Supporting Information

for

Synthesis, conformational stability and molecular structure of 4-aryl- and 4,5-diaryl-1,8-bis(dimethylamino)naphthalenes

Ekaterina A. Filatova,[a] Eugeny A. Ermolenko,[a] Alexander F. Pozharskii,[a] Valery A. Ozeryanskii,[a] Oleg P. Demidov, [b] Anatoly V. Chernyshev, [c] Anatoly V. Metelitsa, [c] Anna V. Gulevskaya*[a]

[a] Department of Chemistry, Southern Federal University, Zorge str. 7, 344090 Rostov-on-Don Russian Federation. E-mail: agulevskaya@sfedu.ru
[b] Department of Chemistry and Pharmacy, North Caucasus Federal University, Pushkin str. 1a, 355017 Stavropol, Russian Federation
[c] Institute of Physical and Organic Chemistry, Southern Federal University, 194/2 Stachka ave., Rostov-on-Don 344090, Russian Federation

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

Table of Contents

EXPERIMENTAL SECTION

General Information: ^{1}H and ^{13}C NMR spectra were recorded on 250, 400 and 600 MHz spectrometers. Chemical shifts are reported in ppm relative to Me_4Si. The electronic absorption spectra of the studied compounds have been recorded on an Agilent 8453 spectrophotometer equipped with a temperature-controlled cell holder at 293 K. Fluorescence emission spectra have been collected using an Eclipse Varian spectrofluorimeter. Mass spectra were performed in electron impact (70 eV) and electrospray ionization (ESI) modes (for HR-ESI MS). Melting points were determined in glass capillaries and are uncorrected. Flash column chromatography was performed on Al_2O_3 and SiO_2. Starting compounds **4a**,[1] **4b**[2] and **6**[2] were synthesized as it was described earlier.

Crystal Structure Determination: X-ray measurements were conducted with Bruker APEX II CCD diffractometer and four-circle diffractometer SyperNova, Single source at offset/far, HyPlx3000. Atomic coordinates, bond lengths, bond angles and thermal paramrters have been deposited at the Cambridge Crystallographic Data Centre (CCDC): CCDC 2243960 (**3a**), CCDC 2243962 (**3b**), CCDC 2243964 (**3c**), CCDC 2243966 (**3d**), CCDC 2243961 (**3a·HBF$_4$**), CCDC 2243963 (**3b·HBF$_4$**), CCDC 2243965 (**3c·HBF$_4$**), CCDC 2243967 (**9**). These data can be obtained free of charge from Cambridge Crystallographic Data Centre.

Synthesis of 4-aryl-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamines 5 (general procedure).

Method A (see Table 1). A mixture of 4-iodo-1,8-bis(dimethylamino)naphthalene **4a** (170 mg, 0.5 mmol), 5% Pd/C (85 mg, 0.04 mmol), PPh_3 (26 mg, 0.1 mmol), arylboronic acid (0.65 mmol), and 2M solution of K_2CO_3 (3 mL) in toluene (3 mL) was stirred at 95 °C for 24 h under argon. The reaction mixture was then diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The extract was dried over Na_2SO_4 and evaporated to dryness on a rotary evaporator. The residue was purified by flash column chromatography on silica (2 × 20 cm) using methylene chloride as the eluent. The first fractions with R_f 0.7–0.9 were separated and thrown out. Then ethyl acetate was used as the eluent. Fraction with R_f 0.4 gave compound **5a–e**.

Method B (see Table 1). A mixture of 4-halogeno-1,8-bis(dimethylamino)naphthalene **4a** or **4b** (0.5 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), arylboronic acid (0.65 mmol) and 2M solution of K_2CO_3 (3 mL) in toluene (3 mL) was stirred at 95 °C for 48 h under argon. Isolation of the reaction product was carried out similarly to that described above in *Method A*.

N^1,N^1,N^8,N^8-Tetramethyl-4-phenylnaphthalene-1,8-diamine (**5a**) was obtained using phenylboronic acid (79 mg, 0.65 mmol). Yield 94 mg (65%). Beige solid with mp 56–57 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (pseudosinglet, 12H), 6.95–7.04 (m, 2H), 7.27–7.29 (m, 2H), 7.36–7.54 (m, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 44.2, 44.3, 111.9, 112.3, 119.5, 120.2, 125.3, 126.5, 126.8, 128.0, 130.4, 133.2, 135.8, 142.1, 150.2, 150.8 ppm. HRMS (ESI): *m/z* calcd. for $C_{20}H_{23}N_2^+$ [M + H$^+$]: 291.1856, found 291.1848.

N^1,N^1,N^8,N^8-Tetramethyl-4-p-tolylnaphthalene-1,8-diamine (**5b**) was obtained using *p*-tolylboronic acid (88 mg, 0.65 mmol). Yield 97 mg (64%). Beige solid with mp 113–114 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 2.82 (pseudosinglet, 12H), 6.87–6.97 (m, 2H), 7.17–7.27 (m, 4H),

7.30–7.36 (m, 2H), 7.39 (dd, J = 8.3, 1.0 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.2, 44.3, 112.0, 112.3, 119.6, 120.3, 125.3, 126.8, 128.8, 130.3, 133.2, 135.8, 136.2, 139.1, 150.1, 150.8 ppm. HRMS (ESI): m/z calcd. for $C_{21}H_{25}N_2^+$ [M + H$^+$]: 305.2012, found 305.2010.

N^1,N^1,N^8,N^8-Tetramethyl-4-m-tolylnaphthalene-1,8-diamine (**5c**) was obtained using *m*-tolylboronic acid (88 mg, 0.65 mmol). Yield 100 mg (66%). Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 2.84 (pseudosinglet, 12H), 6.91−6.98 (m, 2H), 7.13−7.29 (m, 5H), 7.32 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.5, 44.2, 44.3, 111.9, 112.3, 119.6, 120.3, 125.3, 126.7, 127.3, 127.5, 127.9, 131.2, 133.4, 135.8, 137.6, 142.0, 150.2, 150.8 ppm. HRMS (ESI): m/z calcd. for $C_{21}H_{25}N_2^+$ [M + H$^+$]: 305.2012, found 305.2015.

N^1,N^1,N^8,N^8-Tetramethyl-4-o-tolylnaphthalene-1,8-diamine (**5d**) was obtained using *o*-tolylboronic acid (88 mg, 0.65 mmol). Yield 82 mg (54%). Yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 2.85 (pseudosinglet, 12H), 6.87−7.03 (m, 3H), 7.10−7.33 (m, 6H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.2, 44.4, 112.0, 112.4, 119.7, 120.2, 125.3, 125.5, 126.4, 127.1, 129.7, 130.8, 136.1, 137.4 (2C), 141.5, 150.1, 150.8 ppm. HRMS (ESI): m/z calcd. for $C_{21}H_{25}N_2^+$ [M + H$^+$]: 305.2012, found 305.2016.

4-(4-Methoxyphenyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (**5e**) was obtained using (4-methoxyphenyl)boronic acid (99 mg, 0.65 mmol). Yield 80 mg (50%). Beige solid with mp 79−80 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.84 (pseudosinglet, 12H), 3.88 (s, 3H), 6.90–7.02 (m, 4H), 7.18–7.27 (m, 2H), 7.33–7.43 (m, 3H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.3, 44.4, 55.3, 112.0, 112.3, 113.5, 119.6, 120.3, 125.3, 126.8, 131.4, 132.9, 134.5, 136.0, 150.0, 150.8, 158.5 ppm. HRMS (ESI): m/z calcd. for $C_{21}H_{25}N_2O^+$ [M + H$^+$]: 321.1961, found 321.1962.

4-(4-(Dimethylamino)phenyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (**5f**) was obtained from **4a** and (4-(dimethylamino)phenyl)boronic acid (107 mg, 0.65 mmol). Yield 98 mg (59%). Beige solid with mp 157−158 °C (hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.82 (br s, 12H), 3.01 (s, 6H), 6.82 (dm, J = 8.8 Hz, 2H), 6.92 (d, J = 6.9 Hz, 1H), 6.95 (d, J = 7.7 Hz, 1H), 7.19−7.25 (m, 2H), 7.33 (dm, J = 8.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 40.7, 44.3, 44.4, 112.1, 112.2, 112.3 (2C), 119.9, 120.4, 125.0, 126.6, 130.3, 131.1 (2C), 133.6, 136.1, 149.4, 149.7, 150.7 ppm. HRMS (ESI): m/z calcd. for $C_{22}H_{28}N_3^+$ [M + H$^+$]: 334.2278, found 334.2293.

4-(2-(Dimethylamino)phenyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (**5g**) was obtained from **4a** and N,N-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (161 mg, 0.65 mmol). Yield 73 mg (44%). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.47 (s, 6H), 2.87 (br s, 12H), 6.95 (d, J = 7.2 Hz, 1H), 6.98−7.02 (m, 2H), 7.08 (dd, J = 8.2, 1.0 Hz, 1H), 7.19−7.23 (m, 2H), 7.26 (dd, J = 8.3, 1.2 Hz, 1H), 7.28−7.34 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 43.0, 43.9, 44.8, 112.2, 117.2, 120.1, 120.3, 120.5, 124.8, 126.9, 127.7, 132.6, 133.3, 133.5, 135.7, 149.8, 150.6, 152.1 ppm. HRMS (ESI): m/z calcd. for $C_{22}H_{28}N_3^+$ [M + H$^+$]: 334.2278, found 334.2284.

N^4,N^4,N^5,N^5-Tetramethyl-[1,1'-binaphthalene]-4,5-diamine (**5h**) was obtained from **4a** and naphthalen-1-ylboronic acid (112 mg, 0.65 mmol). Yield 104 mg (61%). Beige solid with mp 134−135 °C (hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.85 (br s, 6H), 2.88 (s, 6H), 6.88 (dd, J = 8.3, 1.2 Hz, 1H), 6.90 (dd, J = 7.5, 1.1 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 7.07 (dd, J = 8.2, 7.5 Hz, 1H), 7.25−7.29 (m, 2H), 7.41−7.47 (m, 3H), 7.54 (dd, J = 8.2, 7.0 Hz, 1H), 7.87−7.91 (m, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 44.4, 111.9, 112.4, 120.2, 125.2, 125.4, 125.6, 125.7, 127.0, 127.3, 127.6, 128.0, 128.1, 131.1, 133.4,

133.5, 137.0, 139.9, 150.5, 150.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{25}N_2^+$ [M + H$^+$]: 341.2012, found 341.2003.

N^4,*N*^{4},*N*^{5},*N*^{5}*-Tetramethyl-[1,2'-binaphthalene]-4,5-diamine* (**5i**) was obtained from **4b** and 2-naphthalen-2-ylboronic acid (112 mg, 0.65 mmol). Yield 107 mg (63%). Beige solid with mp 116−117 °C (hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.85 (s, 6H), 2.86 (s, 6H), 6.95 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.48–7.52 (m, 2H), 7.61 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.84–7.88 (m, 1H) 7.88–7.92 (m, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 44.2, 44.3, 111.9, 112.3, 119.5, 120.3, 125.4, 125.6, 126.0, 127.1, 127.3, 127.6, 128.0, 128.7, 129.2, 132.3, 133.0, 133.5, 135.9, 139.6, 150.4, 150.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{25}N_2^+$ [M + H$^+$]: 341.2012, found 341.2022.

N^1,*N*^{1},*N*^{8},*N*^{8}*-Tetramethyl-4-(quinolin-3-yl)naphthalene-1,8-diamine* (**5j**) was obtained from **4b** and quinolin-3-ylboronic acid (112 mg, 0.65 mmol). Yield 101 mg (59%). Light yellow solid with mp 138−139 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.84 (s, 6H), 2.86 (s, 6H), 6.93–7.03 (m, 2H), 7.20–7.38 (m, 3H), 7.55 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.0, 1.5 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.12–8.22 (m, 2H), 9.03 (d, *J* = 2.2 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.1, 44.2, 111.8, 112.6, 118.6, 120.0, 126.0, 126.8, 127.8, 127.9, 128.1, 128.8, 129.2, 129.3, 135.1, 135.8, 136.2, 147.0, 151.0, 151.1, 152.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{24}N_3^+$ [M + H$^+$]: 342.1965, found 342.1959.

N^1,*N*^{1},*N*^{8},*N*^{8}*-Tetramethyl-4-(pyren-1-yl)naphthalene-1,8-diamine* (**5k**) was obtained from **4b** and pyren-1-ylboronic acid (160 mg, 0.65 mmol). Yield 71 mg (34%). Dark beige solid with mp 189−190 °C (decomp., hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.90 (br s, 6H), 2.94 (s, 6H), 6.90–6.97 (m, 2H), 7.04–7.13 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.95–8.04 (m, 2H), 8.07–8.17 (m, 3H), 8.19 (d, *J* = 7.6 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.5, 112.0, 112.5, 120.2, 120.4, 124.5, 124.8(4), 124.8(7), 124.9(4), 125.0, 125.5, 125.9, 126.3, 127.1, 127.2, 127.5, 128.3, 129.0, 130.3, 130.5, 131.2, 131.5, 137.2, 137.5, 150.6, 150.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{30}H_{27}N_2^+$ [M + H$^+$]: 415.2169, found 415.2170.

4-(Anthracen-9-yl)-N^1,*N*^{1},*N*^{8},*N*^{8}*-tetramethylnaphthalene-1,8-diamine* (**5l**) was obtained from **4b** and anthracen-9-ylboronic acid (144 mg, 0.65 mmol). Yield 86 mg (44 %). Light yellow solid with mp 180−181 °C (decomp., hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.93 (s, 6H), 2.97 (s, 6H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.88–7.05 (m, 2H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.20–7.35 (m, 3H), 7.40–7.55 (m, 4H), 8.08 (d, *J* = 8.5 Hz, 2H), 8.55 (s, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.5, 112.1, 112.5, 120.2, 120.3, 125.1, 125.2, 125.5, 126.3, 127.4, 128.3, 128.8, 131.4, 131.5, 136.7, 137.6 (2C), 150.7, 150.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{27}N_2^+$ [M + H$^+$]: 391.2169, found 391.2163.

Synthesis of 4,5-diaryl**-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamines 3a–d and 4-bromo-5-(4-(dimethylamino)phenyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (7) (general procedure).** A mixture of 4,5-dibromo-1,8-bis(dimethylamino)naphthalene **6** (186 mg, 0.5 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), arylboronic acid (1.2 mmol) and 2M solution of K_2CO_3 (3 mL) in toluene (3 mL) was stirred at 95 °C for 24 h or 48 h (see Table 2) under argon. The reaction mixture was then diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The extract was dried over Na_2SO_4 and evaporated to dryness

on a rotary evaporator. The residue was purified by flash column chromatography on silica (2 × 30 cm) using methylene chloride as the eluent. The first fractions with R_f 0.7–0.9 were separated and thrown out. Then ethyl acetate was used as the eluent. Fraction with R_f 0.4–0.5 gave compound **3a**–**d** or **7**.

N^1,N^1,N^8,N^8-Tetramethyl-4,5-diphenylnaphthalene-1,8-diamine (**3a**) was obtained using phenylboronic acid (146 mg, 1.2 mmol). Yield 101 mg (55%). Light yellow solid with mp 161–162 °C (hexane). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.88 (s, 12H), 6.81–6.84 (m, 2H), 6.87–6.90 (m, 4H), 6.92 (dm, J = 7.7 Hz, 2H), 6.93–6.97 (m, 4H), 7.18 (dm, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 44.0, 110.8, 121.7, 125.0, 127.1, 130.0, 130.2, 132.9, 133.7, 143.9, 150.0. HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{27}N_2^+$ [M + H^+]: 367.2169, found 367.2171.

N^1,N^1,N^8,N^8-Tetramethyl-4,5-di-m-tolylnaphthalene-1,8-diamine (**3b**) was obtained using *m*-tolylboronic acid (163 mg, 1.2 mmol). Yield 95 mg (48%). Yellow solid with mp 155–156 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.10 (br. s, 6H), 2.90 (s, 12H), 6.60–6.67 (m, 3H), 6.70–7.05 (m, 7H), 7.24 (dm, J = 7.8 Hz, 2H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.2, 44.1, 110.8, 121.6, 125.7, 126.6, 126.9, 129.9, 131.4, 133.0, 133.7, 136.0, 143.7, 150.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{31}N_2^+$ [M + H^+]: 395.2482, found 395.2490.

$N^{4'}$,$N^{4'}$,$N^{5'}$,$N^{5'}$-Tetramethyl-[1,1',8',1''-ternaphthalene]-4',5'-diamine (**3c**) was obtained using naphthalen-1-ylboronic acid (206 mg, 1.2 mmol). Yield 119 mg (51%). Light yellow solid with mp 218−220 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.95 (s, 12H), 6.28 (dd, J = 8.1, 7.0 Hz, 2H), 6.42 (dd, J = 7.0, 1.3 Hz, 2H), 6.93–7.02 (m, 4H), 7.05 (dm, J = 7.7 Hz, 2H), 7.18–7.32 (m, 4H), 7.40 (dd, J = 8.2, 0.8 Hz, 2H), 7.51 (dd, J = 8.2, 1.0 Hz, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 44.2, 110.8, 120.6, 123.5, 124.6, 125.0, 125.7, 126.7, 127.6 (2C), 130.3, 130.6, 132.6, 132.7, 136.7, 140.5, 150.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{31}N_2^+$ [M + H^+]: 467.2482, found 467.2482.

$N^{4'}$,$N^{4'}$,$N^{5'}$,$N^{5'}$-Tetramethyl-[2,1',8',2''-ternaphthalene]-4',5'-diamine (**3d**) was obtained using naphthalen-2-ylboronic acid (206 mg, 1.2 mmol). Yield 123 mg (53%). Yellow solid with mp 198−199 °C (hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.92 (s, 12H), 6.92–7.15 (m, 9H), 7.17–7.45 (m, 9H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 44.1, 110.9, 121.6, 124.6, 125.1, 126.1, 126.8, 127.3 (2C), 128.7, 130.1, 131.1, 132.5, 132.8, 134.4, 141.2, 150.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{31}N_2^+$ [M + H^+]: 467.2482, found 467.2482.

4-Bromo-5-(4-(dimethylamino)phenyl)-N^1,N^1,N^8,N^8-tetramethylnaphthalene-1,8-diamine (**7**) was obtained using (4-(dimethylamino)phenyl)boronic acid (198 mg, 1.2 mmol). Yield 101 mg (49%). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.79 (s, 6H), 2.82 (s, 6H), 2.98 (s, 6H), 6.62 (d, J = 6.4 Hz, 1H), 6.74 (dm, J = 8.7 Hz, 2H), 6.87 (d, J = 6.0 Hz, 1H), 7.14 (dm, J = 8.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (150.0 MHz, $CDCl_3$): δ = 40.7, 43.8, 43.9, 111.0, 111.4, 111.5, 111.9, 122.6, 130.3, 131.0, 132.1, 132.2, 133.1, 133.7, 149.4, 149.6, 149.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{22}H_{26}BrN_3^+$ [M + H^+]: 412.1383, found 412.1366.

Synthesis of 4-bromo-N^1,N^1,N^8,N^8-tetramethyl-5-(pyridin-3-yl)naphthalene-1,8-diamine (8) and of N^3,N^3,N^4,N^4-tetramethylacenaphtho[1,2-*b*]pyridine-3,4-diamine (9). A mixture of 4,5-dibromo-1,8-bis(dimethylamino)naphthalene **6** (186 mg, 0.5 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), pyridin-3-ylboronic acid (148 mg, 1.2 mmol), and 2M solution of K_2CO_3 (3 mL) in toluene (3 mL) was stirred at 95

°C for 48 h under argon. Then the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The extract was evaporated to dryness on a rotary evaporator. The residue was purified by flash column chromatography on silica (2 × 20 cm) using ethyl acetate as the eluent. The first yellow-orange fractions with R_f 0.7–0.8 gave compound **9**. The second yellow fractions with R_f 0.4–0.5 gave compound **8**. Crude product **9** was repurified by TLC on Al_2O_3, using CH_2Cl_2 as the eluent.

4-Bromo-N^1,N^1,N^8,N^8-tetramethyl-5-(pyridin-3-yl)naphthalene-1,8-diamine (**8**) was obtained as a yellow oil. Yield 26 mg (14%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.81 (s, 6H), 2.82 (s, 6H), 6.66 (d, J = 8.2 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.24–7.30 (m, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.58 (ddd, J = 7.8, 2.2, 1.7 Hz, 1H), 8.50–8.57 (m, 2H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 43.6(8), 43.7(3), 110.2, 111.0, 111.5, 122.0, 122.6, 128.3, 131.1, 132.9, 133.4, 137.1, 139.4, 147.2, 150.3, 150.7, 150.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{21}BrN_3^+$ [M + H$^+$]: 370.0913, found 370.0918.

N^3,N^3,N^4,N^4-tetramethylacenaphtho[1,2-b]pyridine-3,4-diamine (**9**) was obtained as a yellow solid with mp 105−106 °C (hexane). Yield 71 mg (49 %). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.94 (s, 6H), 2.96 (s, 6H), 7.02 (d, J = 7.7 Hz, 1H), 7.07–7.15 (m, 2H), 7.85 (d, J = 7.7 Hz, 1H), 8.01 (dd, J = 7.6, 1.5 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 8.44 (dd, J = 5.0, 1.5 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.3, 44.4, 113.4, 114.1, 117.6, 119.7, 122.2, 122.7, 125.3, 126.7, 127.2, 132.2 (2C), 136.1, 146.0, 152.5, 153.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{20}N_3^+$ [M + H$^+$]: 290.1652, found 290.1652.

Synthesis of 3,4-bis(dimethylamino)-7-methylacenaphtho[1,2-*b*]pyridin-7-ium iodide (12). A mixture of **9** (289 mg, 0.1 mmol), methyl iodide (28 mg, 0.012 mL, 0.2 mmol) in acetone (1 mL) was stirred at room temperature for 24 h. The red precipitate was filtered off, washed with diethyl ether, and dried on air.

3,4-Bis(dimethylamino)-7-methylacenaphtho[1,2-b]pyridin-7-ium iodide (**12**) was obtained as a red solid with mp >300 °C (decomp.). Yield 29 mg (68%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 2.99 (s, 6H), 3.12 (s, 6H), 4.62 (s, 3H), 7.20–7.30 (m, 2H), 7.67 (dd, J = 7.6, 6.3 Hz, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.57 (d, J = 6.2 Hz, 1H), 8.88 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 43.1, 43.3, 46.1, 111.1, 112.4, 112.8, 112.9, 117.0, 119.1, 127.4, 131.1, 132.3, 134.0, 136.8, 139.1, 144.7, 155.0, 157.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{22}N_3^+$ [M + H$^+$]: 304.1808, found 304.1800.

8-(Dimethylamino)-N,N-dimethyl-4,5-diarylnaphthalen-1-aminium tetrafluoroborates 3·HBF$_4$ (general procedure). To a solution of compound **3** (0.04 mmol) in EtOAc (3 mL) was added 40% aqueous HBF_4 (0.0075 mL, 1.1 equiv.). The reaction mixture was thoroughly stirred for several minutes. The resulting precipitate was filtered off, washed with Et_2O and dried in a vacuum, giving desired salts in high yields.

3a·HBF$_4$ was obtained as a colorless solid with mp 246−247 °C. Yield 15 mg (83%). ^{1}H NMR (250 MHz, CD_3CN): δ = 3.13 (s, 6H), 3.14 (s, 6H), 6.93 (br s, 10H), 7.54 (dm, J = 7.9 Hz, 2H), 7.94 (d, J = 7.9 Hz, 2H), 19.40 (s, 1H) ppm. ^{13}C NMR (62.9 MHz, CD_3CN): δ = 45.8, 121.0, 121.2, 126.5, 127.6, 129.7, 131.2, 131.6, 142.0, 142.1, 143.8 ppm.

3b·HBF$_4$ was obtained as a colorless solid with mp 269−271 °C. Yield 16 mg (86%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.99 (s, 3H), 2.15 (s, 3H), 3.21 (s, 12H), 6.25−7.10 (m, 8H), 7.60 (dm, J = 7.9 Hz,

2H), 8.20 (dm, J = 7.9 Hz, 2H), 19.24 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 21.2, 46.2, 121.2, 121.8, 126.3, 126.7, 127.3, 127.5, 127.8, 130.8, 130.9, 131.8, 136.4, 136.6, 141.6, 141.8, 144.6 ppm.

3c·HBF$_4$ was obtained as a colorless solid with mp >300 °C (decomp.). Yield 17 mg (79 %). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 3.29 (s, 12H), 6.23−6.33 (m, 2H), 6.38 (dd, J = 7.0, 1.1 Hz, 2H), 7.15 (dm, J = 8.0 Hz, 4H), 7.30−7.50 (m, 6H), 7.65 (dd, J = 7.7, 1.3 Hz, 2H), 8.23 (dm, J = 7.9 Hz, 2H), 19.38 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 46.2, 46.4, 120.9, 121.9, 123.5, 125.7, 125.9, 126.2, 127.0, 127.2, 128.3, 131.9, 132.1, 132.6, 133.8, 138.2, 139.6, 145.2 ppm.

3d·HBF$_4$ was obtained as a colorless solid with mp >300 °C (decomp.). Yield 20 mg (91%). ^{1}H NMR (250 MHz, DMSO-d_6): δ = 3.26 (s, 12H), 7.05−7.50 (m, 13H), 7.60−7.80 (m, 3H), 8.27 (dm, J = 7.9 Hz, 2H), 19.24 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 46.2, 121.3, 122.0, 126.0, 126.2, 127.1, 127.7, 127.9, 128.8, 129.2, 131.4, 132.1, 132.3, 139.2, 139.5, 141.5, 144.7 ppm.

4-(Dimethylamino)-N,N-dimethylacenaphtho[1,2-*b*]pyridin-3-aminium tetrafluoroborate 10. To a solution of compound **9** (26 mg, 0.09 mmol) in EtOAc (3 mL) was added 40% aqueous HBF_4 (0.015 mL, 0.09 mmol). The reaction mixture was thoroughly stirred for several minutes. The resulting precipitate was filtered off, washed with Et_2O and dried in a vacuum, giving yellow-orange salt 10 (32 mg, 93%). Mp >300 °C (decomp.). ^{1}H NMR (250 MHz, CD_3CN): δ = 3.20 (d, J = 2.5 Hz, 6H), 3.22 (d, J = 2.8 Hz, 6H), 7.44 (dd, J = 7.7, 5.1 Hz, 1H), 8.00−8.10 (m, 2H), 8.20 (d, J = 7.6 Hz, 1H), 8.30−8.40 (m, 2H), 8.57 (dd, J = 5.1, 1.4 Hz, 1H), 16.42 (br s, 1H) ppm. ^{13}C NMR (62.9 MHz, CD_3CN): δ = 46.2, 46.3, 116.9, 122.9, 123.2, 123.4, 123.5, 123.6, 130.4, 132.6, 133.4, 133.5, 134.8, 145.5, 147.1, 147.9, 157.3 ppm.

References

[1] O. V. Ryabtsova , A. F. Pozharskii , V. A. Ozeryanskii, N. V. Vistorobskii, *Russ. Chem. Bull.*, 2001, **50**, 854–859 (doi:10.1023/a:1011311226664)

[2] A. A. Yakubenko, V. V. Karpov, E. Yu. Tupikina, A. S. Antonov. *Organometallics,* 2021, **40**, 3627–3636.

Copies of NMR spectra

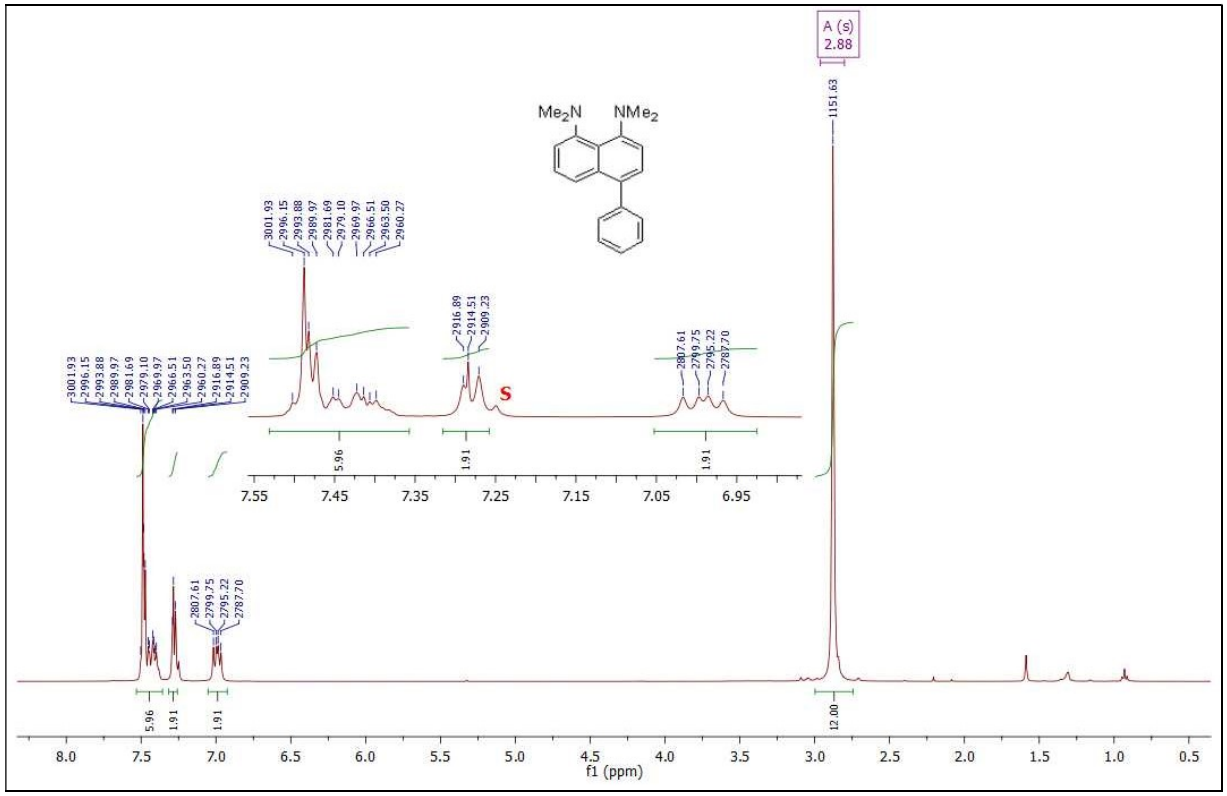

Fig. S1. ^{1}H NMR spectrum of compound **5a** (400 MHz, $CDCl_3$).

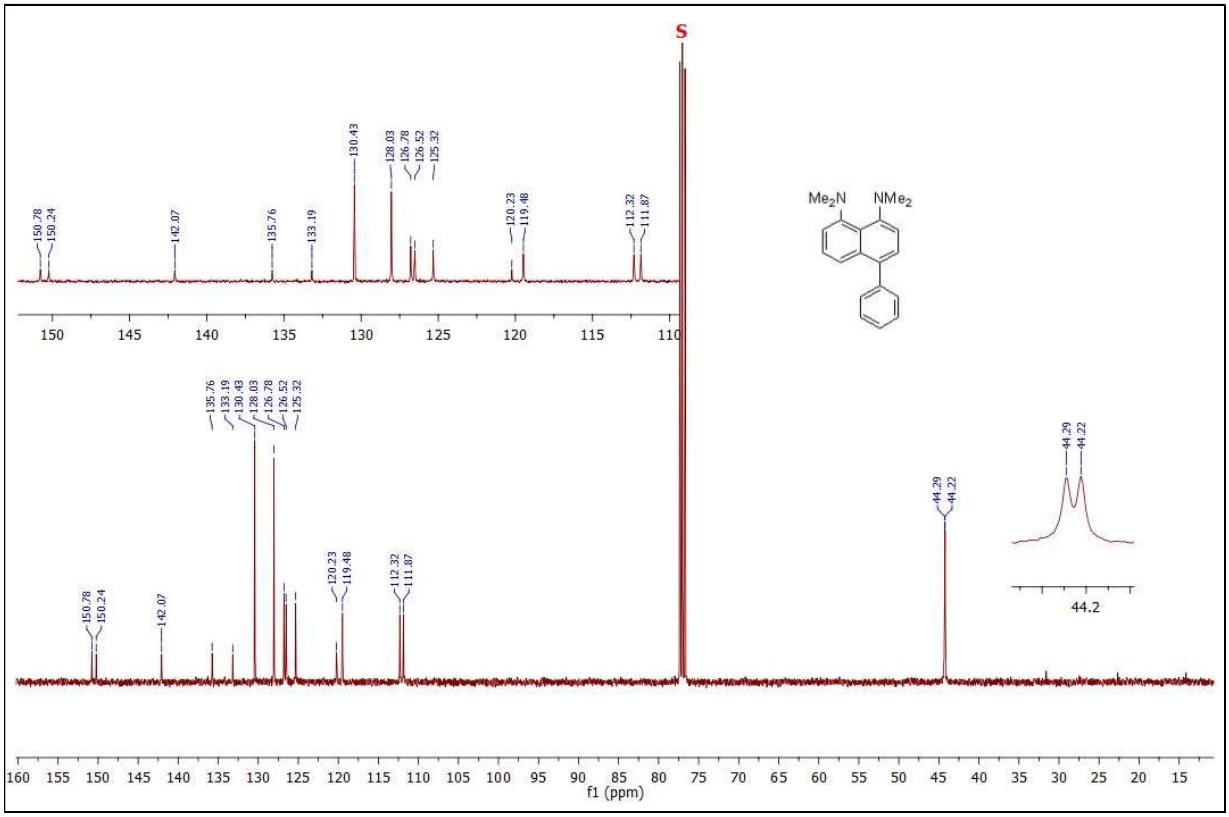

Fig. S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5a** (100.9 MHz, $CDCl_3$).

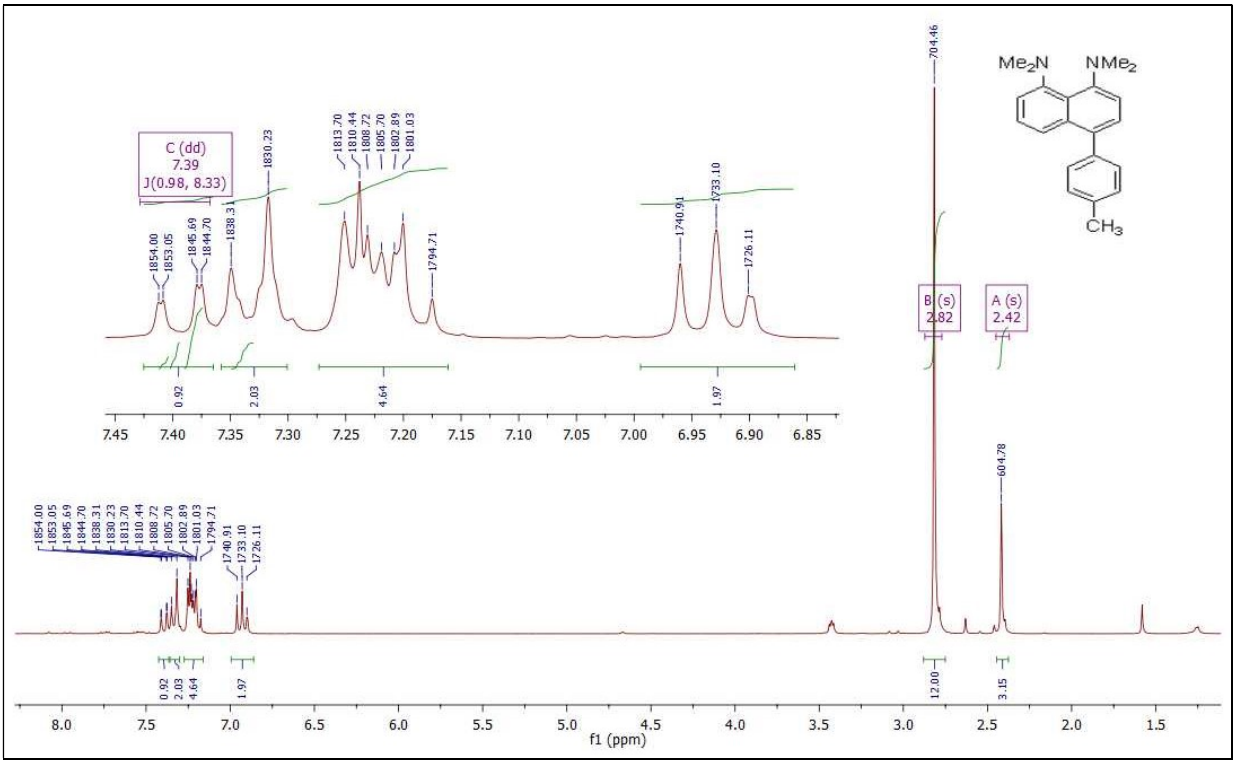

Fig. S3. ^{1}H NMR spectrum of compound **5b** (250 MHz, $CDCl_3$).

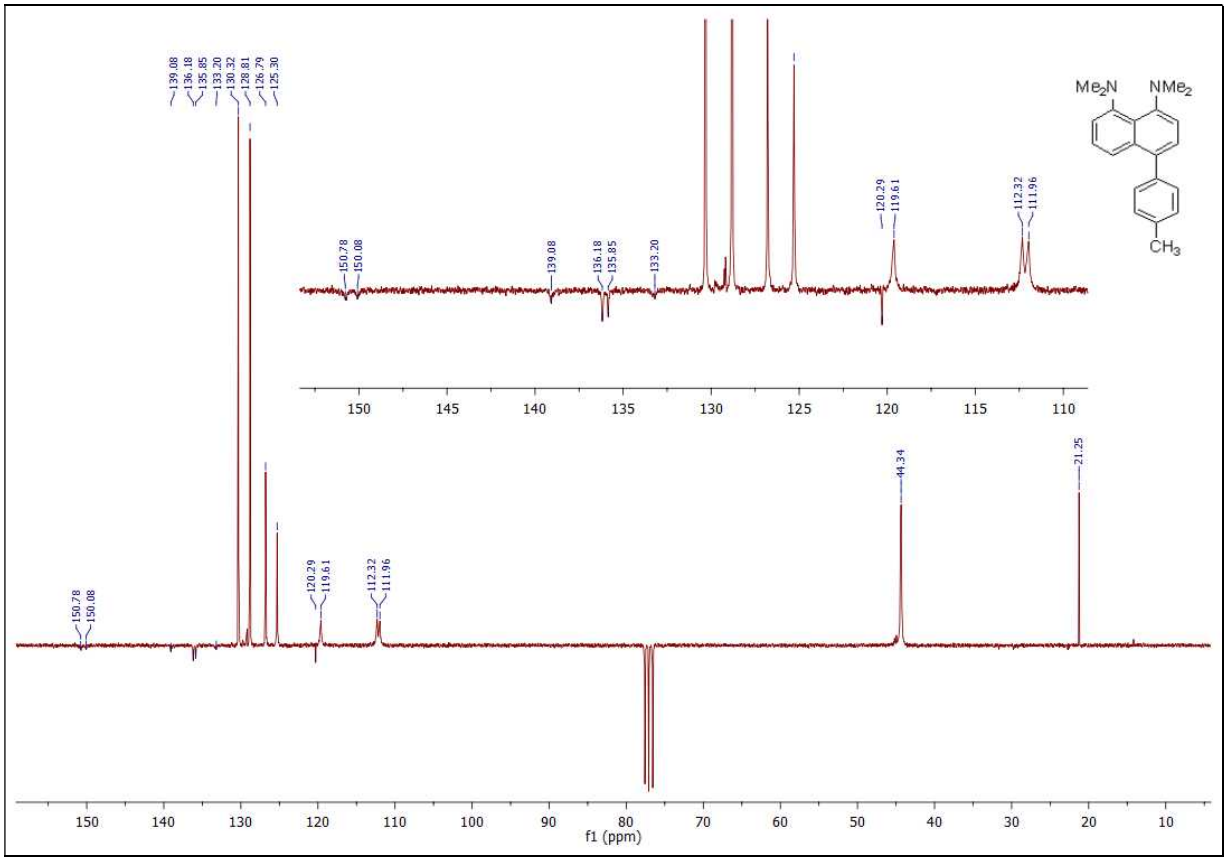

Fig. S4. $^{13}C\{^{1}H\}$ APT-NMR spectrum of **5b** (62.9 MHz, $CDCl_3$).

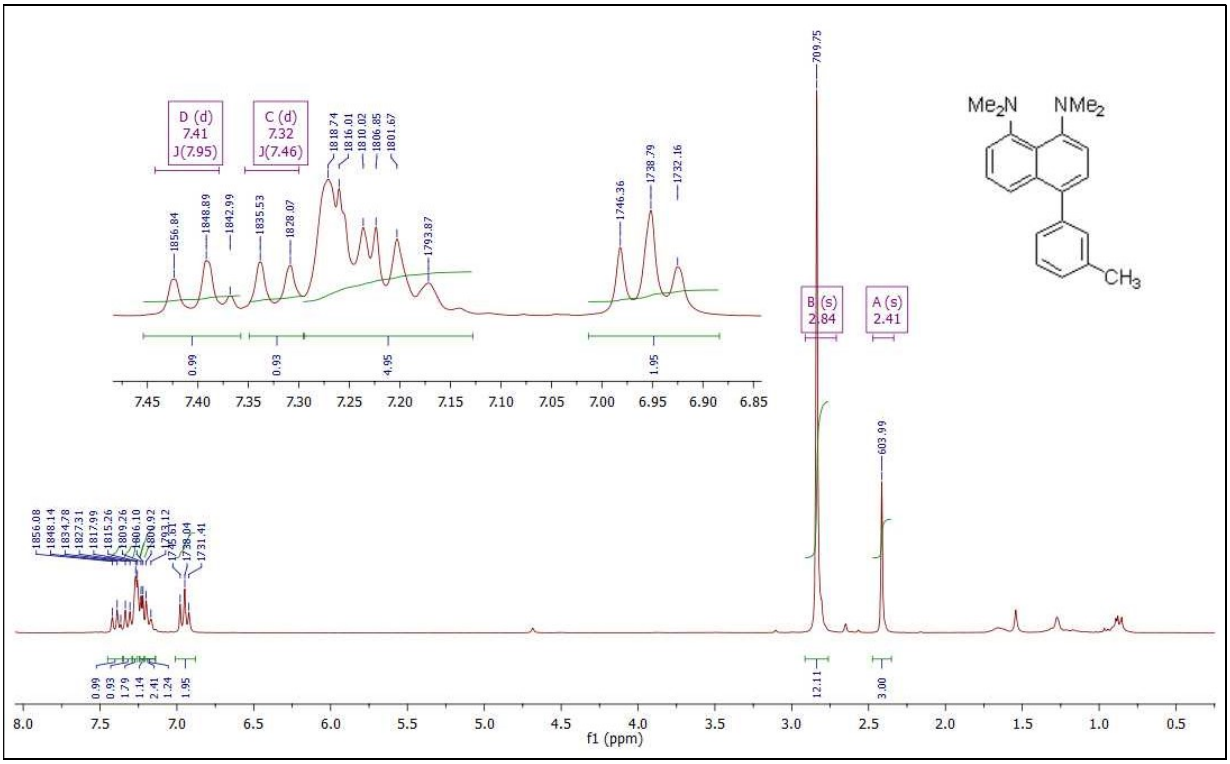

Fig. S5. ^{1}H NMR spectrum of compound **5c** (250 MHz, $CDCl_3$).

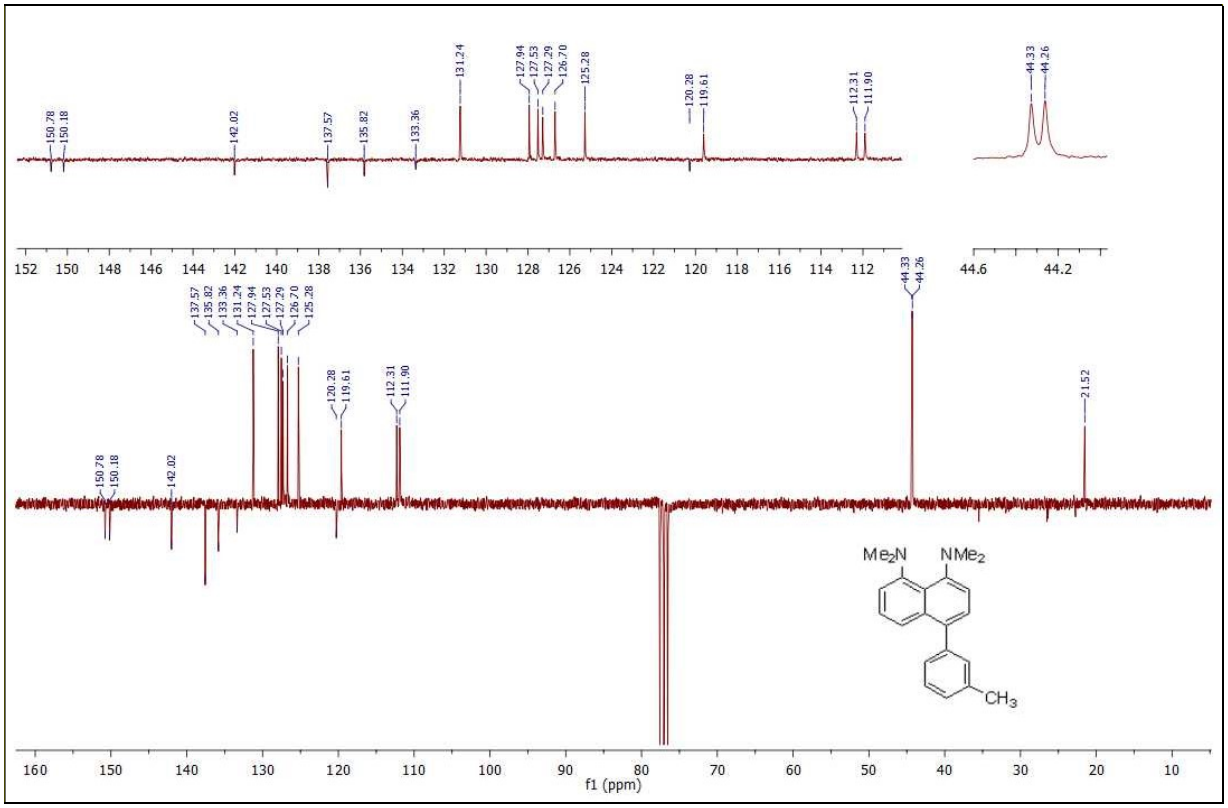

Fig. S6. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5c** (62.9 MHz, $CDCl_3$).

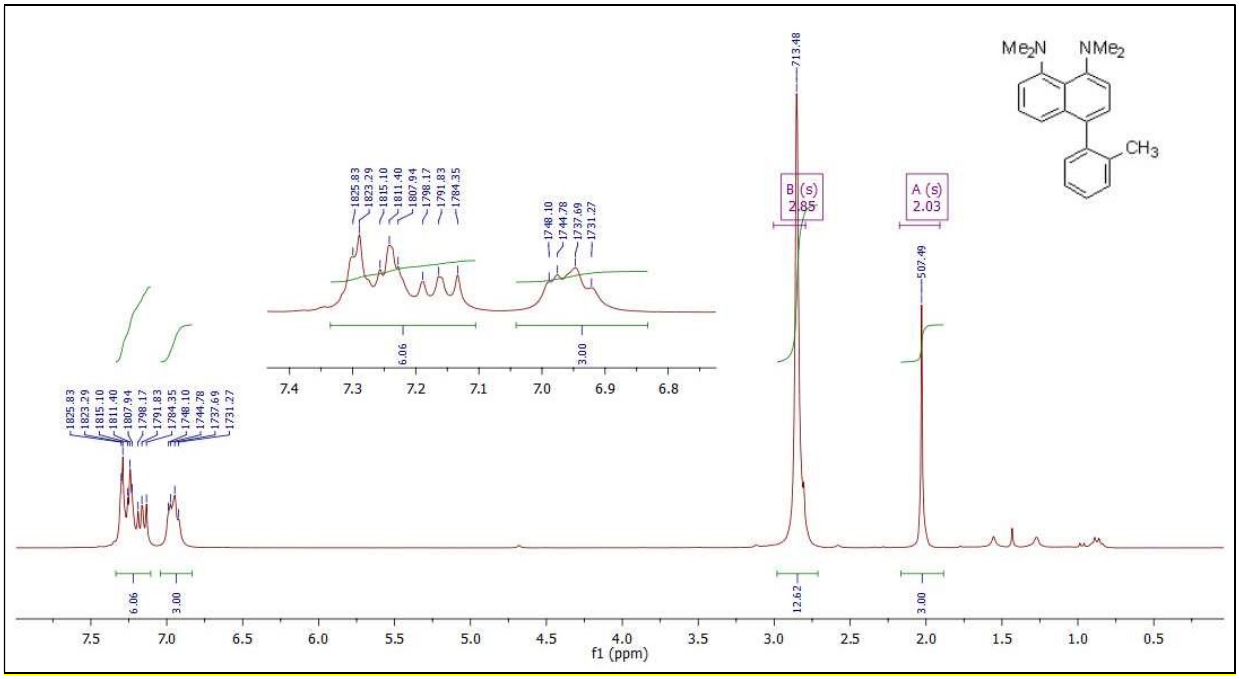

Fig. S7. ^{1}H NMR spectrum of compound **5d** (250 MHz, $CDCl_3$).

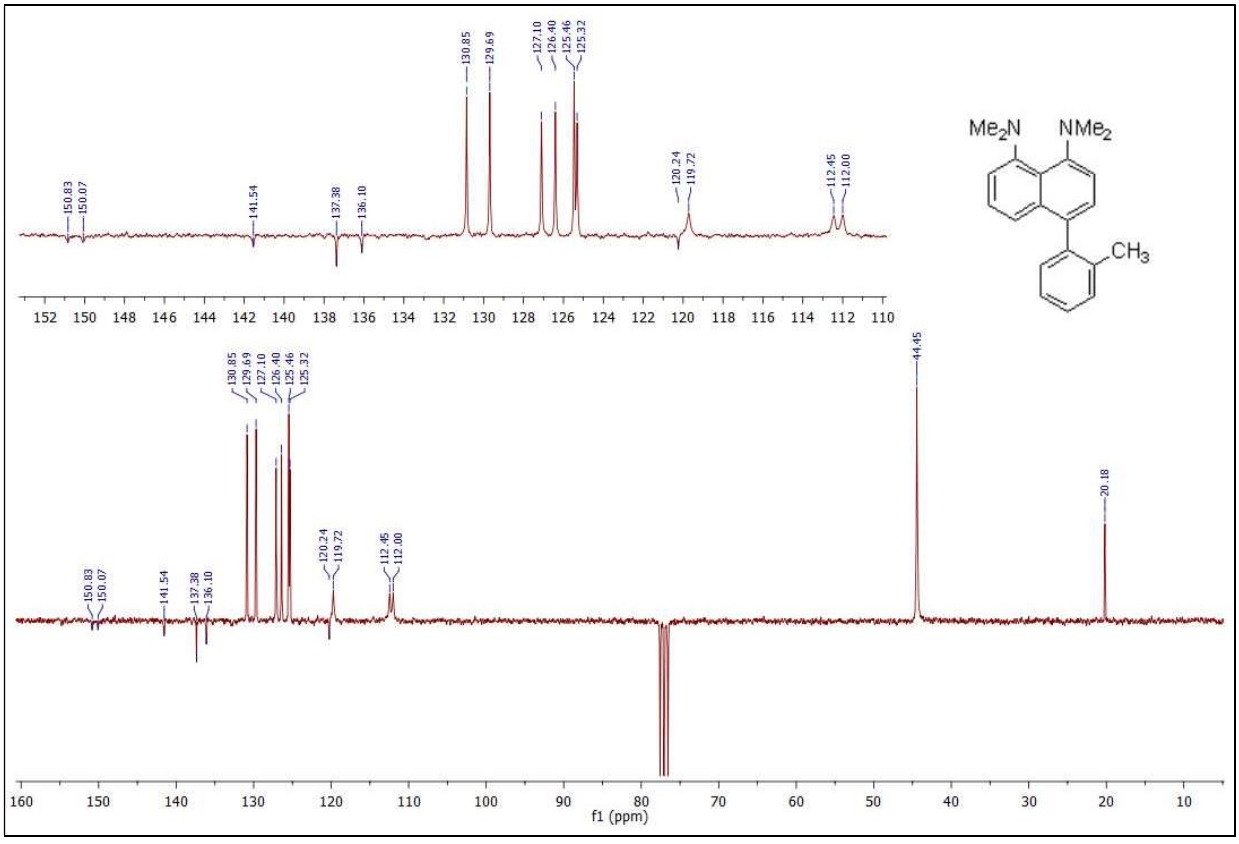

Fig. S8. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5d** (62.9 MHz, $CDCl_3$).

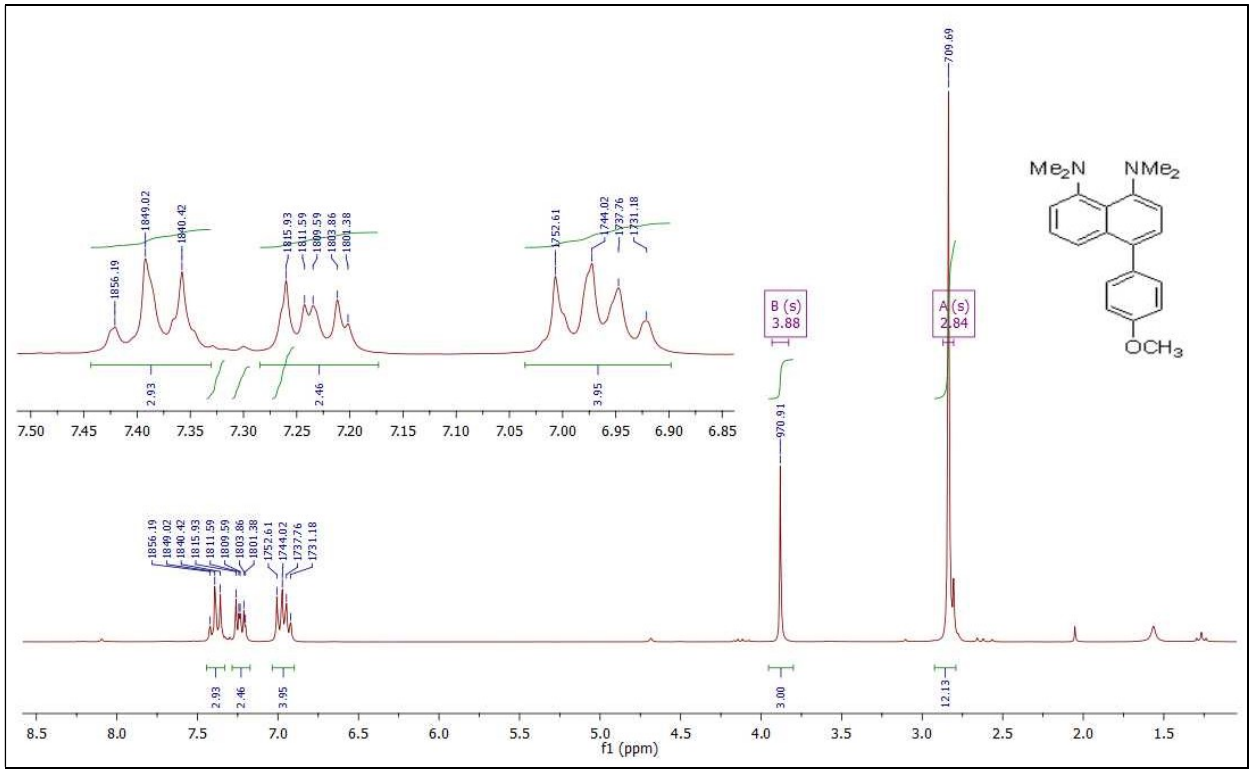

Fig. S9. ^{1}H NMR spectrum of compound **5e** (250 MHz, $CDCl_3$).

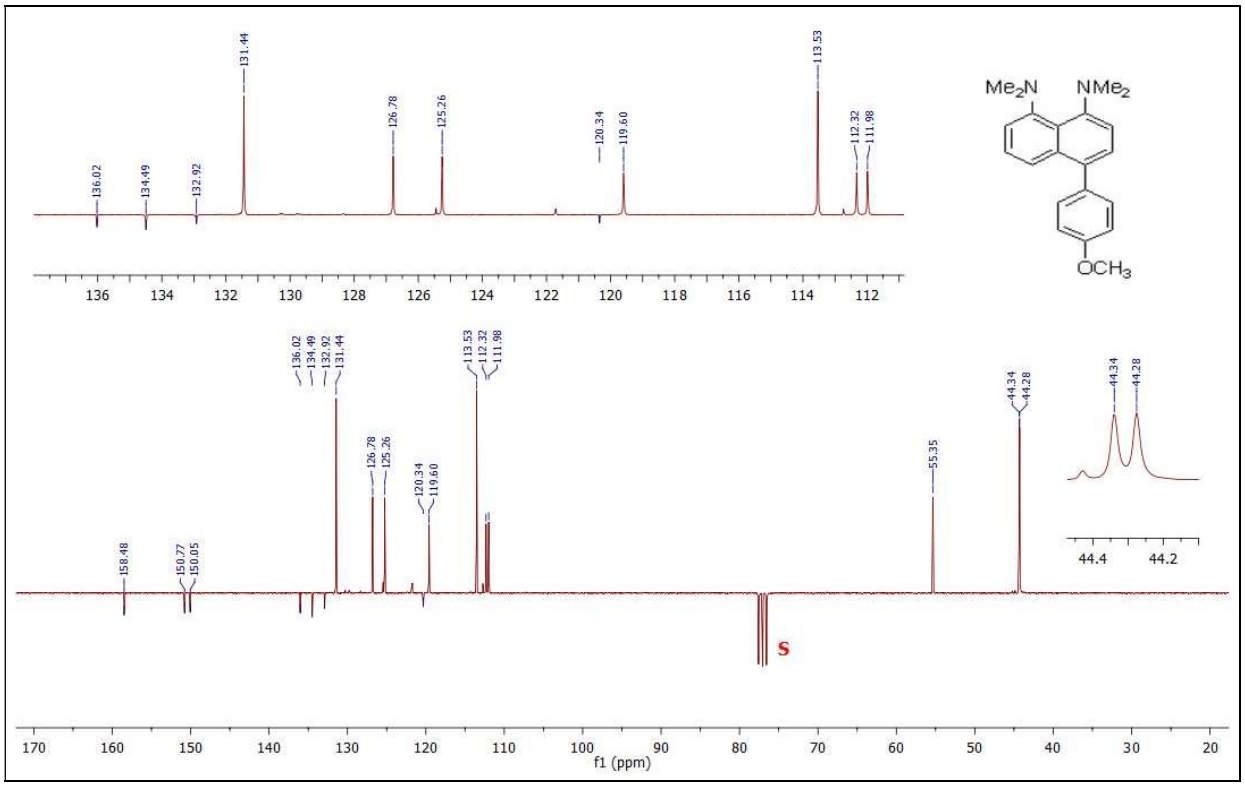

Fig. S10. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5e** (62.9 MHz, $CDCl_3$).

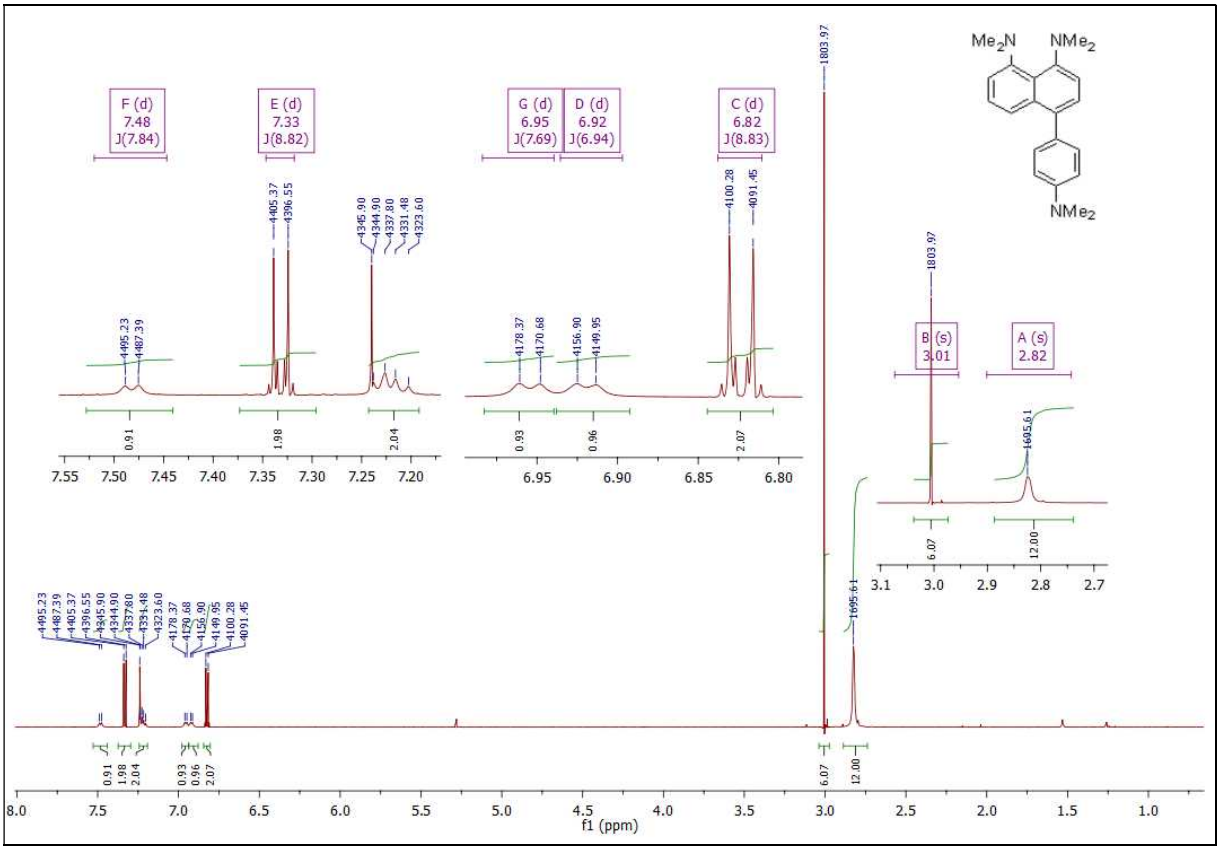

Fig. S11. ^{1}H NMR spectrum of compound **5f** (600 MHz, $CDCl_3$).

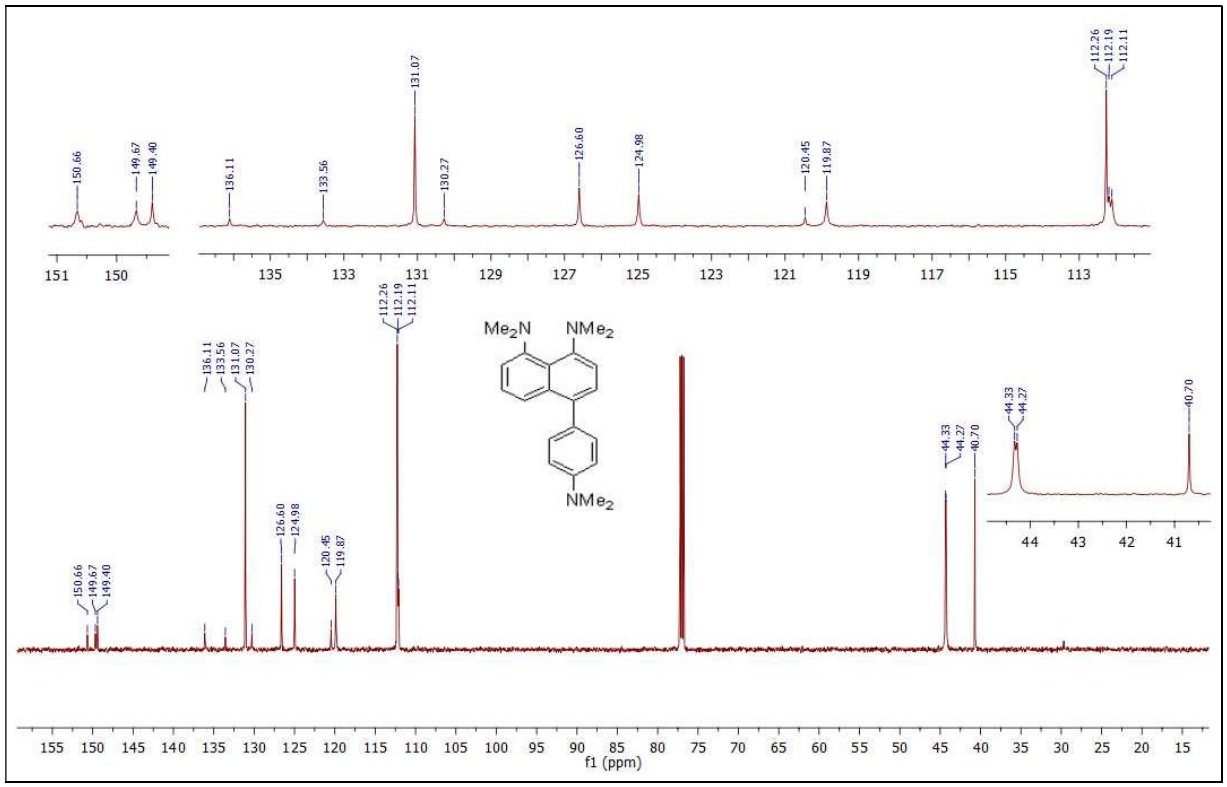

Fig. S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5f** (150 MHz, $CDCl_3$).

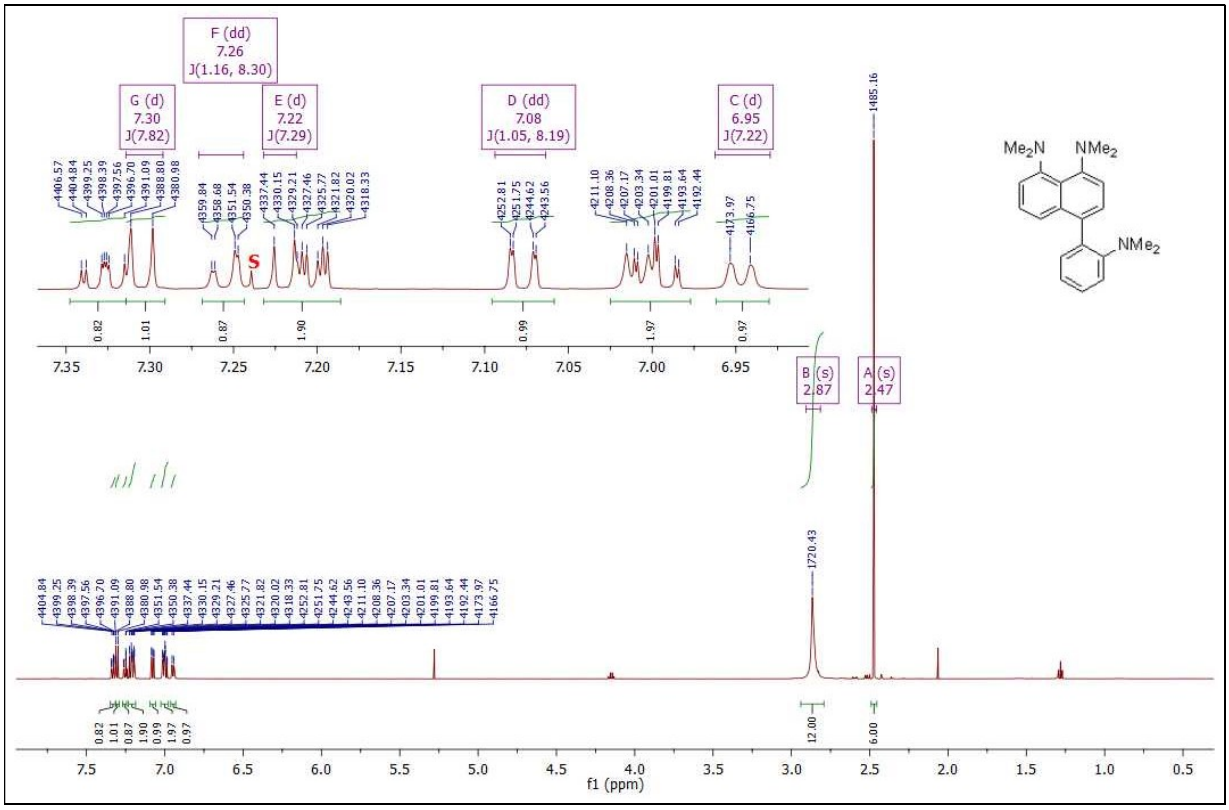

Fig. S13. ^{1}H NMR spectrum of compound **5g** (600 MHz, $CDCl_3$).

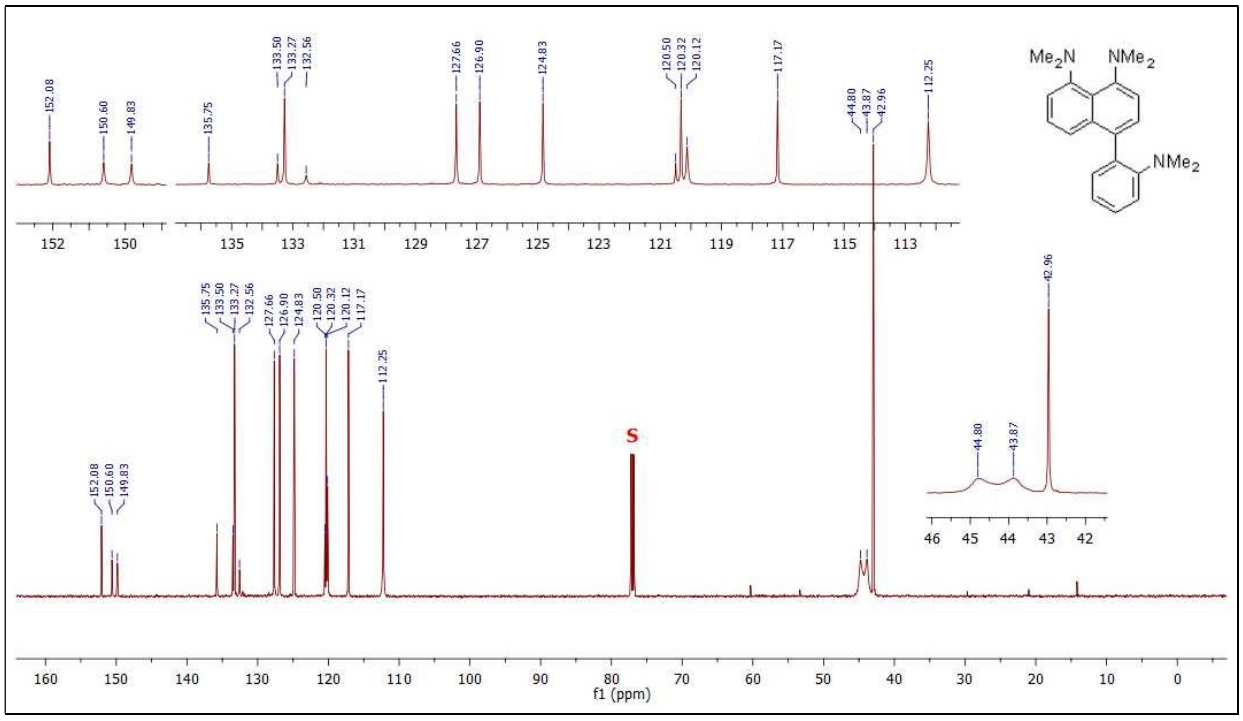

Fig. S14. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5g** (150 MHz, $CDCl_3$).

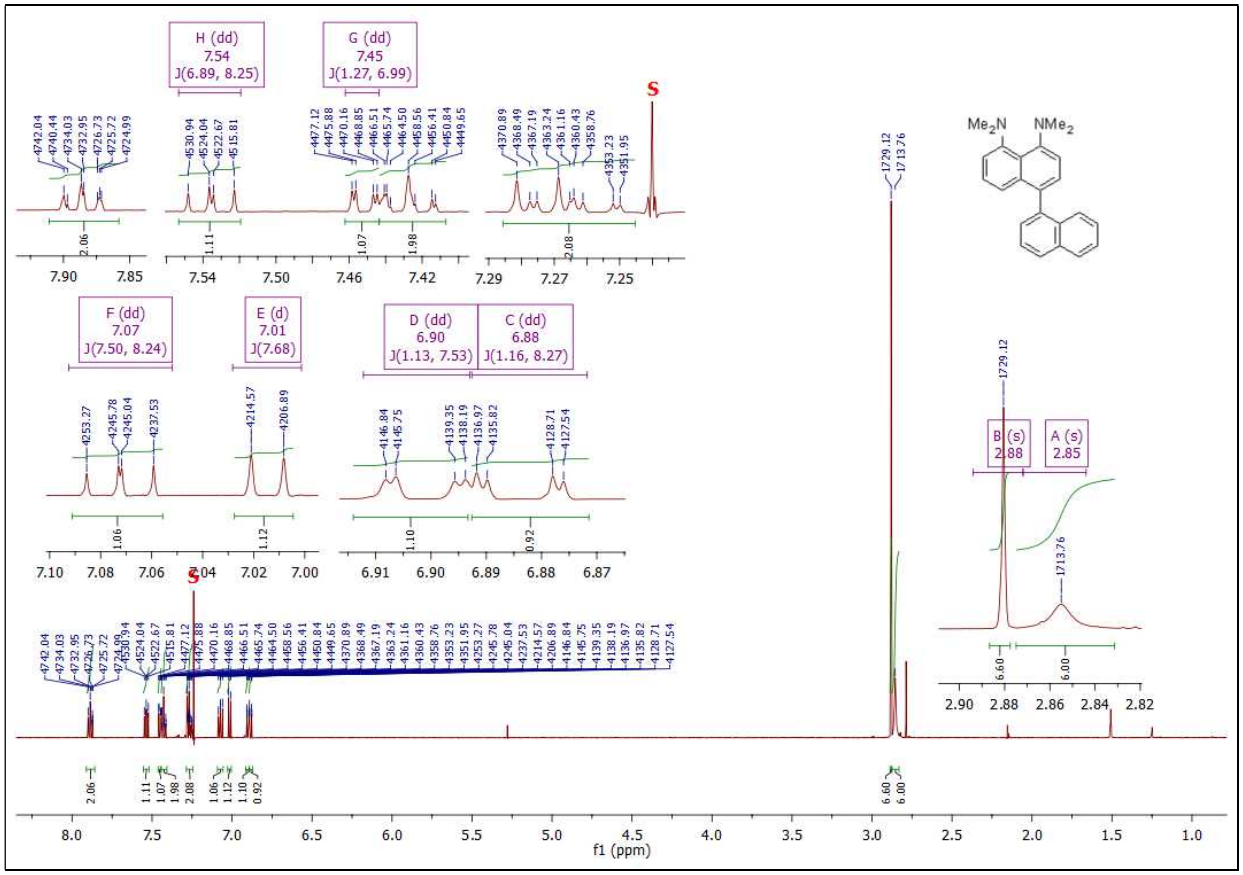

Fig. S15. ^{1}H NMR spectrum of compound **5h** (600 MHz, $CDCl_3$).

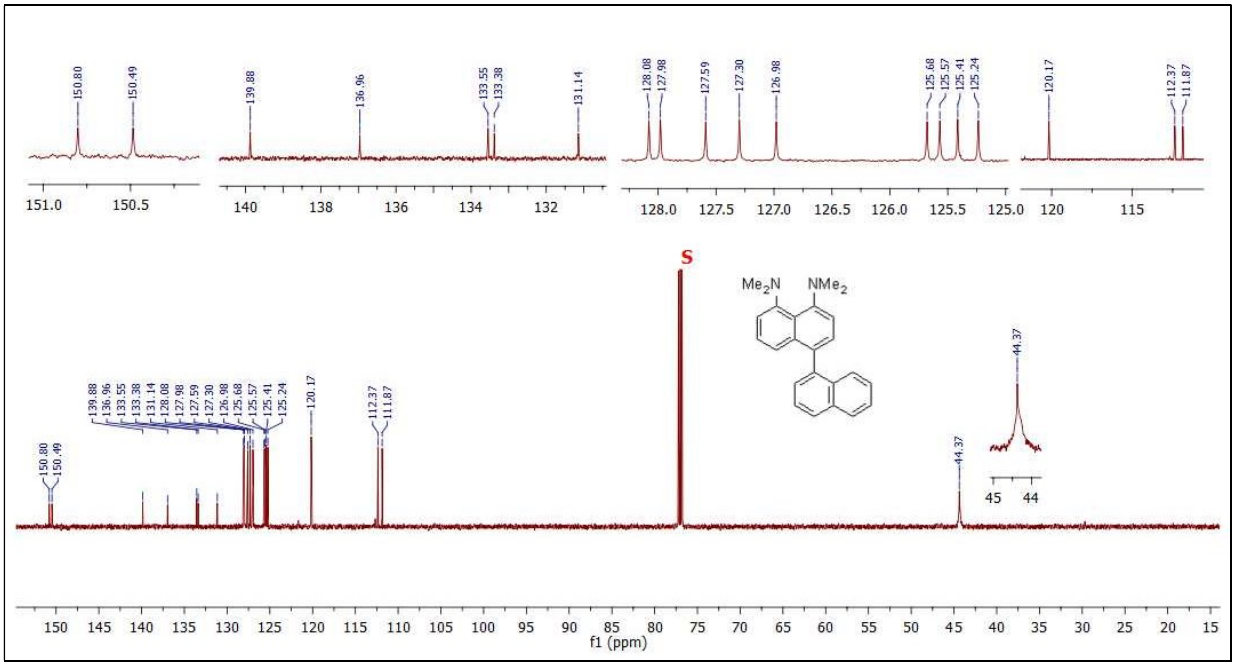

Fig. S16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5h** (150 MHz, $CDCl_3$).

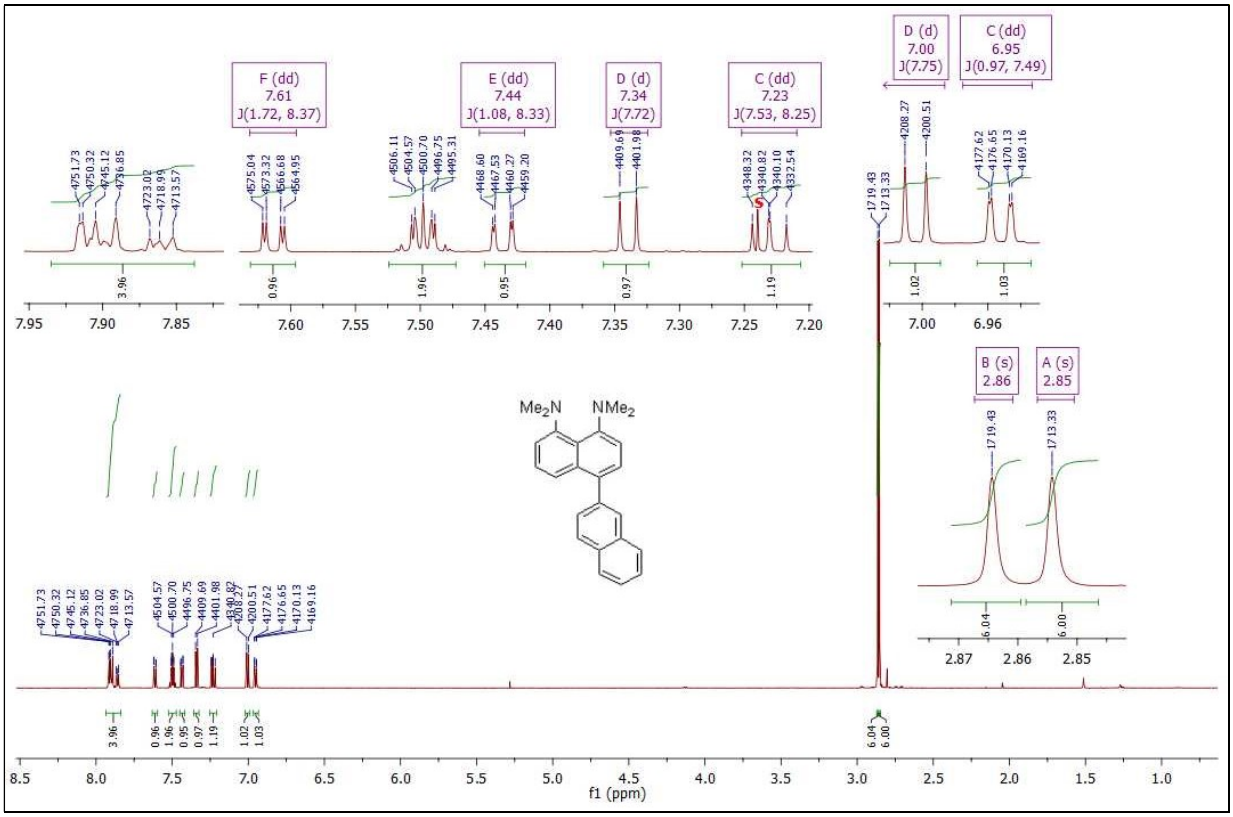

Fig. S17. ^{1}H NMR spectrum of compound **5i** (600 MHz, $CDCl_3$).

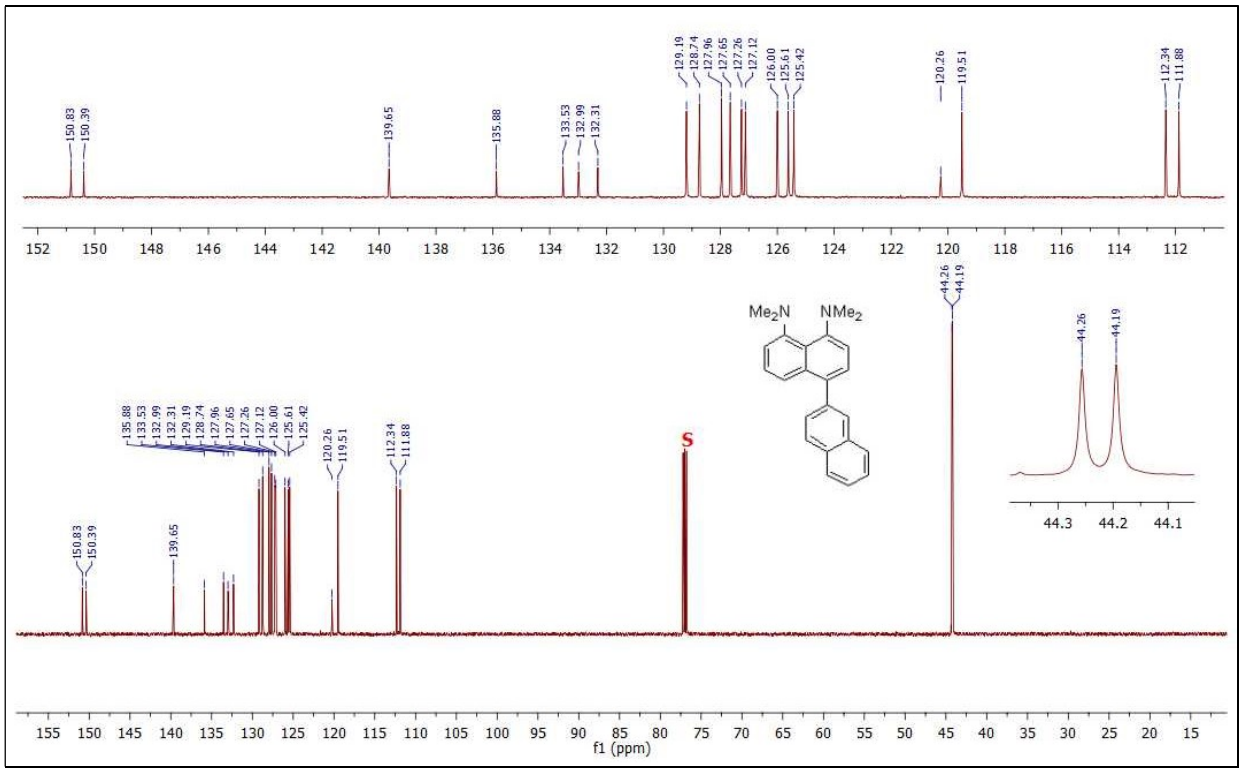

Fig. S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5i** (150 MHz, $CDCl_3$).

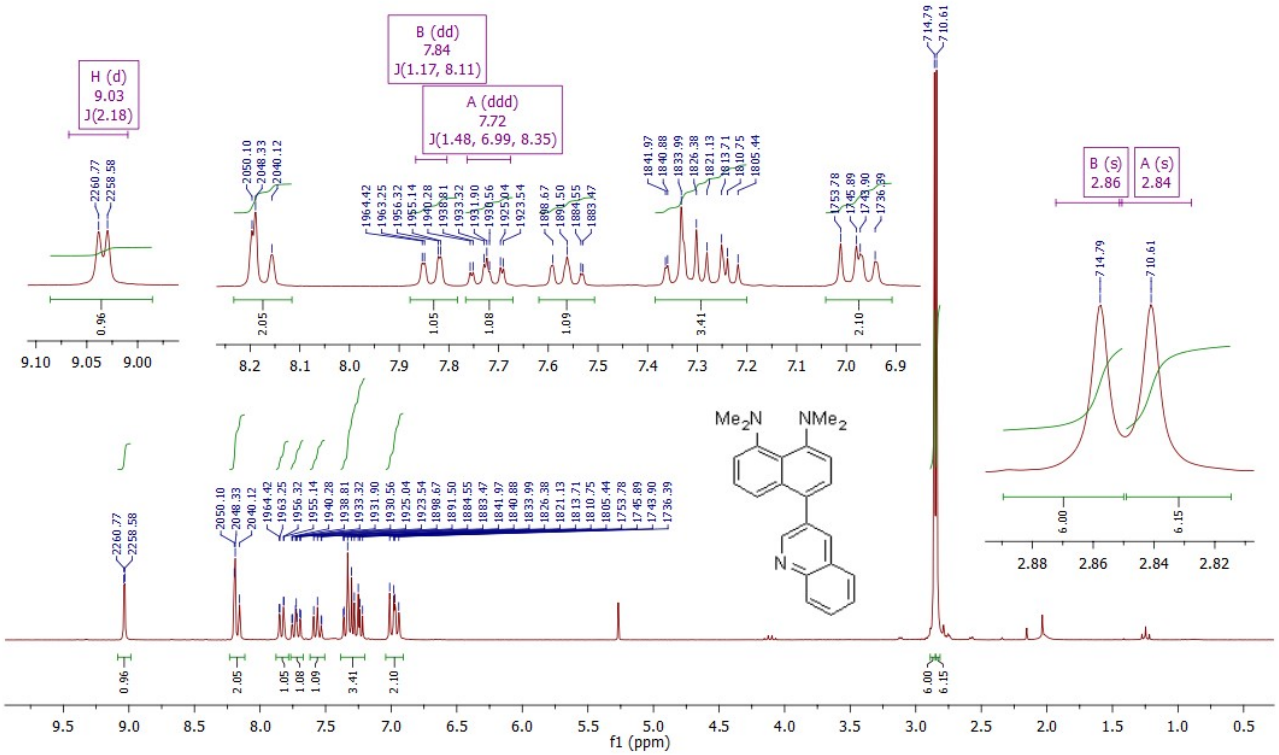

Fig. S19. ^{1}H NMR spectrum of compound **5j** (250 MHz, $CDCl_3$).

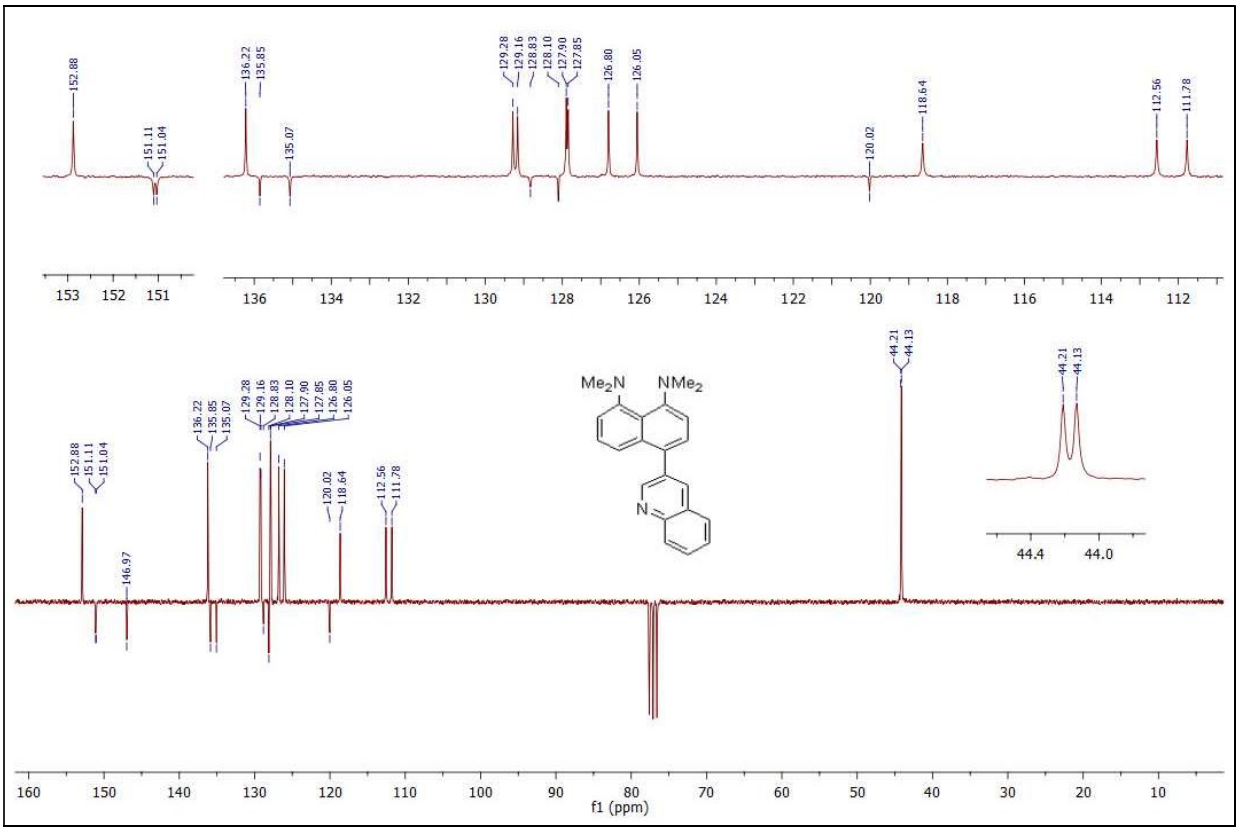

Fig. S20. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5j** (62.9 MHz, $CDCl_3$).

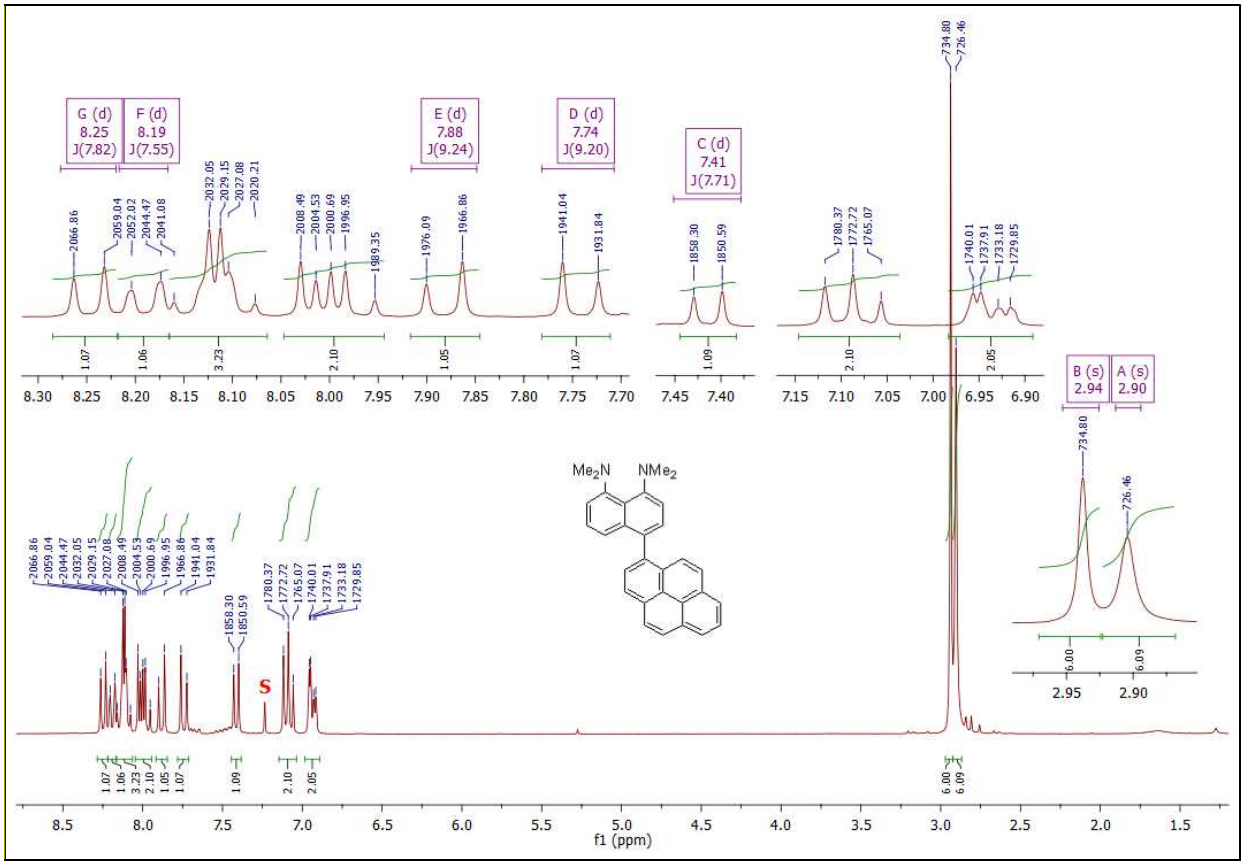

Fig. S21. ^{1}H NMR spectrum of compound **5k** (250 MHz, $CDCl_3$).

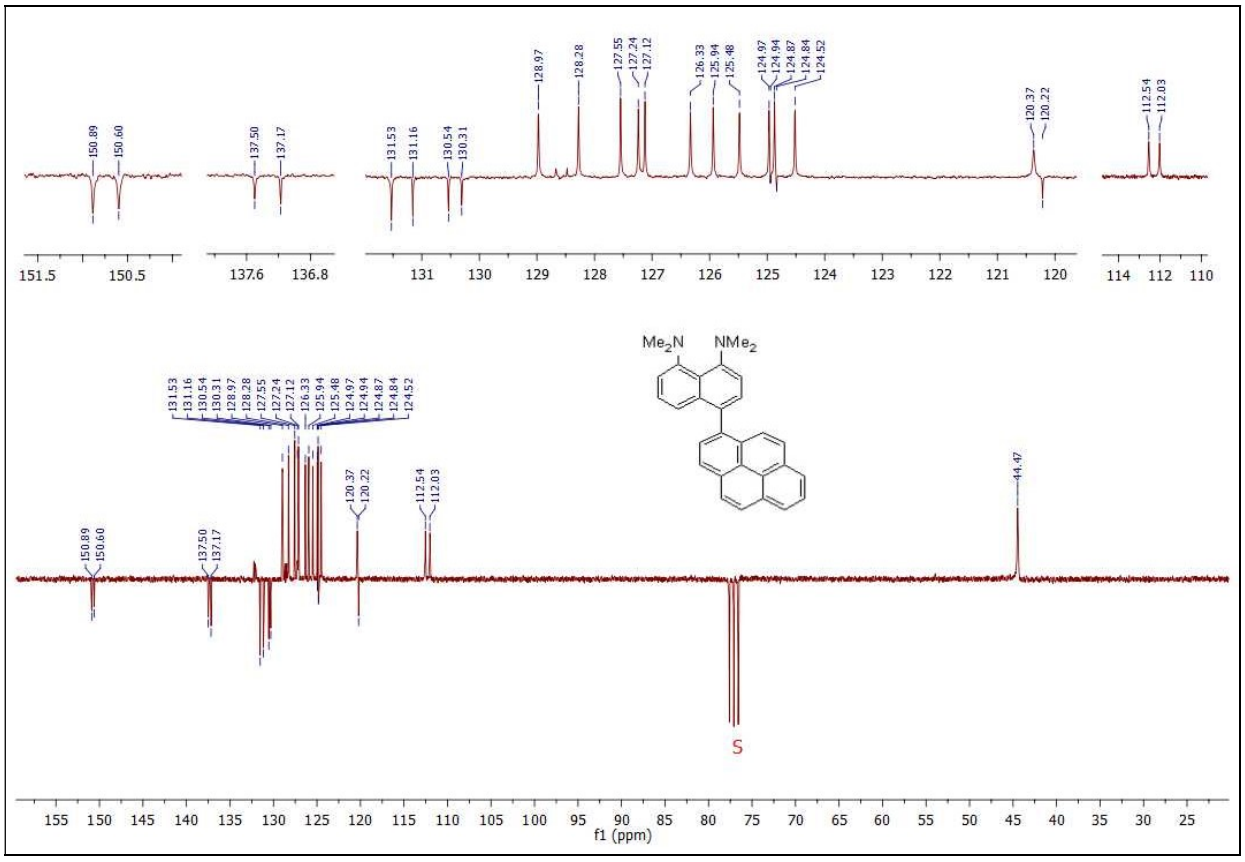

Fig. S22. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5k** (62.9 MHz, $CDCl_3$).

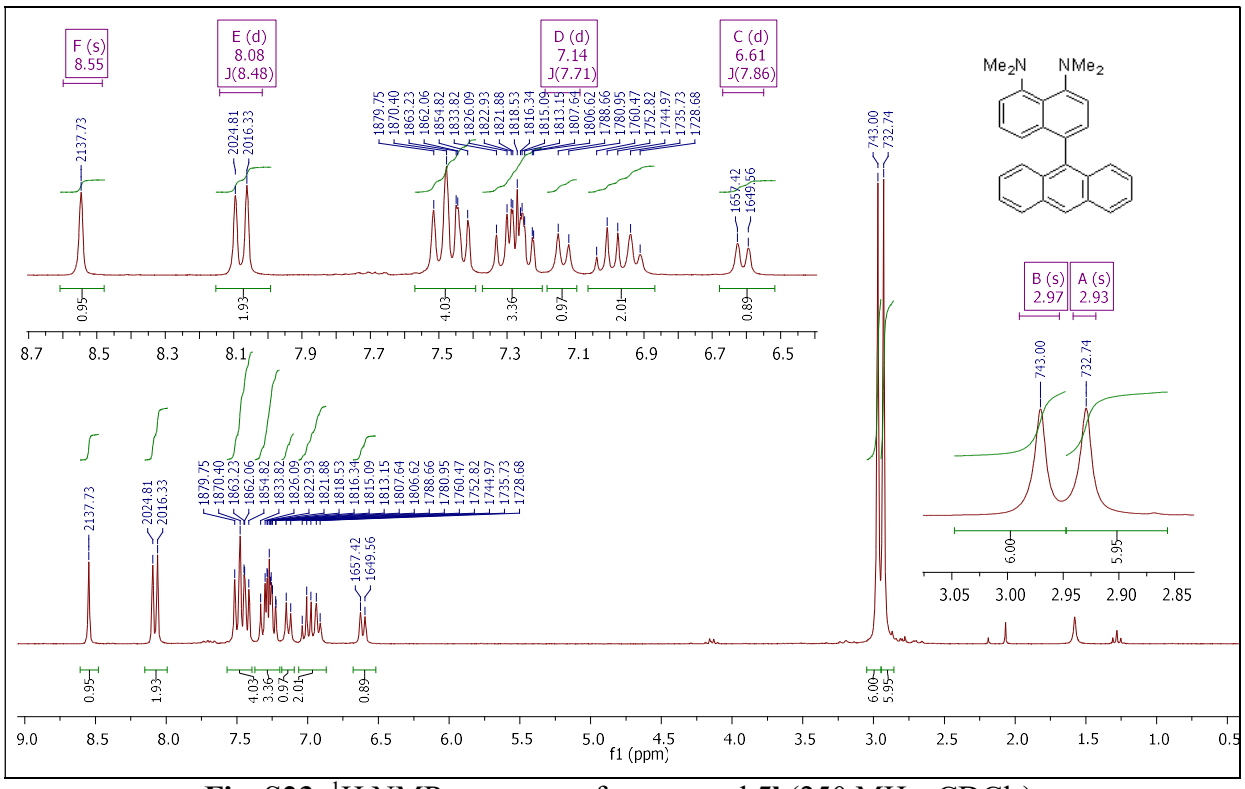

Fig. S23. ^{1}H NMR spectrum of compound **5l** (250 MHz, $CDCl_3$).

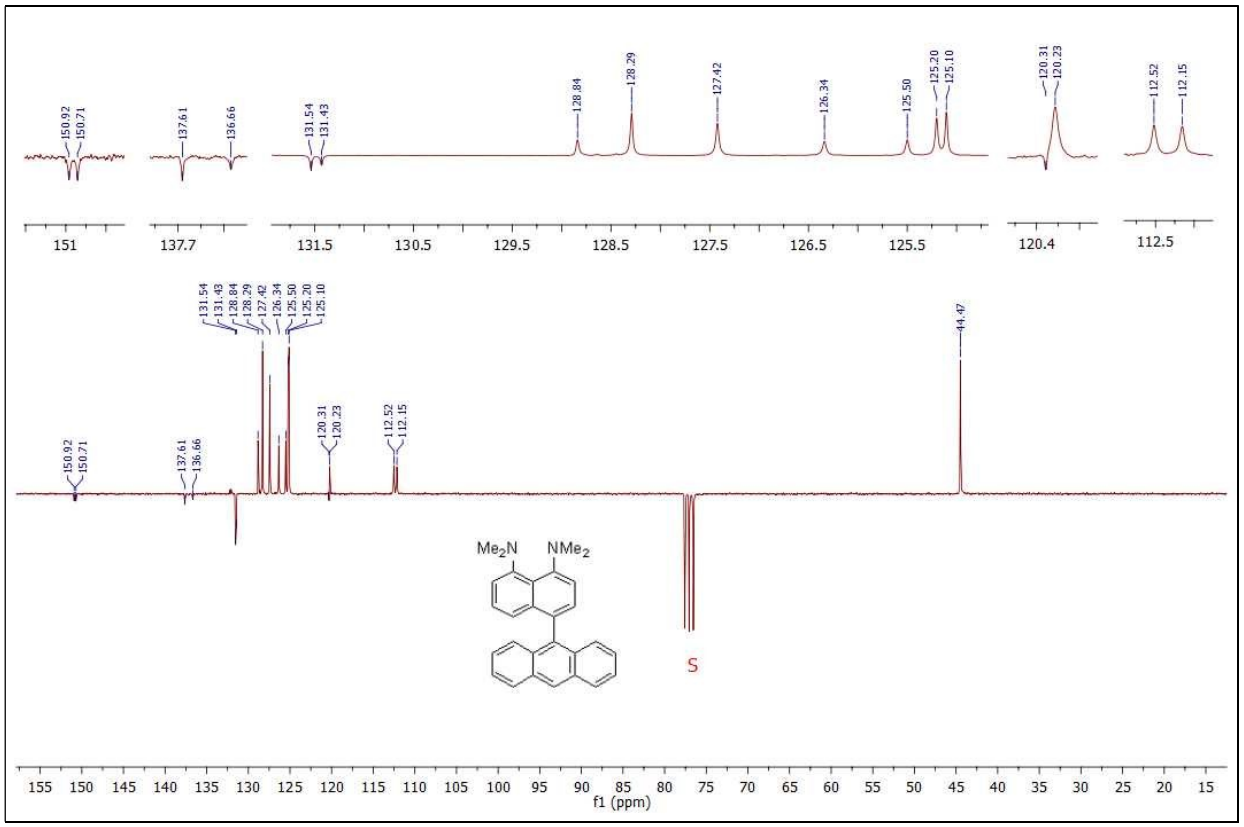

Fig. S24. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **5l** (62.9 MHz, $CDCl_3$).

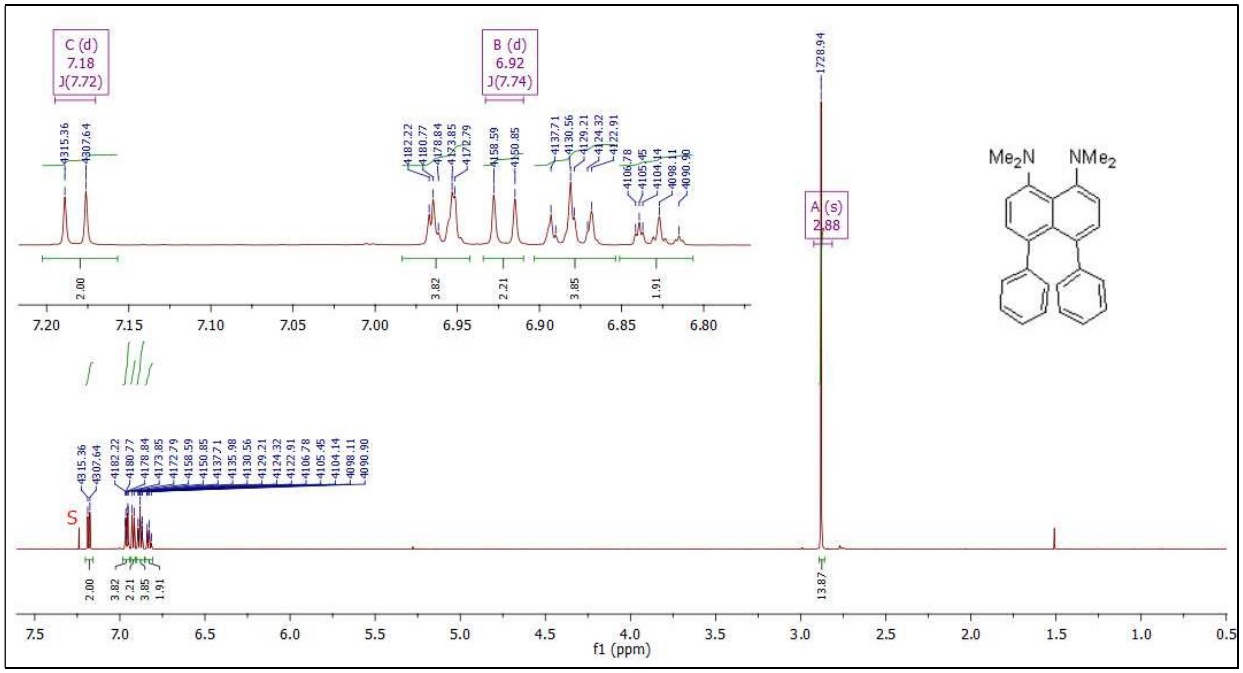

Fig. S25. ^{1}H NMR spectrum of compound **3a** (600 MHz, $CDCl_3$).

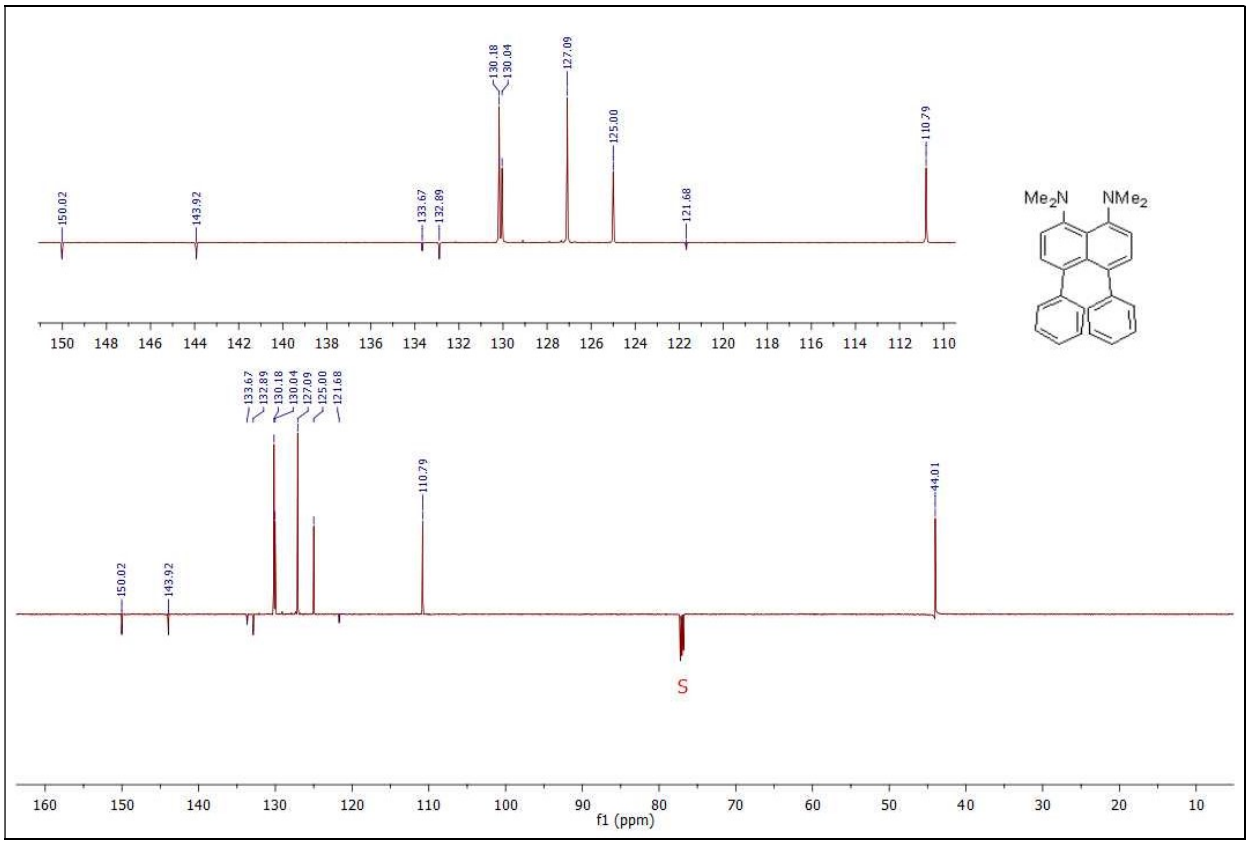

Fig. S26. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **3a** (150 MHz, $CDCl_3$).

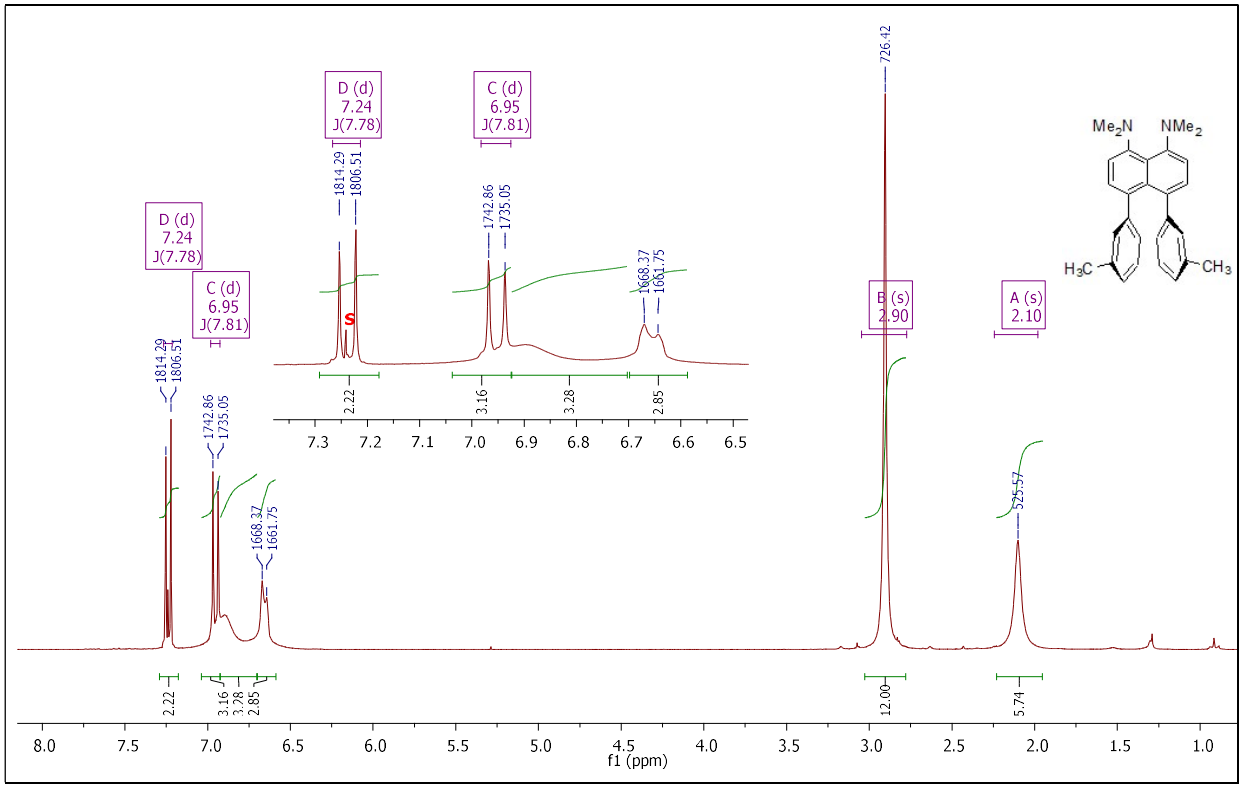

Fig. S27. ^{1}H NMR spectrum of compound **3b** (250 MHz, $CDCl_3$).

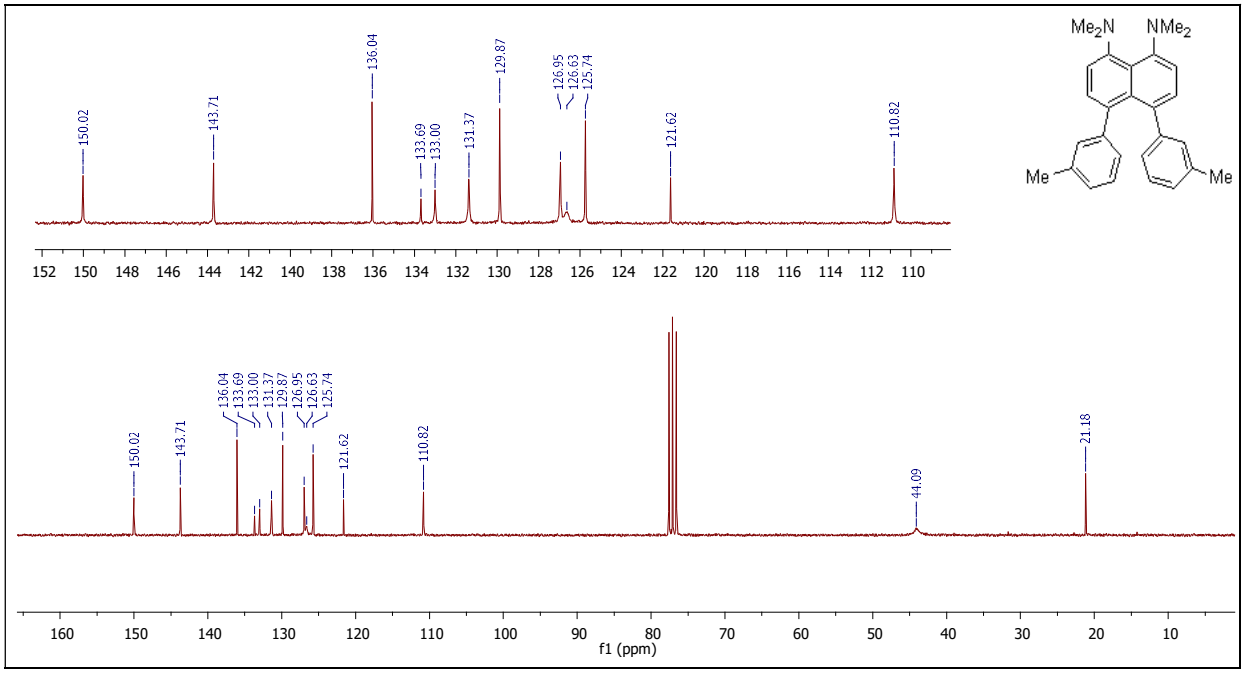

Fig. S28. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3b** (62.9 MHz, $CDCl_3$).

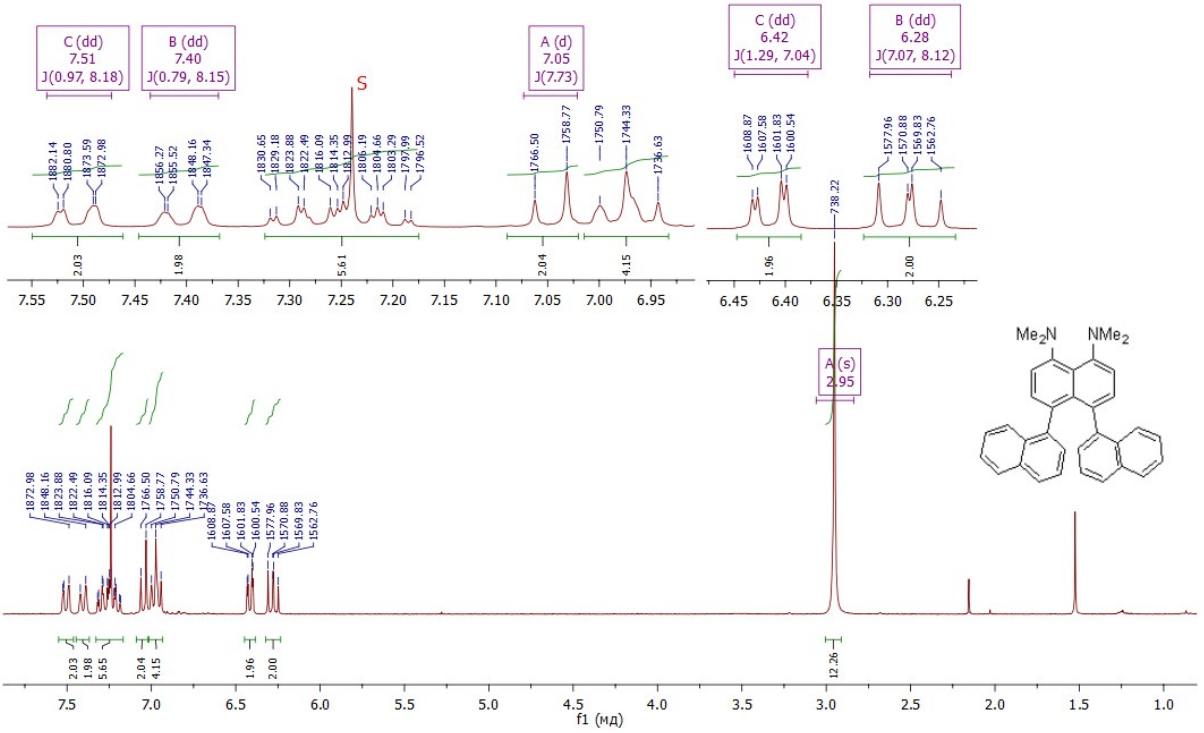

Fig. S29. ^{1}H NMR spectrum of compound **3c** (250 MHz, $CDCl_3$).

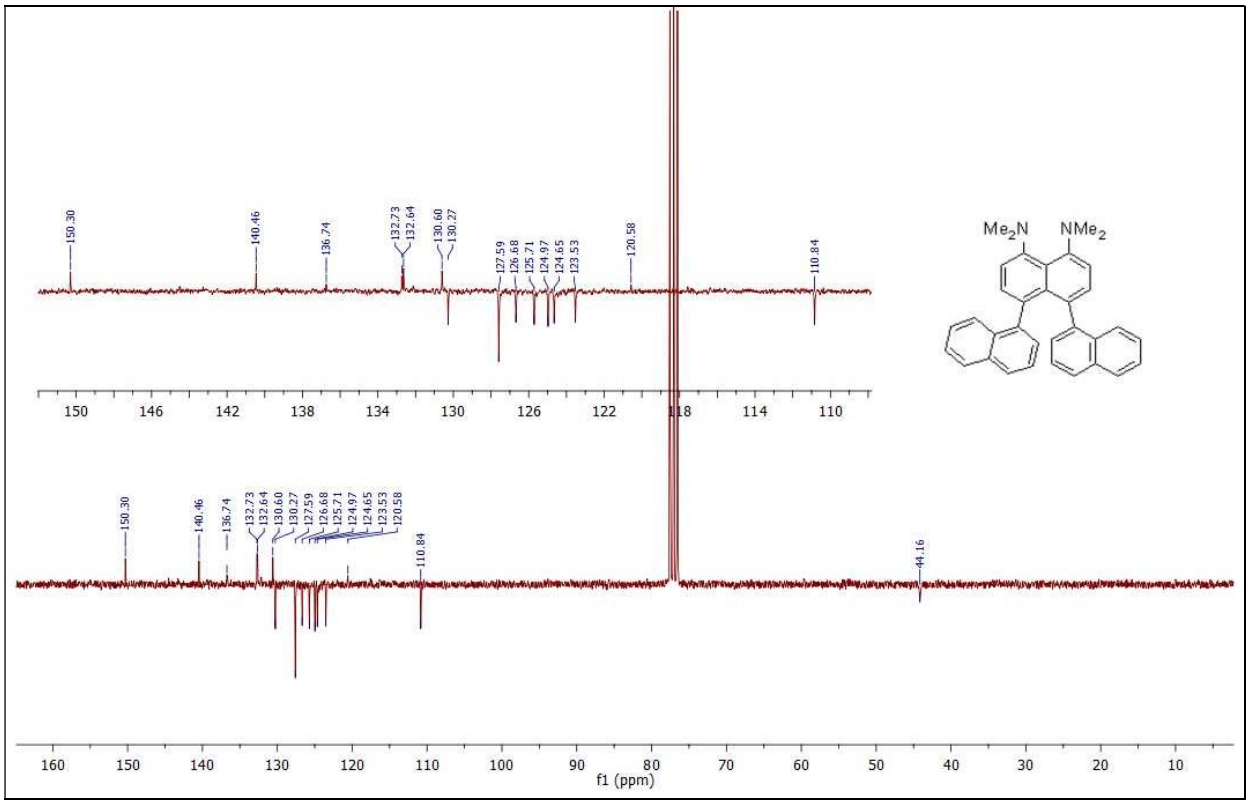

Fig. S30. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **3c** (62.9 MHz, $CDCl_3$).

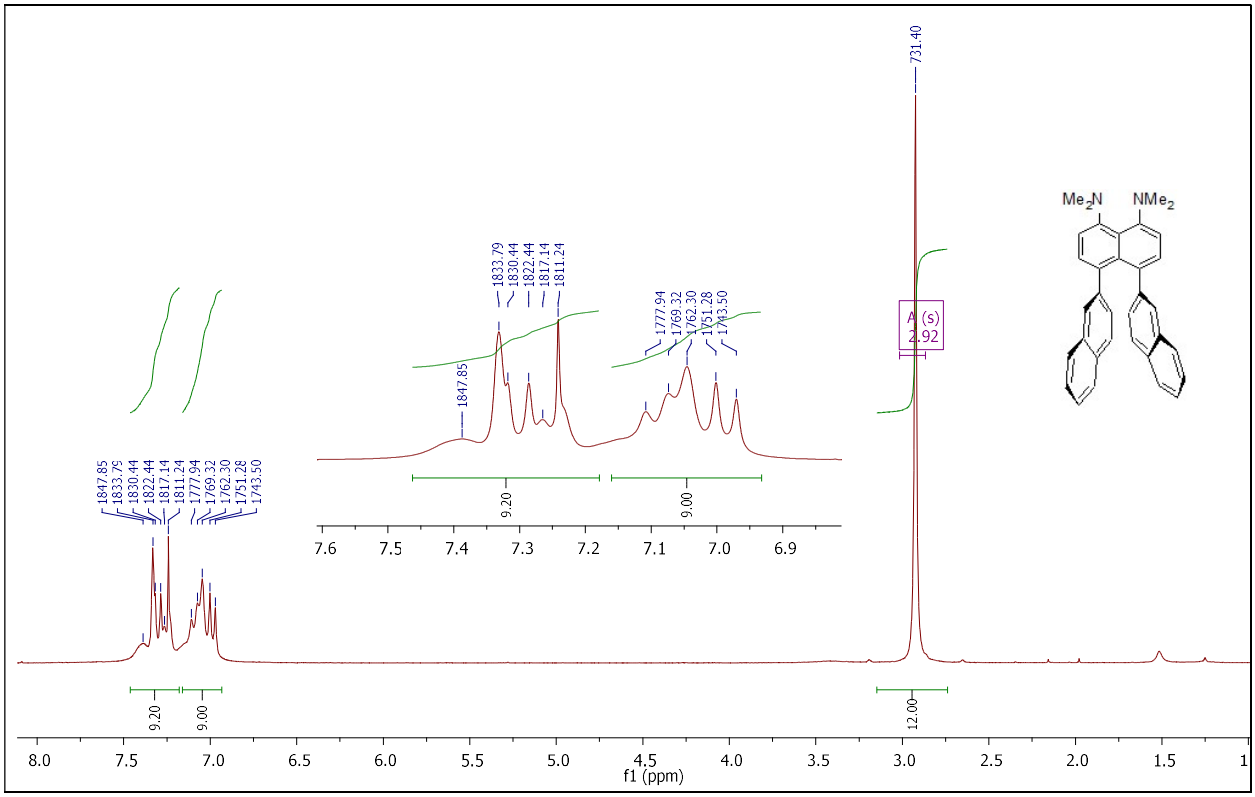

Fig. S31. ^{1}H NMR spectrum of compound **3d** (250 MHz, $CDCl_3$).

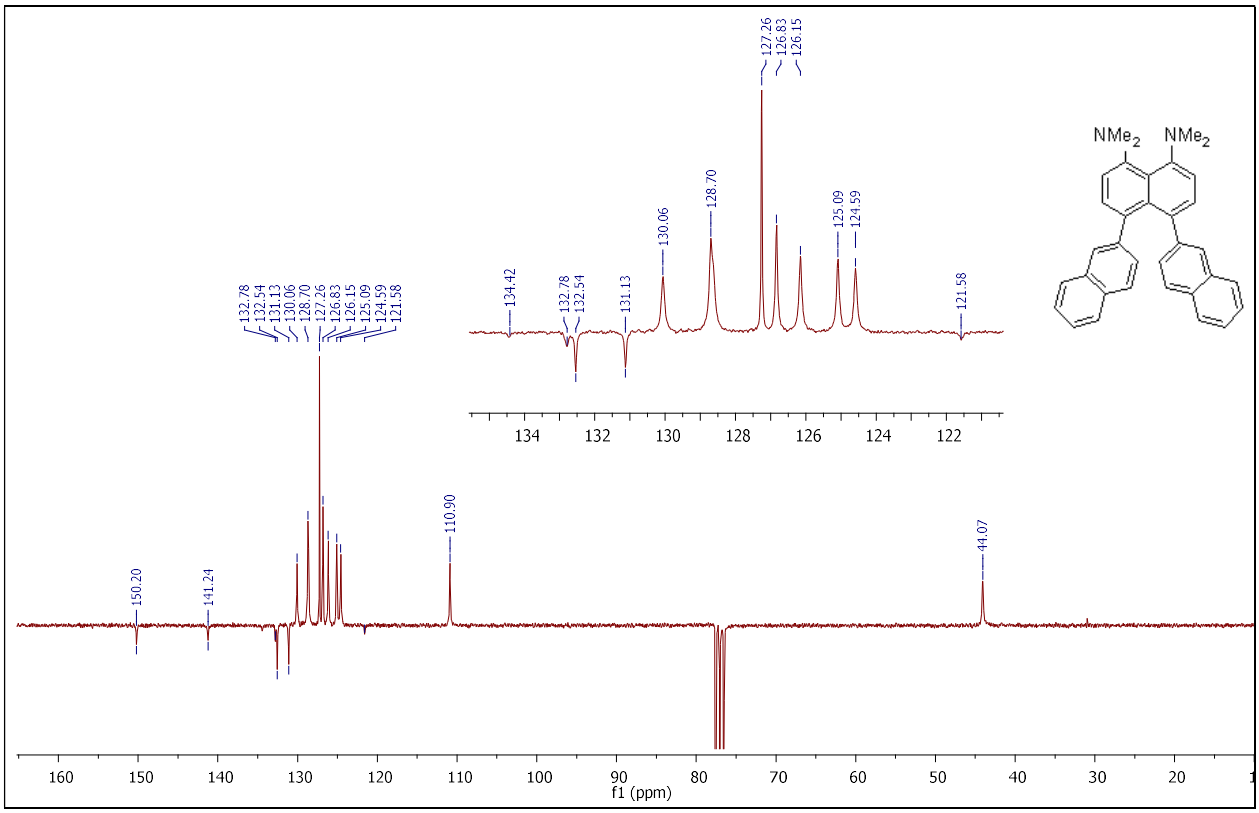

Fig. S32. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **3d** (62.9 MHz, $CDCl_3$).

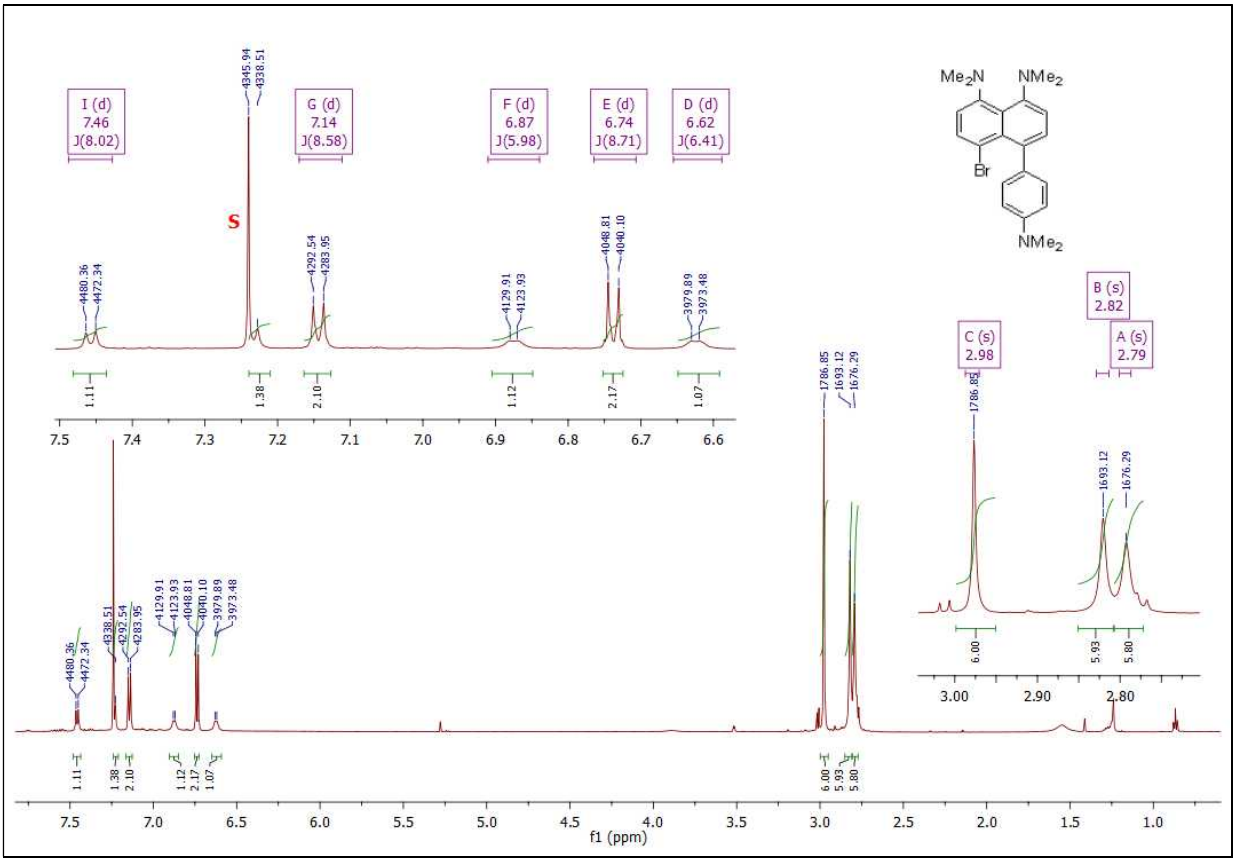

Fig. S33. ^{1}H NMR spectrum of compound **7** (600 MHz, $CDCl_3$).

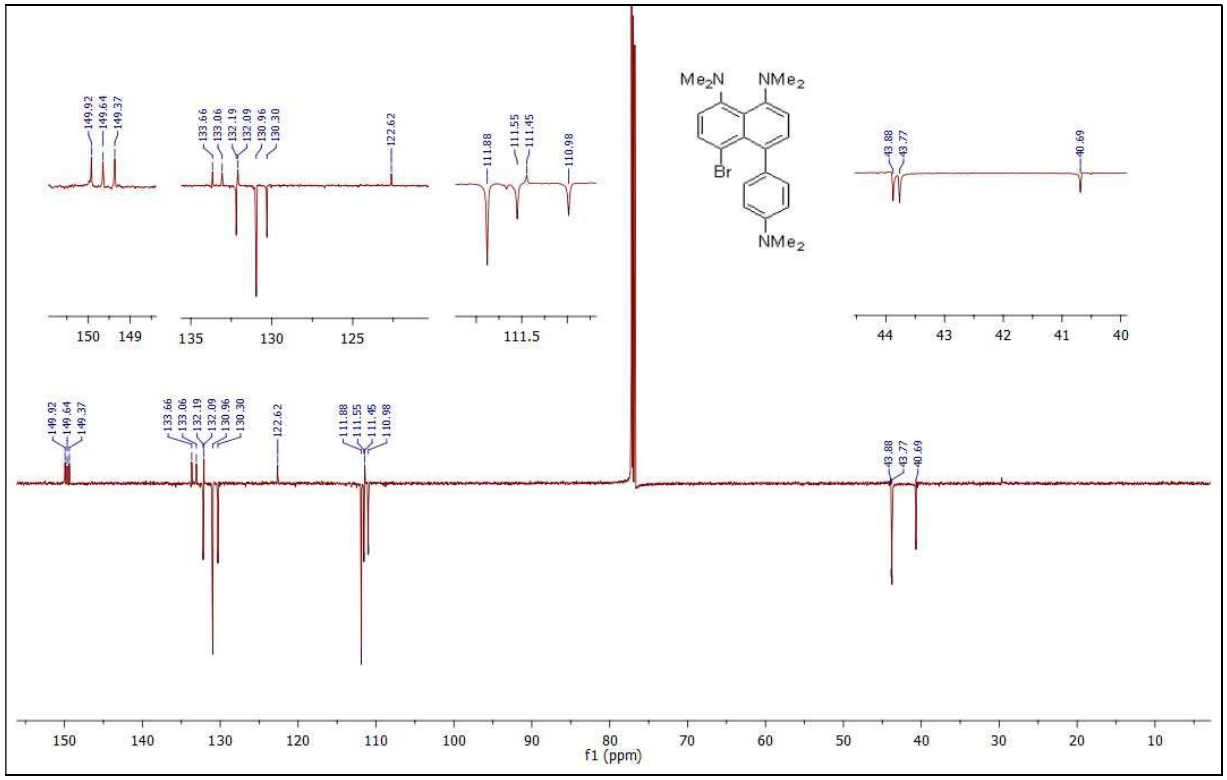

Fig. S34. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **7** (150 MHz, $CDCl_3$).

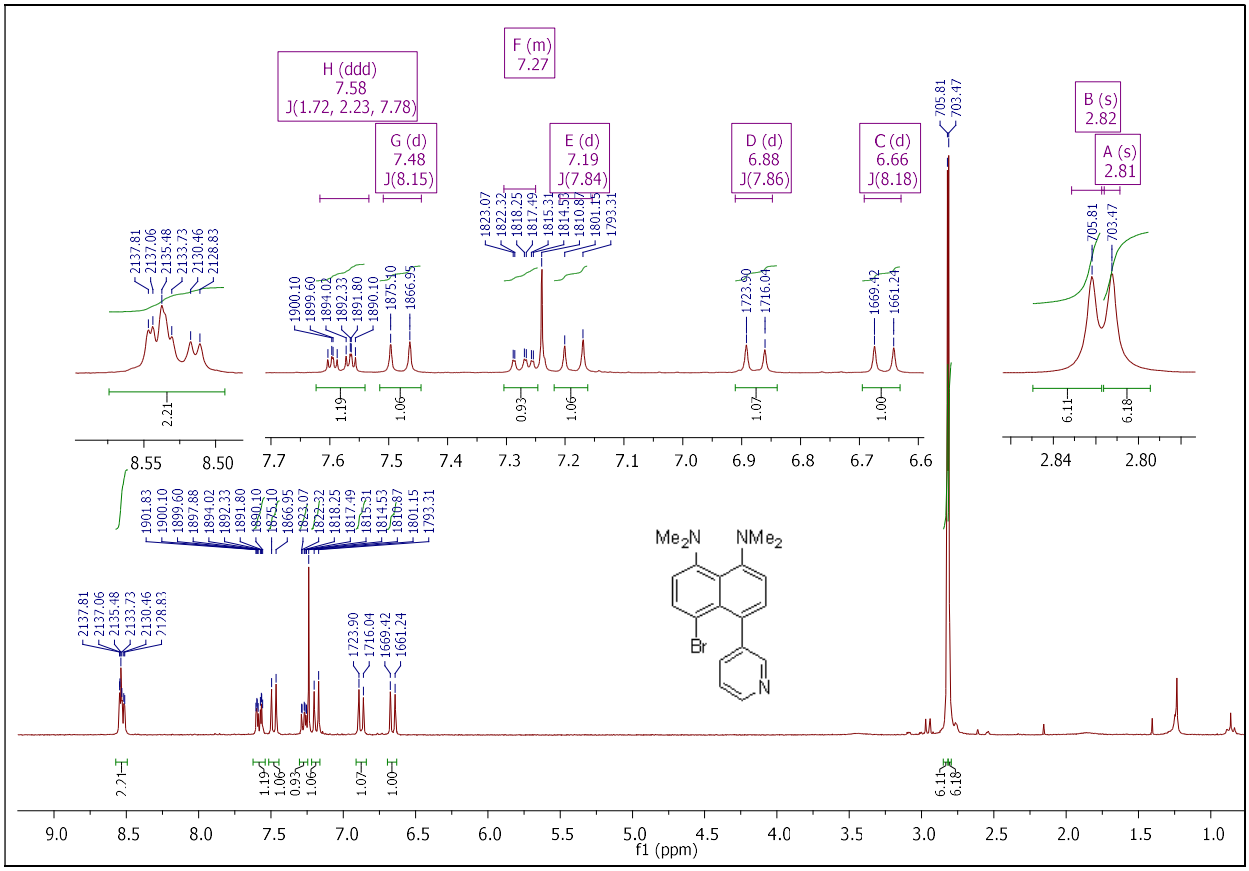

Fig. S35. ^{1}H NMR spectrum of compound **8** (250 MHz, DMSO-d$_6$).

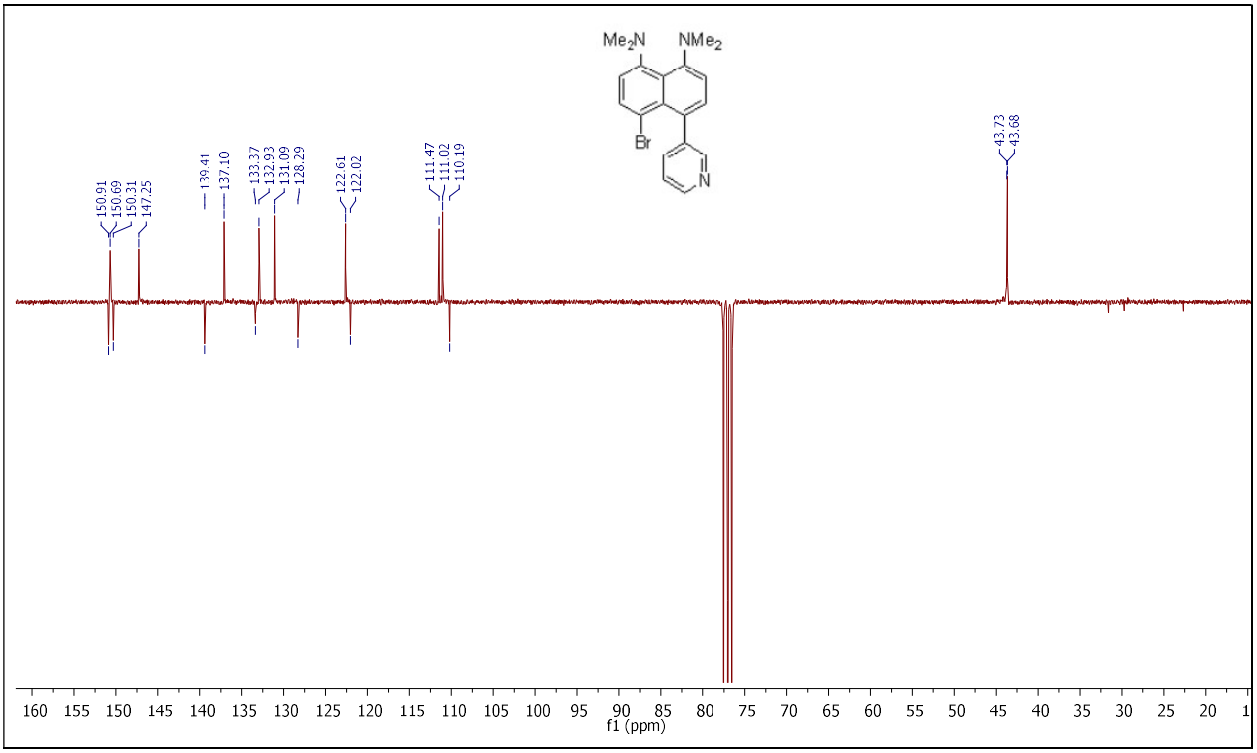

Fig. S36. ^{13}C{^{1}H} APT-NMR spectrum of compound **8** (62.9 MHz, DMSO-d$_6$).

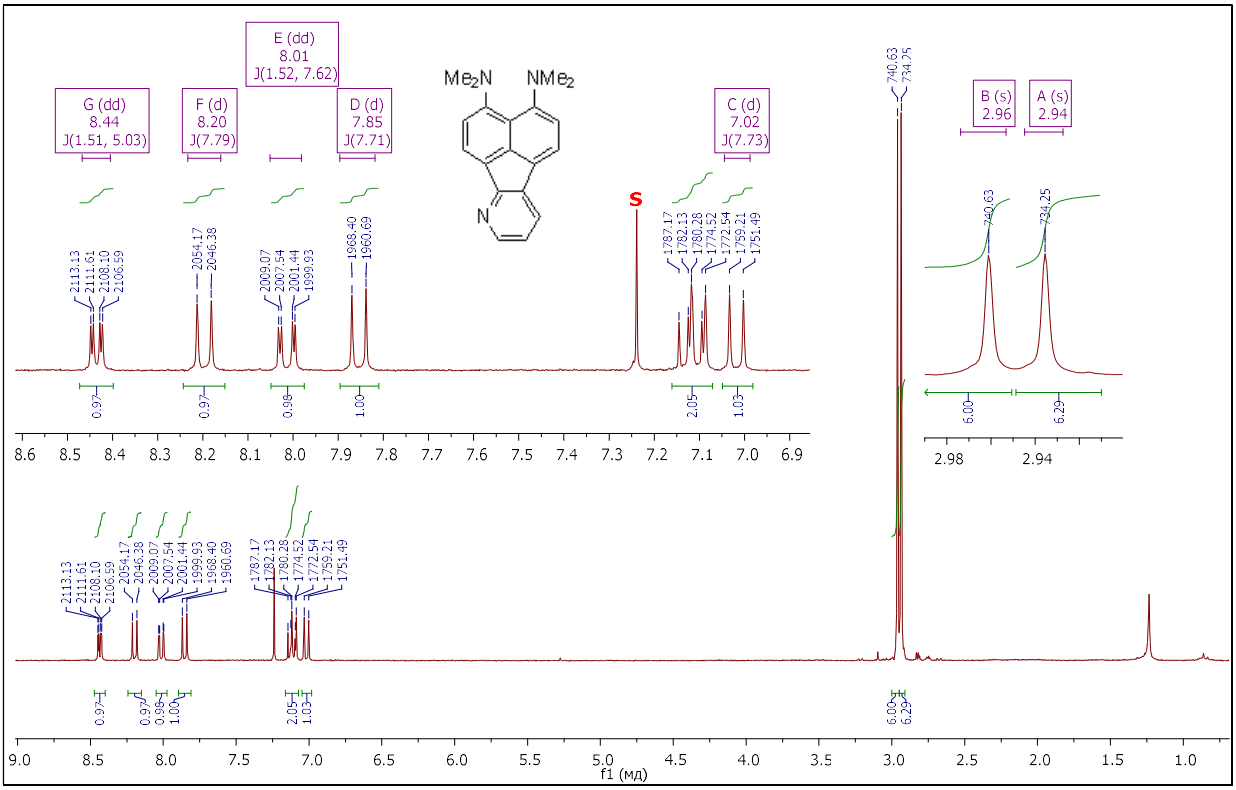

Fig. S37. ^{1}H NMR spectrum of compound **9** (250 MHz, $CDCl_3$).

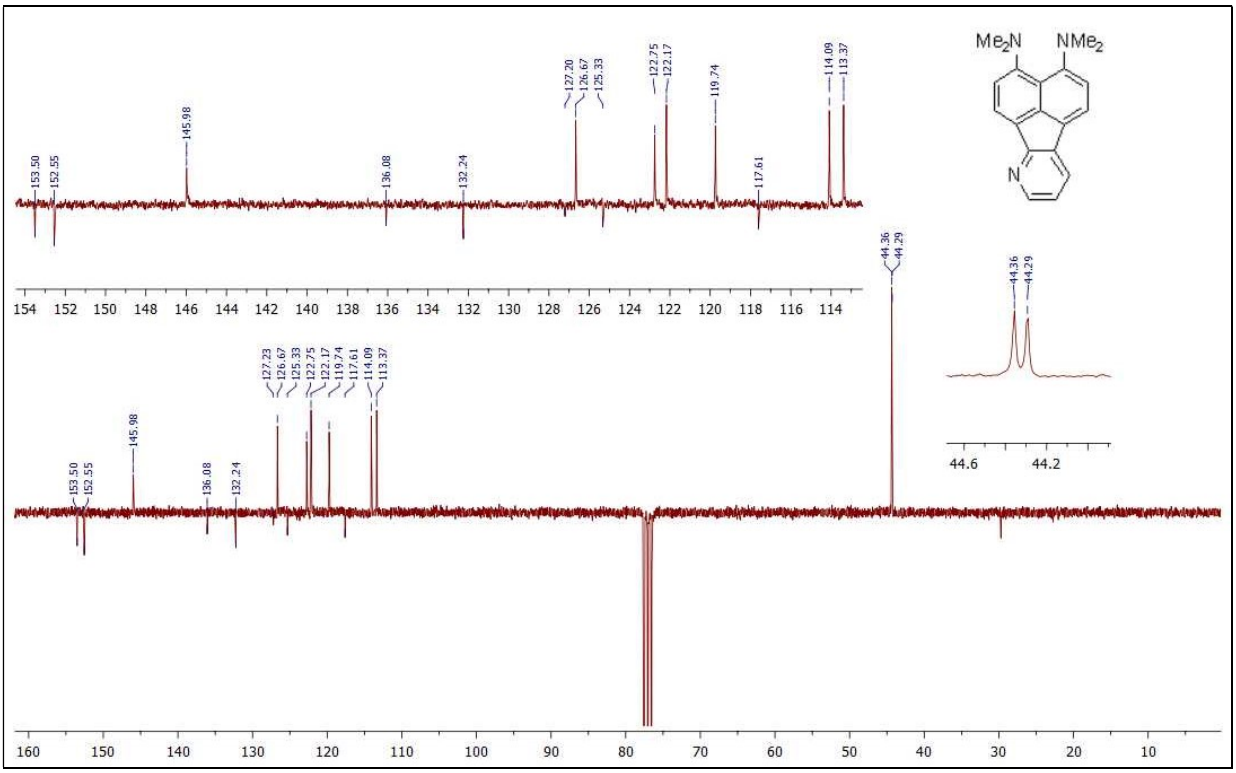

Fig. S38. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **9** (62.9 MHz, $CDCl_3$).

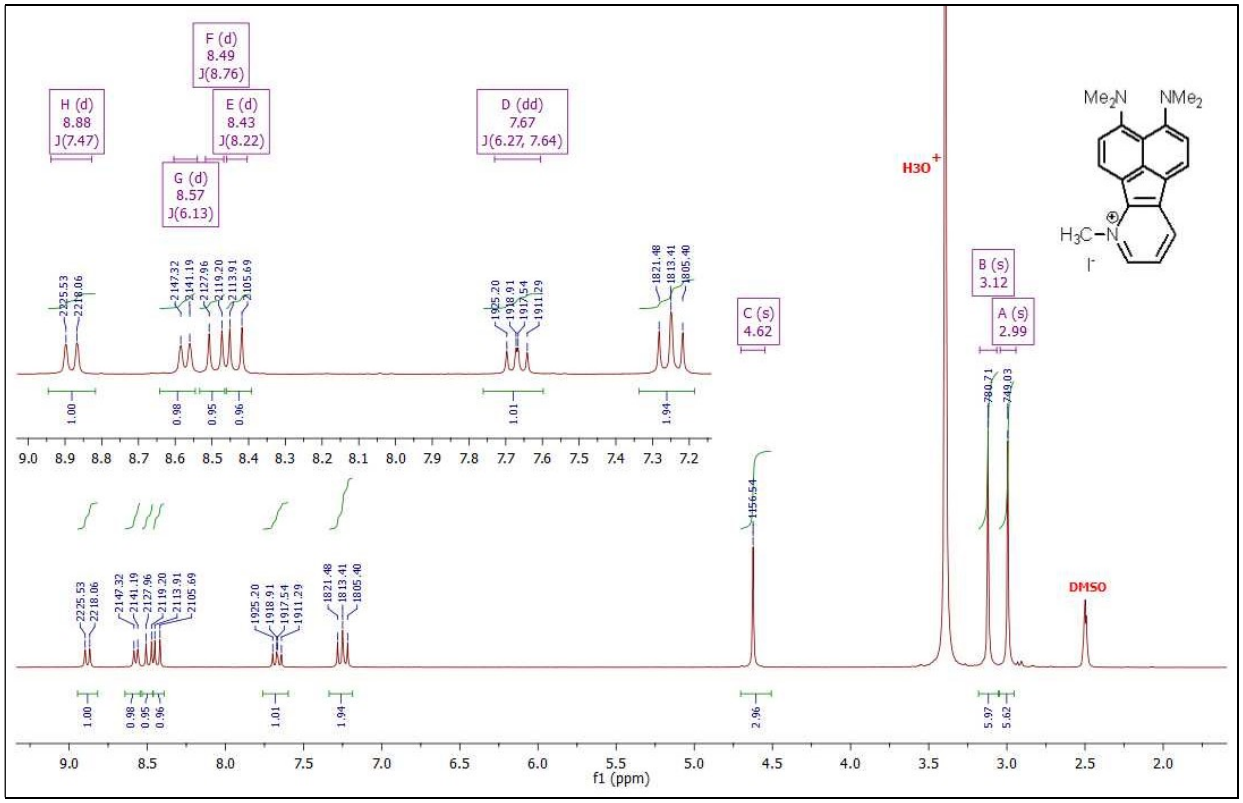

Fig. S39. ^{1}H NMR spectrum of compound **12** (250 MHz, DMSO-d_6).

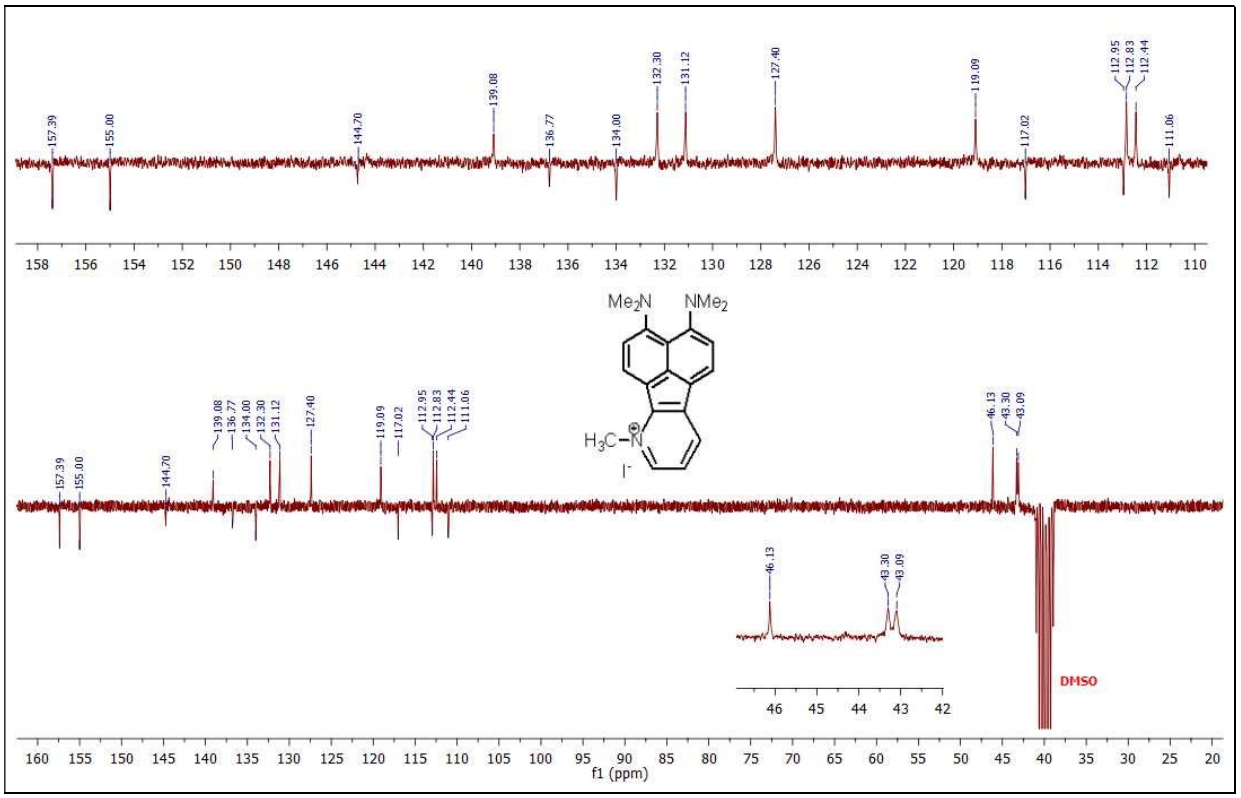

Fig. S40. ^{13}C{^{1}H} APT-NMR spectrum of compound **12** (62.9 MHz, DMSO-d_6).

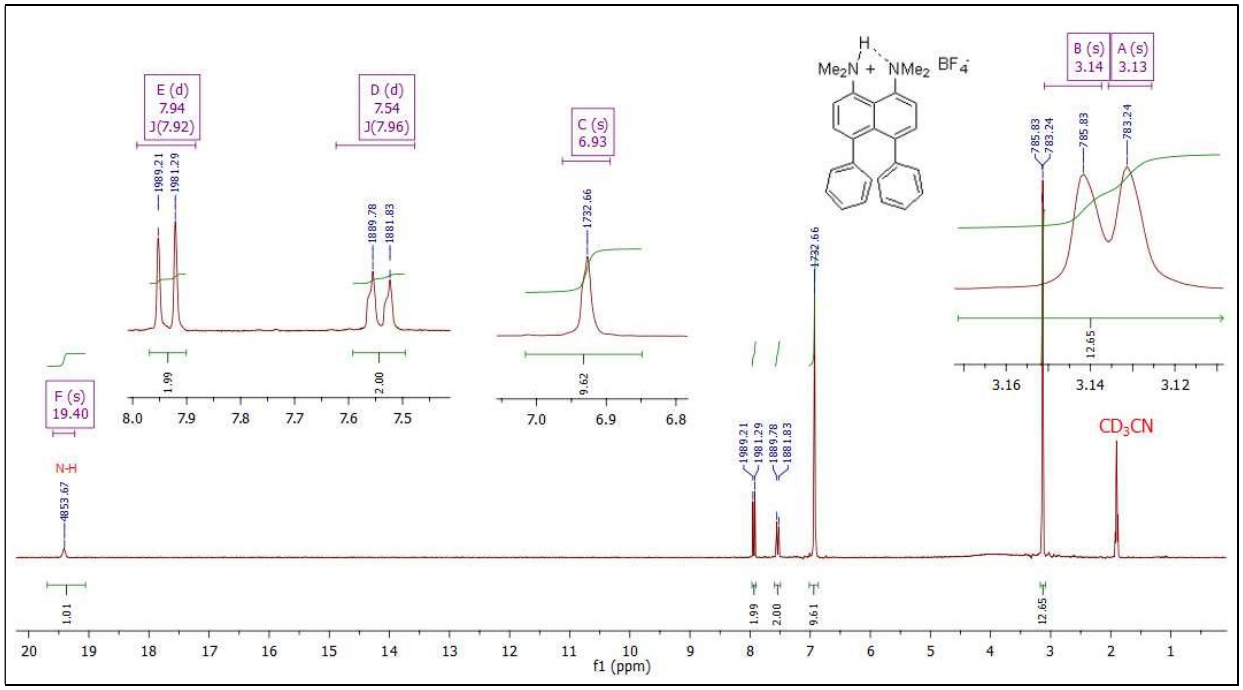

Fig. S41. ^{1}H NMR spectrum of compound **3a·HBF$_4$** (250 MHz, CD_3CN).

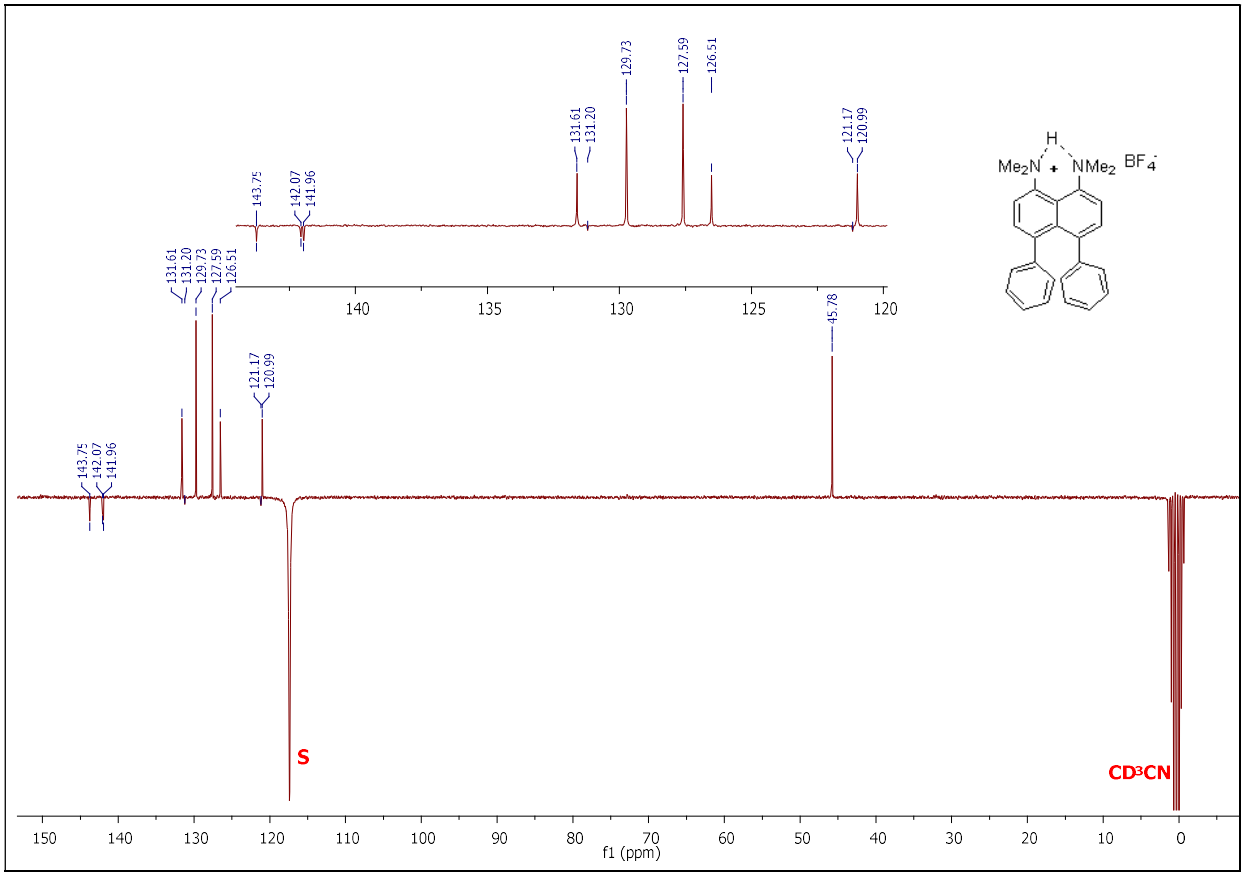

Fig. S42. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **3a·HBF$_4$** (62.9 MHz, CD_3CN).

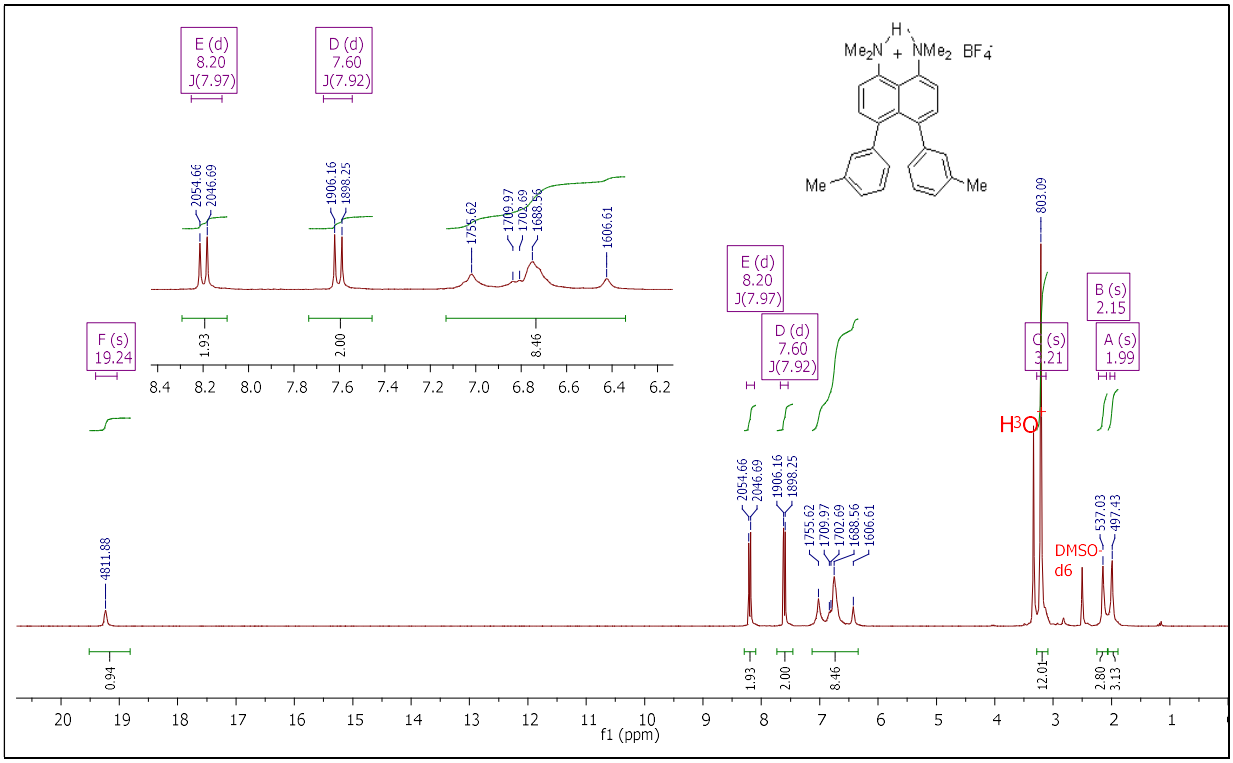

Fig. S43. ^{1}H NMR spectrum of compound **3b·HBF$_4$** (250 MHz, DMSO-d$_6$).

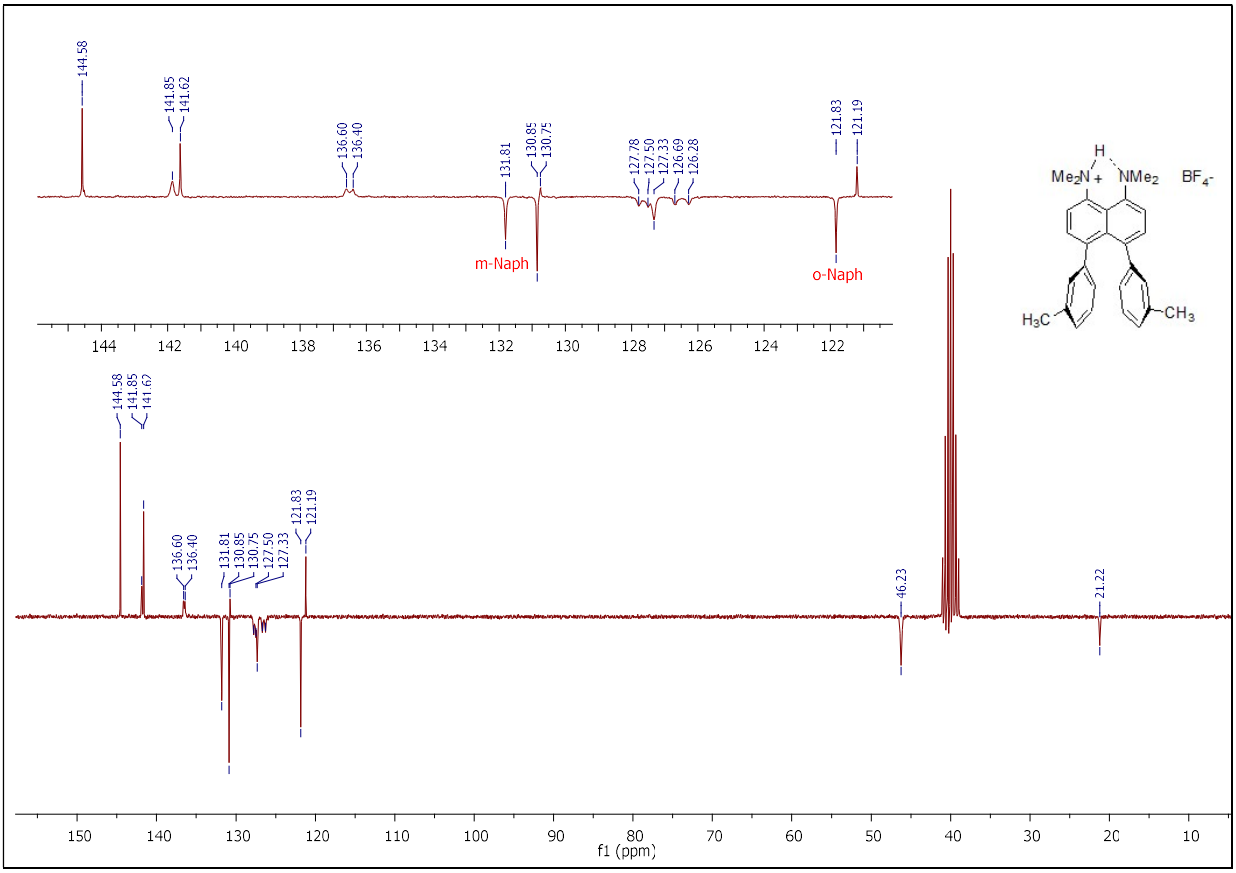

Fig. S44. ^{13}C{^{1}H} APT-NMR spectrum of compound **3b·HBF$_4$** (62.9 MHz, DMSO-d$_6$)

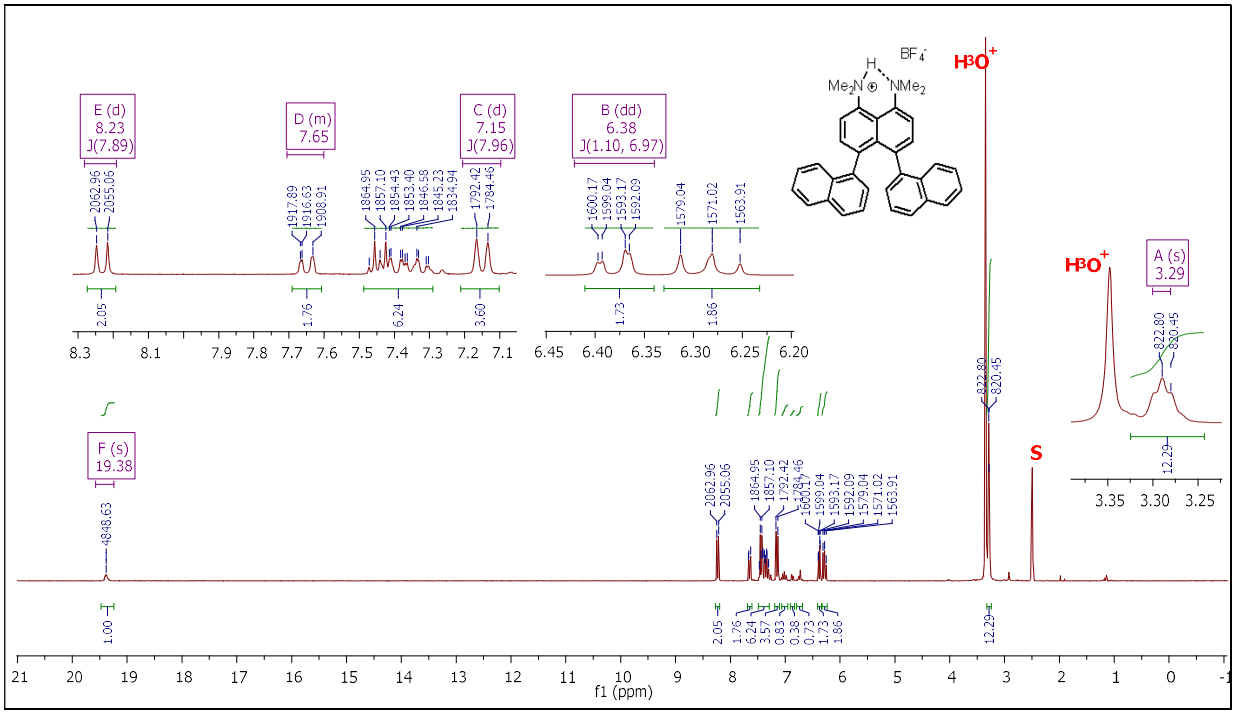

Fig. S45. ^{1}H NMR spectrum of compound **3c·HBF$_4$** (250 MHz, DMSO-d$_6$).

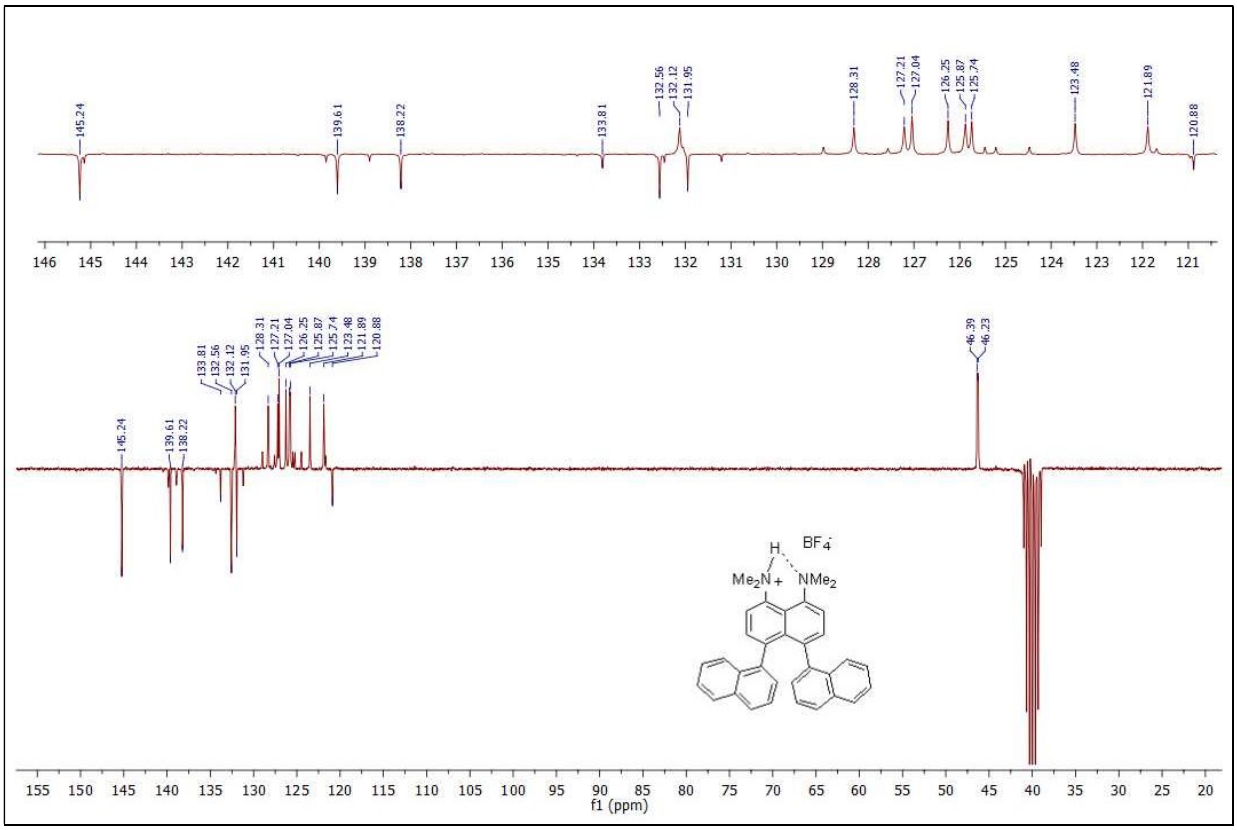

Fig. S46. ^{13}C{^{1}H} APT-NMR spectrum of compound **3c·HBF$_4$** (62.9 MHz, DMSO-d$_6$).

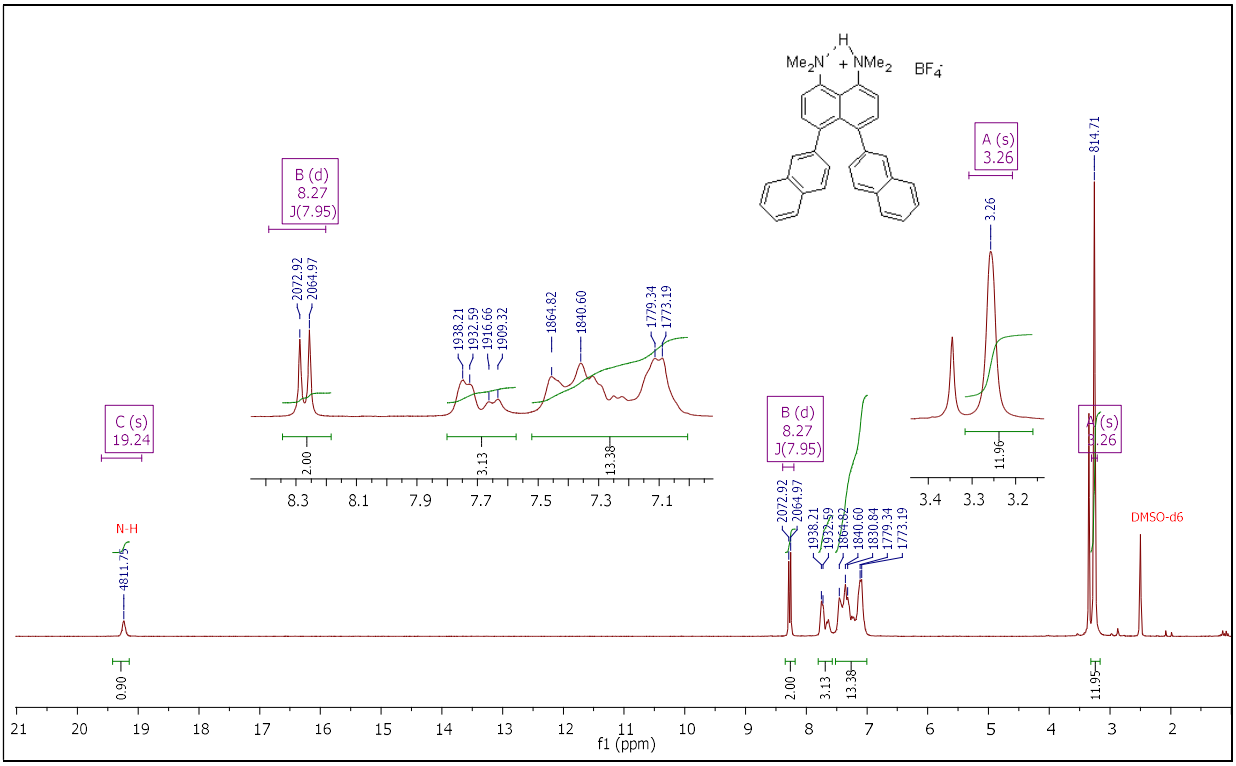

Fig. S47. ^{1}H NMR spectrum of compound **3d·HBF$_4$** (250 MHz, DMSO-d$_6$).

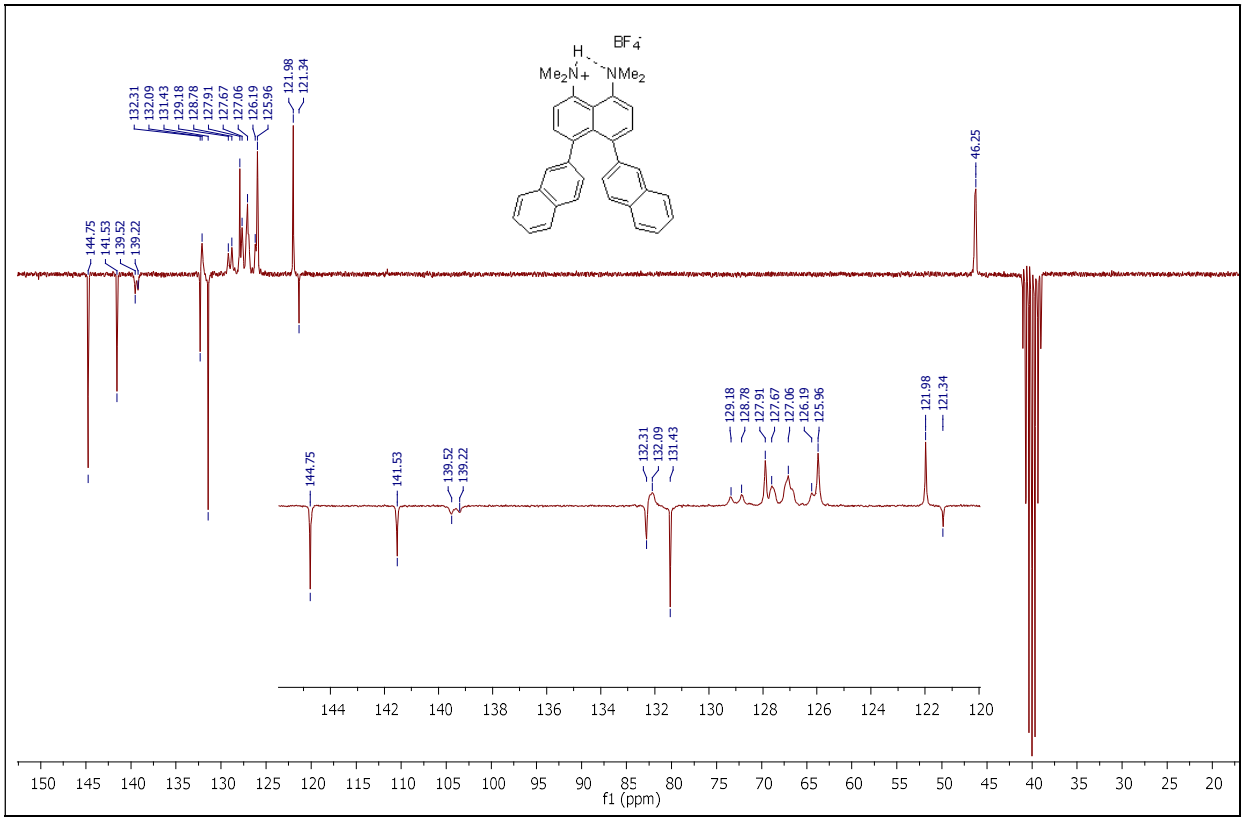

Fig. S48. ^{13}C{^{1}H} APT-NMR spectrum of compound **3d·HBF$_4$** (62.9 MHz, DMSO-d$_6$).

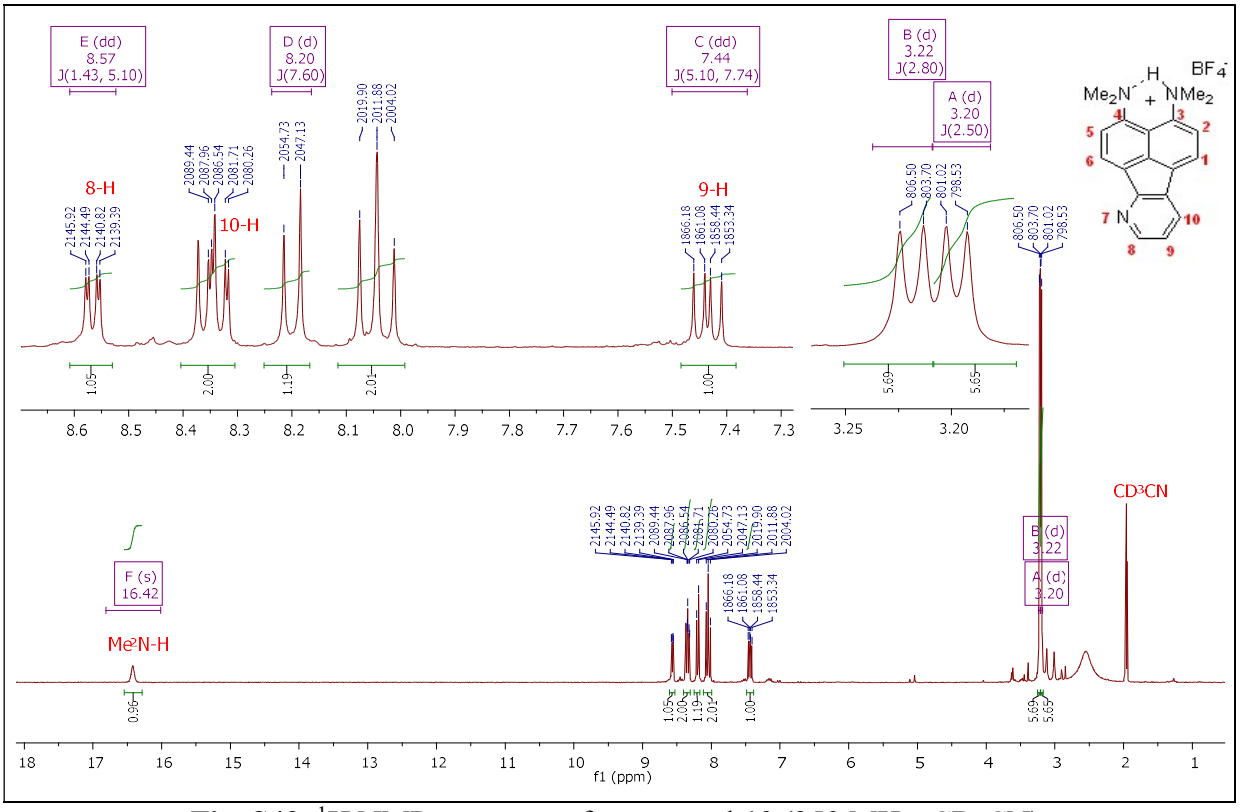

Fig. S49. ^{1}H NMR spectrum of compound **10** (250 MHz, CD_3CN).

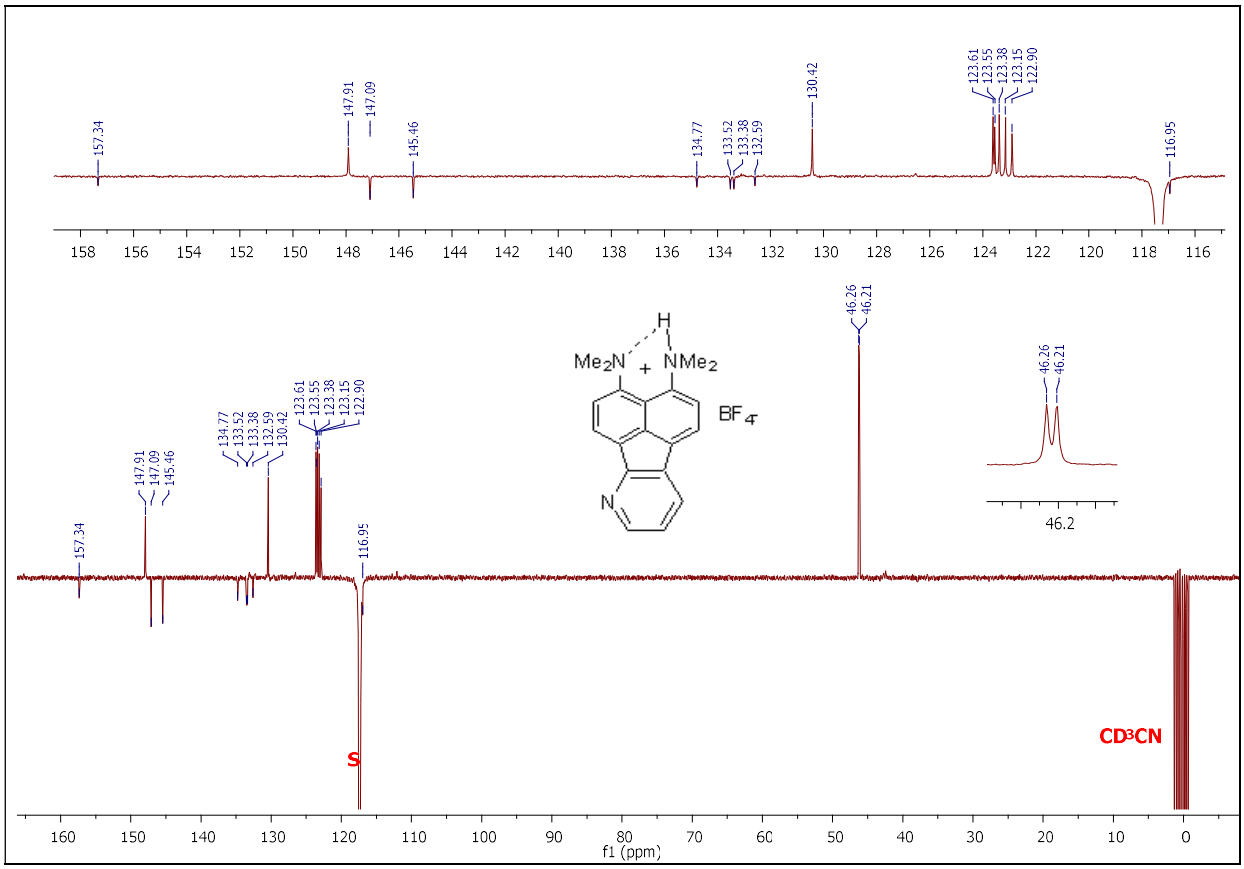

Fig. S50. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **10** (62.9 MHz, CD_3CN).

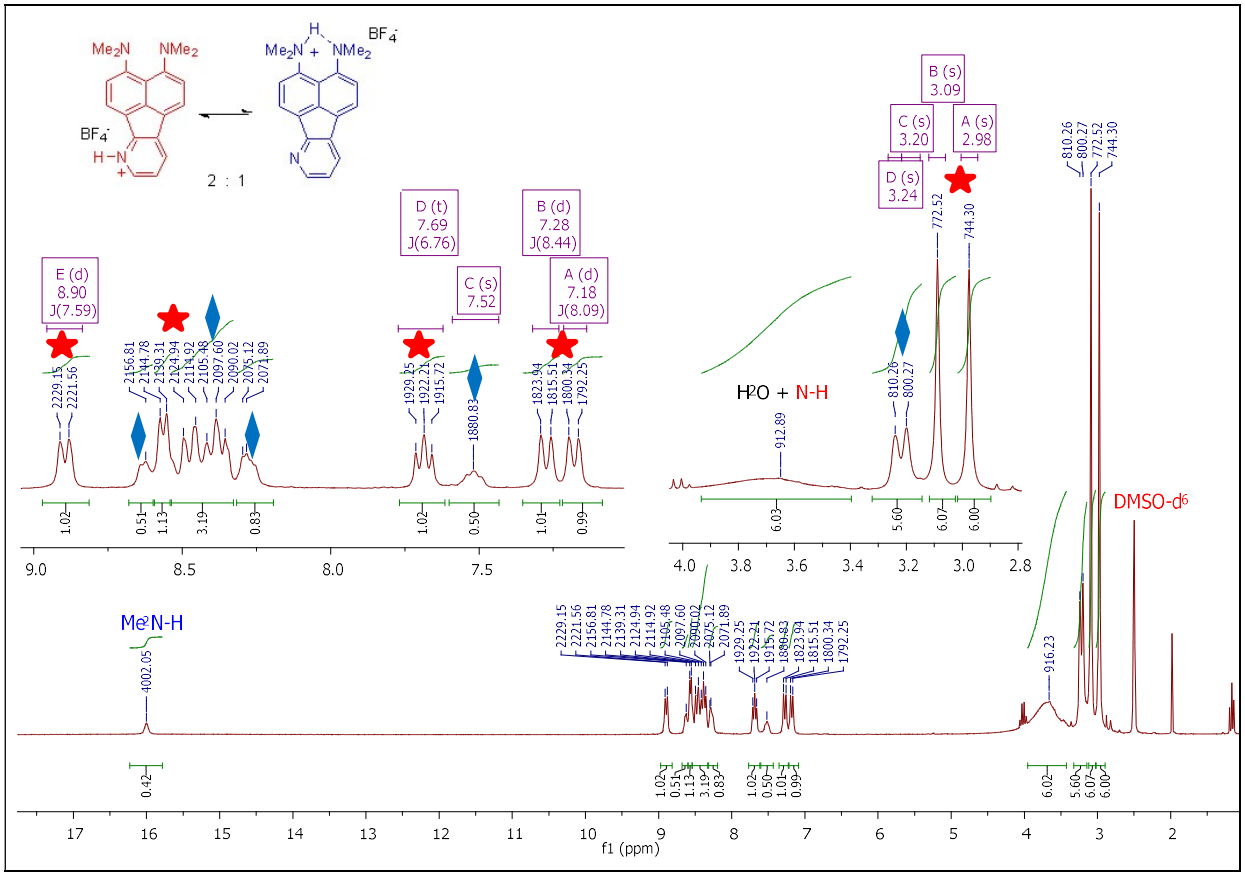

Fig. S51. ^{1}H NMR spectrum of mixture of compounds, **11:10** ratio = 2:1 (250 MHz, DMSO-d_6).

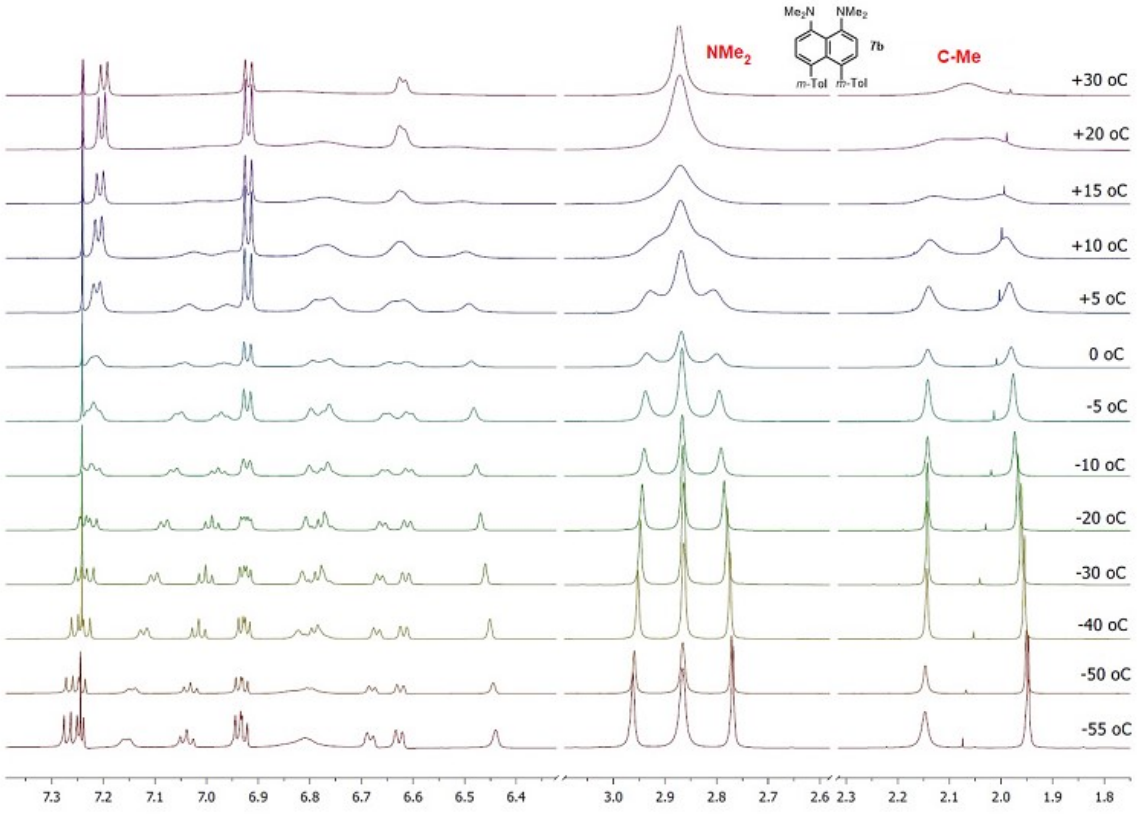

Fig. S52. Variable-temperature ^{1}H NMR spectra of **3b** ($CDCl_3$, 600 MHz).

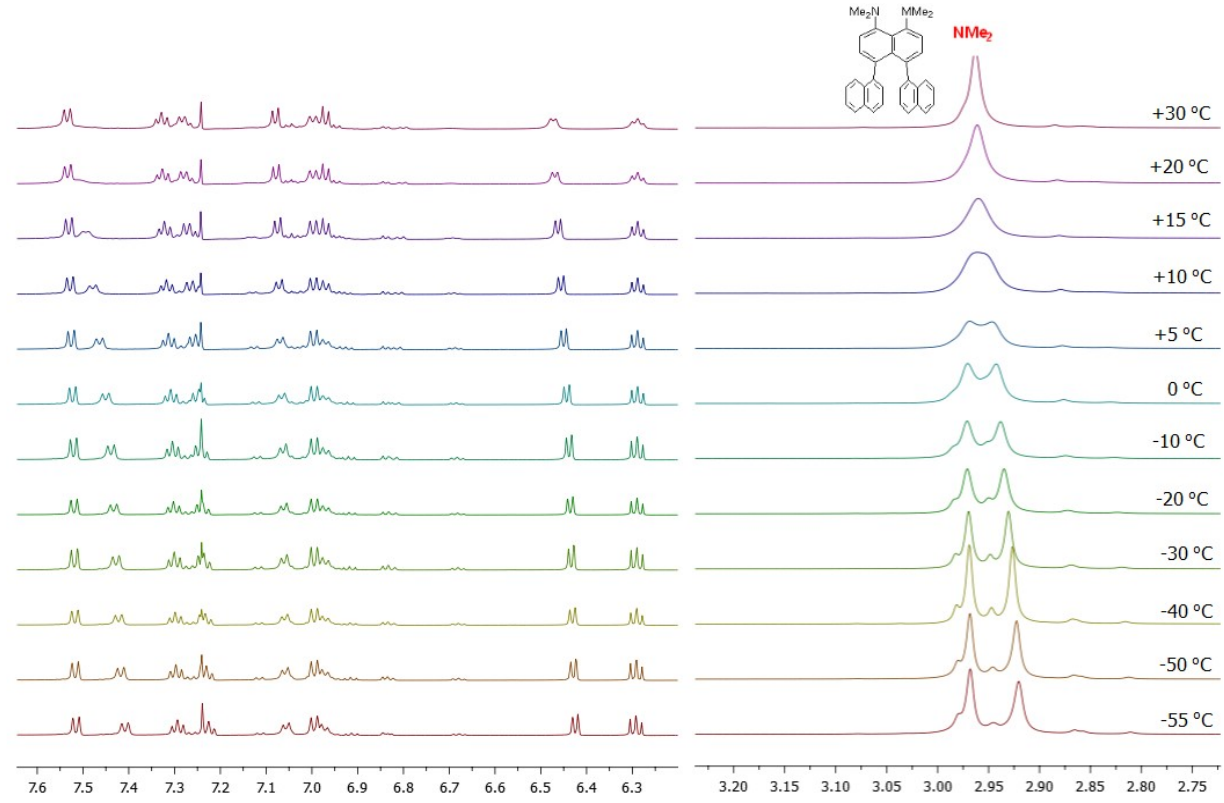

Fig. S53. Variable-temperature ^{1}H NMR spectra of **3c** ($CDCl_3$, 600 MHz).

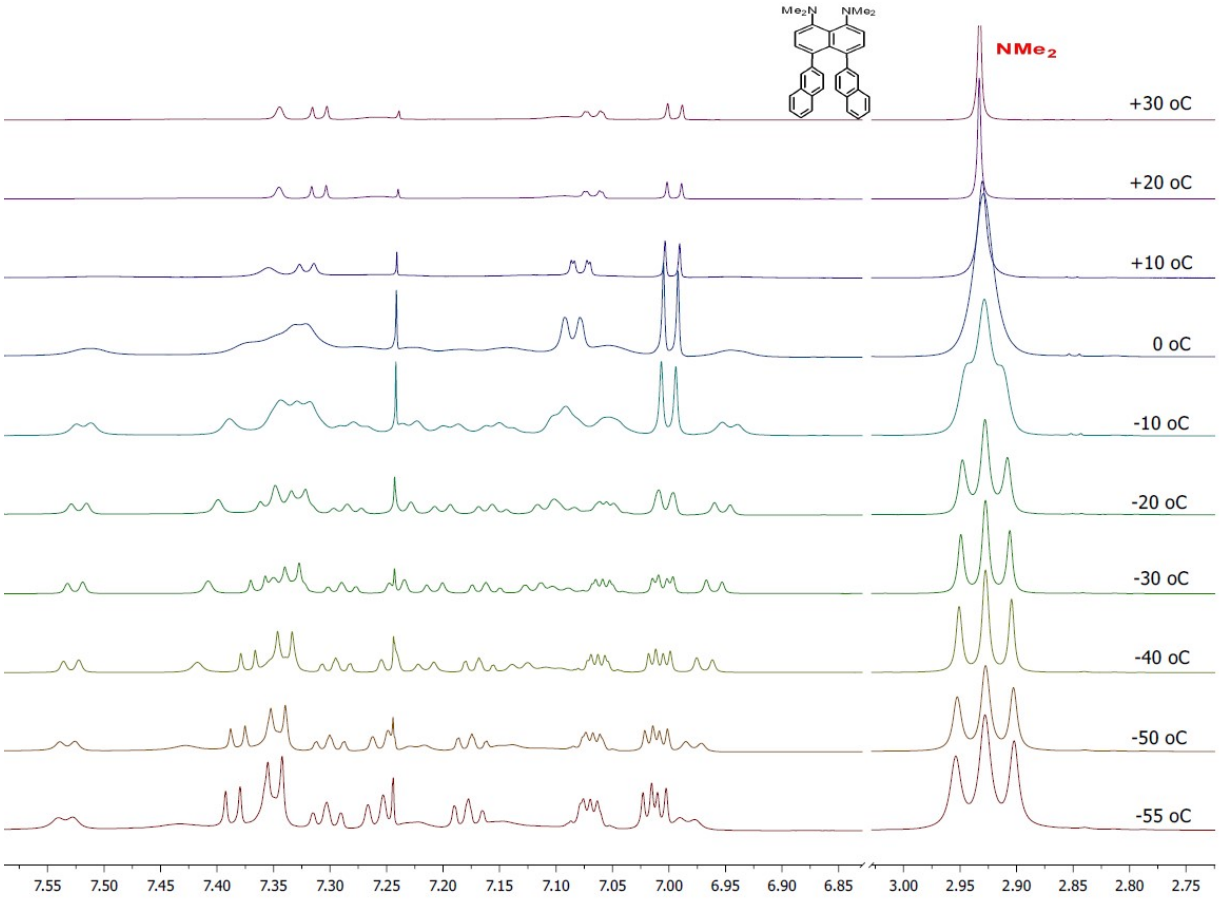

Fig. S54. Variable-temperature ^{1}H NMR spectra of **3d** ($CDCl_3$, 600 MHz).

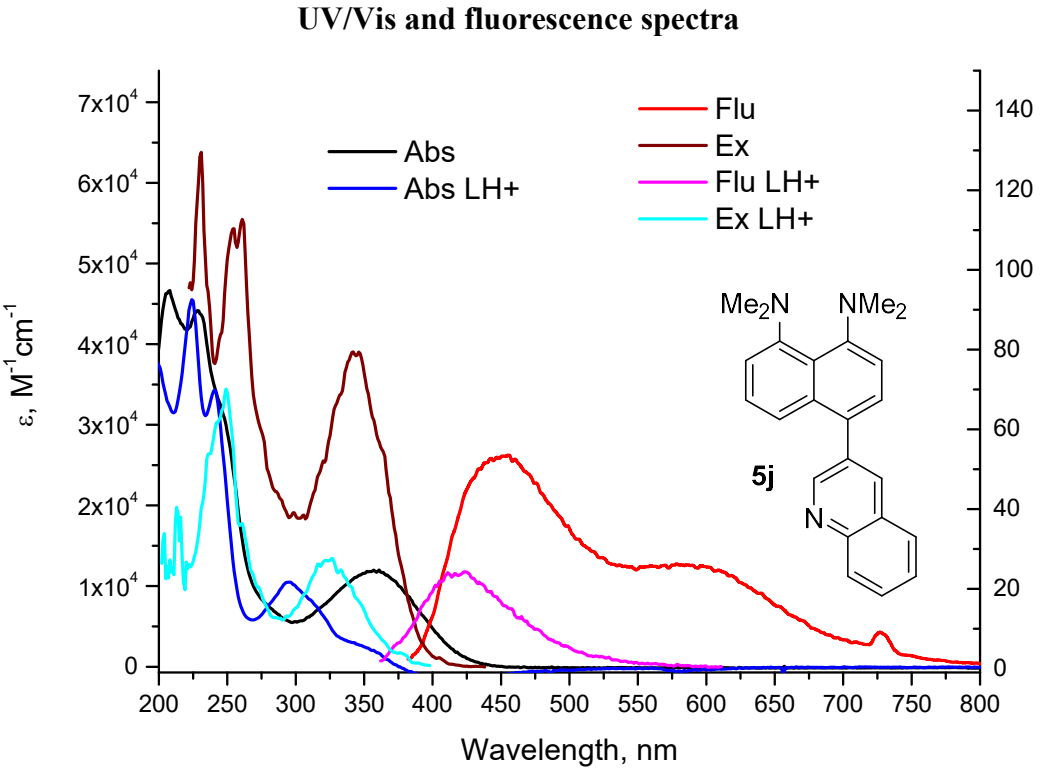

Fig. S55. Absorption, excitation, and emission spectra of **5j** (L) and its protonated form **5j-H**$^+$ (LH+) in MeCN, T = 293 K.

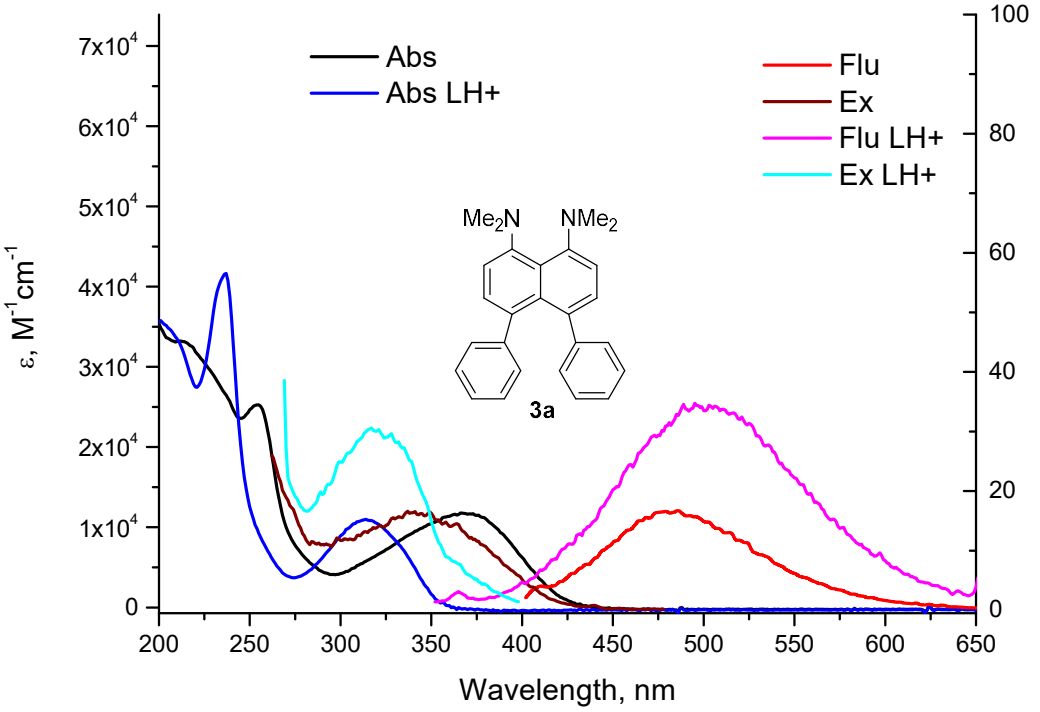

Fig. S56. Absorption, excitation, and emission spectra of **3a** (L) and its protonated form **3a-H**$^+$ (LH+) in MeCN, T = 293 K.

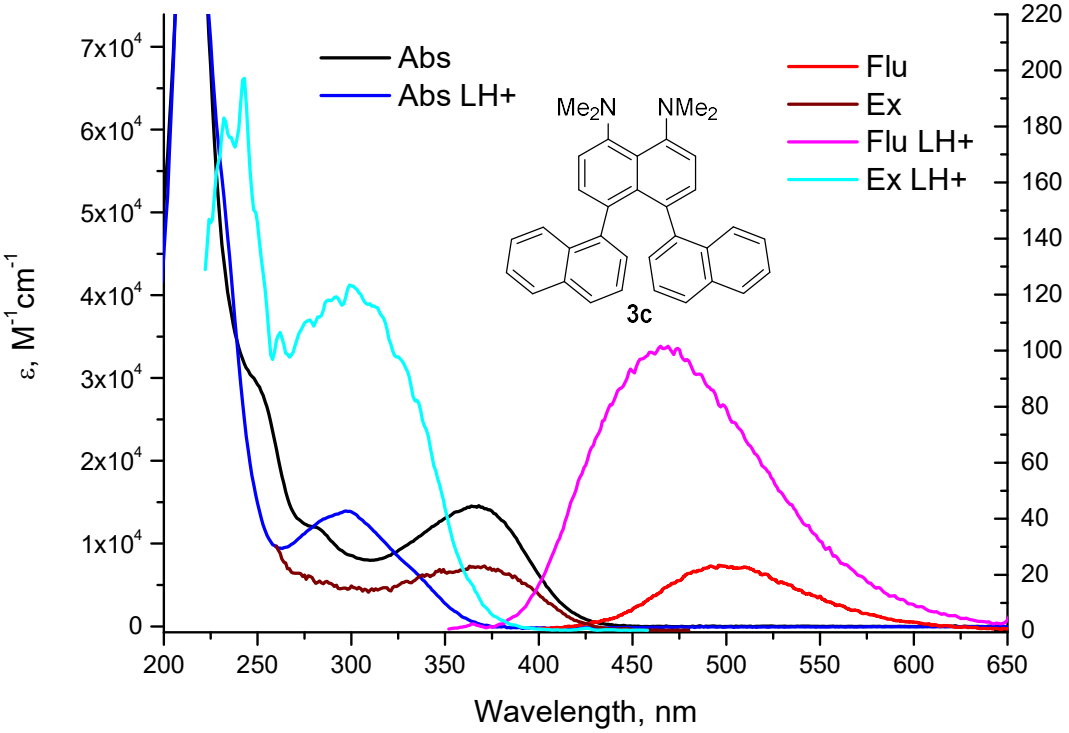

Fig. S57. Absorption, excitation, and emission spectra of **3c** (L) and its protonated form **3c-H**$^+$ (LH+) in MeCN, T = 293 K.

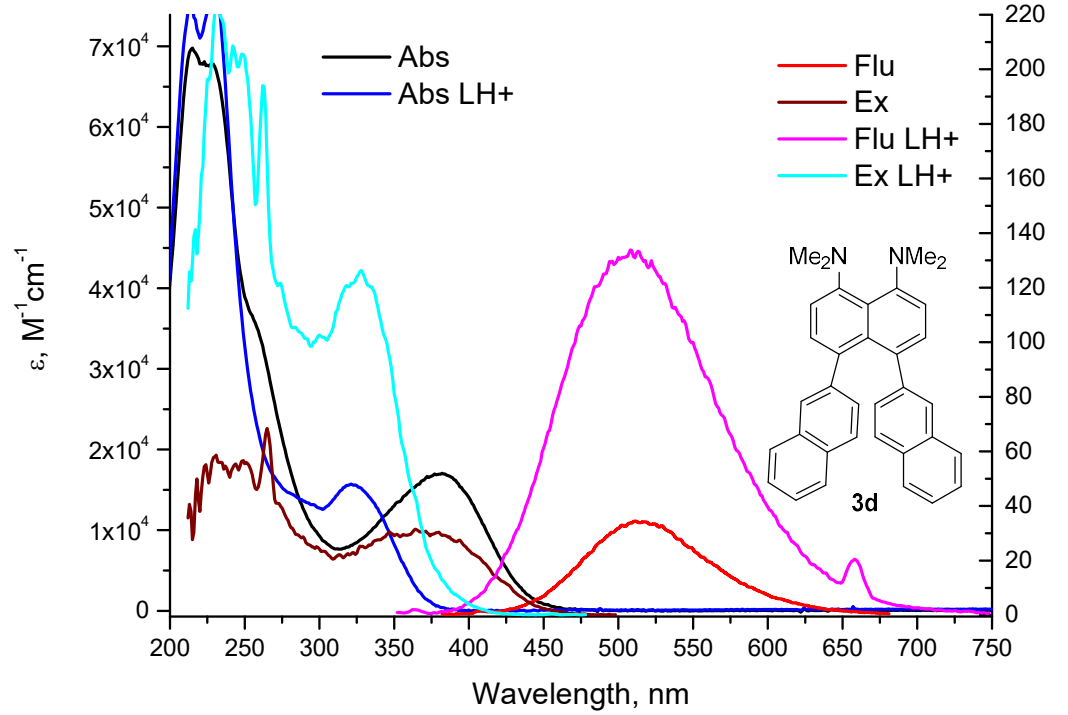

Fig. S58. Absorption, excitation, and emission spectra of **3d** (L) and its protonated form **3d-H**$^+$ (LH+) in MeCN, T = 293 K.