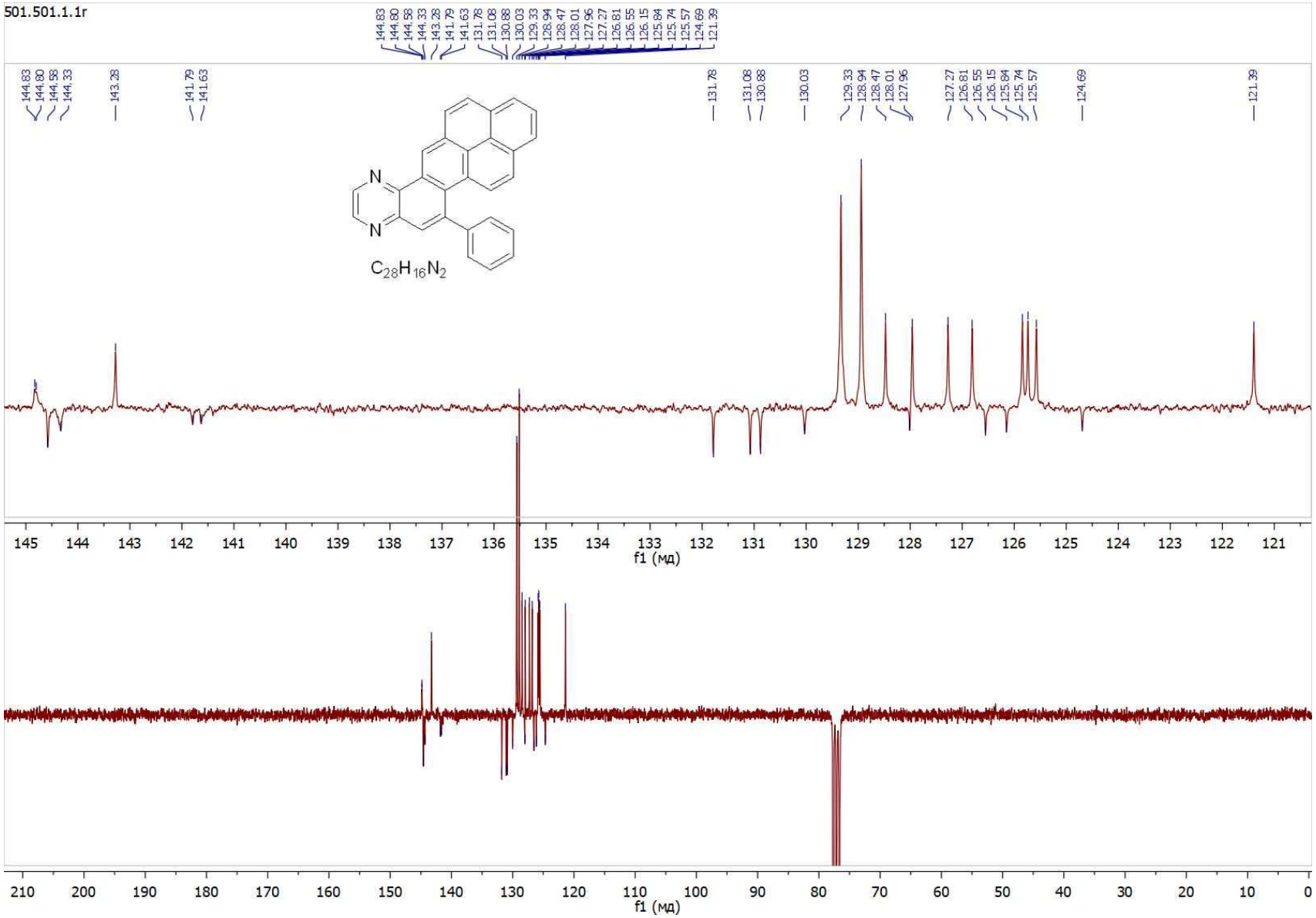


Figure S15. ^{13}C NMR APT spectrum of **6b** ($CDCl_3$, 62.9 MHz)

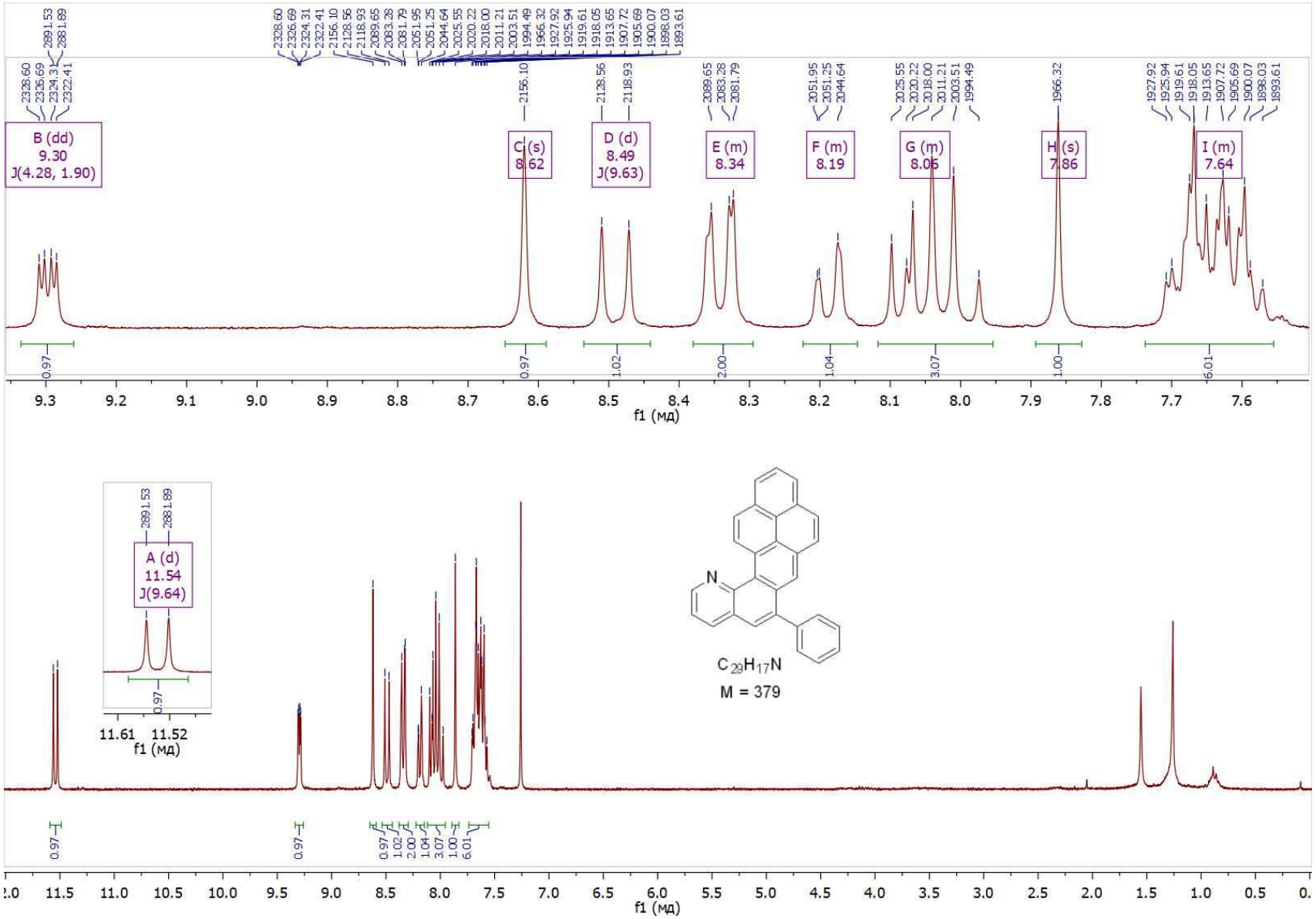


Figure S16. ^{1}H NMR spectrum of **5c** ($CDCl_3$, 250 MHz)

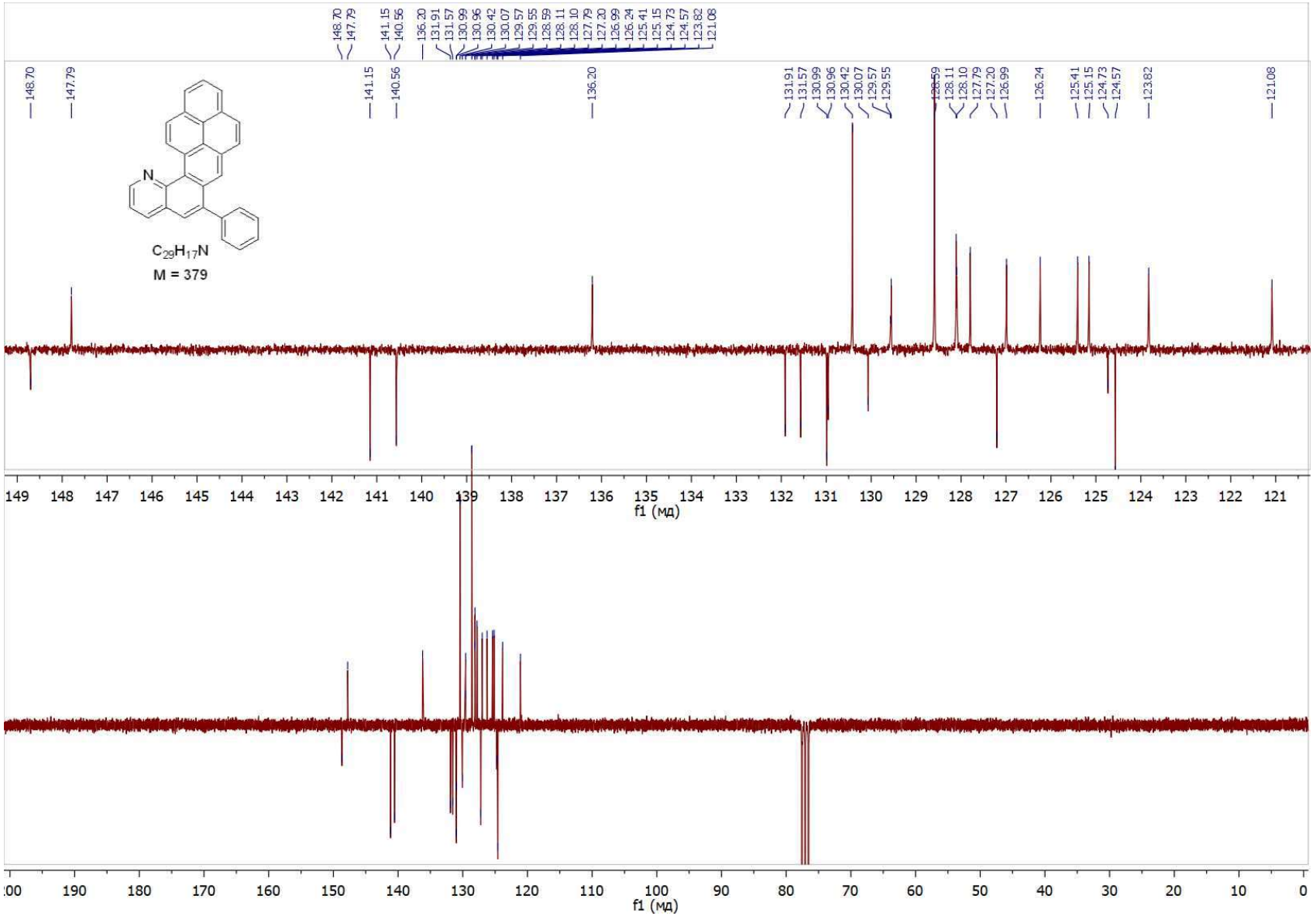


Figure S17. ^{13}C NMR APT spectrum of **5c** ($CDCl_3$, 62.9 MHz)

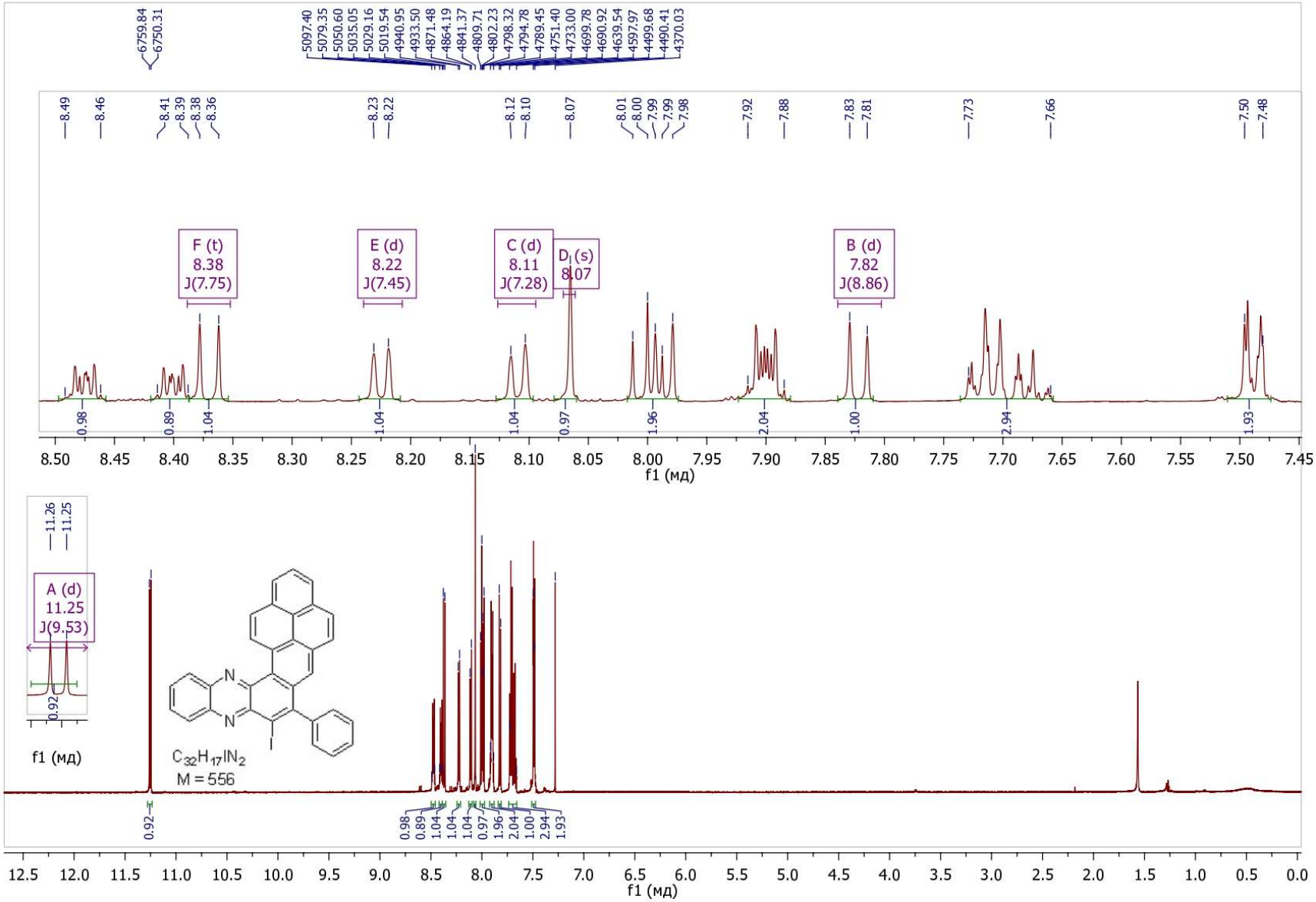


Figure S18. ^{1}H NMR spectrum of **7a** ($CDCl_3$, 600 MHz)

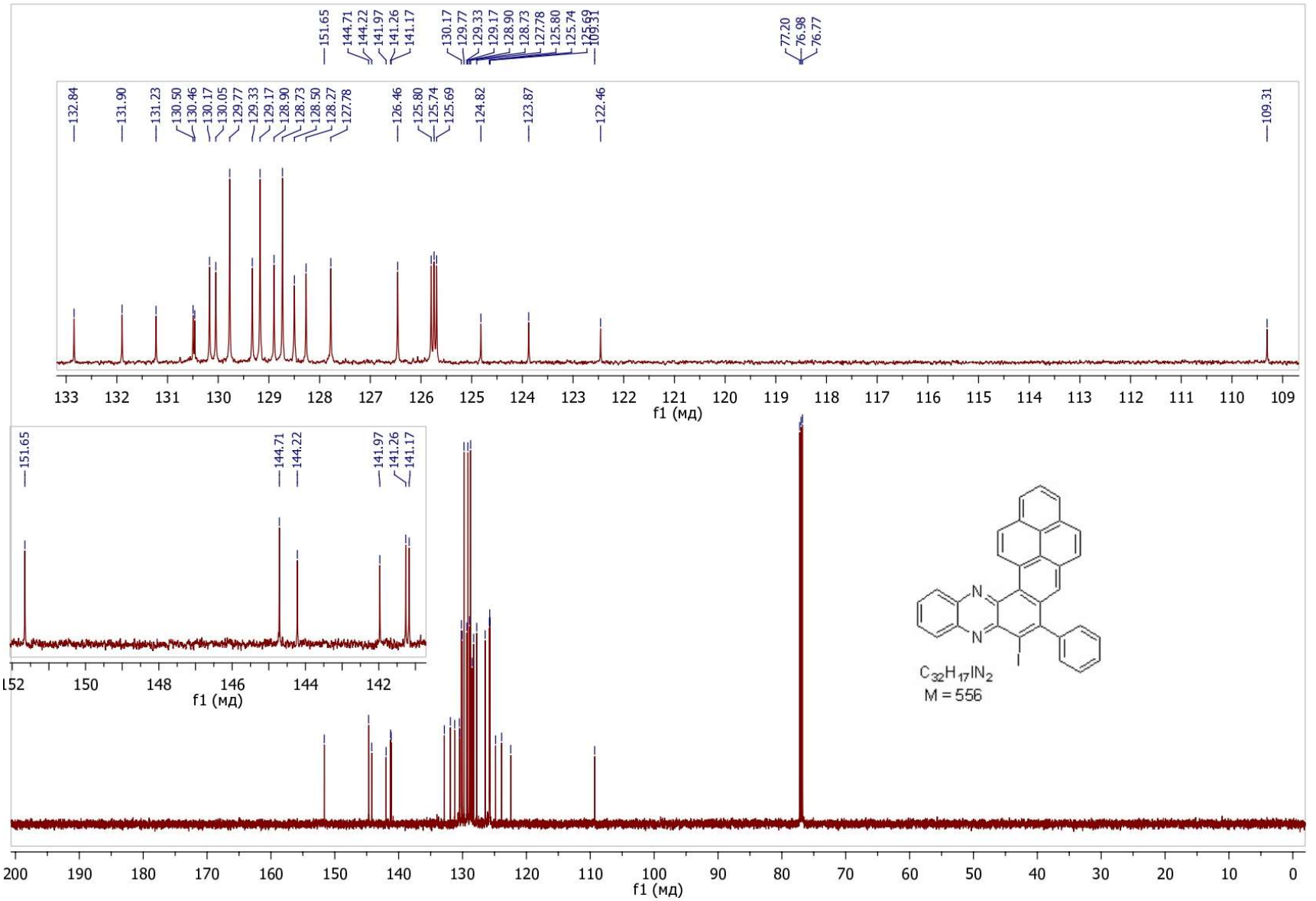


Figure S19. ^{13}C NMR spectrum of **7a** ($CDCl_3$, 150 MHz)

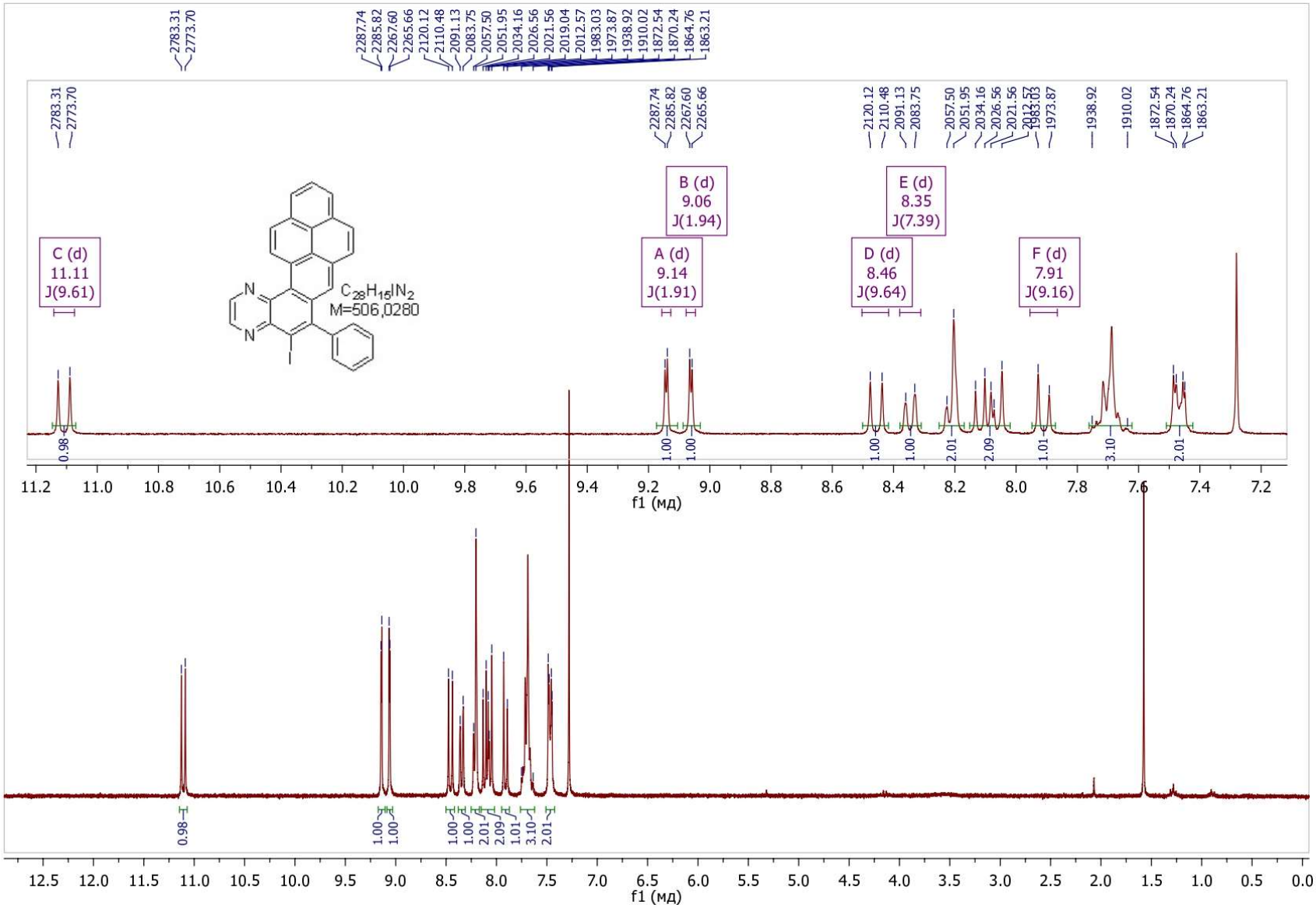


Figure S20. ^{1}H NMR spectrum of **7b** ($CDCl_3$, 250 MHz)

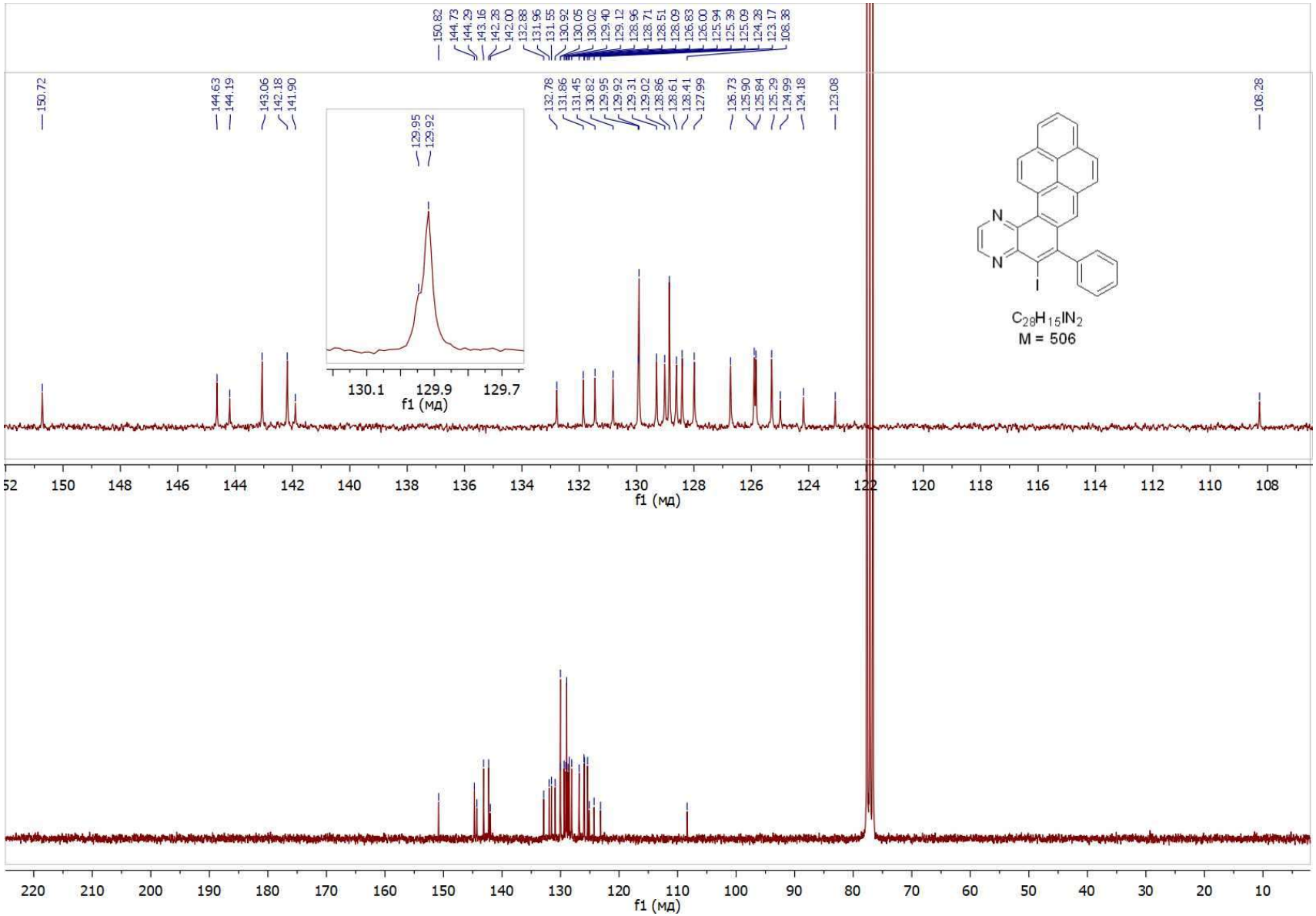


Figure S21. ^{13}C NMR spectrum of **7b** ($CDCl_3$, 62.9 MHz)

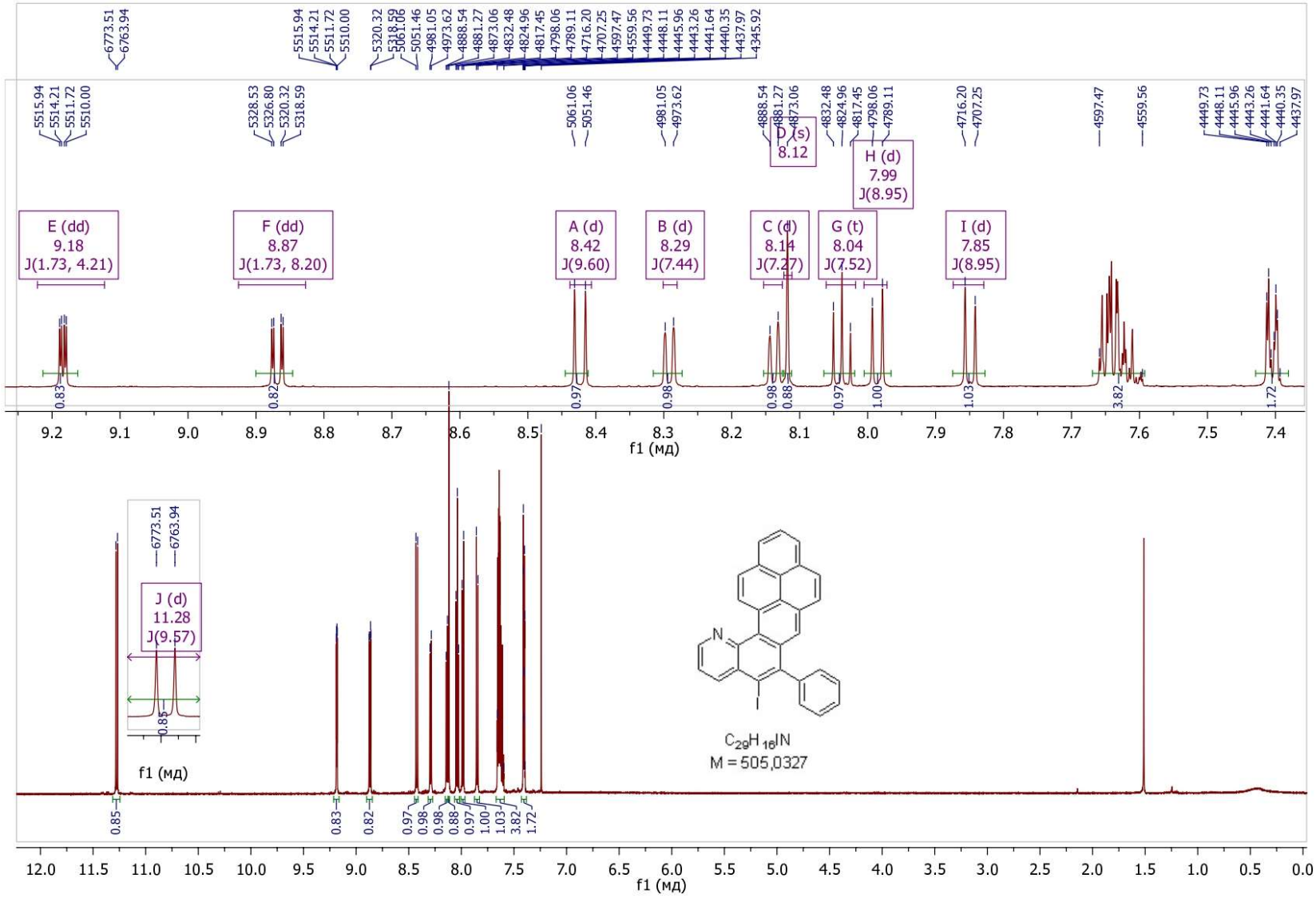


Figure S22. ^{1}H NMR spectrum of **7c** ($CDCl_3$, 600 MHz)

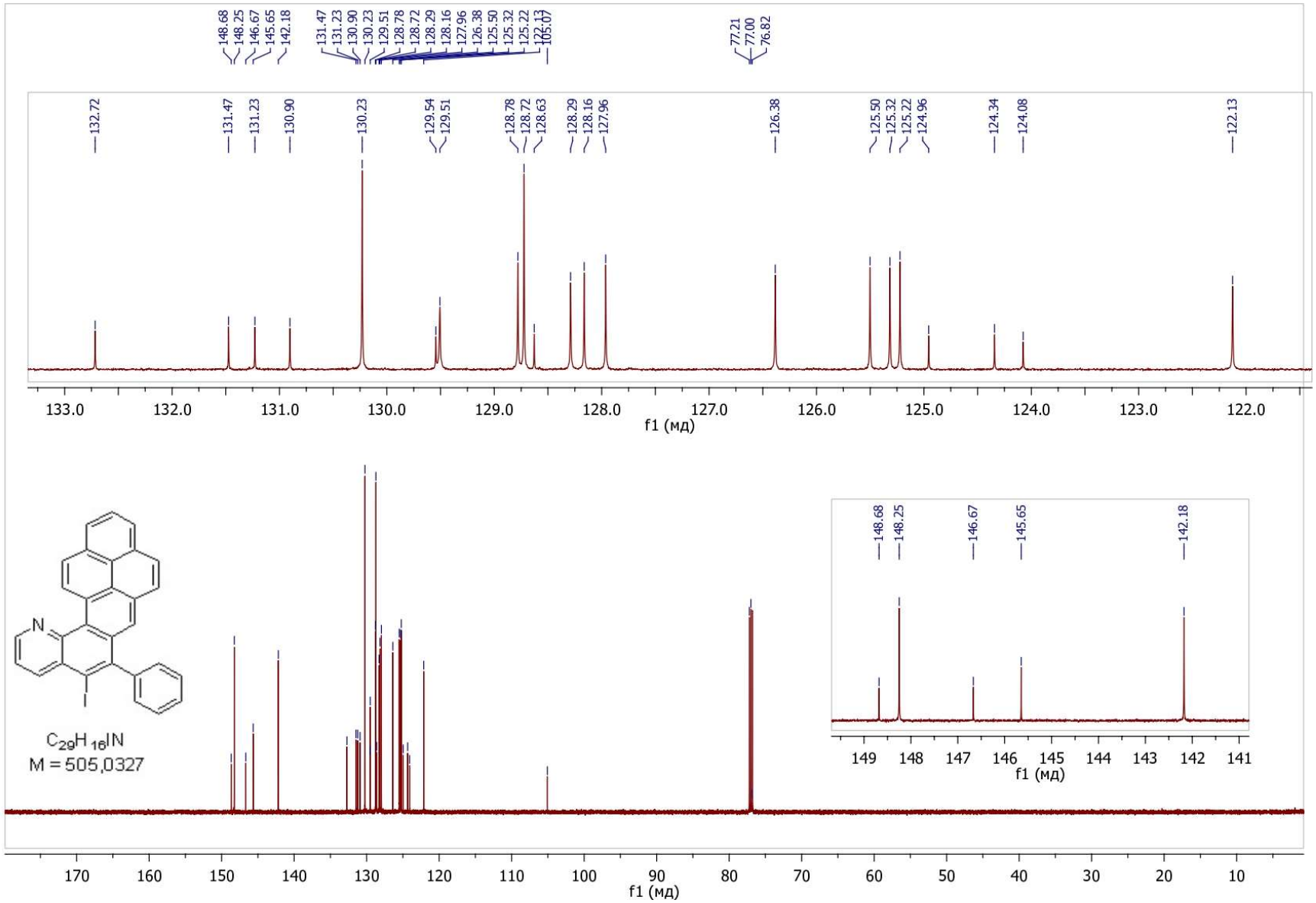


Figure S23. ^{13}C NMR spectrum of **7c** ($CDCl_3$, 150 MHz)

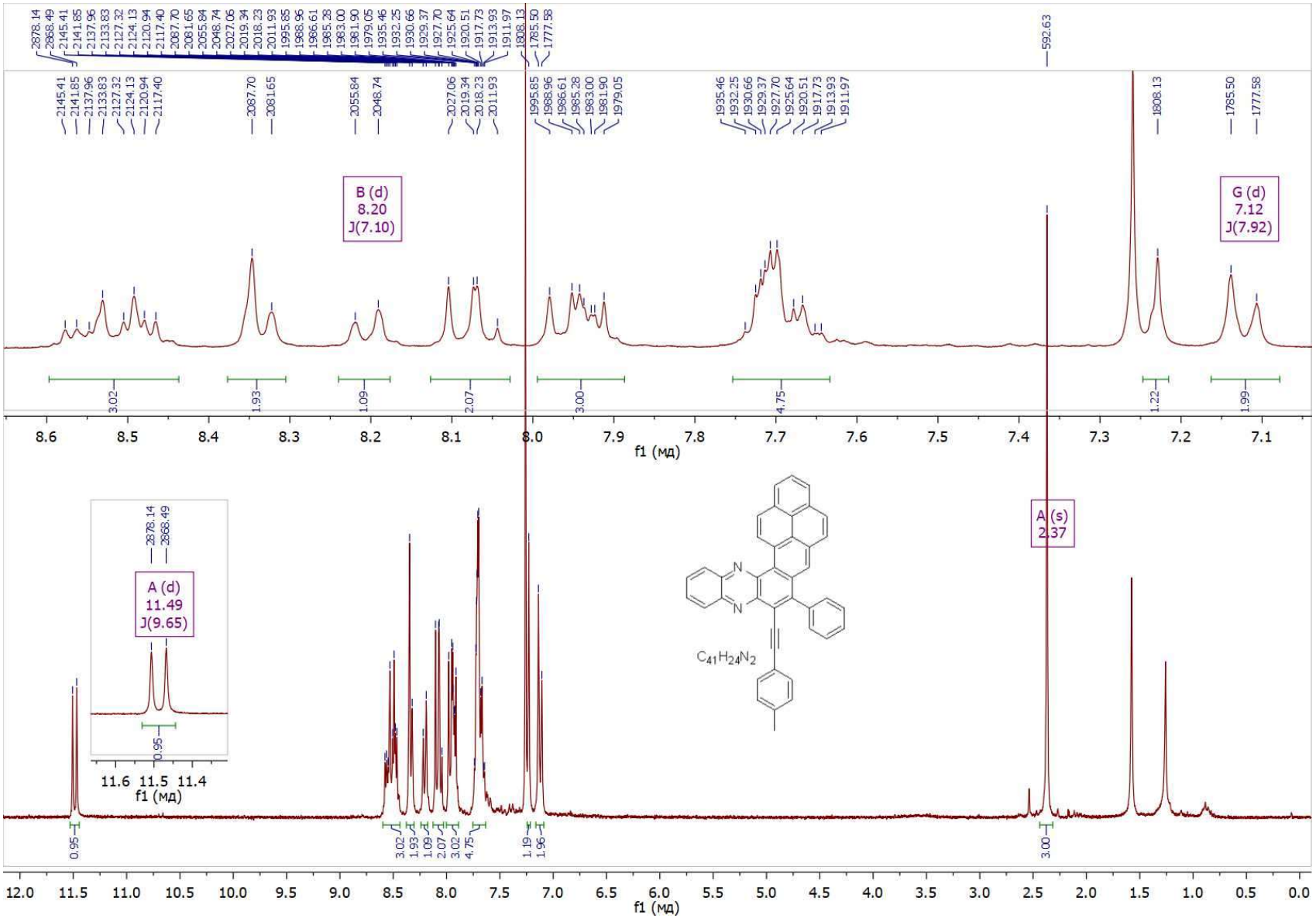


Figure S24. ^{1}H NMR spectrum of **8a** ($CDCl_3$, 250 MHz)

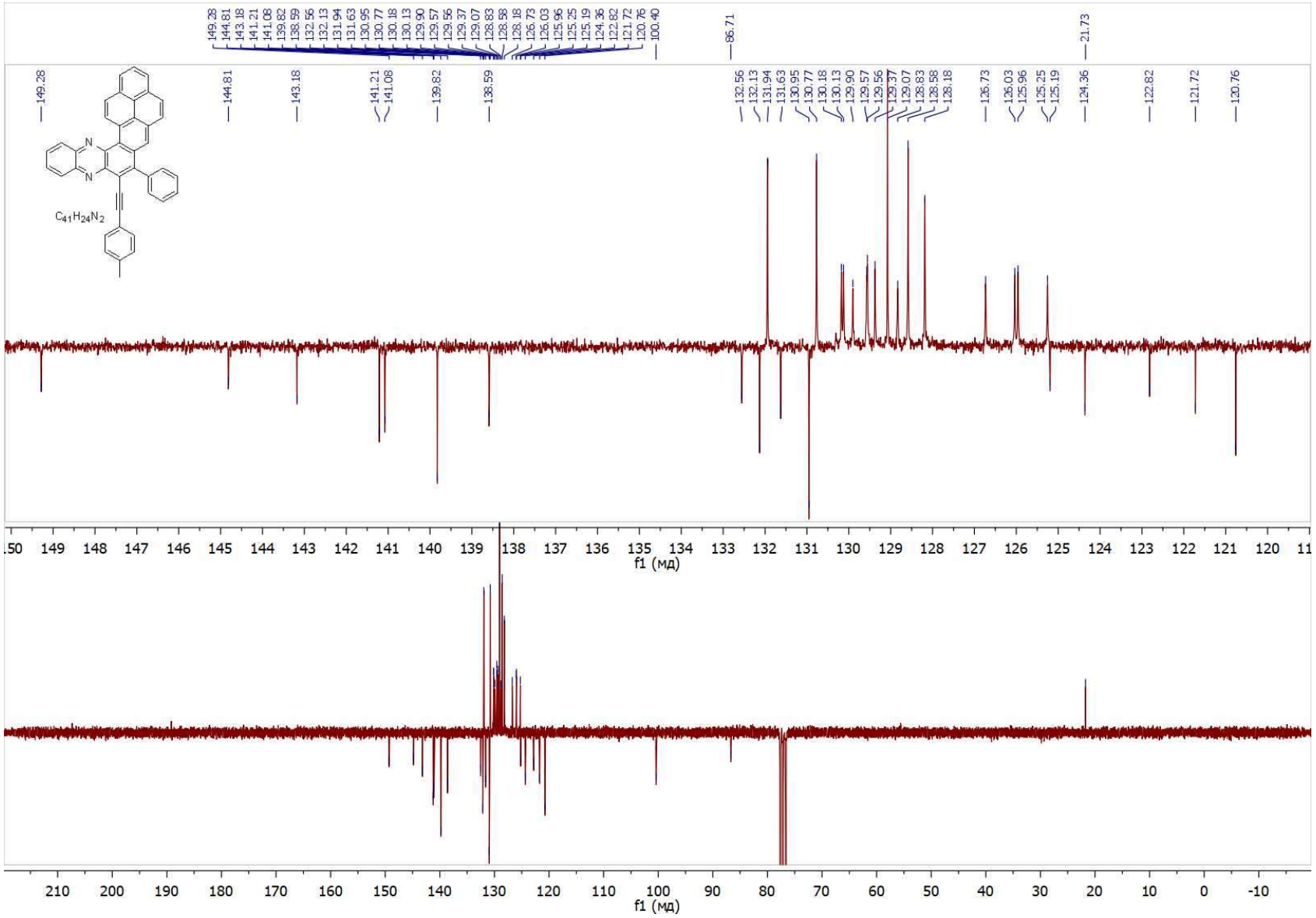


Figure S25. ^{13}C NMR APT spectrum of **8a** ($CDCl_3$, 62.9 MHz)

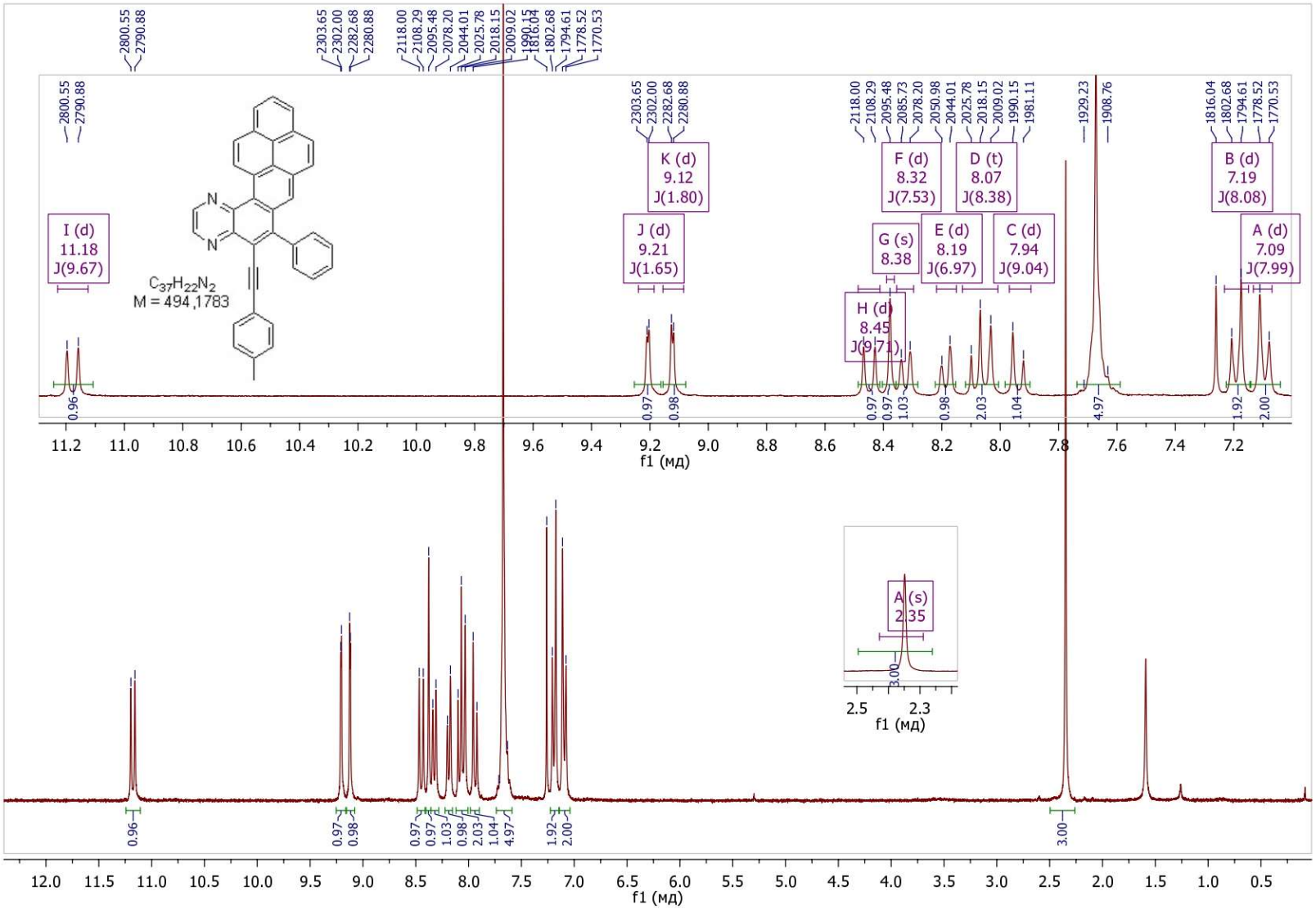


Figure S26. ^{1}H NMR spectrum of **8b** ($CDCl_3$, 250 MHz)

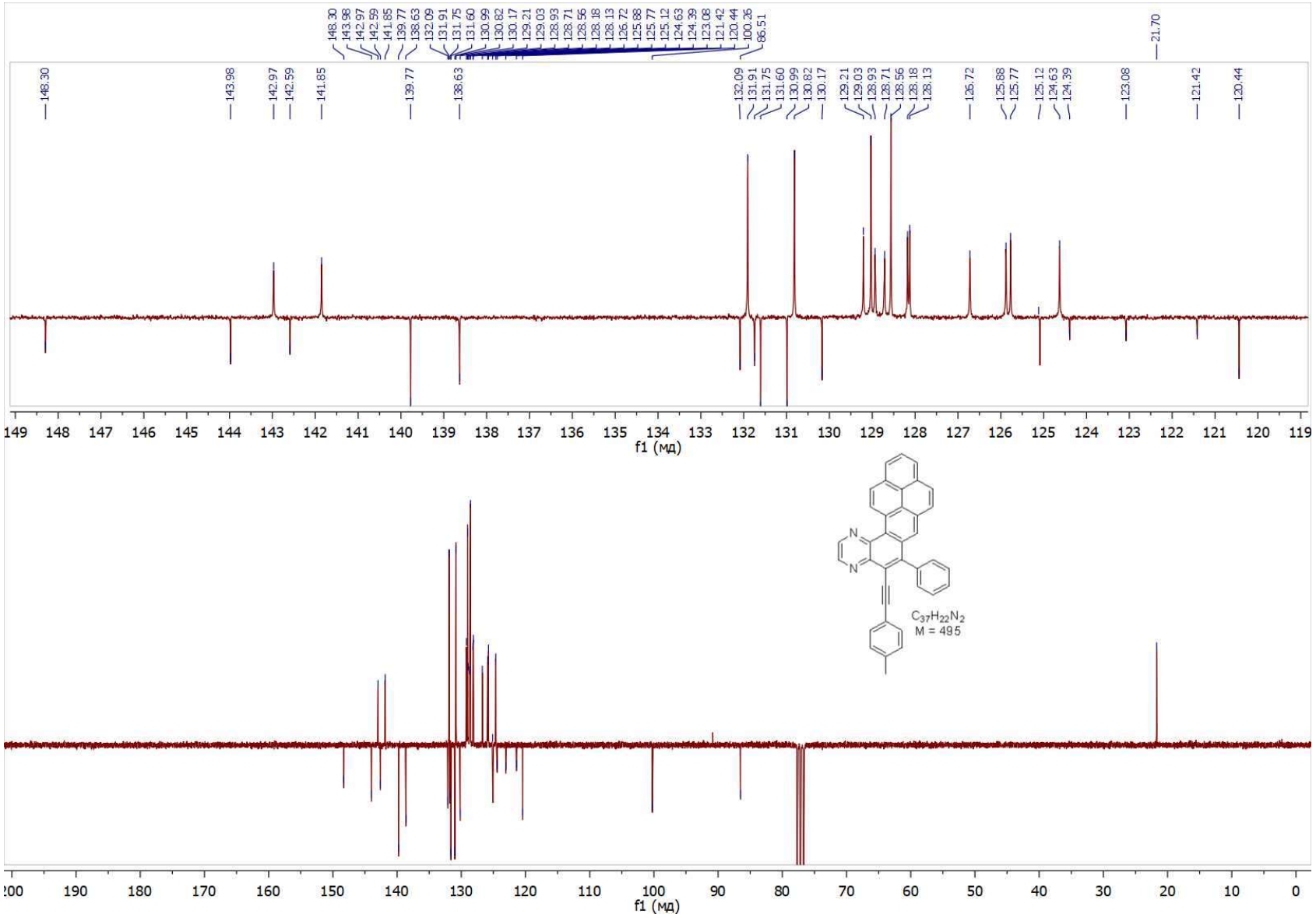


Figure S27. ^{13}C NMR APT spectrum of **8b** ($CDCl_3$, 62.9 MHz)

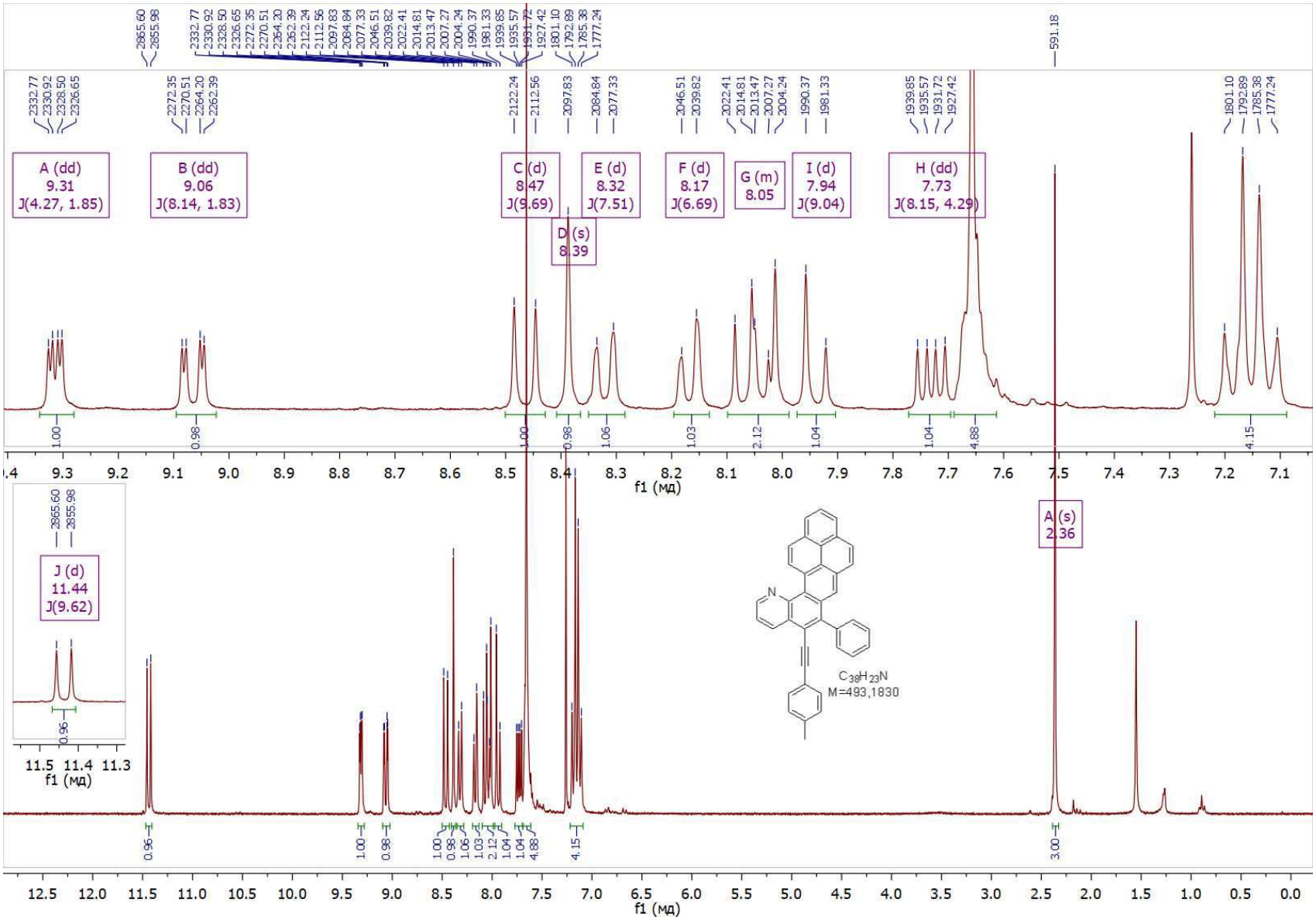


Figure S28. ^{1}H NMR spectrum of **8c** ($CDCl_3$, 250 MHz)

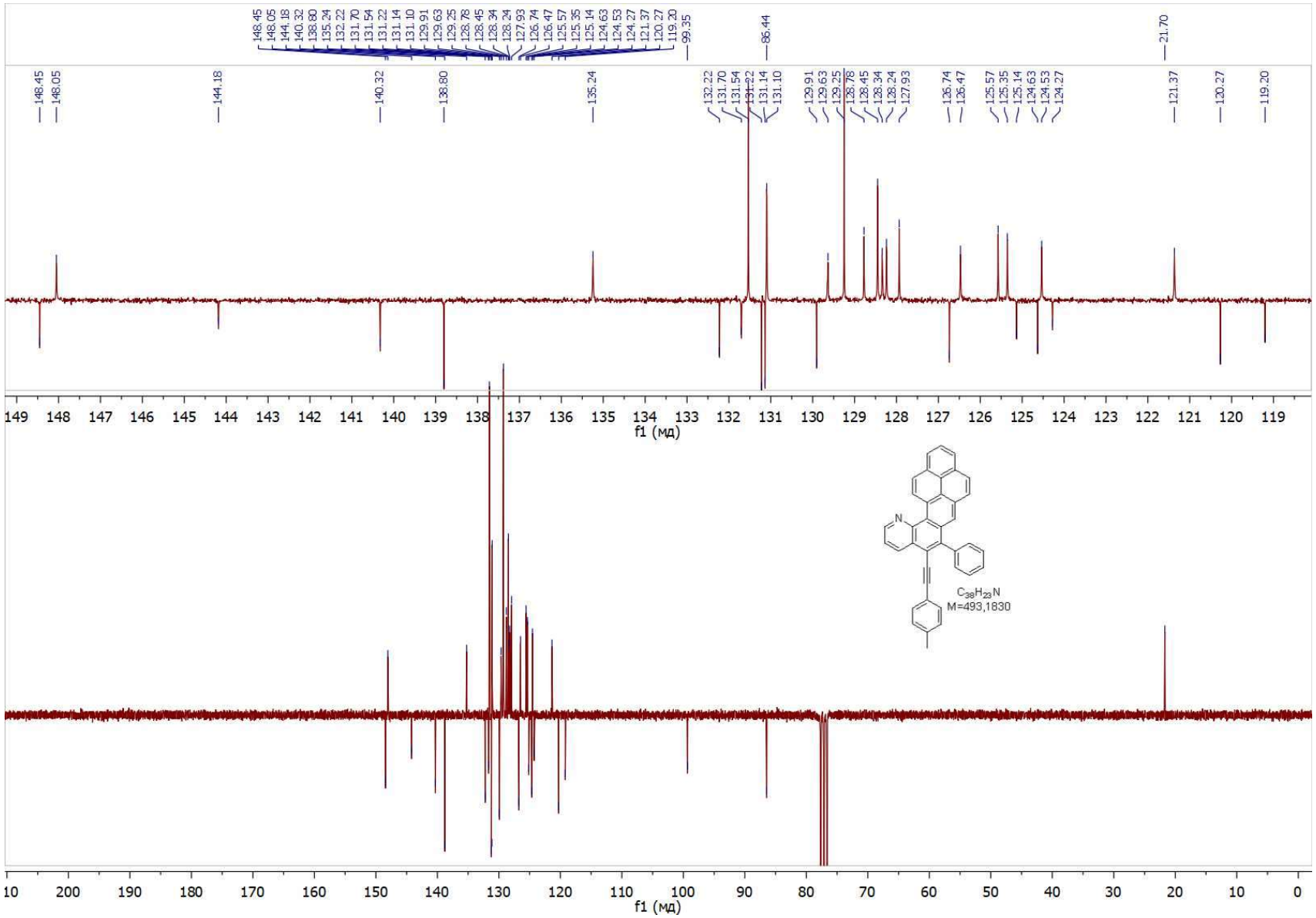


Figure S29. ^{13}C NMR APT spectrum of **8c** ($CDCl_3$, 62.9 MHz)

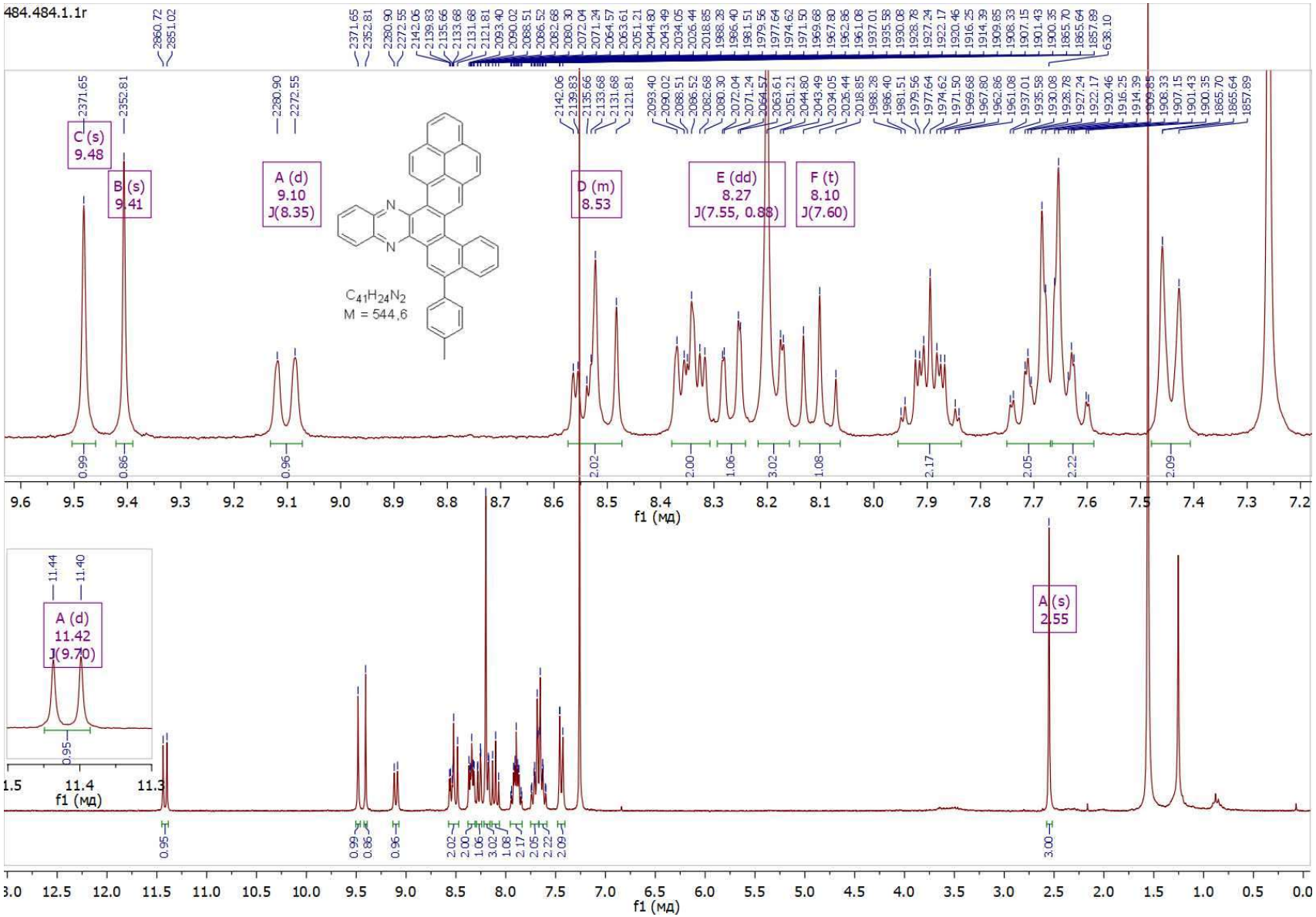


Figure S30. ^{1}H NMR spectrum of **9a** ($CDCl_3$, 250 MHz)

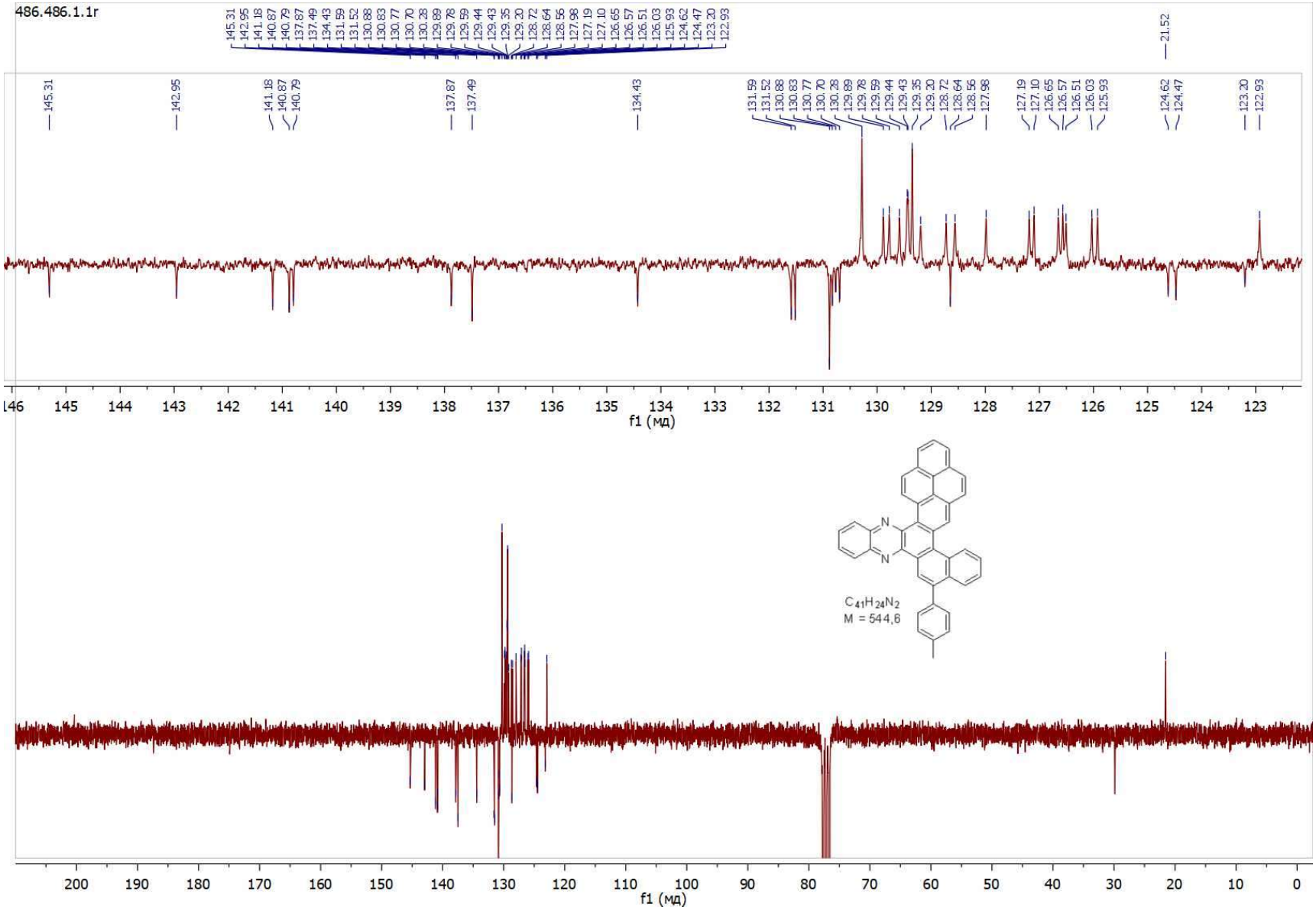


Figure S31. ^{13}C NMR APT spectrum of **9a** ($CDCl_3$, 62.9 MHz)

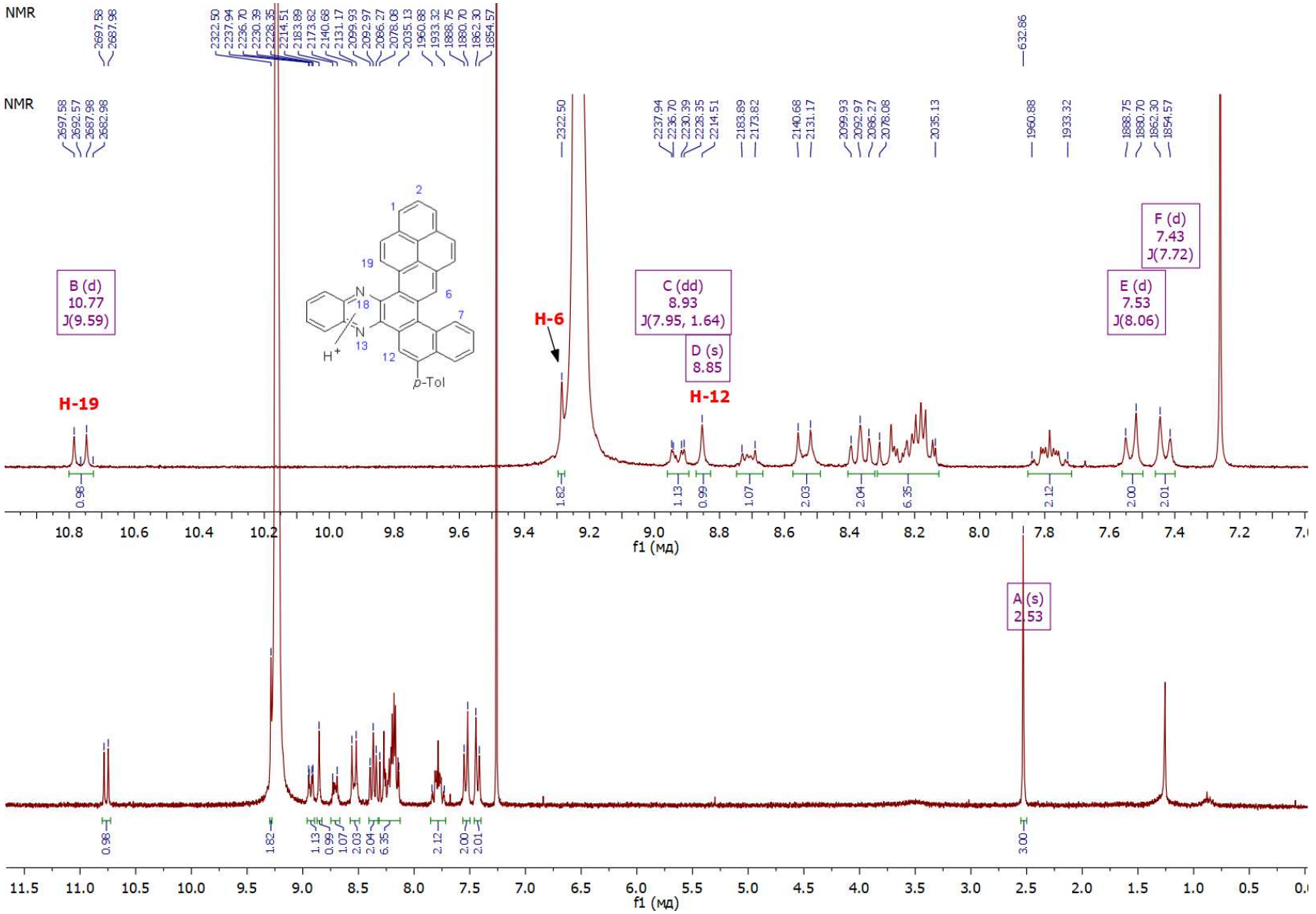


Figure S32. ^{1}H NMR spectrum of **9a** ($CDCl_3$, CF_3COOH, 250 MHz)

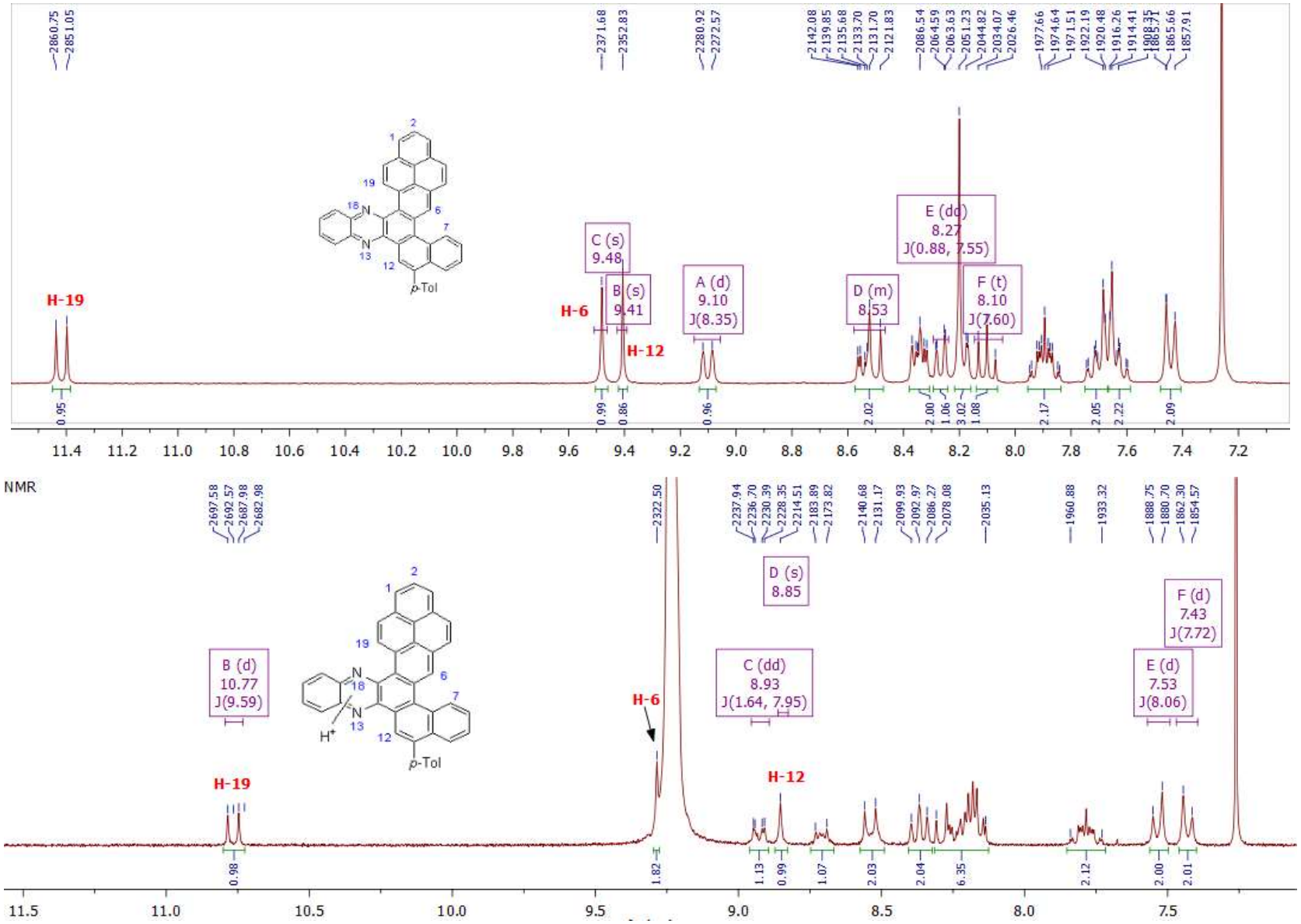


Figure S33. Fragments of ^{1}H NMR spectra of **9a** in $CDCl_3$ and $CDCl_3/CF_3COOH$ (250 MHz)

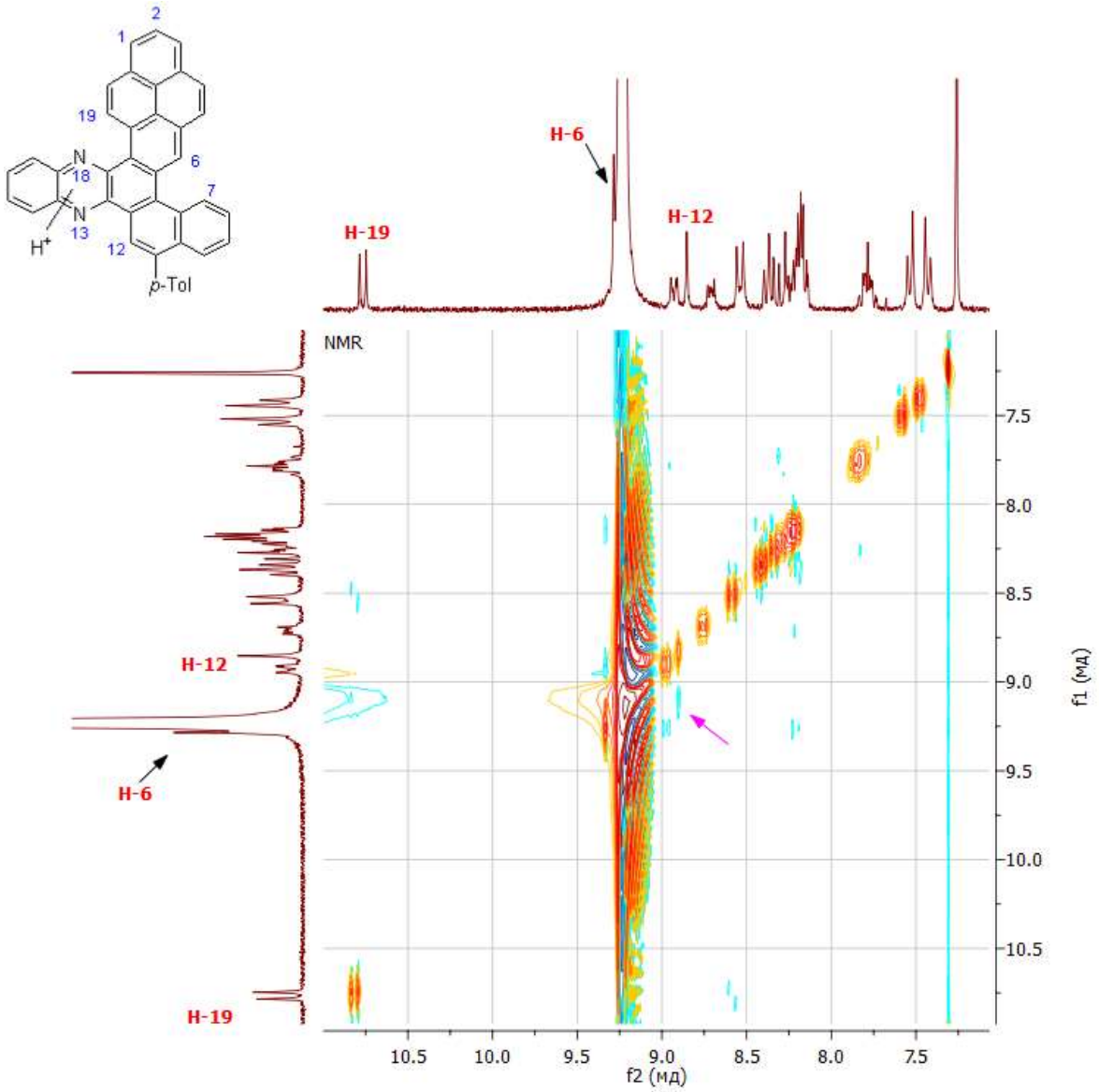


Figure S34. ^{1}H-^{1}H NOESY spectrum of **9a** in $CDCl_3/CF_3COOH$ (250 MHz)

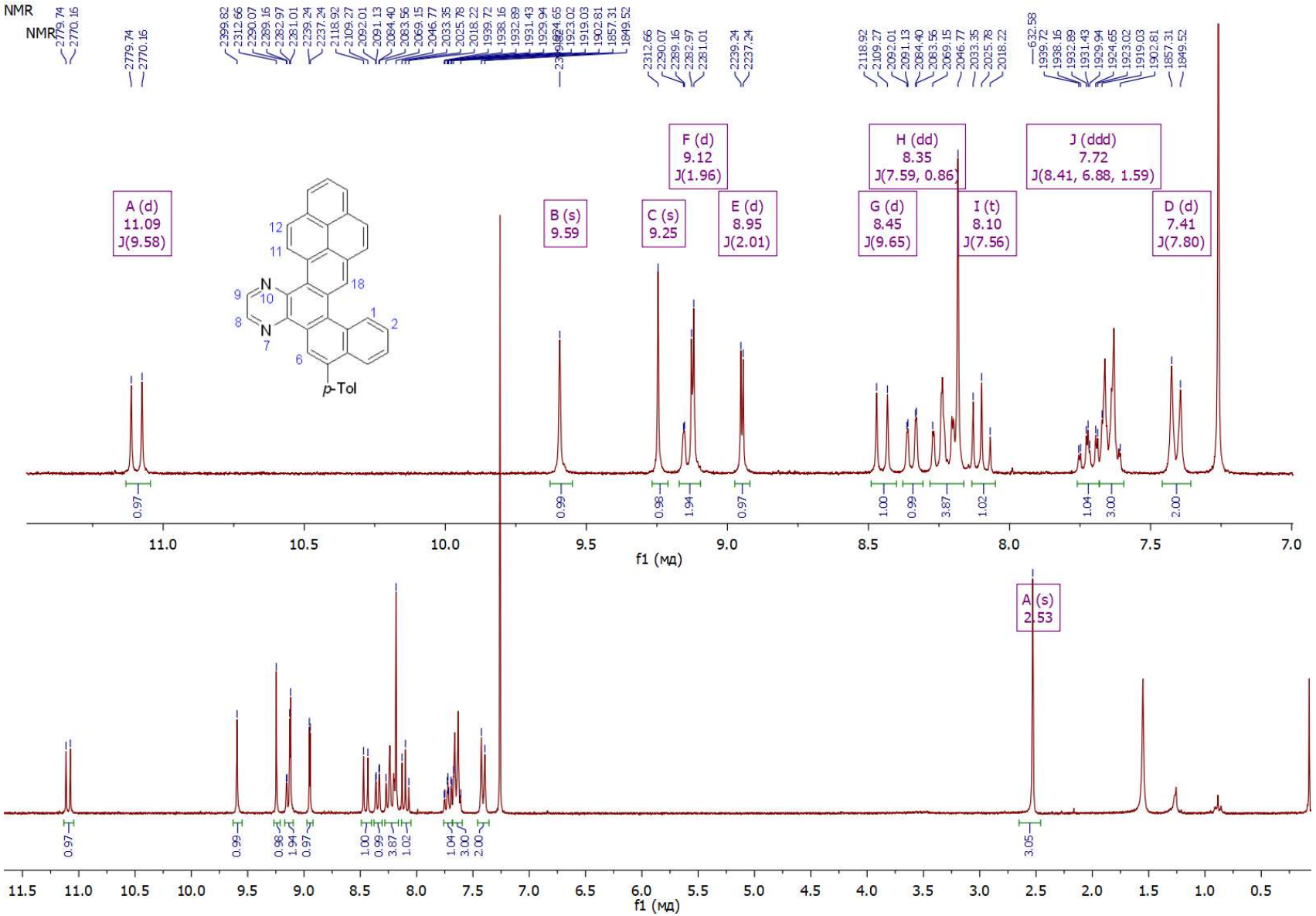


Figure S35. ^{1}H NMR spectrum of **9b** ($CDCl_3$, 250 MHz)

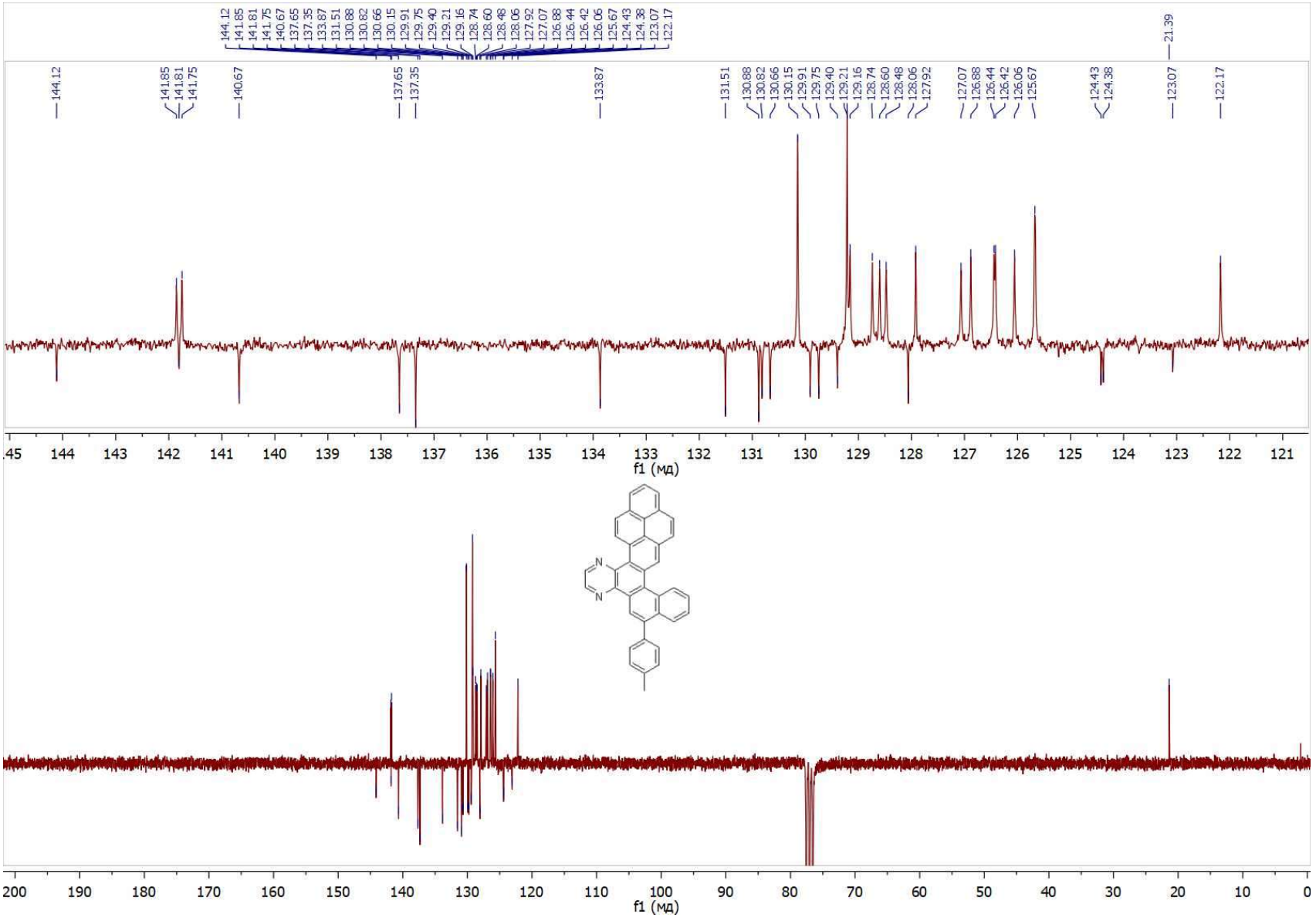


Figure S36. ^{13}C NMR APT spectrum of **9b** ($CDCl_3$, 62.9 MHz)

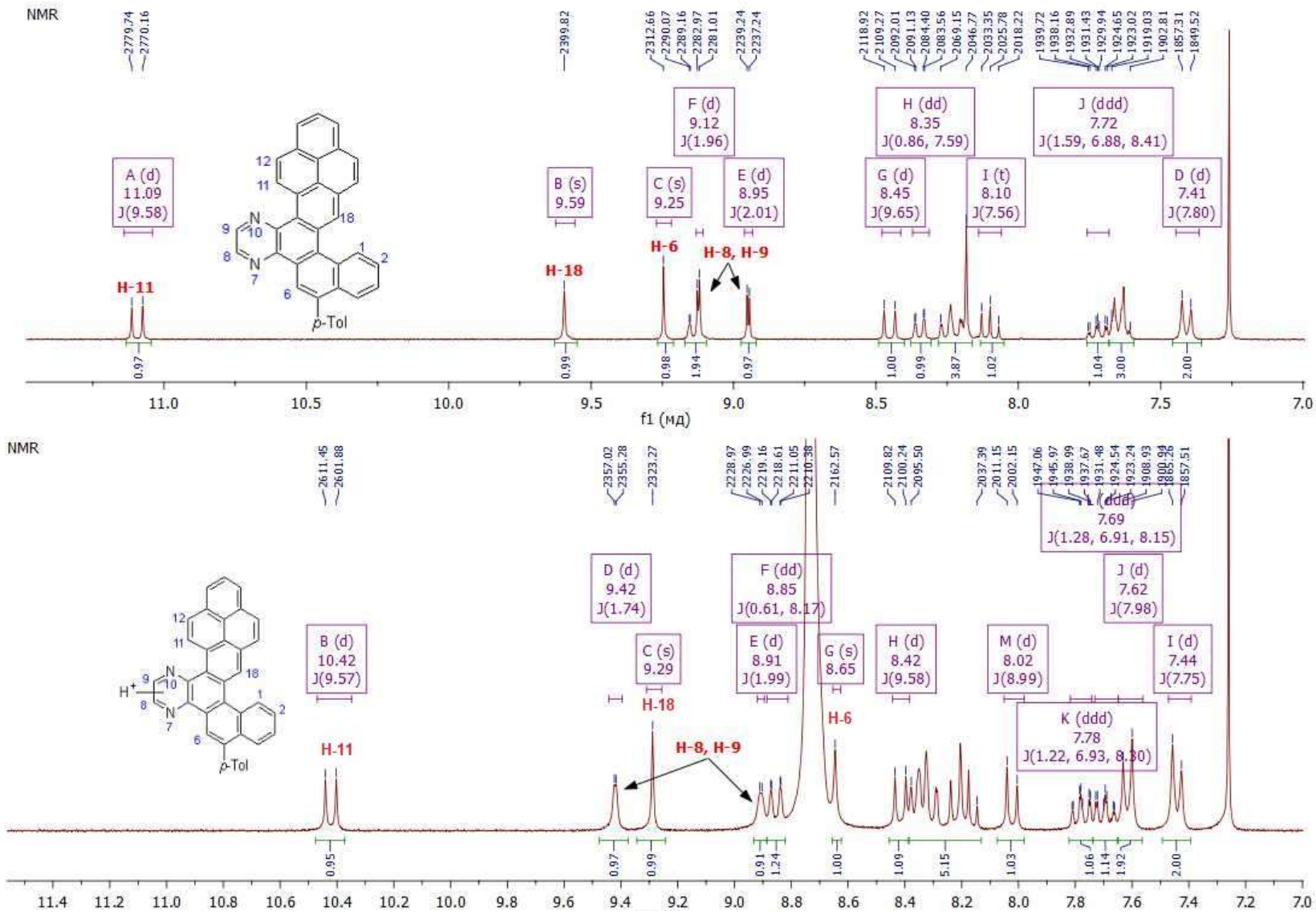


Figure S37. Fragments of ^{1}H NMR spectra of **9b** in $CDCl_3$ and $CDCl_3/CF_3COOH$ (250 MHz)

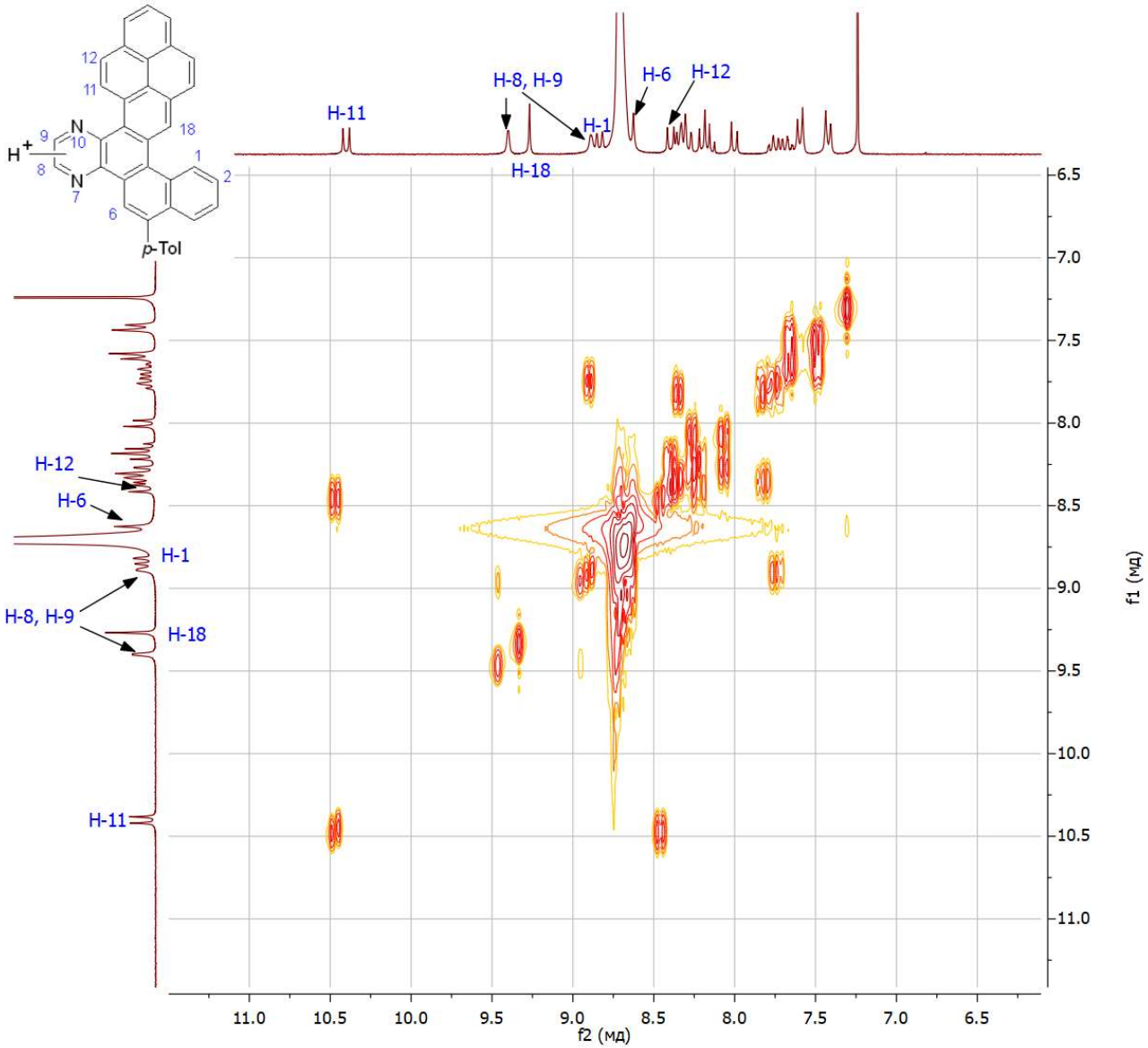


Figure S38. ^{1}H-^{1}H COSY spectrum of **9b** in $CDCl_3/CF_3COOH$ (250 MHz)

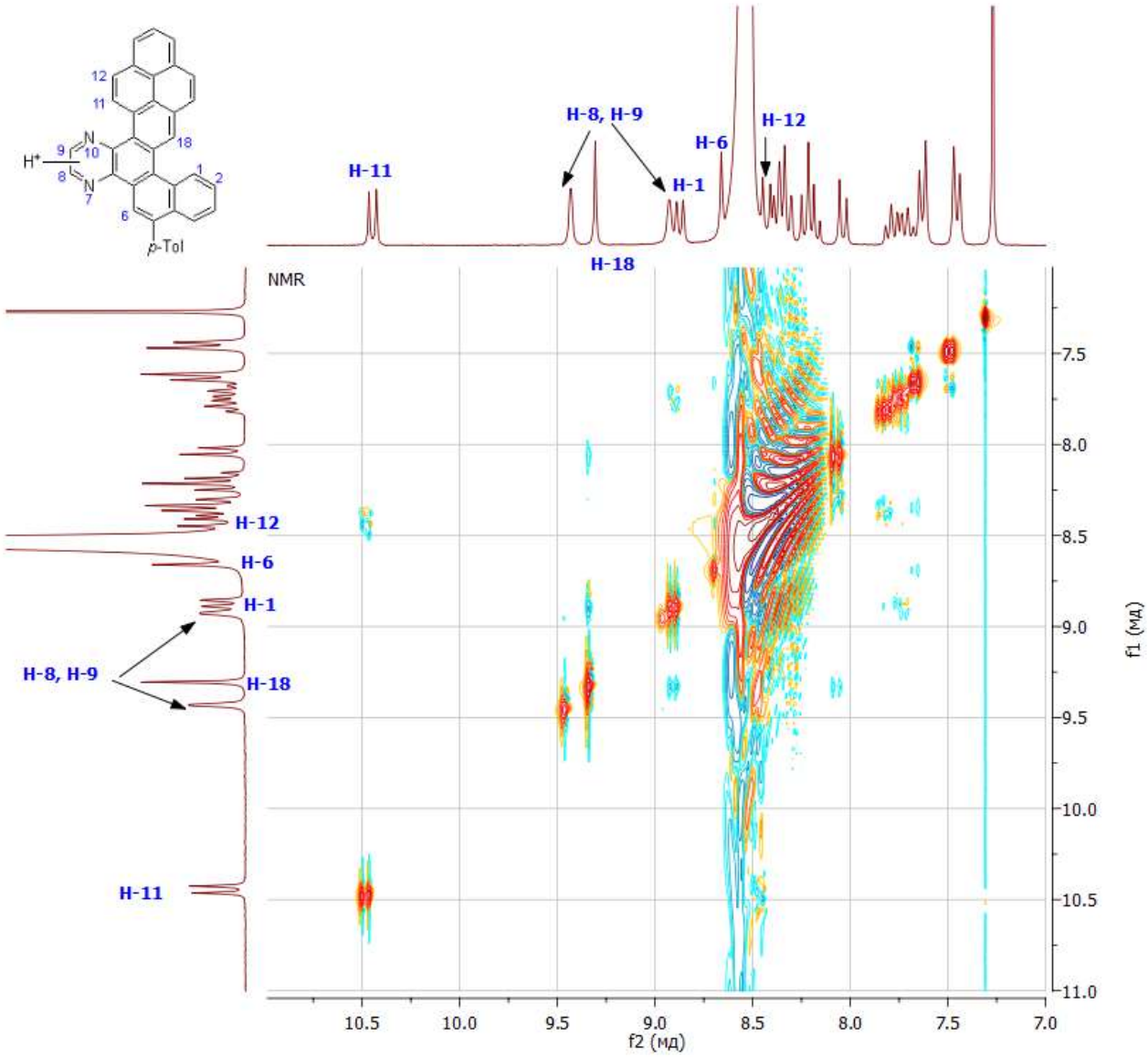


Figure S39. ^{1}H-^{1}H NOESY spectrum of **9b** $CDCl_3/CF_3COOH$ (250 MHz)

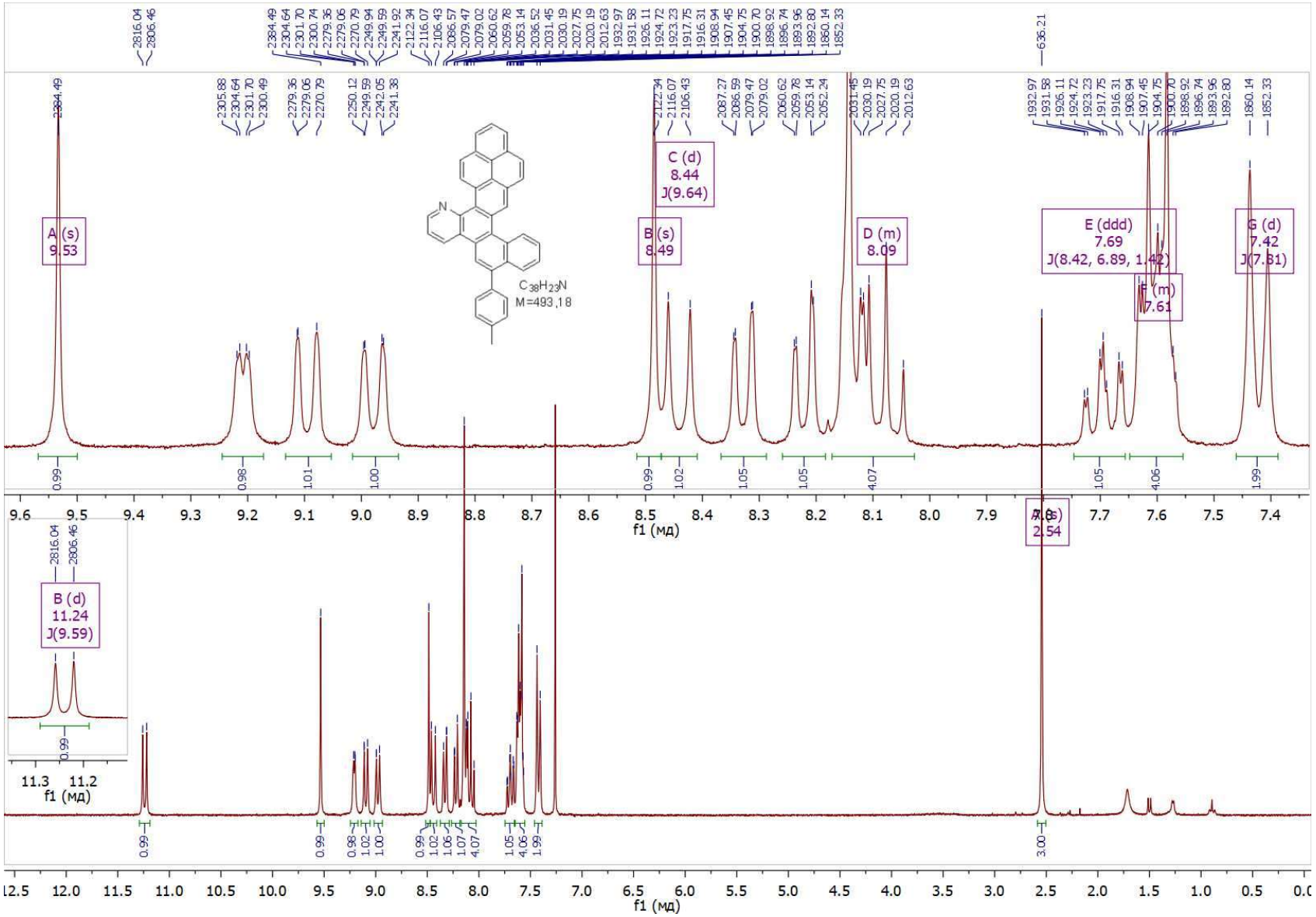


Figure S40. ^{1}H NMR spectrum of **9c** ($CDCl_3$, 250 MHz)

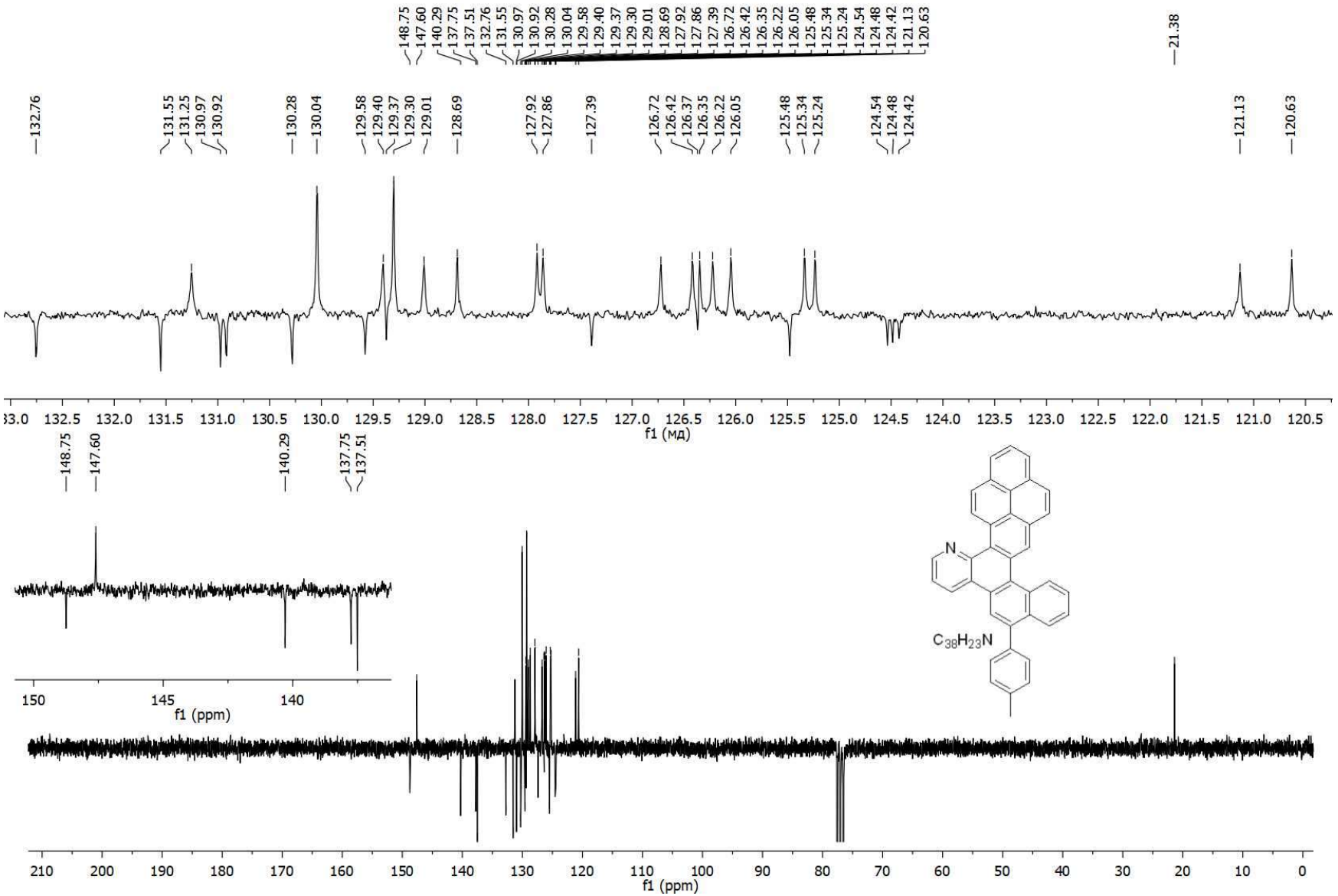


Figure S41. ^{13}C NMR APT spectrum of **9c** ($CDCl_3$, 62.9 MHz)

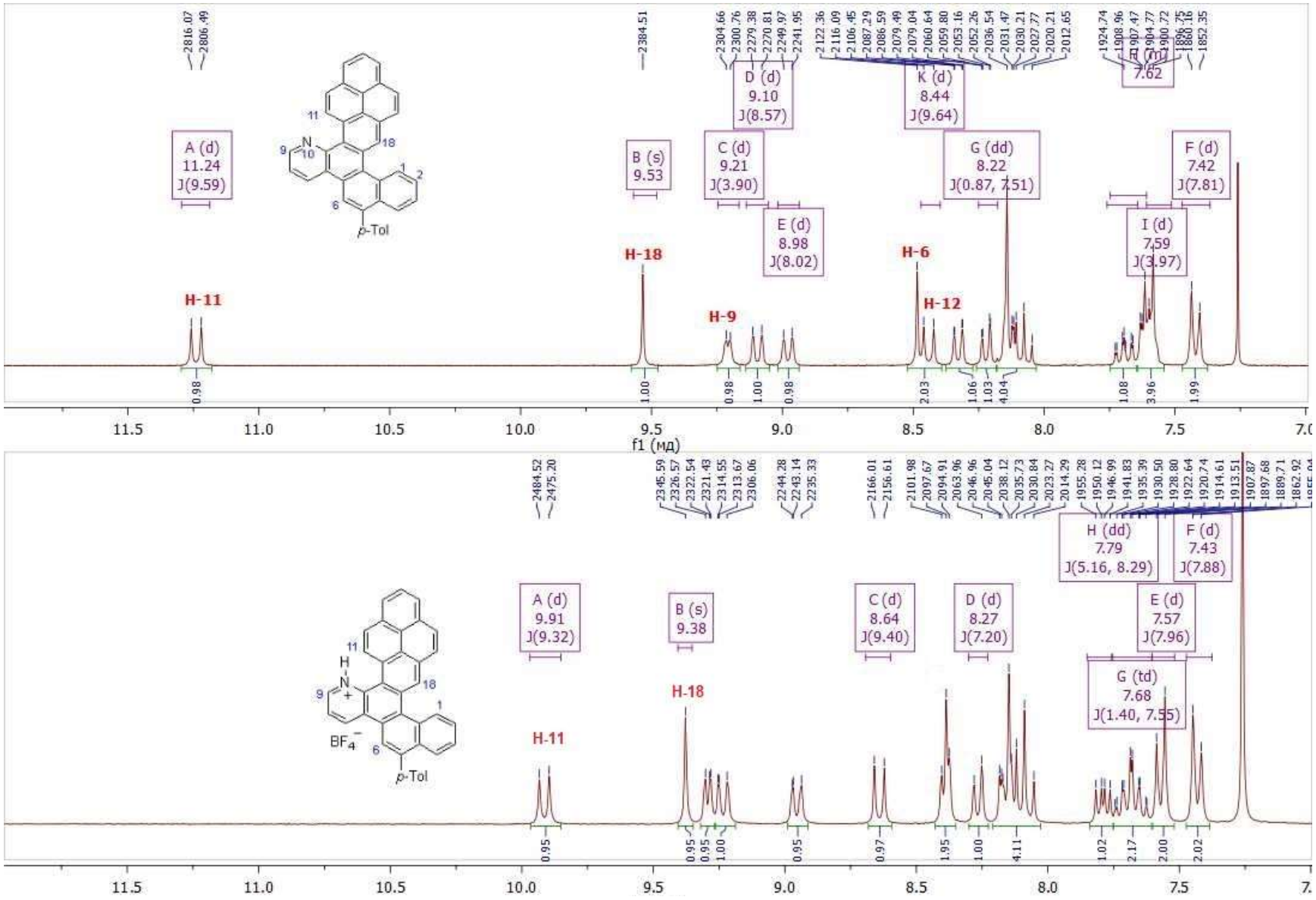


Figure S42. Fragments of ^{1}H NMR spectra of **9c** and salt **9c•HBF$_4$** ($CDCl_3$, 250 MHz)

Crystal Structure Determination: X-Ray measurements were conducted with Bruker APEX II CCD diffractometer and four-circle diffractometer SuperNova, Single source at offset/far, HyPix3000. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2145243 (**7b**) and CCDC 2145242 (**9c**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

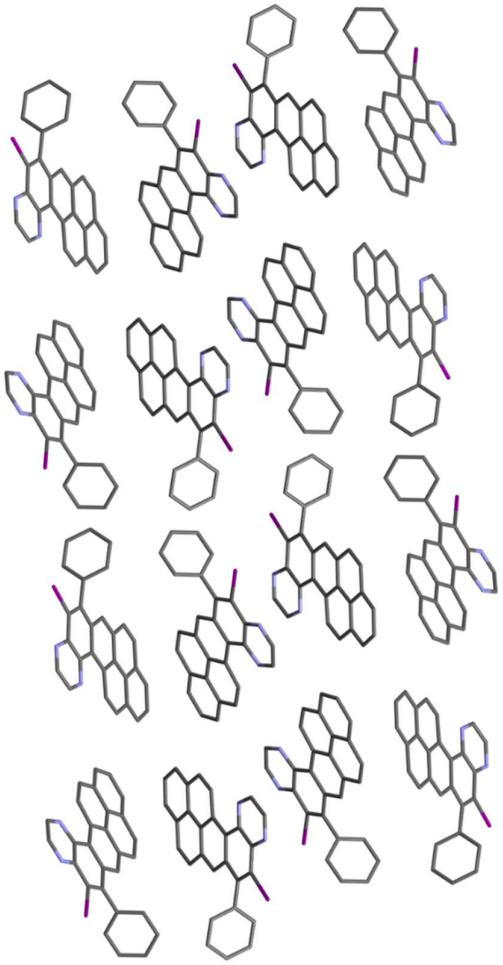


Figure S43. Crystal packing of **7b** (view along *b* axis)

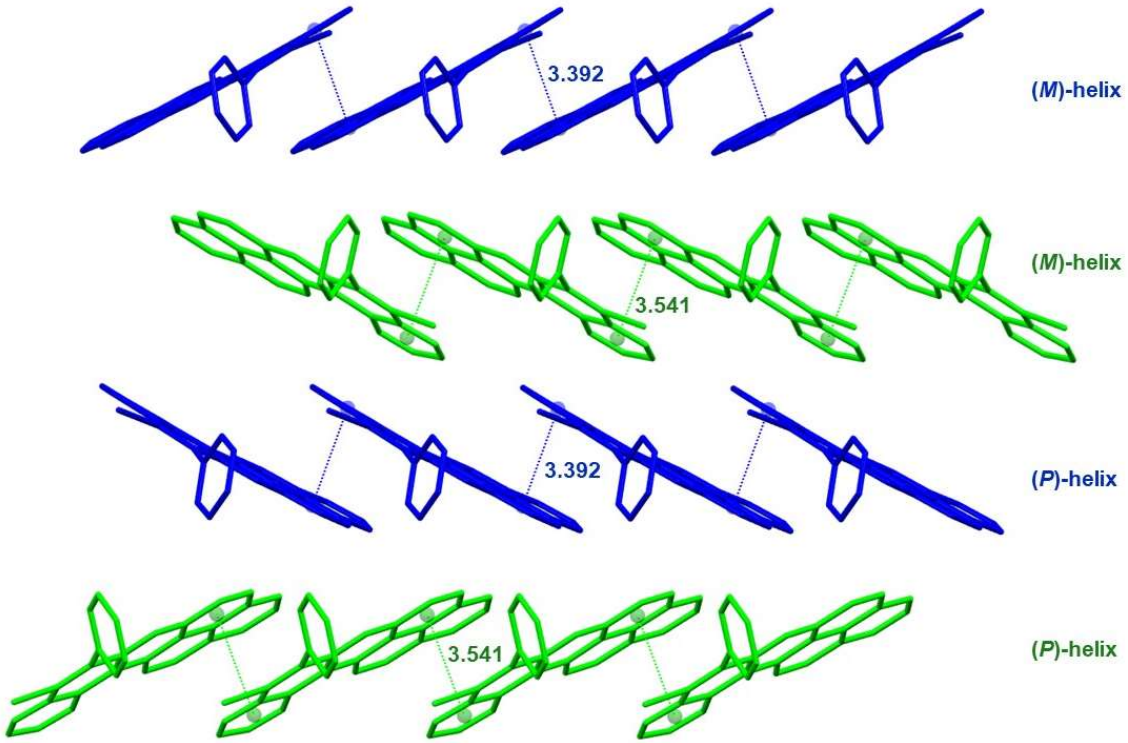


Figure S44. Crystal packing of **7b** (view along *a* axis). Molecules are colored by symmetry equivalence

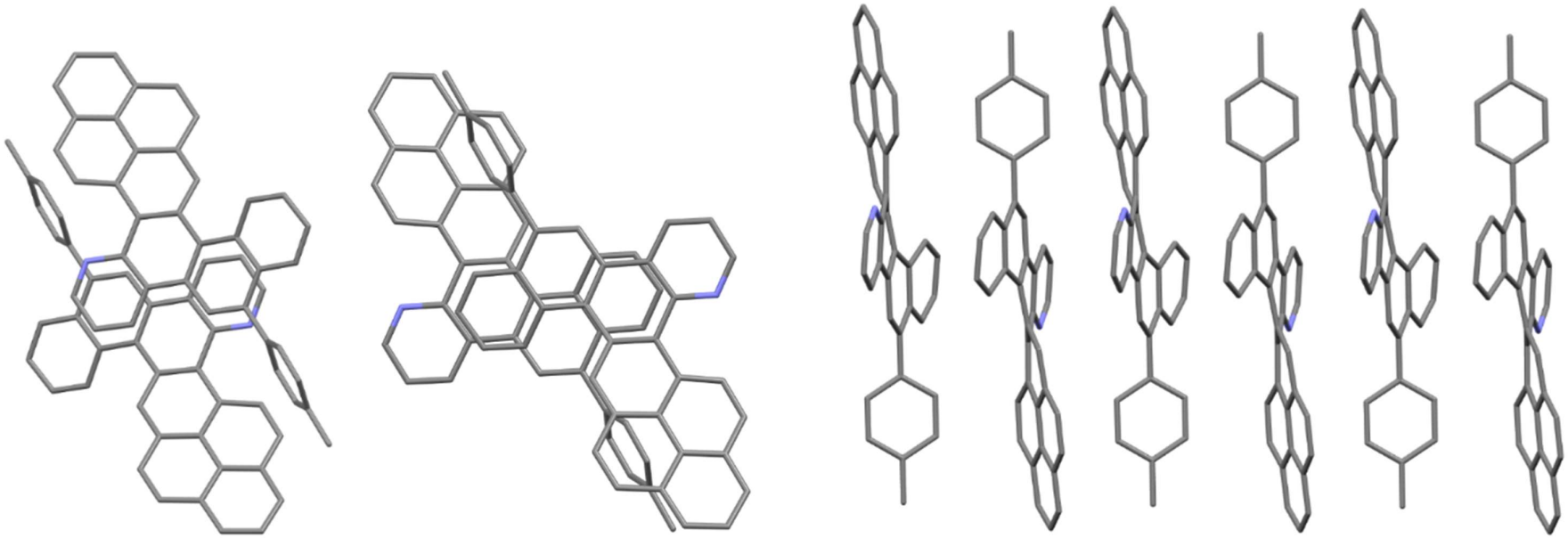


Figure S45. Crystal packing of **9c** (pairs and layer, view along a^* axis and b* axis, respectively)

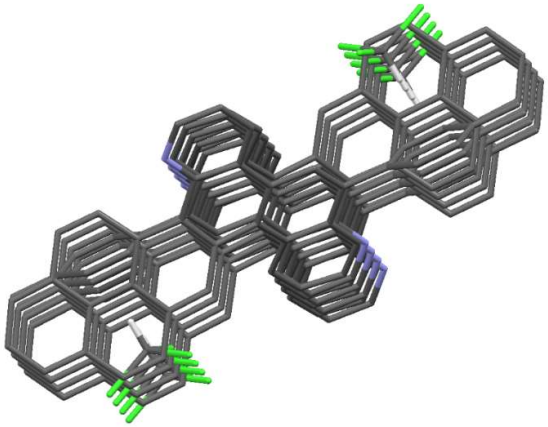


Figure S46. Crystal packing of **9c** (view along *a* axis)

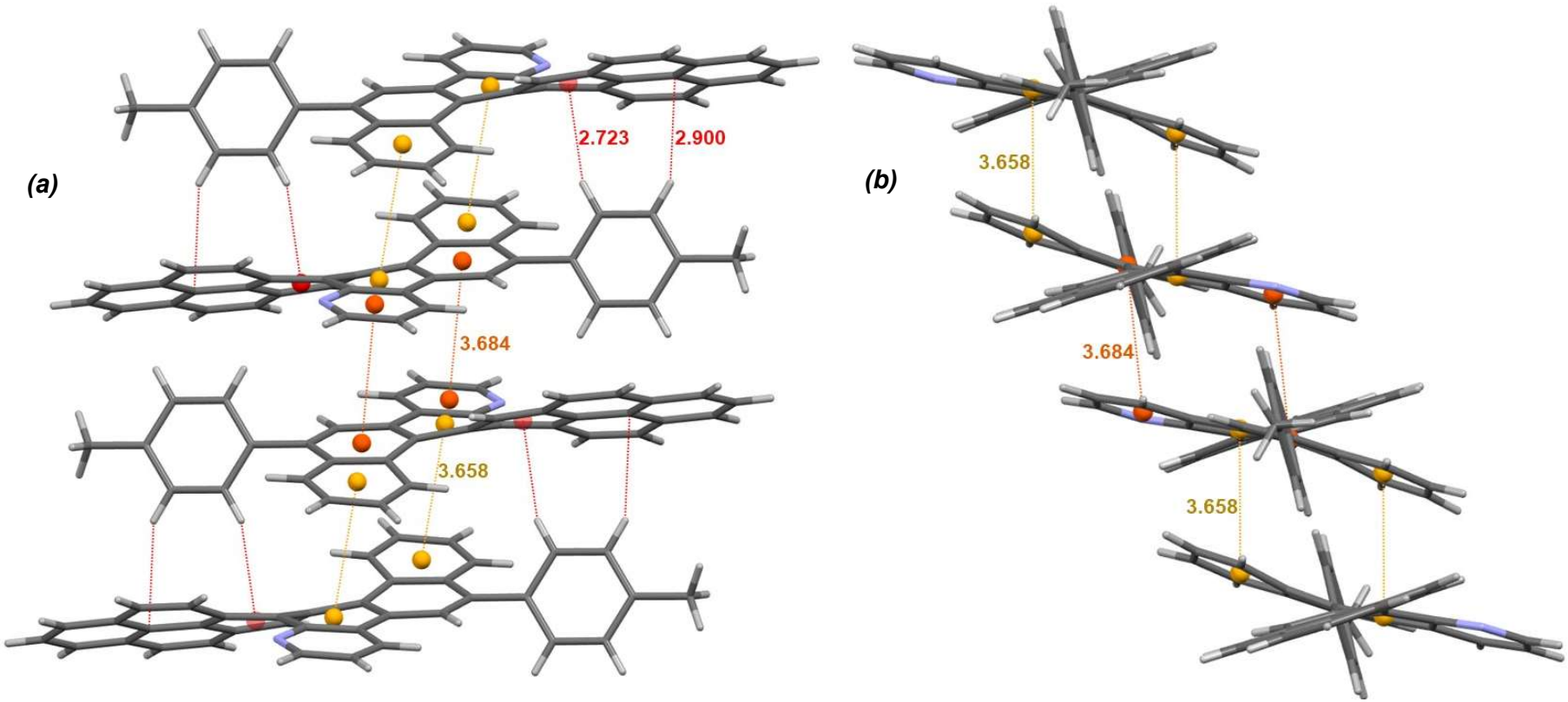


Figure S47. Crystal packing of **9c** (view along *b* axis (*a*) and along *c* axis (*b*))

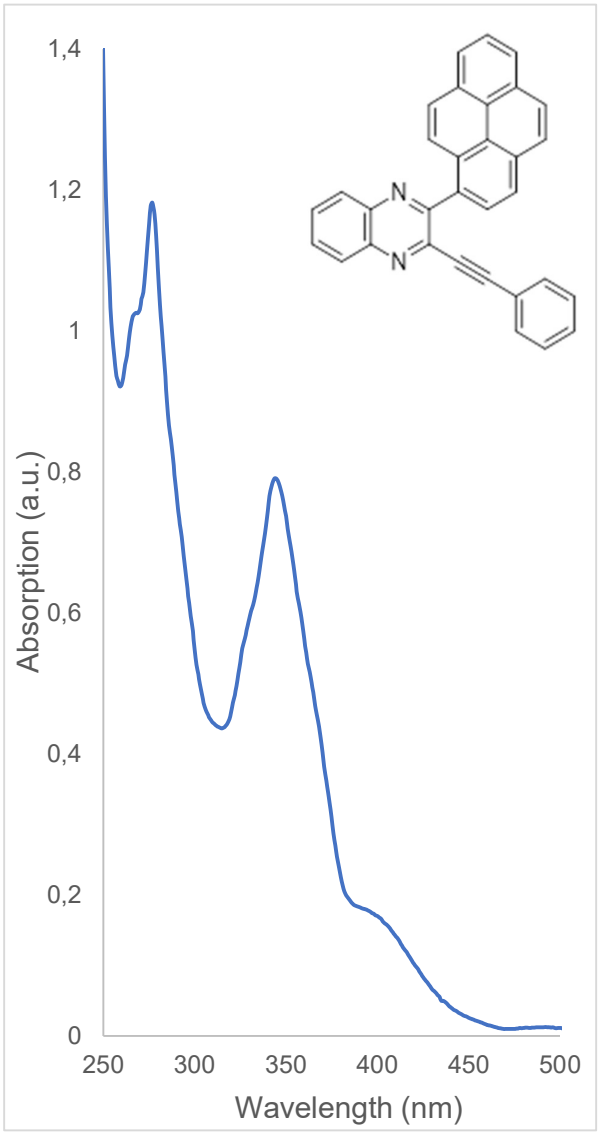


Figure S48. Absorption spectrum of **2a** in $CHCl_3$

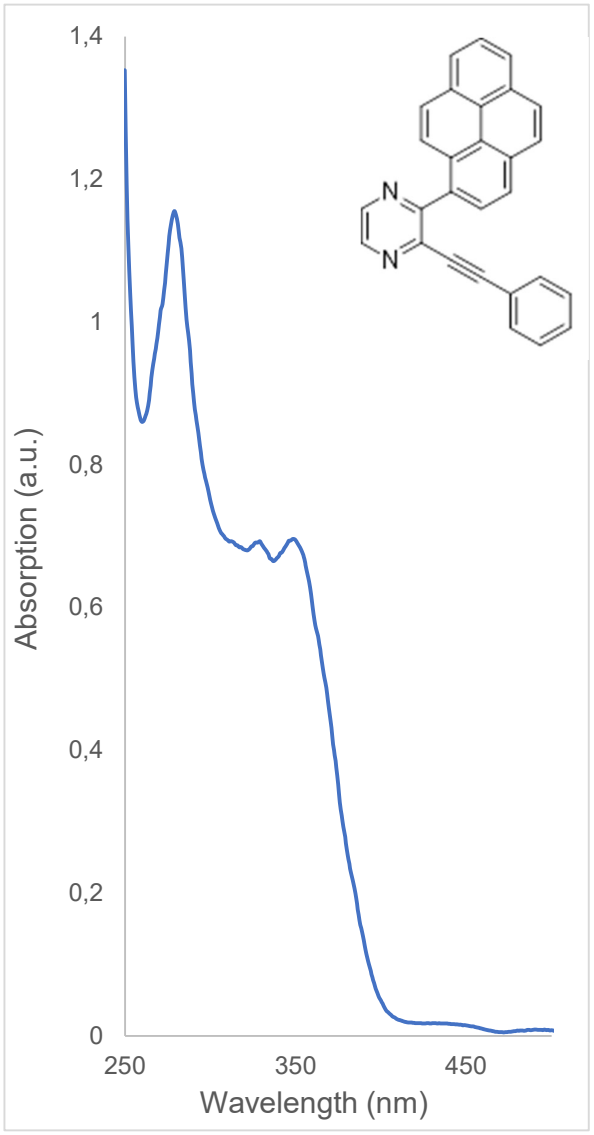


Figure S49. Absorption spectrum of **2b** in $CHCl_3$

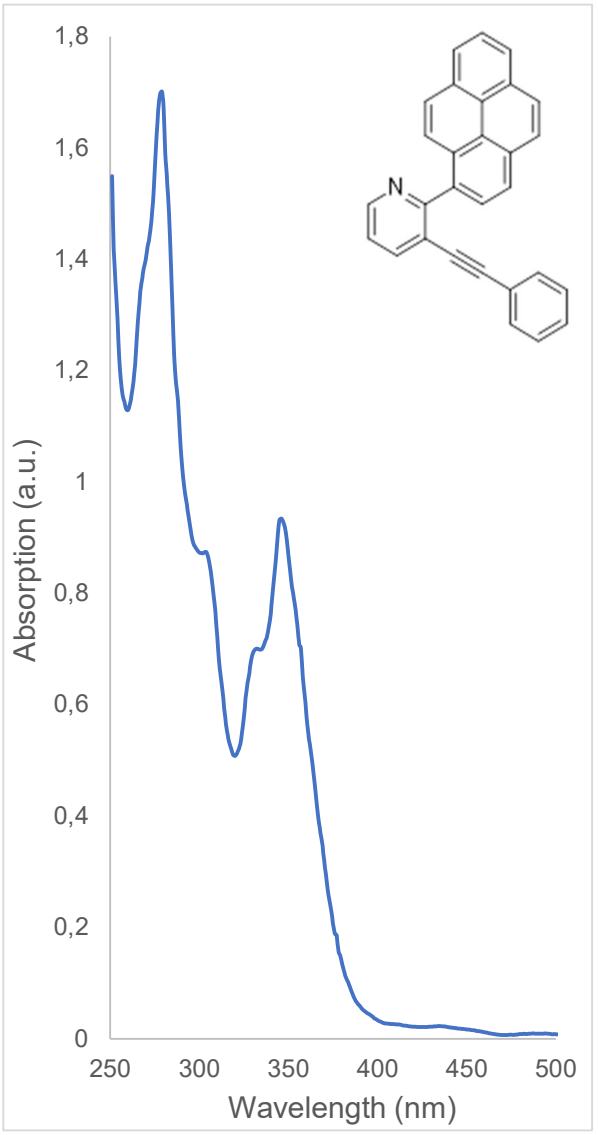


Figure S50. Absorption spectrum of **2c** in $CHCl_3$

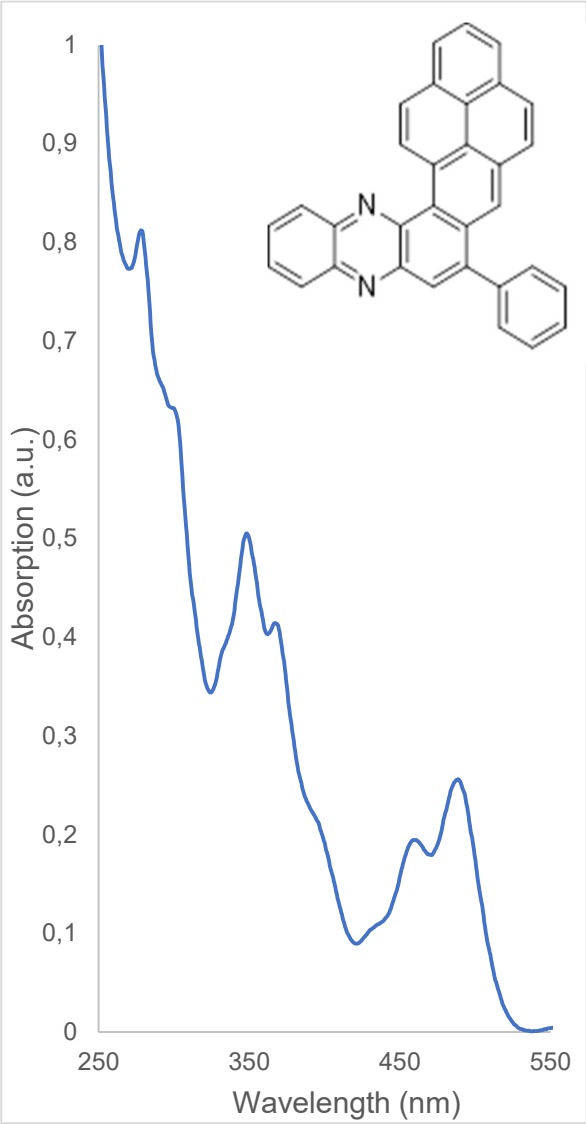


Figure S51. Absorption spectrum of **5a** in $CHCl_3$

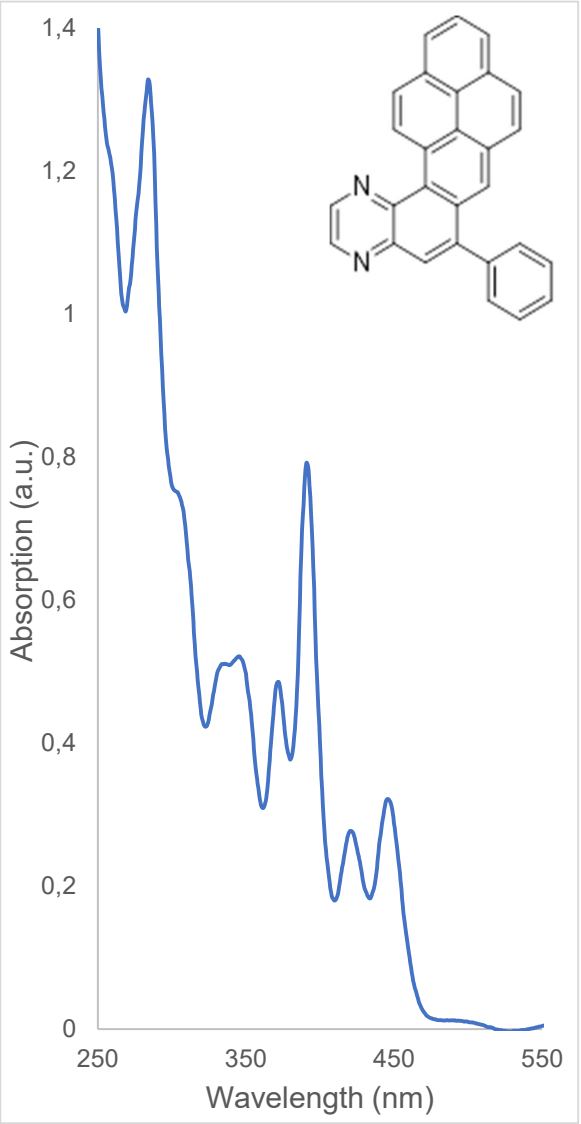


Figure S52. Absorption spectrum of **5b** in $CHCl_3$

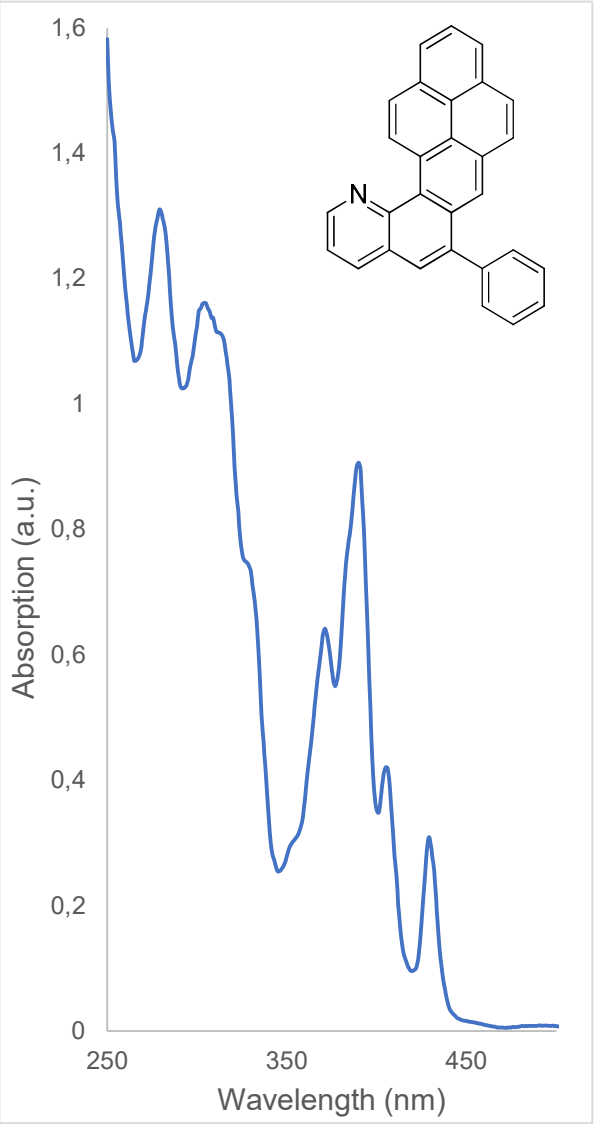


Figure S53. Absorption spectrum of **5c** in $CHCl_3$

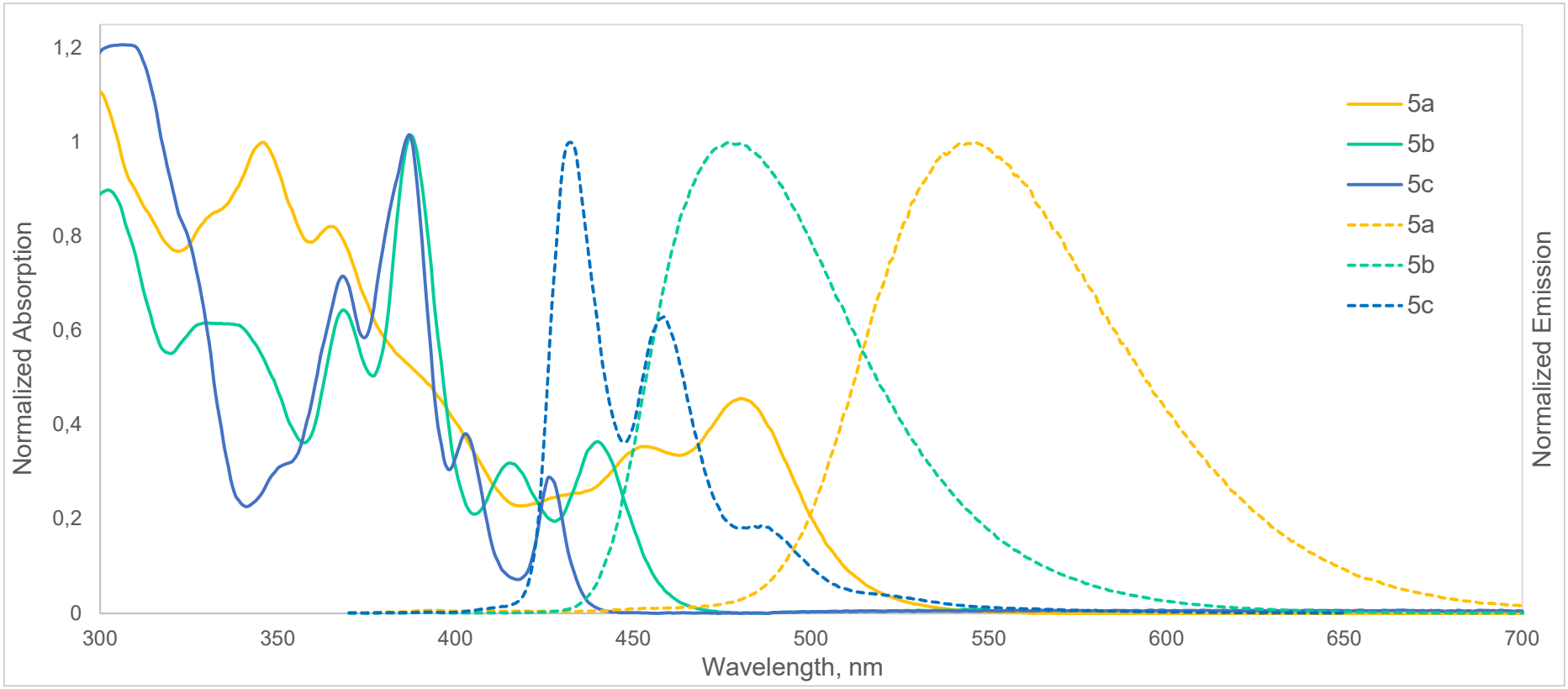


Figure S54. Normalized absorption (solid line) and emission spectra (dashed line) of helicenes **5** in acetonitrile solution (λ_{ex} = 350 nm (**5a, 5b**), 300 nm (**5c**)). The absorption spectra were normalized to the maximum at ~350 nm (**5a**) and ~390 nm (**5b**, **5c**)

Table S1. Photophysical properties of [4]helicenes **5**.

Compound	λ_{max}^{abs}, nm	λ_{max}^{em}, nm[a]	E_g^{opt}, eV[b]	Stokes shift, cm^{-1}	Φ_{FL}[c]
5a	480	546	2.48	2518	0.24
5b	440	477	2.77	1763	0.71
5c	426	432, 459, sh 489	2.93	326	0.42

[a] Excitation at 350 nm (**9a, 9b**) and 300 nm (**9c**). [b] The optical band gap was estimated from the intersection between the absorption and emission bands. [c] Calculated relative to anthracene in EtOH (Φ = 0.28)[1]

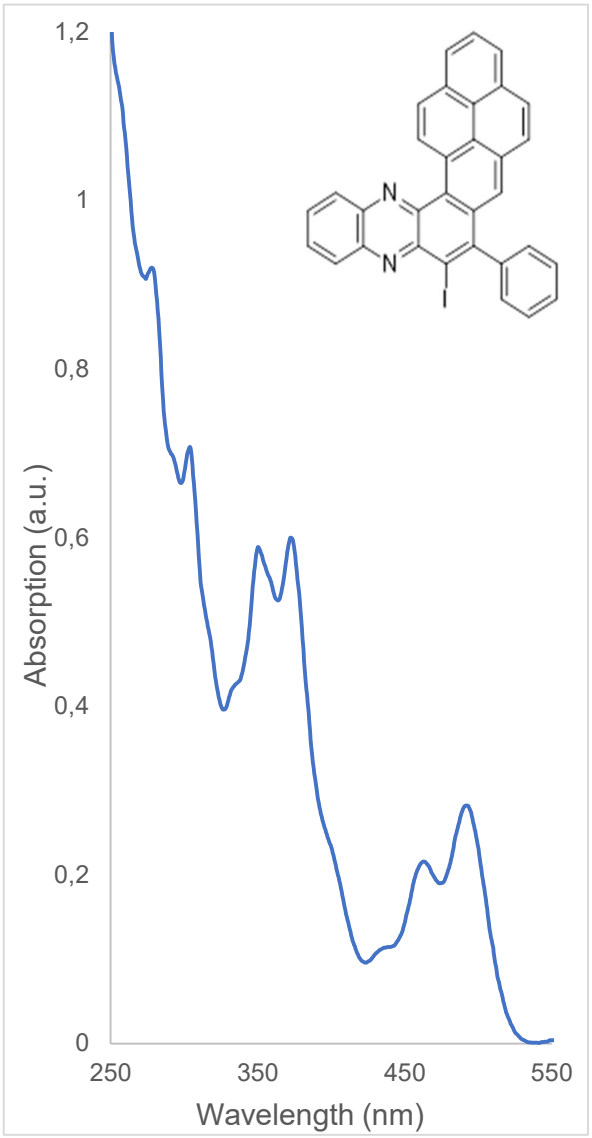


Figure S55. Absorption spectrum of **7a** in $CHCl_3$

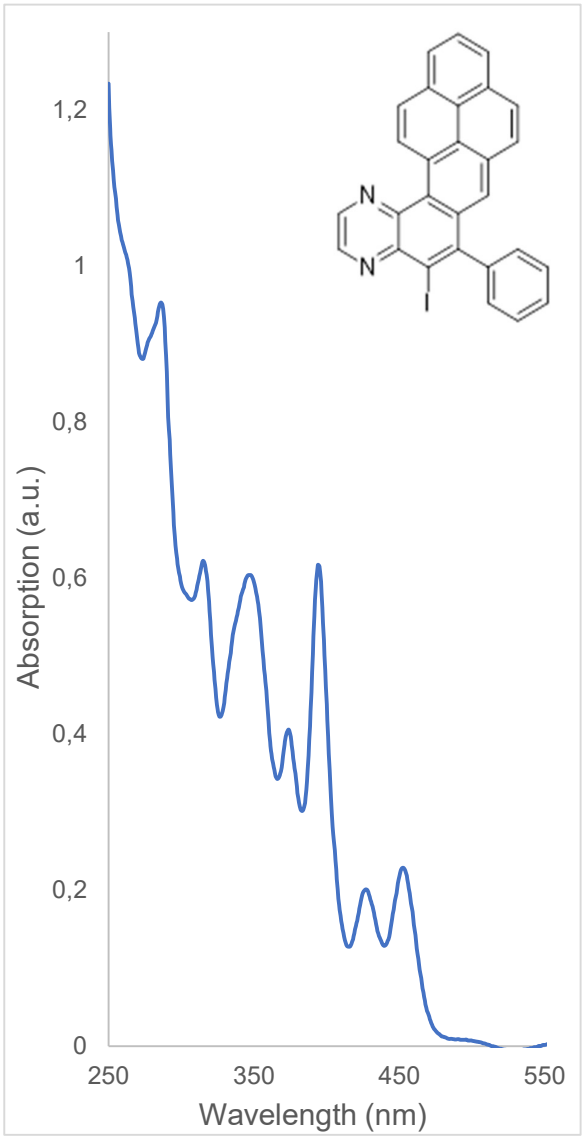


Figure S56. Absorption spectrum of **7b** in $CHCl_3$

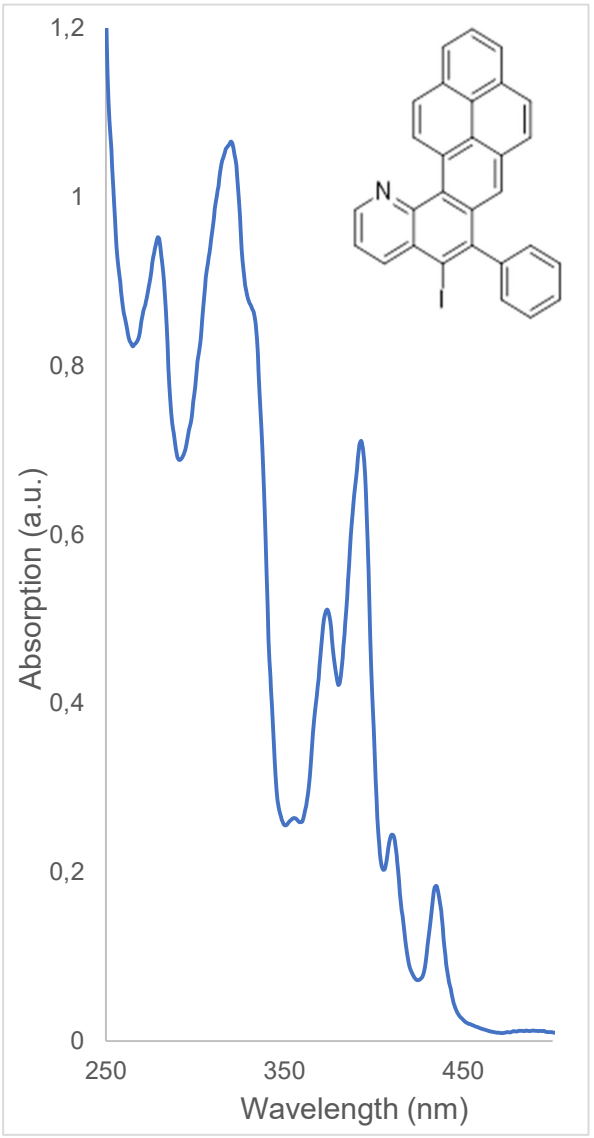


Figure S57. Absorption spectrum of **7c** in $CHCl_3$

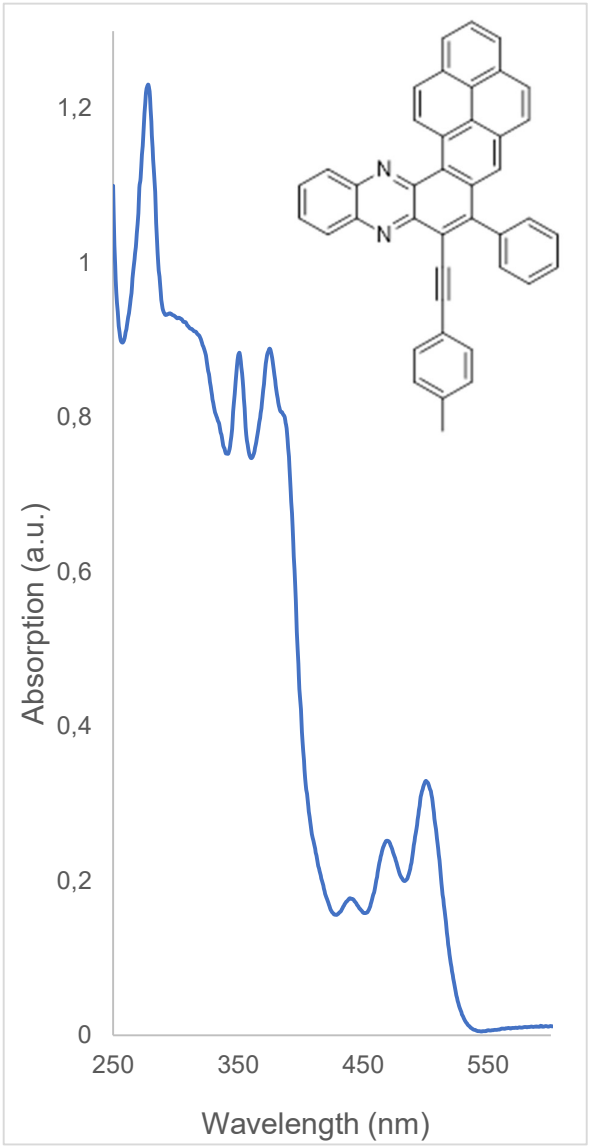


Figure S58. Absorption spectrum of **8a** in $CHCl_3$

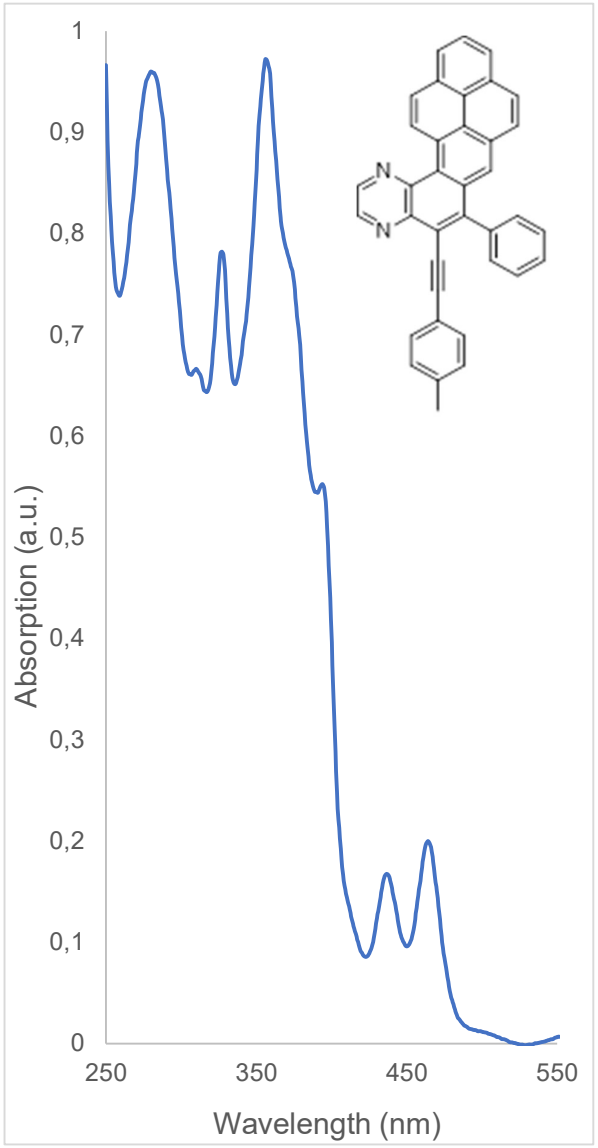


Figure S59. Absorption spectrum of **8b** in $CHCl_3$

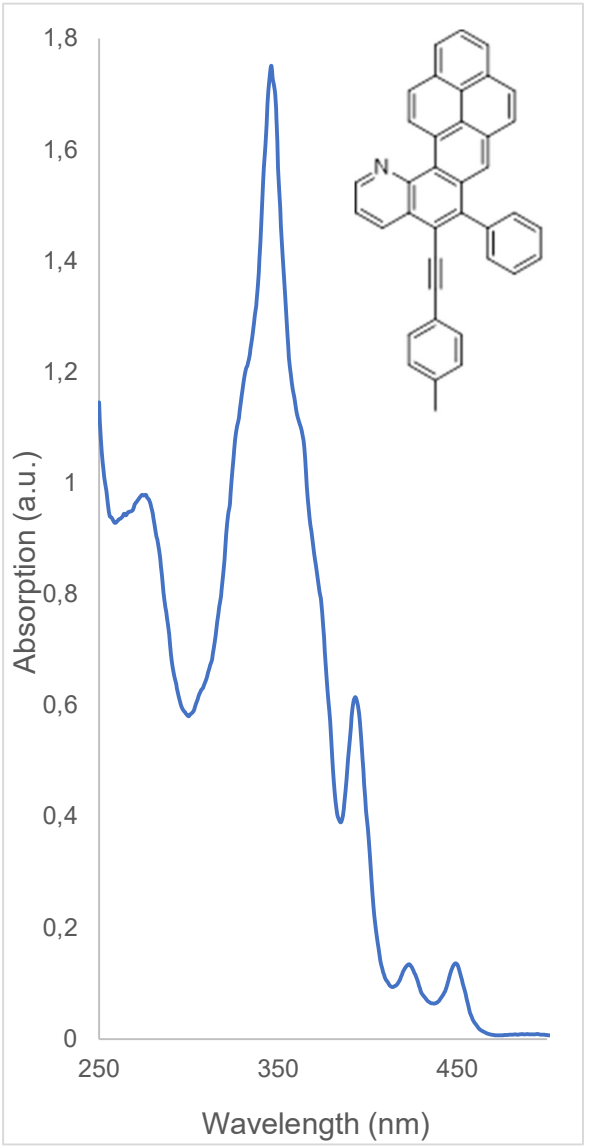


Figure S60. Absorption spectrum of **8c** in $CHCl_3$

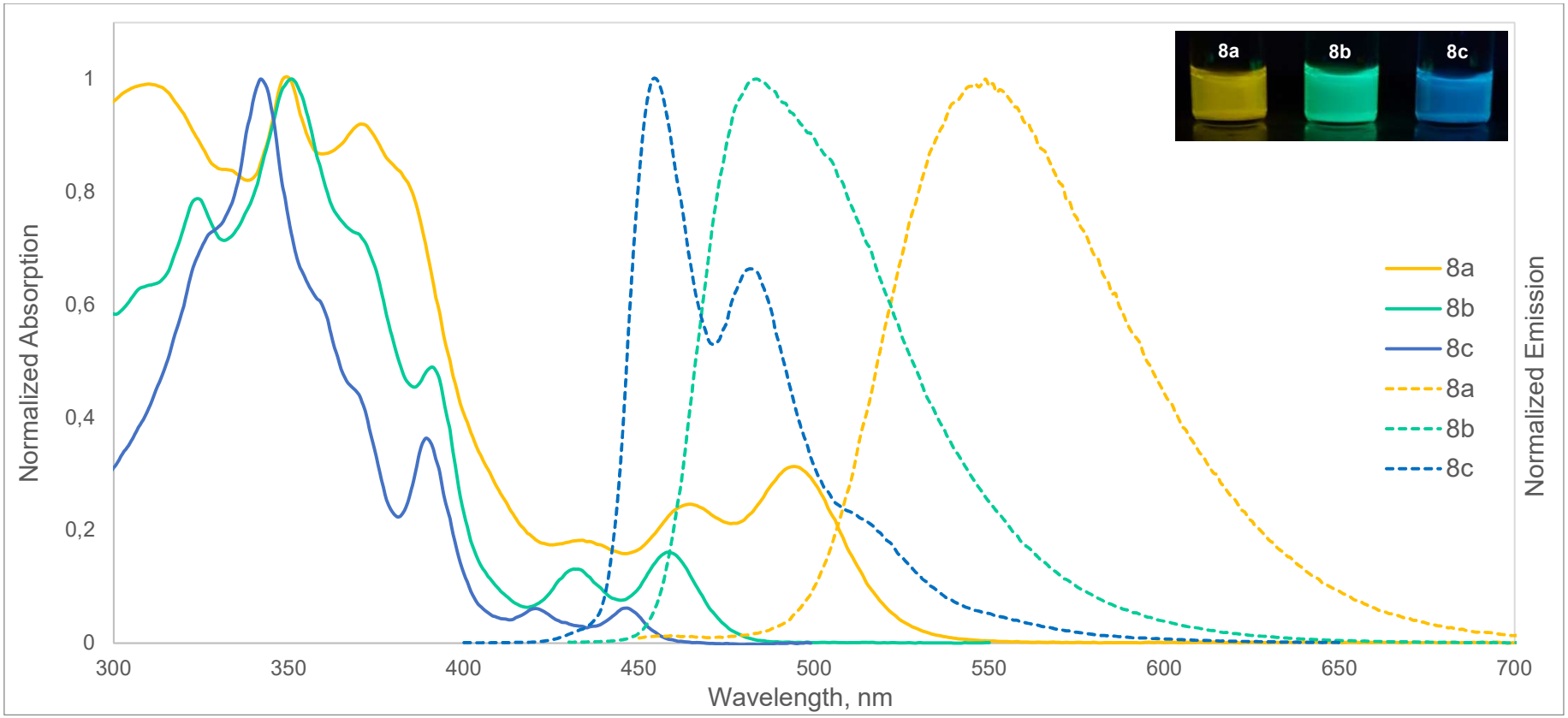


Figure S61. Normalized absorption (solid line) and emission spectra (dashed line) of alkynes **8** in acetonitrile solution (λ_{ex} = 350 nm). The absorption spectra were normalized to the maximum at ~350 nm

Table S2. Photophysical properties of alkynes **8**.

Compound	λ_{max}^{abs}, nm	λ_{max}^{em}, nm[a]	E_g^{opt}, eV[b]	Stokes shift, cm^{-1}	Φ_{FL}[c]
8a	493	549	2.45	2069	0.28
8b	458	483, sh 506	2.70	1130	0.57
8c	446	454, 482, sh 517	2.85	395	0.38

[a] Excitation at 350 nm. [b] The optical band gap was estimated from the intersection between the absorption and emission bands. [c] Calculated relative to anthracene in EtOH (Φ = 0.28) [1]

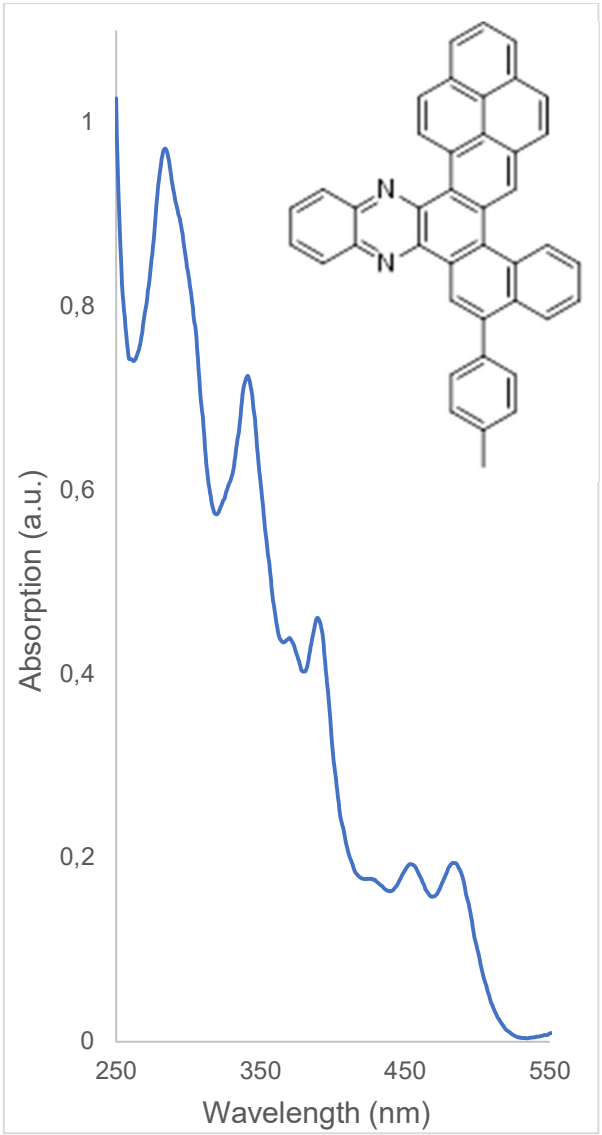


Figure S62. Absorption spectrum of **9a** in $CHCl_3$

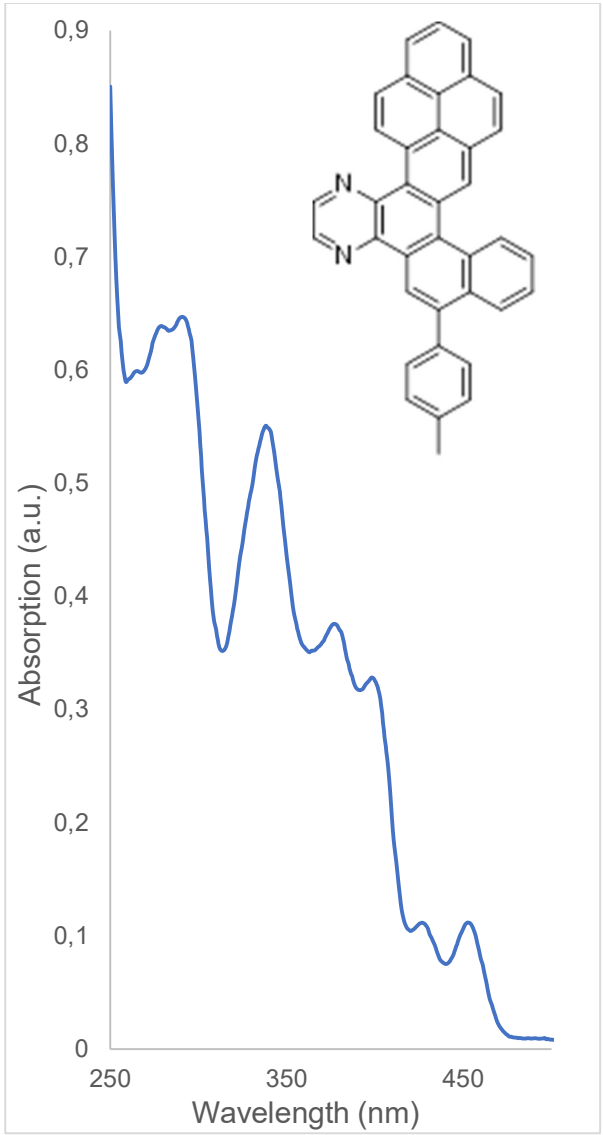


Figure S63. Absorption spectrum of **9b** in $CHCl_3$

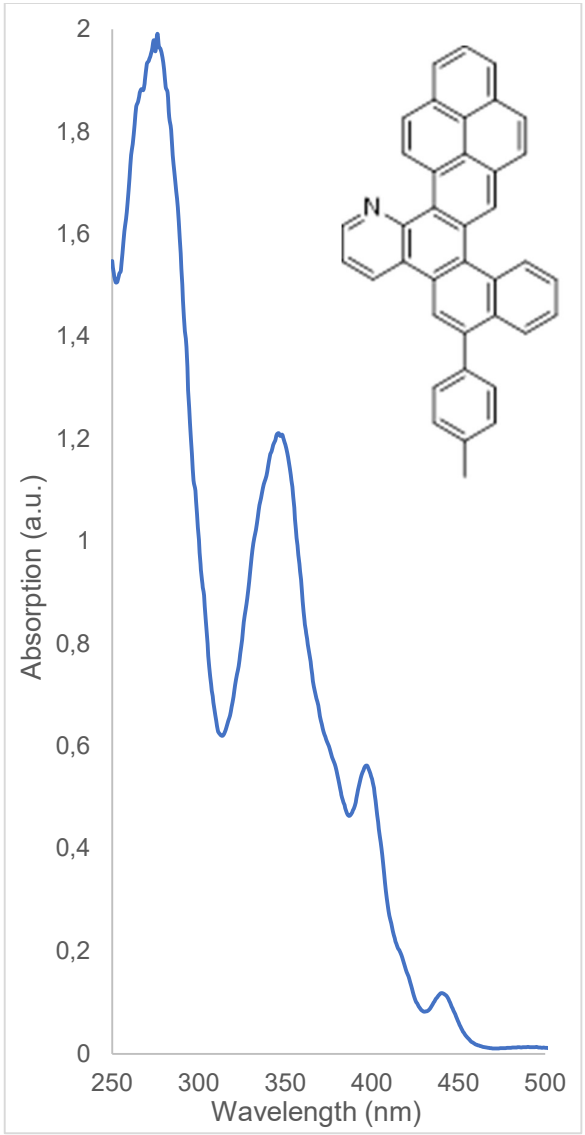


Figure S64. Absorption spectrum of **9c** in $CHCl_3$

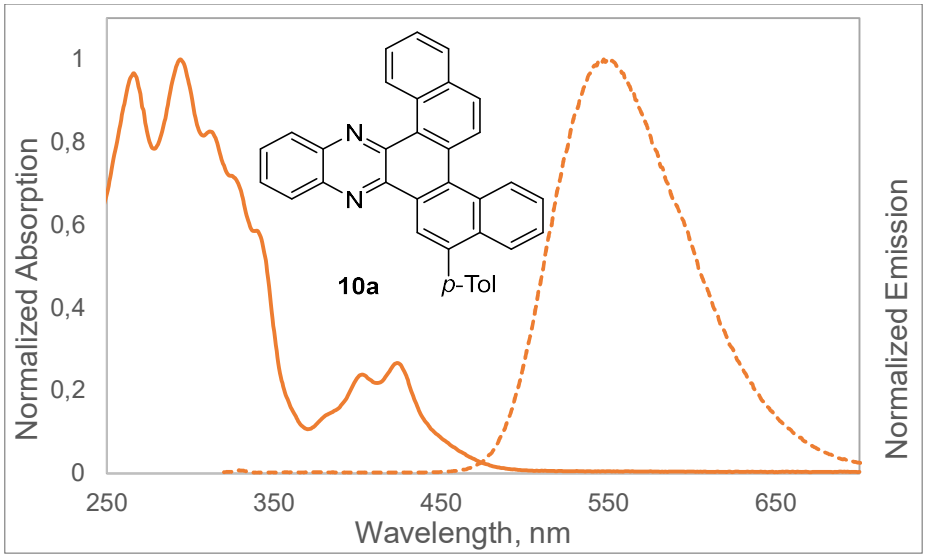


Figure S65. Normalized absorption (solid line) and emission spectra (dashed line) of previously reported quinoxaline containing S-shaped double [4]helicene **10a**[4] in acetonitrile solution (λex = 300 nm)

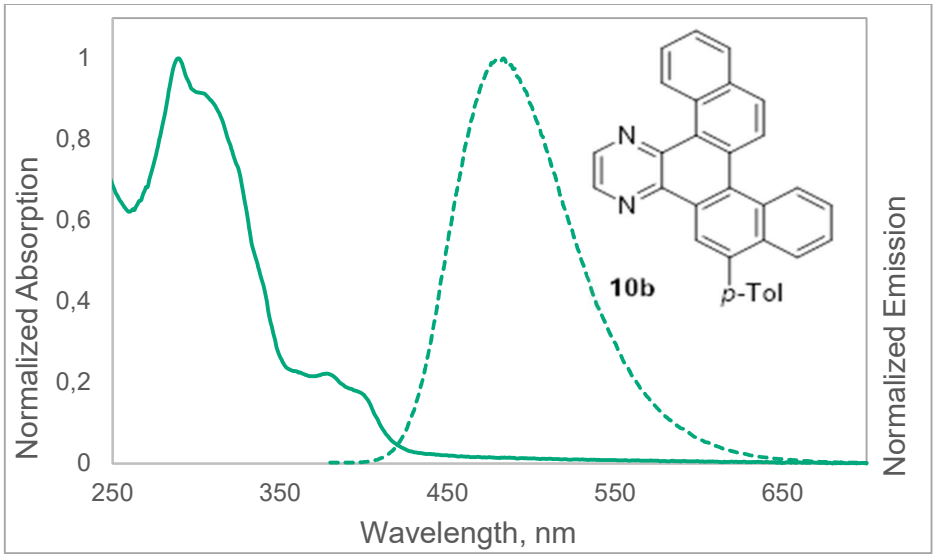


Figure S66. Normalized absorption (solid line) and emission spectra (dashed line) of previously reported pyrazine containing S-shaped double [4]helicene **10b**[4]] in acetonitrile solution (λex = 300 nm)

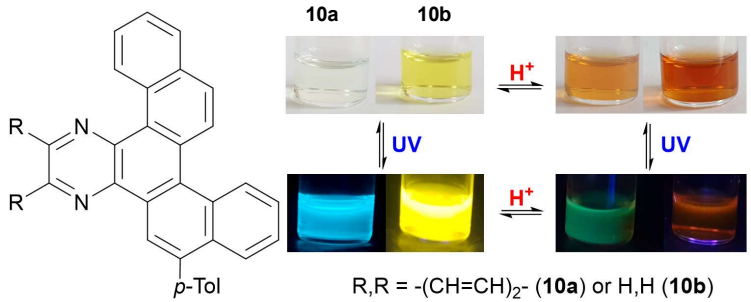


Figure S67. Acetonitrile solutions of helicenes **10a** without acid (top, left) and with HBF_4 (top, right) under daylight. The same solutions under UV irradiation (365 nm, bottom)

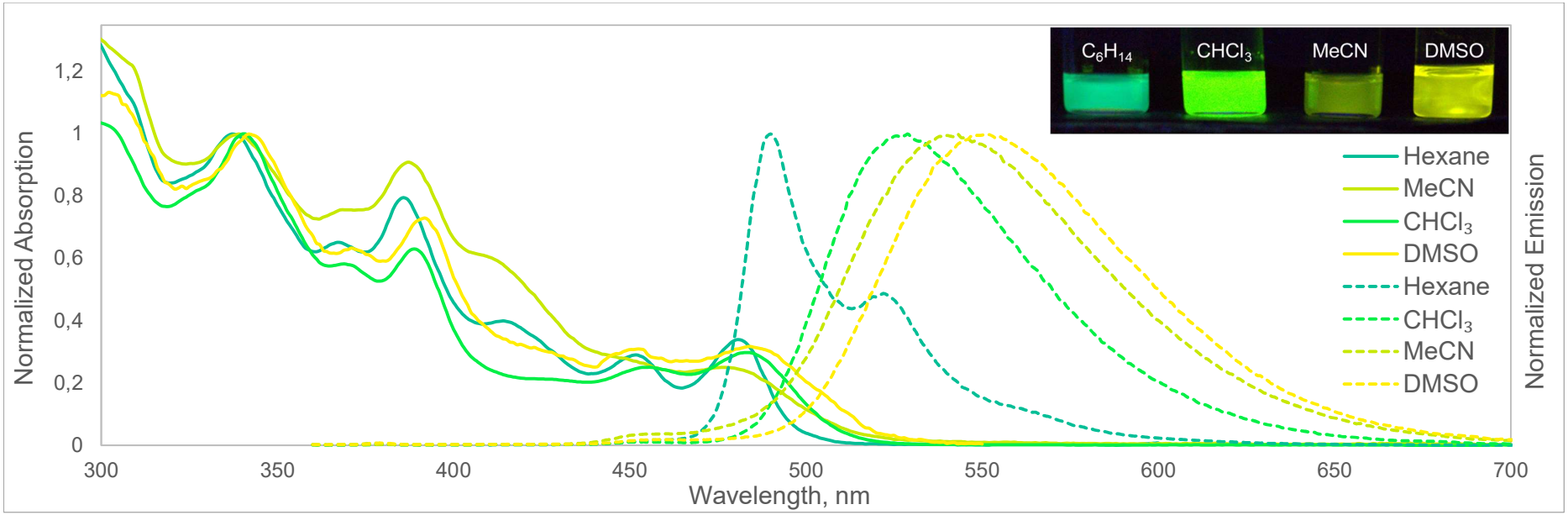


Figure S68. Normalized absorption (solid line) and emission spectra (dashed line) of **9a** in different solvents (λ_{ex} = 340 nm). The absorption spectra were normalized to the maximum at ~350 nm

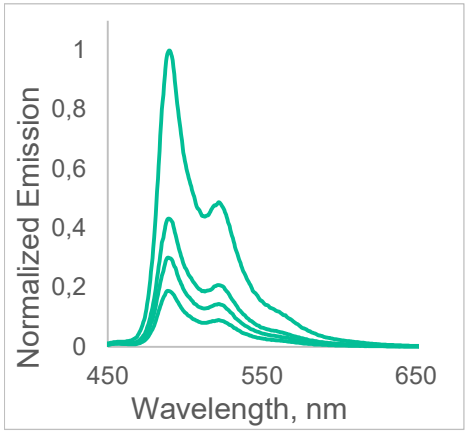


Figure S69. Normalized emission spectra of **9a** at different concentrations in hexane solution

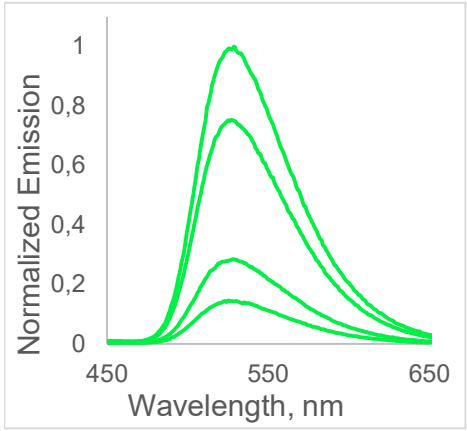


Figure S70. Normalized emission spectra of **9a** at different concentrations in $CHCl_3$ solution

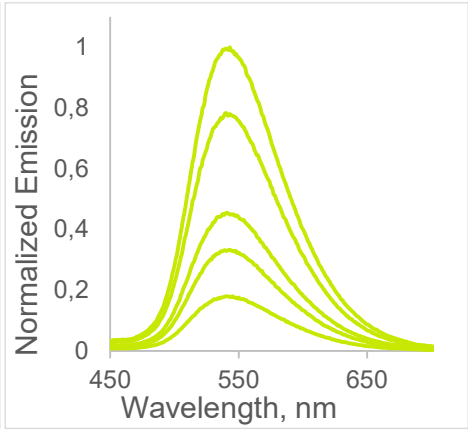


Figure S71. Normalized emission spectra of **9a** at different concentrations in MeCN solution

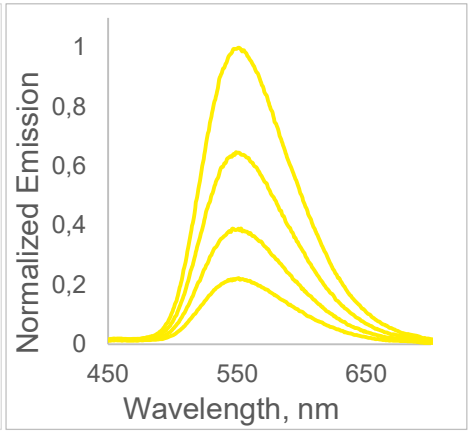


Figure S72. Normalized emission spectra of **9a** at different concentrations in DMSO solution

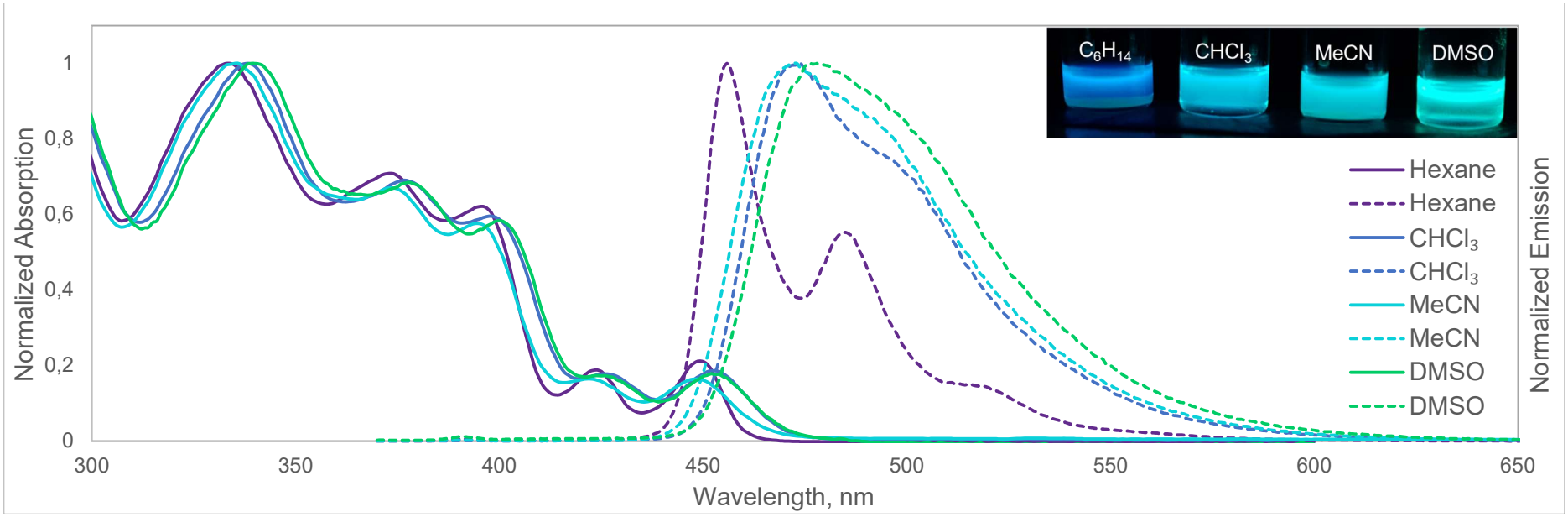


Figure S73. Normalized absorption (solid line) and emission spectra (dashed line) of **9b** in different solvents (λ_{ex} = 350 nm). The absorption spectra were normalized to the maximum at ~350 nm

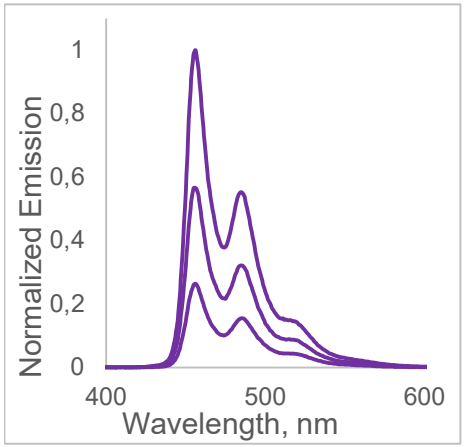


Figure S74. Normalized emission spectra of **9b** at different concentrations in hexane solution

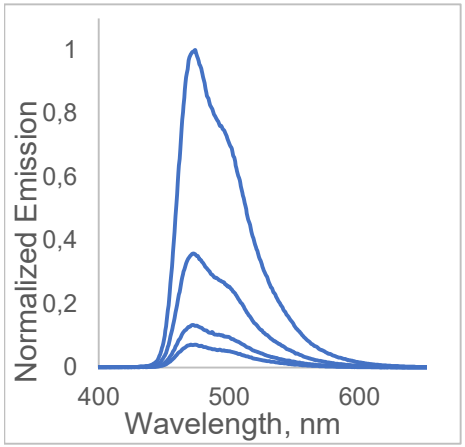


Figure S75. Normalized emission spectra of **9b** at different concentrations in $CHCl_3$ solution

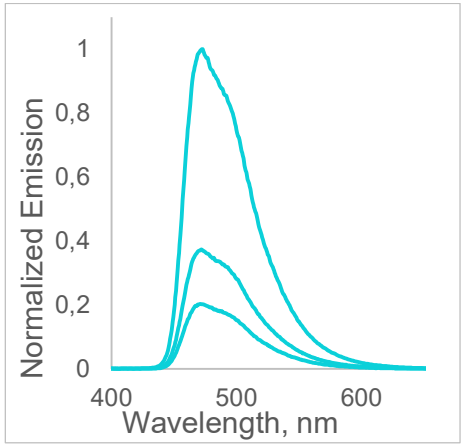


Figure S76. Normalized emission spectra of **9b** at different concentrations in MeCN solution

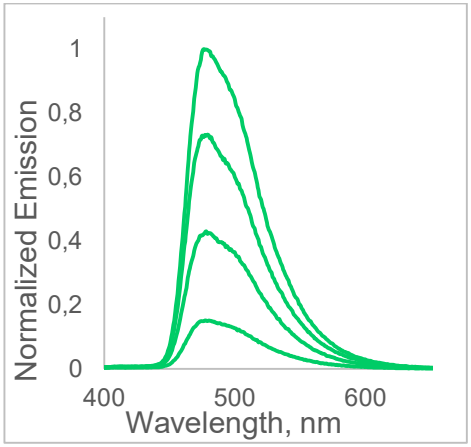


Figure S77. Normalized emission spectra of **9b** at different concentrations in DMSO solution

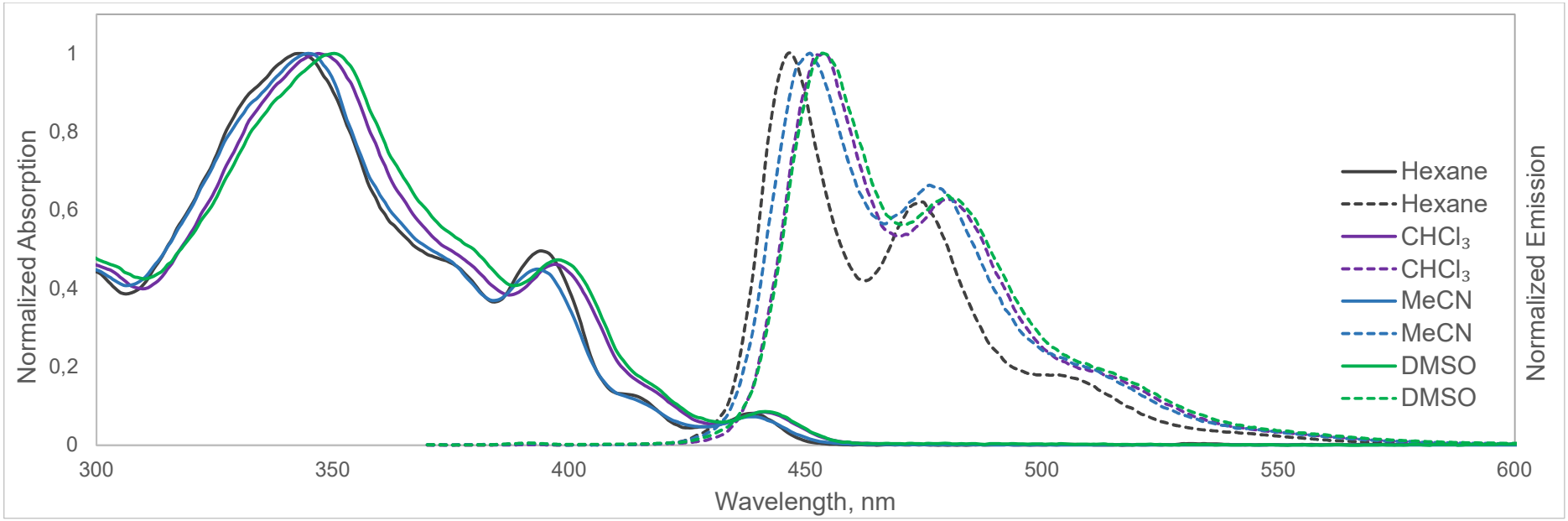


Figure S78. Normalized absorption (solid line) and emission spectra (dashed line) of **9c** in different solvents (λ_{ex} = 350 nm). The absorption spectra were normalized to the maximum at ~350 nm

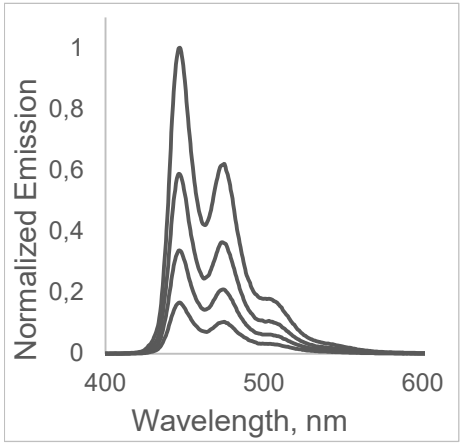


Figure S79. Normalized emission spectra of **9c** at different concentrations in hexane solution

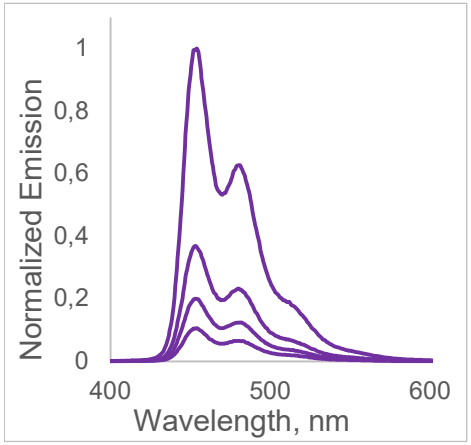


Figure S80. Normalized emission spectra of **9c** at different concentrations in $CHCl_3$ solution

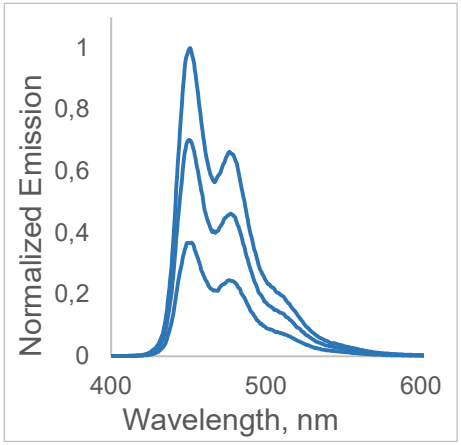


Figure S81. Normalized emission spectra of **9c** at different concentrations in MeCN solution

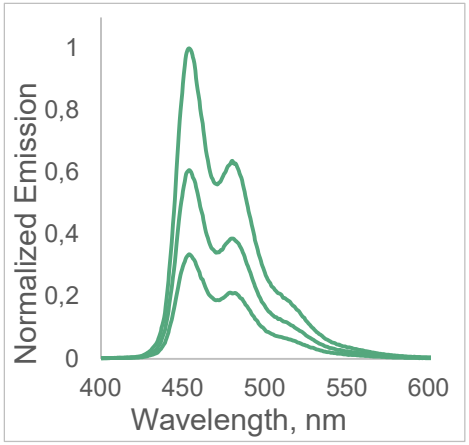


Figure S82. Normalized emission spectra of **9c** at different concentrations in DMSO solution

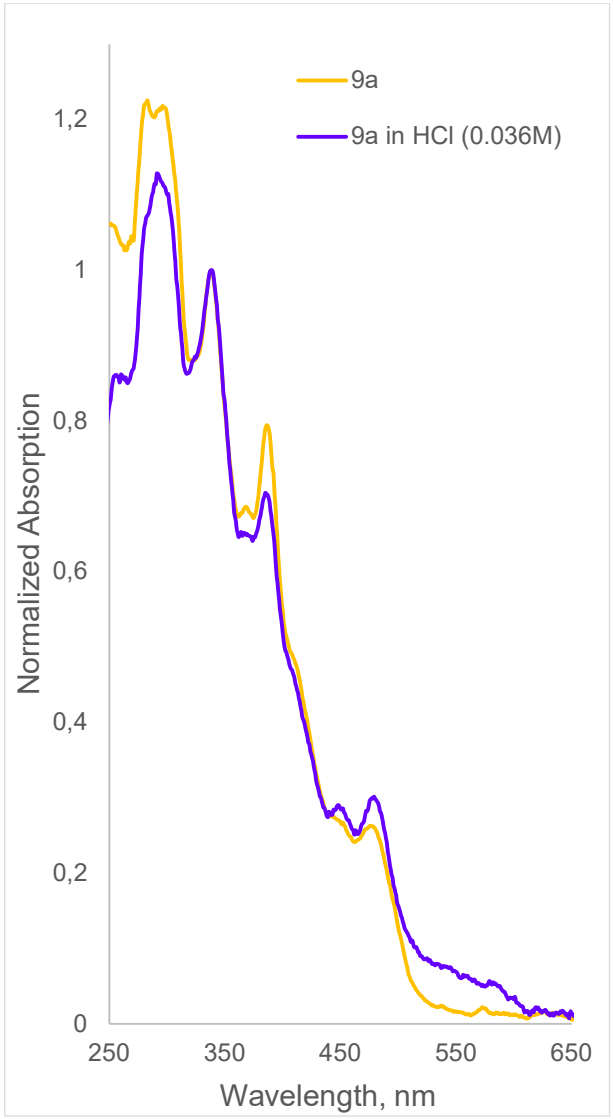


Figure S83. Normalized absorption spectrum of **9a** in MeCN (orange) and acidified MeCN (purple)

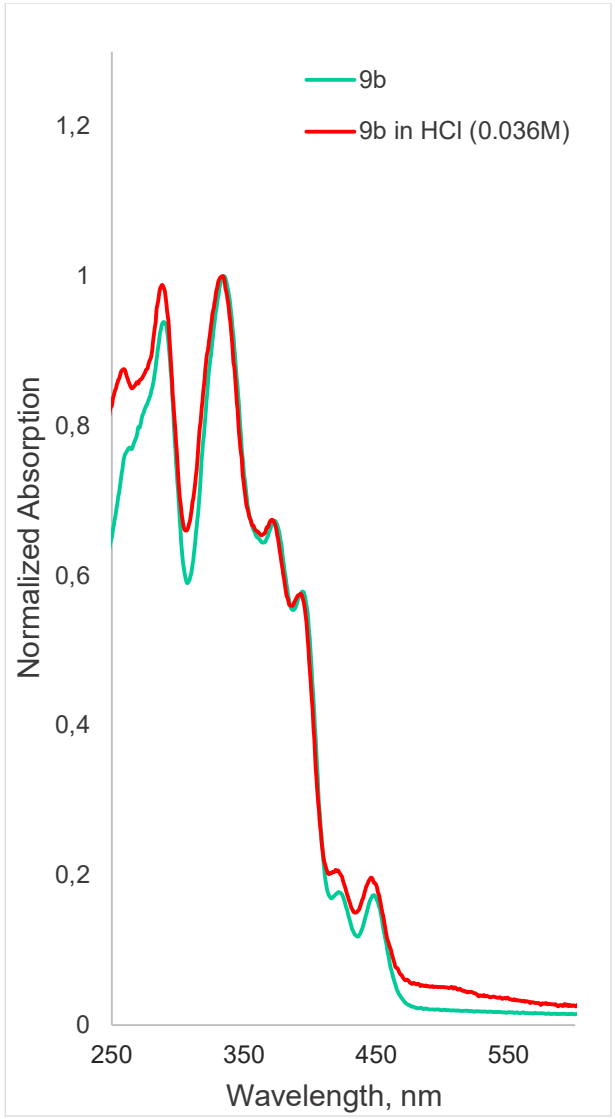


Figure S84. Normalized absorption spectrum of **9b** in MeCN (turquoise) and acidified MeCN (red)

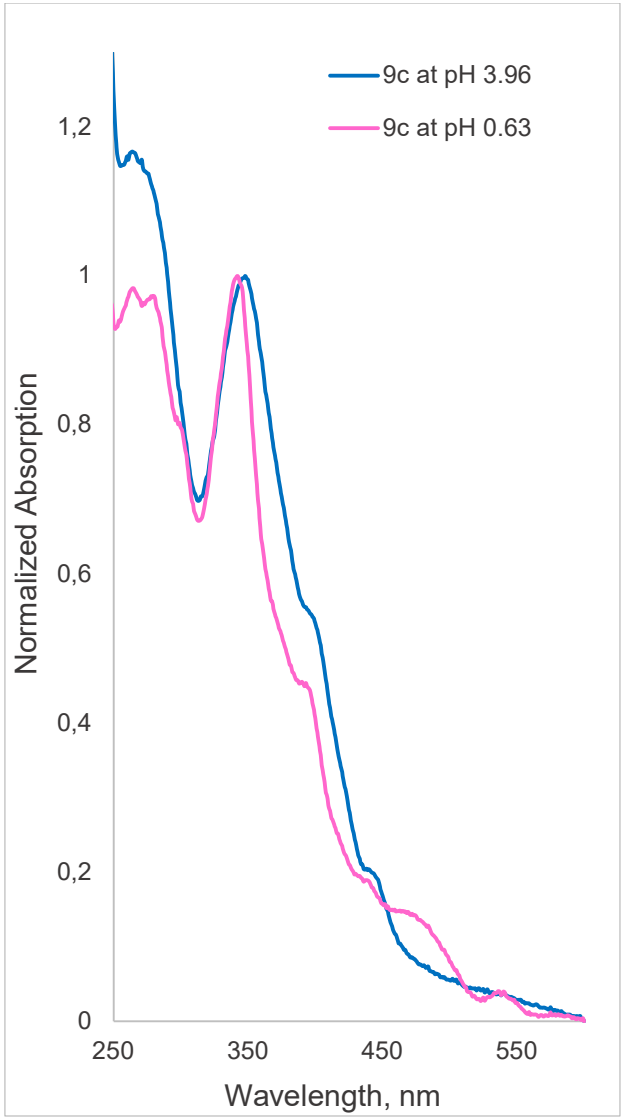


Figure S85. Normalized absorption spectrum of **9c** in MeCN at pH 3.96 (blue) and at pH 0.63 (pink)

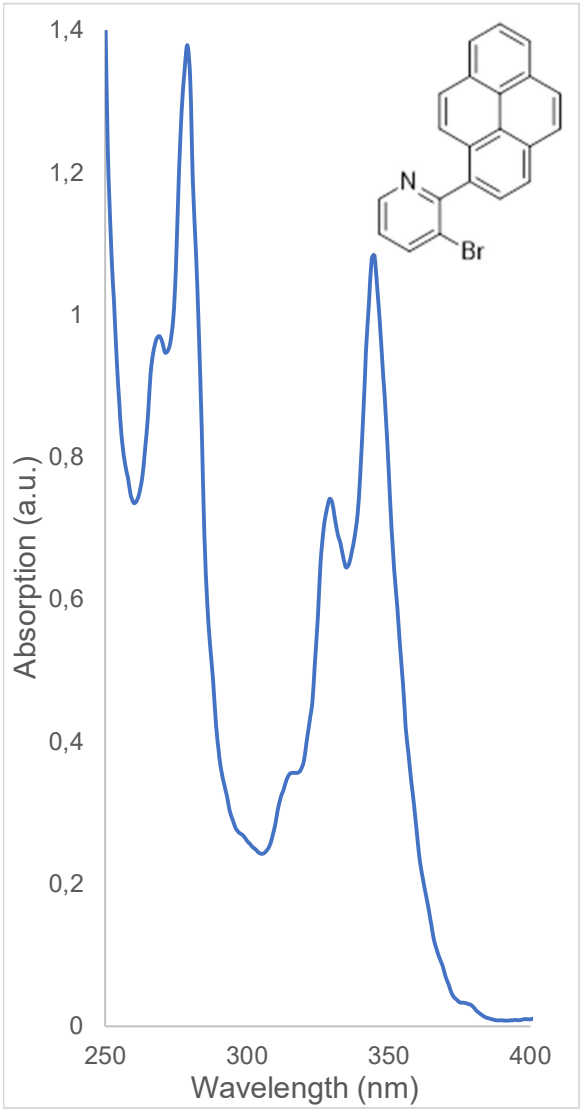


Figure S86. Absorption spectrum of **4** in $CHCl_3$

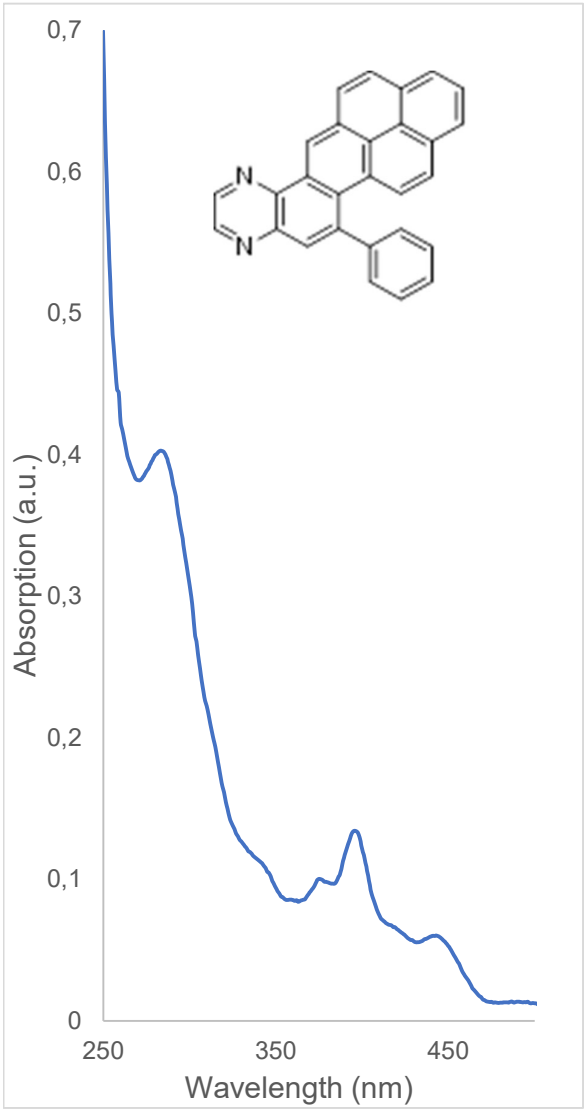


Figure S87. Absorption spectrum of **6b** in $CHCl_3$

References

1. K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oishic, S. Tobita, *Phys. Chem. Chem. Phys.,* 2009, **11**, 9850–9860.
2. C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, *Nature protocols,* 2013, **8**, 1535–1550.
3. A. Kowalczyk, N. Boens, V. Van den Bergh, F. C. De Schryver, *J. Phys. Chem*., 1994, **98**, 8585–8590.
4. A. V. Gulevskaya, E. A. Shvydkova, D. I. Tonkoglazova, *Eur. J. Org. Chem,* 2018, 5030–5043.