Supporting Information

for

Unexpected pyrazine ring annulation in the Cu-catalyzed reaction of aryl bromides with 1,2-diamines. Synthesis of novel pyrazino[2,3-*f*]perimidine fluorophores

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Experimental details, copies of NMR spectra, photophysical studies

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EXPERIMENTAL SECTION

General Information: ^{1}H and ^{13}C NMR spectra were recorded on 250 MHz spectrometers. Chemical shifts are reported in ppm relative to Me_4Si. The UV-vis spectra were recorded on a Varian Cary 50 Probe spectrophotometer. Fluorescence emission spectra were collected using a Cary Eclipse Varian spectrofluorometer. Mass spectra were performed in electrospray ionization (ESI) modes (HR-ESI MS). Melting points were determined in glass capillaries and are uncorrected. X-ray measurements were conducted with diffractometer SyperNova, Dual, Cu at home/near, AtlasS2'. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC): CCDC 2528976 (**3b**), CCDC 2528980 (**4a**). These data can be obtained free of charge from Cambridge Crystallographic Data Centre.

Starting 6-bromo-1,3-dimethyl-1*H*-perimidin-2(3*H*)-one **1**[1] was synthesized as it was described earlier.

General procedure for arylation of NH-heterocycles with 6-bromo-1,3-dimethyl-1*H*-perimidin-2(3*H*)-one 1 (Table 1). A mixture of 6-bromo-1,3-dimethyl-1*H*-perimidin-2(3*H*)-one **1** (116 mg, 0.4 mmol), NH-heterocycle **2** (0.48 mmol), CuI (30 mg, 0.16 mmol, 40 mol%), diamine ligand (0.32 mmol, 80 mol%), K_3PO_4 (170 mg, 0.8 mmol) and 3 mL o-xylene or DMF was flushed with argon and stirred at 120 °C for 72 h. The reaction mixture was evaporated to dryness on air. The residue was purified by column chromatography on silica using dichloromethane as eluent. The colorless fraction with R_f 0.4 gave N-arylation product **3**. From the next colorless fraction with R_f 0.3 a mixture of starting compound **1** and 1,3-dimethyl-1*H*-perimidin-2(3*H*)-one **5** were isolated. Elution was then continued using a mixture of CH_2Cl_2-EtOAc (10:1, v/v) as the eluent. The yellow fluorescent under UV fraction with R_f 0.2 (CH_2Cl_2-EtOAc (10:1, v/v)) gave 4,6-dimethyl-4*H*-pyrazino[2,3-*f*]perimidin-5(6*H*)-one **4a** or 4,6-dimethyl-9,10,11,12-tetrahydro-4*H*-quinazolino[5,4-*ab*]phenazin-5(6*H*)-one **4b**.

6-(1H-Indol-1-yl)-1,3-dimethyl-1H-perimidin-2(3H)-one **3a** was obtained as white crystals with mp 265-268 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.75 (dd, *J* = 6.4, 2.4 Hz, 1 H), 7.49 (d, *J* = 8.1 Hz, 1 H), 7.29-7.36 (m, 2 H), 7.12-7.22 (m, 2 H), 6.99-7.03 (m, 1 H), 6.82 (d, *J* = 8.5 Hz, 1 H), 6.75 (d, *J* = 3.1 Hz, 1 H), 6.67-6.71 (m, 2 H), 3.55 (s, 3 H), 3.52 ppm (s, 3 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.8, 138.0, 137.8, 131.6, 129.5, 128.9, 128.4, 128.0, 127.3, 122.1, 121.0, 120.1, 115.3, 114.9, 110.7, 105.0, 103.5, 102.8, 31.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{21}H_{17}N_3NaO$ $[M + Na]^+$: 350.1264, found 350.1277.

6-(9H-Carbazol-9-yl)-1,3-dimethyl-1H-perimidin-2(3H)-one **3b** was obtained as white crystals with mp 281-283 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.19-8.23 (m, 2 H), 7.57 (d, *J* = 8.1 Hz, 1 H), 7.21-7.37 (m, 5 H), 7.02 (dd, *J* = 7.2, 1.1 Hz, 2 H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 2 H), 3.58 (s, 3 H), 3.53 ppm (s, 3 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.8, 141.9, 138.4, 138.2, 131.8, 128.9, 125.9, 125.6, 123.2, 120.4, 119.7, 115.7, 115.1, 110.1, 105.1, 104.0, 31.02, 30.98 ppm. HRMS (ESI): *m/z* calcd. for $C_{25}H_{19}N_3NaO$ $[M + Na]^+$: 400.1420, found 400.1429.

4,6-Dimethyl-4H-pyrazino[2,3-f]perimidin-5(6H)-one **4a** was obtained as yellow crystals with mp 239-240 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 2.0 Hz, 1H), 8.69-8.73 (m, 2 H), 7.73 (t, *J* = 8.1 Hz, 1 H), 7.05 (dd, *J* = 8.0, 0.6 Hz, 1 H), 6.95 (s, 1 H), 3.58 (s, 3 H), 3.55 ppm (s, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.3, 145.1, 144.7, 140.8, 140.0, 137.6, 137.3, 131.6, 129.6, 117.4, 114.6, 109.9, 101.4, 31.2, 31.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{15}H_{13}N_4O$ $[M + H]^+$ 265.1084, found 265.1075; *m/z* calcd. for $C_{15}H_{12}N_4NaO$ $[M + Na]^+$ 287.0903, found 287.0903.

4,6-Dimethyl-9,10,11,12-tetrahydro-4H-quinazolino[5,4-ab]phenazin-5(6H)-one **4b** was obtained as yellow crystals with mp 221-222 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 7.6 Hz, 1 H), 7.59 (t, *J* = 8.0 Hz, 1 H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.75 (br s, 1 H), 3.48 (s, 3 H), 3.47 (s, 3 H), 3.11-3.16 (m, 4 H), 2.01-2.06 ppm (m, 4 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 153.8, 150.3, 149.8, 142.1, 138.7, 137.2, 135.0, 131.3, 129.0, 116.9, 114.2, 108.9, 101.1, 32.80, 32.78, 31.1, 30.8, 23.0, 22.9. HRMS (ESI): *m/z* calcd. for $C_{19}H_{19}N_4O$ $[M + H]^+$ 319.1553, found 319.1558.

Isolated *1,3-dimethyl-1H-perimidin-2(3H)-one* **5** was identical to authentic material[2].

General procedure for Cu-catalyzed reaction of 6-bromo-1,3-dimethyl-1*H*-perimidin-2(3*H*)-one with various 1,2-diamines (Tables 2,3). A mixture of 6-bromo-1,3-dimethyl-1*H*-perimidin-2(3*H*)-one **1** (116 mg, 0.4 mmol), diamine (0.8 mmol), CuBr (57 mg, 0.4 mmol), K_2CO_3 (221 mg, 1.6 mmol) and 2 mL DMSO was flushed with argon and stirred at 120 °C for 48 h. The reaction mixture was then evaporated to dryness on air. The residue was purified by column chromatography on Al_2O_3 using a mixture CH_2Cl_2–petroleum ether (1:1, v/v) as eluent. From the colorless fraction with R_f 0.4 starting compound **1** was regenerated. Next colorless fraction with R_f 0.3 gave 1,3-dimethyl-1*H*-perimidin-2(3*H*)-one **5**. The yellow fluorescent under UV fraction with R_f 0.1-0.2 gave compound **4**.

Inseparable mixture of *4,6,9-trimethyl-4H-pyrazino[2,3-f]perimidin-5(6H)-one* **4c** and *4,6,10-trimethyl-4H-pyrazino[2,3-f]perimidin-5(6H)-one* **4c'** (2:1 ratio) was obtained as a yellow solid (for ^{1}H NMR spectrum see Fig. S9). HRMS (ESI): *m/z* calcd. for $C_{16}H_{15}N_4O$ $[M + H]^+$ 279.1240, found 279.1237.

4,6-Dimethyl-4H-quinazolino[5,4-ab]phenazin-5(6H)-one **4d** was obtained as orange crystals with mp 256-258 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.85 (d, *J* = 8.0 Hz, 1 H), 8.18 (dd, *J* = 8.2, 1.4 Hz, 1 H), 8.04-8.09 (m, 1 H), 7.67-7.82 (m, 3 H), 7.06 (d, *J* = 7.9 Hz, 1 H), 6.83 (s, 1 H), 3.54 (s, 3 H), 3.50 ppm (s, 3 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.0, 145.2, 143.5, 140.8, 140.7, 139.5, 137.2, 131.4, 130.4, 129.9, 129.6, 128.4, 128.1, 118.9, 114.3, 111.8, 100.6, 31.3, 31.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{19}H_{15}N_4O$ $[M + H]^+$ 315.1240, found 315.1245; *m/z* calcd. for $C_{19}H_{14}N_4NaO$ $[M + Na]^+$ 337.1060, found 337.1061.

4,6-Dimethyl-4H-benzo[h]quinazolino[5,4-ab]phenazin-5(6H)-one **4e** was obtained as orange crystals with mp >285 °C (decomp.). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.32-9.36 (m, 1 H), 8.94 (d, *J* = 8.2 Hz, 1 H), 7.92-8.06 (m, 3 H), 7.74-7.81 (m, 3 H), 7.11 (s, 1 H), 7.07 (d, *J* = 7.9 Hz, 1 H), 3.65 (s, 3 H), 3.53 ppm (s, 3 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.3, 143.6, 142.2, 140.3, 138.2, 137.4, 133.6, 131.5, 130.6, 129.7, 129.3, 128.1, 127.4, 127.3, 125.0, 118.4, 114.5, 111.0, 101.5, 31.4, 31.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{23}H_{17}N_4O$ $[M + H]^+$ 365.1397, found 365.1388.

Isolated *1,3-dimethyl-1H-perimidin-2(3H)-one* **5** was identical to authentic material[2].

General procedure for Cu-catalyzed reactions of 4-bromo-*N^1,N^1,N^8,N^8*-tetramethylnaphthalene-1,8-diamine 7 and 4-bromo-*N,N*-dimethylaniline 8 with ethylenediamine. A mixture of arylbromide (0.5 mmol), ethylenediamine (0.07 mL, 1 mmol), $Cu(OAc)_2{\cdot}H_2O$ (116 mg, 0.5 mmol), K_2CO_3 (276 mg, 2 mmol) and 2 mL DMSO was flushed with argon and stirred at 120 °C for 48 h. The reaction mixture was then evaporated to dryness on air. The residue was purified by column chromatography.

N^6,N^6,N^7,N^7-Tetramethylbenzo[f]quinoxaline-6,7-diamine **9** was obtained from compound **7** as a yellow oil. Column chromatography was carried out on Al_2O_3 using a mixture EtOAc–petroleum ether (1:10, v/v) as eluent. From the colorless fraction with R_f 0.6 starting compound **7** was regenerated. Compound **9** was isolated from the fraction with R_f 0.4. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.82 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.68 (d, *J* = 2.2 Hz, 1 H), 8.60 (d, *J* = 2.2 Hz, 1 H), 7.60 (t, *J* = 7.9 Hz, 1 H), 7.24 (dd, *J* = 7.8, 1.1 Hz, 1 H), 7.18 (s, 1 H), 2.92 (s, 6 H), 2.85 ppm (s, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 152.7, 151.0, 144.4, 144.2, 139.4, 139.0, 134.8, 127.5, 120.7, 117.1, 116.7, 107.6, 44.0, 43.3 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{19}N_4$ $[M + H]^+$ 267.1604, found 267.1609.

N,N-Dimethylquinoxalin-6-amine **10** was obtained from compound **8** as a yellow oil (mp 32-34 °C [3,4]). Column chromatography was carried out on Al_2O_3 using a mixture CH_2Cl_2–petroleum ether (1:1, v/v) as eluent. Compound **10** was isolated from the fraction with R_f 0.1. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.68 (br s, 1 H), 8.54 (br s, 1 H), 7.94 (d, *J* = 9.4 Hz, 1 H), 7.42 (dd, *J* = 9.4, 2.7 Hz, 1 H), 7.09 (d, *J* = 2.7 Hz, 1 H), 3.17 ppm (s, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 151.1, 145.1, 145.0, 140.4, 137.1, 129.8, 119.6, 105.5, 40.5 ppm. HRMS (ESI): *m/z* calcd. for $C_{10}H_{12}N_3$ $[M + H]^+$ 174.1026, found 174.1026.

Cu-Catalyzed reactions of 1-bromonaphthalene 11 with ethylenediamine. A mixture of 1-bromonaphthalene **11** (0.21 mL, 1.5 mmol), ethylenediamine (0.20 mL, 3 mmol), CuBr (216 mg, 1.5 mmol), K_2CO_3 (818 mg, 6 mmol) and 4 mL DMSO was flushed with argon and stirred at 130 °C for 48 h. The reaction mixture was then evaporated to dryness on air. The residue was purified by column chromatography on Al_2O_3 using a mixture CH_2Cl_2–petroleum ether (1:1, v/v) as eluent. The first fraction with R_f 0.7 gave N^1,N^2-di(naphthalen-1-yl)ethane-1,2-diamine **13**.

N^1,N^2-Di(naphthalen-1-yl)ethane-1,2-diamine **13** was obtained as a beige crystals with mp 119-121°C (122–124 °C [5,6]). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.80-7.85 (m, 4 H), 7.33-7.51 (m, 8 H), 6.77 (dd, *J* = 7.4, 0.9 Hz, 2 H), 4.72 (br. s, 2 H), 3.74 ppm (s, 4 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 143.3, 134.4, 128.7, 126.6, 125.9, 125.0, 123.8, 120.0, 118.2, 104.9, 43.5 ppm. HRMS (ESI): *m/z* calcd. For $C_{22}H_{21}N_2$ $[M + H]^+$ 313.1699, found 313.1701.

Cu-Catalyzed reactions of 4-bromo-*N*-butyl-1,8-naphthalimide 12 with ethylenediamine. A mixture of 4-bromo-*N*-butyl-1,8-naphthalimide **12** (100 mg, 0.3 mmol), ethylenediamine (0.04 mL, 0.6 mmol), CuBr (43 mg, 0.3 mmol), K_2CO_3 (166 mg, 1.2 mmol) and 2 mL DMSO was flushed with argon and stirred at 130 °C for 48 h. The reaction mixture was then evaporated to dryness on air. The residue was purified by column chromatography on Al_2O_3 using a mixture CH_2Cl_2–petroleum ether (1:1, v/v). The first fraction with R_f 0.7 gave *N*-butyl-1,8-naphthalimide **15** (10 mg, 13%). Subsequent elution was carried out using a mixture CH_2Cl_2–EtOAc (3:1, v/v). Fraction with R_f 0.2 gave 4,4'-(ethane-1,2-diylbis(azanediyl))bis(N-butyl-1,8-naphthalimide) **14** (43 mg, 51%).

4,4'-(Ethane-1,2-diylbis(azanediyl))bis(N-butyl-1,8-naphthalimide) **14** was obtained as yellow crystals with mp 281–283 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 8.59 (d, *J* = 8.4 Hz, 2 H), 8.41 (d, *J* =7.2 Hz, 2 H), 8.24 (d, *J* = 8.5 Hz, 2 H), 7.63 (t, *J* = 7.9 Hz, 2 H), 7.51 (br s, 2 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 4.03 (t, *J* = 7.2 Hz, 4 H), 3.79-3.81 (m, 4 H), 1.56-1.68 (m, 4 H), 1.27-1.42 (m, 4 H), 0.92 ppm (t, *J* = 7.3 Hz, 6 H). ^{13}C NMR (62.9 MHz, CF_3COOD): δ = 168.4, 166.0, 144.4, 134.7, 133.8, 129.5, 127.6, 127.5, 122.2, 122.0, 115.8, 45.0, 41.7, 29.6, 19.7, 12.0 ppm. HRMS (ESI): *m/z* calcd. for $C_{34}H_{34}N_4O_4Na$, $[M + Na]^+$ 585.2472, found 585.2390; *m/z* calcd. for $C_{34}H_{32}D_2N_4O_4Na$, $[M + Na]^+$ 587.2598, found 587.2552.

Isolated *N-butyl-1,8-naphthalimide* **15** was identical to authentic material[7].

4,6,8-Trimethyl-5-oxo-5,6-dihydro-4*H*-pyrazino[2,3-*f*]perimidin-8-ium iodide 16. To a solution of 4,6-dimethyl-4*H*-pyrazino[2,3-*f*]perimidin-5(6*H*)-one **4a** (26 mg, 0.1 mmol) in dichloromethane (4 mL) methyl iodide (0.07 mL, 1 mmol) was added. The reaction mixture was stirred at 35-40 °C for 48 h and then evaporated to dryness. The residue was rinsed with small portion of dichloromethane yielding **16** (20 mg, 49%). Compound **16** was obtained as a red solid with mp 233–235 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ = 9.14 (d, *J* = 3.5 Hz, 1 H), 9.10 (d, *J* =3.5 Hz, 1 H), 8.67 (d, *J* = 8.1 Hz, 1 H), 8.04 (t, *J* = 8.2 Hz, 1 H), 7.58 (d, *J* = 8.1 Hz, 1 H), 6.94 (s, 1 H), 4.50 (s, 3 H), 3.64 (s, 3 H), 3.53 ppm (s, 3 H). ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 149.3, 147.2, 142.6, 140.3, 138.3, 138.3, 137.0, 133.3, 129.3, 118.0, 114.4, 113.8, 90.7, 45.7, 32.6, 31.9 ppm. HRMS (ESI): *m/z* calcd. for $C_{16}H_{15}N_4O$, $[M + H]^+$ 279.1240, found 279.1248.

Copies of NMR spectra

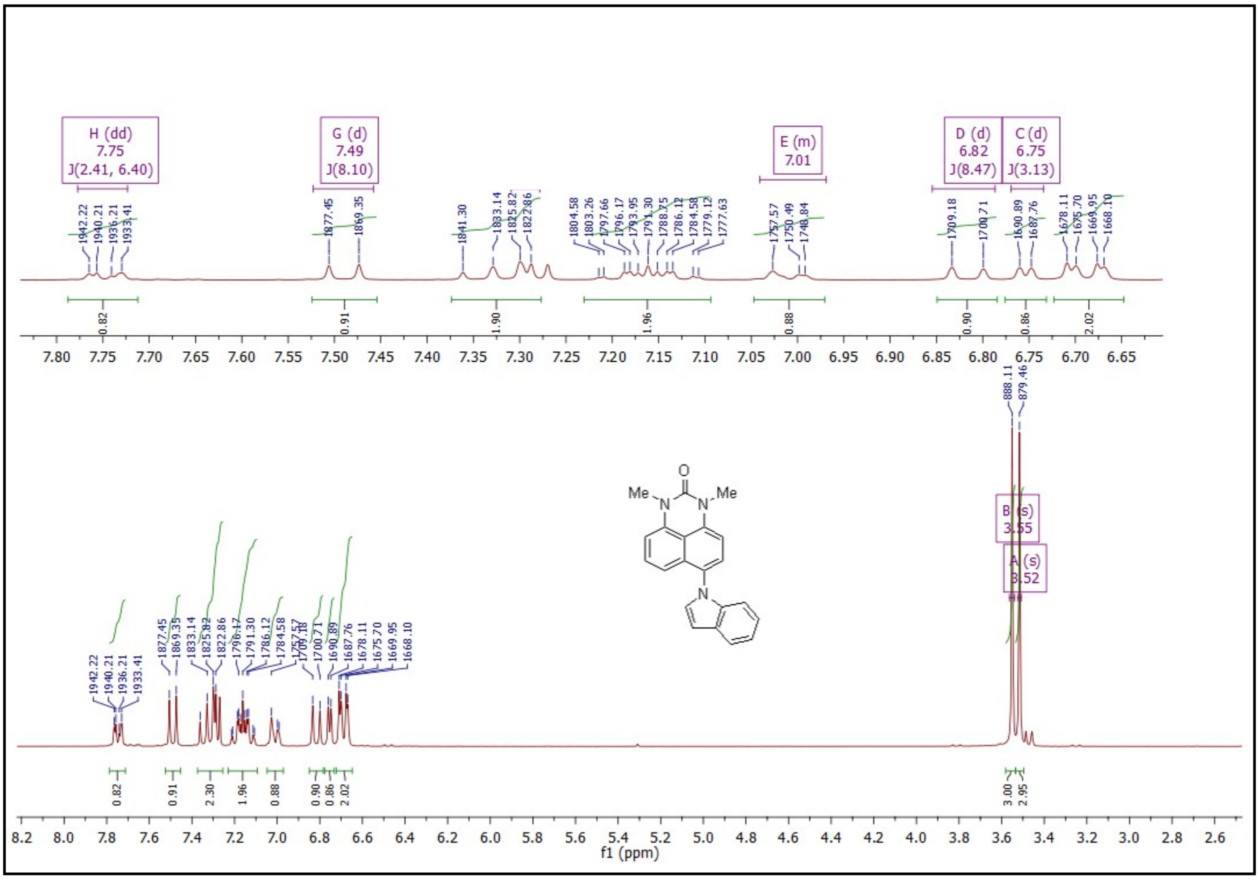


Fig. S1. ^{1}H NMR spectrum of compound **3a** (250 MHz, CDCl$_3$).

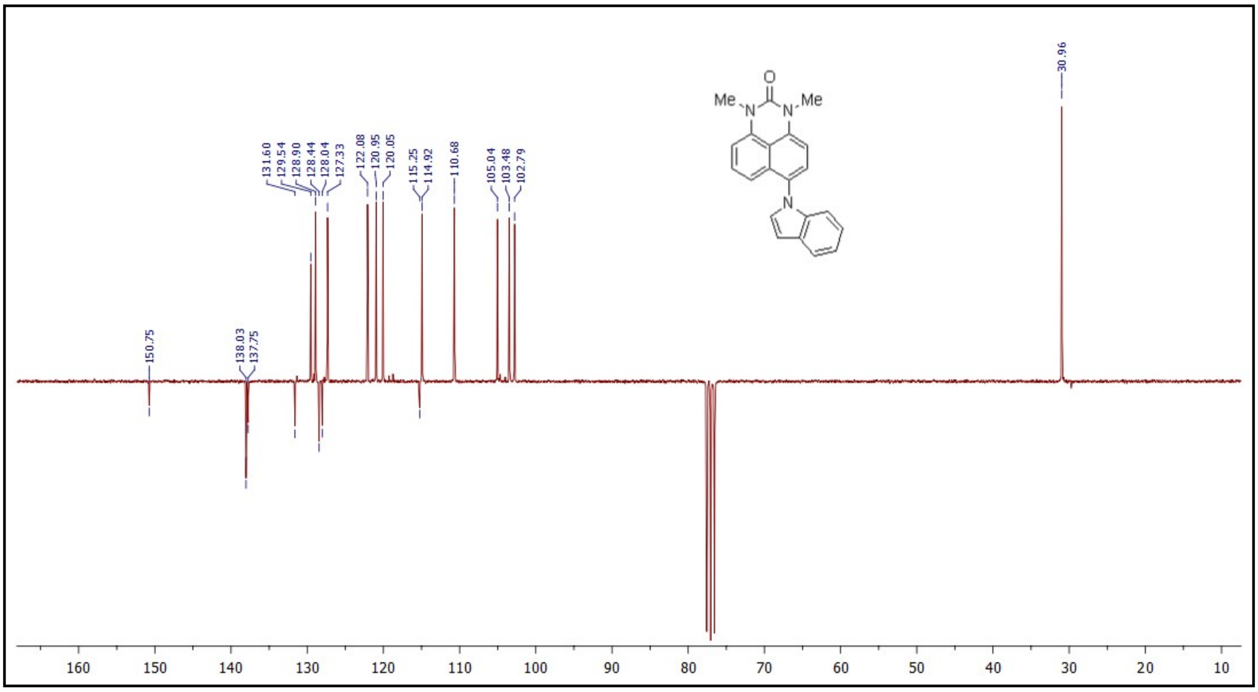


Fig. S2. ^{13}C{^{1}H} APT-NMR spectrum of compound **3a** (62.9 MHz, CDCl$_3$).

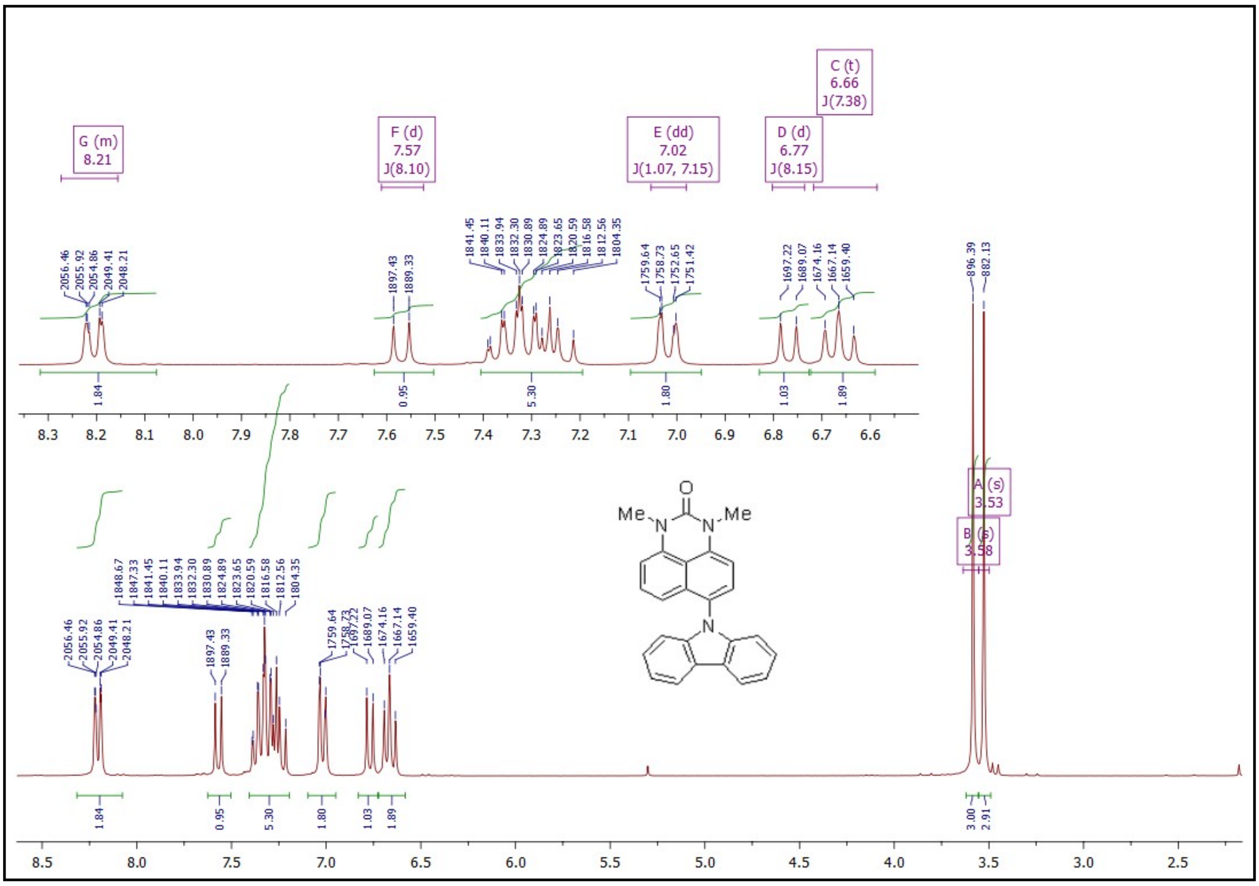


Fig. S3. ^{1}H NMR spectrum of compound **3b** (250 MHz, CDCl$_3$).

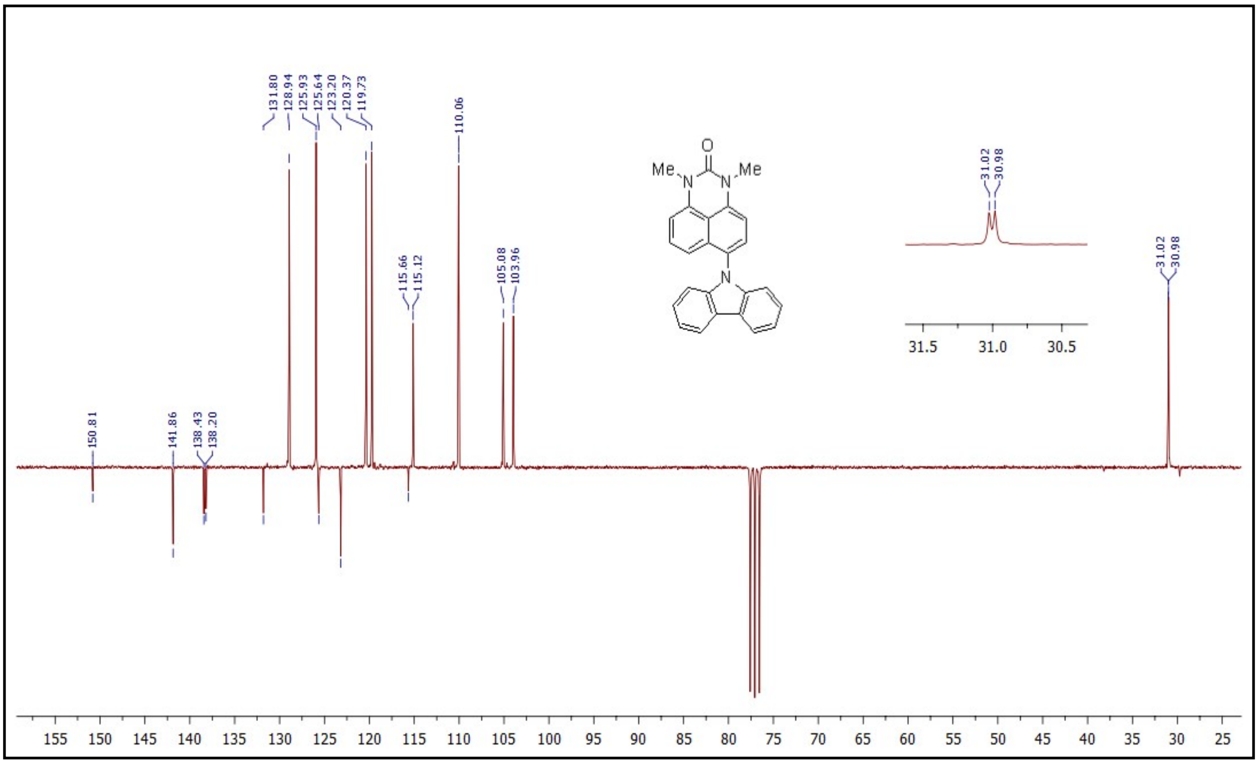


Fig. S4. ^{13}C{^{1}H} APT-NMR spectrum of compound **3b** (62.9 MHz, CDCl$_3$).

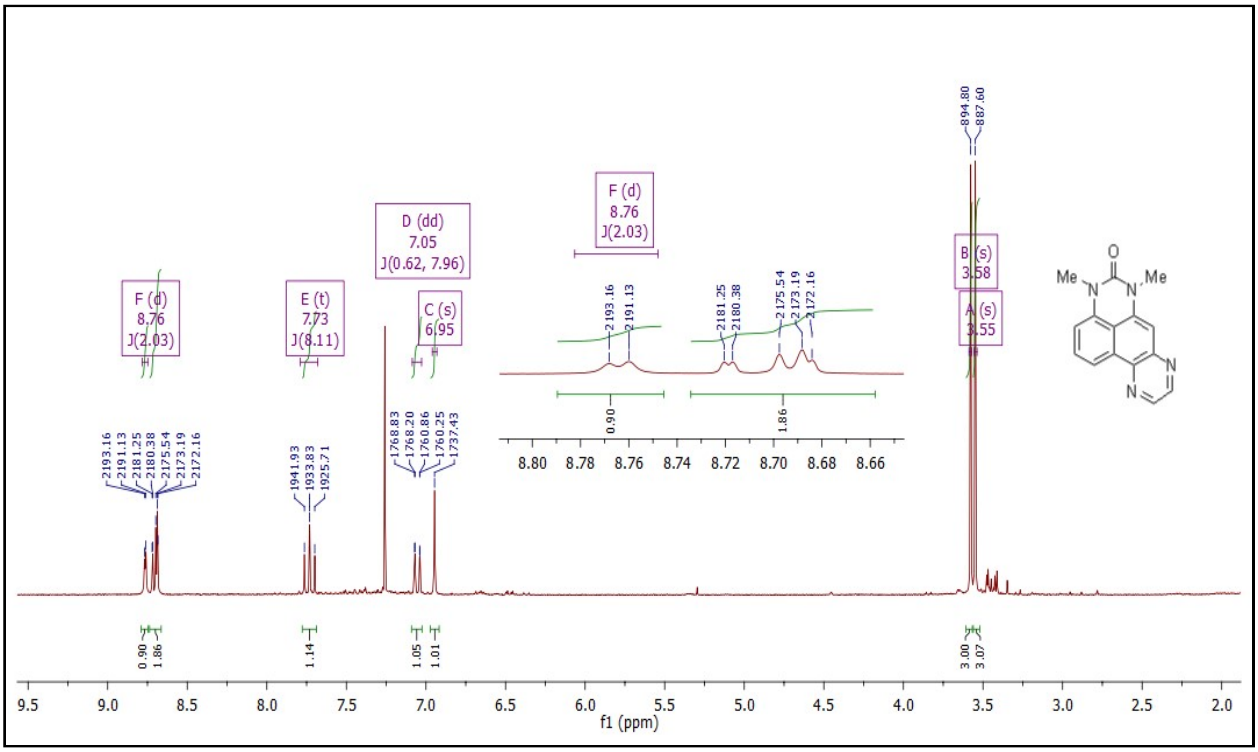


Fig. S5. ^{1}H NMR spectrum of compound **4a** (250 MHz, CDCl$_3$).

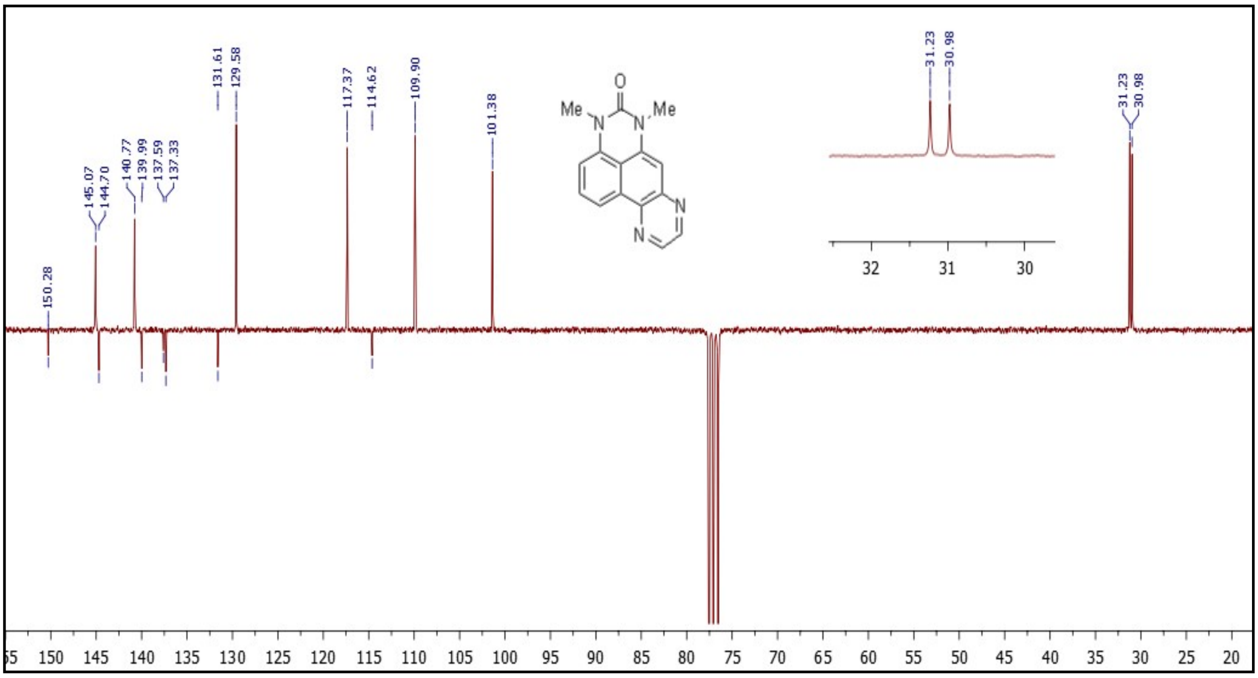


Fig. S6. ^{13}C{^{1}H} APT-NMR spectrum of compound **4a** (62.9 MHz, CDCl$_3$).

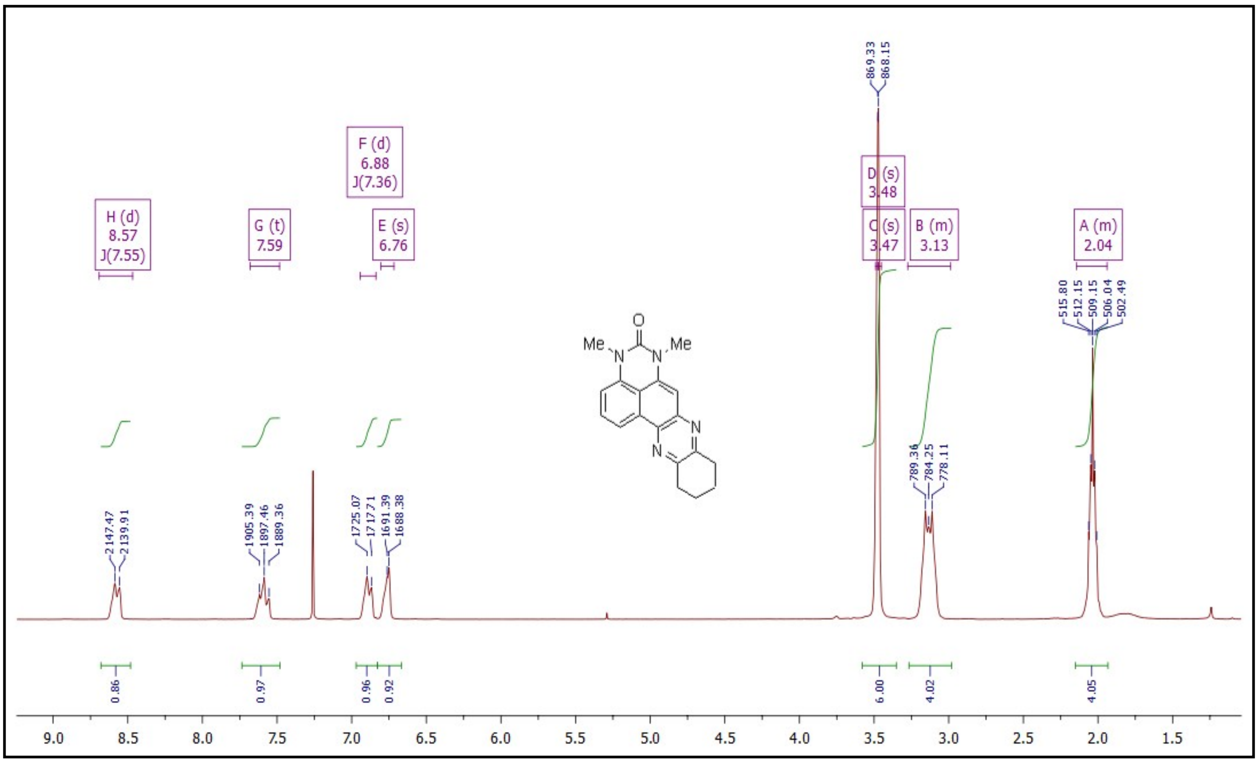


Fig. S7. ^{1}H NMR spectrum of compound **4b** (250 MHz, $CDCl_3$).

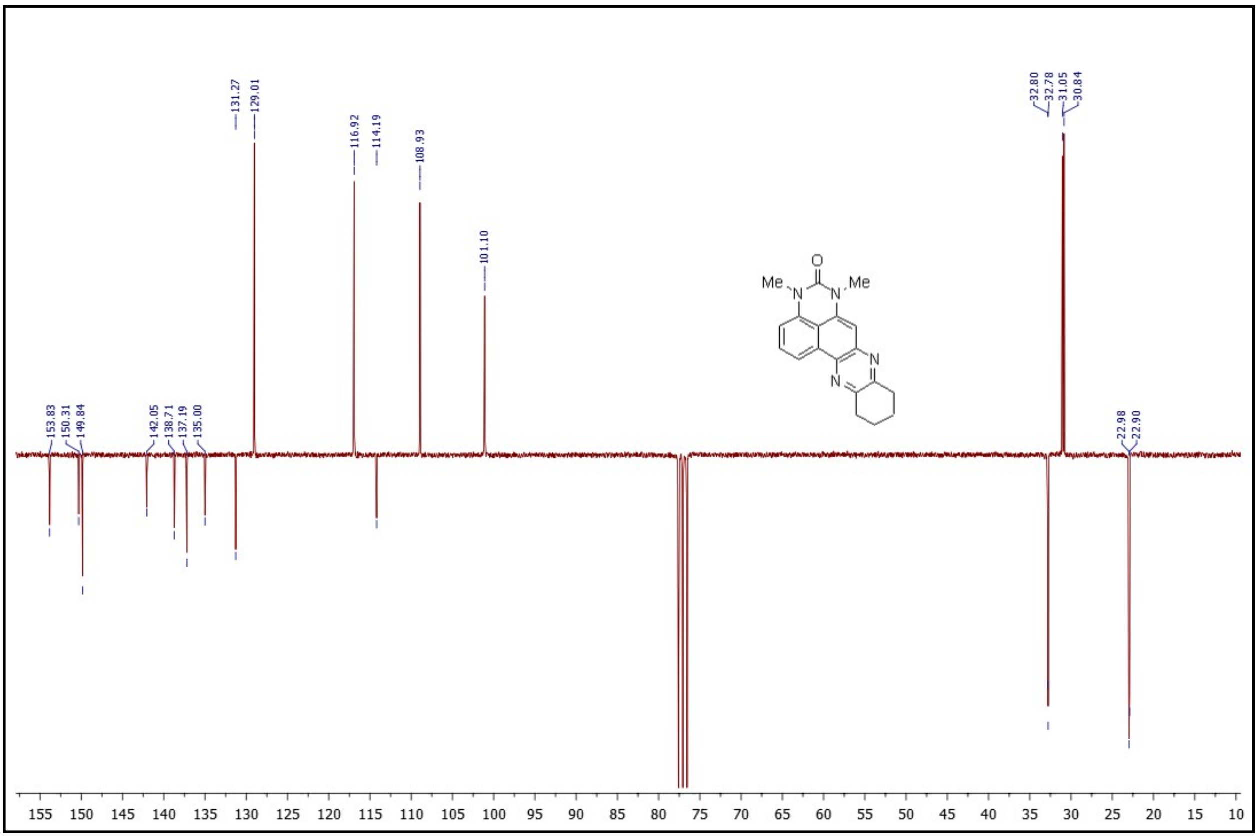


Fig. S8. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **4b** (62.9 MHz, $CDCl_3$).

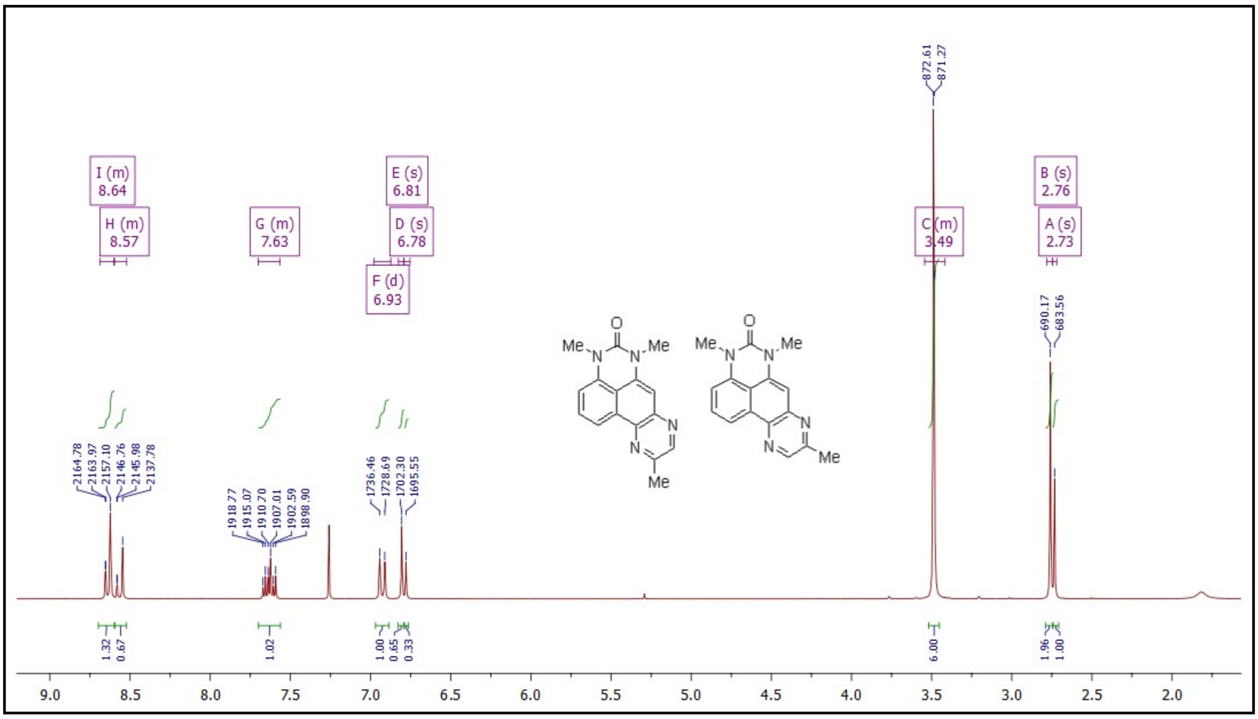


Fig. S9. ^{1}H NMR spectrum of a mixture of isomeric compounds **4c** and **4c'** (250 MHz, CDCl$_3$).

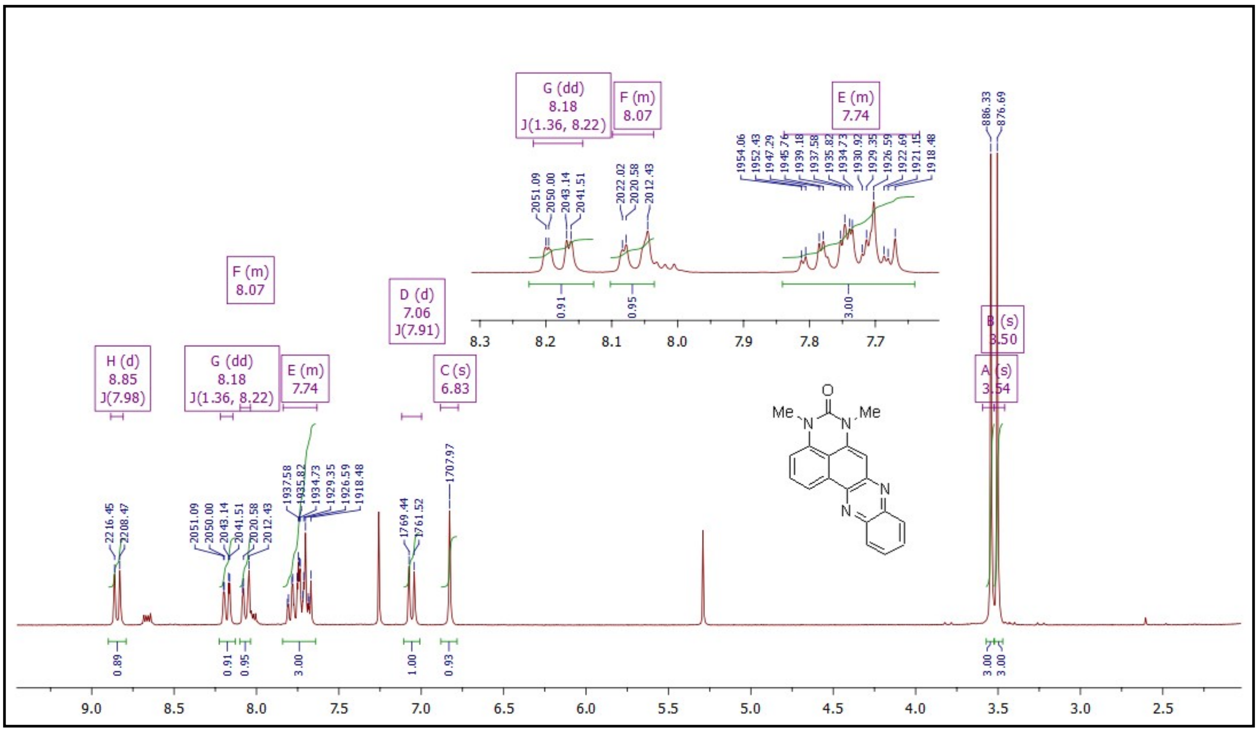


Fig. S10. ^{1}H NMR spectrum of compound **4d** (250 MHz, CDCl$_3$).

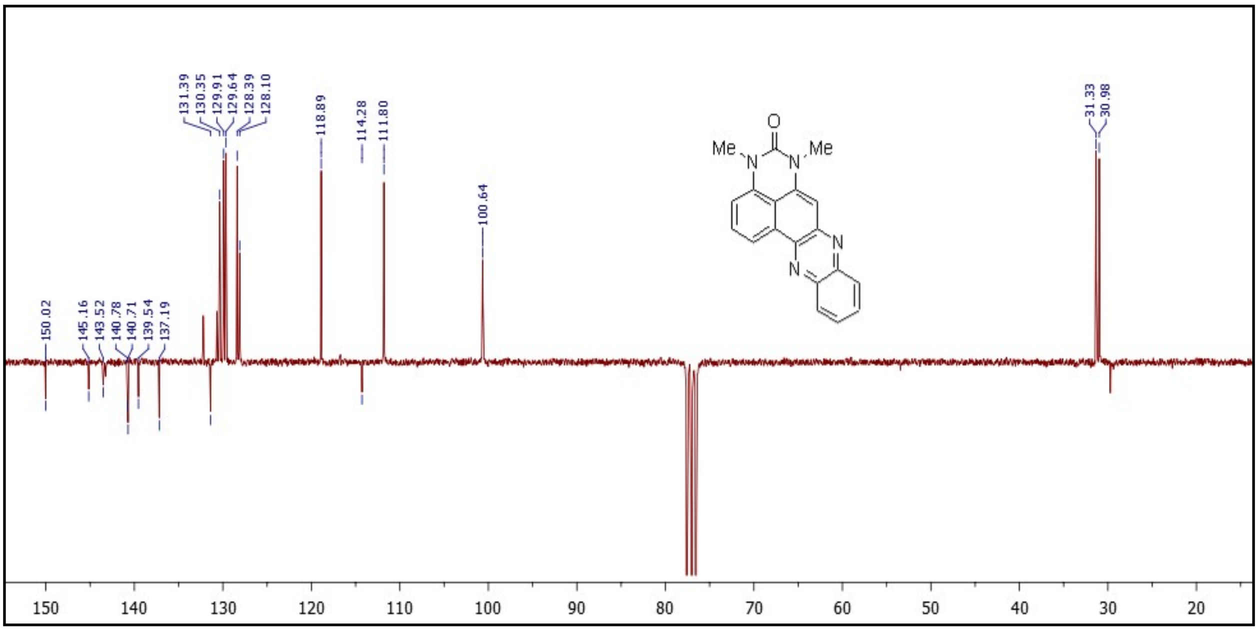


Fig. S11. ^{13}C{^{1}H} APT-NMR spectrum of compound **4d** (62.9 MHz, CDCl$_3$).

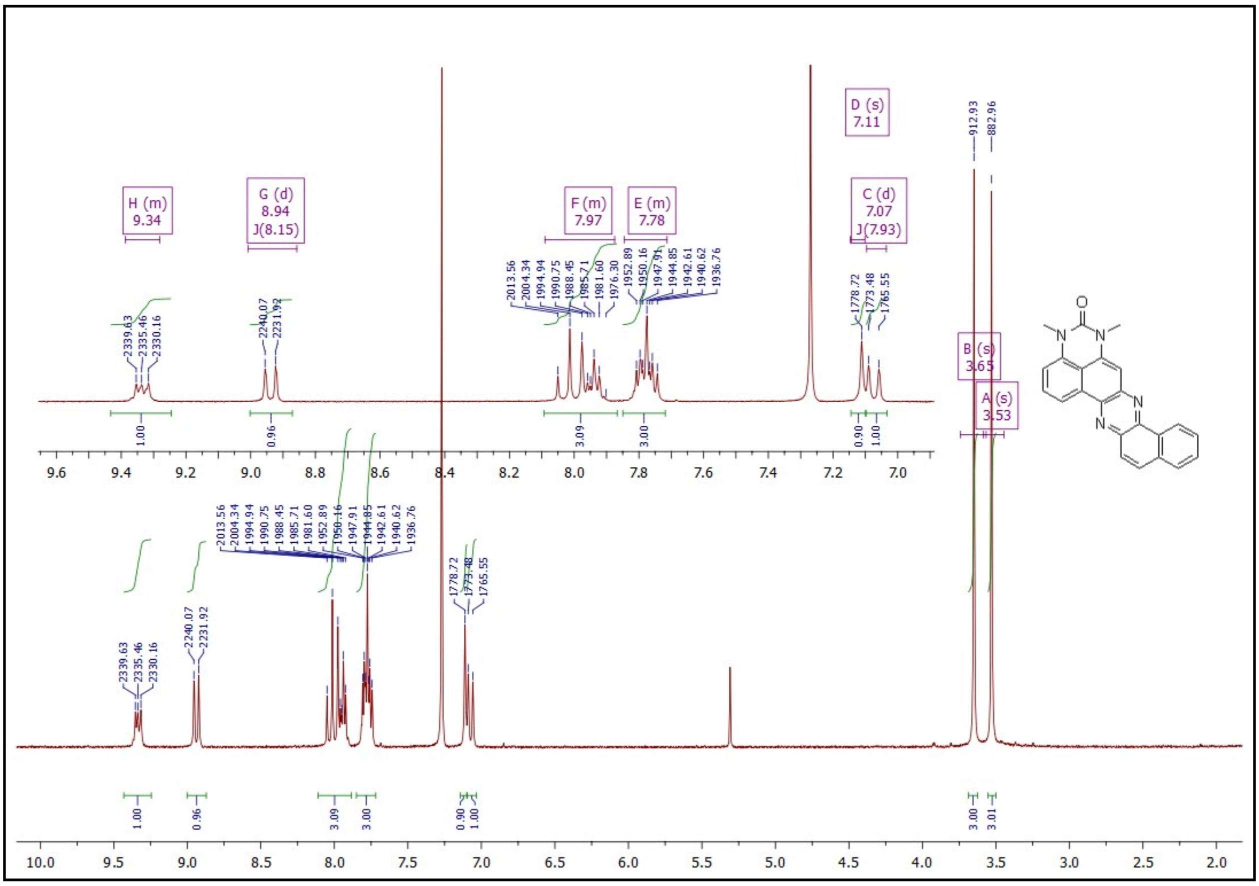


Fig. S12. ^{1}H NMR spectrum of compound **4e** (250 MHz, CDCl$_3$).

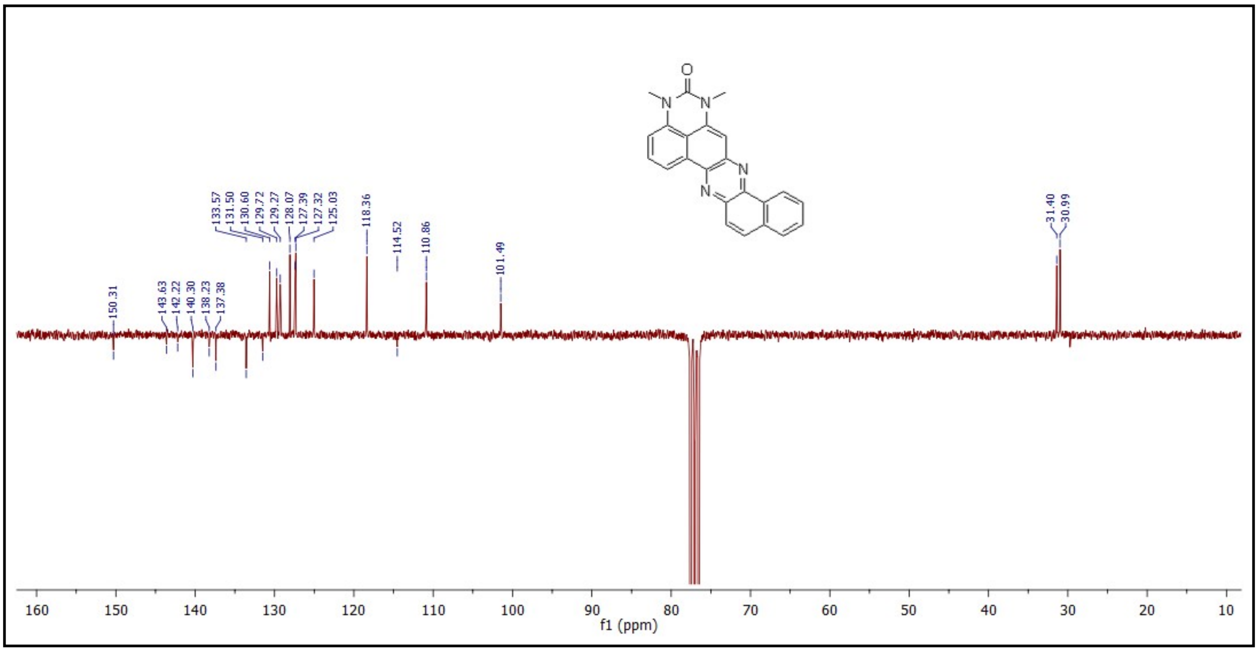


Fig. S13. ^{13}C{^{1}H} APT-NMR spectrum of compound **4e** (62.9 MHz, CDCl$_3$).

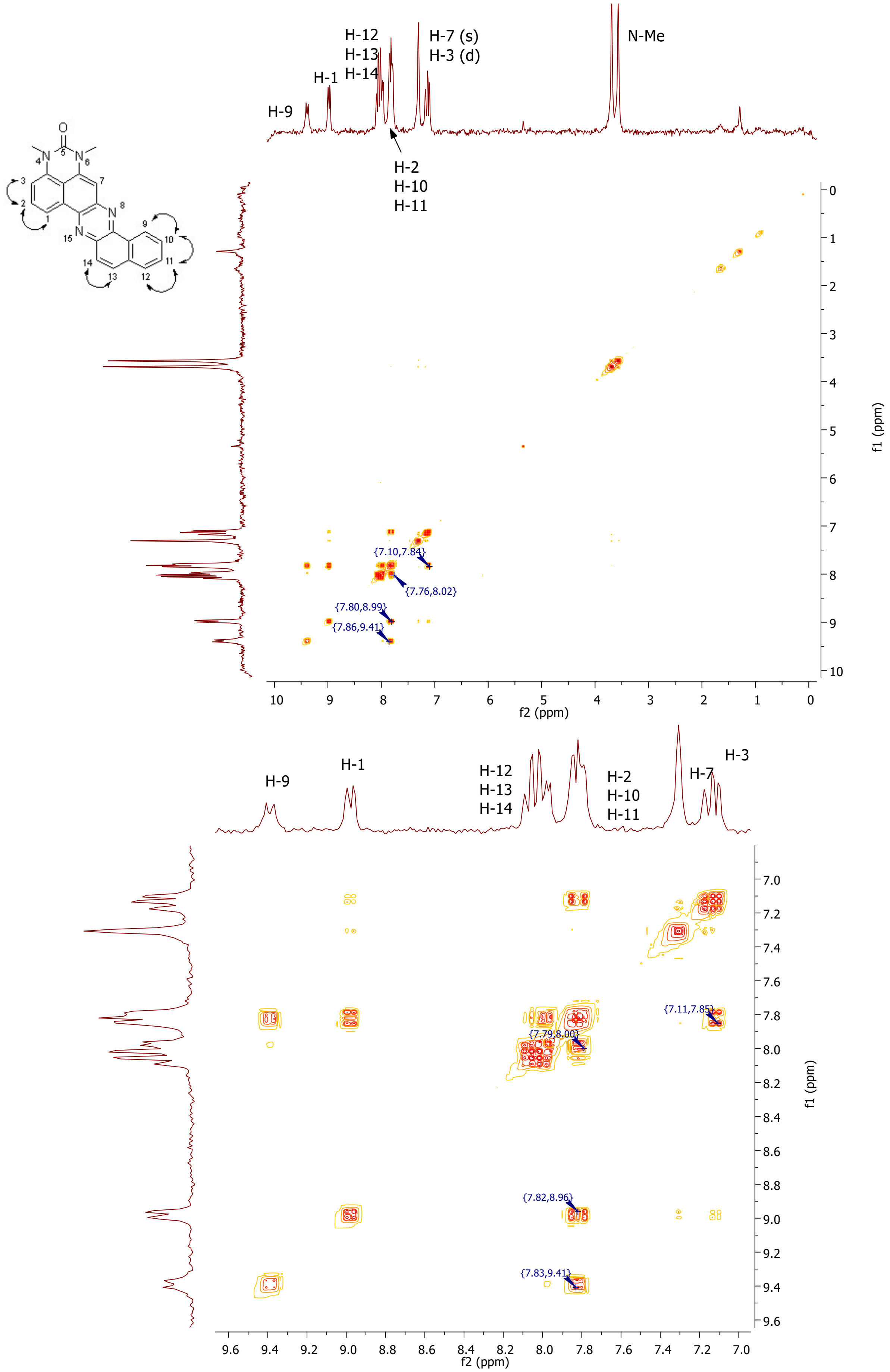
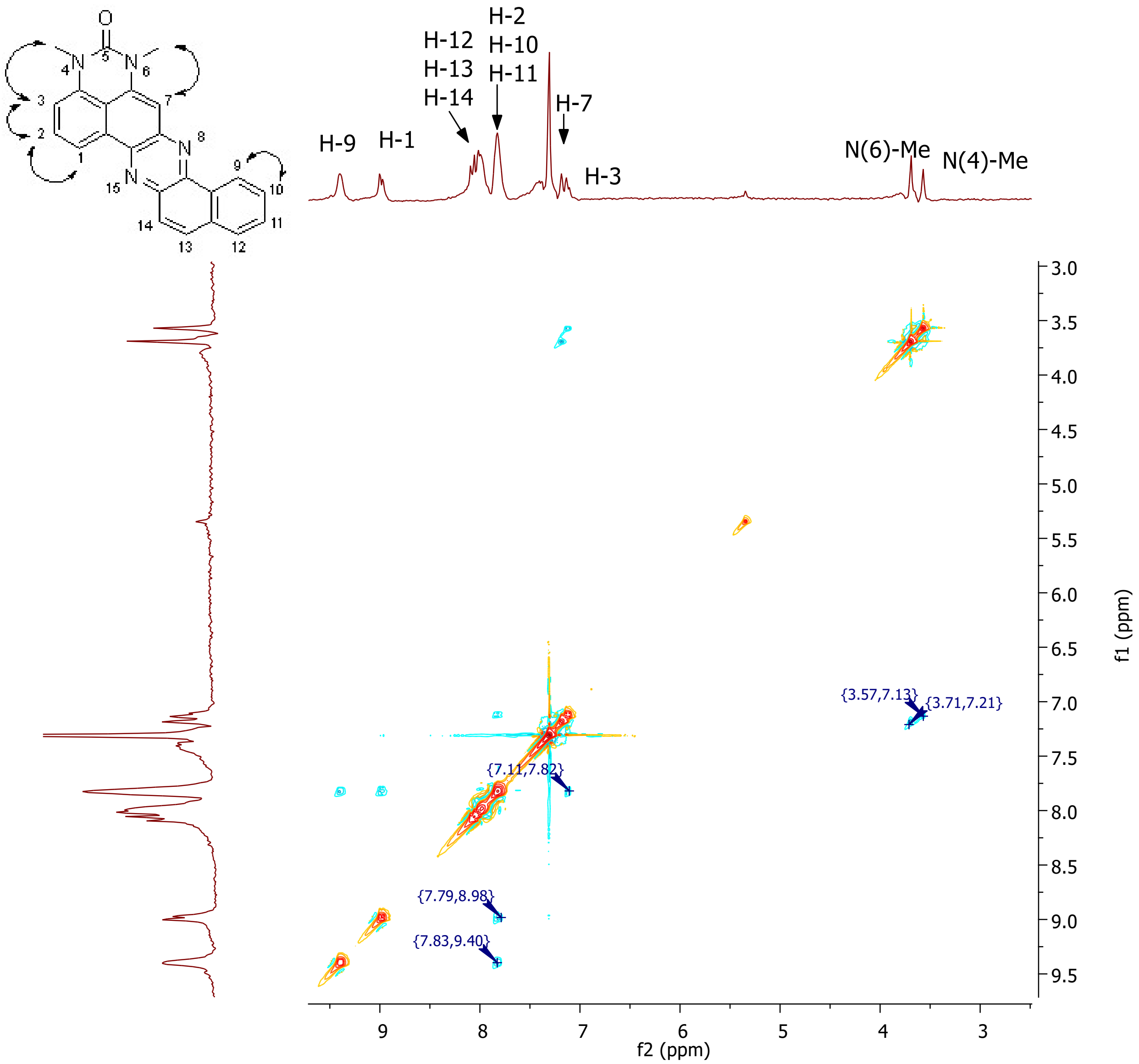
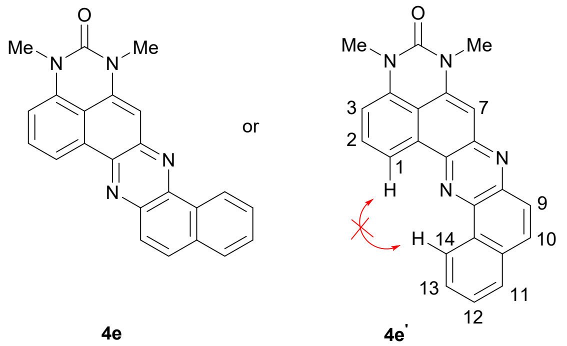


Fig. S14. ^{1}H-^{1}H COSY spectrum of compound **4e** (250 MHz, $CDCl_3$).





4e or **4e'**

Fig. S15. NOESY spectrum of compound **4e** (250 MHz, $CDCl_3$).

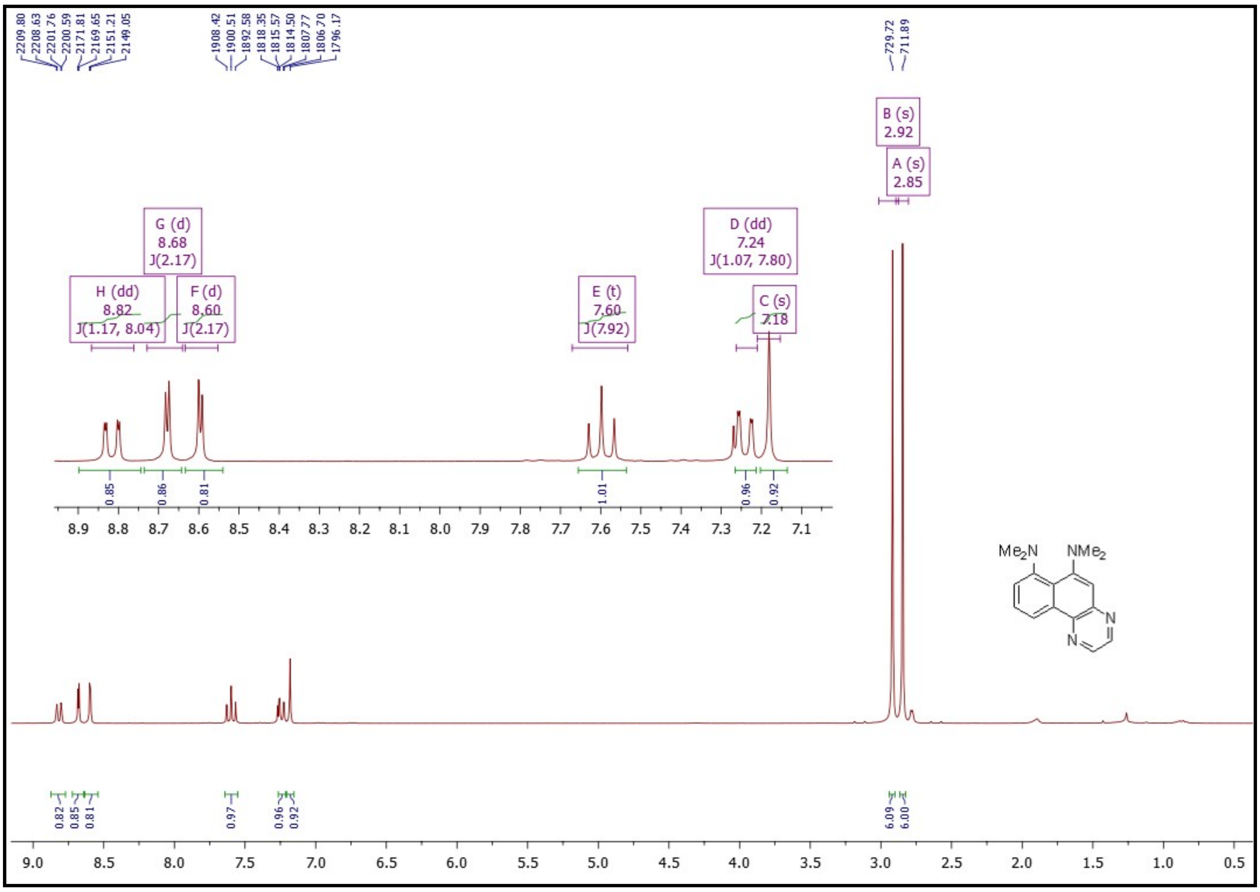


Fig. S16. ^{1}H NMR spectrum of compound **9** (250 MHz, CDCl$_3$).

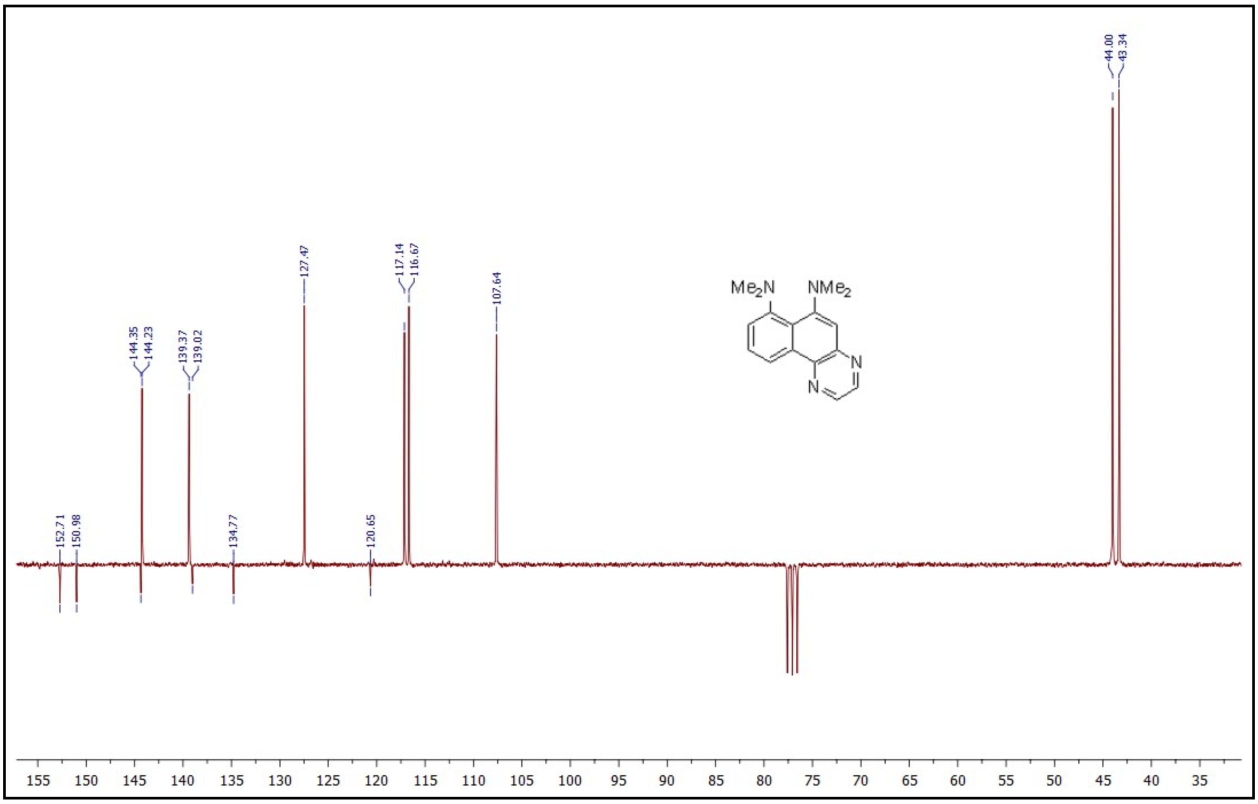


Fig. S17. ^{13}C{^{1}H} APT-NMR spectrum of compound **9** (62.9 MHz, CDCl$_3$).

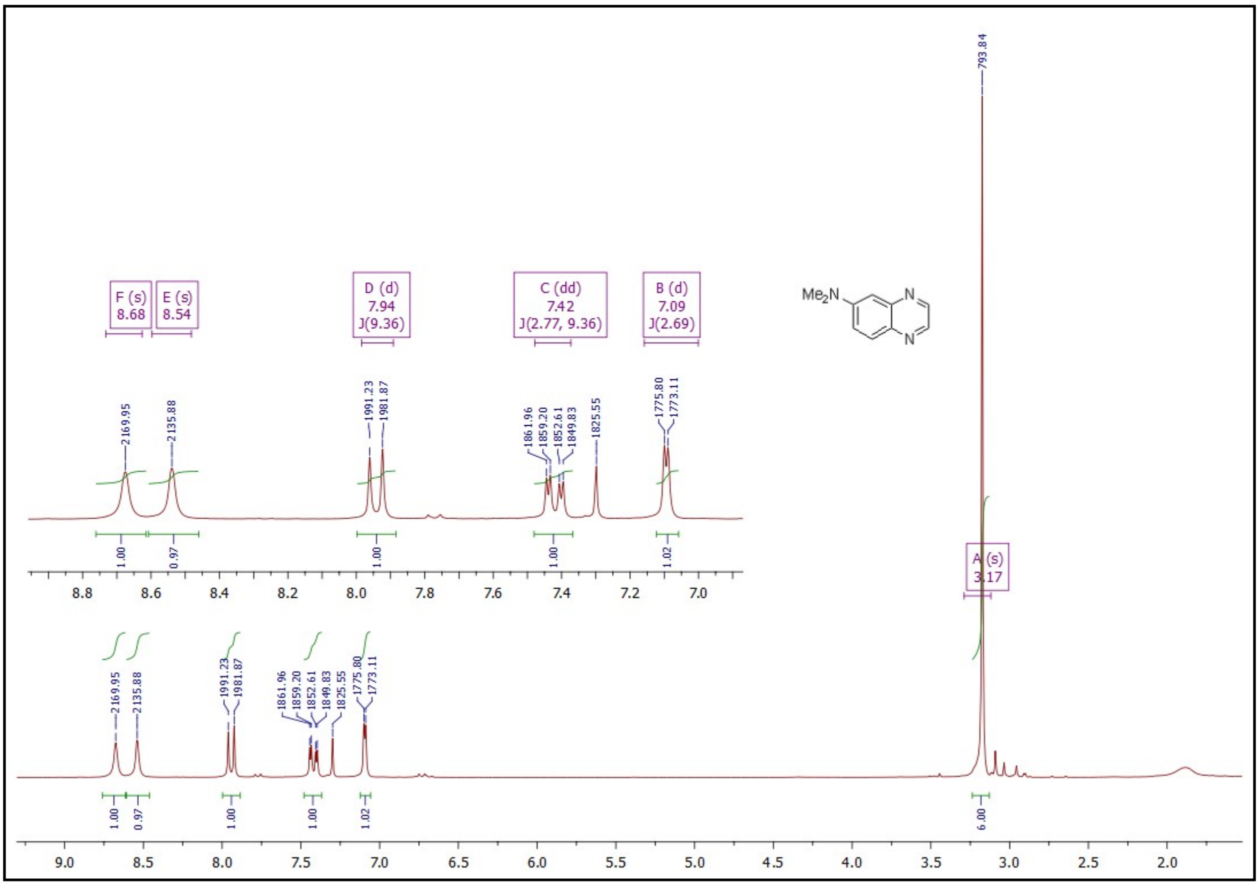


Fig. S18. ^{1}H NMR spectrum of compound **10** (250 MHz, CDCl$_3$).

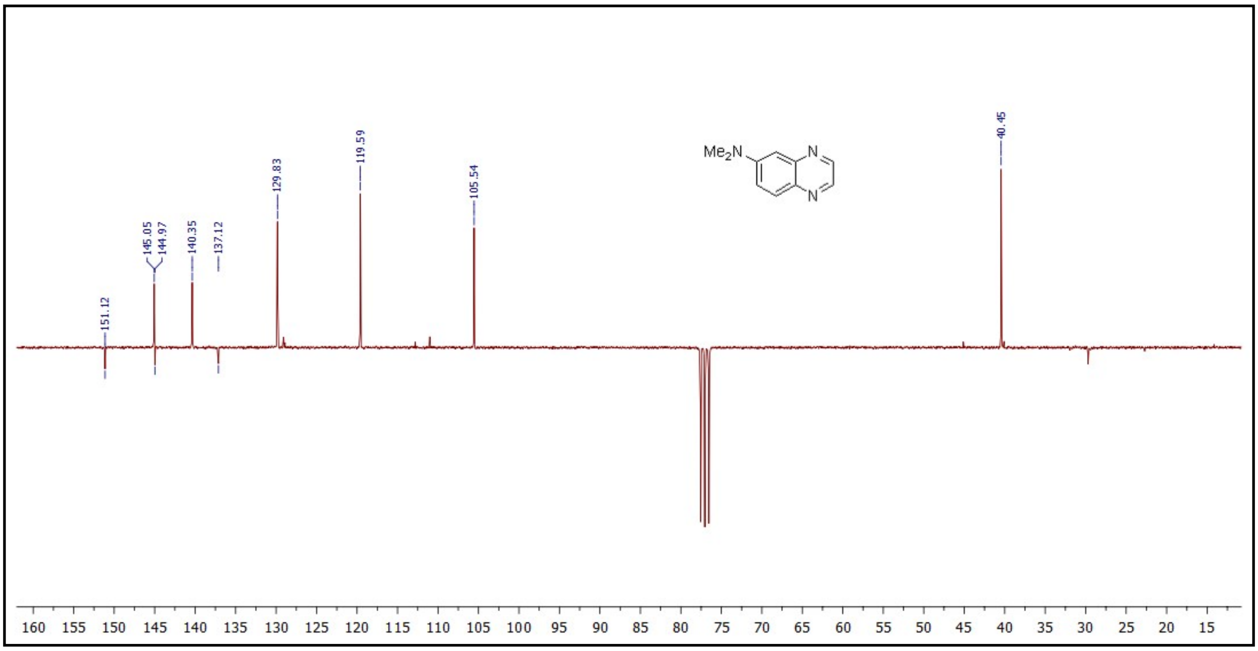


Fig. S19. ^{13}C{^{1}H} APT-NMR spectrum of compound **10** (62.9 MHz, CDCl$_3$).

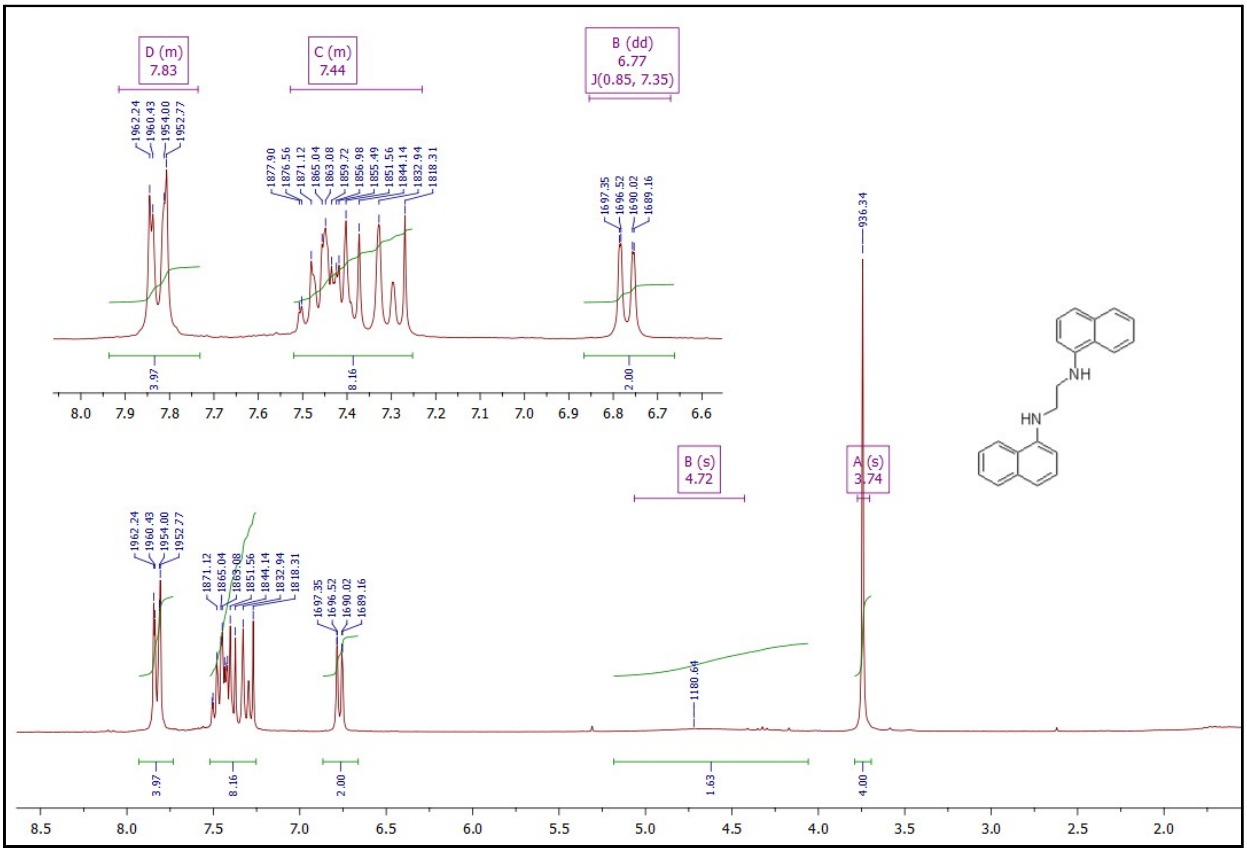


Fig. S20. ^{1}H NMR spectrum of compound **13** (250 MHz, CDCl$_3$).

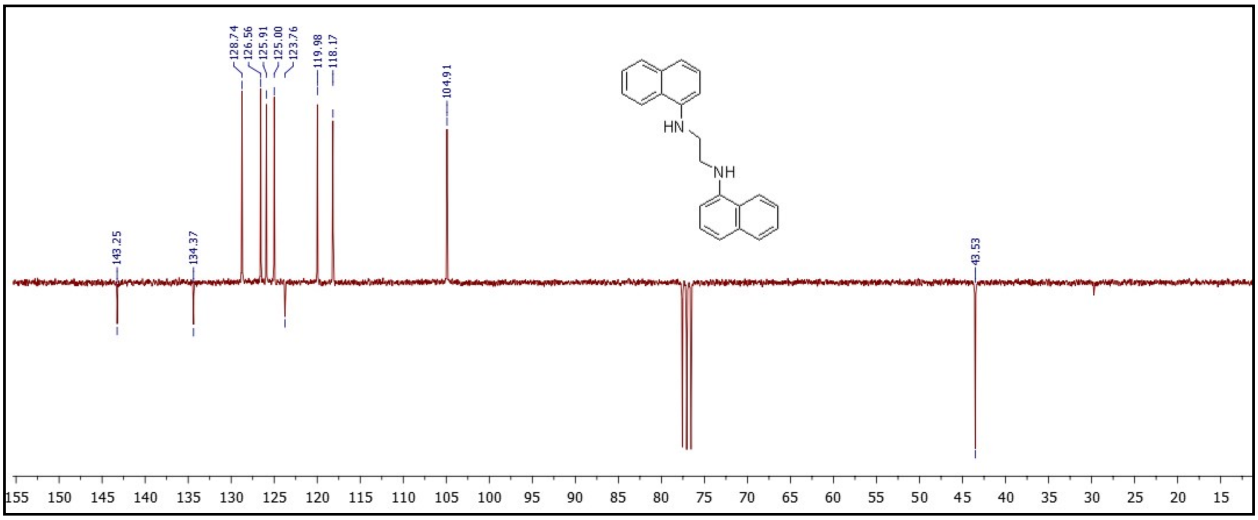


Fig. S21. ^{13}C{^{1}H} APT-NMR spectrum of compound **13** (62.9 MHz, CDCl$_3$).

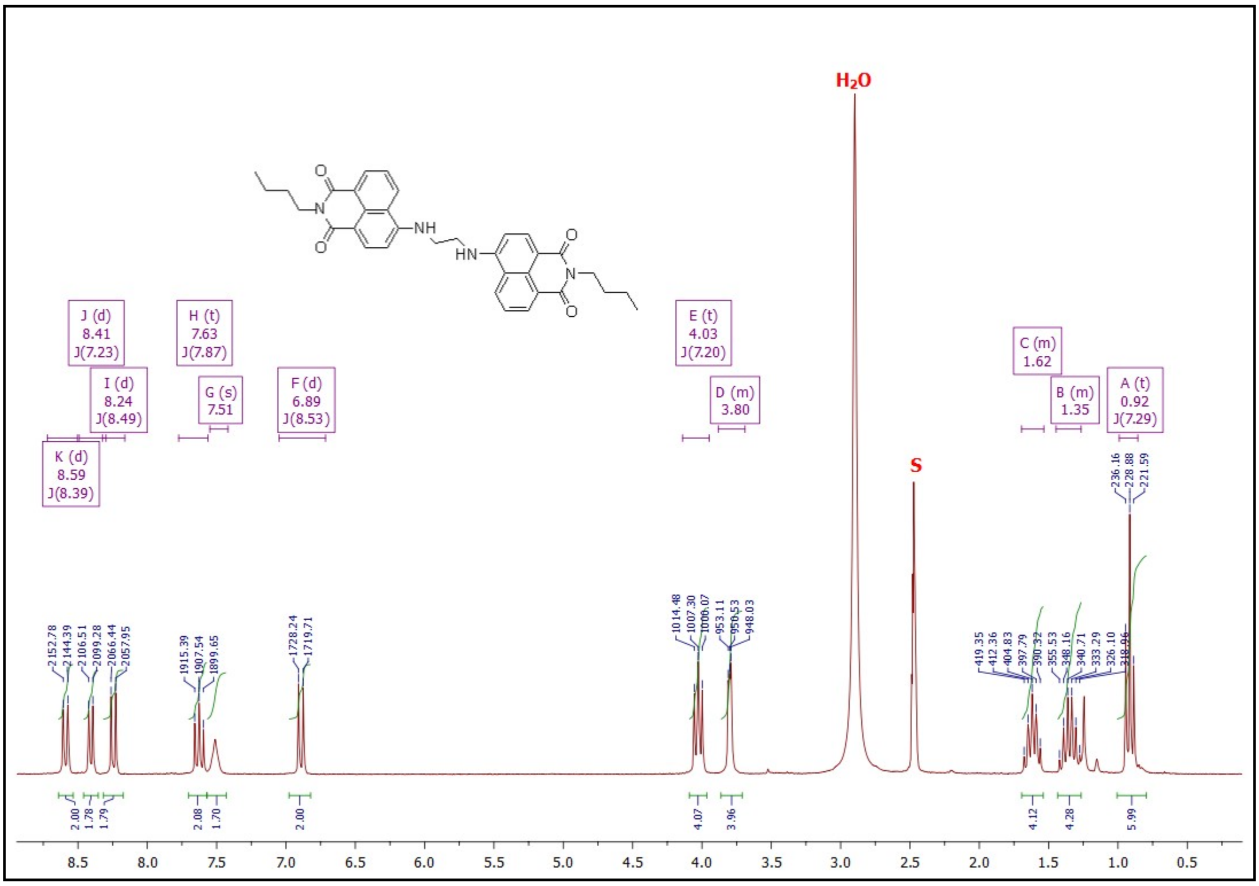


Fig. S22. ^{1}H NMR spectrum of compound **14** (250 MHz, DMSO-d_6).

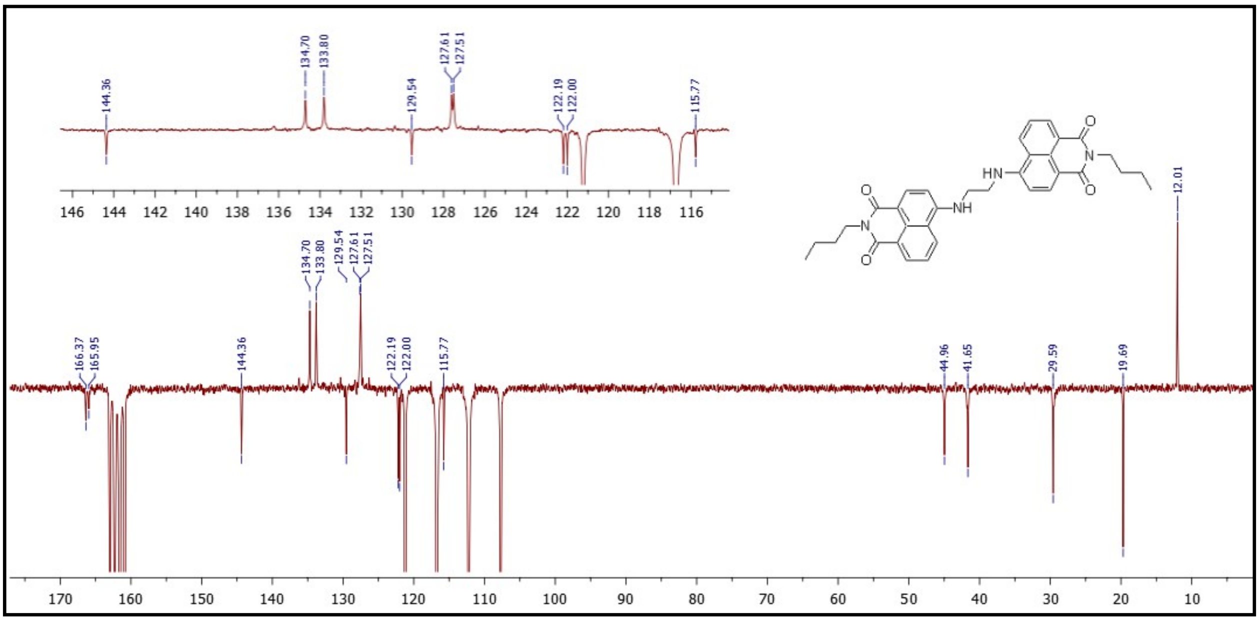


Fig. S23. ^{13}C{^{1}H} APT-NMR spectrum of compound **14** (62.9 MHz, CF_3COOD).

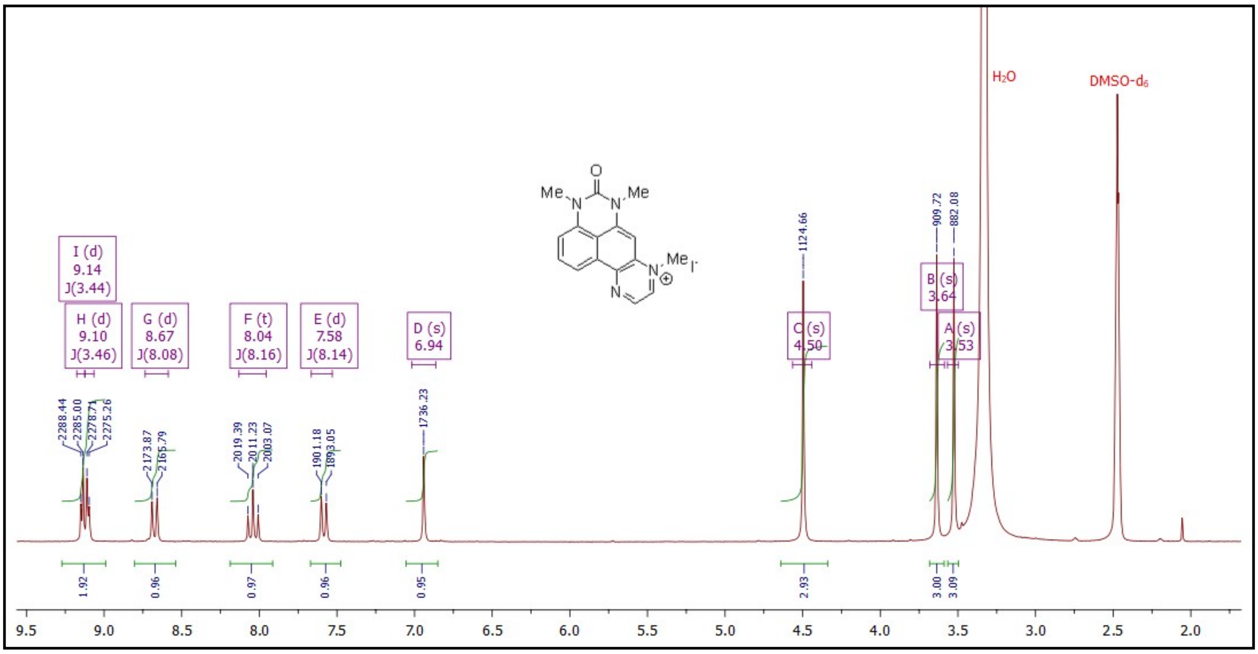


Fig. S24. ^{1}H NMR spectrum of compound **16** (250 MHz, DMSO-d_6).

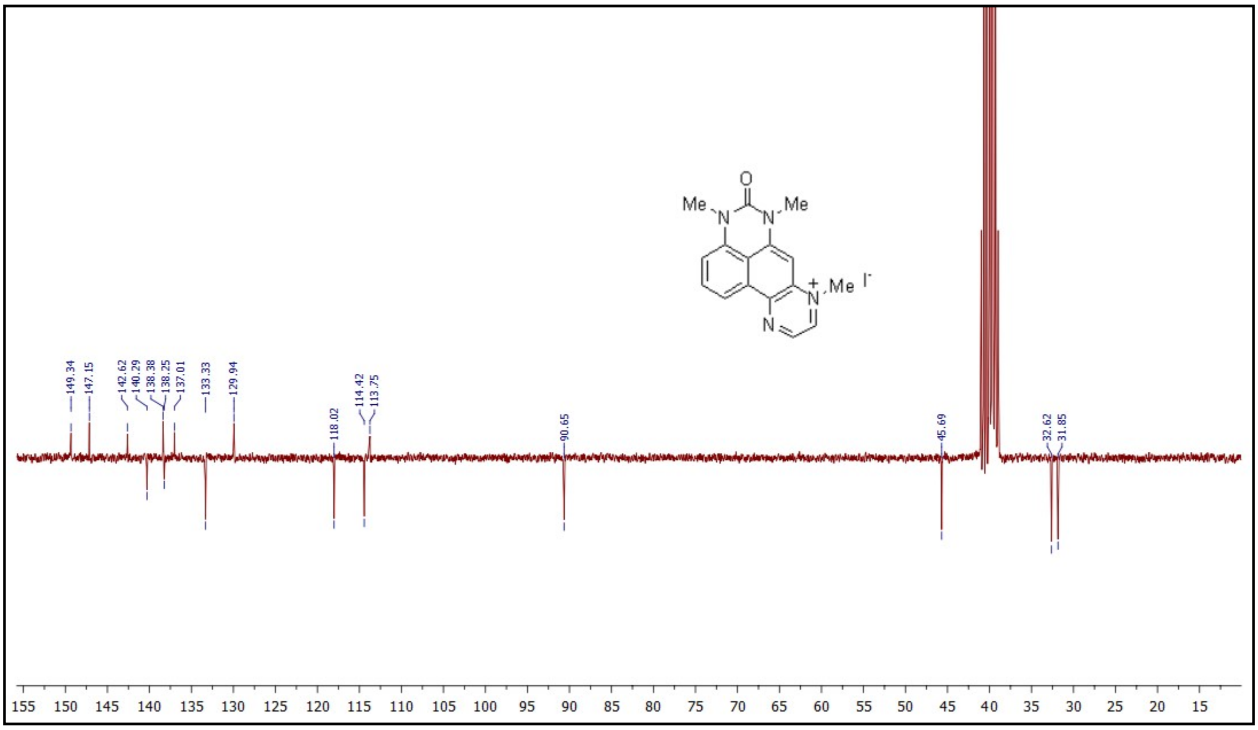


Fig. S25. ^{13}C{^{1}H} APT-NMR spectrum of compound **16** (62.9 MHz, DMSO-d_6).

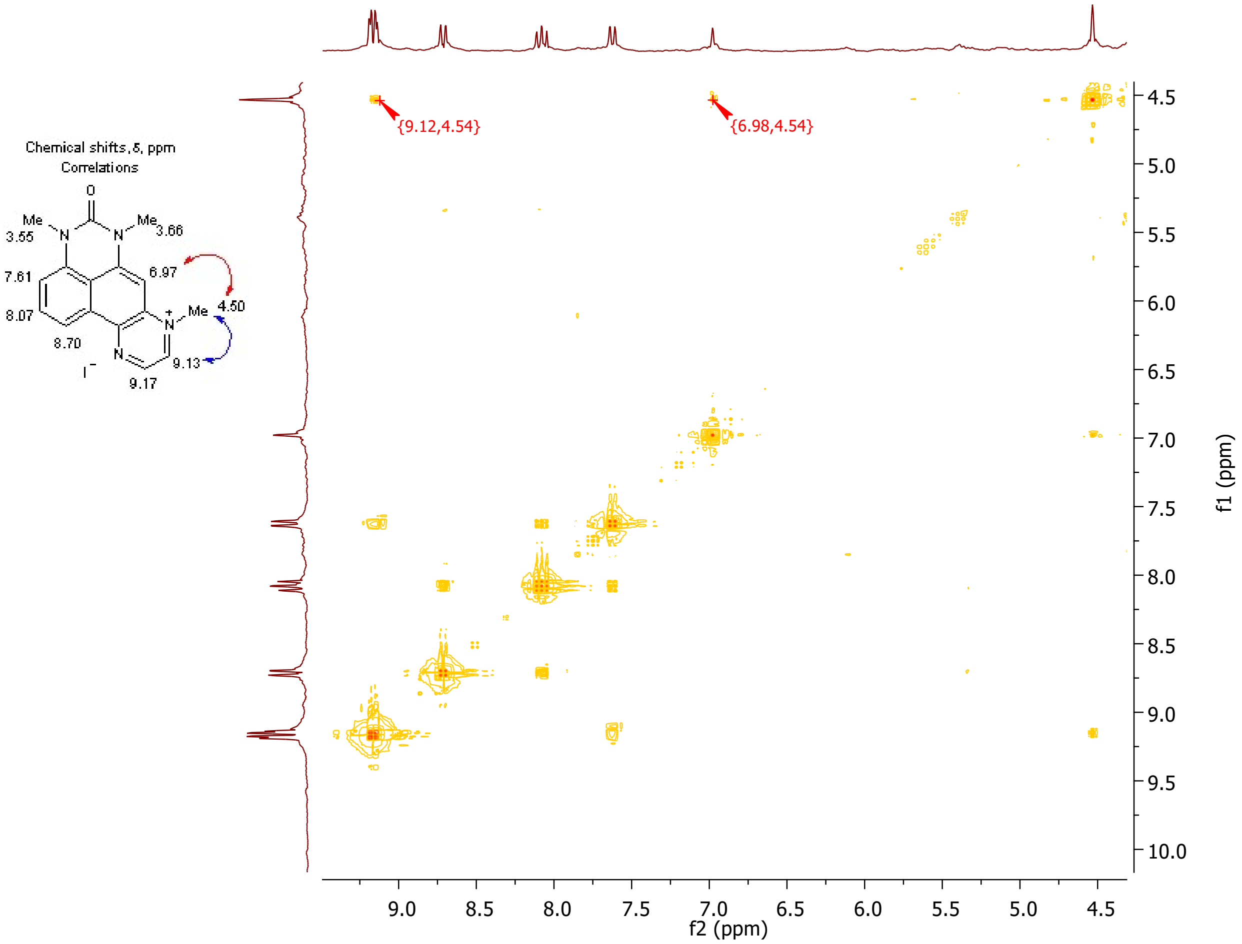


Fig. S26. NOESY spectrum of compound **16** (250 MHz, DMSO-d_6).

Photophysical studies

Emission quantum yields were determined by relative method with a solution of anthracene in degassed EtOH as a standard ($\Phi = 0.28$)[8] and solutions of studied compounds in DMSO using Equation 1[9]:

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

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.

The X-ray structural analysis data for compound **4a** allowed us to determine ***the change in dipole moment (μ_E - μ_G) upon photoexcitation using the Lippert-Matagi equation 2***[10].

$$\nu_A - \nu_E = 2\Delta f(\mu_E - \mu_G)^2/hca^3 + \text{const} \qquad \text{(Eq. 2)},$$

where $\nu_A - \nu_E$ – the Stokes shift (in cm^{-1});
$\mu_E - \mu_G$ – the magnitude of the change in the dipole moment from the ground state to the excited state (in $cm^{5/2} \cdot g^{1/2} \cdot s^{-1}$, to convert to Debye (D), the value should be multiplied by 10^{18});
h – the Plank's constant ($6.626 \cdot 10^{-27}$ $g \cdot cm^2 \cdot s^{-1}$);
c – the velocity of light in the vacuum ($3 \cdot 10^{10}$ $cm \cdot s^{-1}$);
a – the Onsager cavity radius (in cm). The radius a can be calculated using Equation 3.

$$a = (3M / 4N\pi d)^{1/3} \qquad \text{(Eq. 3)},$$

where M – molecular weight, $g \cdot mol^{-1}$; N – the Avogadro number; d – density of the crystals of **4a**, $g \cdot cm^{-3}$ (from X-ray data).
Δf – the orientation polarizability parameter of the solvent, it is determined using Equation 4

$$\Delta f = (\varepsilon - 1) / (2\varepsilon + 1) - (n^2 - 1) / (2n^2 - 1) \qquad \text{(Eq. 4)},$$

where ε – the static dielectric constant of the solvent; n – the refractive index of the solvent.
The calculation results for compound **4a** in various solvents are presented in the graph (Fig. S27). The change in dipole moment for compound **4a** was determined from the slope of the graph and amounted to ~6.3 D.

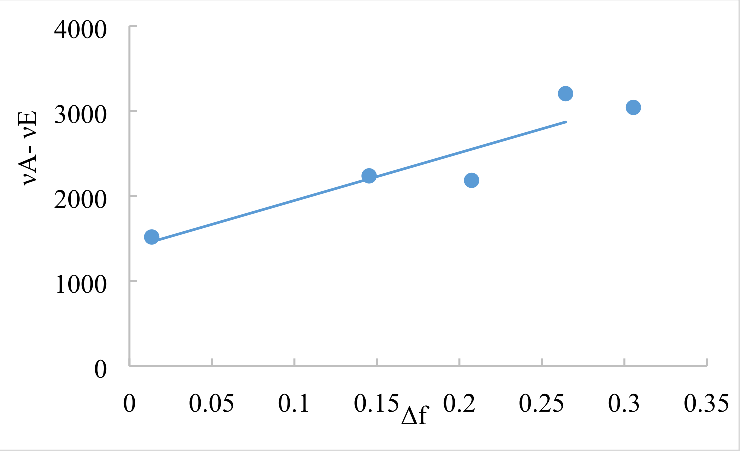


Fig. S27. Lippert–Mataga plot for **4a**.

Protolytic equilibrium constant of compounds **4a,d** was estimated in DMSO – H_2O solution (1:1, v/v) by direct fluorimetric titration as a function of p*H* using the fluorescence emission spectra. To adjust the p*H* of the solutions, 0.1 M and 1M solution of HCl, 0.1 M solution of disodium citrate and 0.1M solution of sodium hydroxide were used. To measure the p*H* values a p*H*-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 Equation 5[11]:

$$pK_a = pH + \lg\frac{F_{max} - F_i}{F_i - F_{min}} \qquad \text{(Eq. 5)}$$

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.

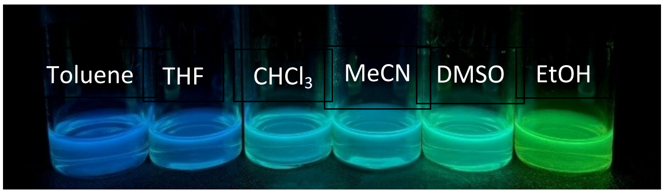
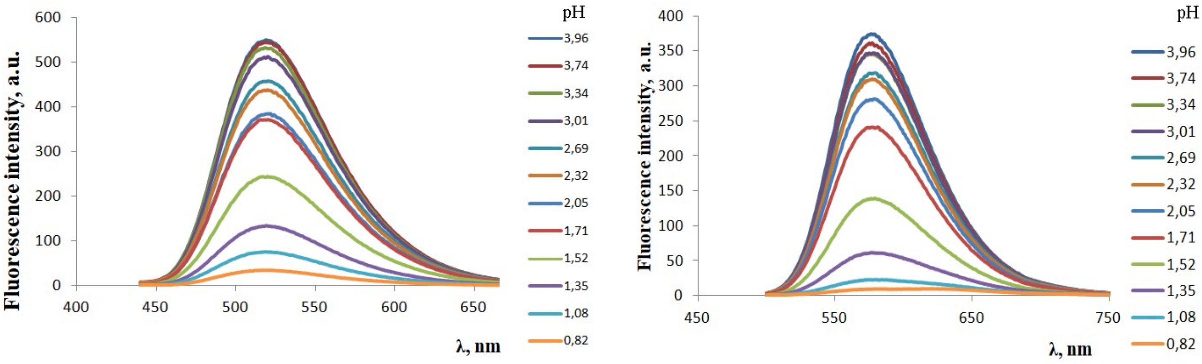


Figure S28. Fluorescence of compound **4a** in different solvents.

a ***b***

Fig. S29. Solutions of compounds **4a** (*a*) and **4d** (*b*) in MeCN and MeCN/1M HCl (10:1) under UV-light (365 nm).



4a **4d**

a ***b***

Fig. S30. p*H*-Dependent emission spectra of **4a** (*a*) and **4d** (*b*) in DMSO/H_2O (1:1)

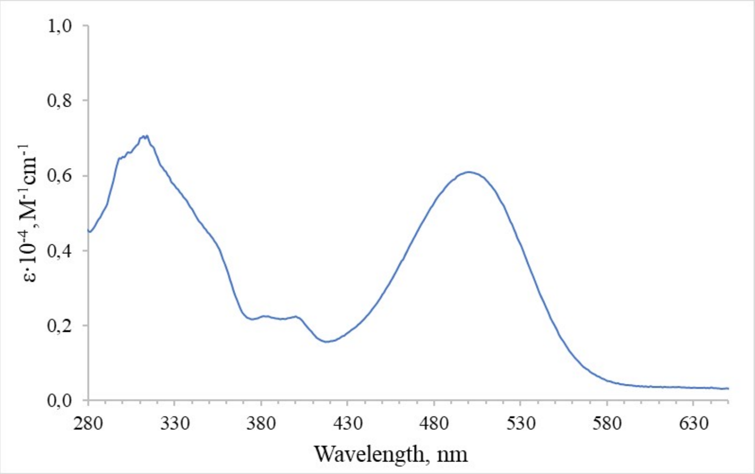


Fig. S31. UV/Vis absorption spectrum of salt **16** in DMSO.

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