



## Supporting Information

for

### **Synthesis, crystal structures and properties of carbazole-based [6]helicenes fused with an azine ring**

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**Experimental procedures and analytical data, copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all new compounds, X-ray data for 9c and 10a–c, HPLC spectra of helicenes 10a–c, UV–vis and fluorescence spectra of 10a–c**

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## Experimental section

**General information:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 250 MHz spectrometer (Bruker DPX-250). Chemical shifts were reported in ppm relative to  $\text{Me}_4\text{Si}$ . The UV-vis spectra were recorded on a Varian Cary 50 Probe spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer. 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. Flash column chromatography was performed on silica gel (70–230 mesh, Aldrich). Reactions were monitored by thin layer chromatography (silica gel 60  $\text{F}_{254}$ ) and visualized using UV. Commercial alkynes, 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole, catalysts, ICl, 2,3-dihaloazines, diisopropylamine, triethylamine,  $\text{PPh}_3$ , TFA, triflic acid, anhydrous DMSO, THF were used as received.

**9-Ethyl-3-(3-(phenylethynyl)quinoxalin-2-yl)-9*H*-carbazole (2a):** A stirred mixture of 2-chloro-3-(phenylethynyl)quinoxaline **1a** [1] (132 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (161 mg, 0.5 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (58 mg, 0.05 mmol),  $\text{K}_2\text{CO}_3$  (345 mg, 2.5 mmol), 1,4-dioxane (8 mL) and water (4 mL) was heated at 100 °C for 17 h under argon. After evaporation of the reaction mixture the residue was diluted with water (50 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15$  mL). The extract was dried over  $\text{Na}_2\text{SO}_4$ . Flash column chromatography was carried out on silica gel ( $3.5 \times 50$  cm) using  $\text{CH}_2\text{Cl}_2$  as the eluent. The yellow fraction with  $R_f$  0.45 gave compound **2a** (203 mg, 96%). Compound **2a** was obtained as lemon yellow needles with mp 158–160 °C (EtOH).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.47 (t,  $J$  = 7.1 Hz, 3 H), 4.42 (q,  $J$  = 7.1 Hz, 2 H), 7.21–7.35 (m, 4 H), 7.43–7.57 (m, 5 H), 7.70–7.78 (m, 2 H), 8.12–8.18 (m, 3 H), 8.29 (dd,  $J$  = 8.6, 1.4 Hz, 1 H), 9.03 (d,  $J$  = 1.0 Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 37.8, 89.3, 94.9, 108.4, 108.8, 119.4, 120.8, 121.9, 122.4, 122.7, 123.2, 126.1, 127.9, 128.2, 128.5, 128.8, 129.2, 129.5, 129.8, 130.6, 132.3, 138.3, 140.6, 140.7, 140.9, 141.1, 155.5 ppm. HRMS (ESI):  $\text{MH}^+$ , found 424.1815.  $\text{C}_{30}\text{H}_{22}\text{N}_3$  requires 424.1808.  $\text{M}+\text{Na}^+$ , found 446.1633.  $\text{C}_{30}\text{H}_{21}\text{N}_3\text{Na}$  requires 446.1628.

Another catalytic systems, *e.g.*  $\text{Pd}(\text{PPh}_3)_4/\text{K}_3\text{PO}_4/\text{THF}$  (80 °C, 24 h, 36% yield) and  $\text{Pd}(\text{PPh}_3)_4/\text{K}_3\text{PO}_4/1,4\text{-dioxane}$  (100 °C, 24 h, 44% yield), were less effective.

**9-Ethyl-3-(3-(phenylethynyl)pyrazin-2-yl)-9H-carbazole (2b):** Synthesis of compound **2b** was carried out similarly to **2a** from 2-chloro-3-(phenylethynyl)pyrazine **1b** [1] (108 mg, 0.5 mmol). Flash column chromatography was performed on silica gel (2 × 20 cm) using ethylacetate - petroleum ether (1:3, v/v) as the eluent. From the yellow fraction with  $R_f$  0.2–0.3 compound **2b** was isolated (153 mg, 82%). Compound **2b** was obtained as yellowish solid with mp 133–135 °C (CH<sub>3</sub>CN). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.52 (t,  $J$  = 7.2 Hz, 3 H), 4.47 (q,  $J$  = 7.2 Hz, 2 H), 7.26–7.40 (m, 4 H), 7.48–7.59 (m, 5 H), 8.14 (d,  $J$  = 7.7 Hz, 1 H), 8.28 (dd,  $J$  = 8.6, 1.7 Hz, 1 H), 8.54 (d,  $J$  = 2.3 Hz, 1 H), 8.64 (d,  $J$  = 2.3 Hz, 1 H), 9.02 (d,  $J$  = 1.6 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>)  $\delta$  11.1, 35.0, 85.5, 91.5, 105.4, 106.0, 116.6, 117.8, 119.1, 119.2, 119.9, 120.4, 123.2, 124.5, 124.7, 125.6, 126.5, 129.2, 134.2, 137.7, 138.1, 138.6, 139.5, 153.3 ppm. HRMS (ESI): MH<sup>+</sup>, found 374.1666. C<sub>26</sub>H<sub>20</sub>N<sub>3</sub> requires 374.1652. M+Na<sup>+</sup>, found 396.1484. C<sub>26</sub>H<sub>19</sub>N<sub>3</sub>Na requires 396.1471.

**3-(3-Chloroquinoxalin-2-yl)-9-ethyl-9H-carbazole (4a)** was synthesized in a similar manner as described in [1]. A stirred mixture of 2,3-dichloroquinoxaline **3a** (100 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (193 mg, 0.6 mmol), 5% Pd/C (32 mg, 0.015 mmol), PPh<sub>3</sub> (16 mg, 0.06 mmol), 2M aqueous solution K<sub>2</sub>CO<sub>3</sub> (2 mL) and toluene (1 mL) was heated at 100 °C for 24 h under argon. The reaction mixture was then extracted with CHCl<sub>3</sub> (3 × 20 mL). The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and purified by flash column chromatography on silica gel (3.5 × 45 cm) with CHCl<sub>3</sub> as the eluent. The first and second fractions were recovered starting materials: 43 mg (43%) of **3a** and 142 mg (73%) of the boronic acid. The fraction with  $R_f$  0.6 gave compound **4a** (28 mg, 15%). Compound **4a** was obtained as lemon yellow crystals with mp 120–122 °C (EtOH). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.51 (t,  $J$  = 7.2 Hz, 3 H), 4.47 (q,  $J$  = 7.2 Hz, 2 H), 7.31–7.34 (m, 1 H), 7.47–7.59 (m, 3 H), 7.78–7.85 (m, 2 H), 8.04–8.12 (m, 2 H), 8.19–8.22 (m, 2 H), 8.70 (d,  $J$  = 1.2 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>)  $\delta$  13.9, 37.8, 108.3, 108.8, 119.5, 120.8, 122.5, 122.9, 123.1, 126.2, 126.4, 127.3, 127.5, 128.1, 129.2, 130.4 (2C), 140.6, 140.7, 140.8, 141.3, 153.8 ppm. HRMS (ESI): MH<sup>+</sup>, found 358.1107 (<sup>35</sup>Cl); 360.1081 (<sup>37</sup>Cl). C<sub>22</sub>H<sub>17</sub>ClN<sub>3</sub> requires 358.1106 (<sup>35</sup>Cl); 360.1078 (<sup>37</sup>Cl). M+Na<sup>+</sup>, found 380.0924 (<sup>35</sup>Cl); 382.0902 (<sup>37</sup>Cl). C<sub>22</sub>H<sub>16</sub>ClN<sub>3</sub>Na requires 380.0925 (<sup>35</sup>Cl); 382.0897 (<sup>37</sup>Cl).

**3-(3-Bromopyridin-2-yl)-9-ethyl-9H-carbazole (4b) and 3,3'-(pyridine-2,3-diyl)bis(9-ethyl-9H-carbazole) (5b).** A stirred mixture of 2,3-dibromopyridine **3b** (119 mg, 0.5 mmol), 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (161 mg, 0.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58

mg, 0.05 mmol), K<sub>2</sub>CO<sub>3</sub> (345 mg, 2.5 mmol), 1,4-dioxane (8 mL) and water (4 mL) was heated at 100 °C for 17 h under argon. After evaporation of the reaction mixture the residue was diluted with water (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The extract was dried over Na<sub>2</sub>SO<sub>4</sub>. Flash column chromatography on silica gel (3.5 × 55 cm) was then carried out using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. From the colorless fraction with *R<sub>f</sub>* 0.3 compound **4b** was isolated (142 mg, 80%). The yellowish fraction with *R<sub>f</sub>* 0.2 gave compound **5b** (20 mg, 8%).

**3-(3-Bromopyridin-2-yl)-9-ethyl-9H-carbazole (4b).** Yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.52 (t, *J* = 7.1 Hz, 3 H), 4.46 (q, *J* = 7.1 Hz, 2 H), 7.17 (dd, *J* = 8.0, 4.6 Hz, 1 H), 7.28–7.34 (m, 1 H), 7.47–7.58 (m, 3 H), 7.91 (d, *J* = 8.5 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 7.7 Hz, 1 H), 8.55 (s, 1 H), 8.72 (d, *J* = 4.6 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 13.9, 37.7, 107.9, 108.7, 119.2, 120.1, 120.7, 121.9, 122.6, 122.7, 123.3, 125.9, 127.3, 130.4, 140.2, 140.5, 141.4, 148.1, 159.0 ppm. HRMS (ESI): MH<sup>+</sup> (<sup>81</sup>Br), found 353.0476; MH<sup>+</sup> (<sup>79</sup>Br), found 351.0497. C<sub>19</sub>H<sub>16</sub>BrN<sub>2</sub> requires 353.0472 (<sup>81</sup>Br), 351.0491 (<sup>79</sup>Br).

**3,3'-(Pyridine-2,3-diyl)bis(9-ethyl-9H-carbazole) (5b).** Yellowish oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.38 (t, *J* = 7.2 Hz, 3 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 7.12–7.27 (m, 5 H), 7.34–7.52 (m, 6 H), 7.90 (dd, *J* = 7.7, 1.6 Hz, 1 H), 7.97 (d, *J* = 7.7 Hz, 1 H), 8.05 (d, *J* = 7.7 Hz, 1 H), 8.12 (br s, 1 H), 8.38 (d, *J* = 1.3 Hz, 1 H), 8.77 (dd, *J* = 4.7, 1.6 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 13.7(8), 13.8(0), 37.5(8), 37.6(2), 107.6, 108.2, 108.4, 108.6, 118.8, 118.9, 120.5, 120.6, 121.2, 121.5, 122.3, 122.9, 123.0, 123.2, 123.4, 125.5, 125.8, 127.8, 128.2, 131.4, 131.5, 136.7, 139.1, 139.2, 139.6, 140.3, 147.9, 158.1 ppm. HRMS (ESI): MH<sup>+</sup>, found 466.2287. C<sub>33</sub>H<sub>28</sub>N<sub>3</sub> requires 466.2278.

**9-Ethyl-3-(3-(phenylethynyl)pyridin-2-yl)-9H-carbazole (6)** was synthesized in a similar manner as described in [1]. A stirred mixture of 3-(3-bromopyridin-2-yl)-9-ethyl-9H-carbazole **4b** (92 mg, 0.25 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (18 mg, 0.025 mmol), CuI (2 mg, 0.01 mmol), *i*-Pr<sub>2</sub>NH (0.5 mL) and DMSO (2.5 mL) was heated at 80 °C for 20 min under argon. A solution of phenylacetylene (93 mg, 0.1 mL, 0.75 mmol) in *i*-Pr<sub>2</sub>NH (1 mL) was then added by portions for 1 h. The reaction mixture was stirred at 80 °C for 24 h, evaporated without heating to remove *i*-Pr<sub>2</sub>NH, treated with H<sub>2</sub>O (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by flash column chromatography on silica gel (3.5 × 30 cm) with CH<sub>2</sub>Cl<sub>2</sub> as the eluent. The fraction with *R<sub>f</sub>* 0.2 and violet fluorescence gave compound **6** (69 mg, 74%). Compound **6** was obtained as a yellow brown oil. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.55 (t, *J* = 7.2 Hz, 3 H), 4.50 (q, *J* = 7.2 Hz, 2 H), 7.27–7.37

(m, 5 H), 7.48–7.60 (m, 5 H), 8.04 (dd,  $J = 7.8, 1.7$  Hz, 1 H), 8.19 (d,  $J = 7.8$  Hz, 1 H), 8.30 (dd,  $J = 8.6, 1.7$  Hz, 1 H), 8.76 (dd,  $J = 4.8, 1.7$  Hz, 1 H), 9.01 (d,  $J = 1.4$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.9, 37.8, 88.5, 94.4, 108.0, 108.7, 117.5, 119.2, 120.6, 120.7, 121.8, 122.6, 123.1, 123.4, 125.7, 127.5, 128.4, 128.5, 130.2, 131.5, 140.4(9), 140.5(2), 141.0, 148.6, 160.2$  ppm. HRMS (ESI):  $\text{MH}^+$ , found 373.1711.  $\text{C}_{27}\text{H}_{21}\text{N}_2$  requires 373.1699.

**1-Ethyl-7-iodo-6-phenyl-1*H*-carbazolo[3,4-*a*]phenazine (7a)** was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)quinoxalin-2-yl)-9*H*-carbazole **2a** (85 mg, 0.2 mmol) in dry  $\text{CH}_3\text{CN}$  (17 mL) a solution of ICl (33 mg, 0.2 mmol) in dry  $\text{CH}_3\text{CN}$  (2 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark. The yellow orange needles precipitate of **7a** (48 mg) was filtered off and washed on the filter with  $\text{CH}_3\text{CN}$  (2 mL). The filtrate was then evaporated to dryness. The residue was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL) and saturated  $\text{Na}_2\text{S}_2\text{O}_3$  solution (5 mL). The organic layer was separated and dried over  $\text{Na}_2\text{SO}_4$  and purified by flash column chromatography on silica gel ( $2.5 \times 55$  cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The bright yellow orange fraction with  $R_f$  0.85 gave 24 mg of cyclization product **7a**. Total yield was 72 mg (65%). 1-Ethyl-7-iodo-6-phenyl-1*H*-carbazolo[3,4-*a*]phenazine **7a** was obtained as yellow orange needles with mp 248–250 °C (EtOH).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.50$  (t,  $J = 7.2$  Hz, 3 H), 4.52 (q,  $J = 7.2$  Hz, 2 H), 6.29 (d,  $J = 8.4$  Hz, 1 H), 6.63 (ddd,  $J = 8.2, 7.0, 1.2$  Hz, 1 H), 7.27–7.30 (m, 1 H), 7.37 (d,  $J = 7.9$  Hz, 1 H), 7.43–7.52 (m, 3 H), 7.63–7.66 (m, 2 H), 7.82–7.92 (m, 2 H), 7.95 (d,  $J = 9.0$  Hz, 1 H), 8.38–8.47 (m, 2 H), 9.81 (d,  $J = 9.0$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 37.8, 107.9, 110.8, 112.2, 118.0, 118.8, 123.3, 124.4, 124.8, 125.4, 128.5, 128.8, 128.9, 129.5, 129.6, 129.9, 130.6, 132.5, 139.5, 141.5, 141.6, 142.5, 142.6, 143.0 (2C), 146.4, 149.0 ppm. HRMS (ESI):  $\text{MH}^+$ , found 550.0785.  $\text{C}_{30}\text{H}_{21}\text{IN}_3$  requires 550.0775.  $\text{M}+\text{Na}^+$ , found 572.0584.  $\text{C}_{30}\text{H}_{20}\text{IN}_3\text{Na}$  requires 550.0594.

When using a 1.5-fold excess of ICl, a hardly separable mixture of **7a** and its 4-iodo derivative **8a** in a 7.7:1 ratio was obtained.

**7-Ethyl-13-iodo-12-phenyl-7*H*-quinoxalino[5,6-*c*]carbazole (7b)** was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)pyrazin-2-yl)-9*H*-carbazole **2b** (59 mg, 0.16 mmol) in dry  $\text{CH}_3\text{CN}$  (2 mL) a solution of ICl (15 mg, 0.09 mmol) in dry  $\text{CH}_3\text{CN}$  (1.5 mL) was added. After 1 h, the next portion of the solution of ICl (5 mg, 0.03 mmol) in dry  $\text{CH}_3\text{CN}$  (1.5 mL) was added. The stirred

reaction mixture was kept at room temperature for 20 h in the dark and then evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (5 mL). The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The extract was purified by flash column chromatography on silica gel (2 × 25 cm) with ethyl acetate - petroleum ether (1:3, v/v) as the eluent. The yellow fraction with *R<sub>f</sub>* 0.45 gave 46 mg (75%) of cyclization product **7b**. 7-Ethyl-13-iodo-12-phenyl-7*H*-quinoxalino[5,6-*c*]carbazole **7b** was obtained as yellow needles with mp 217–219 °C (EtOH). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.49 (t, *J* = 7.2 Hz, 3 H), 4.51 (q, *J* = 7.2 Hz, 2 H), 6.20 (d, *J* = 8.5 Hz, 1 H), 6.67 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1 H), 7.31 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1 H), 7.42 (d, *J* = 7.9 Hz, 1 H), 7.48–7.65 (m, 5 H), 7.98 (d, *J* = 9.0 Hz, 1 H), 8.90 (d, *J* = 1.8 Hz, 1 H), 8.97 (d, *J* = 1.8 Hz, 1 H), 9.62 (d, *J* = 9.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 13.9, 37.7, 107.9, 111.3, 111.7, 116.8, 118.8, 123.4, 123.6, 124.5, 125.3, 126.0, 128.6, 128.8, 130.0, 132.5, 139.1, 140.4, 141.3, 141.7, 143.9, 144.0, 146.7, 147.4 ppm. HRMS (ESI): MH<sup>+</sup>, found 500.0625. C<sub>26</sub>H<sub>19</sub>IN<sub>3</sub> requires 500.0618.

When using equimolar amount of ICl, a hardly separable mixture of **7b** and its 4-iodo derivative **8b** in a 10:1 ratio (69% total yield) was obtained.

**7-Ethyl-10,13-diiodo-12-phenyl-7*H*-quinoxalino[5,6-*c*]carbazole (**8b**):** To a suspension of 7-ethyl-13-iodo-12-phenyl-7*H*-quinoxalino[5,6-*c*]carbazole **7b** (25 mg, 0.05 mmol) in dry CH<sub>3</sub>CN (4 mL), a solution of ICl (24 mg, 0.15 mmol) in dry CH<sub>3</sub>CN (2 mL) was added. The reaction mixture was stirred at room temperature for 24 h in the dark. After evaporation in air without heating the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (5 mL). The extract dried over Na<sub>2</sub>SO<sub>4</sub> and purified by flash column chromatography on silica gel (2 × 25 cm) using a mixture of ethyl acetate - petroleum ether (1:3, v/v) as the eluent. The cyclization product **8b** (30 mg, 97%) was isolated from the yellow fraction with *R<sub>f</sub>* 0.5. Compound **8b** was obtained as a yellow solid with mp 254–255 °C (EtOH). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.51 (t, *J* = 7.2 Hz, 3 H), 4.53 (q, *J* = 7.2 Hz, 2 H), 6.44 (d, *J* = 1.4 Hz, 1 H), 7.18 (d, *J* = 8.7 Hz, 1 H), 7.55–7.62 (m, 5 H), 7.66–7.75 (m, 1 H), 7.97 (d, *J* = 9.0 Hz, 1 H), 8.92 (d, *J* = 1.8 Hz, 1 H), 8.99 (d, *J* = 1.8 Hz, 1 H), 9.66 (d, *J* = 9.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 13.8, 37.8, 83.0, 109.9, 111.3, 111.9, 115.8, 124.4, 125.1, 126.4, 128.9, 129.9, 130.0, 132.1, 133.1, 133.5, 138.2, 140.4, 141.1, 141.6, 144.0, 144.2, 145.9, 147.2 ppm. HRMS (ESI): MH<sup>+</sup>, found 625.9576. C<sub>26</sub>H<sub>18</sub>I<sub>2</sub>N<sub>3</sub> requires 625.9585.

**7-Ethyl-13-iodo-12-phenyl-7H-quinolino[8,7-*c*]carbazole (7c)** was synthesized in a similar manner as described in [1]. To a stirred suspension of 9-ethyl-3-(3-(phenylethynyl)pyridin-2-yl)-9H-carbazole **6** (74 mg, 0.2 mmol) in dry CH<sub>3</sub>CN (6 mL) a solution of ICl (52 mg, 0.3 mmol) in dry CH<sub>3</sub>CN (3 mL) was added. The reaction mixture was kept at room temperature for 24 h in the dark. The yellow orange needles precipitate of **7c** (51 mg) was filtered off and washed on the filter with CH<sub>3</sub>CN (2 mL). The filtrate was then evaporated to dryness. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL). The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub> and purified by flash column chromatography on silica gel (2.5 × 25 cm) with CH<sub>2</sub>Cl<sub>2</sub> as the eluent. The yellow fraction with *R<sub>f</sub>* 0.7 gave 11 mg of cyclization product **7c**. Total yield of **7c** was 62 mg (62%). Compound **7c** was obtained as yellow needles with mp 196–197 °C. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.55 (t, *J* = 7.0 Hz, 3 H), 4.58 (q, *J* = 7.0 Hz, 2 H), 6.25 (d, *J* = 8.4 Hz, 1 H), 6.68 (t, *J* = 7.6 Hz, 1 H), 7.28–7.34 (m, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.52–7.65 (m, 6 H), 7.99 (d, *J* = 9.0 Hz, 1 H), 8.81 (d, *J* = 8.2 Hz, 1 H), 9.01 (d, *J* = 3.4 Hz, 1 H), 9.78 (d, *J* = 9.0 Hz, 1 H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 13.9, 37.7, 107.8, 108.6, 110.9, 116.5, 118.5, 122.0, 123.6, 124.0, 124.1, 125.2, 126.8, 127.3, 128.5, 128.6, 129.9, 132.8, 139.0, 141.4, 142.8, 143.7, 146.4, 147.7, 149.4 ppm. HRMS (ESI): MH<sup>+</sup>, found 499.0681. C<sub>27</sub>H<sub>19</sub>IN<sub>2</sub> requires 499.0666.

**1-Ethyl-6-phenyl-7-(*p*-tolylethynyl)-1H-carbazolo[3,4-*a*]phenazine (9a):** A stirred mixture of 1-ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-*a*]phenazine **7a** (110 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (14 mg, 0.02 mmol), CuI (2 mg, 0.01 mmol), Et<sub>3</sub>N (3 mL) and dry THF (5 mL) was heated at 85 °C for 20 min under argon. A solution of *p*-tolylacetylene (35 mg, 0.3 mmol) and Et<sub>3</sub>N (2 mL) in dry THF (2 mL) was then added by portions for 3 h. The reaction mixture was stirred for total 24 h at 85 °C. After subsequent evaporation, the residue was treated with H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 mL). The extract was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Flash column chromatography on silica gel (3.5 × 55 cm) was then carried out using CH<sub>2</sub>Cl<sub>3</sub> as the eluent. The yellow orange fraction with *R<sub>f</sub>* 0.6 (yellow fluorescence under UV 356 nm) gave 90 mg (84%) of compound **9a**. The product was then heated with hexane (3 mL) for crystallization and filtered off. 1-Ethyl-7-iodo-6-phenyl-1H-carbazolo[3,4-*a*]phenazine **9a** was obtained as orange needles with orange fluorescence in the solid state under UV (356 nm) and mp 214–217 °C (ethyl acetate - petroleum ether, 1:3, v/v). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.54 (t, *J* = 7.1 Hz, 3 H), 2.41 (s, 3 H), 4.56 (q, *J* = 7.1 Hz, 2 H), 6.42 (d, *J* = 8.4 Hz, 1 H), 6.70 (ddd, *J* = 8.0, 6.7, 1.0 Hz, 1 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 7.27–7.34 (m, 1 H), 7.36–7.45 (m, 3 H), 7.46–7.55 (m, 3 H), 7.82–8.00 (m, 5 H), 8.39–8.44 (m, 1 H),



8.46–8.50 (m, 1 H), 9.81 (d,  $J = 8.9$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.8, 21.7, 37.7, 87.8, 100.1, 107.9, 110.7, 118.5, 118.8, 120.9, 121.6, 123.4, 123.9, 124.7, 125.5, 125.6, 128.2, 128.4, 129.0, 129.2, 129.3, 129.6, 130.0, 130.1, 131.7, 131.9, 138.4, 139.5, 141.5, 141.8, 142.2, 142.4, 142.5, 142.6, 146.3$  ppm. HRMS (ESI):  $\text{MH}^+$ , found 538.2265.  $\text{C}_{39}\text{H}_{28}\text{N}_3$  requires 538.2278.

**7-Ethyl-12-phenyl-13-(*p*-tolylethynyl)-7*H*-quinoxalino[5,6-*c*]carbazole (9b):** A stirred mixture of 7-ethyl-13-iodo-12-phenyl-7*H*-quinoxalino[5,6-*c*]carbazole **7b** (50 mg, 0.1 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (7 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol),  $\text{Et}_3\text{N}$  (3 mL) was heated at 85 °C for 20 min under argon. A solution of *p*-tolylacetylene (23 mg, 0.2 mmol) in  $\text{Et}_3\text{N}$  (1.6 mL) was then dropped for 3 h. The reaction mixture was stirred at 85 °C for total 24 h. followed by evaporation. The residue was then diluted with  $\text{H}_2\text{O}$  (50 mL) and extracted with  $\text{CHCl}_3$  ( $3 \times 10$  mL). The extract was dried over  $\text{Na}_2\text{SO}_4$ . Flash column chromatography on silica gel ( $2 \times 20$  cm) was carried out using a mixture of ethyl acetate - petroleum ether (1:3, v/v) as the eluent. Compound **9b** (40 mg, 82%) was isolated from the yellow fraction with  $R_f$  0.3 (yellow-green fluorescence under UV 356 nm). Compound **9b** was synthesized as yellow plates with green fluorescence in the solid state under UV (356 nm) and mp 152–154 °C (hexane).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.54$  (t,  $J = 7.2$  Hz, 3 H), 2.38 (s, 3 H), 4.57 (q,  $J = 7.2$  Hz, 2 H), 6.28 (d,  $J = 8.5$  Hz, 1 H), 6.69 (ddd,  $J = 8.1, 7.3, 0.8$  Hz, 1 H), 7.14 (d,  $J = 7.9$  Hz, 2 H), 7.28–7.36 (m, 3 H), 7.42–7.53 (m, 4 H), 7.78–7.82 (m, 2 H), 7.99 (d,  $J = 9.0$  Hz, 1 H), 9.03 (dd,  $J = 4.1, 1.9$  Hz, 2 H), 9.59 (d,  $J = 9.0$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.0, 21.6, 37.8, 88.5, 101.2, 108.0, 111.6, 117.3, 118.9, 120.3, 121.4, 123.1, 123.3, 124.6, 125.4, 125.7, 128.4, 128.6, 129.0, 129.6, 131.9, 132.0, 138.9, 139.2, 140.6, 141.4, 141.6, 141.9, 143.4, 144.0, 145.6$  ppm. HRMS (ESI):  $\text{MH}^+$ , found 488.2099.  $\text{C}_{35}\text{H}_{26}\text{N}_3$  requires 488.2121.  $\text{M}+\text{Na}^+$ , found 510.1916.  $\text{C}_{35}\text{H}_{25}\text{N}_3\text{Na}$  requires 510.1946.

**7-Ethyl-12-phenyl-13-(*p*-tolylethynyl)-7*H*-quinolino[8,7-*c*]carbazole (9c):** Compound **9c** was obtained similarly to **9a** starting from **7c** (50 mg, 0.1 mmol). The reaction was carried out at 80–82 °C. Flash column chromatography was carried out on silica gel ( $3.5 \times 45$  cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The yellow fraction with  $R_f$  0.6 and light blue fluorescence under UV (356 nm) gave compound **9c** (43 mg, 88%) as yellow prisms ( $\text{CH}_2\text{Cl}_2$ ) with mp 210–212 °C (EtOH).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.53$  (t,  $J = 7.2$  Hz, 3 H), 2.40 (s, 3 H), 4.56 (q,  $J = 7.2$  Hz, 2 H), 6.36 (d,  $J = 8.3$  Hz, 1 H), 6.68

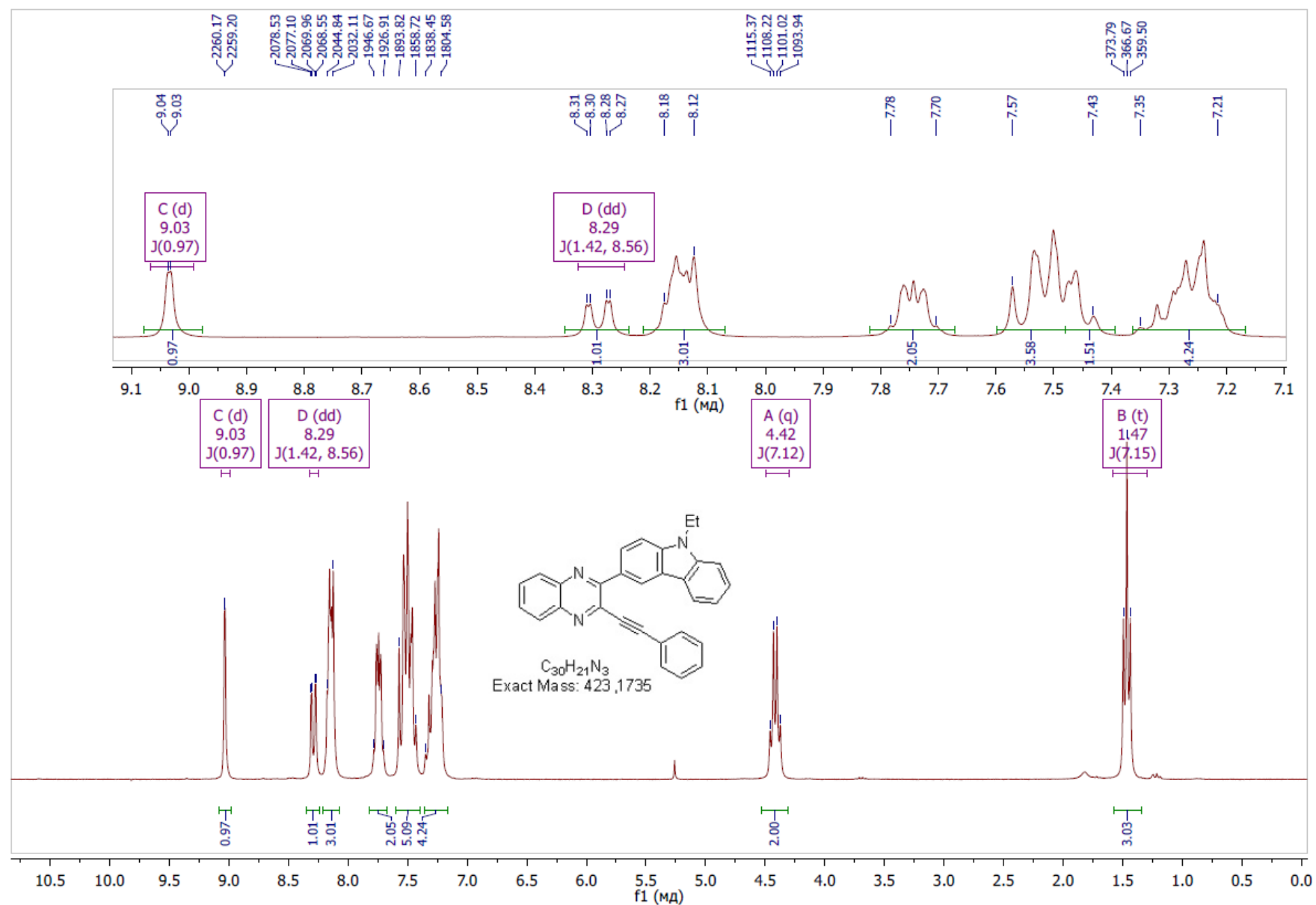
(ddd,  $J = 8.3, 7.0, 1.1$  Hz, 1 H), 7.18 (d,  $J = 7.9$  Hz, 2 H), 7.25–7.35 (m, 3 H), 7.42 (d,  $J = 8.1$  Hz, 1 H), 7.46–7.52 (m, 3 H), 7.63 (dd,  $J = 8.2, 4.4$  Hz, 1 H), 7.77–7.81 (m, 2 H), 7.96 (d,  $J = 9.1$  Hz, 1 H), 8.98 (dd,  $J = 8.2, 1.7$  Hz, 1 H), 9.10 (dd,  $J = 4.4, 1.7$  Hz, 1 H), 9.74 (d,  $J = 9.1$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.9, 21.6, 37.7, 87.6, 99.1, 107.9, 111.0, 117.1, 118.6, 119.8, 120.4, 121.1, 123.5, 123.6, 124.1, 124.5$  (2C), 125.4, 128.0, 128.2, 129.2, 129.7, 131.3, 132.1, 135.6, 138.6 (2C), 139.2, 141.3, 141.4, 142.2, 148.7 ppm. HRMS (ESI):  $\text{MH}^+$ , found 487.2180.  $\text{C}_{36}\text{H}_{27}\text{N}_2$  requires 487.2174.

**8-Ethyl-17-*p*-tolyl-8*H*-carbazolo[3,4-*a*]naphtho[1,2-*c*]phenazine (10a)** was synthesized in a similar manner as described in [1, compound **14c**]. To a solution of compound **9a** (54 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL)  $\text{CF}_3\text{SO}_3\text{H}$  (0.1 mL) was added. The dark red reaction mixture was kept at room temperature for 24 h in the dark. Then it was mixed with saturated aqueous  $\text{K}_2\text{CO}_3$  (50 mL) and separated in a separating funnel. The yellow  $\text{CH}_2\text{Cl}_2$  phase was dried over  $\text{Na}_2\text{SO}_4$  and purified by flash column chromatography on silica gel (2 × 50 cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The bright yellow fraction with  $R_f$  0.9 gave the cyclization product (50 mg, 92 %). Compound **10a** was obtained as a yellow orange solid with mp 294–295 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.61$  (t,  $J = 7.2$  Hz, 3 H), 2.58 (s, 3 H), 4.62 (q,  $J = 7.2$  Hz, 2 H), 6.71 (d,  $J = 8.1$  Hz, 1 H), 6.81 (t,  $J = 7.4$  Hz, 1 H), 7.18 (d,  $J = 7.8$  Hz, 1 H), 7.39 (d,  $J = 7.6$  Hz, 1 H), 7.46–7.52 (m, 4 H), 7.77 (d,  $J = 7.8$  Hz, 2 H), 7.81–7.90 (m, 2 H), 7.94 (d,  $J = 8.9$  Hz, 1 H), 8.20 (d,  $J = 8.3$  Hz, 1 H), 8.32–8.39 (m, 3 H), 9.48 (s, 1 H), 9.66 (d,  $J = 8.9$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.0, 21.4, 37.9, 108.2, 109.6, 118.0, 120.2, 122.7, 123.4, 123.8, 124.9, 125.3, 125.4, 125.7, 126.4, 126.9, 127.1, 128.8, 129.0, 129.1, 129.2$  (2C), 129.4, 129.5, 129.6, 130.3, 130.7, 132.4, 137.3, 137.8, 140.0, 140.7, 141.7, 141.8, 141.9, 142.2, 143.8 ppm. UV-vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  nm (lg  $\epsilon$ ): 264 (4.75), 303 (4.72), sh 324 (4.59), 357 (4.36), 374 (4.46), 433 (4.23), end absorption up to 507 nm. HRMS (ESI):  $\text{MH}^+$ , found 538.2285.  $\text{C}_{39}\text{H}_{28}\text{N}_3$  requires 538.2278.

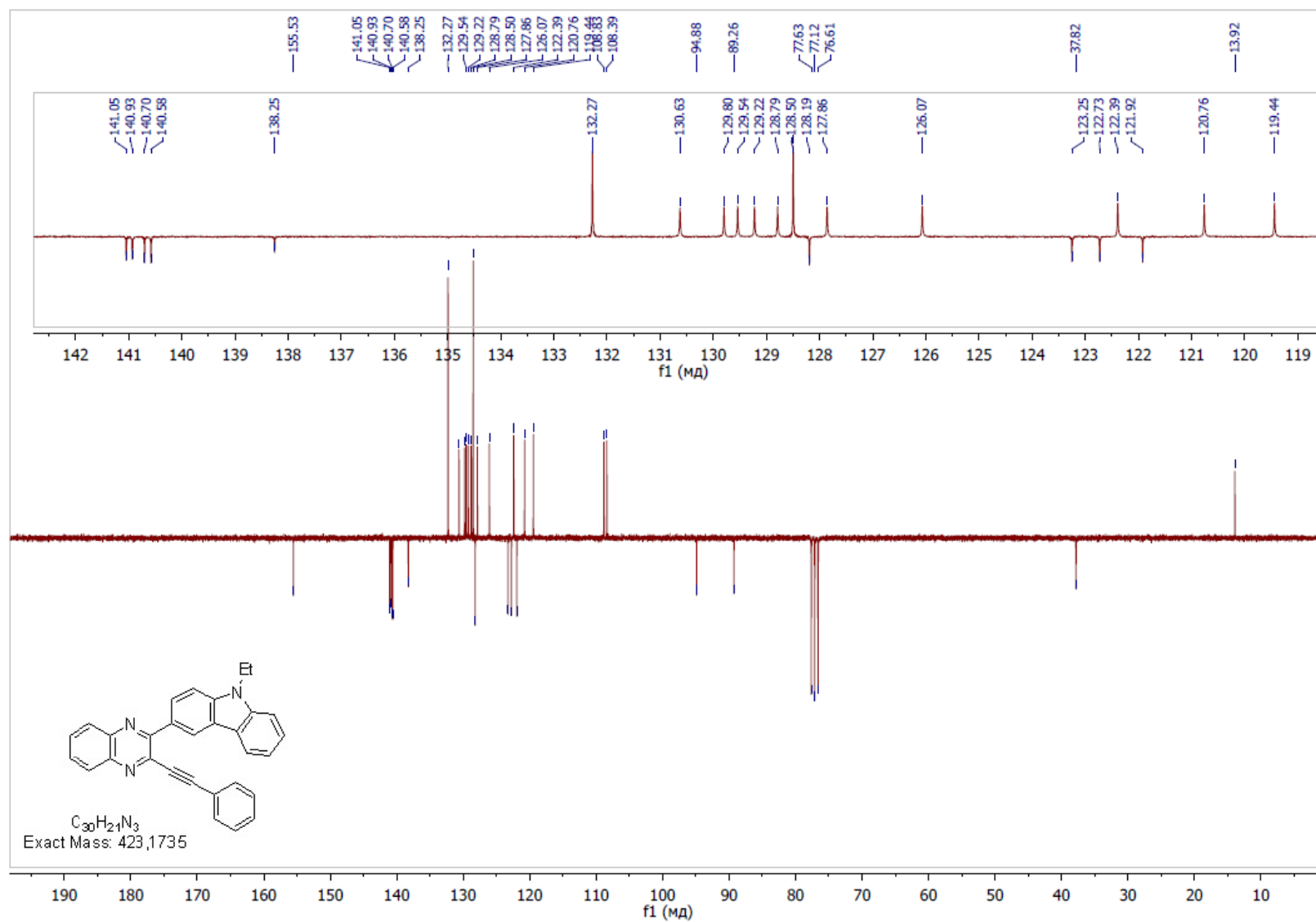
**7-Ethyl-16-*p*-tolyl-7*H*-naphtho[1',2';7,8]quinoxalino[5,6-*c*]carbazole (10b)**: Compound **10b** was obtained similarly to **10a** starting from 7-ethyl-12-phenyl-13-(*p*-tolylethynyl)-7*H*-quinoxalino[5,6-*c*]carbazole **9b** (49 mg, 0.1 mmol). Flash column chromatography was carried out on silica gel (2 × 40 cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The yellow fraction with  $R_f$  0.3 gave the cyclization product **10b** (40 mg, 82%) as a yellow orange solid with mp 225–227 °C (hexane).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.61$  (t,  $J = 7.2$  Hz, 3H), 2.56 (s, 3 H), 4.63 (q,  $J = 7.2$  Hz, 2H), 6.73 (d,  $J = 7.9$  Hz, 1 H), 6.80–

6.86 (m, 1 H), 7.18 (ddd,  $J = 8.1, 7.2, 0.9$  Hz, 1 H), 7.37–7.55 (m, 5 H), 7.76 (d,  $J = 7.9$  Hz, 2 H), 7.98 (d,  $J = 8.9$  Hz, 1 H), 8.21 (d,  $J = 8.2$  Hz, 1 H), 8.37 (d,  $J = 8.4$  Hz, 1 H), 8.90 (d,  $J = 2.0$  Hz, 1 H), 8.94 (d,  $J = 2.0$  Hz, 1 H), 9.30 (s, 1 H), 9.50 (d,  $J = 8.9$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.0, 21.4, 37.9, 108.3, 110.1, 118.0, 119.5, 121.8, 122.8, 123.4, 124.6, 125.1, 125.4, 125.7, 126.2, 126.4, 126.7, 127.6, 128.9, 129.0, 129.1, 130.3, 130.7, 131.8, 137.2, 137.7, 139.7, 140.1, 140.6, 141.3, 142.1, 142.7, 143.2$  ppm. UV-vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 294 (4.57), 323 (4.54), 359 (4.35), 397 (4.03), 418 nm (3.96). HRMS (ESI):  $\text{MH}^+$ , found 488.2120.  $\text{C}_{35}\text{H}_{26}\text{N}_3$  requires 488.2121.  $\text{M}+\text{Na}^+$ , found 510.1929.  $\text{C}_{35}\text{H}_{25}\text{N}_3\text{Na}$  requires 510.1946.

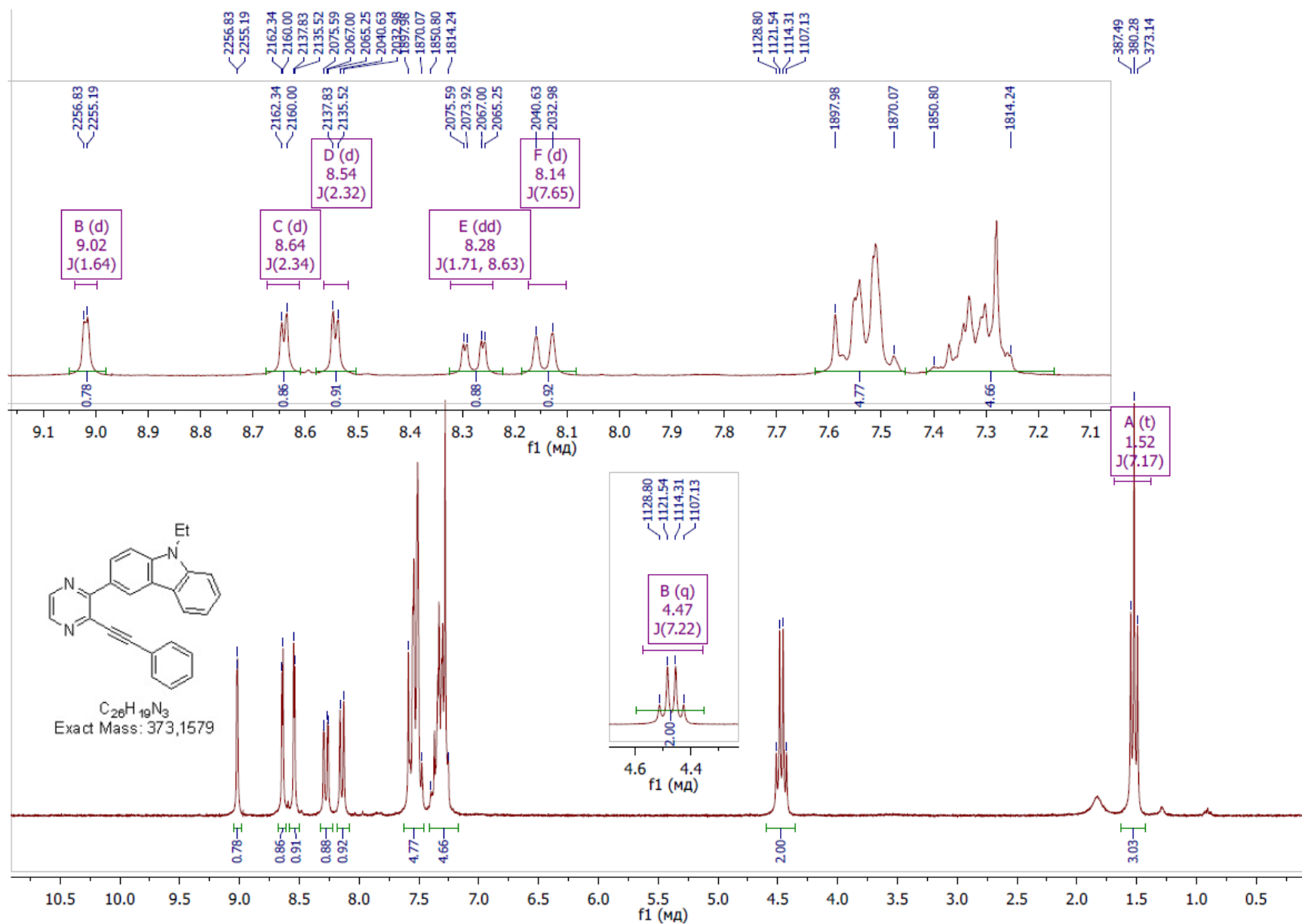
**7-Ethyl-16-*p*-tolyl-7*H*-naphtho[2',1';5,6]quinolino[8,7-*c*]carbazole (10c)** was synthesized in a similar manner as described in [1, compound **14a**]. A dark solution of 7-ethyl-12-phenyl-13-(*p*-tolylethynyl)-7*H*-quinolino[8,7-*c*]carbazole **9c** (49 mg, 0.1 mmol) in  $\text{CF}_3\text{COOH}$  (3 mL) was heated at 85 °C for 24 h. The reaction mixture was evaporated to dryness, treated with saturated  $\text{K}_2\text{CO}_3$  (2 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL), extracted in a separating funnel and separated. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and purified by flash column chromatography on silica gel (2.5 × 30 cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The yellow fraction with  $R_f$  0.5 gave cyclization product **10c** (46 mg, 94 %). Compound **10c** was obtained as a yellow orange solid with mp 223–225 °C (EtOH).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.60$  (t,  $J = 7.2$  Hz, 3 H), 2.57 (s, 3 H), 4.62 (q,  $J = 7.2$  Hz, 2 H), 6.68 (d,  $J = 7.9$  Hz, 1 H), 6.80 (ddd,  $J = 7.9, 7.0, 0.8$  Hz, 1 H), 7.16 (ddd,  $J = 8.2, 7.1, 1.1$  Hz, 1 H), 7.38 (ddd,  $J = 8.0, 7.0, 1.1$  Hz, 1 H), 7.46–7.58 (m, 5 H), 7.73 (d,  $J = 8.0$  Hz, 2 H), 7.98 (d,  $J = 8.9$  Hz, 1 H), 8.14 (d,  $J = 8.0$  Hz, 1 H), 8.37 (d,  $J = 8.2$  Hz, 1 H), 8.61 (s, 1 H), 8.96 (dd,  $J = 8.4, 1.4$  Hz, 1 H), 9.03 (dd,  $J = 4.4, 1.5$  Hz, 1 H), 9.61 (d,  $J = 8.9$  Hz, 1 H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1, 21.4, 37.9, 108.2, 109.8, 117.7, 119.3, 120.7, 120.8, 123.0, 123.3, 123.5, 124.7, 125.1, 125.7, 125.8, 125.9, 126.0, 126.1, 126.2, 127.4, 129.2, 129.3, 130.2, 130.7, 130.9, 131.1, 137.4, 137.9, 139.6, 140.2, 140.8, 147.7, 148.8$  ppm. UV-vis ( $\text{CH}_2\text{Cl}_2$ ),  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 265 (4.63), 285 (4.53), sh 306 (4.48), 324 (4.56), 371 (4.08), sh 388 (3.96), 411 nm (3.79). HRMS (ESI):  $\text{MH}^+$  found 487.2175.  $\text{C}_{36}\text{H}_{27}\text{N}_2$  requires 487.2169.



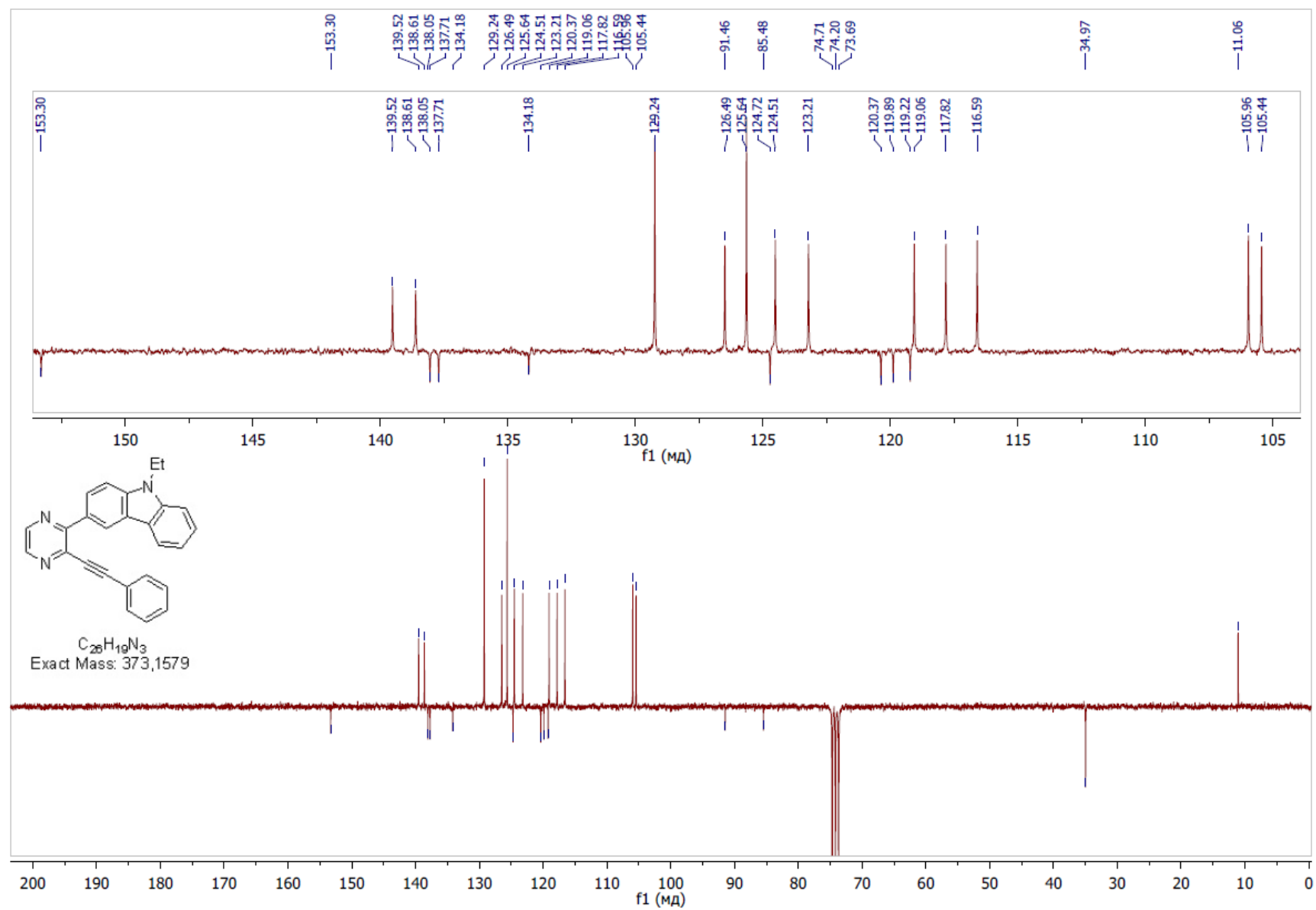
**Figure S1.** <sup>1</sup>H NMR spectrum of **2a** (CDCl<sub>3</sub>, 250 MHz)



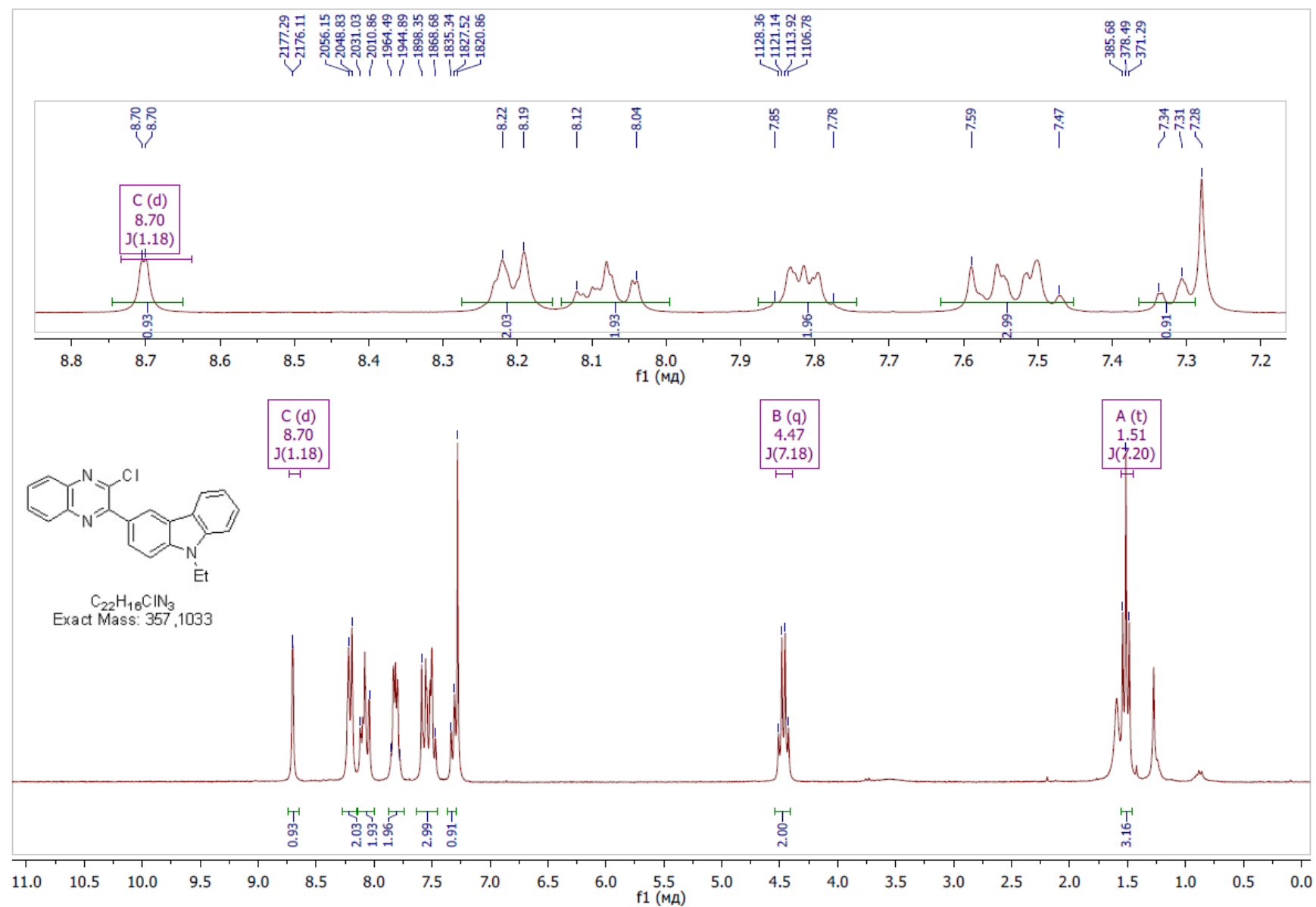
**Figure S2.** <sup>13</sup>C NMR APT spectrum of **2a** (CDCl<sub>3</sub>, 62.9 MHz)



**Figure S3.** <sup>1</sup>H NMR spectrum of **2b** (CDCl<sub>3</sub>, 250 MHz)

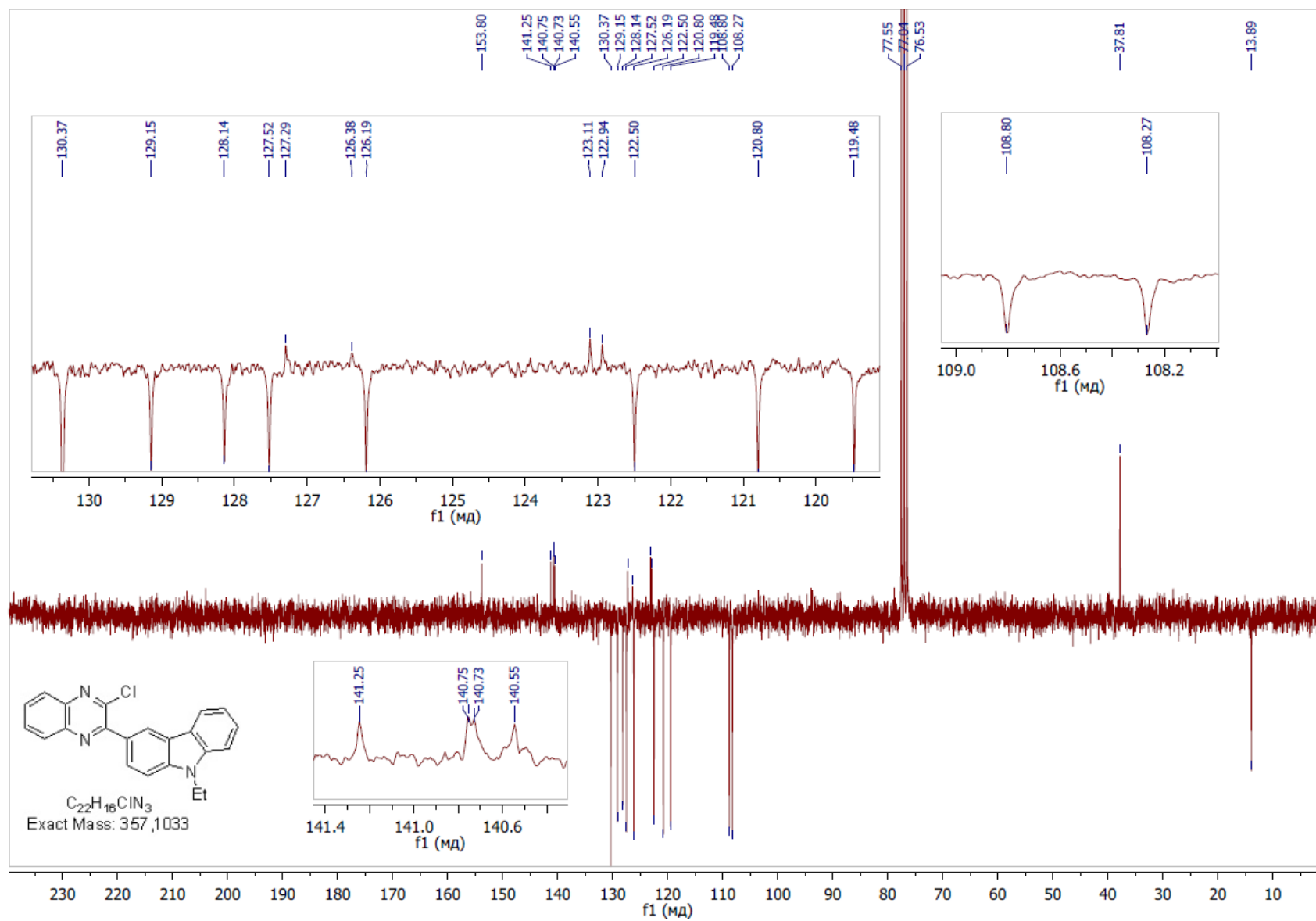


**Figure S4.** <sup>13</sup>C NMR APT spectrum of **2b** (CDCl<sub>3</sub>, 62.9 MHz)

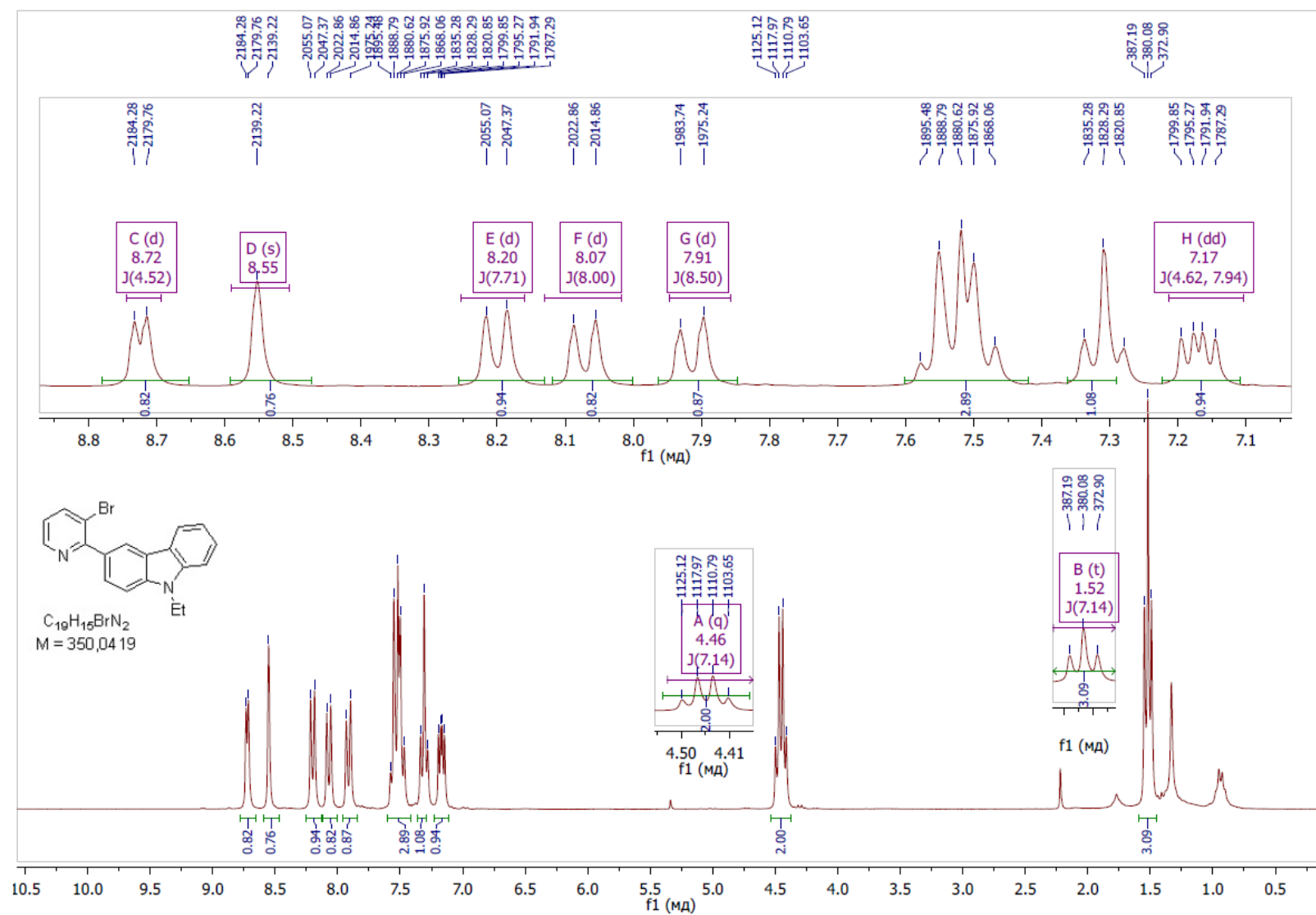


**Figure S5.**  $^1H$  NMR spectrum of **4a** (CDCl<sub>3</sub>, 250 MHz)

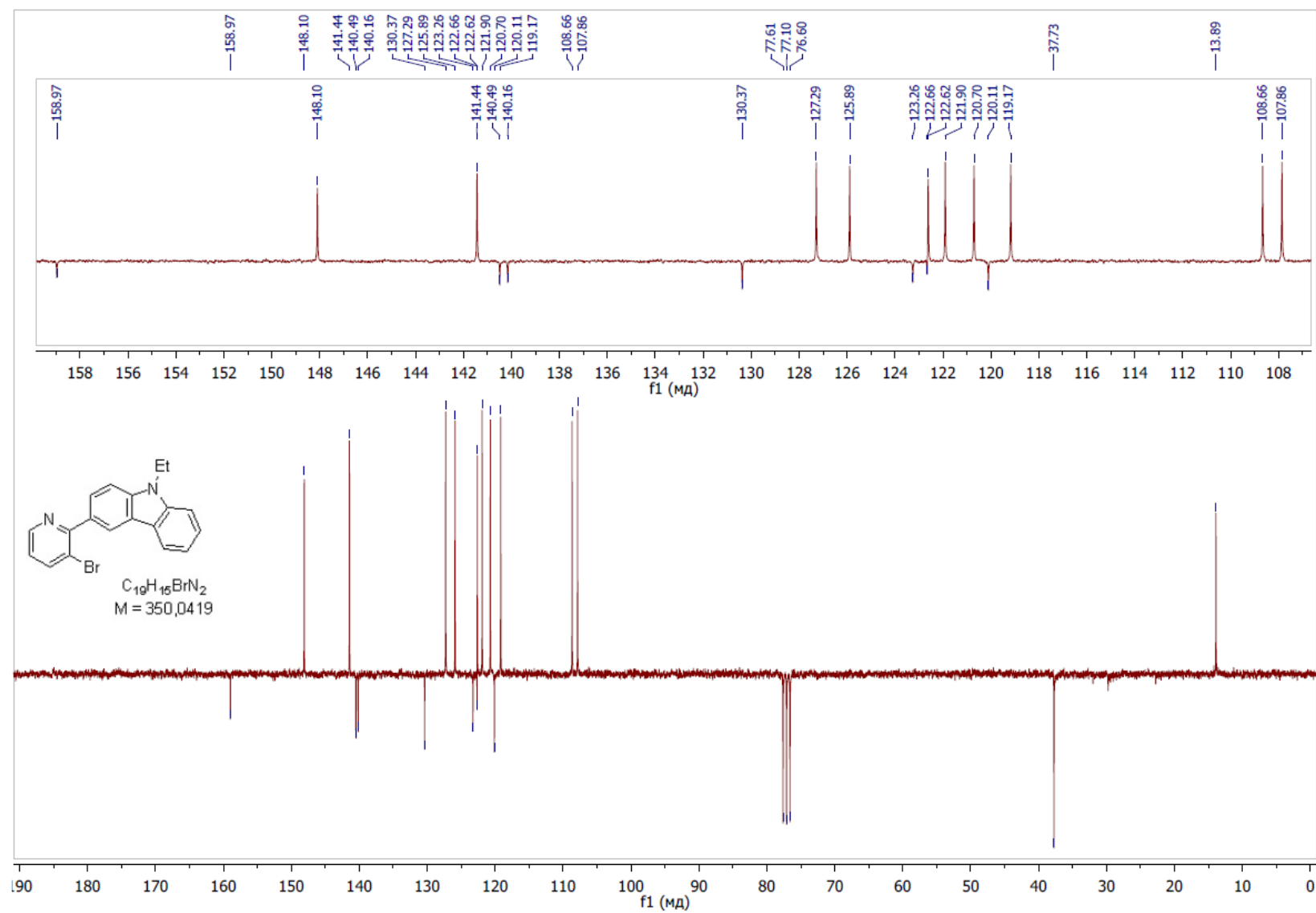




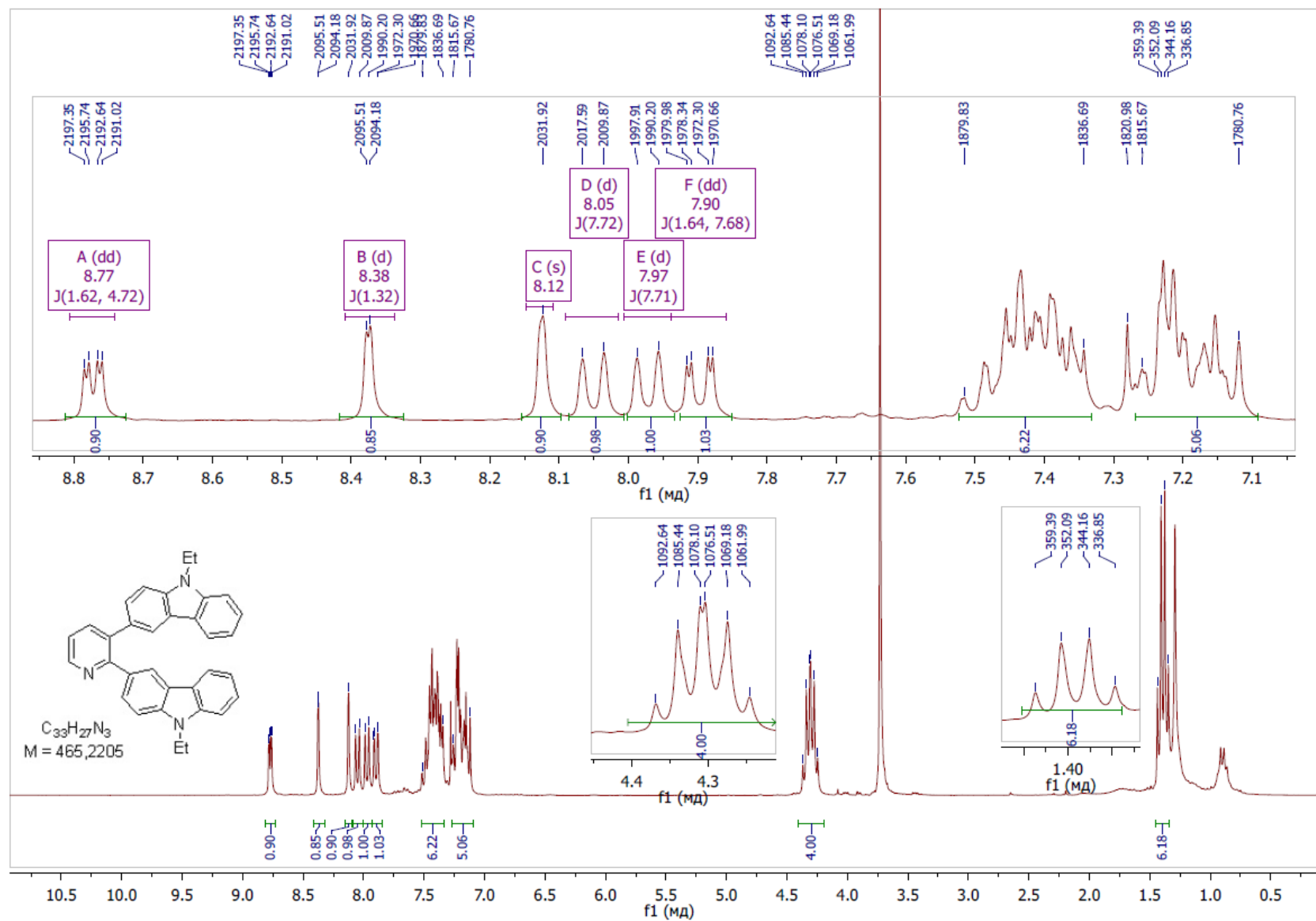
**Figure S6.**  $^{13}\text{C}$  NMR APT spectrum of **4a** ( $\text{CDCl}_3$ , 62.9 MHz)



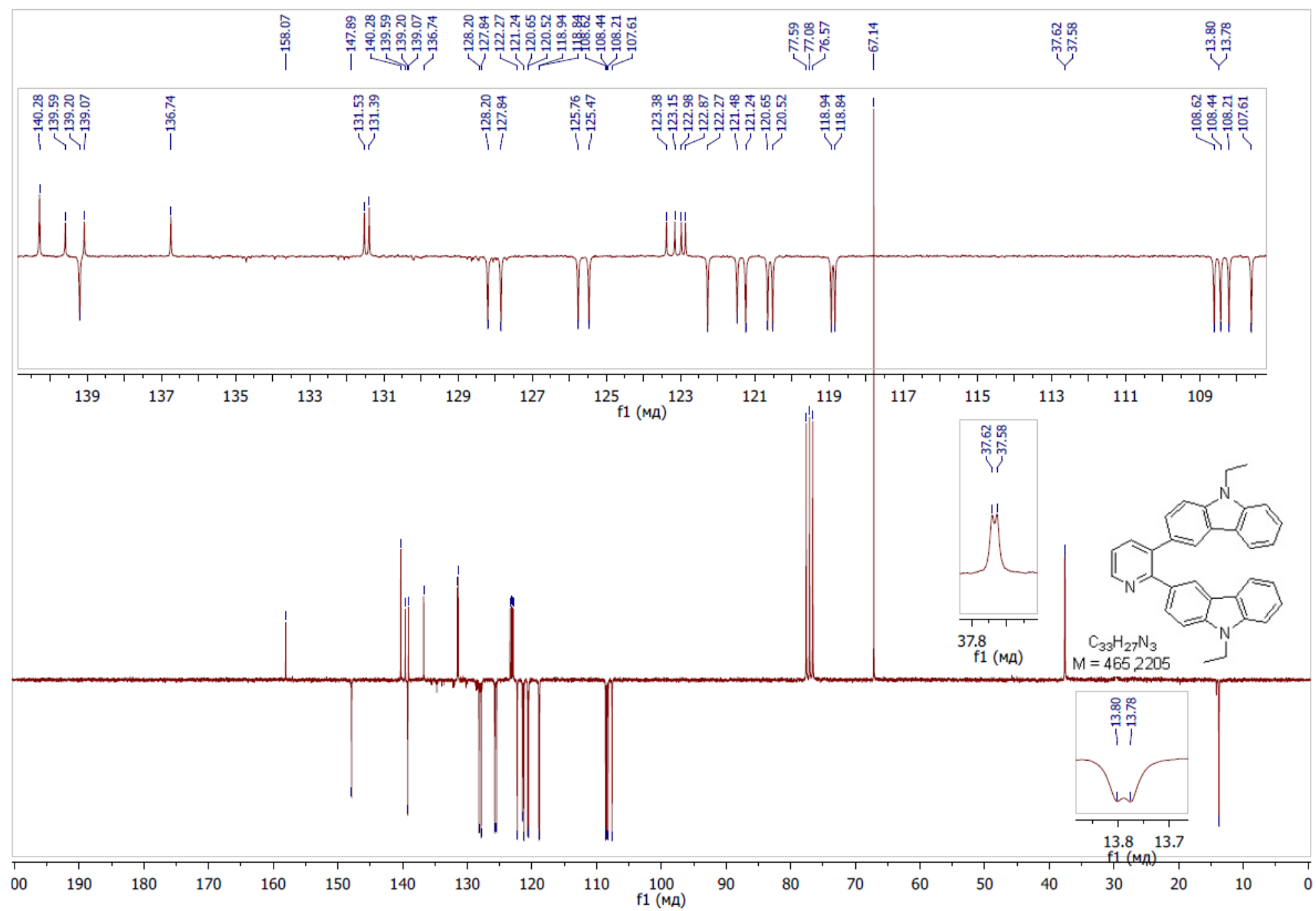
**Figure S7.**  $^1H$  NMR spectrum of **4b** (CDCl<sub>3</sub>, 250 MHz)



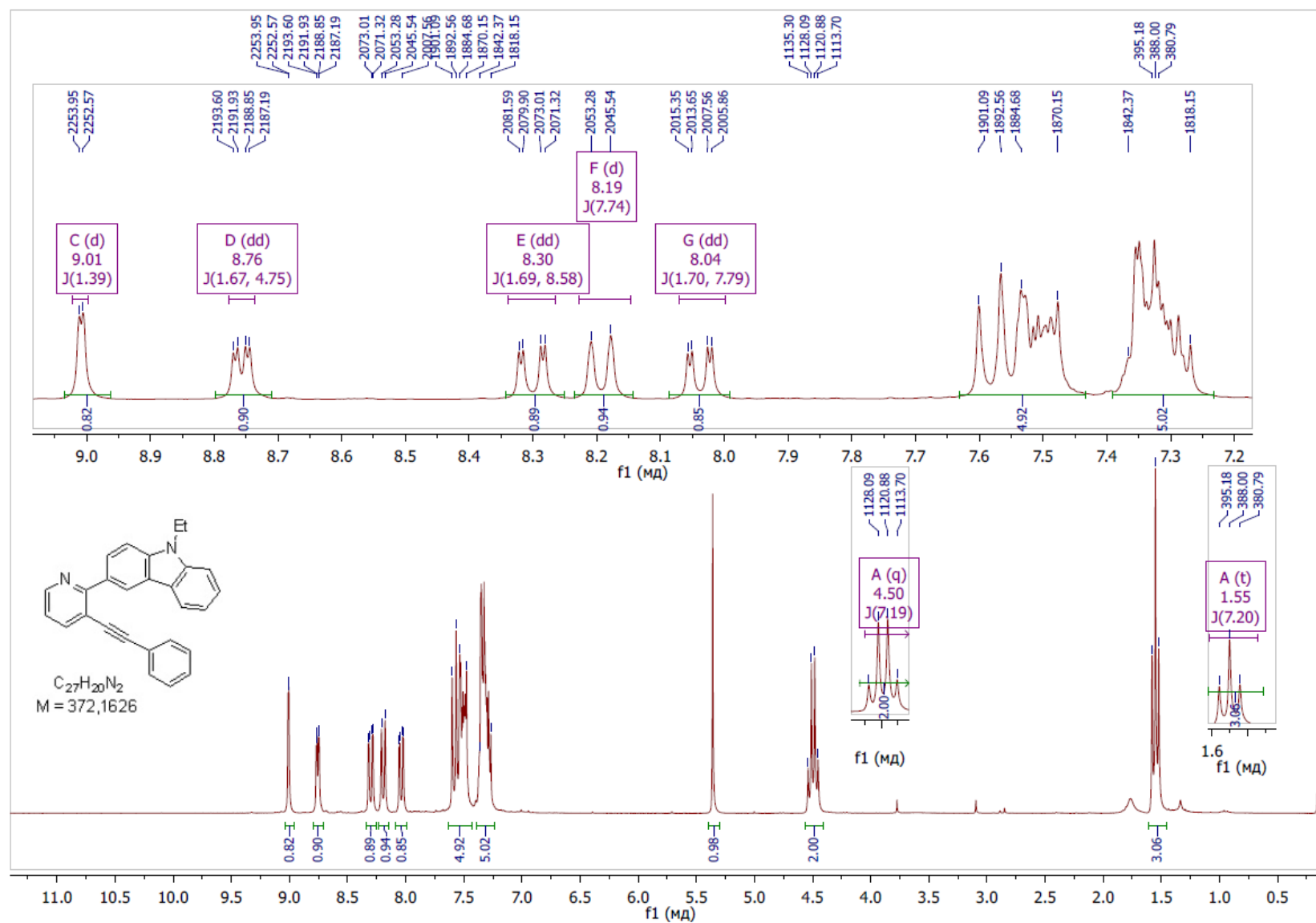
**Figure S8.**  $^{13}C$  NMR APT spectrum of **4b** ( $CDCl_3$ , 62.9 MHz)



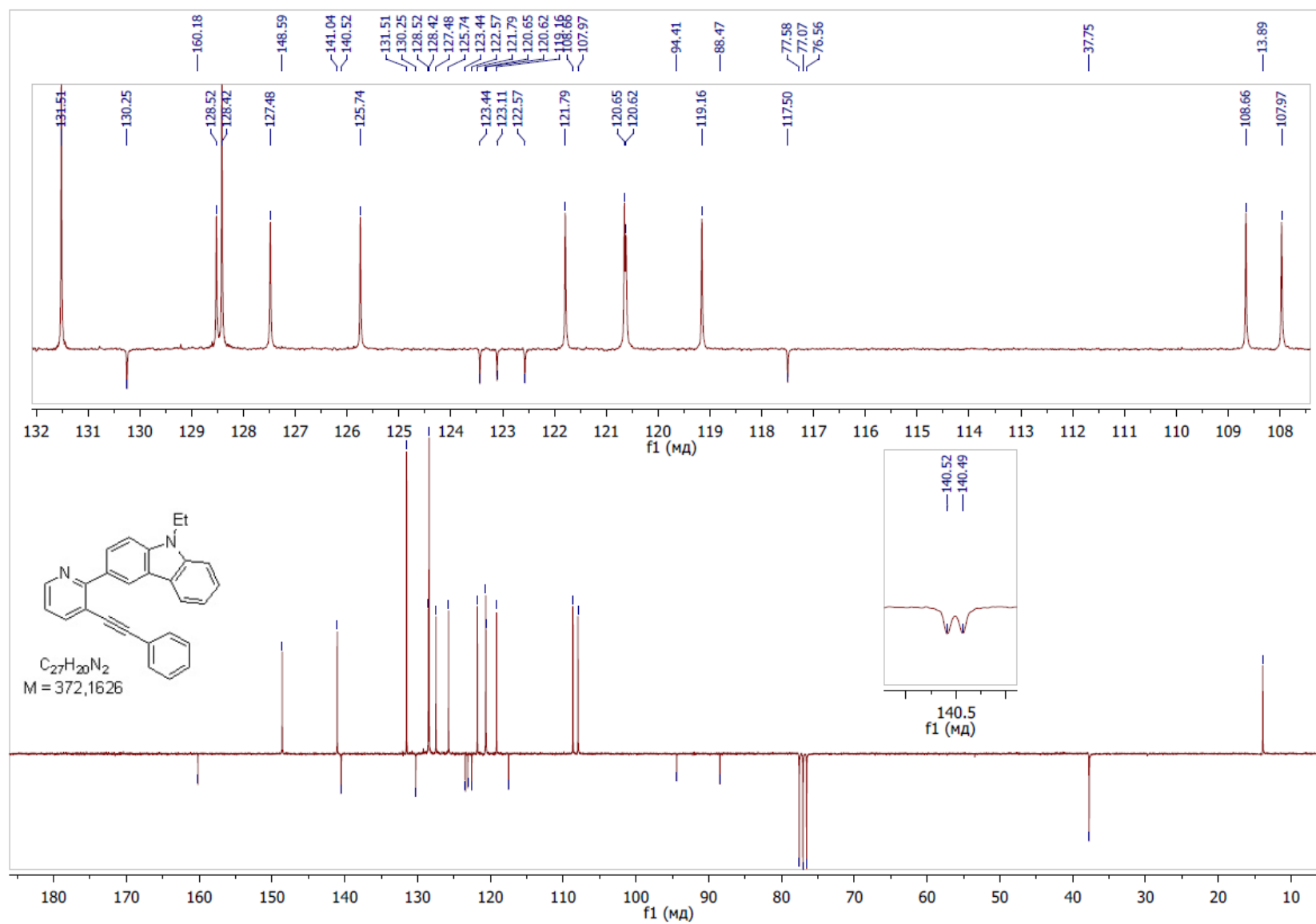
**Figure S9.**  $^1H$  NMR spectrum of **5b** (CDCl<sub>3</sub>, 250 MHz)



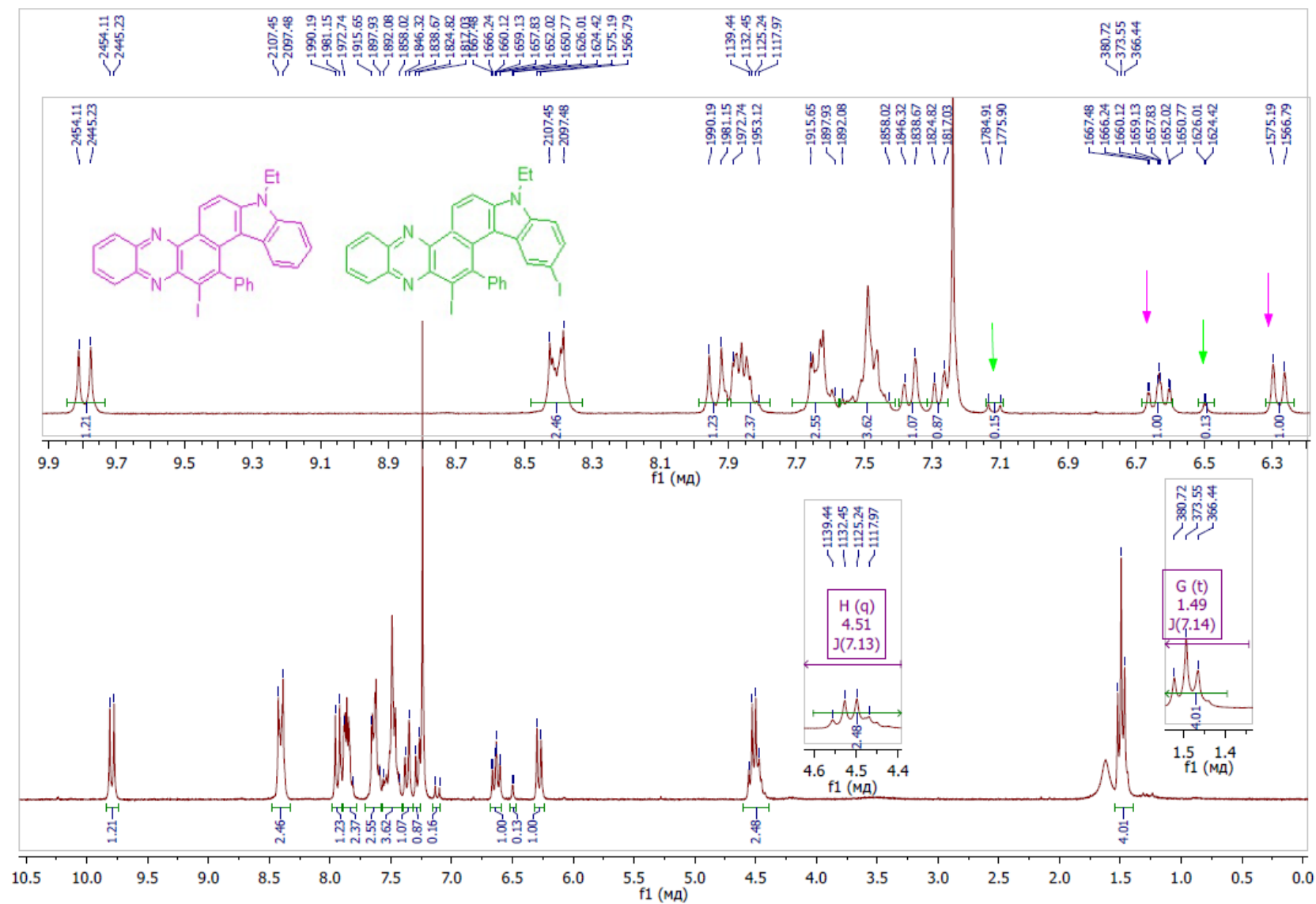
**Figure S10.**  $^{13}\text{C}$  NMR APT spectrum of **5b** ( $\text{CDCl}_3$ , 62.9 MHz)



**Figure S11.**  $^1\text{H}$  NMR spectrum of **6** (CDCl<sub>3</sub>, 250 MHz)

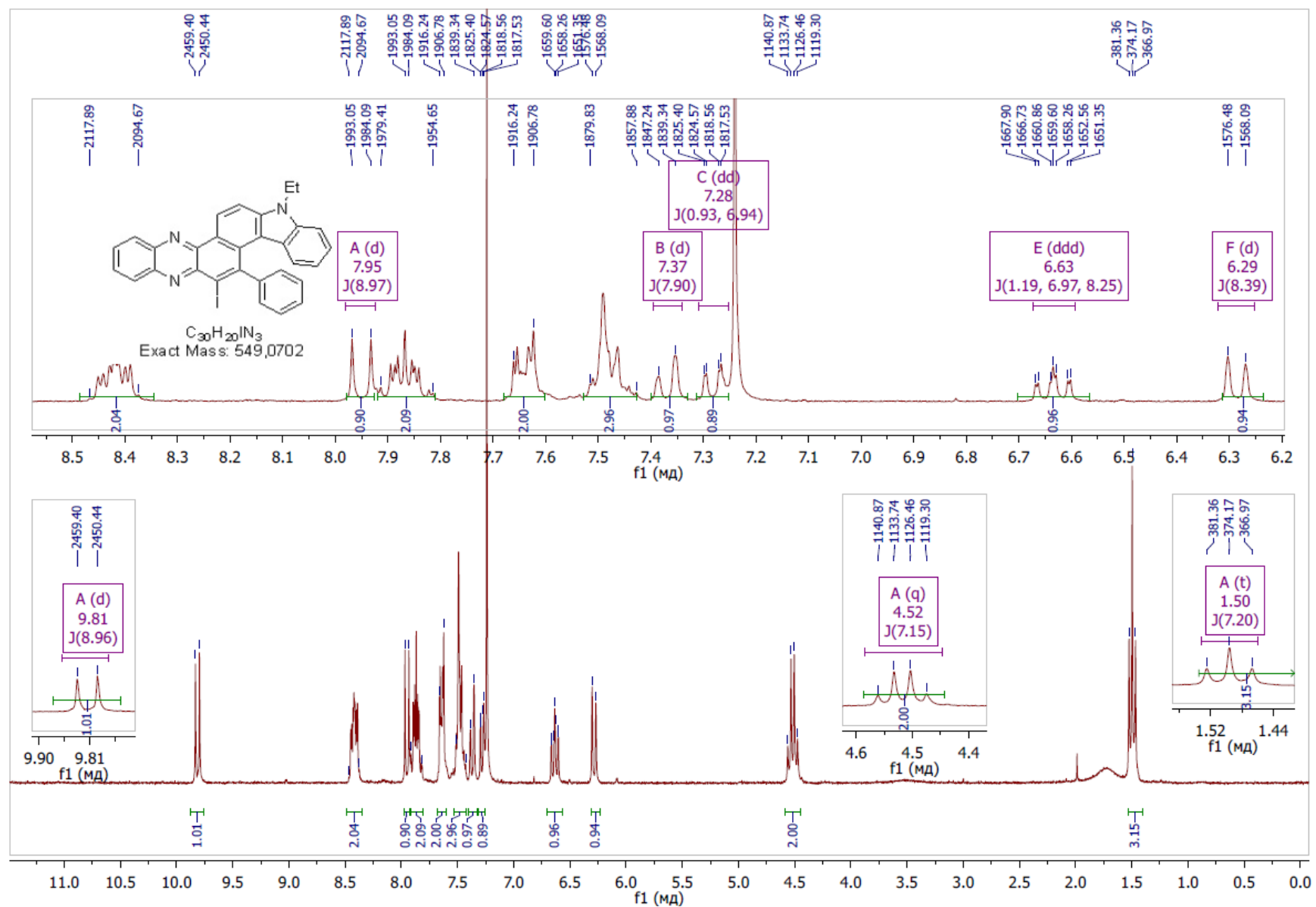


**Figure S12.**  $^{13}C$  NMR APT spectrum of **6** ( $CDCl_3$ , 62.9 MHz)

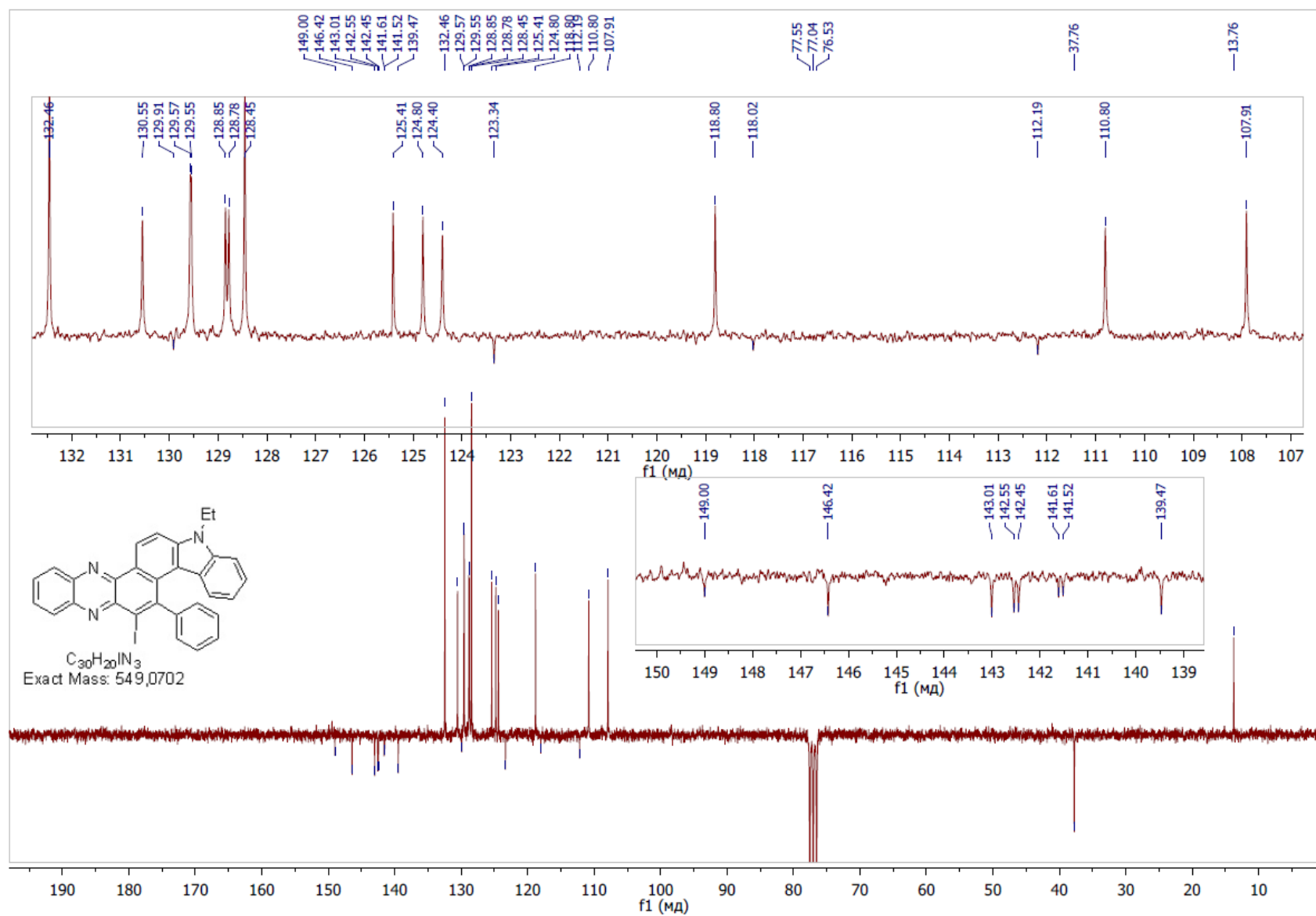


**Figure S13.** <sup>1</sup>H NMR spectrum of the mixture **7a** and **8a** (CDCl<sub>3</sub>, 250 MHz)



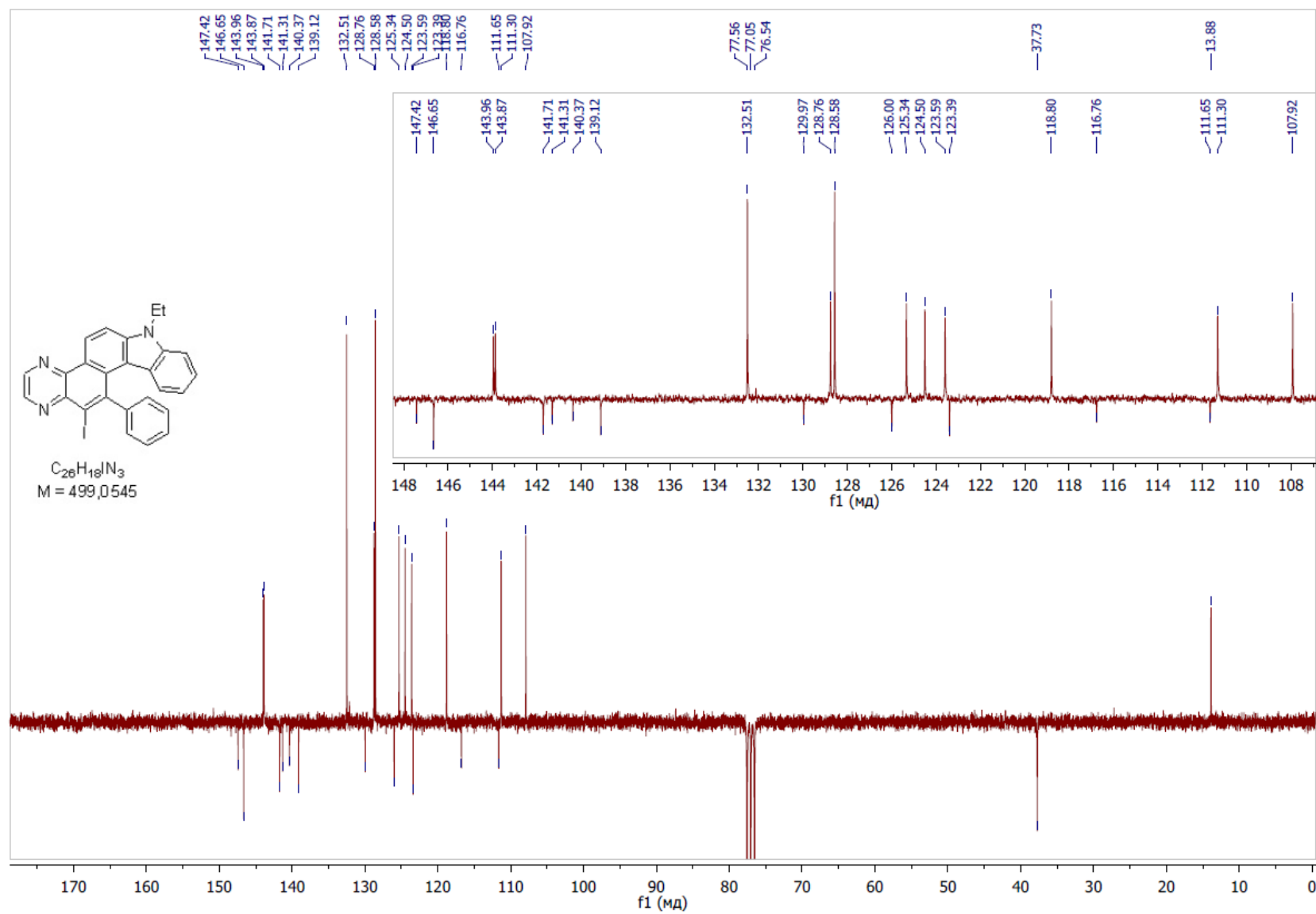


**Figure S14.** <sup>1</sup>H NMR spectrum of **7a** (CDCl<sub>3</sub>, 250 MHz)



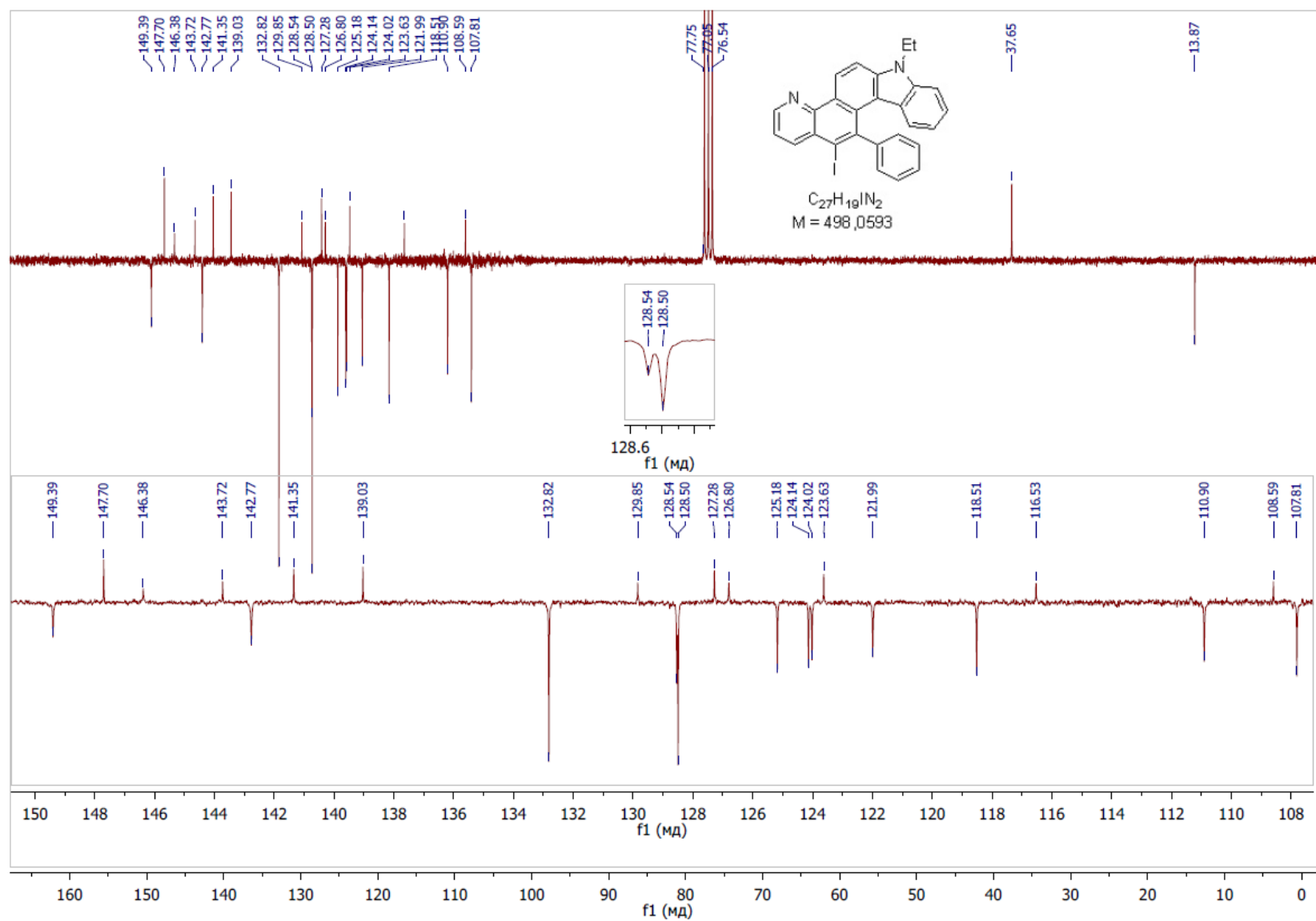
**Figure S15.** <sup>13</sup>C NMR APT spectrum of **7a** (CDCl<sub>3</sub>, 62.9 MHz)



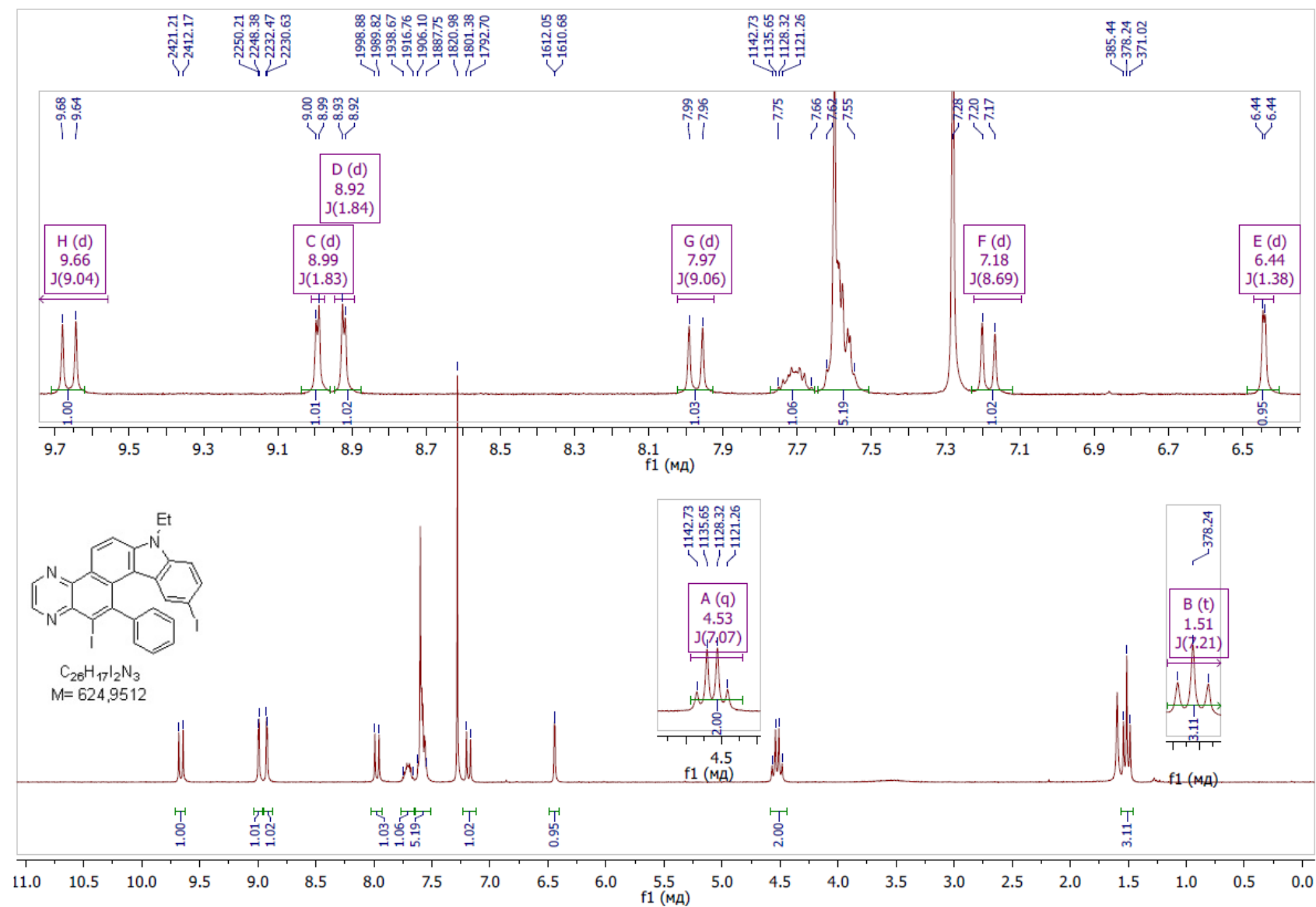


**Figure S17.**  $^{13}C$  NMR APT spectrum of **7b** (CDCl<sub>3</sub>, 62.9 MHz)

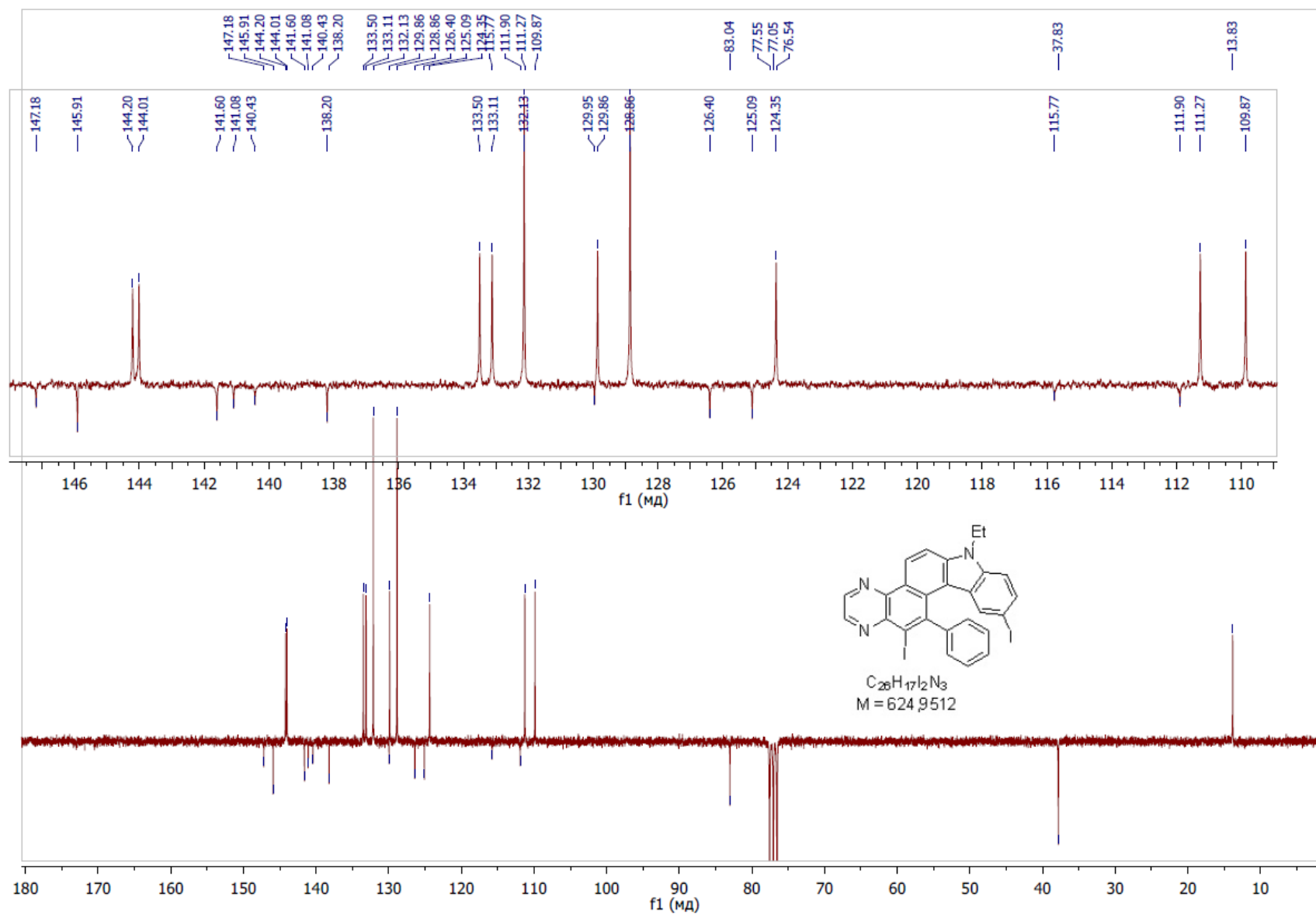




**Figure S19.**  $^{13}\text{C}$  NMR APT spectrum of **7c** ( $\text{CDCl}_3$ , 62.9 MHz)



**Figure S20.**  $^1H$  NMR spectrum of **8b** ( $CDCl_3$ , 250 MHz)



**Figure S21.** <sup>13</sup>C NMR APT spectrum of **8b** (CDCl<sub>3</sub>, 62.9 MHz)



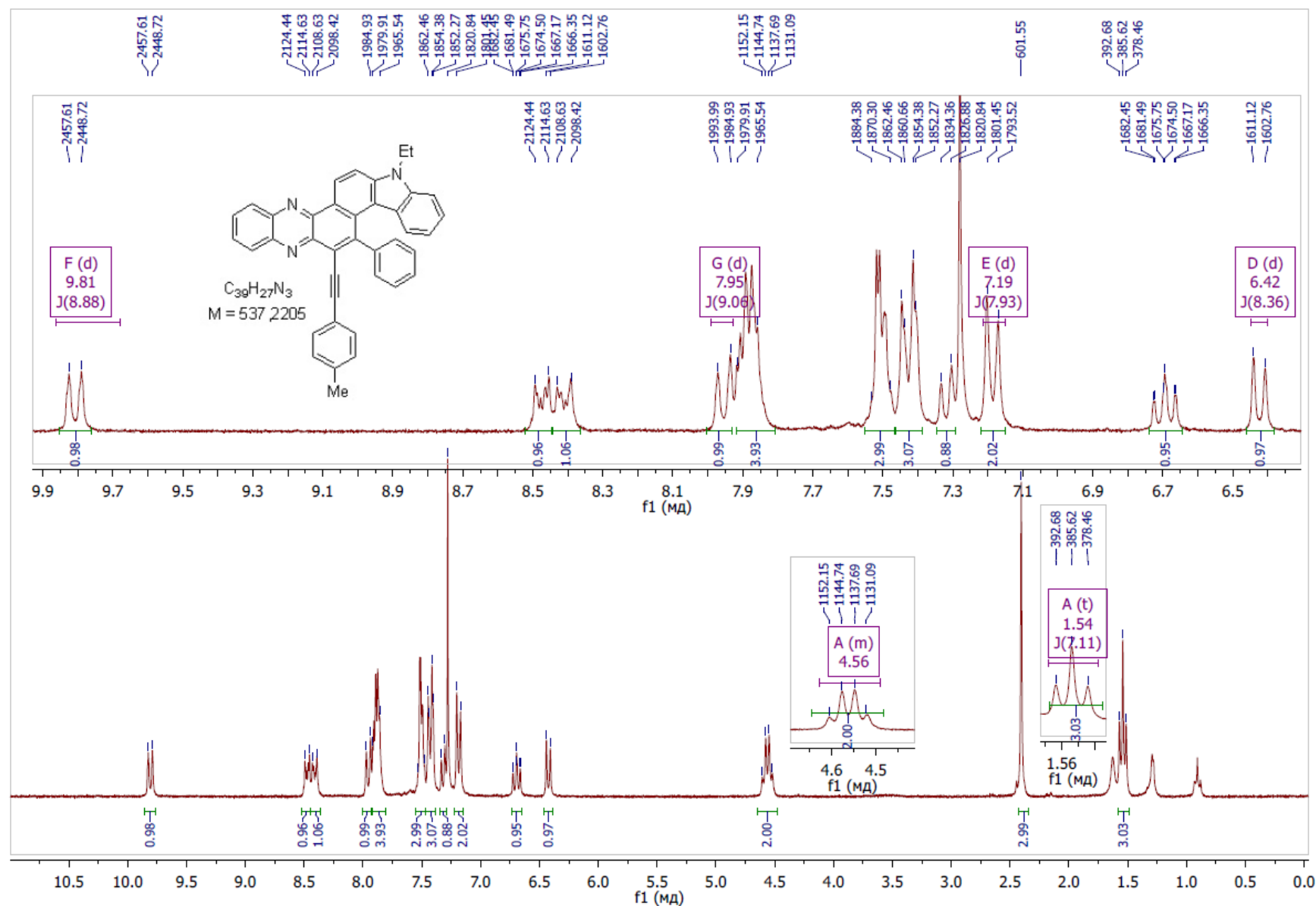
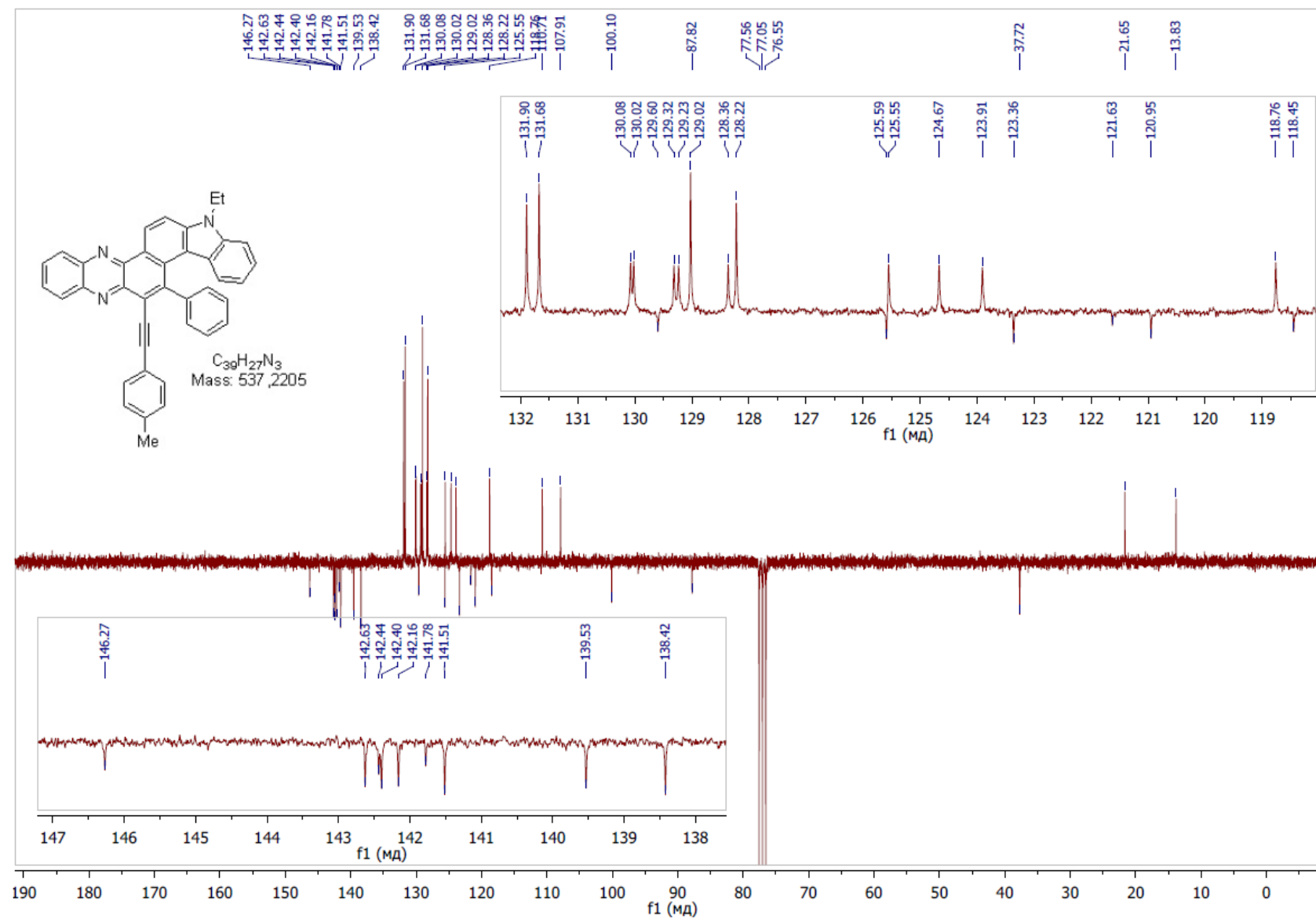


Figure S22. <sup>1</sup>H NMR spectrum of **9a** (CDCl<sub>3</sub>, 250 MHz)



**Figure S23.**  $^{13}\text{C}$  NMR APT spectrum of **9a** (CDCl<sub>3</sub>, 62.9 MHz)

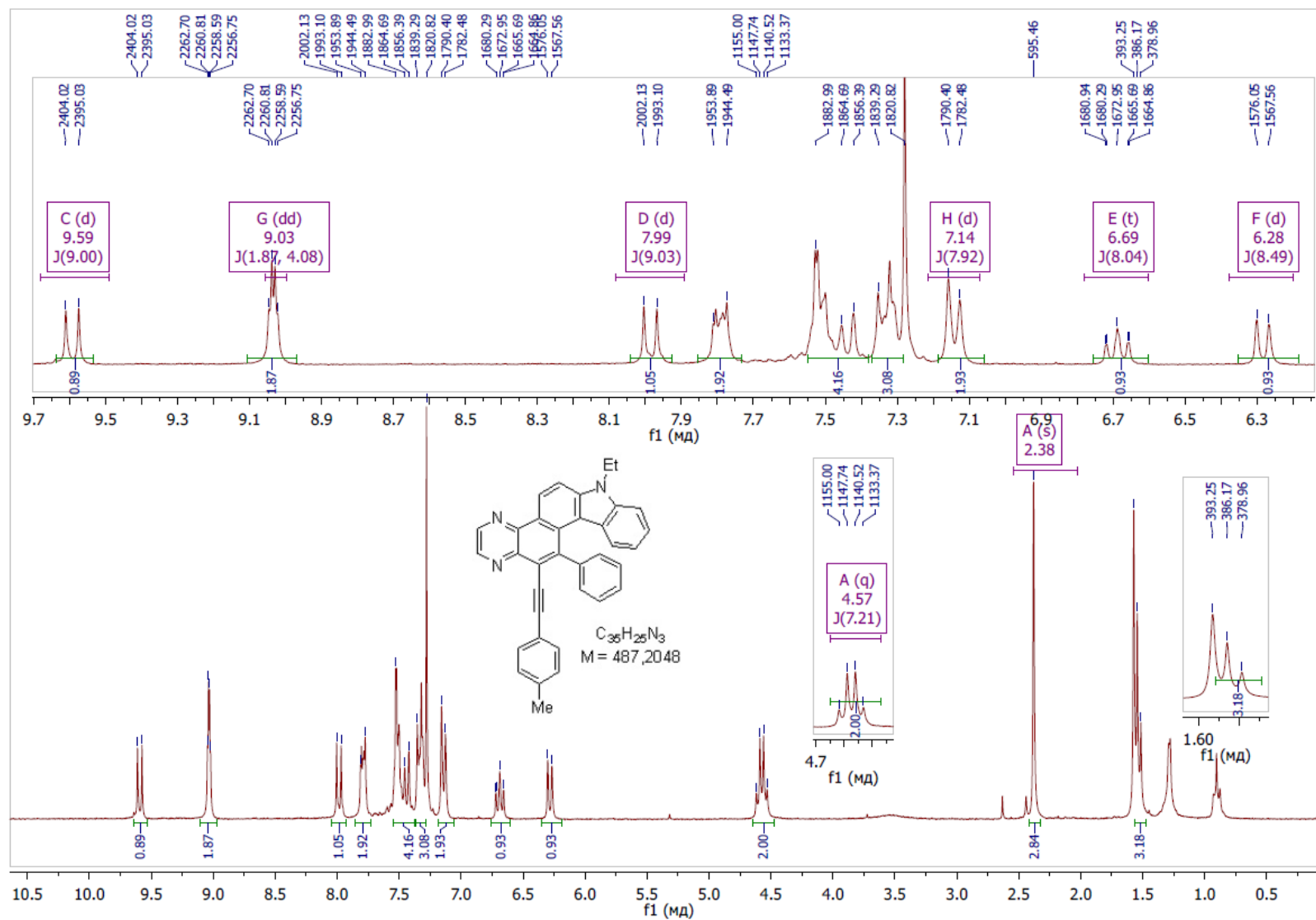
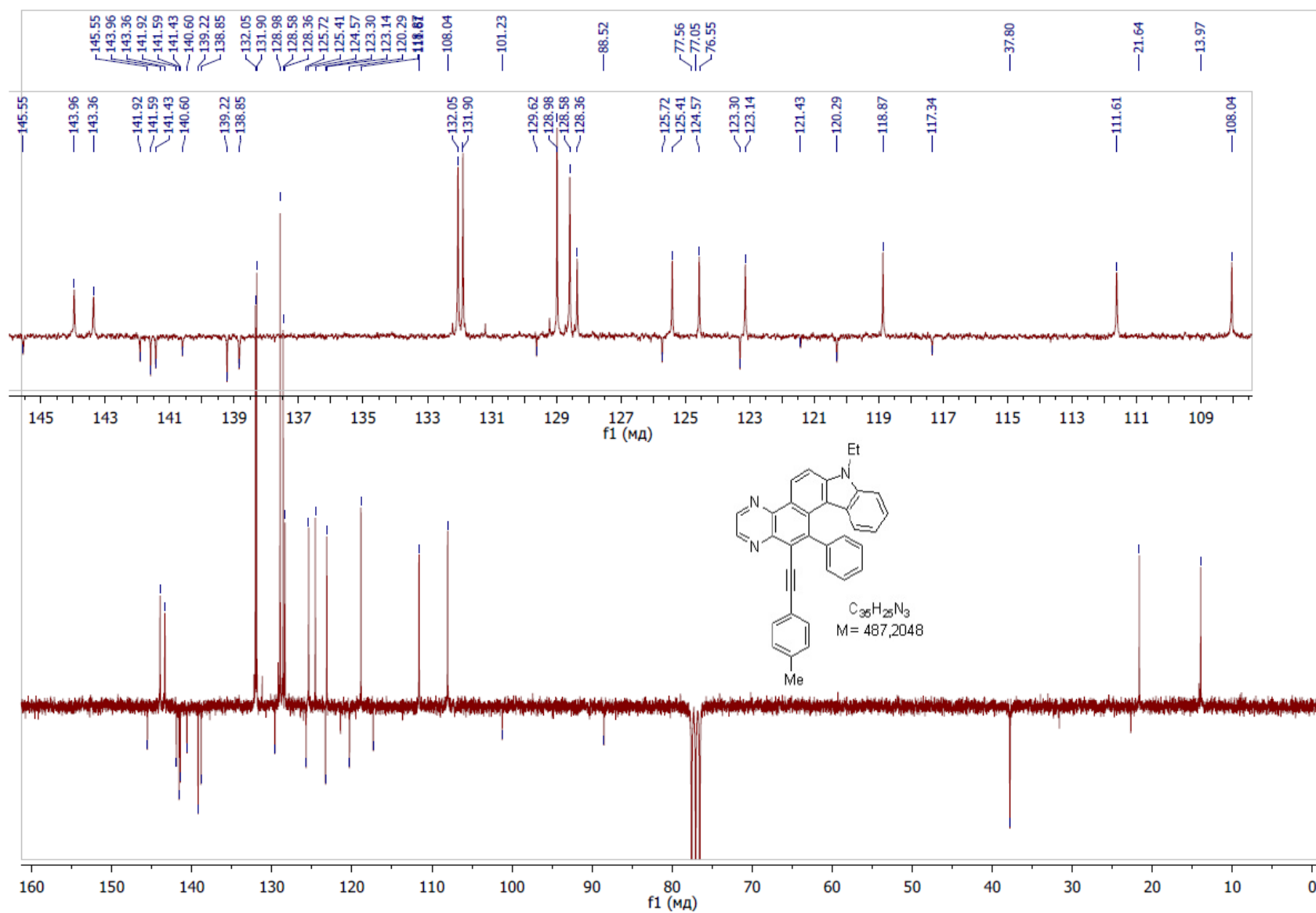


Figure S24. <sup>1</sup>H NMR spectrum of **9b** (CDCl<sub>3</sub>, 250 MHz)



**Figure S25.**  $^{13}\text{C}$  NMR APT spectrum of **9b** ( $\text{CDCl}_3$ , 62.9 MHz)

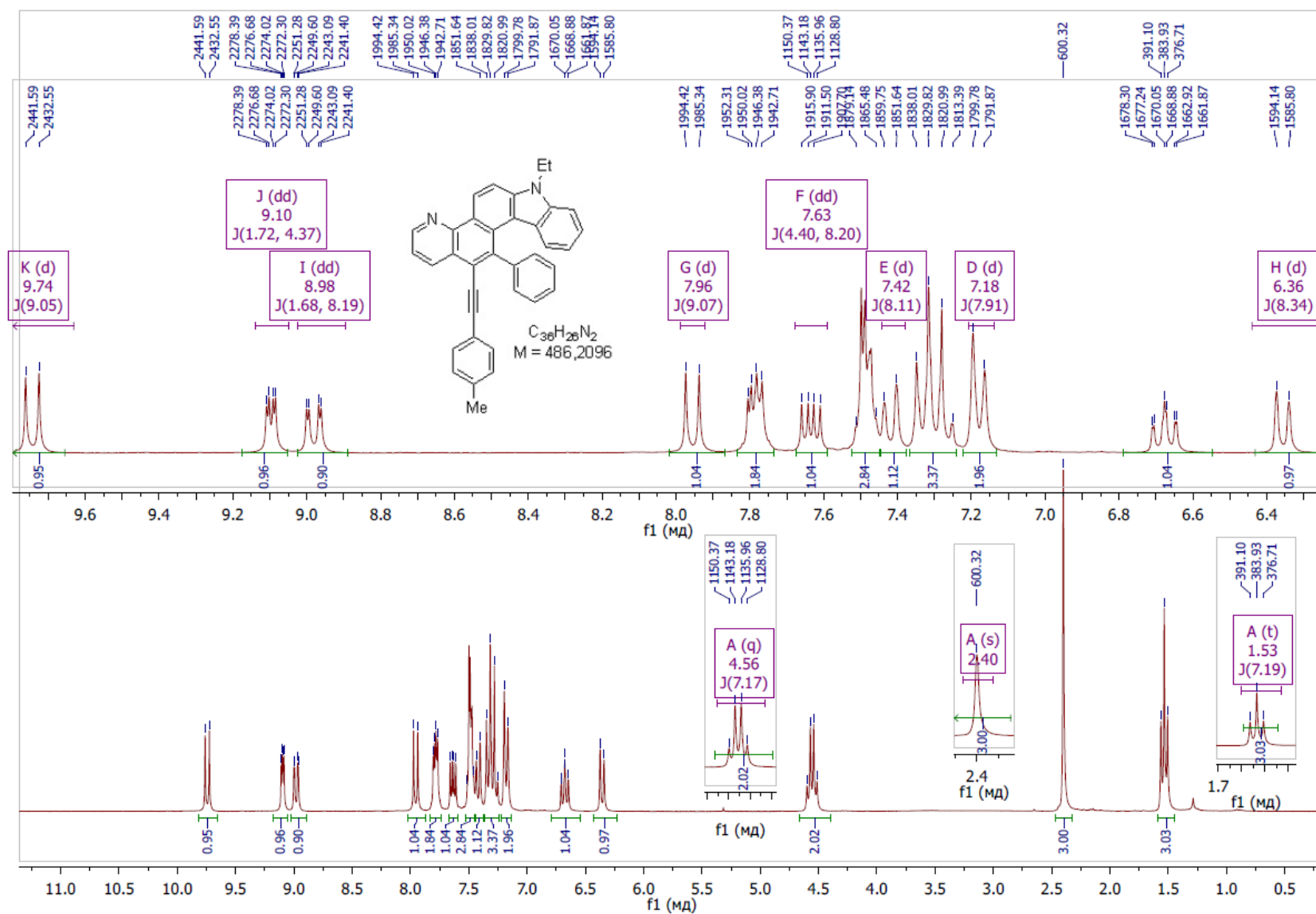
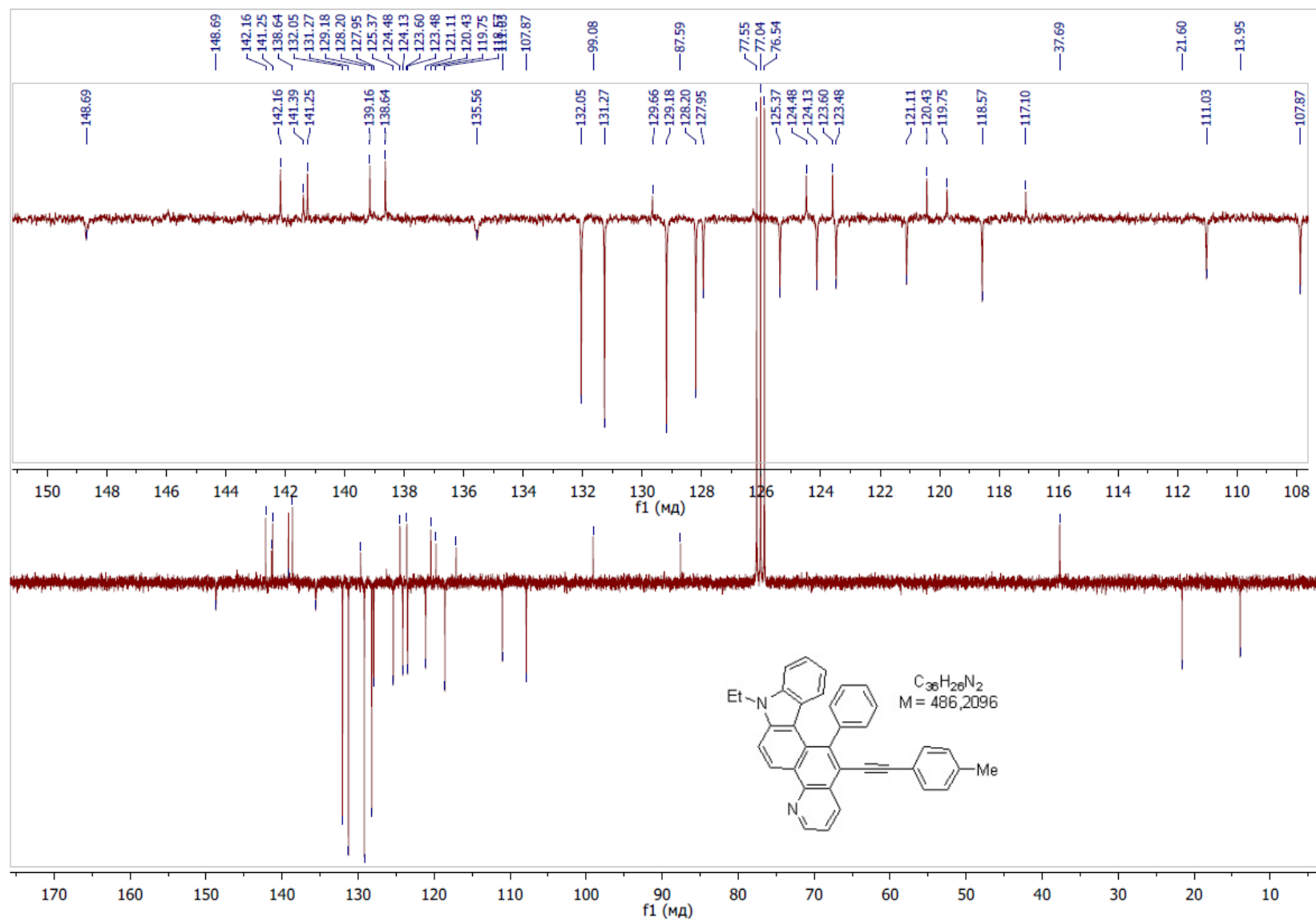
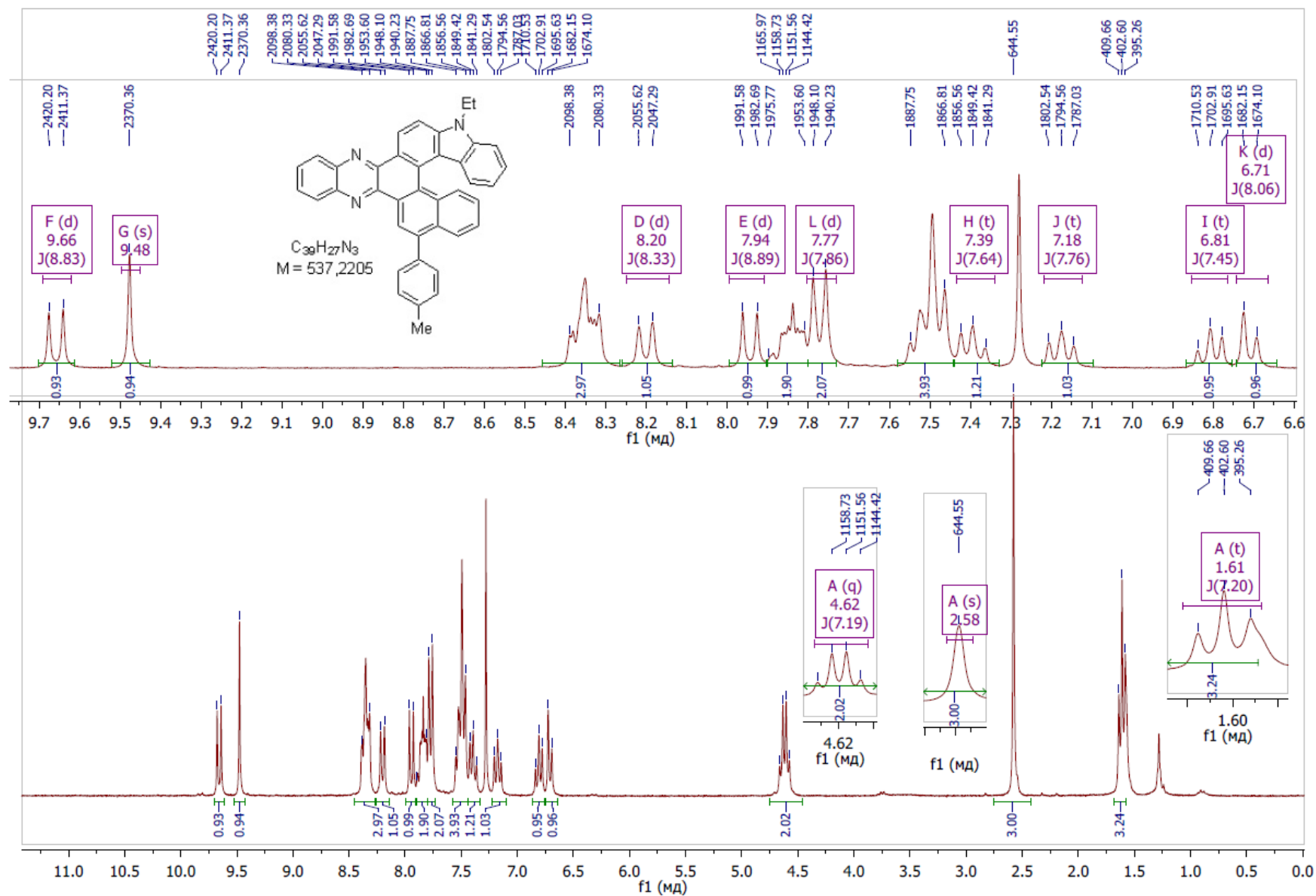


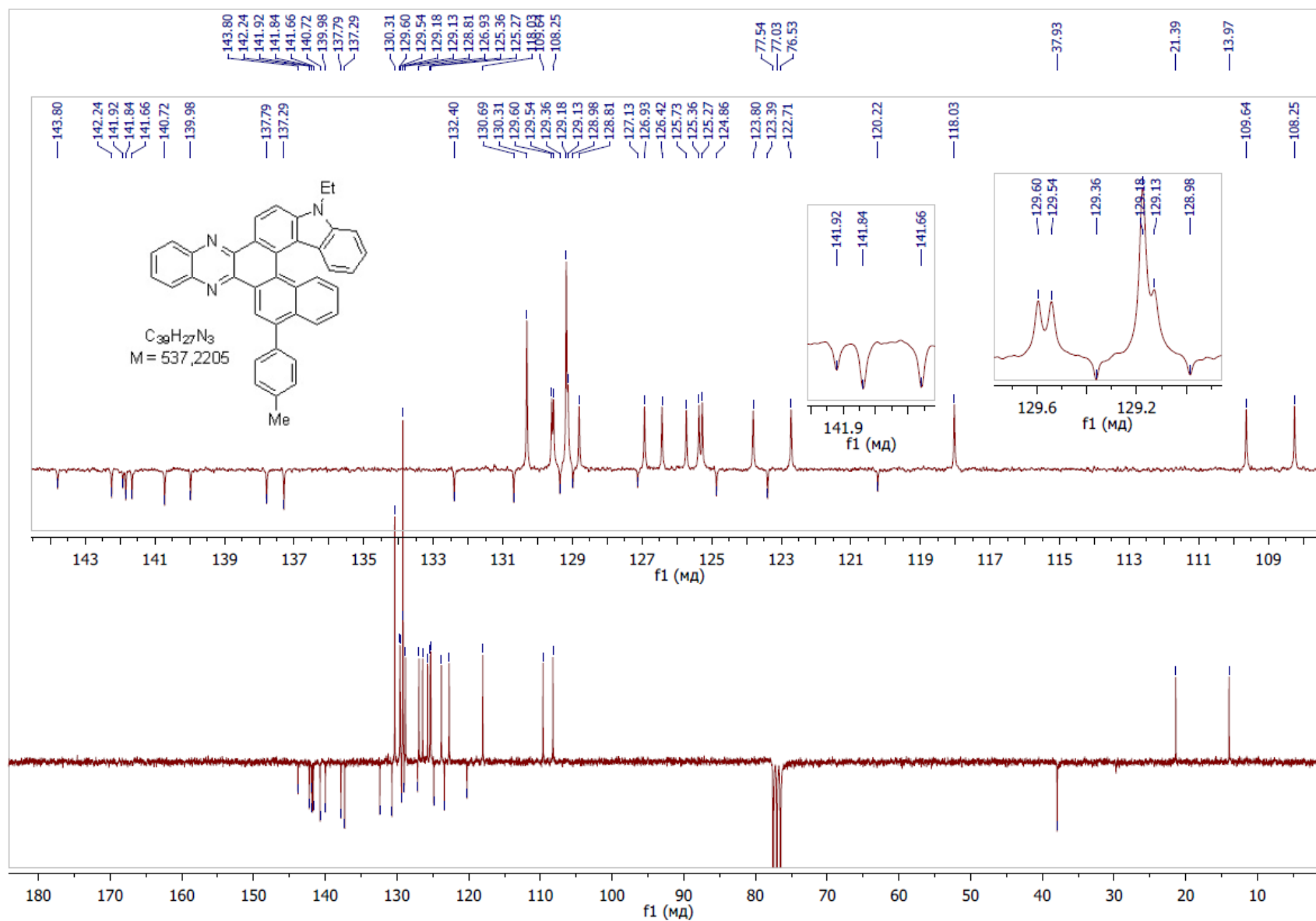
Figure S26. <sup>1</sup>H NMR spectrum of **9c** (CDCl<sub>3</sub>, 250 MHz)



**Figure S27.**  $^{13}\text{C}$  NMR APT spectrum of **9c** ( $\text{CDCl}_3$ , 62.9 MHz)

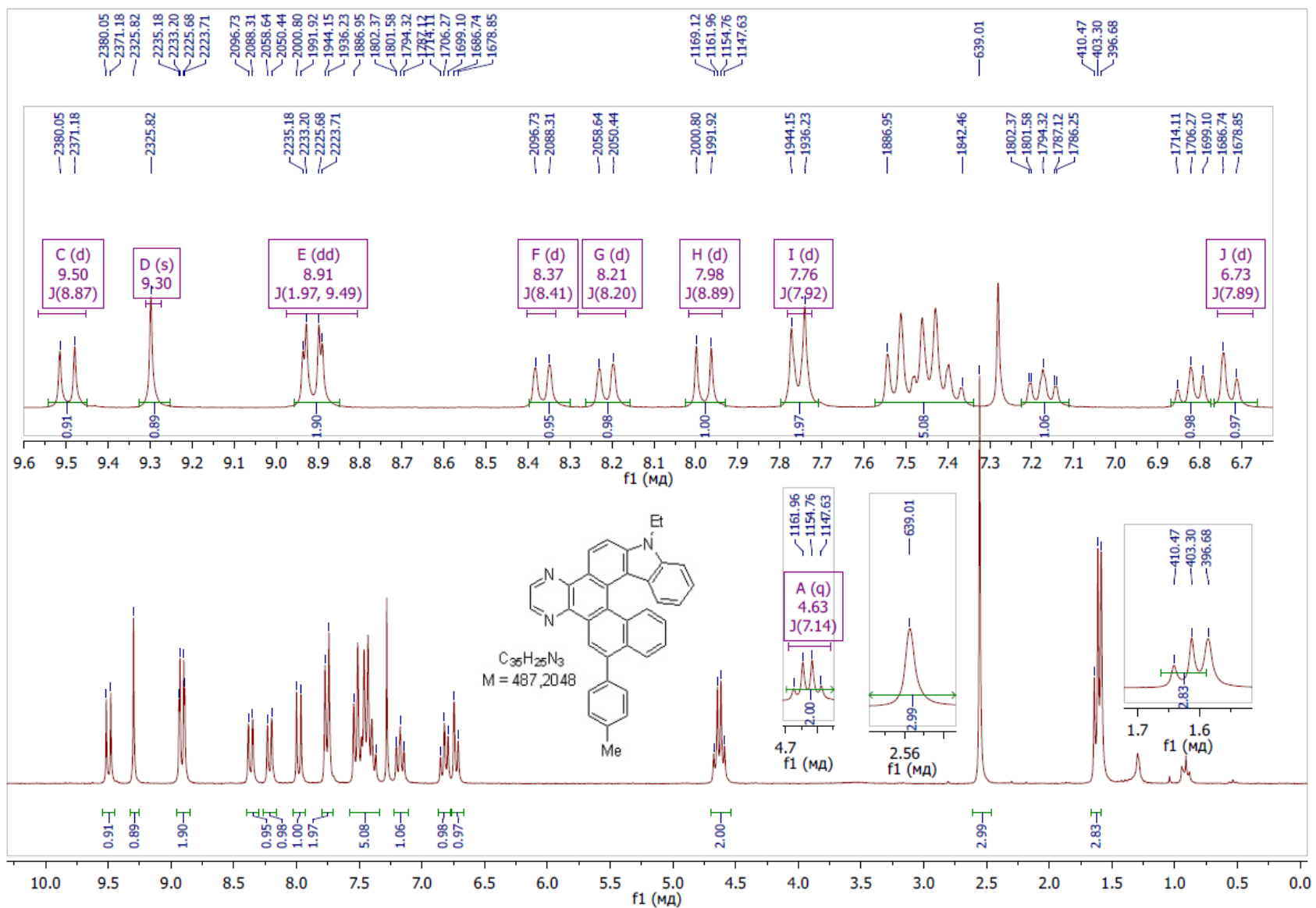


**Figure S28.**  $^1\text{H}$  NMR spectrum of **10a** ( $\text{CDCl}_3$ , 250 MHz)

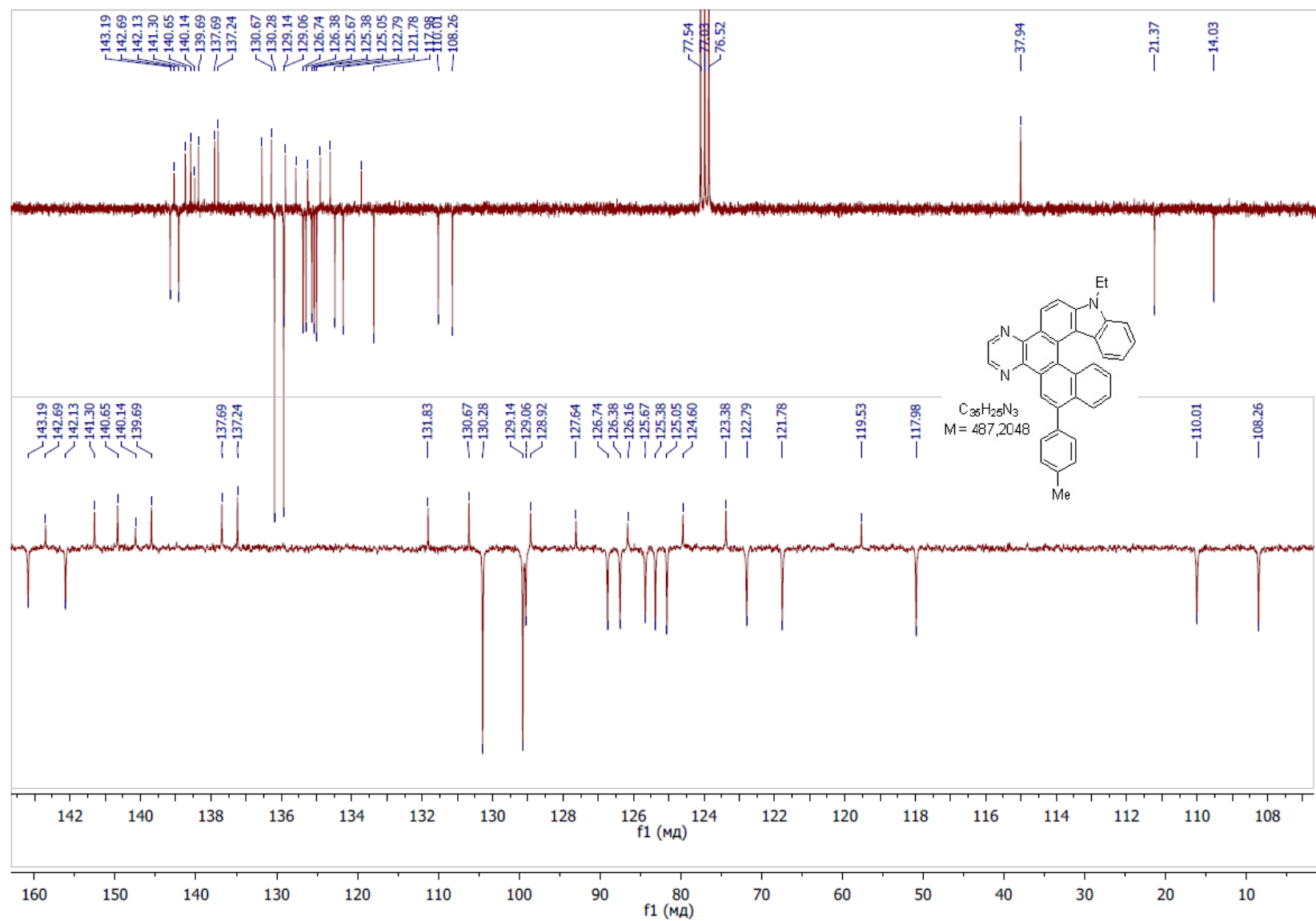


**Figure S29.**  $^{13}C$  NMR APT spectrum of **10a** ( $CDCl_3$ , 62.9 MHz)





**Figure S30.**  $^1H$  NMR spectrum of **10b** ( $CDCl_3$ , 250 MHz)



**Figure S31.**  $^{13}C$  NMR APT spectrum of **10b** ( $CDCl_3$ , 62.9 MHz)

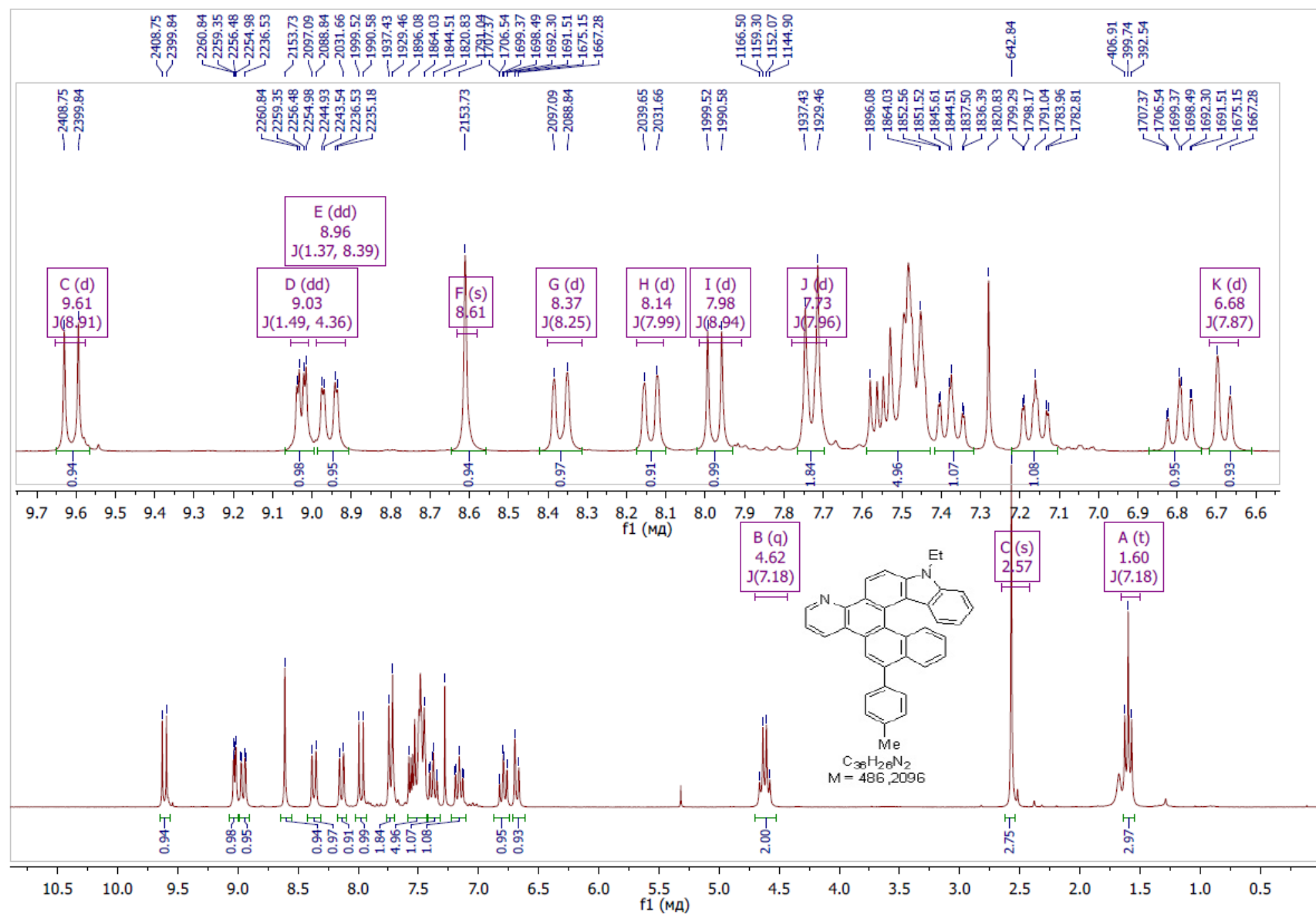
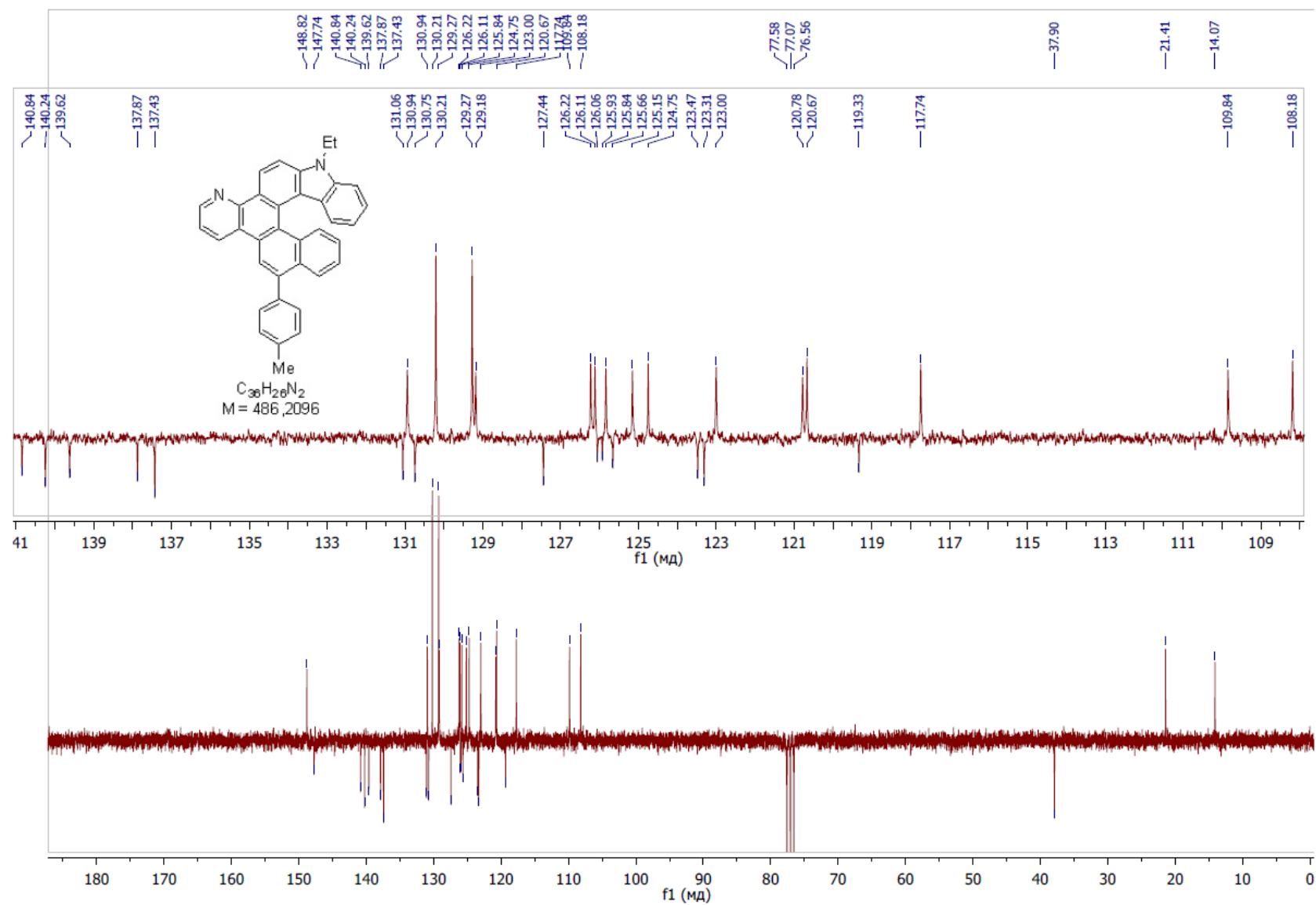
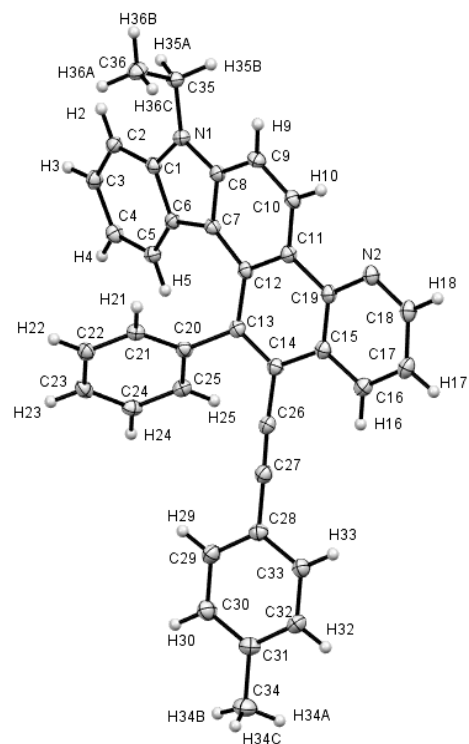


Figure S32. <sup>1</sup>H NMR spectrum of **10c** (CDCl<sub>3</sub>, 250 MHz)

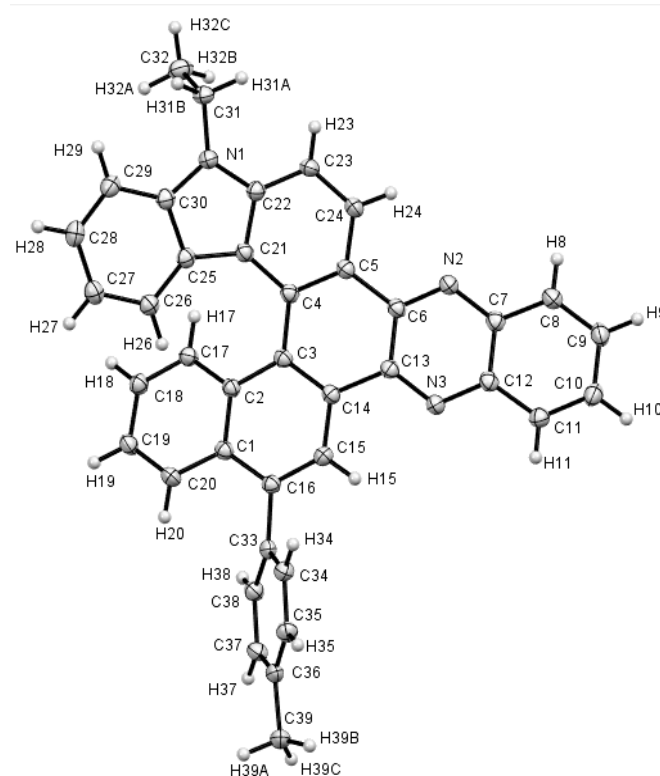


**Figure S33.**  $^{13}C$  NMR APT spectrum of **10c** ( $CDCl_3$ , 62.9 MHz)

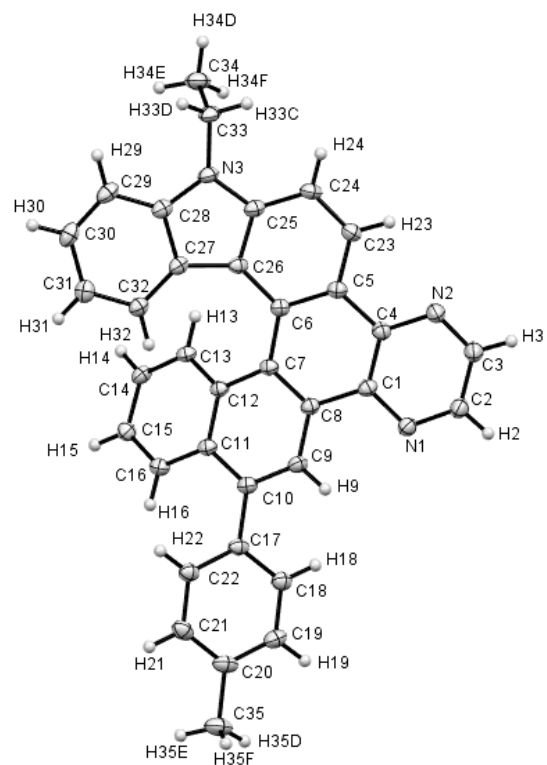
**Crystal structure determination:** X-ray measurements were conducted with Bruker APEX II CCD diffractometer and four-circle diffractometer SuperNova, Single source at offset/far, HyPix3000. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2034941 (**9c**), CCDC 2034943 (**10a**), CCDC 2034944 (**10b**), and CCDC 2034945 (**10c**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



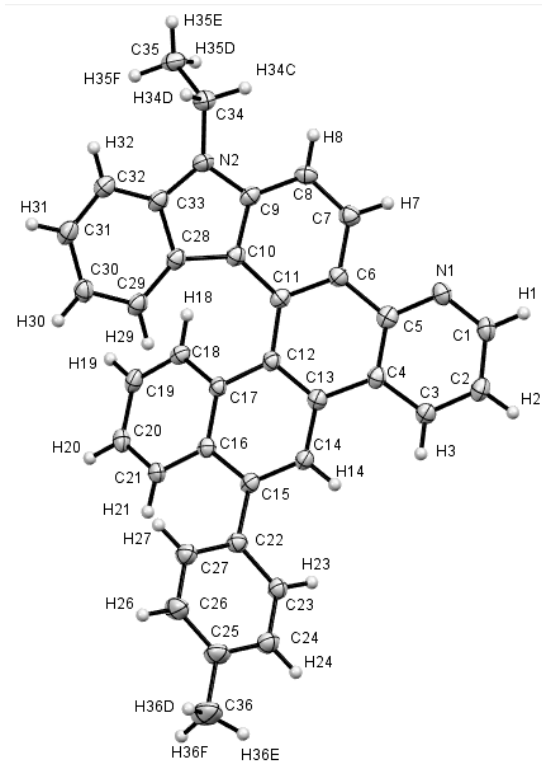
**Figure S34.** Molecular structure of compound **9c** showing 50% probability amplitude displacement ellipsoids.



**Figure S35.** Molecular structure of compound **10a** showing 50% probability amplitude displacement ellipsoids.



**Figure S36.** Molecular structure of compound **10b** showing 50% probability amplitude displacement ellipsoids (one of two independent molecules).



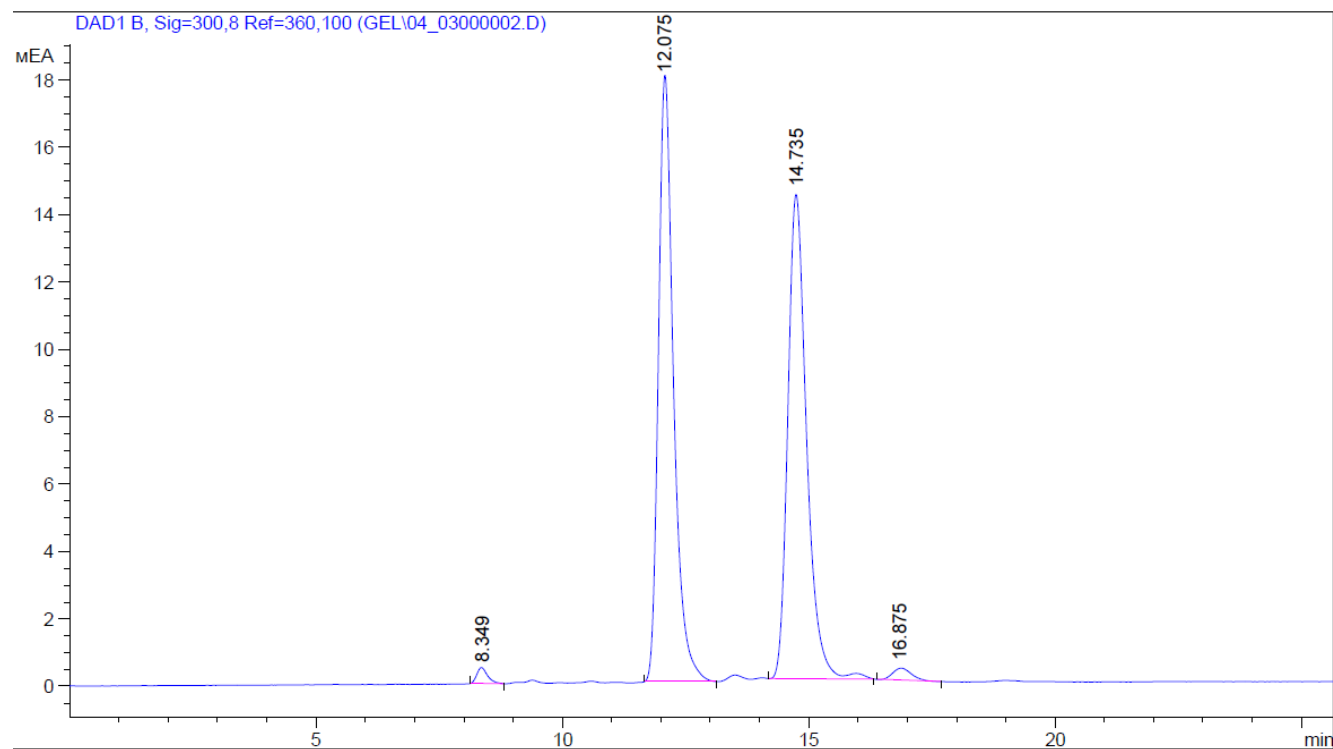
**Figure S37.** Molecular structure of compound **10c** showing 50% probability amplitude displacement ellipsoids (one of two independent molecules).

**Table S1.** Crystal data and structure refinement for compounds **9c** and **10a-c**

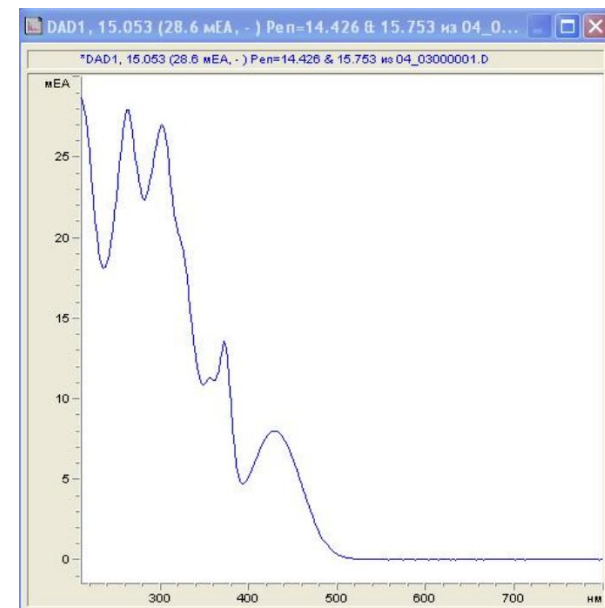
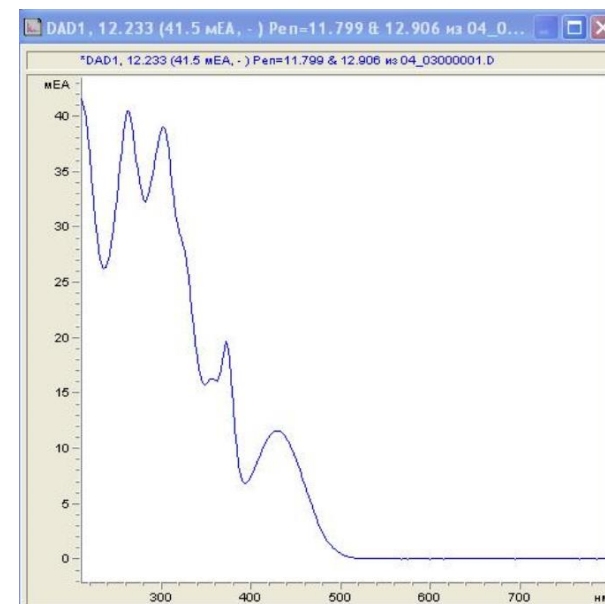
Compound	<b>9c</b>	<b>10a</b>	<b>10b</b>	<b>10c</b>
Empirical formula	C <sub>36</sub> H <sub>26</sub> N <sub>2</sub>	C <sub>39</sub> H <sub>27</sub> N <sub>3</sub>	2(C <sub>35</sub> H <sub>25</sub> N <sub>3</sub> )	2(C <sub>36</sub> H <sub>26</sub> N <sub>2</sub> )
Formula weight	486.59	537.63	975.16	937.17
<i>T</i> [K]	100.01(10)	100.01(16)	100.01(10)	100.00(13)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pca</i> 2 <sub>1</sub>
<i>a</i> [Å]	11.61830(10)	9.65530(10)	13.02350(10)	7.97570(10)
<i>b</i> [Å]	8.88780(10)	28.6719(2)	16.31390(10)	14.9619(2)
<i>c</i> [Å]	24.9720(3)	9.54660(10)	23.8982(2)	41.6111(6)
$\alpha$ [°]	90	90	90	90
$\beta$ [°]	102.2950(10)	92.2720(10)	105.5260(10)	90
$\gamma$ [°]	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	2519.49(5)	2640.76(4)	4892.23(7)	4965.52(12)
<i>Z</i>	4	4	4	4
<i>D<sub>c</sub></i> [g cm <sup>-3</sup> ]	1.283	1.352	1.324	1.302
$\mu$ [mm <sup>-1</sup> ]	0.571	0.612	0.602	0.580
No. of refl. collected/ unique	42146/5308 [ <i>R</i> <sub>int</sub> = 0.0342]	35450/5037 [ <i>R</i> <sub>int</sub> = 0.0256]	64970/ 9345 [ <i>R</i> <sub>int</sub> = 0.0285]	32512/8860 [ <i>R</i> <sub>int</sub> = 0.0439]
No. of parameters	346	382	690	690
<i>R</i> indices (all data)	<i>R</i> <sub>I</sub> = 0.0408 <i>wR</i> <sub>2</sub> = 0.1057	<i>R</i> <sub>I</sub> = 0.0357 <i>wR</i> <sub>2</sub> = 0.0883	<i>R</i> <sub>I</sub> = 0.0400 <i>wR</i> <sub>2</sub> = 0.1056	<i>R</i> <sub>I</sub> = 0.0471 <i>wR</i> <sub>2</sub> = 0.1167
<i>R</i> -factor [%]	3.82	3.43	3.66	4.37
CCDC Dep. No.	2034941	2034943	2034944	2034945

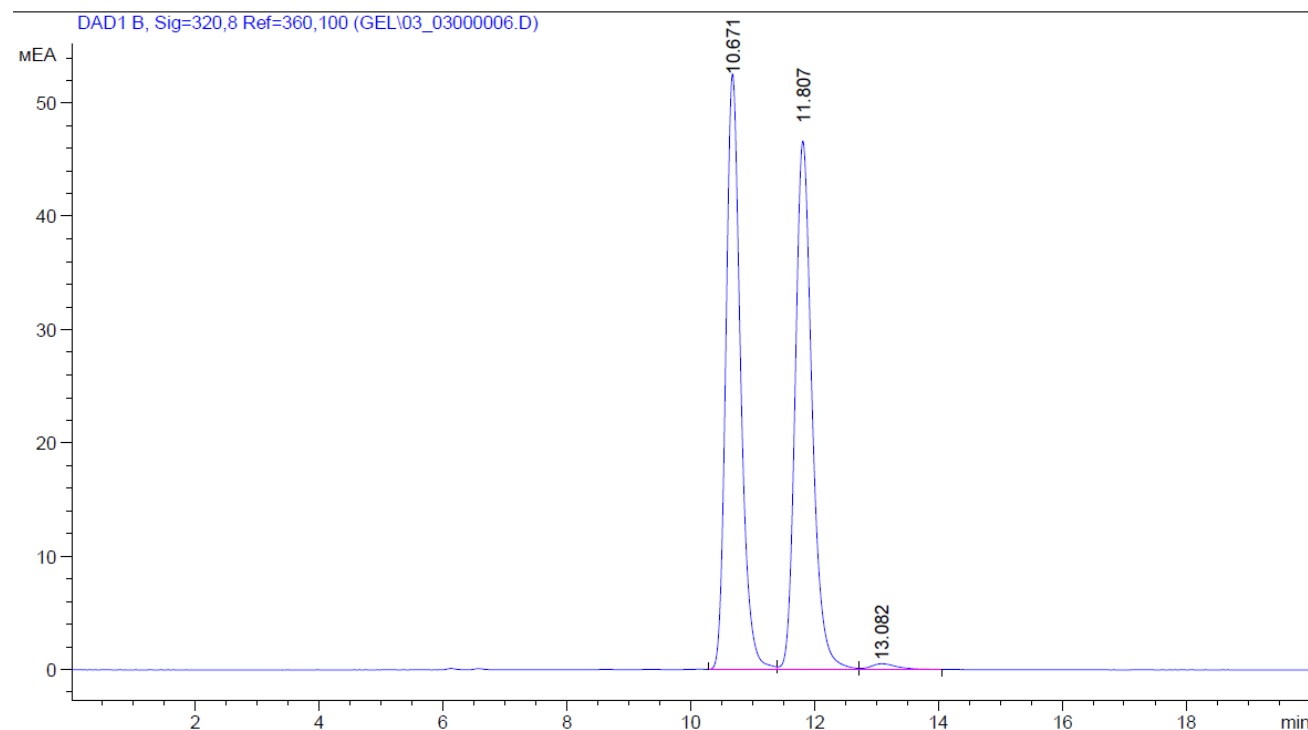
**The HPLC separations** were performed at 25 °C using Agilent 1200 equipment on the column Kromasil 5-Cellucoat (4.6 mm × 250 mm, particle size 5 µm), photodiode array detector; mobile phase is CH<sub>3</sub>CN of HPLC grade; injection of 5 µL of analyte solution in CH<sub>3</sub>CN; nominal flow rate is 0.8 mL min<sup>-1</sup>; UV detection at fixed wavelength 300 nm (for **10a**) and 320 nm (for **10b,c**).



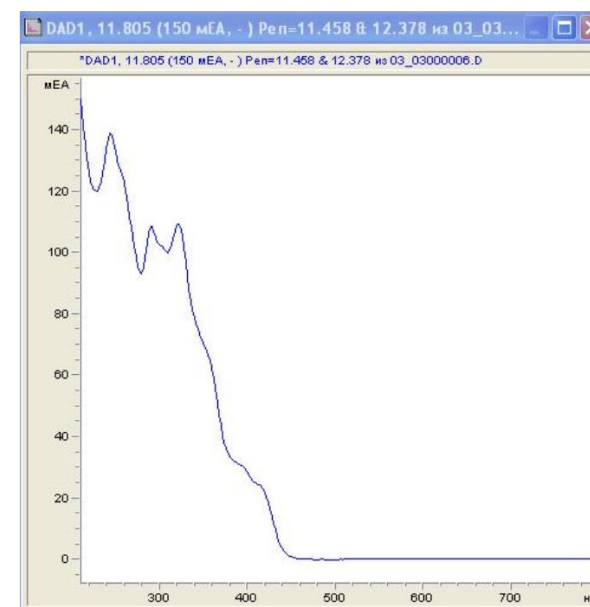
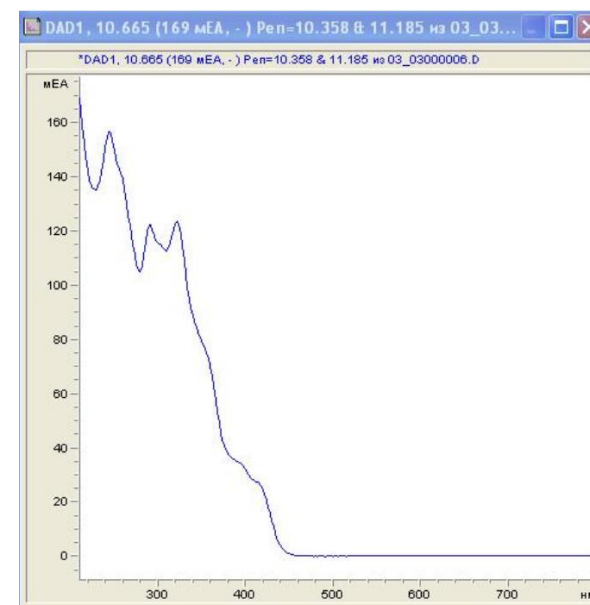


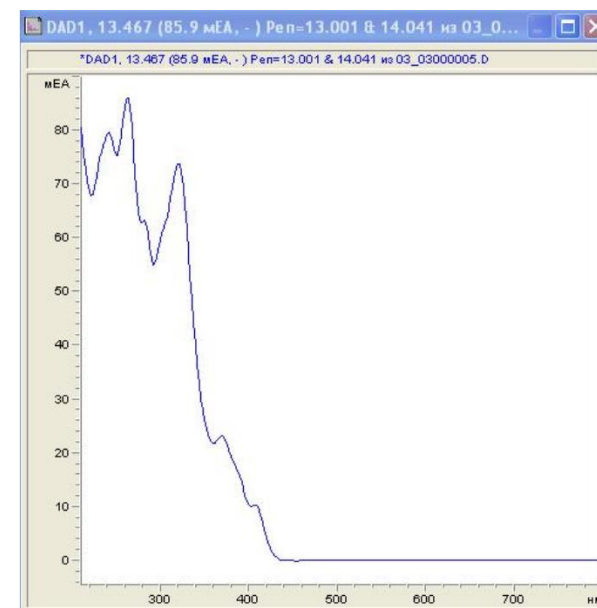
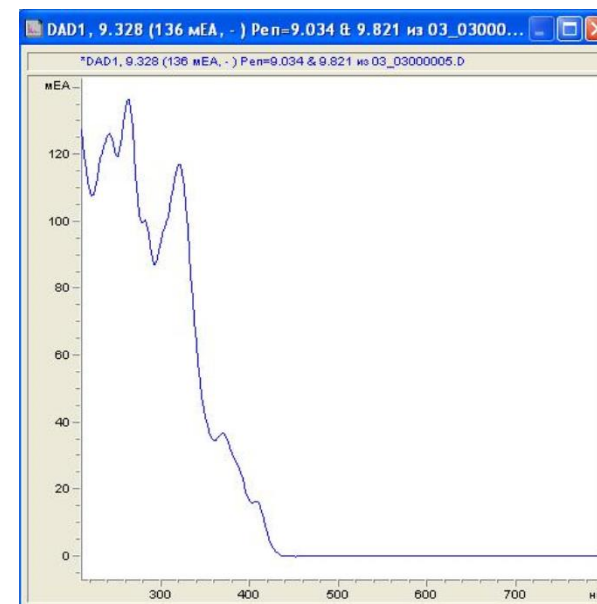
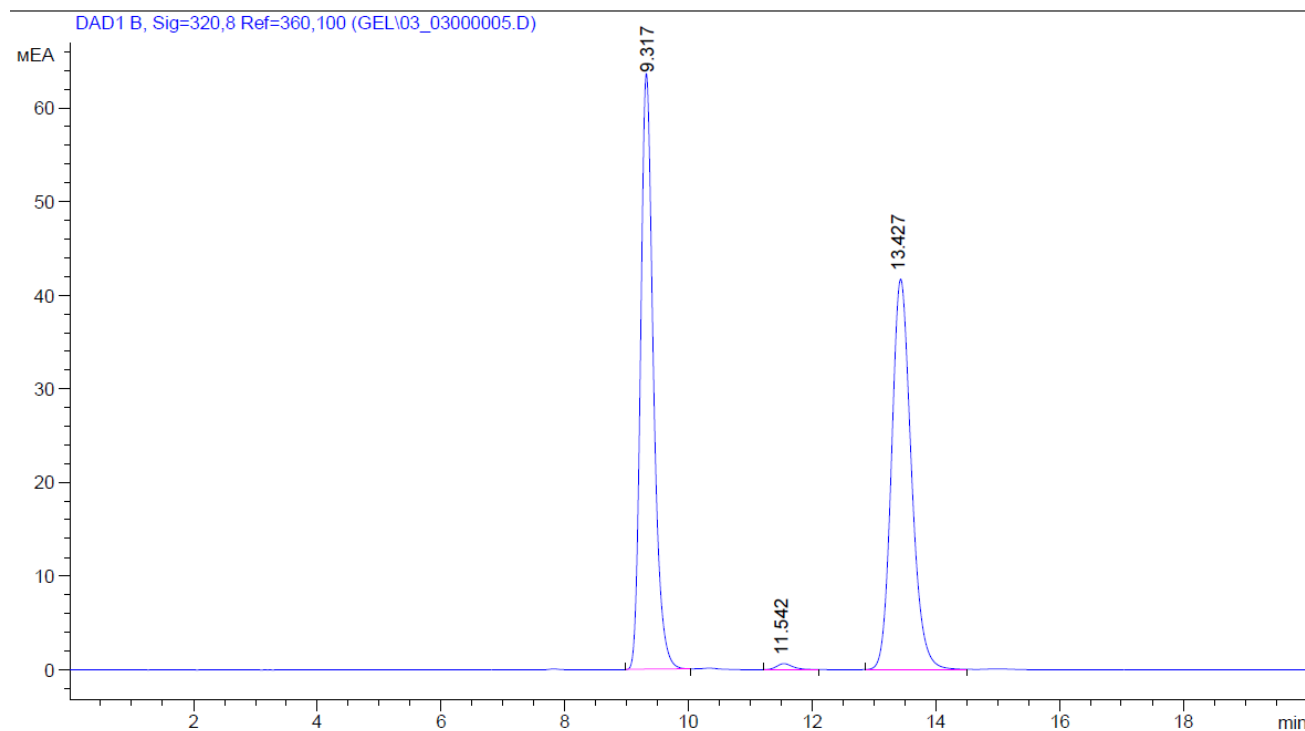
**Figure S38.** Chromatogram (UV-detection) of *(P,M)*-10a on Kromasil 5-Cellucoat (mobile phase CH<sub>3</sub>CN)



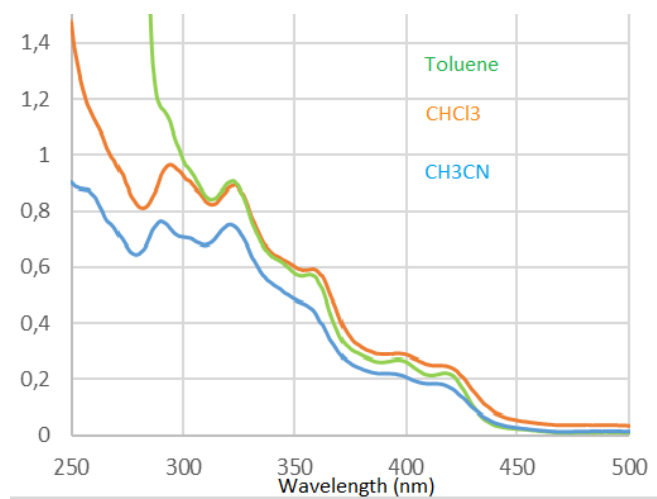


**Figure S39.** Chromatogram (UV-detection) of *(P,M)*-**10b** on Kromasil 5-Cellucoat  
(mobile phase CH<sub>3</sub>CN)

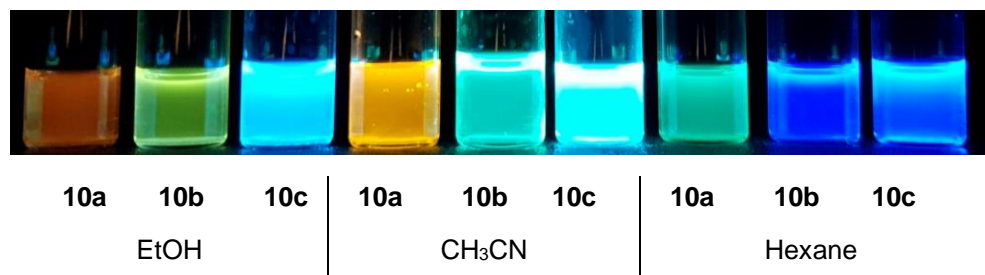




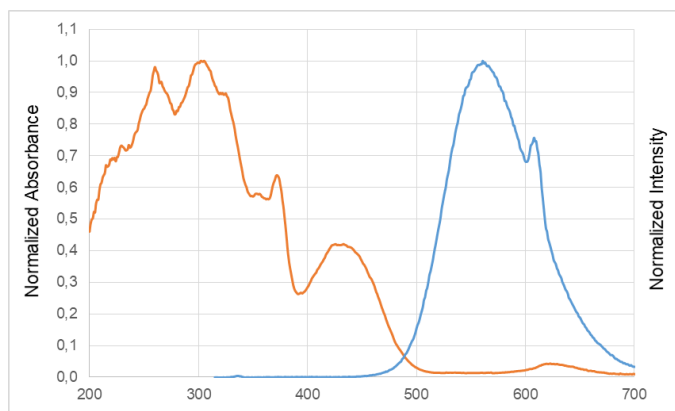
**Figure S40.** Chromatogram (UV-detection) of (*P,M*)-**10c** on Kromasil 5-Cellucoat (mobile phase CH<sub>3</sub>CN)



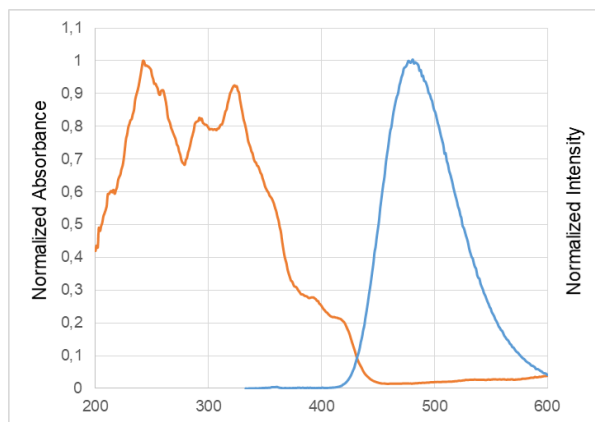
**Figure S41:** UV-vis spectra of [6]helicene **10b** in different solvents.



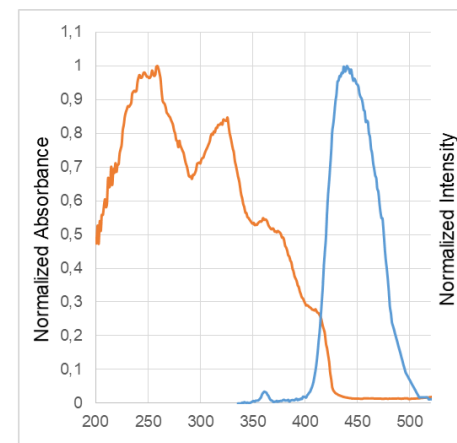
**Figure S42:** Solutions of [6]helicenes **10** in different solvents under UV irradiation (365 nm).



**Figure S43:** Normalized absorption and fluorescence spectra of **10a** in acetonitrile.



**Figure S44:** Normalized absorption and fluorescence spectra of **10b** in acetonitrile.



**Figure S45:** Normalized absorption and fluorescence spectra of **10c** in acetonitrile.

## References

1. Gulevskaya, A. V.; Shvydkova, E. A.; Tonkoglazova, D. I. *Eur. J. Org. Chem.* **2018**, 5030–5043. doi:10.1002/ejoc.201800613