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Supplementary Information

**A new family of 1,4-diaryl-1,3-butadiynes based on the “proton sponge”: synthesis,  
electronic and chemical properties**

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General Information .....	S2
Experimental Procedures and Characterization Data .....	S2
Copies of NMR Spectra (Figures S1–S23).....	S9
Copies of UV-vis absorption spectra (Figures S24–S32).....	S32
Copies of cyclic voltammograms (Figures S33–S36) .....	S37

### General Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on 250 and 600 MHz spectrometers. Chemical shifts were reported in ppm relative to  $\text{Me}_4\text{Si}$ . The UV-vis spectra were recorded on Varian Cary 50 Probe spectrophotometer in  $\text{CHCl}_3$ . CHN analysis was accomplished by combustion analysis (Dumas and Pregl method). The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source. Melting points were determinate in glass capillaries on a Stuart SMP 30 device and are uncorrected. Flash column chromatography was performed on  $\text{Al}_2\text{O}_3$ .

### Experimental Procedures and Characterization Data

**Interaction of 2,7-diiodo-1,8-bis(dimethylamino)naphthalene 5 with 4-ethynyl-1,8-bis(dimethylamino)naphthalene 6: Method A.**  $\text{CuI}$  (6 mg, 0.03 mmol),  $\text{Pd}_2\text{dba}_3$  (12 mg, 0.012 mmol),  $\text{Ph}_3\text{P}$  (24 mg, 0.09 mmol) were added to 2,7-diiodo- $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine **5** (321 mg, 0.69 mmol) in dry toluene (5 mL) and  $\text{Et}_3\text{N}$  (3 mL) under a slow stream of argon. To the reaction mixture stirred at 60 °C a solution of 4-ethynyl-1,8-bis(dimethylamino)naphthalene **6** (72 mg, 0.3 mmol) in  $\text{Et}_3\text{N}$  (2 mL) was added in portions over 2 h. The stirring was continued for 17 h at 60–65 °C. The solvent was evaporated to dryness. The residue was purified by flash column chromatography on  $\text{Al}_2\text{O}_3$  ( $2 \times 20$  cm) with  $\text{CH}_2\text{Cl}_2$  as the eluent. The first orange fraction with  $R_f$  0.5 gave 33 mg (46%) of diyne **2**. The second orange fraction with  $R_f$  0.3–0.4 gave 55 mg (32%) of compound **8**.

**Method B.**  $\text{Pd}(\text{PPh}_3)_4$  (12 mg, 0.012 mmol) was added to 2,7-diiodo- $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine **5** (107 mg, 0.23 mmol) in dry piperidine (3 mL) under a slow stream of argon. To the stirred reaction mixture a solution of 4-ethynyl-1,8-bis(dimethylamino)naphthalene **6** (24 mg, 0.1 mmol) in piperidine (2 mL) was added by portions for 1 h at 60 °C. The stirring was continued for 17 h at 55–60 °C. The solvent was evaporated to dryness. The residue was purified by flash column chromatography on  $\text{Al}_2\text{O}_3$  ( $2 \times 20$  cm) with hexane/ $\text{CH}_2\text{Cl}_2$  (1:1, v/v) as the eluent. The orange fraction with  $R_f = 0.3$ –0.4 gave 37 mg (64%) of compound **8**.

4,4'-(Buta-1,3-diyne-1,4-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **2** was obtained as a dark orange solid with mp 214–215 °C ( $\text{CH}_3\text{CN}$ ). HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{32}\text{H}_{35}\text{N}_4^+$  [ $\text{M}+\text{H}^+$ ],  $\text{C}_{32}\text{H}_{36}\text{N}_4^{2+}$  [ $\text{M}+2\text{H}^+$ ]: 475.2856, 238.1465, found 475.2843, 238.1474.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.78 (s, 12H), 2.85 (s, 12H), 6.81 (d,  $J$  = 8.0 Hz, 2H), 6.94 (d,  $J$  = 7.6 Hz, 2H), 7.39–7.42 (m, 2H), 7.62 (d,  $J$  = 8.0 Hz, 2H), 7.96 (dd,  $J$  = 8.2, 1.0, 2H) ppm.  $^{13}\text{C}$

NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 43.8, 44.0, 78.0, 82.2, 111.3, 111.4, 112.9, 119.1, 119.5, 126.7, 132.2, 138.4, 151.1, 151.9 ppm. UV/vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (log  $\epsilon$ ): 352 sh (4.21), 419 nm (4.52).

*2-((4,5-Bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-iodo-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine 8* was obtained as a yellow solid with mp 132–134 °C (EtOH). HRMS (ESI):  $m/z$  calcd. for C<sub>30</sub>H<sub>34</sub>IN<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 577.1823, found 577.1822. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.81 (s, 6H), 2.86 (s, 6H), 2.98 (s, 6H), 3.16 (s, 6H), 6.89 (d,  $J$  = 8.0 Hz, 1H), 6.98 (dd,  $J$  = 7.5, 1.1 Hz, 1H), 7.20 (d,  $J$  = 8.5 Hz, 1H), 7.41–7.43 (m, 1H), 7.49 (d,  $J$  = 8.4 Hz, 1H), 7.55 (d,  $J$  = 8.4 Hz, 1H), 7.63 (d,  $J$  = 8.0 Hz, 1H), 7.82 (d,  $J$  = 8.5 Hz, 1H), 8.04 (dd,  $J$  = 8.2, 1.1 Hz, 1H) ppm. <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>):  $\delta$  = 43.6, 44.1, 44.2, 45.7, 93.0, 95.9, 103.5, 111.7, 113.1, 113.4, 119.6, 120.2, 125.5, 126.6, 126.7, 130.2, 131.8, 132.1, 136.9, 137.1, 137.7, 151.0, 151.3, 151.6, 151.7 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  [(log  $\epsilon/m^{-1} \text{ cm}^{-1}$ )]: 277 sh [4.65], 346 sh [4.28], 399 [4.41] nm.

**Synthesis of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine 10:** CuI (4 mg, 0.02 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (7 mg, 0.01 mmol) were added to 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-iodo-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **8** (115 mg, 0.2 mmol) in dry toluene (5 mL) and Et<sub>3</sub>N (5 mL) under a slow stream of argon. To the reaction mixture stirred at 80 °C trimethylsilylacetylene (78 mg, 0.11 mL, 0.8 mmol) was added in portions for 2 h. The stirring was continued for 15 h at 80 °C. The solvent was evaporated to dryness. The residue was purified by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (2 × 20 cm) with *n*-hexane/EtOAc (15:1, v/v) as the eluent. The first orange fraction with R<sub>f</sub> 0.8–0.9 gave 58 mg of compound **9** with small amount of desilylated product **10**. The second orange fraction with R<sub>f</sub> 0.4 gave 26 mg of desilylated product **10**. The mixture of products **9** and **10** isolated from the first fraction was re-purified by column chromatography on Al<sub>2</sub>O<sub>3</sub> (1 × 20 cm), which led to complete desilylation and obtaining 43 mg of **10**. The total yield of compound **10** was 69 mg (73%).

*2-((4,5-Bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine 10* was obtained as a yellow solid with mp 136–137 °C (EtOAc). HRMS (ESI):  $m/z$  calcd. for C<sub>32</sub>H<sub>35</sub>N<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 475.2856, found 475.2856; calcd. for C<sub>32</sub>H<sub>36</sub>N<sub>4</sub><sup>2+</sup> [M+2H<sup>+</sup>]: 238.1465, found 238.1458. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.80 (s, 6H), 2.85 (s, 6H), 3.13 (s, 6H), 3.19 (s, 6H), 3.38 (s, 1H), 6.89 (d,  $J$  = 7.9 Hz, 1H), 6.97 (dd,  $J$  = 7.5, 1.0 Hz, 1H), 7.31 (d,  $J$  = 8.3 Hz, 1H), 7.33 (d,  $J$  = 8.3 Hz, 1H), 7.35 (d,  $J$  = 8.3 Hz, 1H), 7.40–7.43 (m, 1H), 7.51 (d,  $J$  = 8.3 Hz, 1H), 7.61 (d,  $J$  = 7.9 Hz, 1H), 8.03 (dd,  $J$  = 8.2, 1.0 Hz, 1H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.1, 44.2, 44.9, 45.1, 82.4, 84.9, 93.7, 94.7, 111.8,

113.1, 113.8, 115.8, 118.2, 119.7, 119.8, 123.5(0), 123.5(3), 126.5, 126.6, 130.0, 131.7, 132.0, 137.6(7), 137.7(2), 151.2, 151.4, 152.1, 153.8 ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  [(log  $\epsilon/m^{-1}$  cm<sup>-1</sup>): 284 [4.68], 358 sh [4.39], 401 [4.46] nm.

**Synthesis of N,N,1-trimethyl-1*H*-benzo[*g*]indol-9-amine 12:** A mixture of CuI (95 mg, 0.5 mmol) and 2-ethynyl-1,8-bis(dimethylamino)naphthalene **11** (238 mg, 1.0 mmol) in *i*-Pr<sub>2</sub>NH (4 mL) was reflux for 20 h. The reaction mixture is evaporated to dryness and the residue was purified by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (2.0 × 20 cm) with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:10, v/v) as the eluent. Colorless fraction with R<sub>f</sub> 0.6 gave 58 mg (26%) of compound **12**. The sample was identical to that obtained by us earlier [E. A. Filatova, A. F. Pozharskii, A. V. Gulevskaya and V. A. Ozeryanskii, *J. Org. Chem.*, 2015, **80**, 872–881].

**Synthesis of 2,2'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) 1** (Table 1, entry 2): A mixture of CuI (190 mg, 1 mmol), 2-ethynyl-1,8-bis(dimethylamino)naphthalene **11** (476 mg, 2 mmol) and TMEDA (116 mg, 0.15 mL, 1 mmol) in *i*-Pr<sub>2</sub>NH (9 mL) was stirred at room temperature for 20 h. Then it was poured into a porcelain dish and evaporated to dryness in a strong stream of air. The residue was purified by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (2.5 × 20 cm) with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (10:1, v/v) as the eluent. The dark-orange fraction with R<sub>f</sub> 0.2 was separated, and the crude product was purified additionally by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (2.5 × 20 cm) with the same eluent. Yield 331 mg (70%). Compound **1** was obtained as a dark amber solid with mp 84–85 °C (hexane). MS (*m/z*) (rel intensity) 476 (M+2H<sup>+</sup>; 19), 474 (M<sup>+</sup>; 57), 459 (100), 443 (20), 429 (20). Anal. calcd for C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>: C, 80.98; H, 7.22; N, 11.80; found: C, 80.92; H, 7.31; N, 11.57. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  2.77 (s, 12H), 3.15 (s, 12H), 6.93 (dd, *J* = 6.0, 2.5 Hz, 2H), 7.23–7.29 (m, 6H), 7.34 (d, *J* = 8.4 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  44.6, 44.7, 79.8, 84.2, 112.5, 113.7, 121.5, 122.0, 122.3, 126.8, 130.7, 138.2, 151.7, 153.7 ppm. UV/vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (lg  $\epsilon$ ): 282 (4.70), 317 sh (4.45), 350 sh (4.27), 429 nm (4.33).

**Synthesis of 4,4'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) 2** was carried out similarly to compound **1** using 4-ethynyl-1,8-bis(dimethylamino)naphthalene **6** (476 mg, 2 mmol) instead of 2-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **11**. Yield 370 mg (78%). Diyne **2** was obtained as a bright yellow solid with mp 214–215 °C (CH<sub>3</sub>CN). The sample was identical to that obtained in the Sonogashira reaction between 2,7-diiodo-1,8-bis(dimethylamino)naphthalene **5** with 4-ethynyl-1,8-bis(dimethylamino)naphthalene **6**.

**Synthesis of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) 3** was carried out similarly to compound **1** using 2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-7-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **15** (95 mg, 0.2 mmol) instead of 2-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **11**, CuI (19 mg, 0.1 mmol), TMEDA (23 mg, 0.03 mL, 0.2 mmol) and *i*-Pr<sub>2</sub>NH (4 mL). Flash column chromatography was carried out on Al<sub>2</sub>O<sub>3</sub> (1.0 × 20 cm) with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (10:1, v/v) as the eluent. The orange fraction with R<sub>f</sub> 0.25 was separated. The solution was concentrated on a rotary evaporator to 4 mL. The target compound **3** was filtered off. Yield 45 mg (47%). Compound **3** was obtained as a yellow orange solid with metallic luster and mp 262–264 °C (decomp.). HRMS (ESI): *m/z* calcd. for C<sub>64</sub>H<sub>68</sub>N<sub>8</sub><sup>2+</sup> [M + 2H<sup>+</sup>]: 474.2778, found 474.2780. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 2.79 (s, 12H), 3.17 (s, 12H), 3.18(3) (s, 12H), 3.18(6) (s, 12H), 6.96 (dd, *J* = 7.4, 1.4 Hz, 2H), 7.25–7.35 (m, 12H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 44.6, 44.7, 44.9, 45.1, 80.0, 84.0, 95.1, 96.3, 113.7, 114.5, 115.2, 117.5, 121.7, 122.6, 122.7, 122.9, 123.0, 125.2, 126.2, 129.6, 131.2, 131.4, 137.6(9), 137.7(1), 151.3, 151.6, 151.8, 154.4 ppm. UV/vis (CHCl<sub>3</sub>) λ<sub>max</sub> (lg ε): 315 (4.69), 437 nm (4.70).

**Synthesis of salt 3·4HBF<sub>4</sub>**: Tetramer **3** (64 mg, 0.068 mmol) was dissolved in a mixture of EtOAc and CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v; 10 mL). To this mixture 40% aqueous HBF<sub>4</sub> (3 μL, 5 equiv.) was added. The reaction mixture was thoroughly stirred for several minutes and diluted with a double volume of Et<sub>2</sub>O. The resulting precipitate was filtered off, washed with Et<sub>2</sub>O and dried in a vacuum. Yield 80 mg (91%). Compound **3·4HBF<sub>4</sub>** was obtained as a gray-green solid with mp 175–176 °C (decomp.). <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN, 70 °C) δ 3.26–3.30 (m, 12H), 3.40–3.45 (m, 12H), 3.48–3.58 (m, 24H), 7.77–7.84 (m, 3H), 7.88–7.96 (m, 4H), 7.98–8.02 (m, 3H), 8.06–8.19 (m, 8H), 18.84 (br s, 2H, NH), 19.91 (br s, 2H, NH) ppm. <sup>13</sup>C NMR (150 MHz, CD<sub>3</sub>CN) δ 43.8, 44.1, 44.2, 46.9, 84.4, 91.7, 95.3, 97.5, 119.3, 120.8, 121.6, 123.0, 128.9, 130.0, 130.5, 130.6, 130.7, 131.4, 133.0, 133.7, 136.4, 136.5, 143.6, 144.4, 146.4, 146.7 ppm.

**Synthesis of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) 4** was carried out similarly to compound **3** using 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **10** instead of 2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-7-ethynyl-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **15**. Yield 45 mg (47%). Compound **4** was obtained as a yellow solid with mp 205–207 °C (CH<sub>2</sub>Cl<sub>2</sub>). HRMS (ESI): *m/z*

calcd. for  $C_{64}H_{68}N_8^{2+}$  [ $M + 2H^+$ ]: 474.2778, found 474.2784.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  2.81 (s, 12H), 2.85 (s, 12H), 3.19 (s, 12H), 3.21 (s, 12H), 6.89 (d,  $J = 8.0$  Hz, 2H), 6.98 (dd,  $J = 7.6, 1.0$  Hz, 2H), 7.29 (d,  $J = 8.3$  Hz, 2H), 7.33 (d,  $J = 8.3$  Hz, 2H), 7.36 (d,  $J = 8.3$  Hz, 2H), 7.40–7.43 (m, 2H), 7.52 (d,  $J = 8.3$  Hz, 2H), 7.61 (d,  $J = 8.0$  Hz, 2H), 8.03 (d,  $J = 8.1$  Hz, 2H) ppm.  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  44.1, 44.2, 45.1, 45.2, 80.2, 84.1, 93.7, 94.7, 111.8, 113.1, 113.8, 114.8, 117.7, 119.7, 119.8, 123.1, 123.2, 125.6, 126.5, 130.0, 131.5, 132.4, 137.7, 137.8, 151.2, 151.4, 152.0, 154.6 ppm. UV/Vis ( $CHCl_3$ ):  $\lambda_{max}$  [(log  $\epsilon/m^{-1} cm^{-1}$ ): 280 sh [4.92], 369 [4.81], 406 [4.82] nm.

**Synthesis of 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **13**** (Table 1, entry 3): A mixture of 2-ethynyl-1,8-bis(dimethylamino)naphthalene **11** (238 mg, 1.0 mmol), CuI (29 mg, 0.15 mmol),  $I_2$  (127 mg, 0.5 mmol) and TMEDA (116 mg, 0.09 mL, 1.0 mmol) in *i*-Pr<sub>2</sub>NH (10 mL) was stirred at room temperature for 20 h under air. Then the reaction mixture poured into a porcelain dish and evaporated to dryness in air. The residue was purified by flash column chromatography on  $Al_2O_3$  (2.0 × 30 cm) using  $CHCl_3$  as the eluent. The fraction with  $R_f$  0.6 gave 147 mg (64%) of compound **13**. The fraction with  $R_f$  0.2 was eluted using  $CH_2Cl_2/EtOAc$  (10:1, v/v) as the eluent. From this, traces of diyne **1** (5 mg, 2%) was isolated. Compound **13** was obtained as a dark gold solid with mp 77-78 °C. HRMS (ESI):  $m/z$  calcd. for  $C_{31}H_{33}N_4^+$  [ $M+H^+$ ]: 461.2700, found 461.2687.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  2.74 (s, 6H), 2.81 (s, 6H), 3.21 (s, 6H), 4.14 (s, 3H), 6.97–7.00 (m, 2H), 7.12 (dd,  $J = 7.6, 1.1$  Hz, 1H), 7.27–7.36 (m, 4H), 7.42–7.46 (m, 2H), 7.51 (dd,  $J = 7.9, 0.8$  Hz, 1H), 7.57 (d,  $J = 8.4$  Hz, 1H) ppm.  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  37.9, 43.1, 44.7, 44.8, 87.1, 96.6, 108.8, 113.8(6), 113.9, 114.1, 117.7, 120.6, 121.8, 122.2, 122.6, 122.8, 124.3, 124.5, 125.4, 125.9, 126.4, 130.3, 133.7, 134.5, 137.9, 148.6, 151.7, 151.8 ppm. UV/vis ( $CHCl_3$ )  $\lambda_{max}$  (lg  $\epsilon$ ): 278 (4.57), 300 (4.57), 415 nm (4.30).

**Synthesis of salt **13**· $HBF_4$** : Compound **13** (77 mg, 0.17 mmol) was dissolved in a mixture of MeCN and  $CH_2Cl_2$  (1:1, v/v; 4 mL). To this mixture 40% aqueous  $HBF_4$  (0.029 mL, 1 equiv.) was added. The yellow-brown reaction mixture was thoroughly stirred for several minutes and diluted with a double volume of  $Et_2O$ . The resulting precipitate was filtered off, washed with  $Et_2O$ , dried in a vacuum, and recrystallized from MeCN. Yield 72 mg (78%). Compound **13**· $HBF_4$  was obtained as a yellow-brown solid which darken above 175 °C and does not melt up to 250 °C.  $^1H$  NMR (250 MHz,  $CD_3CN$ )  $\delta$  2.73 (s, 6H), 3.24 (d,  $J = 2.9$  Hz, 6H), 3.52 (d,  $J = 1.9$  Hz, 6H), 4.23 (s, 3H), 7.26 (d,  $J = 6.2$  Hz, 1H), 7.37–7.50 (m, 2H), 7.52–7.65 (m, 2H), 7.70–

7.85 (m, 2H), 7.87 (d,  $J = 8.6$  Hz, 1H), 7.98 (dd,  $J = 7.7, 1.1$  Hz, 1H), 8.05–8.12 (m, 2H), 19.25 (br s, 1H, NH) ppm. UV/Vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  [(log  $\epsilon/m^{-1}$  cm<sup>-1</sup>): 280 [4.50], 324 sh [4.25], 387 sh [4.07], 437 [4.25] nm.

**Synthesis of 2,2'-(9,9'-bis(dimethylamino)-1,1'-dimethyl-1*H*,1'*H*-3,3'-bibenzo[*g*]indole-2,2'-diyl)bis(ethyne-2,1-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **14** and 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-**

**tetramethylnaphthalene-1,8-diamine **13**** (Table 1, entry 4): A mixture of 2-ethynyl-1,8-bis(dimethylamino)naphthalene **11** (238 mg, 1.0 mmol), CuI (29 mg, 0.15 mmol), I<sub>2</sub> (127 mg, 0.5 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (28 mg, 0.04 mmol) in *i*-Pr<sub>2</sub>NH (8 mL) was stirred at room temperature for 20 h. Then the reaction mixture was poured out into a porcelain dish and was evaporated to dryness. The residue was purified by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (2.0 × 30 cm) using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. The fraction with  $R_f$  0.6 gave 100 mg (43%) of compound **13**. The fraction with  $R_f$  0.05 was eluted using CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (10:1, v/v) as the eluent. After evaporation of the solvent 50 mg (22%) of compound **14** was isolated. Compound **14** was obtained as a dark yellow solid with mp 226–228 °C (EtOH). HRMS (ESI):  $m/z$  calcd. for C<sub>62</sub>H<sub>63</sub>N<sub>8</sub><sup>+</sup> [M+H<sup>+</sup>]: 919.5170, found 919.5211. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 2.63$  (s, 6H), 2.79 (s, 6H), 2.83 (s, 3H), 2.88 (s, 3H), 4.29 (s, 3H), 6.84 (dd,  $J = 5.9, 2.9$  Hz, 1H), 7.08 (d,  $J = 8.4$  Hz, 1H), 7.13–7.20 (m, 4H), 7.35 (t,  $J = 7.7$  Hz, 1H), 7.40 (dd,  $J = 8.5, 0.5$  Hz, 1H), 7.51 (dd,  $J = 8.4, 0.6$  Hz, 1H), 7.67 (d,  $J = 8.4$  Hz, 1H) ppm. <sup>13</sup>C NMR (120 MHz, CDCl<sub>3</sub>):  $\delta = 38.2, 42.9, 43.4, 44.2, 44.5, 88.1, 99.4, 113.3, 113.6, 114.2, 115.8, 117.6, 121.1, 121.5, 121.8, 122.0, 122.2, 122.8, 123.8, 124.2, 126.0, 126.1, 130.6, 133.9, 134.8, 137.6, 148.7, 150.9, 151.5$  ppm. UV/vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (lg  $\epsilon$ ): 302 (4.91), 346 sh (4.62), 421 nm (4.65).

**Synthesis of N<sup>9</sup>,N<sup>9</sup>,N<sup>9'</sup>,N<sup>9'</sup>,1,1'-hexamethyl-1*H*,1'*H*-[2,2'-bibenzo[*g*]indole]-9,9'-diamine **21**:**

A mixture of 2,2'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **1** (142 mg, 0.3 mmol), CuI (57 mg, 0.3 mmol) in aniline (0.27 mg, 0.27 mL, 0.3 mmol) was stirred at 100 °C for 24 h. The mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and purified by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (1.0 × 20 cm) using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. Two fractions with  $R_f$  0.9 and 0.6 were isolated. The fraction with  $R_f$  0.9 was purified additionally by flash column chromatography on Al<sub>2</sub>O<sub>3</sub> (1.0 × 20 cm) using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2, v/v) as the eluent. After evaporation of the solvent, compound **21** was isolated (76 mg, 57%). The fraction with  $R_f$  0.6 gave 9.5 mg (7%) of compound **13**. Compound **21** was obtained as colorless crystals with mp 229–231 °C (heptane). HRMS (ESI):  $m/z$  calcd. for C<sub>30</sub>H<sub>31</sub>N<sub>4</sub><sup>+</sup> [M+H<sup>+</sup>]: 447.2543, found 447.2539. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  2.86 (s, 12H), 3.93 (s, 6H), 6.89 (s, 2H), 7.17 (dd,  $J =$

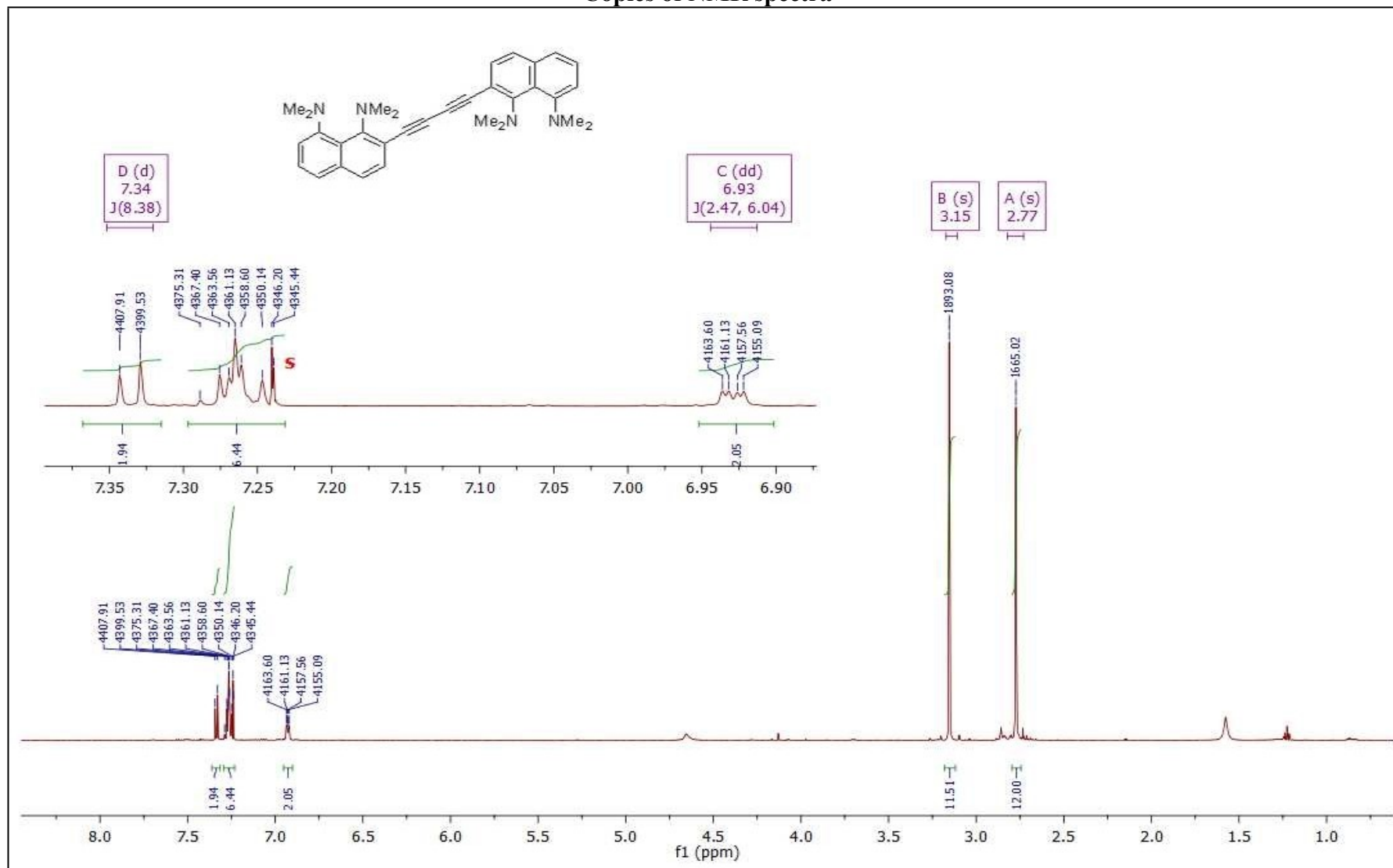
7.5, 1.1 Hz, 2H), 7.34–7.38 (m, 2H), 7.53 (dd,  $J = 8.3, 0.5$  Hz, 2H), 7.58 (dd,  $J = 8.1, 1.0$  Hz, 2H), 7.70 (d,  $J = 8.3$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  38.6, 43.3, 106.3, 113.9, 118.2, 120.7, 122.2, 123.0, 124.0, 126.5, 134.2, 135.4, 135.5, 148.2 ppm. Crystals of 2,2'-biindole **21** suitable for XRD analysis were grown from a 1:1 mixture of petr. eth. and  $\text{CH}_2\text{Cl}_2$ . CCDC 2118209 contains the supplementary crystallographic data for this paper. 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).

**Synthesis of 2,2'-(9,9'-bis(dimethylamino)-1,1'-dimethyl-1*H*,1'*H*-3,3'-bibenzo[*g*]indole-2,2'-diyl)bis(ethyne-2,1-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **14**:** A mixture of 2,2'-(buta-1,3-diyne-1,4-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **1** (142 mg, 0.3 mmol), CuI (6 mg, 0.03 mmol),  $\text{Pd}_2\text{dba}_3$  (14 mg, (0.015 mmol) in DMF (5 mL) was stirred at 100 °C for 3 h. Then the reaction mixture poured into a porcelain dish and evaporated to dryness in a strong stream of air. The residue was purified by flash column chromatography on  $\text{Al}_2\text{O}_3$  (1.0 × 20 cm) using  $\text{CH}_2\text{Cl}_2$  as the eluent. The fraction with  $R_f$  0.6 gave compound **13** (8 mg, 6%). The sample was identical to that obtained in the Glaser-Hay reaction of compound **11** (see Table 1, entry 3). The next fraction with  $R_f$  0.2 was eluted using  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  (10:1, v/v) as the eluent. From this, compound **14** was isolated (70 mg, 51%). The sample was identical to that obtained in the Glaser-Hay reaction of compound **11** (see Table 1, entry 4).

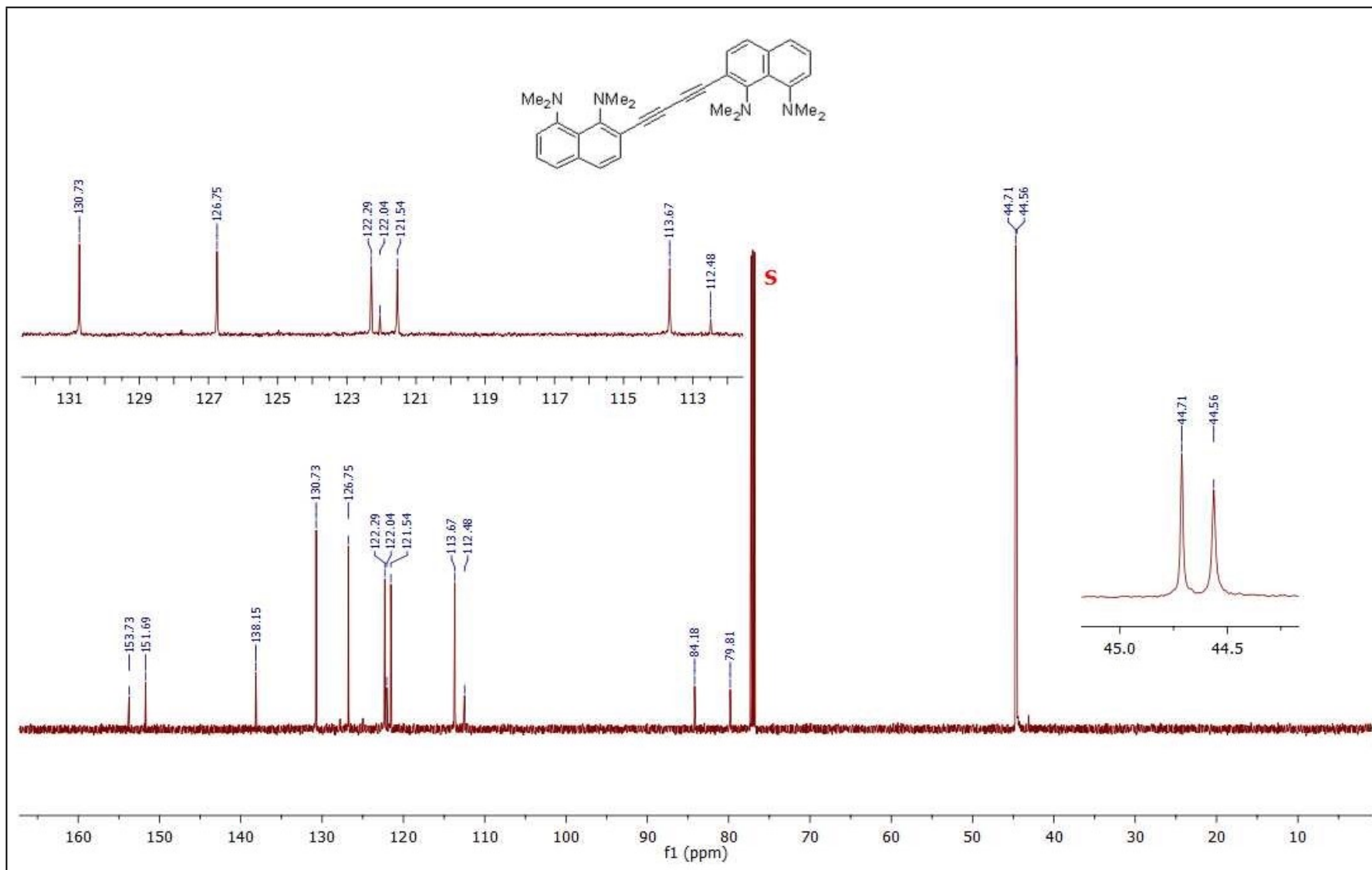
**Synthesis of 4,4'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **22**:** A mixture of 4,4'-(buta-1,3-diyne-1,4-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **2** (142 mg, 0.3 mmol), CuCl (149 mg, 0.15 mmol) and aniline (0.27 mL, 3 mmol) were stirred at 100 °C for 15 h under a slow stream of argon. The cooled reaction mixture was then diluted with  $\text{CH}_2\text{Cl}_2$  (10 mL) and washed with 10% aqueous KOH (10 mL). The organic layer was separated and evaporated to dryness without heating. The residue was purified by flash column chromatography on  $\text{Al}_2\text{O}_3$  (1 × 20 cm) with  $\text{CH}_2\text{Cl}_2$ /petroleum ether (1:1, v/v) as eluent. The first orange fraction with  $R_f$  0.6 gave 40 mg (28%) of the starting compound **2**. The second dark yellow fraction with  $R_f$  0.2 gave 31 mg (18%) of compound **22**. Compound **22** was obtained as a yellow-brown caramel. HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{38}\text{H}_{42}\text{IN}_5^+$  [ $\text{M}+\text{H}^+$ ]: 568.3435, found 568.3435;  $\text{C}_{38}\text{H}_{43}\text{IN}_5^{2+}$  [ $\text{M}+2\text{H}^+$ ] 284.6754, found 284.6761.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  2.74 (s, 12H), 2.76 (s, 12H), 6.48 (s, 2H), 6.70–6.80 (m, 7H), 6.86 (d,  $J = 7.4$  Hz, 2H), 7.04 (br. s, 2H), 7.22 (t,  $J = 7.9$  Hz, 2H), 7.63 (br. s, 2H) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  44.1, 44.2, 110.8, 111.4, 112.0, 120.0, 120.1, 124.4, 125.1, 125.5, 127.3, 127.5, 129.2, 133.2, 137.6, 139.4, 150.2, 150.5 ppm.



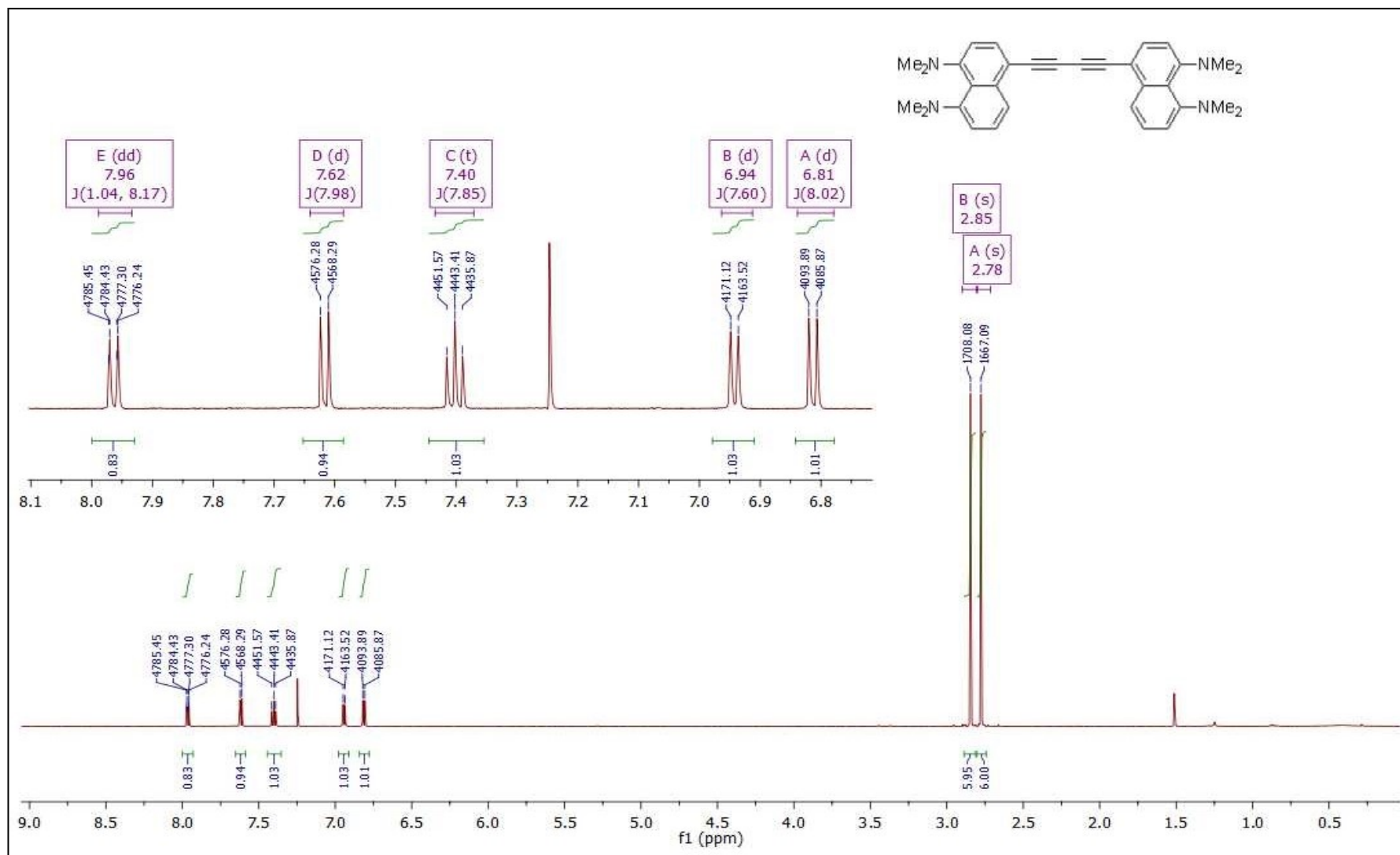
## Copies of NMR spectra



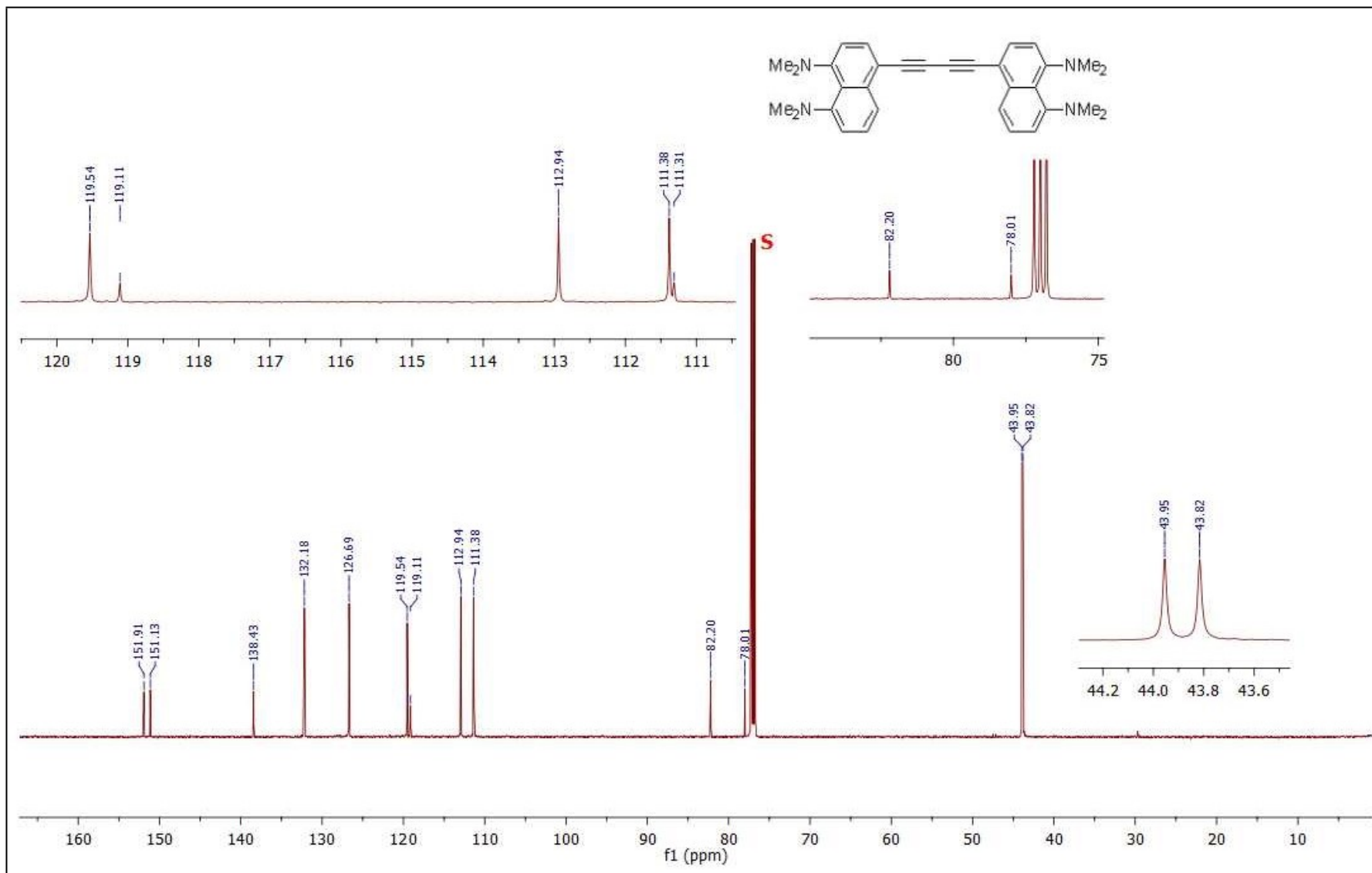
**Fig. S1.** <sup>1</sup>H NMR spectrum of 2,2'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **1** (600 MHz, CDCl<sub>3</sub>).



**Fig. S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,2'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **1** (150 MHz,  $\text{CDCl}_3$ ).

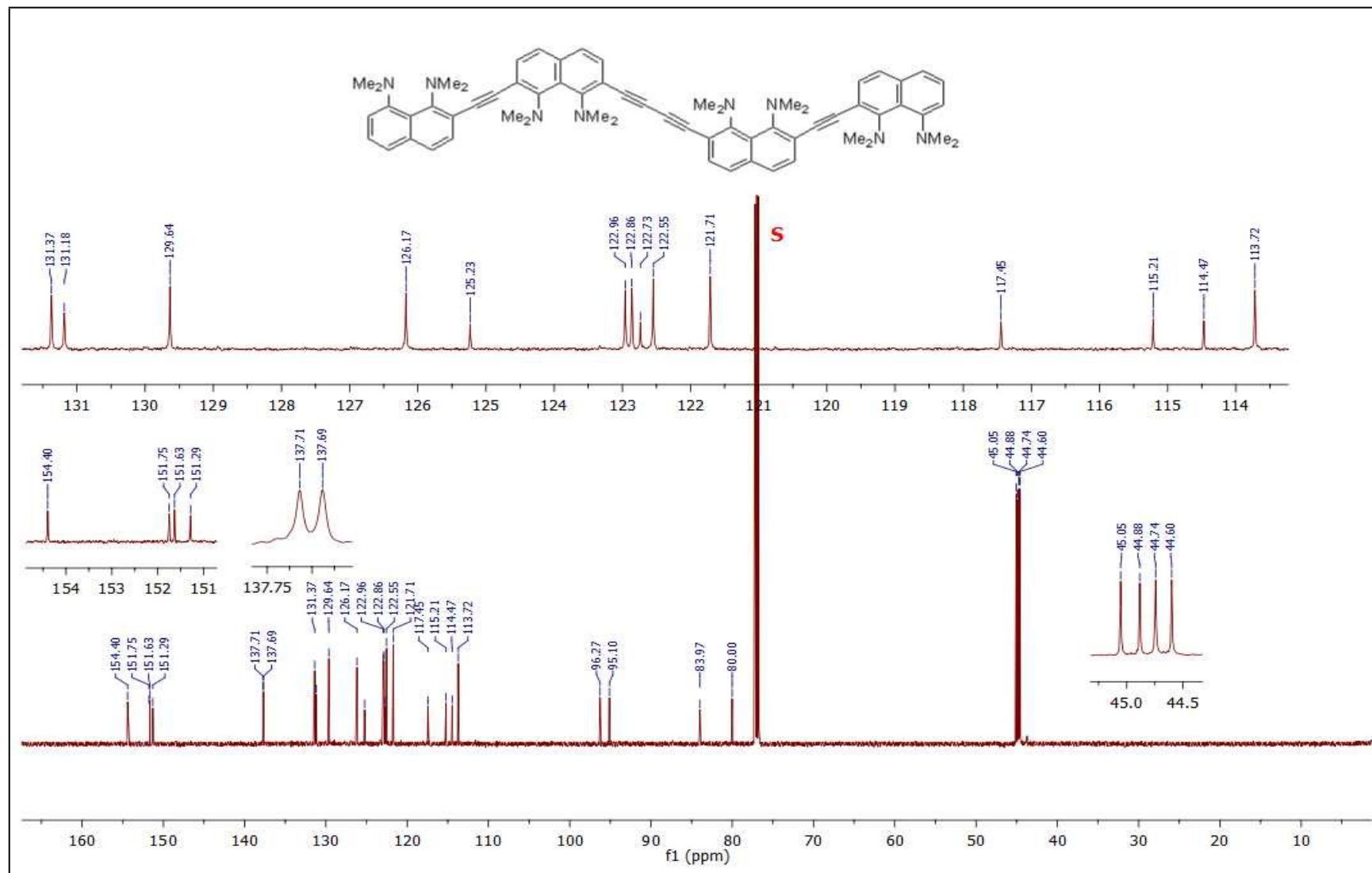


**Fig. S3.** <sup>1</sup>H NMR spectrum of 4,4'-(buta-1,3-diyne-1,4-diyl)bis(N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **2** (600 MHz, CDCl<sub>3</sub>).



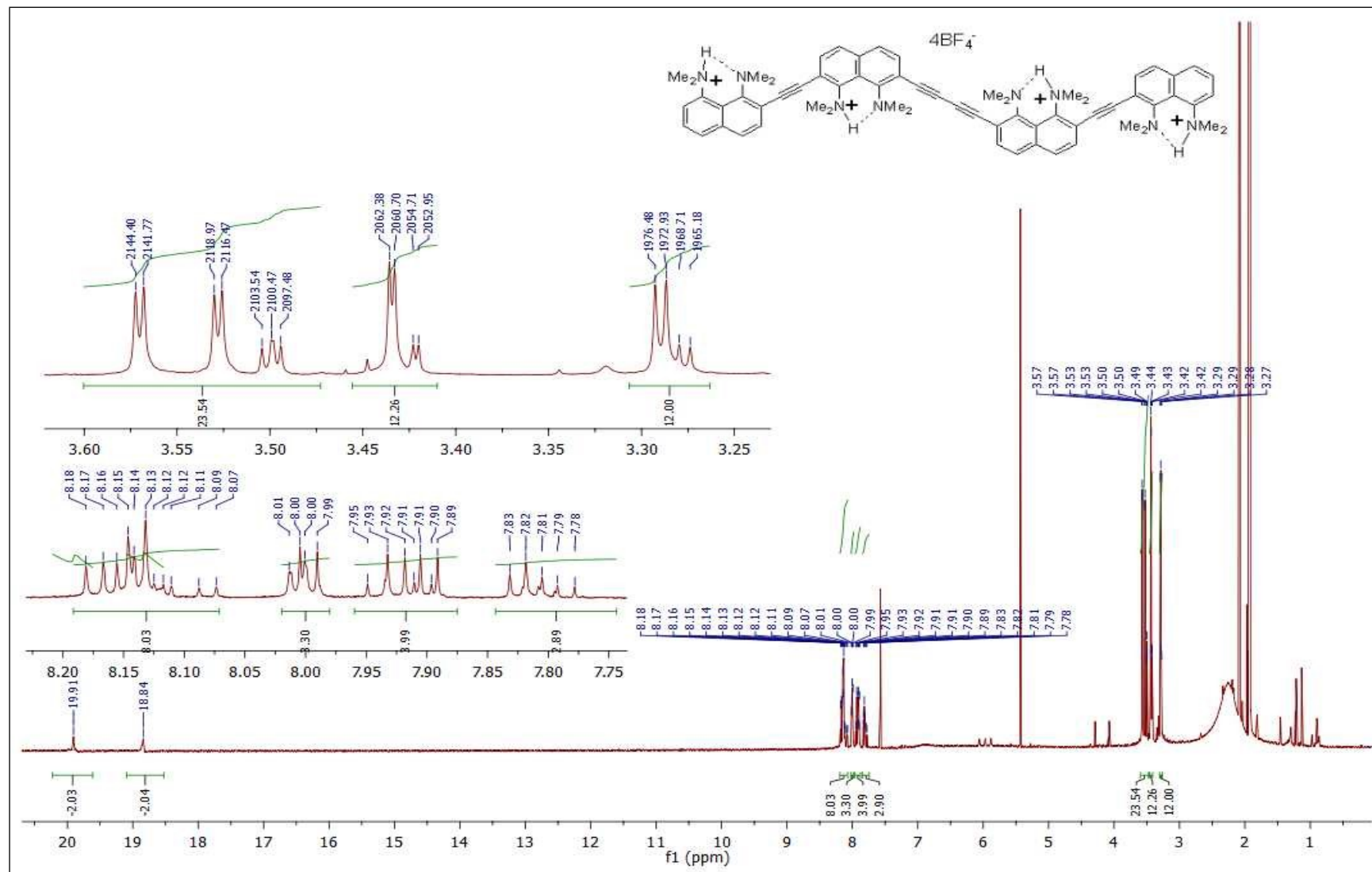
**Fig. S4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 4,4'-(buta-1,3-diyne-1,4-diy)bis( $\text{N}^1,\text{N}^1,\text{N}^8,\text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **2** (150 MHz,  $\text{CDCl}_3$ ).



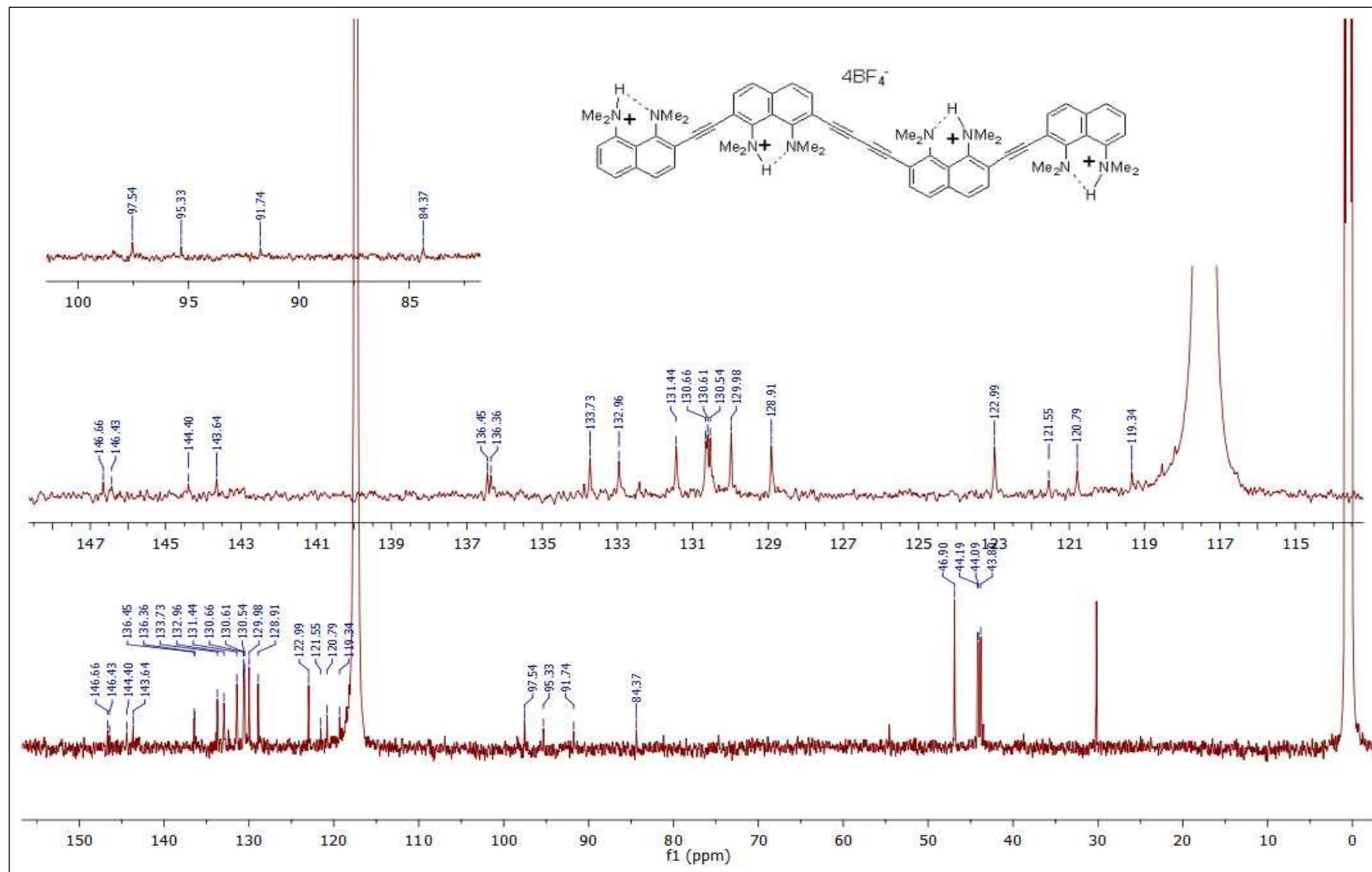


**Fig. S6.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **3** (150 MHz, CDCl<sub>3</sub>).



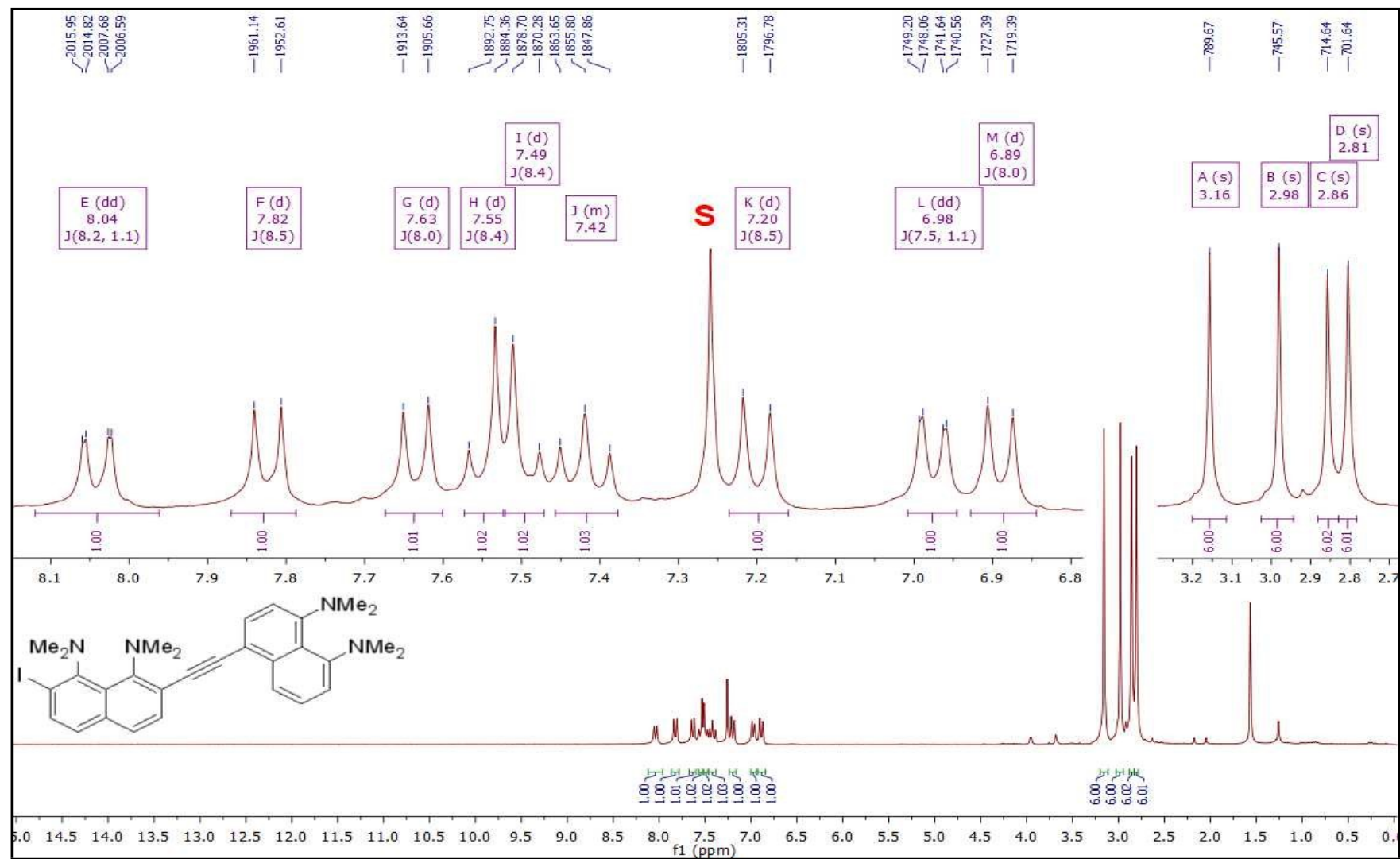


**Fig. S7.** <sup>1</sup>H NMR spectrum of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) salt **3**·4HBF<sub>4</sub> (600 MHz, CD<sub>3</sub>CN).

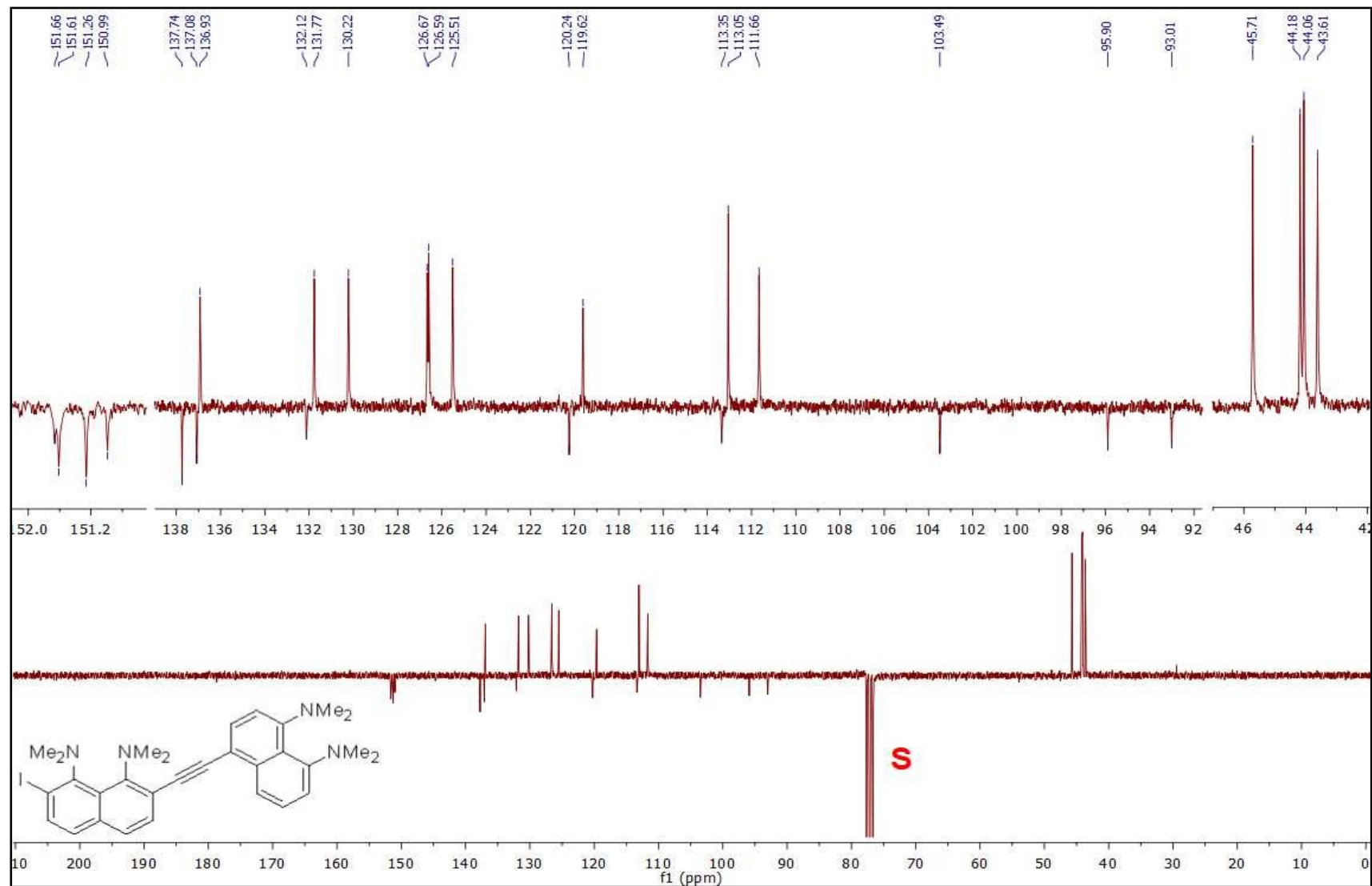


**Fig. S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)- $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine) salt  $3 \cdot 4\text{HBF}_4$  (150 MHz,  $\text{CD}_3\text{CN}$ ).



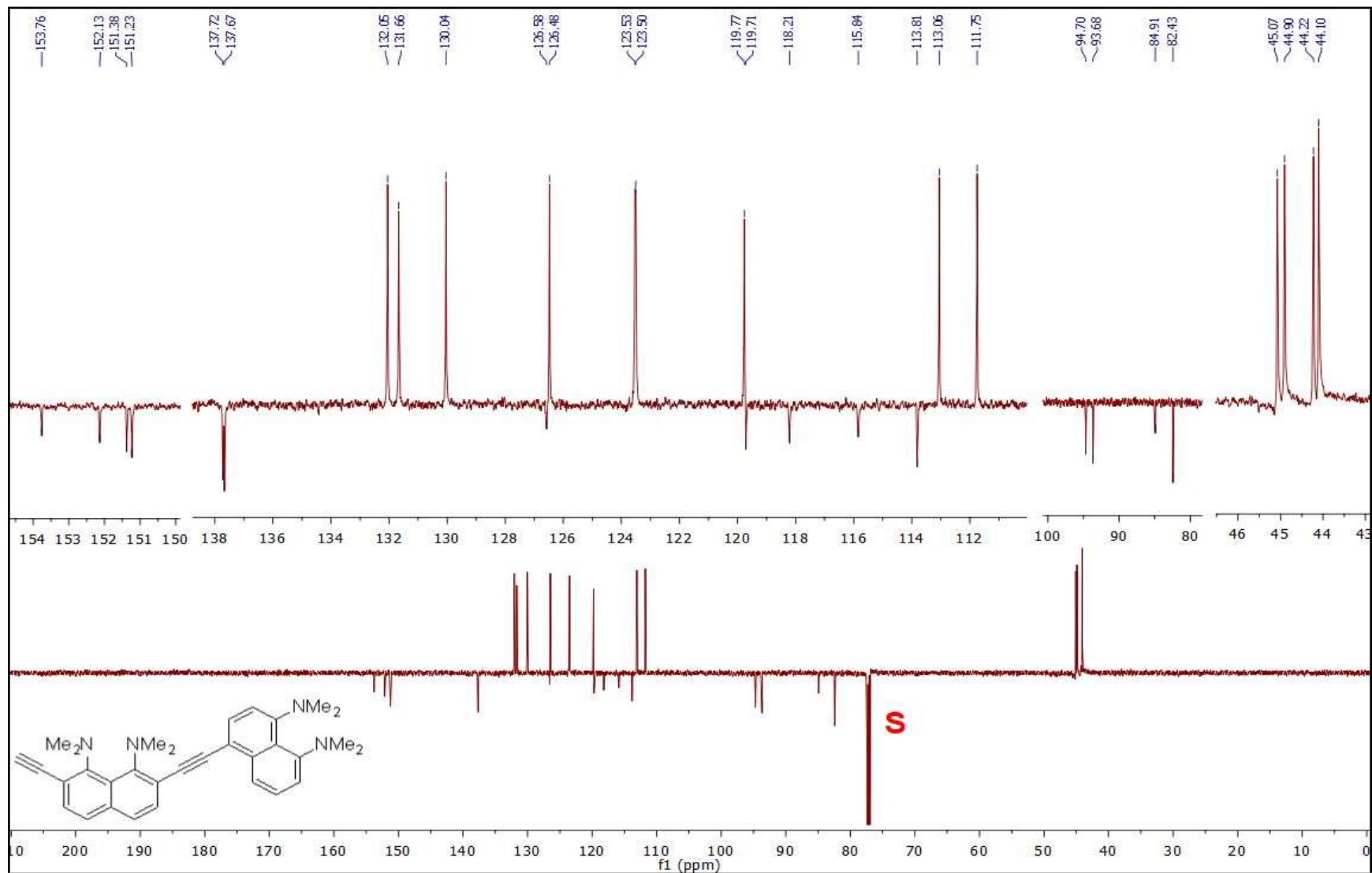


**Fig. S9.**  $^1\text{H}$  NMR spectrum of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-iodo- $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine **8** (250 MHz,  $\text{CDCl}_3$ ).

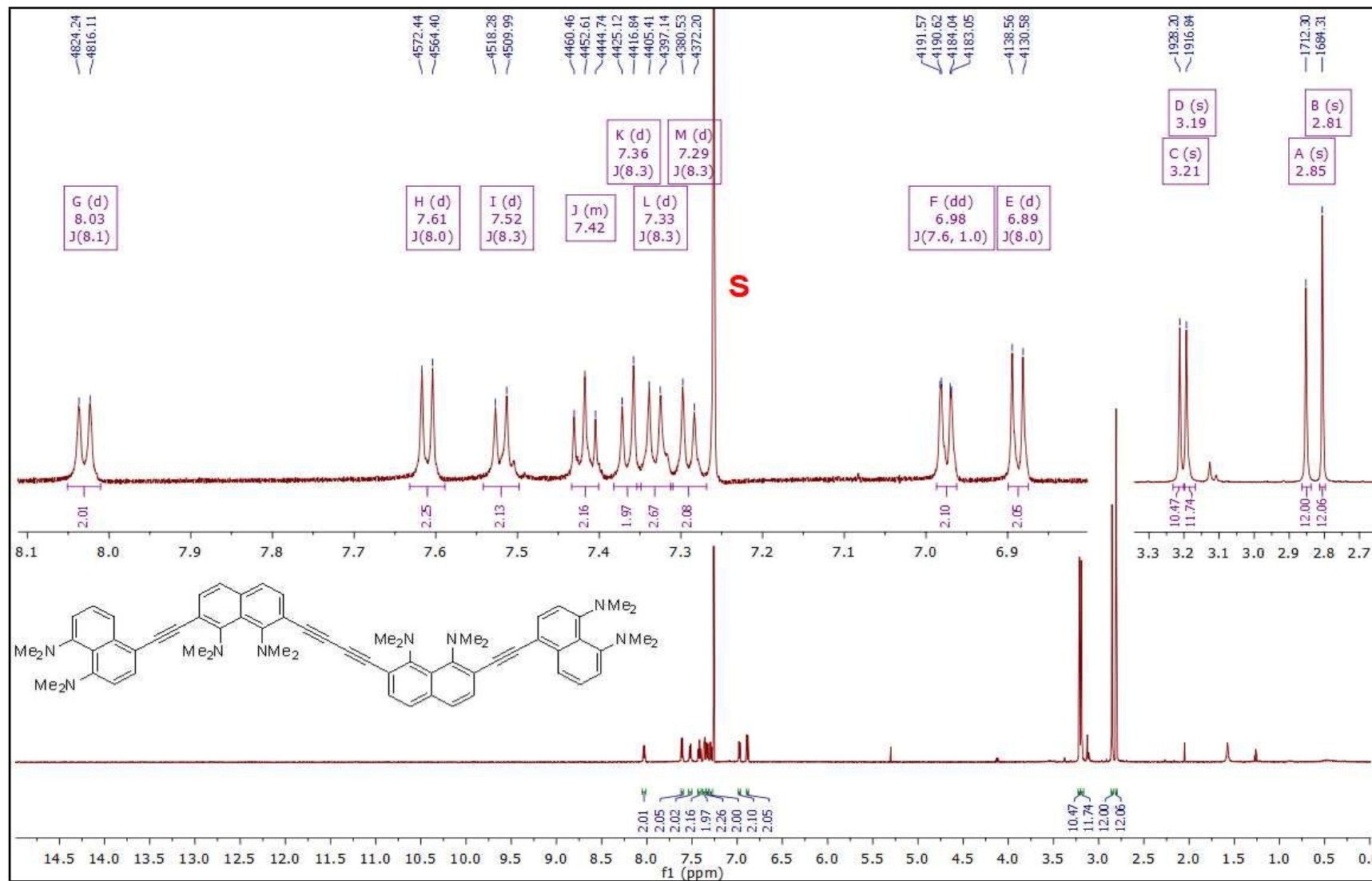


**Fig. S10.**  $^{13}\text{C}\{^1\text{H}\}$  APT-NMR spectrum of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-iodo- $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine **8** (62.9 MHz,  $\text{CDCl}_3$ ).

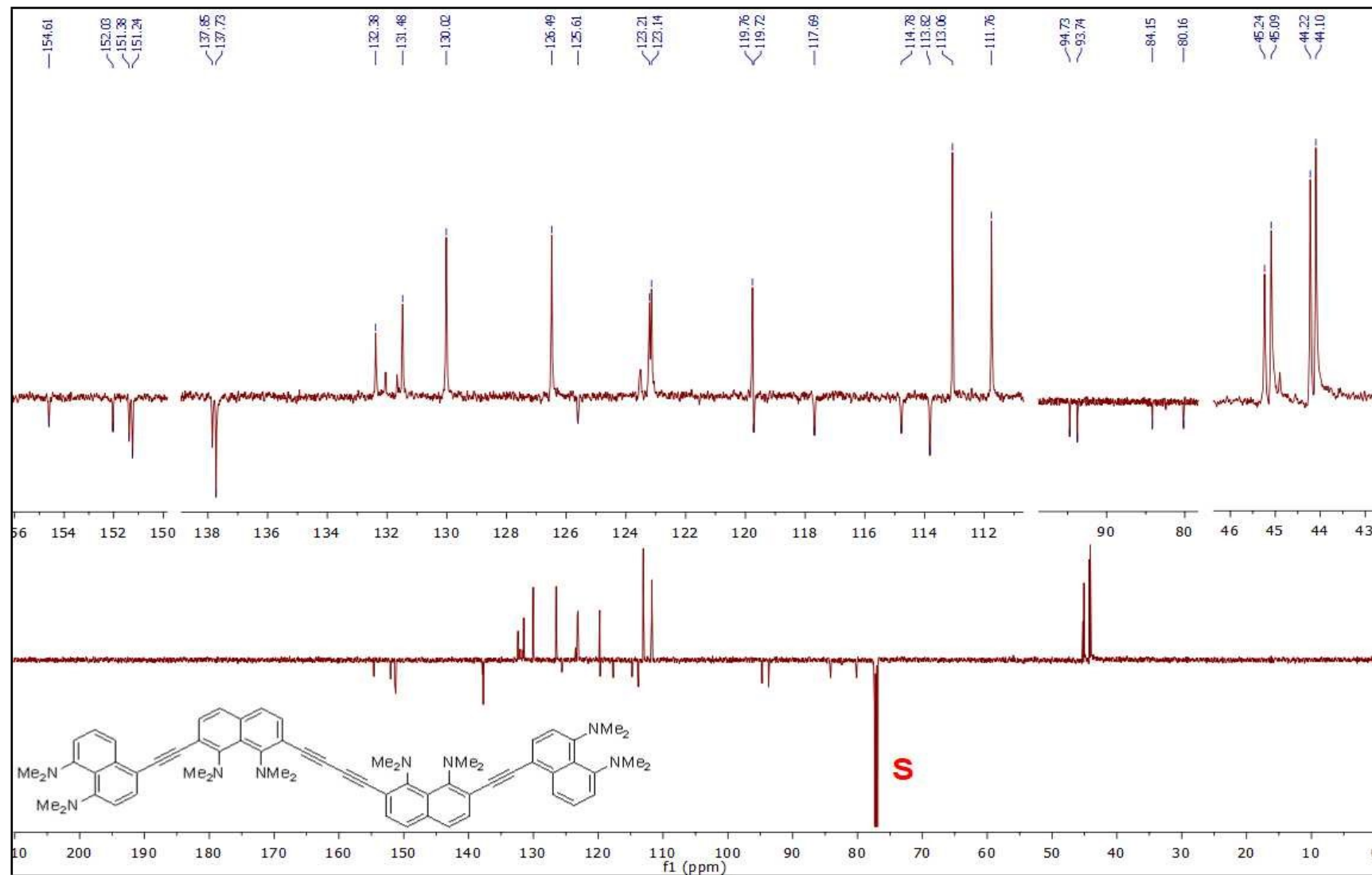




**Fig. S12.**  $^{13}\text{C}\{^1\text{H}\}$  APT-NMR spectrum of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-ethynyl- $\text{N}^1,\text{N}^1,\text{N}^8,\text{N}^8$ -tetramethylnaphthalene-1,8-diamine **10** (150 MHz,  $\text{CDCl}_3$ ).

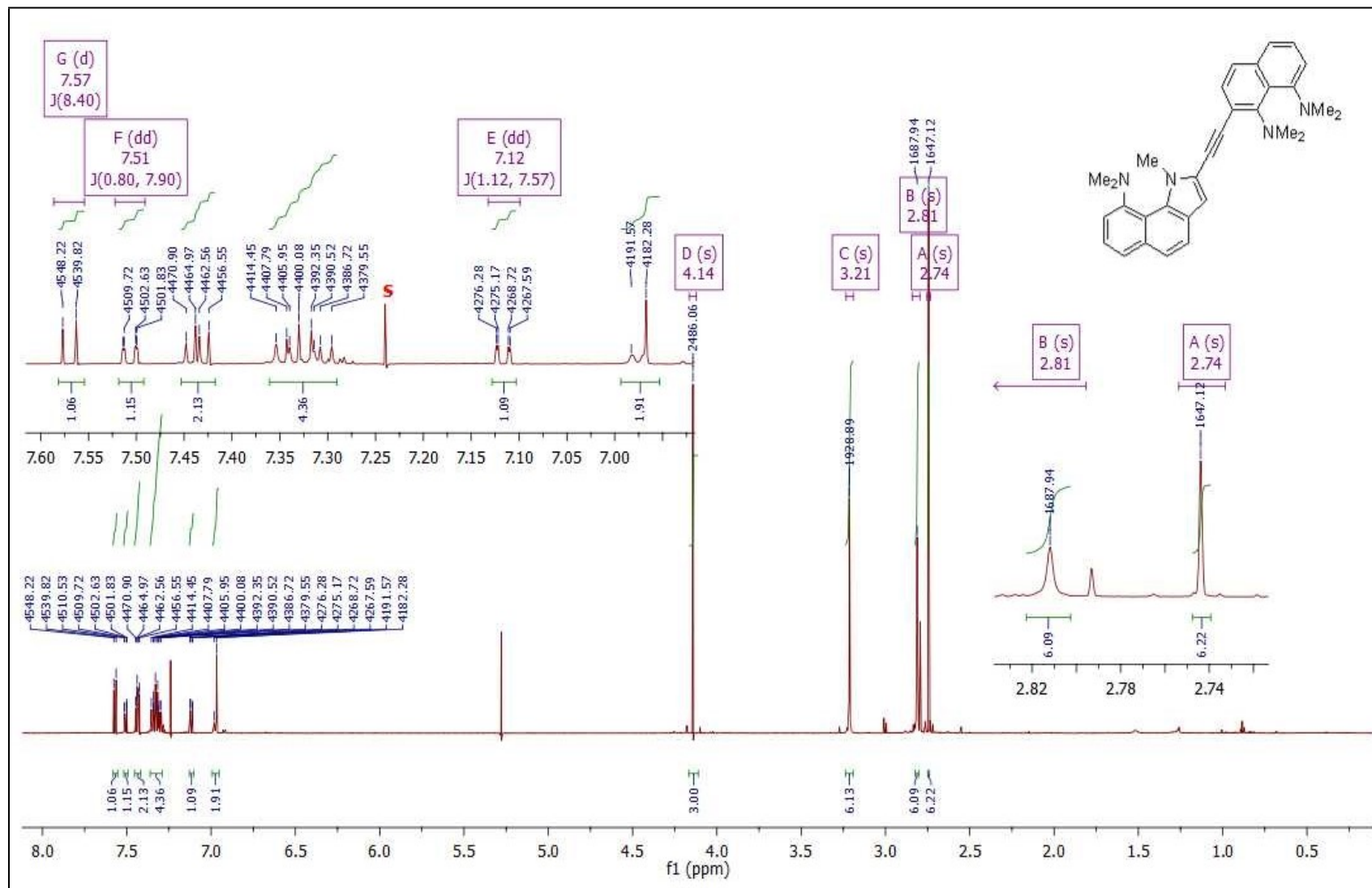


**Fig. S13.**  $^1\text{H}$  NMR spectrum of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **4** (600 MHz,  $\text{CDCl}_3$ ).

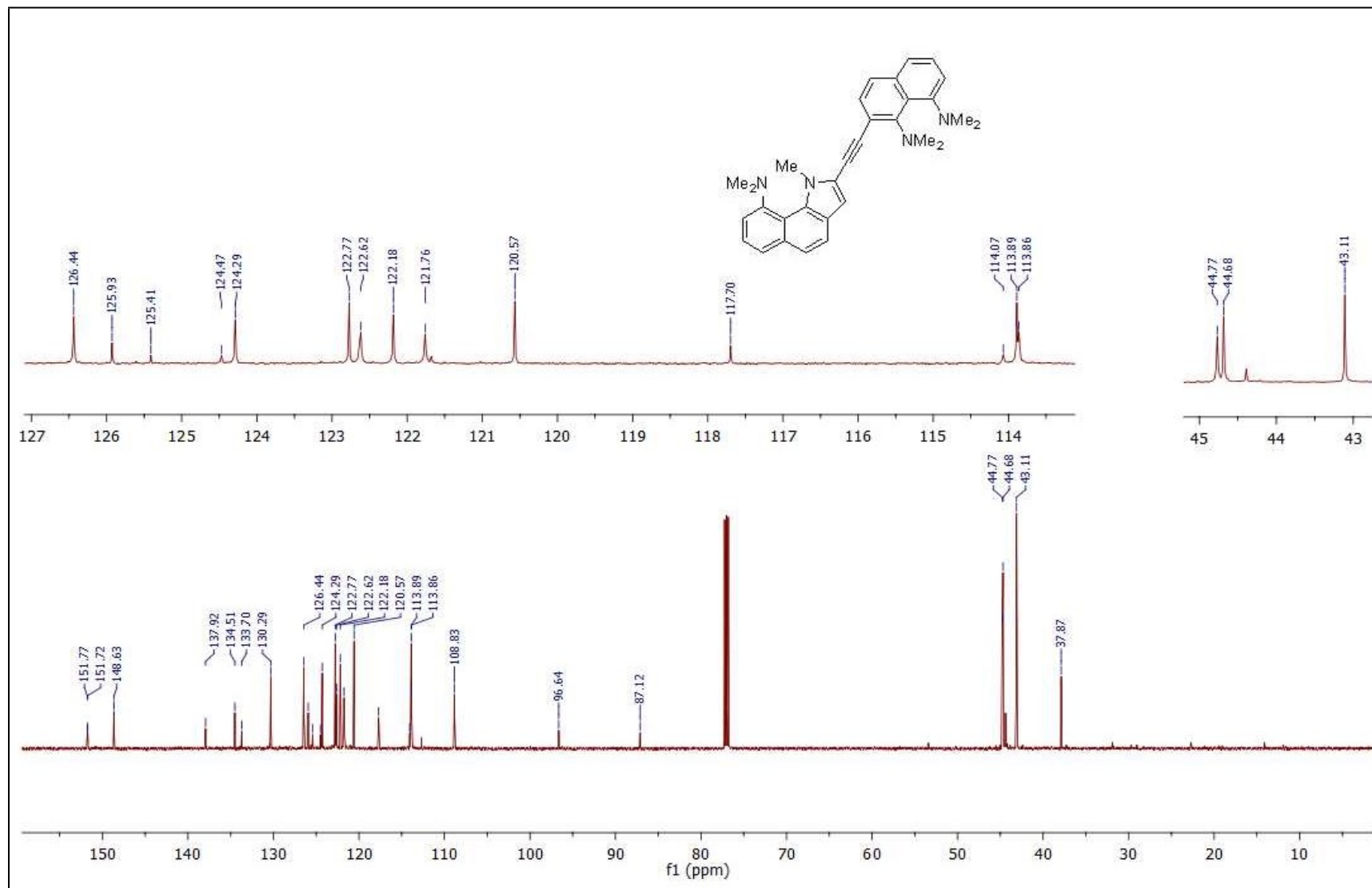


**Fig. S14.**  $^{13}\text{C}\{^1\text{H}\}$  APT-NMR spectrum of 7,7'-(buta-1,3-diyne-1,4-diyl)bis(2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **4** (150 MHz,  $\text{CDCl}_3$ ).



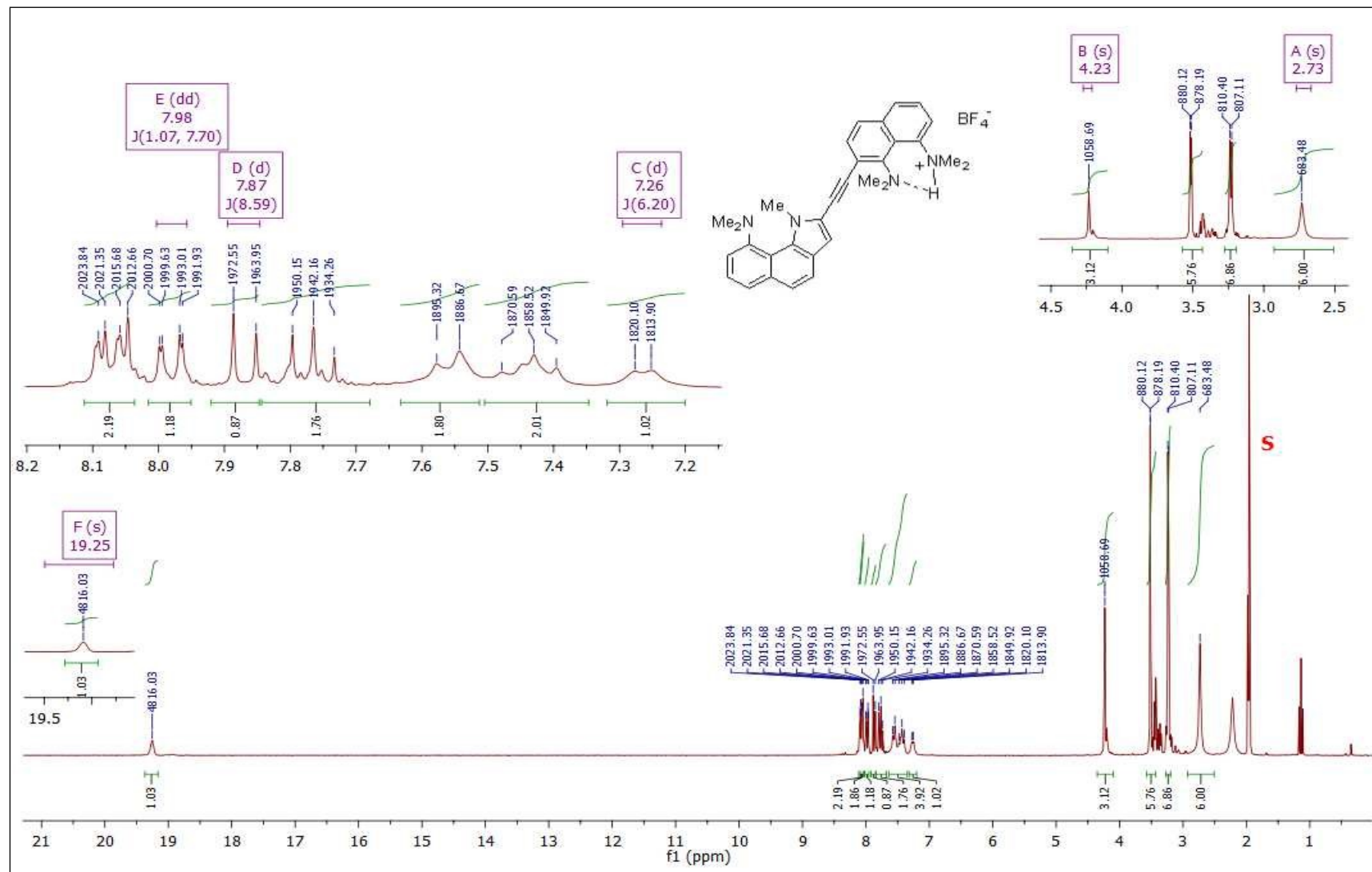


**Fig. S15.**  $^1\text{H}$  NMR spectrum of 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **13** (600 MHz,  $\text{CDCl}_3$ ).

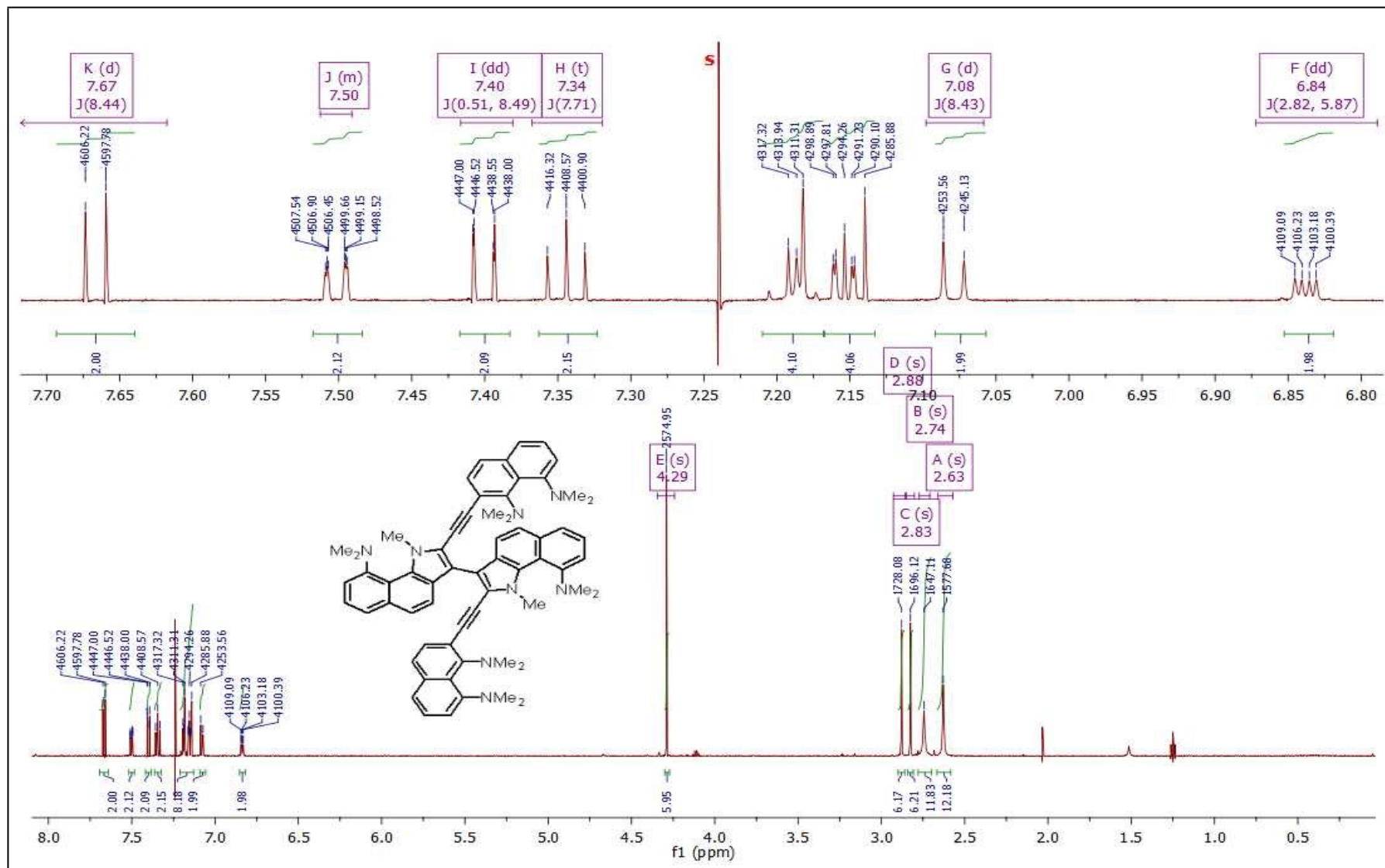


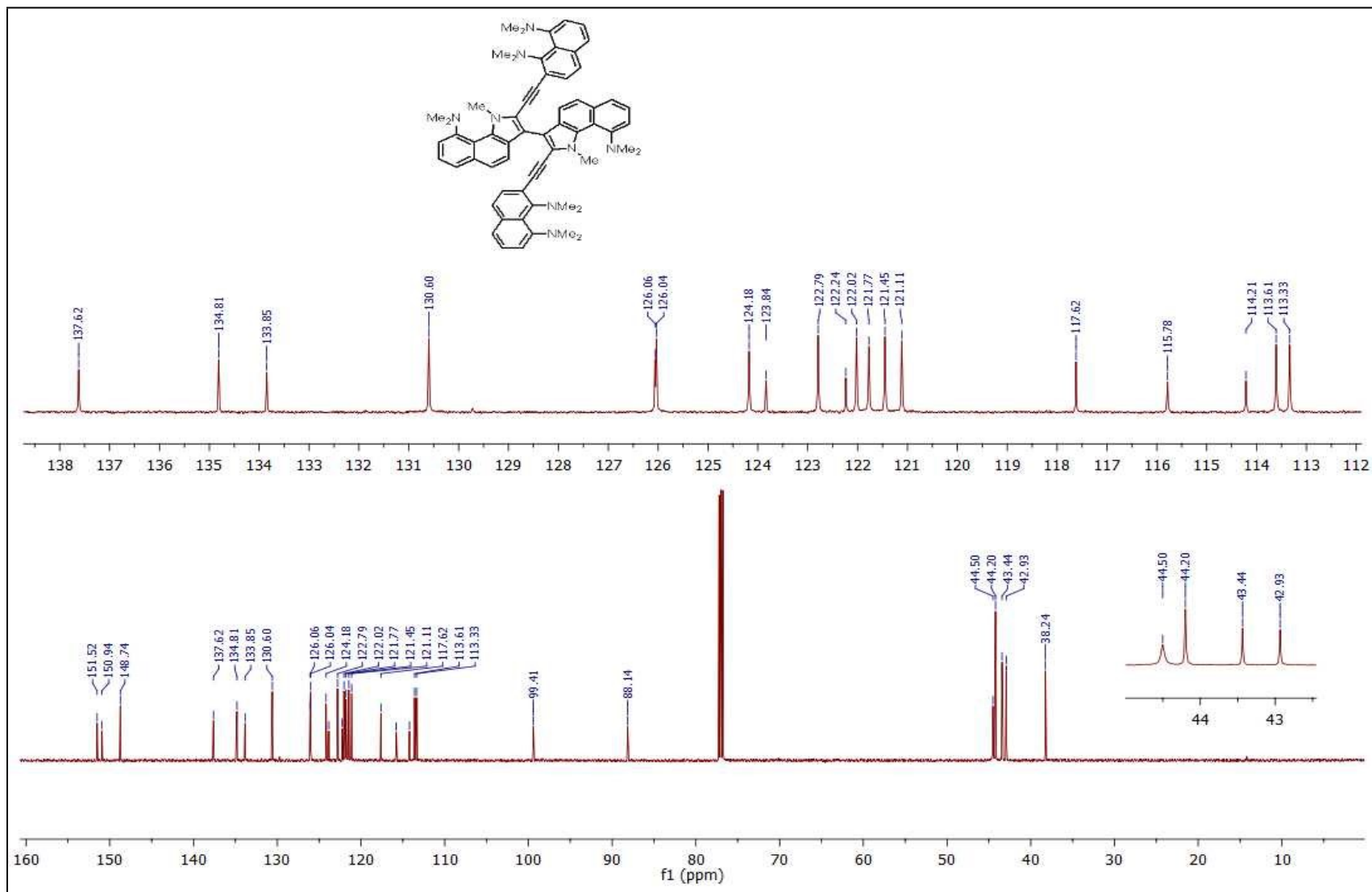
**Fig. S16.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **13** (150 MHz,  $\text{CDCl}_3$ ).



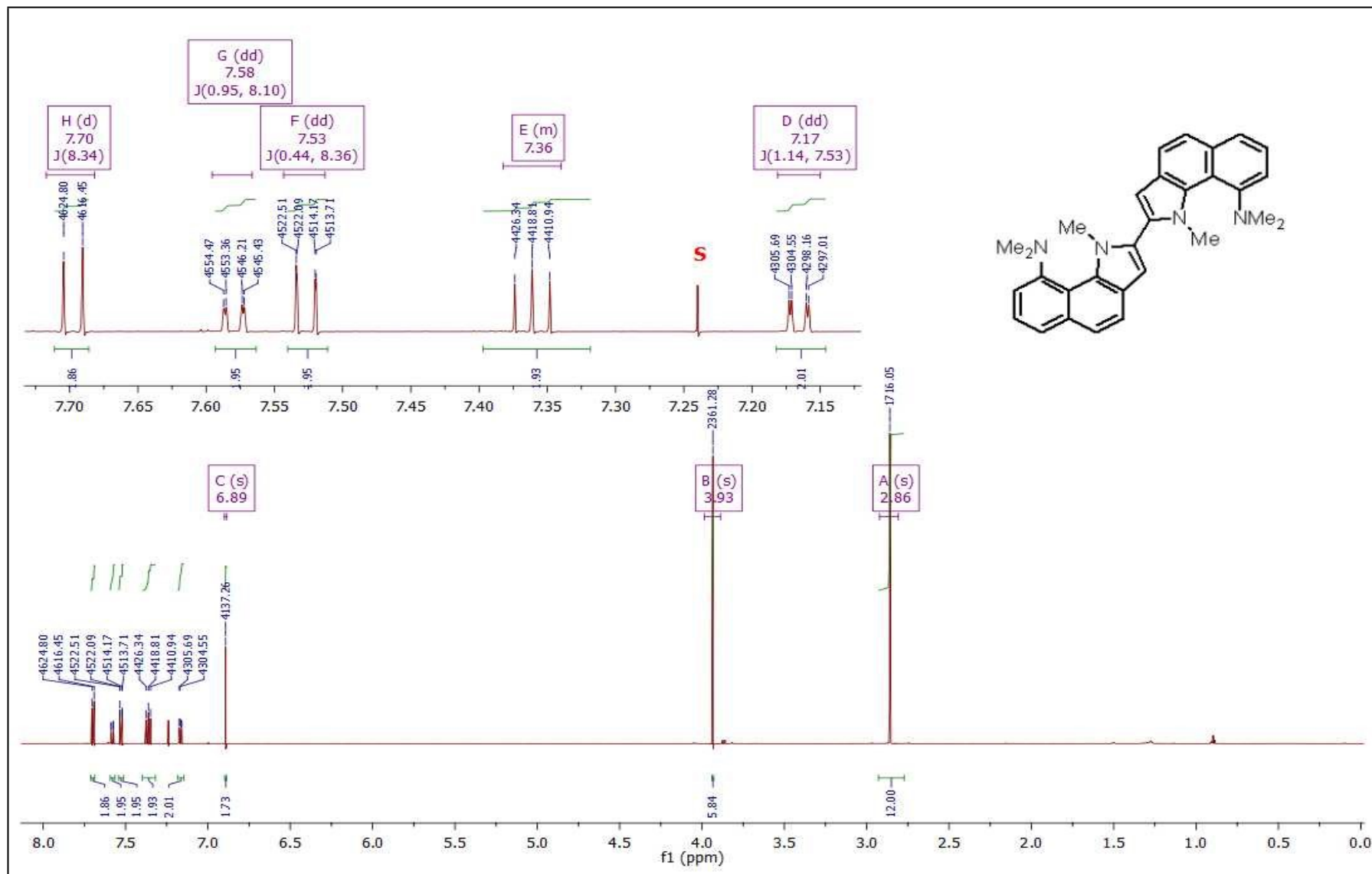


**Fig. S17.** <sup>1</sup>H NMR spectrum of 8-(dimethylamino)-7-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N,N*-dimethylnaphthalen-1-aminium tetrafluoroborate **13**·**HBF<sub>4</sub>** (250 MHz, CD<sub>3</sub>CN).

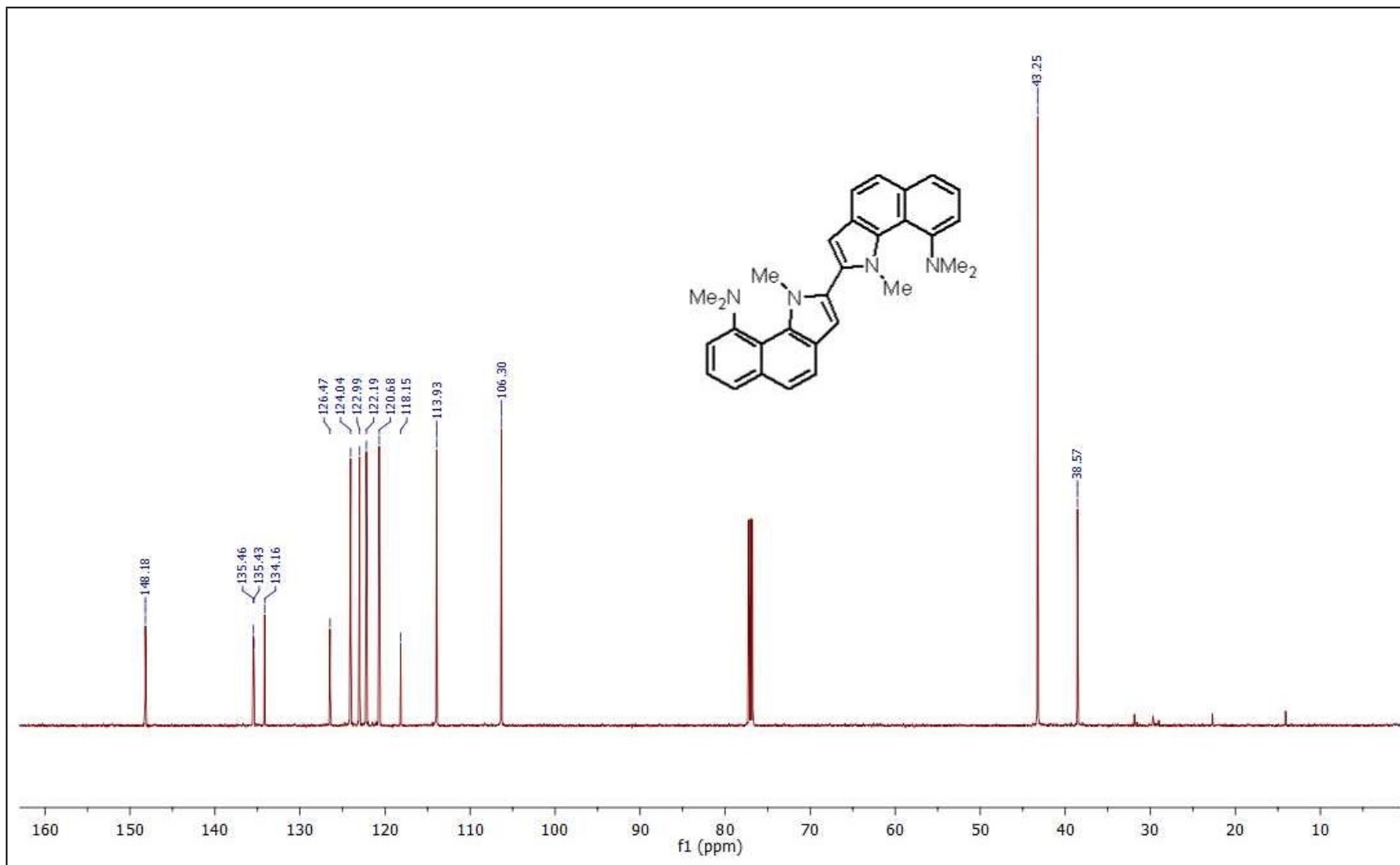




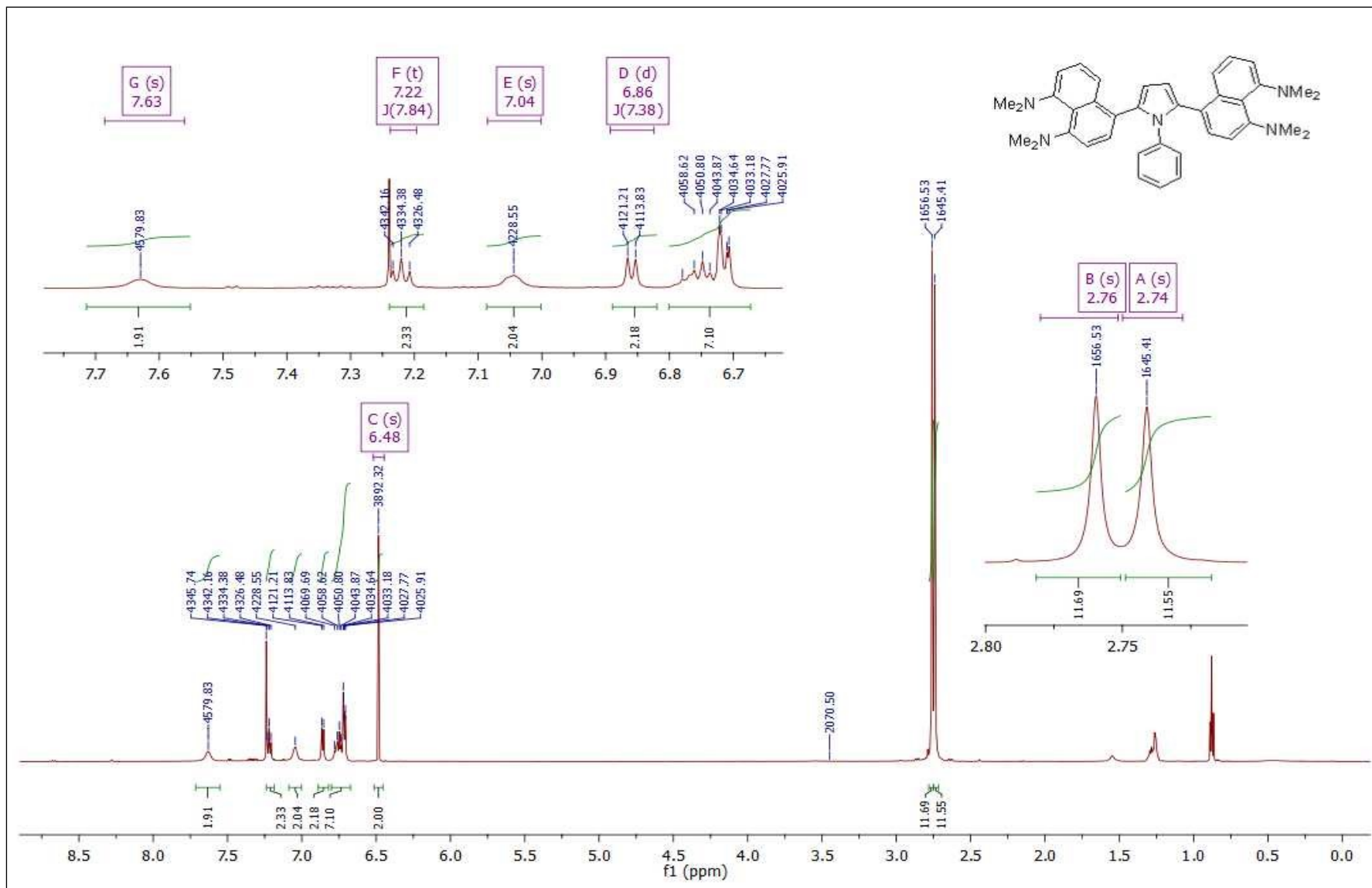
**Fig. S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,2'-(9,9'-bis(dimethylamino)-1,1'-dimethyl-1*H*,1'*H*-3,3'-bibenzo[*g*]indole-2,2'-diyl)bis(ethyne-2,1-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **14** (150 MHz,  $\text{CDCl}_3$ ).



**Fig. S20.** <sup>1</sup>H NMR spectrum of N<sup>9</sup>,N<sup>9</sup>,N<sup>9'</sup>,N<sup>9'</sup>,1,1'-hexamethyl-1*H*,1'*H*-[2,2'-bibenzo[*g*]indole]-9,9'-diamine **21** (600 MHz, CDCl<sub>3</sub>).

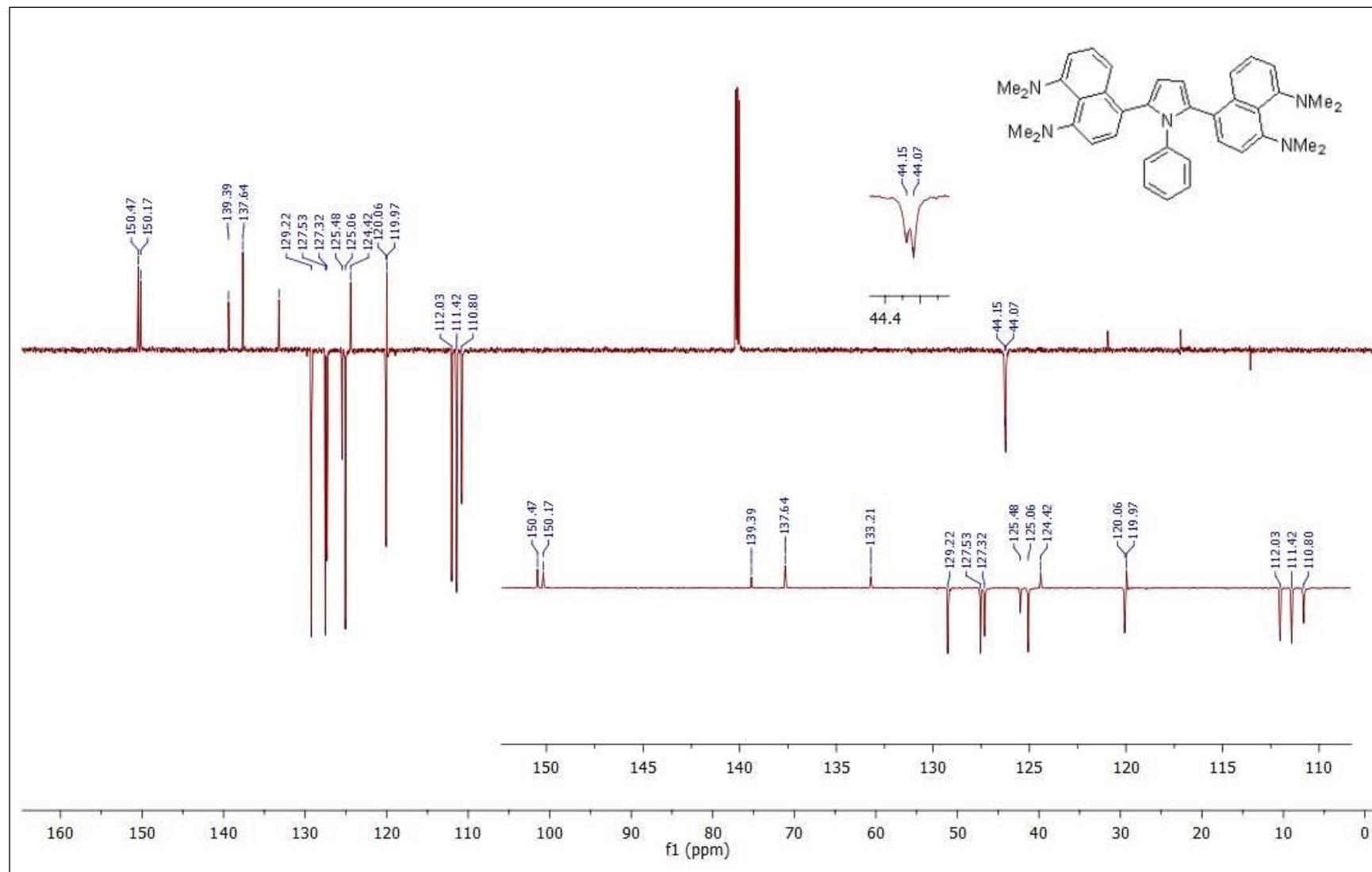


**Fig. S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{N}^9,\text{N}^9,\text{N}^9,\text{N}^9,1,1'$ -hexamethyl- $1H,1'H$ -[2,2'-bibenzo[*g*]indole]-9,9'-diamine **21** (150 MHz,  $\text{CDCl}_3$ ).



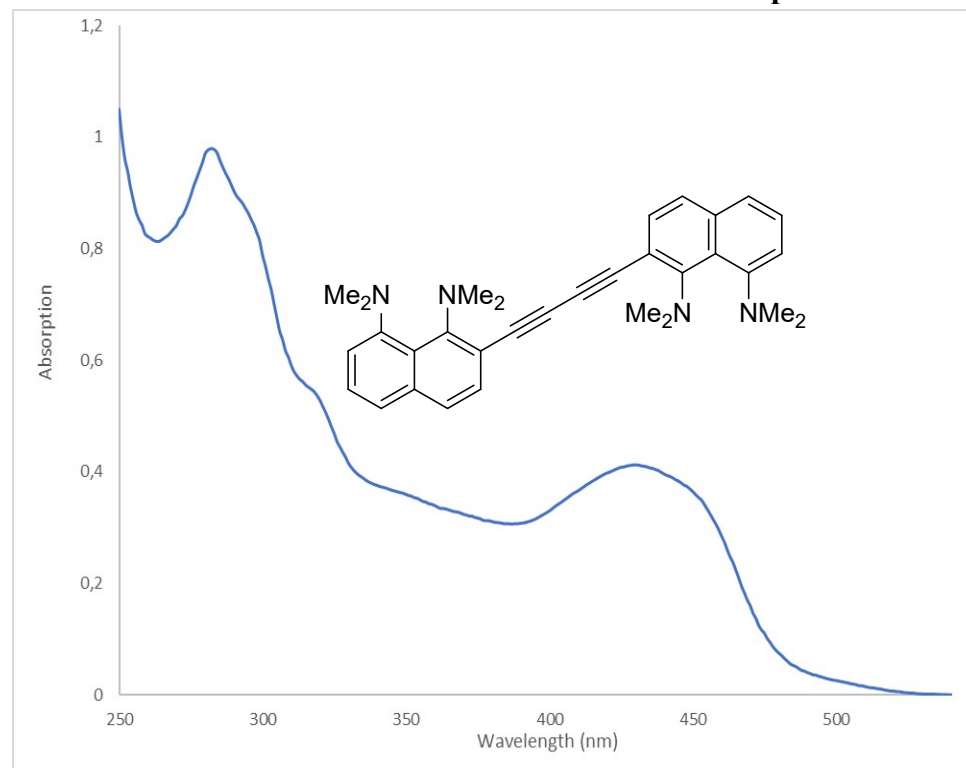
**Fig. S22.** <sup>1</sup>H NMR spectrum of 4,4'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis(*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **22** (600 MHz, CDCl<sub>3</sub>).



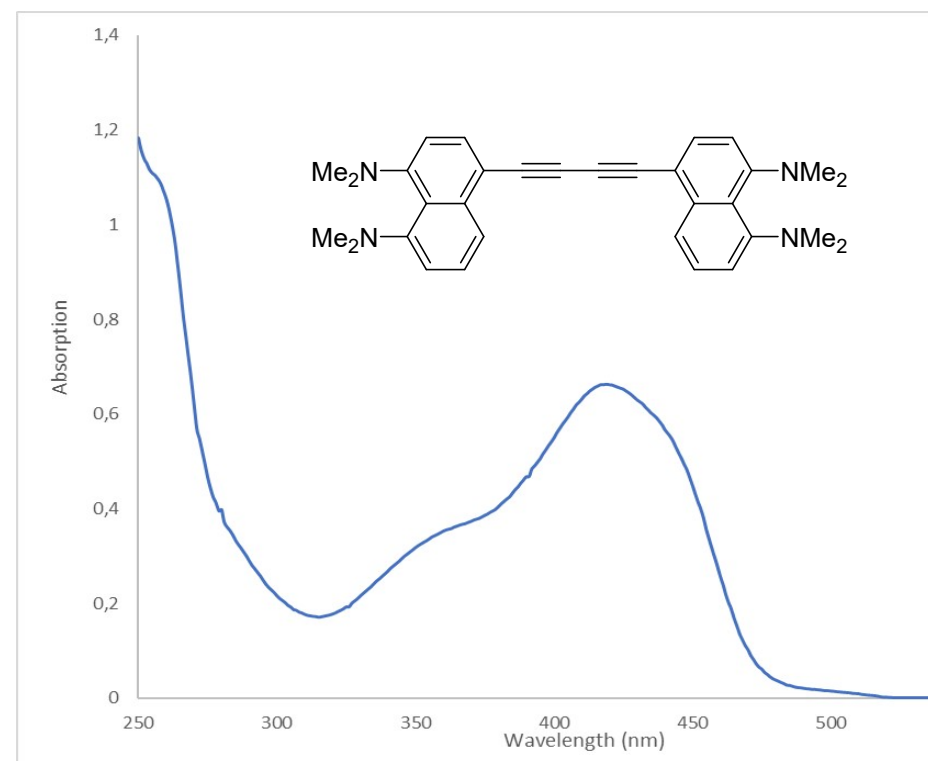


**Fig. S23.**  $^{13}\text{C}\{^1\text{H}\}$  APT-NMR spectrum of 4,4'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **22** (150 MHz,  $\text{CDCl}_3$ ).

## Copies of UV-vis absorption spectra

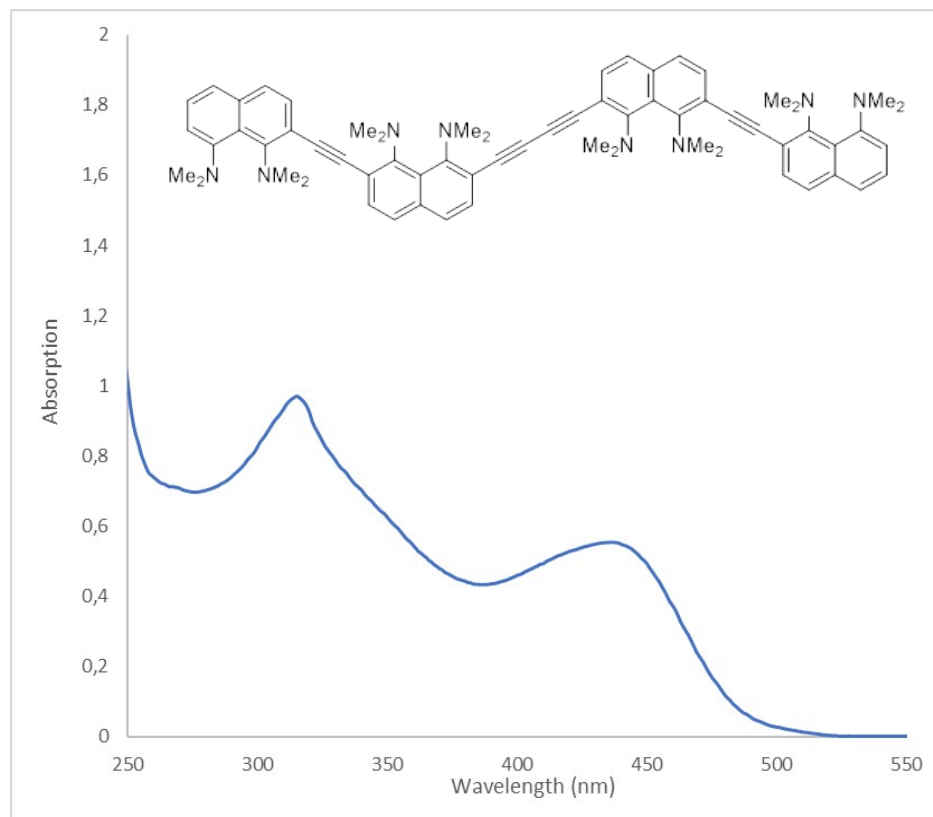


**Fig. S24.** UV-vis absorption spectra of 2,2'-(buta-1,3-diyne-1,4-diyl)-bis( $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine) **1** in  $\text{CHCl}_3$  solution.

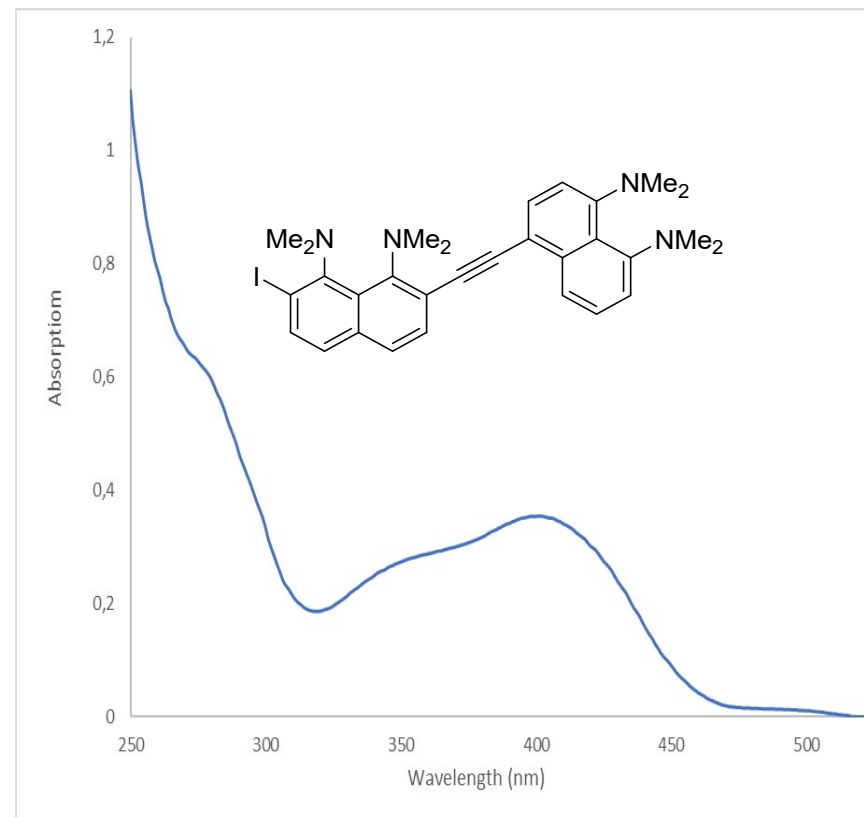


**Fig. S25.** UV-vis absorption spectra of 4,4'-(buta-1,3-diyne-1,4-diyl)-bis( $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine) **2** in  $\text{CHCl}_3$  solution.

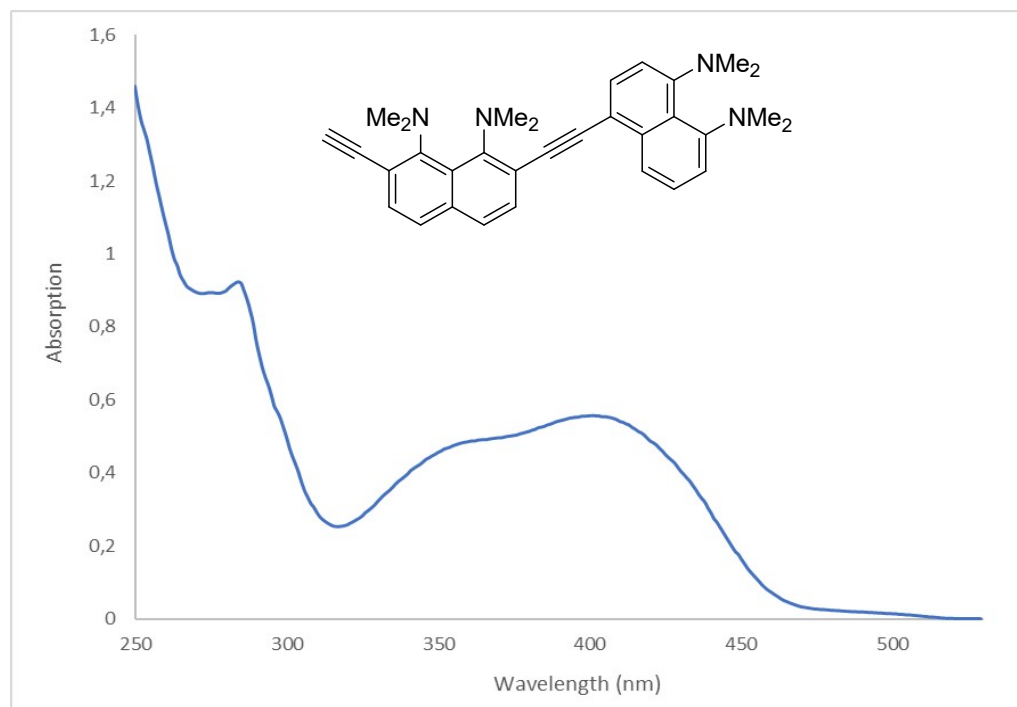




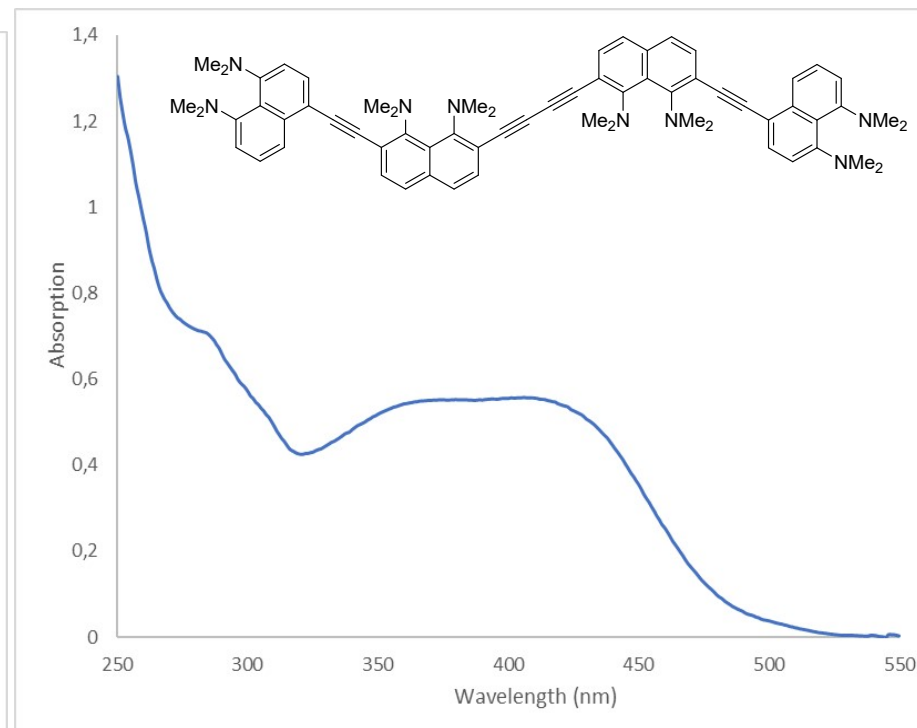
**Fig. S26.** UV-vis absorption spectra of 7,7'-(buta-1,3-diyne-1,4-diyl)-bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **3** in CHCl<sub>3</sub> solution.



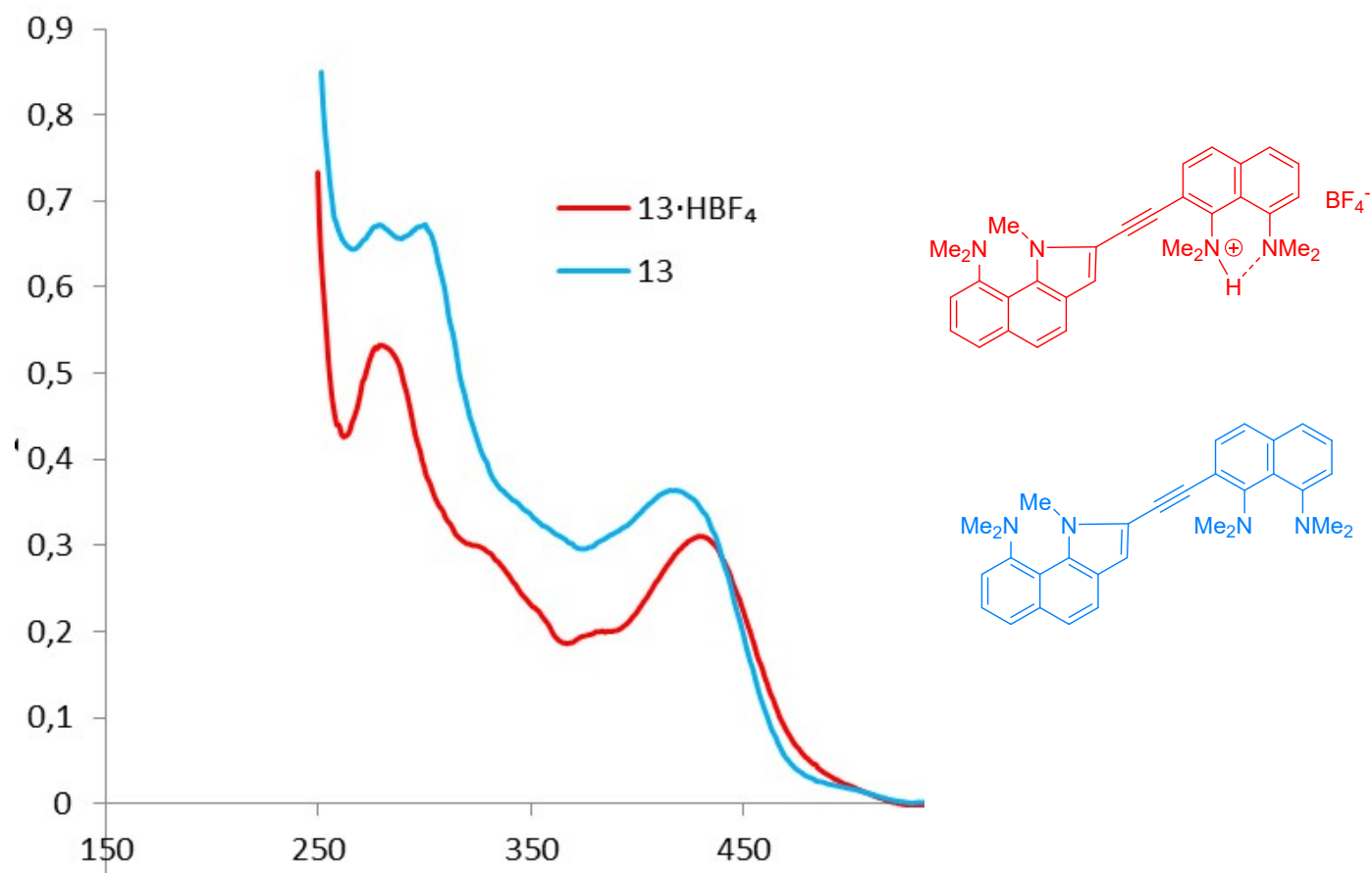
**Fig. S27.** UV-vis absorption spectra of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-iodo-N<sup>1</sup>,N<sup>1</sup>,N<sup>8</sup>,N<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **8** in CHCl<sub>3</sub> solution.



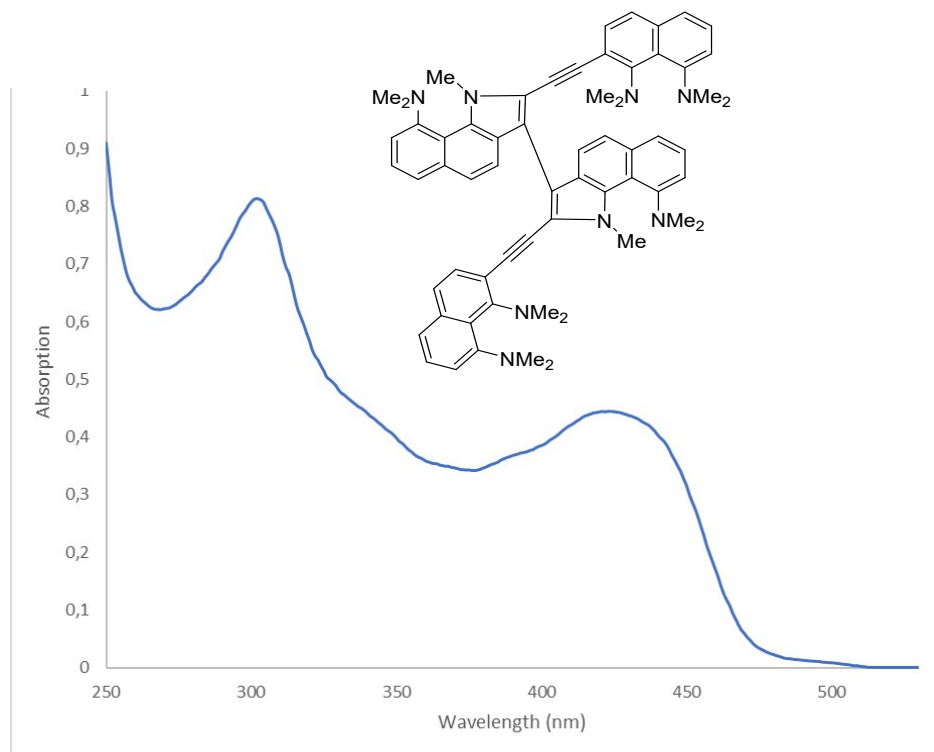
**Fig. S28.** UV-vis absorption spectra of 2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)-7-ethynyl- $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine **10** in  $\text{CHCl}_3$  solution.



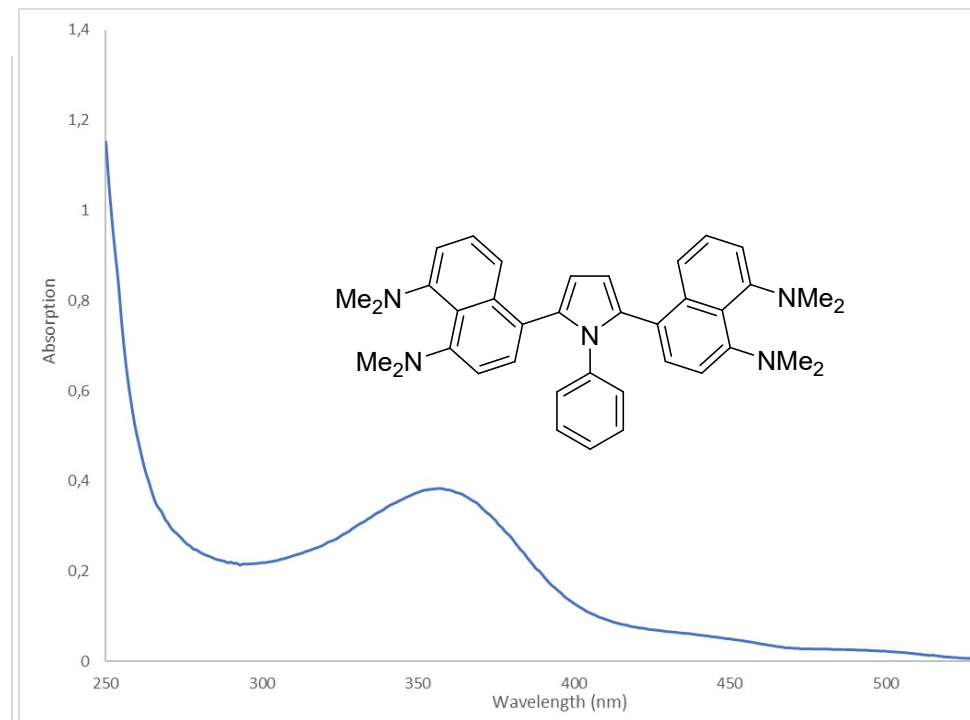
**Fig. S29.** UV-vis absorption spectra of 7,7'-(buta-1,3-diyne-1,4-diyl)-bis(2-((4,5-bis(dimethylamino)naphthalen-1-yl)ethynyl)- $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine) **4** in  $\text{CHCl}_3$  solution.



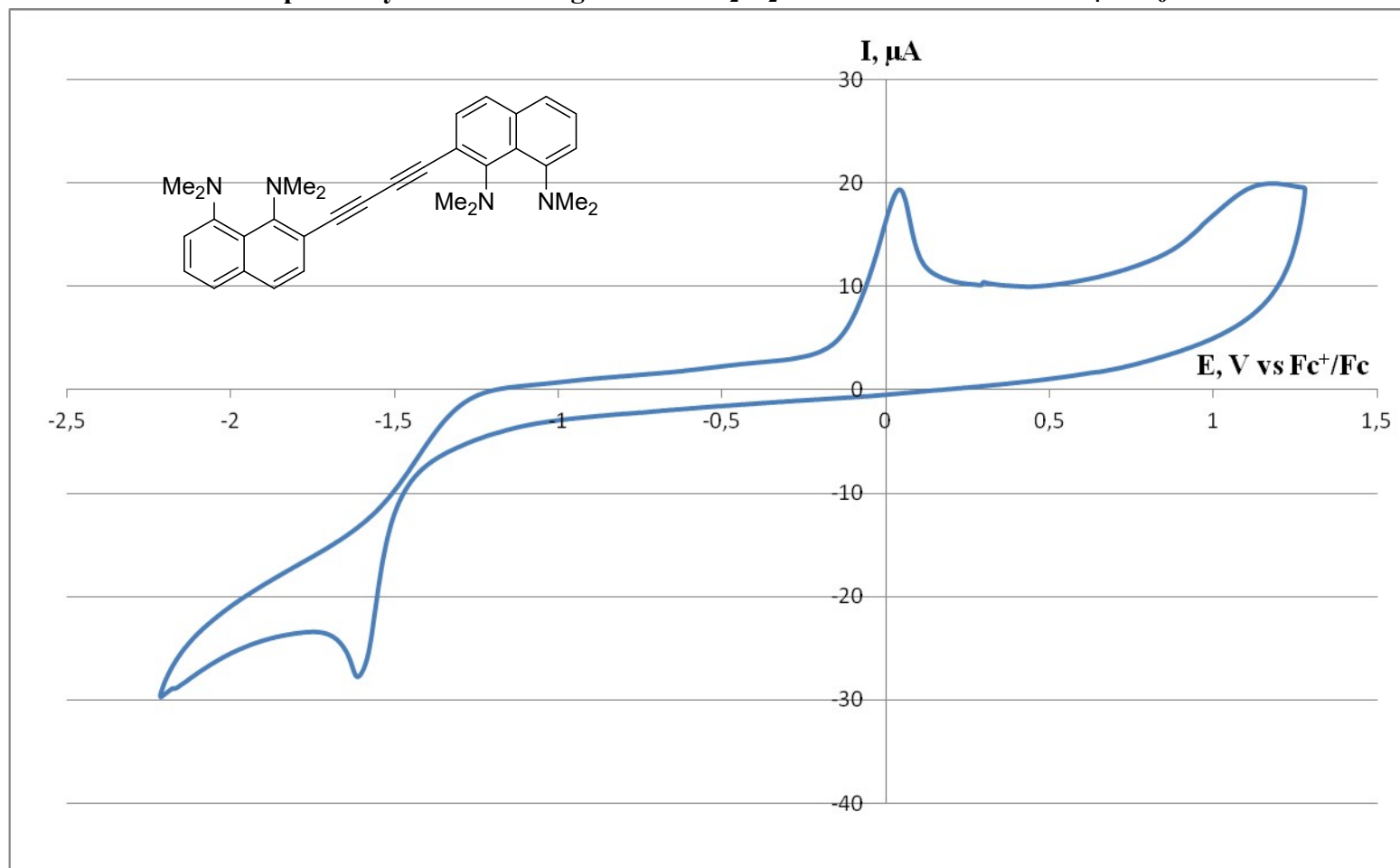
**Fig. S30.** UV-vis absorption spectra of 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **13** and its salt **13·HBF<sub>4</sub>** in CHCl<sub>3</sub> solution.

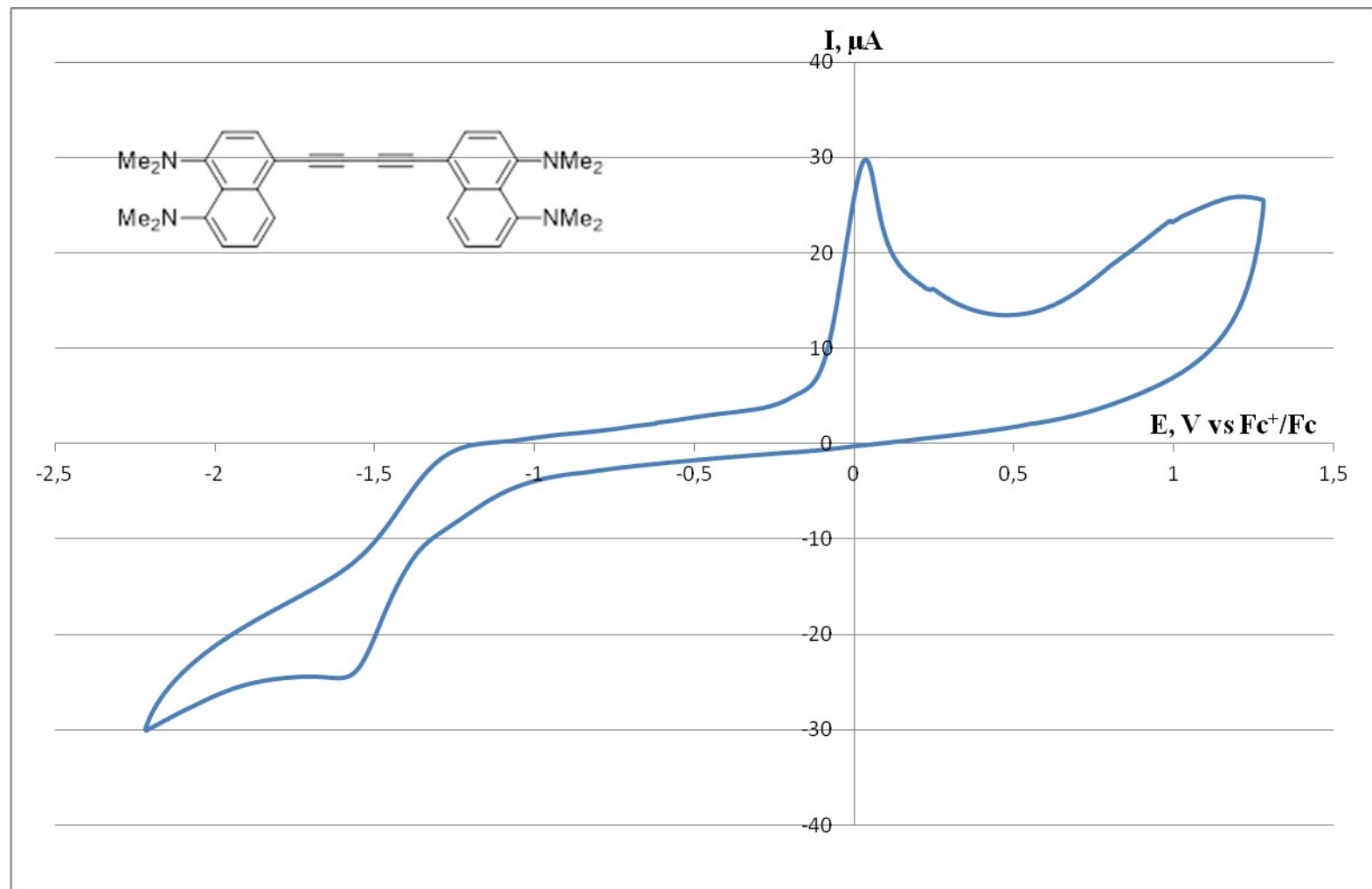


**Fig. S31.** UV-vis absorption spectra of 2,2'-(9,9'-bis(dimethylamino)-1,1'-dimethyl-1*H*,1'*H*-3,3'-bibenzo[*g*]indole-2,2'-diyl)bis(ethyne-2,1-diyl)-bis(*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **14** in CHCl<sub>3</sub> solution.

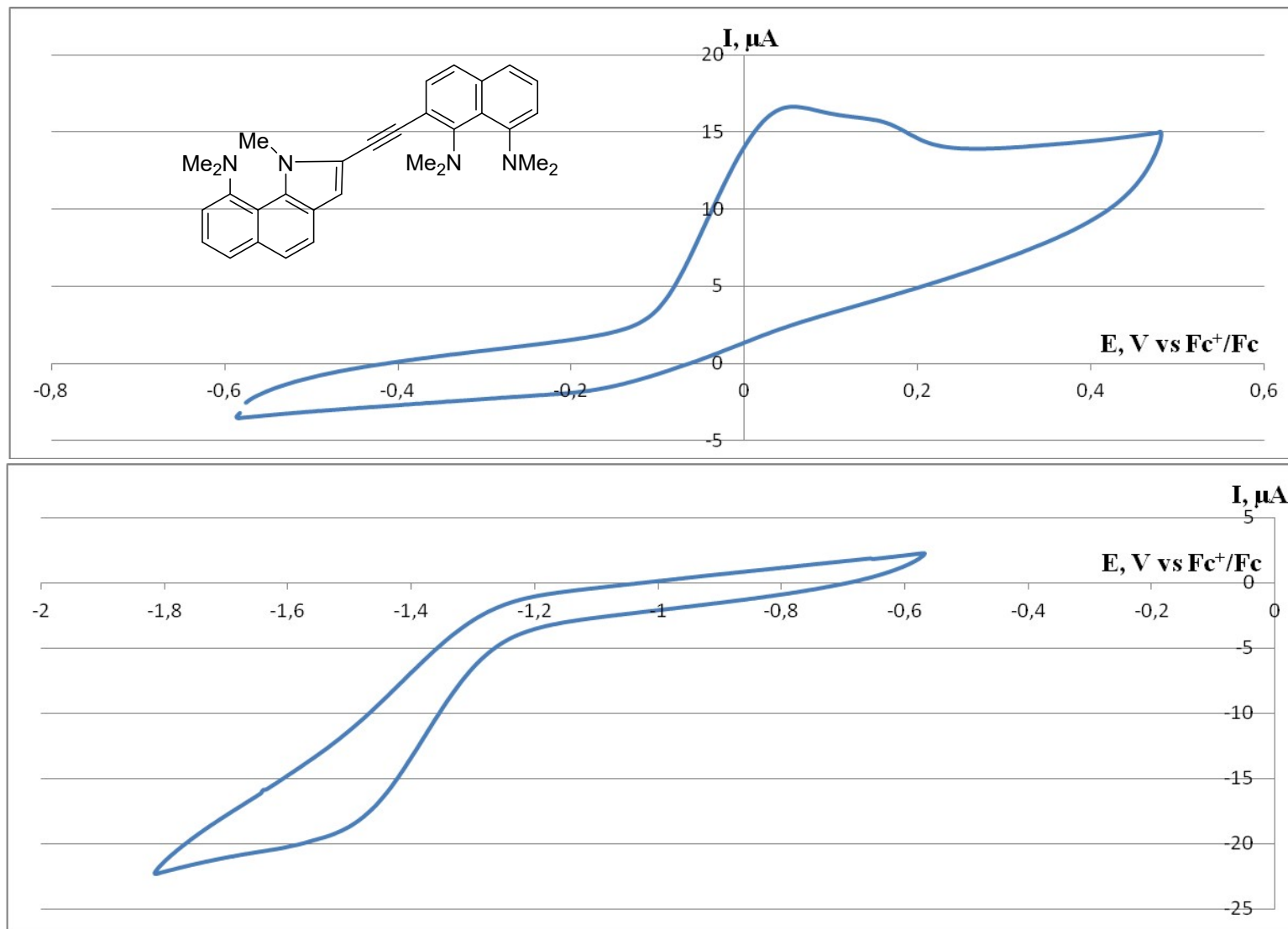


**Fig. S32.** UV-vis absorption spectra of 4,4'-(1-phenyl-1*H*-pyrrole-2,5-diyl)bis(*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine) **22** in CHCl<sub>3</sub> solution.

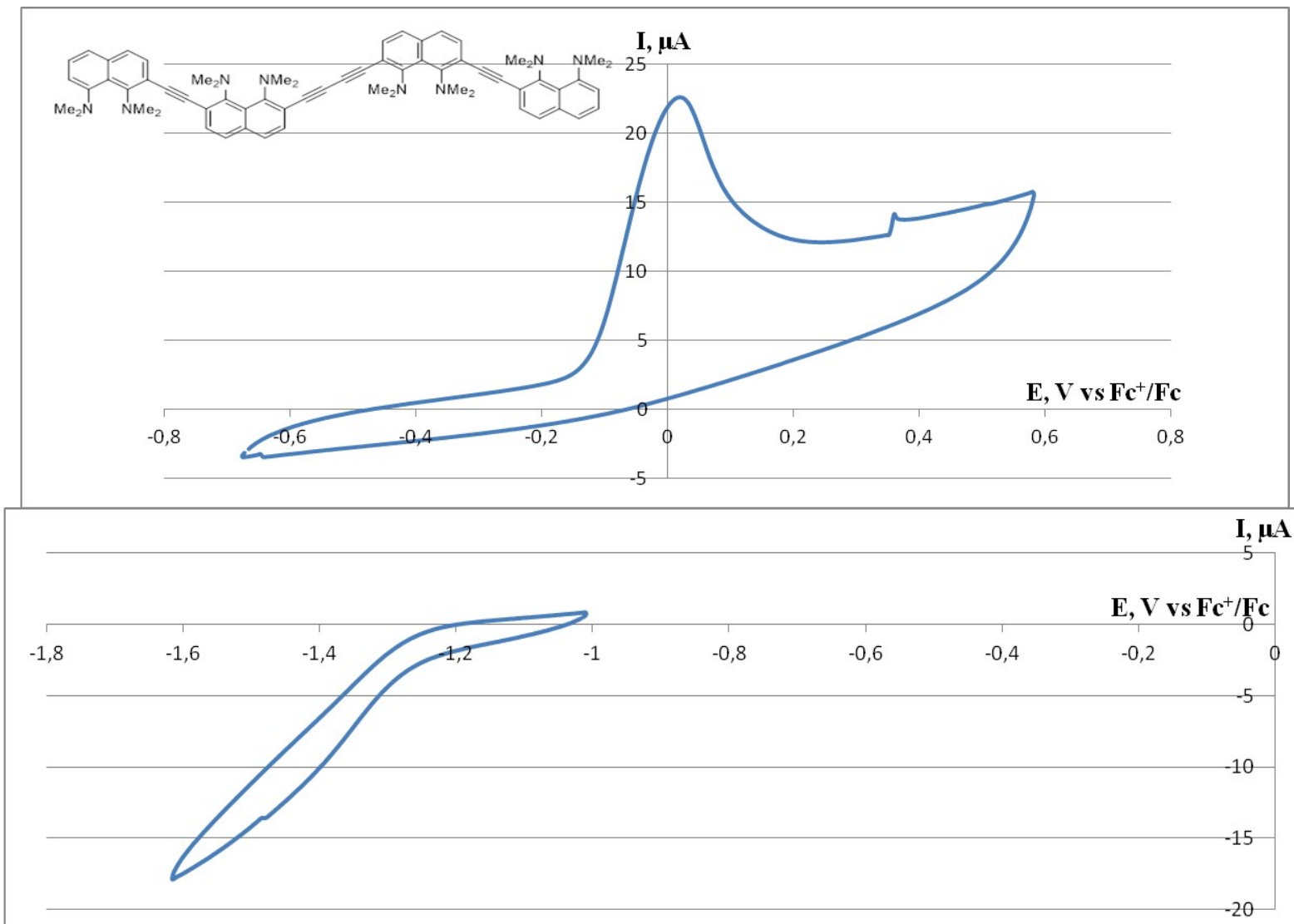
Copies of cyclic voltammograms in  $\text{CH}_2\text{Cl}_2$  solution with 0.1 M  $n\text{-Bu}_4\text{NPF}_6$ **Fig. S33.** Cyclic voltamperogramm of 2,2'-(buta-1,3-diyne-1,4-diyl)-bis( $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **1** in  $\text{CH}_2\text{Cl}_2$ .



**Fig. S34.** Cyclic voltamperogramm of 4,4'-(buta-1,3-diyne-1,4-diyl)-bis( $N^1,N^1,N^8,N^8$ -tetramethylnaphthalene-1,8-diamine) **2** in  $\text{CH}_2\text{Cl}_2$ .



**Fig. S35.** Cyclic voltamperogramm of 2-((9-(dimethylamino)-1-methyl-1*H*-benzo[*g*]indol-2-yl)ethynyl)-*N*<sup>1</sup>,*N*<sup>1</sup>,*N*<sup>8</sup>,*N*<sup>8</sup>-tetramethylnaphthalene-1,8-diamine **13** in  $\text{CHCl}_3$ .



**Fig. S36.** Cyclic voltamperogramm of 7,7'-(buta-1,3-diyne-1,4-diy)l-bis(2-((1,8-bis(dimethylamino)naphthalen-2-yl)ethynyl)- $\text{N}^1, \text{N}^1, \text{N}^8, \text{N}^8$ -tetramethylnaphthalene-1,8-diamine) **3** in  $\text{CHCl}_3$ .