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Supporting Information

for

Synthesis, structure, and properties of switchable cross-conjugated 1,4-diaryl-1,3-butadiynes based on 1,8-bis(dimethylamino)naphthalene

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Experimental section

Table of contents

General information

^{1}H and ^{13}C NMR spectra were recorded on 250 and 600 MHz spectrometers. Chemical shifts were reported in ppm relative to Me_4Si. The UV/Vis spectra of oligomers were recorded on a Varian Cary 50 Probe spectrophotometer in $CHCl_3$ and CH_3CN. The HR-ESI mass-spectra were obtained on a BRUKER maXis spectrometer equipped with an electrospray ionization (ESI) source. Melting points were determined on a Stuart SMP30 instrument in glass capillaries and are uncorrected. Flash column chromatography was performed on Al_2O_3. Commercial aryl- and (trimethylsilyl)acetylenes, amines, $Pd(PPh_3)_2Cl_2$, Pd_2dba_3, anhydrous DMSO were used as received. 2,7-Diiodo-1,8-bis(dimethylamino)naphthalene (**8**) was synthesized as it was described earlier.[1] Copper(I) acetylides were prepared from the corresponding alkynes according to the published procedure.[2]

Experimental procedures and characterization data

2-Iodo-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-(phenylethynyl)naphthalene-1,8-diamine (7a) and *N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-2,7-bis(phenylethynyl)-naphthalene-1,8-diamine (9a)

Method A. To a solution of 2,7-diiodo-1,8-bis(dimethylamino)naphthalene (**8**, 513 mg, 1.1 mmol) in dry pyridine (5 mL) dry copper(I) phenylacetylide (82 mg, 0.5 mmol) was added under argon. The reaction mixture was stirred at 80 °C for 20 h. The solvent was evaporated to dryness. The residue was purified by flash column chromatography on Al_2O_3 (2 × 20 cm) with *n*-hexane as the eluent. The first yellow fraction with R_f = 0.3–0.4 gave 114 mg (52%) of compound **7a**. The second yellow fraction with R_f = 0.1 gave 19 mg (18%) of compound **9a**.

Method B. A mixture of 2,7-diiodo-1,8-bis(dimethylamino)naphthalene (**8**, 513 mg, 1.1 mmol), CuI (9.5 mg, 0.05 mmol), Pd_2dba_3 (18 mg, 0.02 mmol), Ph_3P (39 mg, 0.15 mmol), dry DMSO (5 mL) and Et_3N (3 mL) were stirred for 20 min at 60 °C under argon. To the reaction mixture a solution of ethynylbenzene (52 mg, 0.5 mmol) in Et_3N (2 mL) was then added in portions over 1.5 h. The stirring was continued for 15 h at 60 °C. The reaction mixture was then evaporated without heating to remove the Et_3N. The residue was diluted with water (50 mL) and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and filtered. The solvent was evaporated to dryness. Flash column chromatography was then carried out similarly to *Method A*. Yield **7a**: 136 mg (62%); **9a**: 31 mg (30%).

Compound **7a** was obtained as a yellow solid, mp 105–106 °C (*n*-hexane). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.97 (s, 6 H), 3.12 (s, 6 H), 7.19 (d, J = 8.6 Hz, 1 H), 7.34–7.46 (m, 4 H), 7.49 (d, J = 8.4 Hz, 1 H), 7.53–7.61 (m, 2 H), 7.83 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 43.6, 45.6, 90.0, 95.6, 103.2, 119.1, 124.0, 125.5, 126.6, 128.4, 128.6, 131.2, 131.4, 131.8, 137.3(2), 137.3(3), 151.1, 152.4 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 287 [4.70], 301 [4.66], 332 sh [4.13], 390 sh [3.73] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{22}IN_2^+$ [M+H$^+$]: 441.0823, found 441.0826.

Compound **9a** was obtained as a yellow solid, mp 156–157 °C (EtOH). UV/Vis ($CHCl_3$): λ_{max} [log ε]: 312 [4.83], 321 [4.84], 378 sh [3.96], 405 [4.05] nm. The compound was identical to that previously obtained in our laboratory.[3]

2-Iodo-7-((4-methoxyphenyl)ethynyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (7b) and 2,7-bis((4-methoxyphenyl)ethynyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine (9b)

Method A. Compounds **7b** and **9b** were synthesized similarly to **7a** and **9a** using copper(I) (4-methoxyphenyl)acetylide (97 mg, 0.5 mmol). Flash column chromatography was carried out on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent. The first yellow fraction with R_f = 0.3–0.4 gave compound **7b** (96 mg, 41%). The second yellow fraction was eluted using CH_2Cl_2. Fraction with R_f = 0.3 gave compound **9b** (3 mg, 2.5%).

Method B. Compounds **7b** and **9b** were synthesized similarly to **7a** and **9a** using 1-ethynyl-4-methoxybenzene (66 mg, 0.5 mmol). The purification was carried out similarly to *Method A*. Yield **7b**: 120 mg (51%); **9b**: 25 mg (21%).

Compound **7b** was obtained as a yellow solid, mp 111–112 °C (*n*-hexane). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.97 (s, 6 H), 3.11 (s, 6 H), 3.85 (s, 3 H), 6.92 (d, J = 8.3 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 1 H), 7.42 (d, J = 8.3 Hz, 1 H), 7.45–7.59 (m, 3 H), 7.83 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 43.6, 45.6, 55.5, 88.6, 95.7, 103.4, 114.2, 116.1, 119.5, 125.5, 126.6, 131.4, 132.0, 132.6, 137.0(9), 137.1(2), 151.0, 152.0, 159.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 293–307 [4.66], 342 [4.31], 394 sh [3.65] nm. HRMS (ESI): *m/z* calcd. for $C_{23}H_{24}IN_2O^+$ [M+H$^+$]: 471.0928, found 471.0928.

Compound **9b** was obtained as a yellow solid, mp 161–163 °C ($CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.16 (s, 12 H), 3.84 (s, 6 H), 6.86–6.94 (m, 4 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H), 7.45–7.53 (m, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.9, 55.5, 89.4, 94.5, 114.2, 116.5, 117.4, 123.6, 126.6, 131.3, 132.5, 137.3, 152.4, 159.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 317–323 [4.89], 386 [4.07], 402 [4.06] nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{31}N_2O_2^+$ [M+H$^+$]: 475.2380, found 475.2386.

2-Iodo-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-((4-(trifluoromethyl)phenyl)ethynyl)naphthalene-1,8-diamine (7c) and *N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-2,7-bis((4-(trifluoromethyl)phenyl)ethynyl)naphthalene-1,8-diamine (9c)

Method A. Compounds **7c** and **9c** were synthesized similarly to **7a** and **9a** using copper(I) (4-(trifluoromethyl)phenyl)acetylide (116 mg, 0.5 mmol). Flash column chromatography was carried out on Al_2O_3 (2 × 20 cm) with *n*-hexane as the eluent. The first yellow fraction with R_f = 0.5 gave compound **7c** (114 mg, 45 %). The second yellow fraction with R_f = 0.1–0.2 gave compound **9c** (15 mg, 11 %).

Method B. Compounds **7c** and **9c** were synthesized similarly to **7a** and **9a** using 1-ethynyl-4-(trifluoromethyl)benzene (85 mg, 0.5 mmol). The purification was carried out similarly to *Method A*. Yield **7c**: 135 mg (53 %); **9c**: 30 mg (22 %).

Compound **7c** was obtained as a yellow solid, mp 87–88 °C (EtOH). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.99 (s, 6 H), 3.12 (s, 6 H), 7.19 (d, J = 8.4 Hz, 1 H), 7.43 (d, J = 8.4 Hz, 1 H), 7.49 (d, J = 8.4 Hz, 1 H), 7.65 (s, 4 H), 7.85 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 43.7, 45.7, 92.5, 94.1, 102.7, 118.1, 124.1 (q, J = 272.1 Hz), 125.4(8), 125.5(4) (q, J = 3.7 Hz), 126.5, 127.8, 130.0 (q, J = 32.6 Hz), 131.2, 131.3, 131.5, 137.6, 137.8, 151.2, 152.9 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 289 [4.86], 306 [4.84], 343 [4.76], 369 sh [4.66] nm. HRMS (ESI): *m/z* calcd. for $C_{23}H_{21}F_3IN_2^+$ [M+H$^+$]: 509.0696, found 509.0703.

Compound **9c** was obtained as a yellow solid, mp 148–149 °C (EtOH). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.19 (s, 12 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.41 (d, J = 8.3 Hz, 2 H), 7.63 (s, 8 H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 45.1, 93.4 (2C), 115.7, 123.3, 124.2 (q, J = 272.1 Hz), 125.4(8) (q, J = 3.8 Hz), 125.4(9), 128.1, 129.7 (q, J = 32.6 Hz), 131.2, 131.8, 138.3, 153.2 ppm. UV/Vis (CHCl$_3$): λ_{max} [log ε]: 296 [4.71], 316 [4.78], 329 [4.83], 374 sh [4.07], 415 [4.19] nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{25}F_6N_2^+$ [M+H$^+$]: 551.1917, found 551.1906.

4-((1,8-Bis(dimethylamino)-7-iodonaphthalen-2-yl)ethynyl)benzonitrile (7d) and 4,4'-((1,8-bis(dimethylamino)naphthalene-2,7-diyl)bis(ethyne-2,1-diyl))dibenzonitrile (9d)

Method A. Compounds **7d** and **9d** were synthesized similarly to **7a** and **9a** using copper(I) (4-cyanophenyl)acetylide (95 mg, 0.5 mmol). Flash column chromatography was carried out on Al$_2$O$_3$ (2 × 20 cm) with *n*-hexane/CH$_2$Cl$_2$ 5:1 (v/v) as the eluent. The first yellow fraction with R_f = 0.3 gave compound **7d** (56 mg, 24%). The second yellow fraction with R_f = 0.6–0.7 was eluted using CH$_2$Cl$_2$. From it compound **9d** was isolated (10 mg, 9%).

Method B. Compounds **7d** and **9d** were synthesized similarly to **7a** and **9a** using 4-ethynylbenzonitrile (64 mg, 0.5 mmol). The purification was carried out similarly to *Method A*. Yield **7d**: 114 mg (49%); **9d**: 30 mg (26%).

Compound **7d** was obtained as a yellow solid, mp 153–155 °C (EtOH). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.98 (s, 6 H), 3.11 (s, 6 H), 7.19 (d, J = 8.6 Hz, 1 H), 7.40 (d, J = 8.4 Hz, 1 H), 7.48 (d, J = 8.4 Hz, 1 H), 7.59–7.69 (m, 4 H), 7.85 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 43.7, 45.8, 93.8, 94.7, 102.4, 111.5, 117.6, 118.7, 125.4, 126.4, 128.9, 131.1, 131.3, 131.5, 132.3, 137.7, 138.0, 151.2, 153.1 ppm. UV/Vis (CHCl$_3$): λ_{max} [log ε]: 284 [4.63], 300 sh [4.61], 314 sh [4.58], 343 sh [4.33], 418 sh [3.80] nm. HRMS (ESI): *m/z* calcd. for $C_{23}H_{21}IN_3^+$ [M+H$^+$]: 466.0775, found 466.0770.

Compound **9d** was obtained as an orange solid, mp 211–212 °C (EtOH). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 3.18 (s, 12 H), 7.32 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.56–7.68 (m, 8 H) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 45.2, 93.3, 95.6, 111.2, 115.0, 118.8, 123.2, 125.0, 129.2, 131.4, 132.0, 132.3, 138.6, 153.4 ppm. UV/Vis (CHCl$_3$): λ_{max} [log ε]: 306 [4.66], 331 [4.65], 343 [4.74], 436 [4.21] nm. HRMS (ESI): *m/z* calcd. for $C_{32}H_{25}N_4^+$ [M+H$^+$]: 465.2074, found 465.2080.

2-Iodo-N^1,N^1,N^8,N^8-tetramethyl-7-((4-nitrophenyl)ethynyl)naphthalene-1,8-diamine (7e) and N^1,N^1,N^8,N^8-tetramethyl-2,7-bis((4-nitrophenyl)ethynyl)naphthalene-1,8-diamine (9e)

Method A. Compounds **7e** and **9e** were synthesized similarly to **7a** and **9a** using copper(I) (4-nitrophenyl)acetylide (105 mg, 0.5 mmol). Flash column chromatography was carried out on Al$_2$O$_3$ (2 × 20 cm) with *n*-hexane/CH$_2$Cl$_2$ 5:1 (v/v) as the eluent. The first orange fraction with R_f = 0.3–0.4 gave compound **7e** (73 mg, 30%). The second red fraction with R_f = 0.6–0.7 was eluted using CH$_2$Cl$_2$. From it compound **9e** was isolated (8 mg, 5%).

Method B. Compounds **7e** and **9e** were synthesized similarly to **7a** and **9a** using 1-ethynyl-4-nitrobenzene (74 mg, 0.5 mmol). The purification was carried out similarly to *Method A*. Yield **7e**: 102 mg (42%); **9e**: 13 mg (10%).

Compound **7e** was obtained as a red solid, mp 121–122 °C (EtOH). ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.99 (s, 6 H), 3.12 (s, 6 H), 7.19 (d, J = 8.5 Hz, 1 H), 7.41 (d, J = 8.5 Hz, 1 H), 7.48 (d, J = 8.5 Hz, 1 H), 7.68 (d, J = 7.9 Hz, 2 H), 7.86 (d, J = 8.5 Hz, 1 H), 8.25 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR

(62.9 MHz, $CDCl_3$): δ = 43.8, 45.8, 93.7, 95.7, 102.2, 117.4, 123.9, 125.4, 126.4, 130.9, 131.1, 131.2, 131.7, 137.8, 138.1, 147.0, 151.3, 153.3 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 273 sh [4.69], 320 [4.54], 357 sh [4.44] nm. HRMS (ESI): *m/z* calcd. for $C_{22}H_{21}IN_3O_2^+$ [M+H$^+$]: 486.0673, found 486.0678.

Compound **9e** was obtained as red-brown crystals with a greenish metallic luster, mp 210–211 °C (DCE). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.21 (s, 12 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.42 (d, *J* = 8.3 Hz, 2 H), 7.65 (d, *J* = 8.8 Hz, 4 H), 8.24 (d, *J* = 8.8 Hz, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.3, 93.2, 96.7, 114.7, 123.1, 123.9, 124.7, 131.2, 131.5, 132.1, 138.8, 146.8, 153.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 287 [4.46], 330 [4.66], 365 sh [4.53], 465 [4.28] nm. HRMS (ESI): *m/z* calcd. for $C_{30}H_{25}N_4O_4^+$ [M+H$^+$]: 505.1871, found 505.1867.

***N*^{1},*N*^{1},*N*^{8},*N*^{8}-Tetramethyl-2-(phenylethynyl)-7-((trimethylsilyl)ethynyl)naphthalene-1,8-diamine (10a) and 2-ethynyl-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-(phenylethynyl)naphthalene-1,8-diamine (6a)**

A mixture of iodide **7a** (88 mg, 0.2 mmol), CuI (4 mg, 0.02 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), dry DMSO (4 mL) and Et_3N (4 mL) was stirred at 80 °C for 20 min under argon. To the reaction mixture trimethylsilylacetylene (58 mg, 0.08 mL, 0.6 mmol) was then added in portions over 1 h. The stirring was continued for 15 h at 80 °C. The reaction mixture was then evaporated without heating to remove the Et_3N. The residue was diluted with water (50 mL) and extracted with CH_2Cl_2 (5 × 20 mL). The combined organic extracts were dried over Na_2SO_4 and filtered. The solvent was evaporated to dryness. The residue was treated with *n*-hexane (30 mL) and filtered; the filtrate was evaporated to dryness. The crude product was recrystallized from EtOH. Yield: 74 mg (90%). Compound **10a** was obtained as a yellow solid, mp 132–133 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 3.11 (s, 6 H), 3.16 (s, 6 H), 7.24–7.44 (m, 7 H), 7.52–7.58 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.1, 44.8, 45.0, 90.8, 94.6, 99.5, 106.4, 116.4, 116.6, 123.2, 123.3, 124.3, 126.0, 128.1, 128.5, 131.1, 131.6, 131.9, 137.8, 152.8, 153.5 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 281 [4.57], 294 [4.74], 298 sh [4.73], 312 [4.80], 331 sh [4.06], 370 [3.93], 400 [3.98] nm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{31}N_2Si^+$ [M+H$^+$]: 411.2251, found 411.2254.

The column chromatography of crude product **10a** on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent led to its full desilylation and formation of terminal alkyne **6a**. Compound **6a** was obtained as a yellow solid, mp 85–86 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.13 (s, 6 H), 3.17 (s, 6 H), 3.39 (s, 1 H), 7.28–7.44 (m, 7 H), 7.52–7.59 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.9, 45.0, 82.6, 84.8, 90.7, 94.7, 115.6, 116.7, 123.3, 123.4, 124.3, 126.0, 128.1, 128.5, 131.1, 131.7, 132.0, 137.9, 152.8, 153.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 291 [4.68], 296 [4.67], 308 [4.77], 393 [3.98] nm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{23}N_2^+$ [M+H$^+$]: 339.1856, found 339.1860.

2-((4-Methoxyphenyl)ethynyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-((trimethylsilyl)ethynyl)naphthalene-1,8-diamine (10b) and 2-ethynyl-7-((4-methoxyphenyl)ethynyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-naphthalene-1,8-diamine (6b)

Compound **10b** was obtained similarly to **10a** starting from iodide **7b** (94 mg, 0.2 mmol). Yield: 70 mg (80%). Compound **10b** was obtained as a yellow solid, mp 145–146 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 3.11 (s, 6 H), 3.14 (s, 6 H), 3.84 (s, 3 H), 7.86–7.94 (m, 2 H), 7.24–7.34 (m, 3 H), 7.38 (d, *J* = 8.2 Hz, 1 H), 7.45–7.52 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.1, 44.8, 44.9, 55.5, 89.4, 94.6, 99.5, 106.5, 114.2, 116.5, 116.6, 117.2, 123.3, 123.4, 126.3, 131.6, 131.7, 132.5, 137.6, 152.5, 153.5, 159.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 302 sh [4.73], 315 [4.80], 340 sh [4.15], 375 [4.00], 398 [4.00] nm. HRMS (ESI): *m/z* calcd. for $C_{28}H_{33}N_2OSi^+$ [M+H$^+$]: 441.2357, found 441.2364.

The column chromatography of crude product **10b** on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent led to its full desilylation and formation of terminal alkyne **6b**. Compound **6b** was obtained as a yellow solid, mp 121–122 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (s, 6 H), 3.15 (s, 6 H), 3.38 (s, 1 H), 3.84 (s, 3 H), 6.90 (d, J = 8.2 Hz, 2 H), 7.27–7.43 (m, 4 H), 7.49 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.9, 45.0, 55.5, 82.6, 84.8, 89.3, 94.7, 114.2, 115.7, 116.4, 117.3, 123.4, 123.5, 126.2, 131.7, 131.8, 132.5, 137.7, 152.4, 153.6, 159.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 297 sh [4.63], 312 [4.72], 338 sh [4.05], 405 sh [3.92] nm. HRMS (ESI): *m/z* calcd. for $C_{25}H_{25}N_2O^+$ [M+H$^+$]: 369.1961, found 369.1967.

N^1,*N*^{1},*N*^{8},*N*^{8}-Tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)-7-((trimethylsilyl)ethynyl)-naphthalene-1,8-diamine (10c) and 2-ethynyl-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-((4-(trifluoromethyl)-phenyl)ethynyl)naphthalene-1,8-diamine (6c)

Compound **10c** was obtained similarly to **10a** starting from iodide **7c** (102 mg, 0.2 mmol). Yield: 81 mg (85%). Compound **10c** was obtained as a yellow solid, mp 136–137 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 3.11 (s, 6 H), 3.16 (s, 6 H), 7.23–7.41 (m, 4 H), 7.62 (s, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.1, 44.9, 45.1, 93.2, 93.5, 99.8, 106.4, 115.6, 116.5, 123.1, 123.3, 124.2 (q, J = 272.1 Hz), 125.5 (q, J = 3.8 Hz), 125.7, 128.2, 129.6 (q, J = 32.6 Hz), 131.2, 131.5, 132.3, 138.2, 153.3, 153.5 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 280 sh [4.55], 294 [4.69], 304 sh [4.64], 316 [4.71], 408 [4.02] nm. HRMS (ESI): *m/z* calcd. for $C_{28}H_{30}F_3N_2Si^+$ [M+H$^+$]: 479.2125, found 479.2127.

The column chromatography of crude product **10c** on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent led to its full desilylation and formation of terminal alkyne **6c**. Compound **6c** was obtained as a yellow solid, mp 78–79 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (s, 6 H), 3.17 (s, 6 H), 3.39 (s, 1 H), 7.27–7.42 (m, 4 H), 7.62 (s, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.9, 45.1, 82.8, 84.7, 93.3, 93.4, 115.6, 115.7, 123.3, 123.4, 124.2 (q, J = 272.1 Hz), 125.5 (q, J = 3.9 Hz), 125.7, 128.1, 129.7 (q, J = 32.6 Hz), 131.2, 131.6, 132.5, 138.2, 153.3, 153.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 276 sh [4.58], 291 [4.70], 299 sh [4.68], 313 [4.75], 400 [4.08] nm. HRMS (ESI): *m/z* calcd. for $C_{25}H_{22}F_3N_2^+$ [M+H$^+$]: 407.1730, found 407.1730.

4-((1,8-Bis(dimethylamino)-7-((trimethylsilyl)ethynyl)naphthalen-2-yl)ethynyl)benzonitrile (10d) and 4-((1,8-bis(dimethylamino)-7-ethynylnaphthalen-2-yl)ethynyl)benzonitrile (6d)

Compound **10d** was obtained similarly to **10a** starting from iodide **7d** (93 mg, 0.2 mmol). Yield: 72 mg (83%). Compound **10d** was obtained as a yellow solid, mp 170–172 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 3.11 (s, 6 H), 3.15 (s, 6 H), 7.22–7.38 (m, 4 H), 7.56–7.67 (m, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.0, 44.9, 45.1, 93.0, 95.8, 99.8, 106.3, 111.0, 114.9, 116.3, 118.8, 123.0, 123.2, 125.3, 129.3, 131.4 (2C), 132.2, 132.5, 138.3, 153.5 (2C) ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 283 sh [4.56], 294 [4.62], 307 [4.62], 325 [4.63], 413 [4.06], 442 sh [3.98] nm. HRMS (ESI): *m/z* calcd. for $C_{28}H_{29}N_3Si^+$ [M+H$^+$]: 436.2204, found 436.2206.

The column chromatography of crude product **10d** on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent led to its full desilylation and formation of terminal alkyne **6d**. Compound **6d** was obtained as a yellow solid, mp 138–139 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (s, 6 H), 3.16 (s, 6 H), 3.39 (s, 1 H), 7.26–7.39 (m, 4 H), 7.56–7.67 (m, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 44.9, 45.2, 82.9, 84.6, 93.1, 95.7, 111.0, 115.0, 115.4, 118.8, 123.1, 123.2, 125.3, 129.2, 131.4, 131.5, 132.2, 132.7, 138.4, 153.4, 153.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 288 [4.60], 307 [4.62], 321 [4.64], 407 [4.08], 441 sh [4.08] nm. HRMS (ESI): *m/z* calcd. for $C_{25}H_{22}N_3^+$ [M+H$^+$]: 364.1808, found 364.1814.

***N*^{1},*N*^{1},*N*^{8},*N*^{8}-Tetramethyl-2-((4-nitrophenyl)ethynyl)-7-((trimethylsilyl)ethynyl)naphthalene-1,8-diamine (10e) and 2-ethynyl-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-7-((4-nitrophenyl)ethynyl)naphthalene-1,8-diamine (6e)**

Compound **10e** was obtained similarly to **10a** starting from iodide **7e** (97 mg, 0.2 mmol). Yield: 76 mg (83%). Compound **10e** was obtained as a red solid, mp 142–144 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 3.12 (s, 6 H), 3.17 (s, 6 H), 7.23–7.39 (m, 4 H), 7.60–7.68 (m, 2 H), 8.19–8.27 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.0, 44.9, 45.2, 93.0, 97.0, 99.9, 106.2, 114.6, 116.3, 122.9, 123.2, 123.9, 125.2, 131.3(5), 131.3(9), 131.5, 132.7, 138.4, 146.7, 153.5, 153.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 281 sh [4.54], 290 [4.60], 331 [4.47], 408 [4.03], 460 sh [3.86] nm. HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}N_3O_2Si^+$ [M+H$^+$]: 456.2102, found 456.2103.

The column chromatography of crude product **10e** on Al_2O_3 (2 × 20 cm) with *n*-hexane/CH_2Cl_2 5:1 (v/v) as the eluent led to its full desilylation and formation of terminal alkyne **6e**. Compound **6e** was obtained as a red solid, mp 118–119 °C (EtOH). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.12 (s, 6 H), 3.17 (s, 6 H), 3.39 (s, 1 H), 7.26–7.40 (m, 4 H), 7.60–7.68 (m, 2 H), 8.19–8.26 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 45.0, 45.2, 82.9, 84.6, 93.0, 96.9, 114.8, 115.4, 123.1, 123.2, 123.9, 125.2, 131.3, 131.4(9), 131.5(2), 132.8, 138.5, 146.8, 153.6, 153.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 275 sh [4.52], 284 [4.56], 328 [4.49], 404 [4.05], 456 sh [3.92] nm. HRMS (ESI): *m/z* calcd. for $C_{24}H_{22}N_3O_2^+$ [M+H$^+$]: 384.1707, found 384.1713.

7,7'-(Buta-1,3-diyne-1,4-diyl)bis(*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethyl-2-(phenylethynyl)naphthalene-1,8-diamine) (5a)

A mixture of alkyne **6a** (94 mg, 0.28 mmol), CuI (29 mg, 0.15 mmol), TMEDA (45 µL, 0.3 mmol) and diisopropylamine (5 mL) was stirred at room temperature for 20 h under air. The reaction mixture was then evaporated without heating to remove diisopropylamine. The residue was purified by flash column chromatography on Al_2O_3 (2 × 20 cm) using CH_2Cl_2 as the eluent. The orange fraction with R_f = 0.3 gave compound **5a** (59 mg, 63%) as a yellow-orange solid, mp 208−209 °C (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.18(0) (s, 12 H), 3.18(1) (s, 12 H), 7.27 (dd, *J* = 8.3, 0.5 Hz, 2 H), 7.30 (dd, *J* = 8.2, 0.5 Hz, 2 H), 7.32–7.39 (m, 8 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 7.53–7.55 (m, 2 H), 7.55–7.56 (m, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.0, 45.2, 80.2, 84.1, 90.8, 94.8, 114.7, 116.4, 123.0, 123.1, 124.3, 125.2, 128.1, 128.6, 131.1, 131.8, 132.1, 138.1, 152.7, 154.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 308 sh [4.93], 323 [5.04], 337 sh [4.92], 432 [4.51] nm. HRMS (ESI): *m/z* calcd. for $C_{48}H_{43}N_4^+$ [M+H$^+$]: 675.3482, found 675.3482; calcd. for $C_{48}H_{44}N_4^{2+}$ [M+2H$^+$]: 338.1778, found 338.1771.

7,7'-(Buta-1,3-diyne-1,4-diyl)bis(2-((4-methoxyphenyl)ethynyl)-*N*^{1},*N*^{1},*N*^{8},*N*^{8}-tetramethylnaphthalene-1,8-diamine) (5b)

Compound **5b** was obtained similarly to **5a** starting from alkyne **6b** (103 mg, 0.28 mmol). Yield: 66 mg (64%). Compound **5b** was obtained as a yellow-orange solid, mp 204–205 °C (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.16 (s, 12 H), 3.17 (s, 12 H), 3.84 (s, 6 H), 6.90 (m, 4 H), 7.27 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 7.47–7.49 (m, 4 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.0, 45.2, 55.5, 80.2, 84.1, 89.4, 94.7, 114.3, 114.8, 116.5, 116.9, 123.1, 123.2, 125.5, 131.6, 132.1, 132.5, 137.9, 152.4, 154.6, 159.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 327 [5.10], 338 sh [5.02], 423 [4.54] nm. HRMS (ESI): *m/z* calcd. for $C_{50}H_{47}N_4O_2^{+}$ [M+H$^+$]: 735.3694, found 735.3694; calcd. for $C_{50}H_{48}N_4O_2^{2+}$ [M+2H$^+$]: 368.1883, found 368.1883.

7,7'-(Buta-1,3-diyne-1,4-diyl)bis(N^1,N^1,N^8,N^8-tetramethyl-2-((4-(trifluoromethyl)phenyl)ethynyl)naphthalene-1,8-diamine) (5c)

Compound **5c** was obtained similarly to **5a** starting from alkyne **6c** (101 mg, 0.25 mmol). Yield: 65 mg (64%). Compound **5c** was obtained as a yellow solid, mp 224–225 °C (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.18(0) (s, 12 H), 3.18(3) (s, 12 H), 7.27 (dd, *J* = 8.3, 0.5 Hz, 2 H), 7.30 (dd, *J* = 8.3, 0.5 Hz, 2 H), 7.37–7.40 (m, 4 H), 7.62 (s, 8 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.1, 45.2, 80.3, 84.1, 93.4, 93.5, 114.6, 115.3, 123.0, 123.1, 124.2 (q, *J* = 272.1 Hz), 124.9, 125.5 (q, *J* = 3.7 Hz), 128.1, 129.7 (q, *J* = 32.6 Hz), 131.2, 132.0, 132.2, 138.5, 153.2, 154.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 315 sh [4.99], 327 [5.06], 340 sh [4.98], 437 [4.64] nm. HRMS (ESI): *m/z* calcd. for $C_{50}H_{41}F_6N_4^{+}$ [M+H$^+$]: 811.3230, found 811.3230; calcd. for $C_{50}H_{42}F_6N_4^{2+}$ [M+2H$^+$]: 406.1651, found 406.1659.

4,4'-((Buta-1,3-diyne-1,4-diylbis(1,8-bis(dimethylamino)naphthalene-7,2-diyl))bis(ethyne-2,1-diyl))-dibenzonitrile (5d)

Compound **5d** was obtained similarly to **5a** starting from alkyne **6d** (109 mg, 0.3 mmol). Yield: 72 mg (66%). Compound **5d** was obtained as an orange solid, mp 230–232 °C (decomp.) (DCE). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.17 (s, 12 H), 3.18 (s, 12 H), 7.26 (dd, *J* = 8.3, 0.5 Hz, 2 H), 7.29 (dd, *J* = 8.3, 0.5 Hz, 2 H), 7.37 (d, *J* = 7.0 Hz, 2 H), 7.39 (d, *J* = 7.0 Hz, 2 H), 7.58–7.60 (m, 4 H), 7.63–7.66 (m, 4 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.1(8), 45.2(4), 80.3, 84.0, 93.2, 95.8, 111.2, 114.4, 114.7, 118.8, 122.9, 123.0, 124.6, 129.2, 131.4, 131.9, 132.3, 132.5, 138.6, 153.4, 154.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 318 [5.04], 326 [5.04], 338 [5.06], 385 sh [4.51], 449 [4.54] nm. HRMS (ESI): *m/z* calcd. for $C_{50}H_{41}N_6^{+}$ [M+H$^+$]: 725.3387, found 725.3393; calcd. for $C_{50}H_{42}N_6^{2+}$ [M+2H$^+$]: 363.1730, found 363.1726.

7,7'-(Buta-1,3-diyne-1,4-diyl)bis(N^1,N^1,N^8,N^8-tetramethyl-2-((4-nitrophenyl)ethynyl)naphthalene-1,8-diamine) (5e)

Compound **5e** was obtained similarly to **5a** starting from alkyne **6e** (115 mg, 0.3 mmol). Yield: 73 mg (64%). Compound **5e** was obtained as a dark red solid, mp 234–235 °C (decomp.) (DCE). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.18 (s, 12 H), 3.20 (s, 12 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.38–7.40 (m, 4 H), 7.63–7.66 (m, 4 H), 8.22–8.25 (m, 4 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.2, 45.3, 80.4, 84.1, 93.2, 96.9, 114.4, 122.9, 123.0, 123.9, 124.5, 131.3, 131.5, 132.0, 132.6, 138.7, 146.9, 153.5, 154.6 ppm. UV/Vis ($CHCl_3$): λ_{max} [log ε]: 310 [4.83], 332 [4.86], 453 [4.58] nm. HRMS (ESI): *m/z* calcd. for $C_{48}H_{41}N_6O_4^+$ [$M+H^+$]: 765.3184, found 765.3180.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(7-(arylethynyl)-8-(dimethylamino)-*N,N*-dimethylnaphthalen-1-aminium) bis(tetrafluoroborates) (11) (general procedure)

To a solution of compound **5** (0.025 mmol) in CH_2Cl_2 (5–6 mL) 40% aqueous HBF_4 (2.5-fold excess) was added. The 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 and dried in a vacuum giving rise to the desired salt **11**.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(8-(dimethylamino)-N,N-dimethyl-7-(phenylethynyl)naphthalen-1-aminium) bis(tetrafluoroborate) (**11a**) was obtained in 79% as a gray solid (decomp. > 225 °C). ^{1}H NMR (600 MHz, DMSO-d$_6$): 3.45 (d, *J* = 2.1 Hz, 12 H), 3.54 (d, *J* = 2.9 Hz, 12 H), 7.54–7.58 (m, 6 H), 7.75–7.79 (m, 4 H), 7.96 (d, *J* = 8.5 Hz, 2 H), 7.98 (d, *J* = 8.5 Hz, 2 H), 8.21–8.27 (m, 4 H), 19.76 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d$_6$): 42.8, 43.0, 80.8, 82.9, 84.9, 100.8, 116.6, 118.5, 120.7, 120.9, 129.0, 129.6, 129.8, 130.2, 131.4, 132.6, 133.0, 134.9, 143.0, 146.8 ppm. UV/Vis (CH_3CN): λ_{max} [log ε]: 286 sh [4.67], 306 [4.77], 316 [4.77], 328 sh [4.72], 345 [4.49], 371 [4.39], 382 sh [4.28] nm.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(8-(dimethylamino)-7-((4-methoxyphenyl)ethynyl)-N,N-dimethylnaphthalen-1-aminium) bis(tetrafluoroborate) (**11b**) was obtained in 78% as a pale gray solid (decomp. > 222 °C). ^{1}H NMR (600 MHz, DMSO-d$_6$): 3.44 (d, *J* = 2.1 Hz, 12 H), 3.53 (d, *J* = 3.0 Hz, 12 H), 3.85 (s, 6 H), 7.08–7.12 (m, 4 H), 7.69–7.73 (m, 4 H), 7.92 (d, *J* = 8.5 Hz, 2 H), 7.96 (d, *J* = 8.5 Hz, 2 H), 8.21 (d, *J* = 4.2 Hz, 2 H), 8.22 (d, *J* = 4.2 Hz, 2 H), 19.73 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d$_6$): 42.7, 43.0, 55.5, 80.9, 82.9, 84.0, 101.4, 112.8, 114.8, 116.7, 118.9, 120.8, 129.5, 129.7, 132.5, 133.0, 133.2, 134.7, 142.4, 146.8, 160.7 ppm. UV/Vis (CH_3CN): λ_{max} [log ε]: 273 [4.56], 283 [4.56], 309 sh [4.64], 326 [4.75], 341 [4.78], 370 [4.48], 387 sh [4.31] nm.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(8-(dimethylamino)-N,N-dimethyl-7-((4-(trifluoromethyl)-phenyl)ethynyl)naphthalen-1-aminium) bis(tetrafluoroborate) (**11c**) was obtained in 86% as a pale yellow solid (decomp. > 228 °C). ^{1}H NMR (600 MHz, DMSO-d$_6$): 3.47 (d, *J* = 2.2 Hz, 12 H), 3.53 (d, *J* = 2.8 Hz, 12 H), 7.92 (d, *J* = 8.2 Hz, 4 H), 7.96–8.03 (m, 8 H), 8.25 (d, *J* = 8.7 Hz, 2 H), 8.27 (d, *J* = 8.7 Hz, 2 H), 19.73 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d$_6$): 42.9, 43.1, 80.8, 83.0, 87.1, 98.9, 116.7, 118.0, 120.8, 123.8 (q, *J* = 272.5 Hz), 125.2, 125.9 (q, *J* = 3.1 Hz), 129.6, 129.8, 129.9 (q, *J* = 32.1 Hz), 132.3, 132.9, 133.1, 135.1, 143.7, 146.8 ppm. UV/Vis (CH_3CN): λ_{max} [log ε]: 290 sh [4.74], 312 [4.80], 320 [4.80], 331 sh [4.73], 347 sh [4.51], 371 [4.38], 382 sh [4.30] nm.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(7-((4-cyanophenyl)ethynyl)-8-(dimethylamino)-N,N-dimethyl-naphthalen-1-aminium) bis(tetrafluoroborate) (**11d**) was obtained in 76% as a beige solid (decomp. > 227 °C). ^{1}H NMR (600 MHz, DMSO-d$_6$): 3.46 (d, *J* = 2.2 Hz, 12 H), 3.52 (d, *J* = 2.8 Hz, 12 H), 7.95–7.98 (m, 4 H), 7.99–8.01 (m, 4 H), 8.02–8.06 (m, 4 H), 8.25 (d, *J* = 8.8 Hz, 2 H), 8.27 (d, *J* = 8.8 Hz, 2 H), 19.76 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d$_6$): 43.0, 43.1, 80.8, 83.0, 88.3, 98.8, 112.3, 116.7, 117.9, 118.2, 120.7, 125.7, 129.6, 129.8, 132.3, 132.8, 132.9(5), 133.0(4), 135.2, 143.8, 146.8 ppm. UV/Vis (CH_3CN): λ_{max} [log ε]: 285 sh [4.60], 305 sh [4.73], 321 [4.76], 339 [4.71], 371 [4.33], 383 sh [4.24] nm.

2,2'-(Buta-1,3-diyne-1,4-diyl)bis(8-(dimethylamino)-N,N-dimethyl-7-((4-nitrophenyl)ethynyl)-naphthalen-1-aminium) bis(tetrafluoroborate) (**11e**) was obtained in 80% as a gray solid (decomp. > 230 °C). ^{1}H NMR (600 MHz, DMSO-d_6): 3.47 (d, J = 2.3 Hz, 12 H), 3.53 (d, J = 2.8 Hz, 12 H), 8.01 (d, J = 8.5 Hz, 2 H), 8.02 (d, J = 8.5 Hz, 2 H), 8.04–8.07 (m, 4 H), 8.26 (d, J = 8.8 Hz, 2 H), 8.28 (d, J = 8.8 Hz, 2 H), 8.36–8.40 (m, 4 H), 19.77 (s, 2 H) ppm. ^{13}C NMR (62.9 MHz, DMSO-d_6): 43.0, 43.1, 80.8, 83.1, 89.0, 98.5, 116.6, 117.8, 120.8, 124.0, 127.6, 129.7, 129.8, 132.8, 133.0, 133.1, 135.2, 144.0, 146.8, 147.8 ppm. UV/Vis (CH_3CN): λ_{max} [log ε]: 284 sh [4.36], 307 sh [4.46], 325 [4.54], 347 [4.56], 369 sh [4.37], 385 sh [4.19] nm.

Copies of NMR spectra

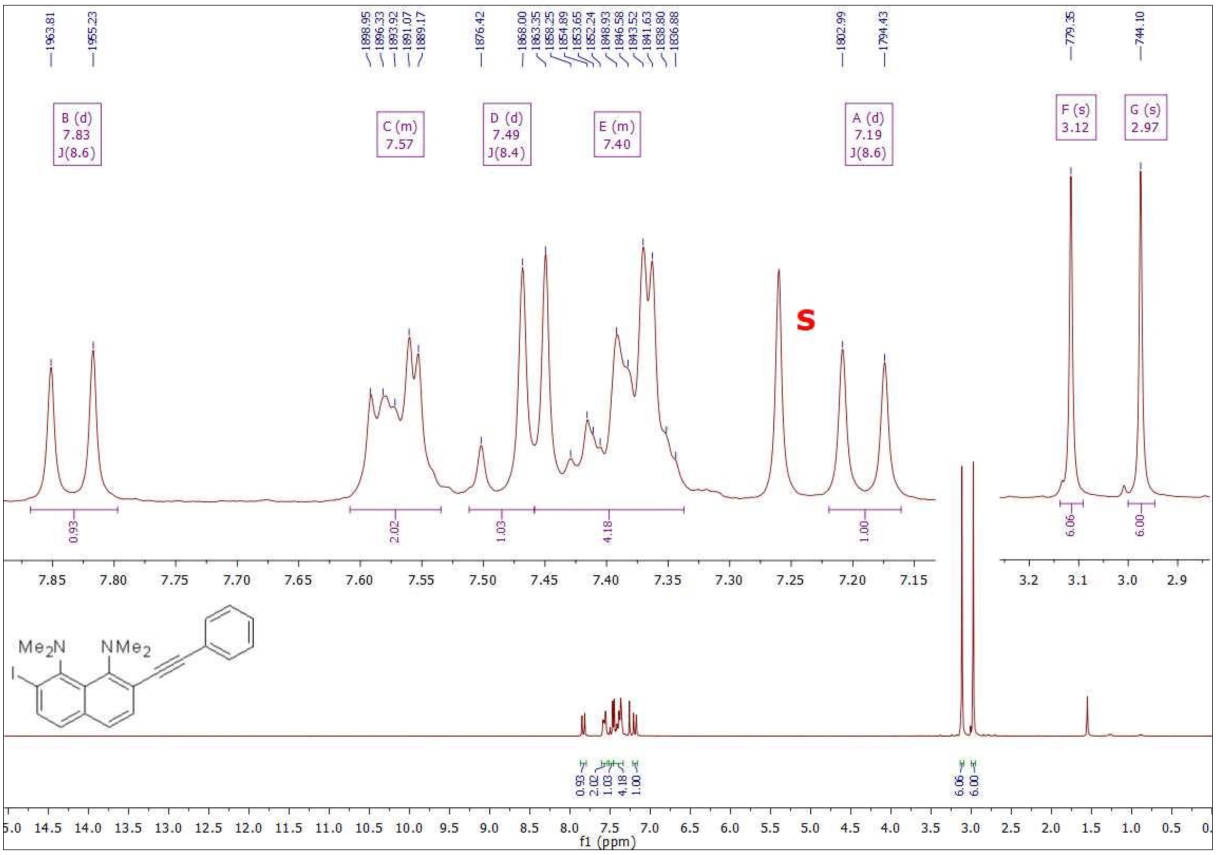

Figure S1. ^{1}H NMR spectrum of compound **7a** (250 MHz, $CDCl_3$).

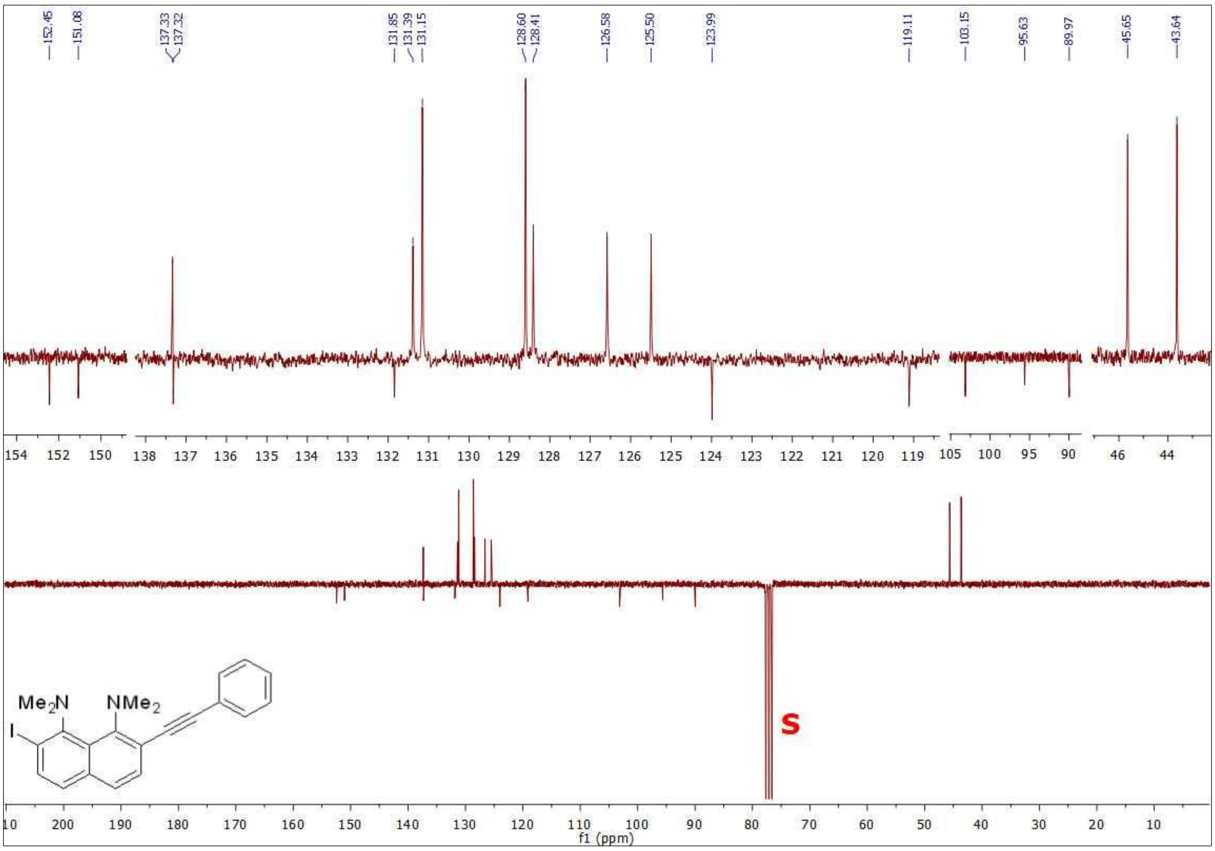

Figure S2. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **7a** (62.9 MHz, $CDCl_3$).

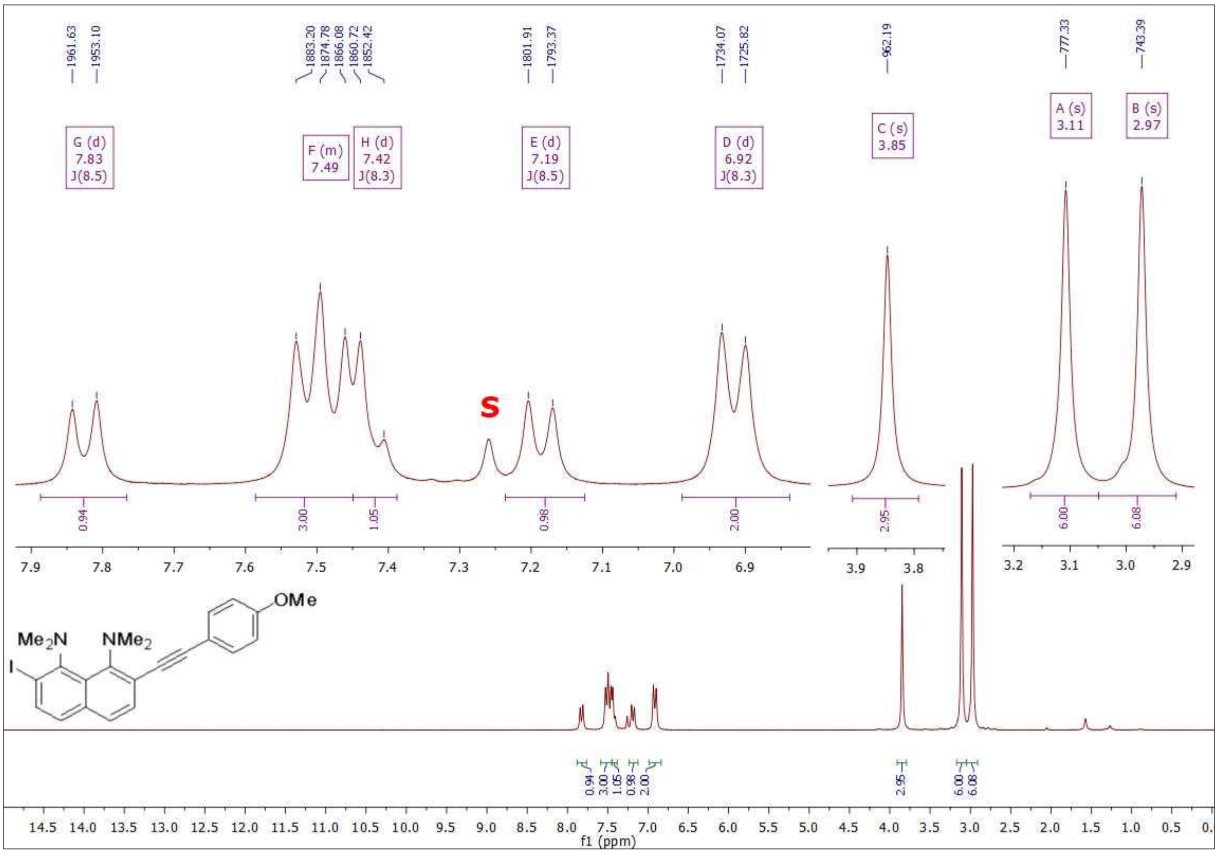

Figure S3. ^{1}H NMR spectrum of compound **7b** (250 MHz, $CDCl_3$).

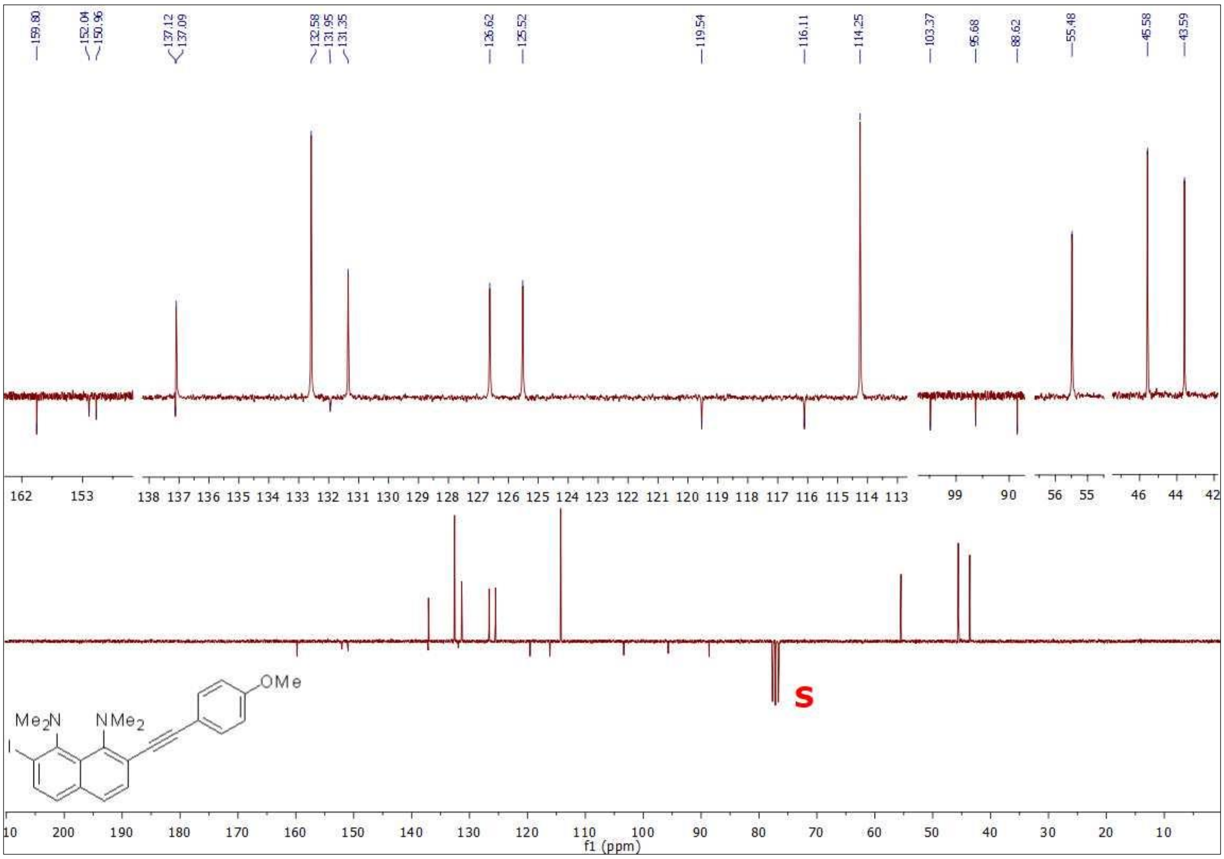

Figure S4. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **7b** (62.9 MHz, $CDCl_3$).

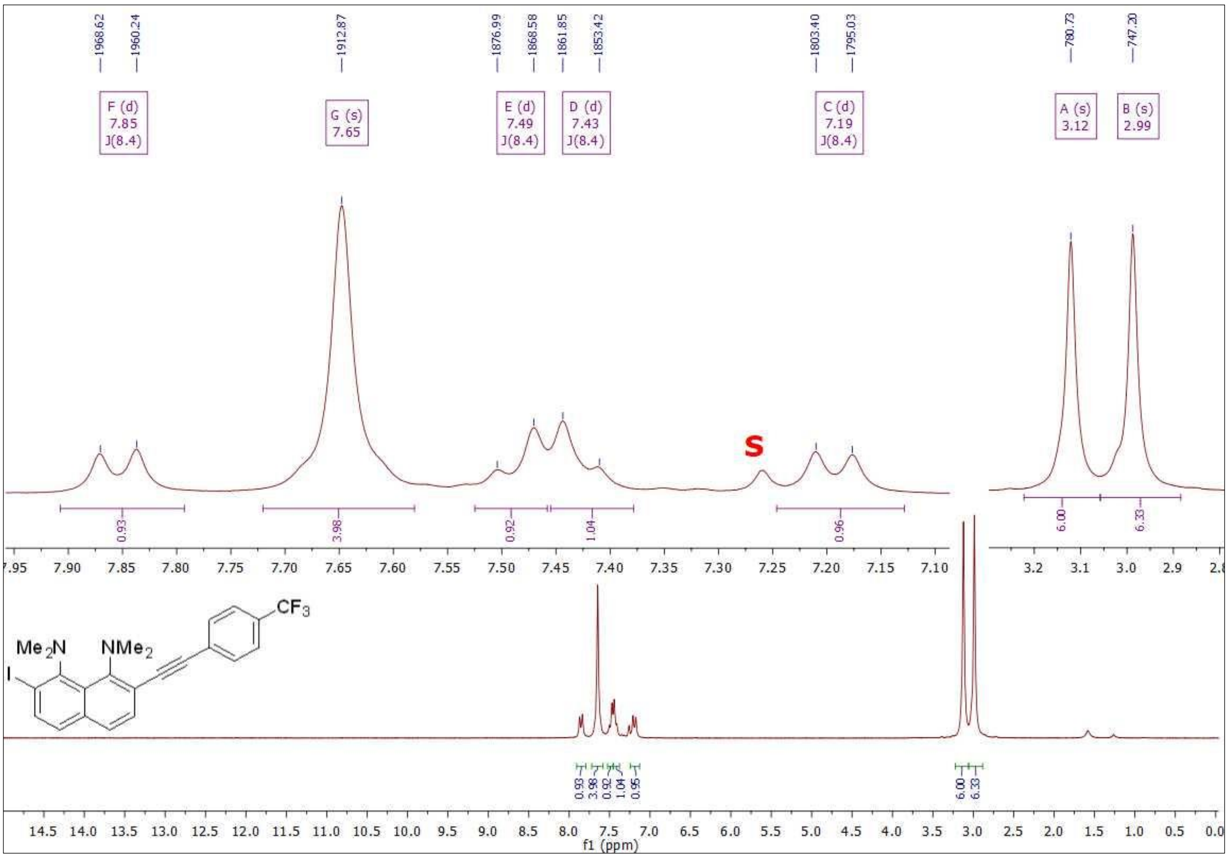

Figure S5. ^{1}H NMR spectrum of compound **7c** (250 MHz, CDCl$_3$).

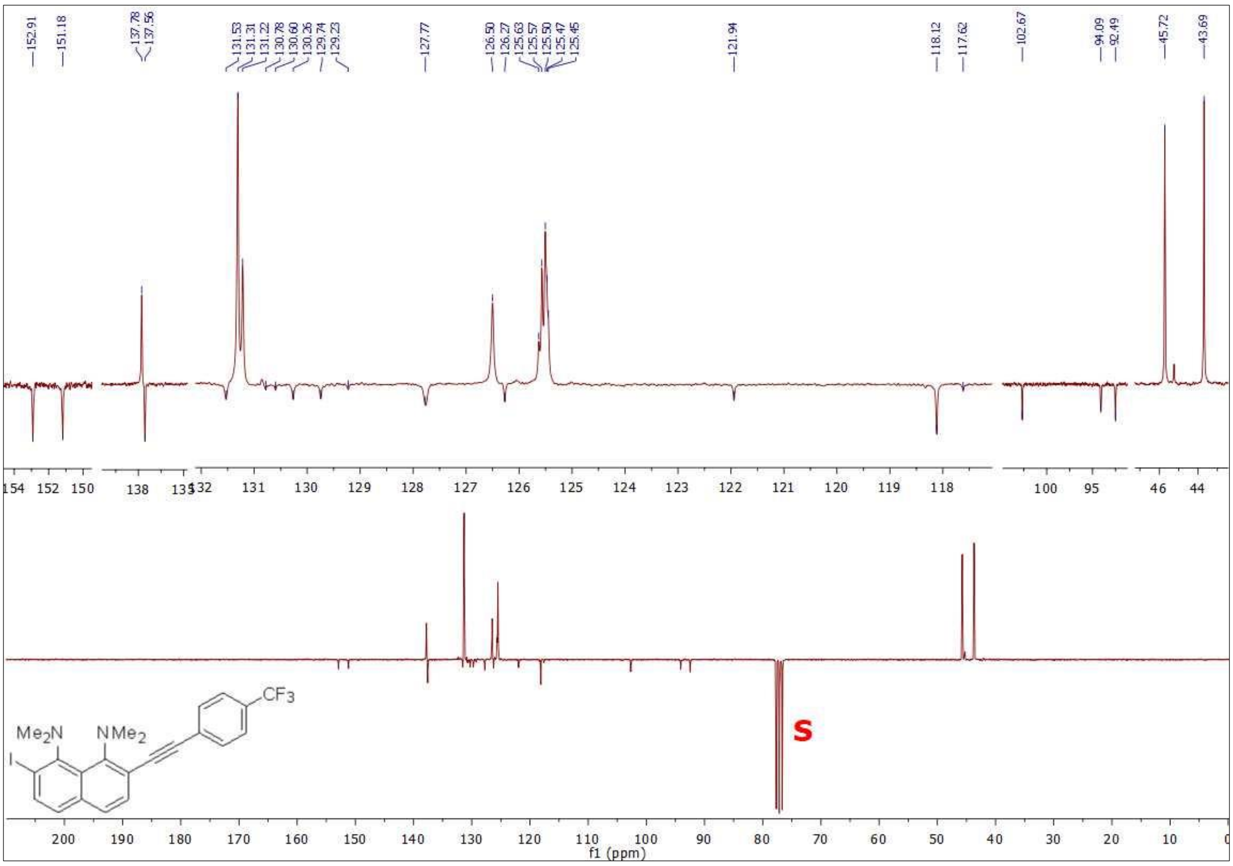

Figure S6. ^{13}C{^{1}H} APT-NMR spectrum of compound **7c** (62.9 MHz, CDCl$_3$).

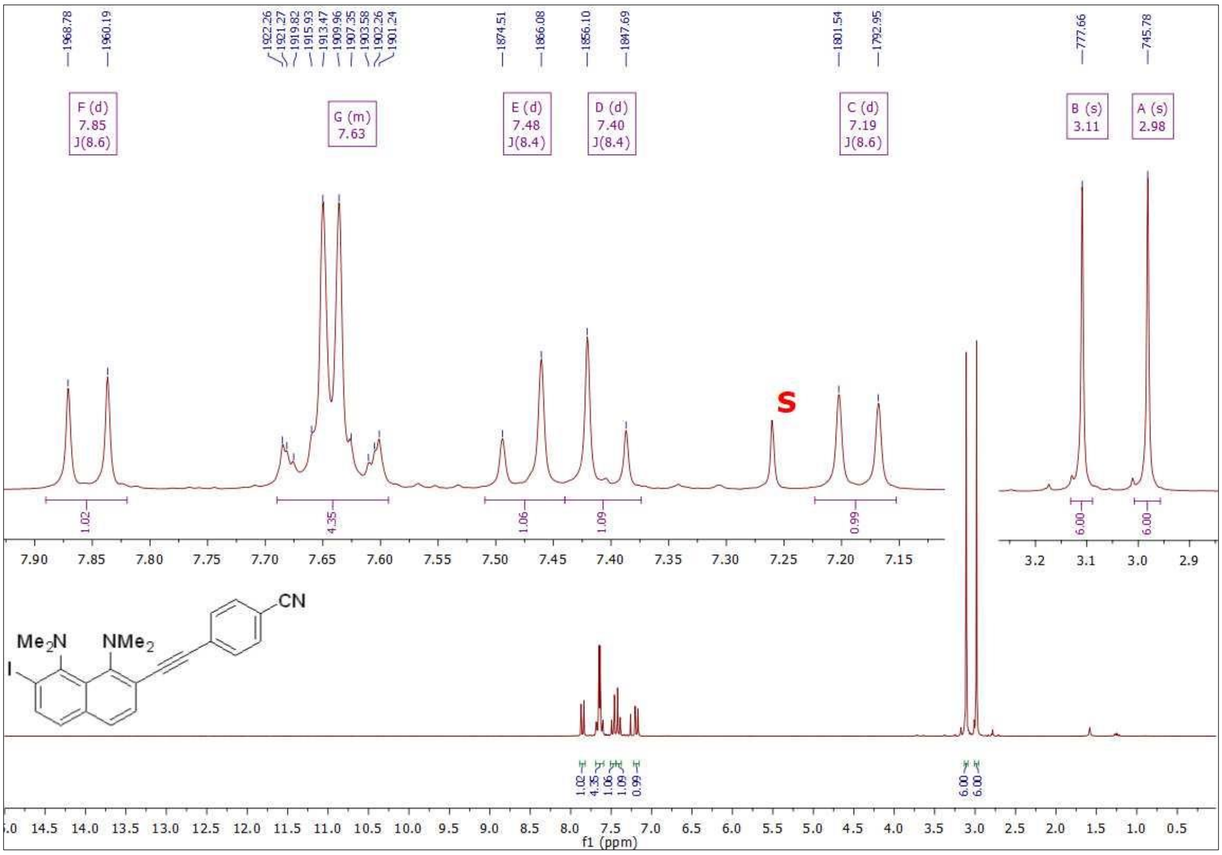

Figure S7. ^{1}H NMR spectrum of compound **7d** (250 MHz, CDCl$_3$).

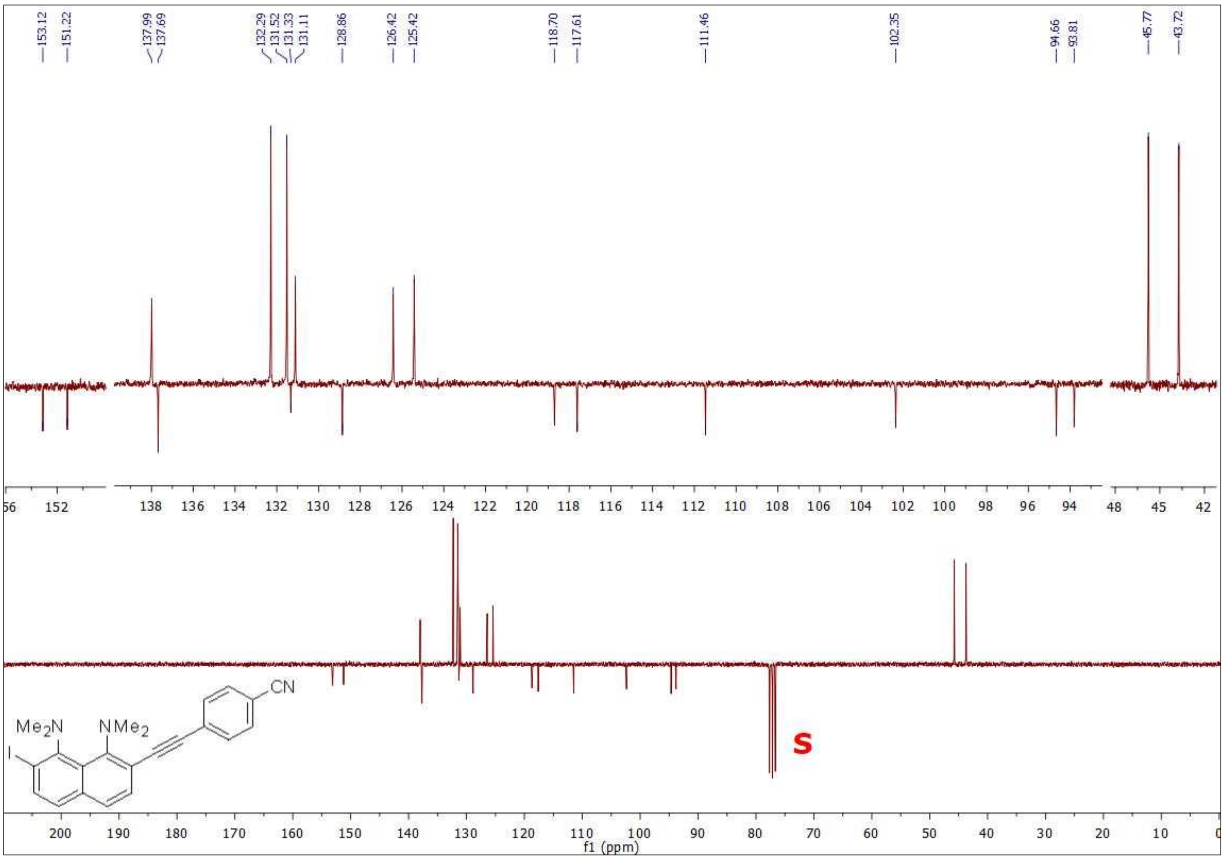

Figure S8. ^{13}C{^{1}H} APT-NMR spectrum of compound 7**d** (62.9 MHz, CDCl$_3$).

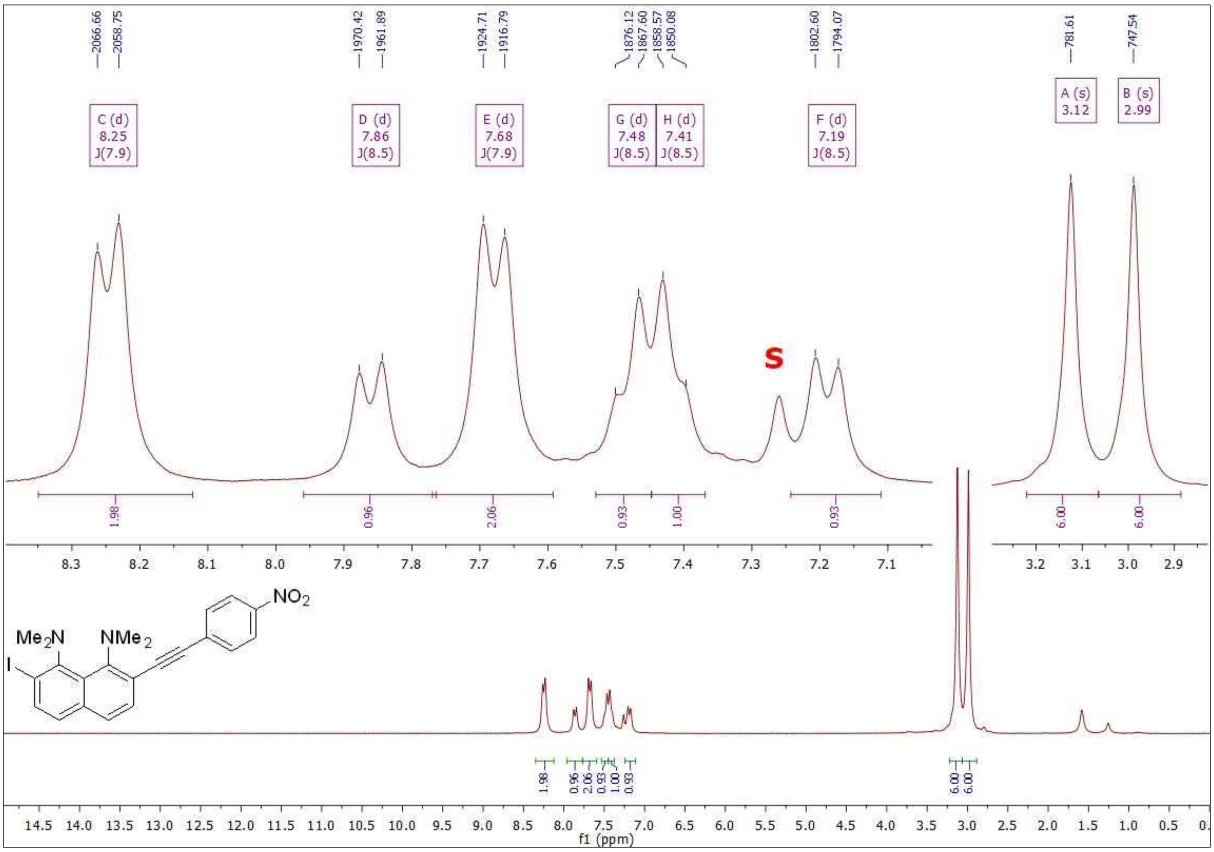

Figure S9. ^{1}H NMR spectrum of compound **7e** (250 MHz, CDCl$_3$).

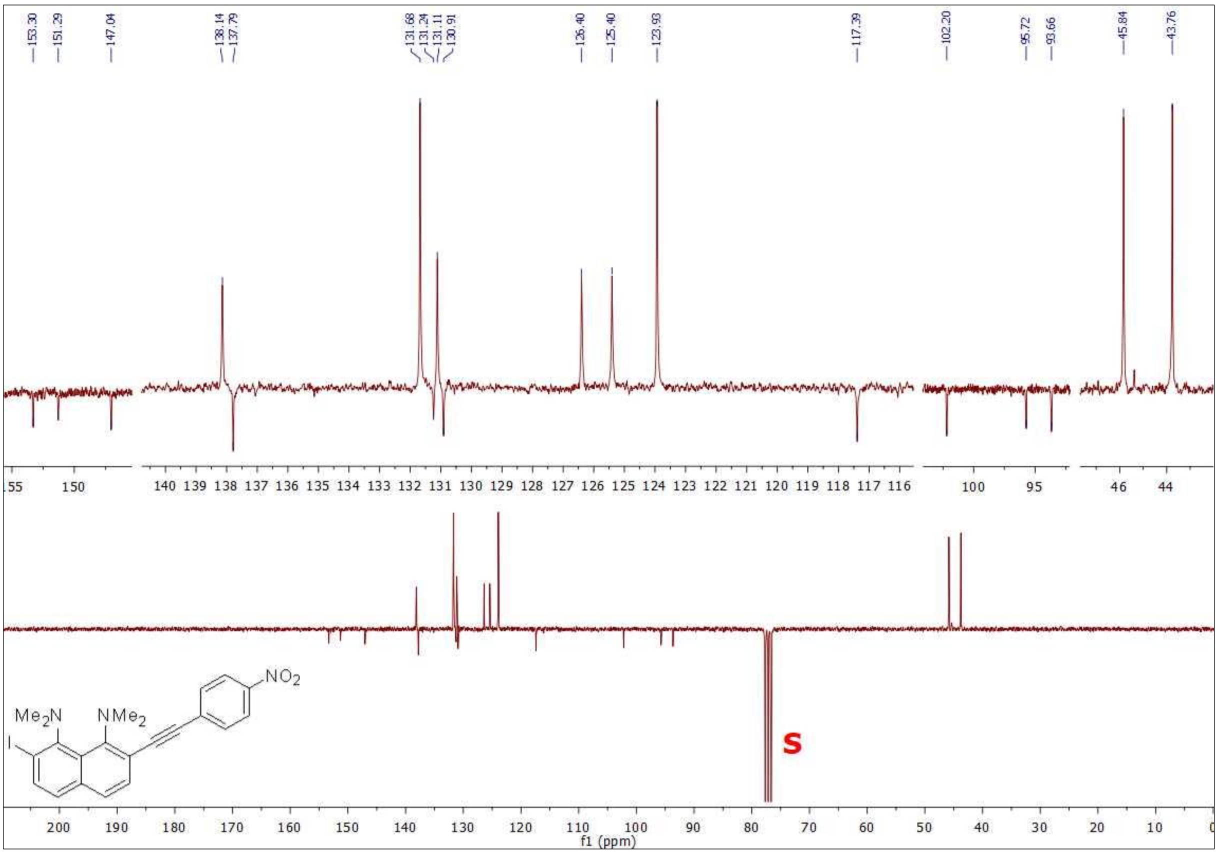

Figure S10. ^{13}C{^{1}H} APT-NMR spectrum of compound **7e** (62.9 MHz, CDCl$_3$).

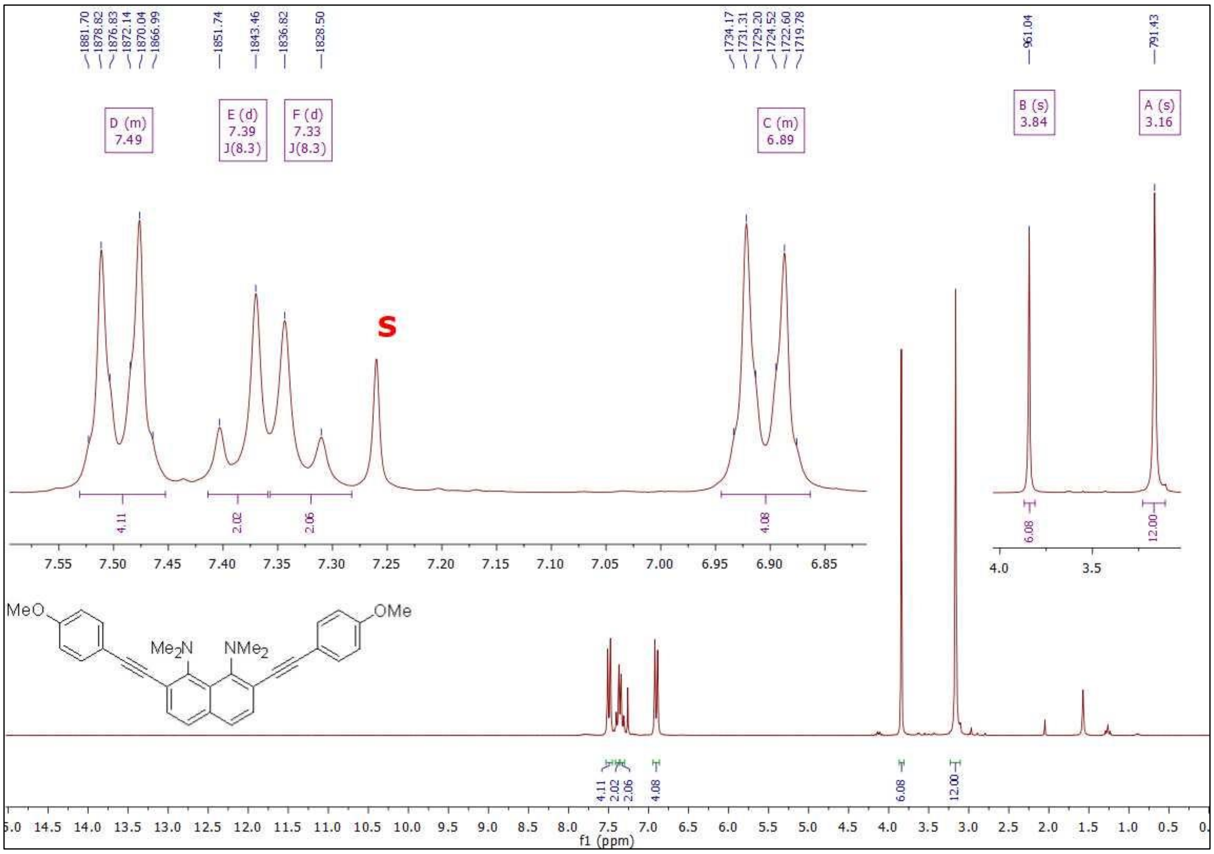

Figure S11. ^{1}H NMR spectrum of compound **9b** (250 MHz, CDCl$_3$).

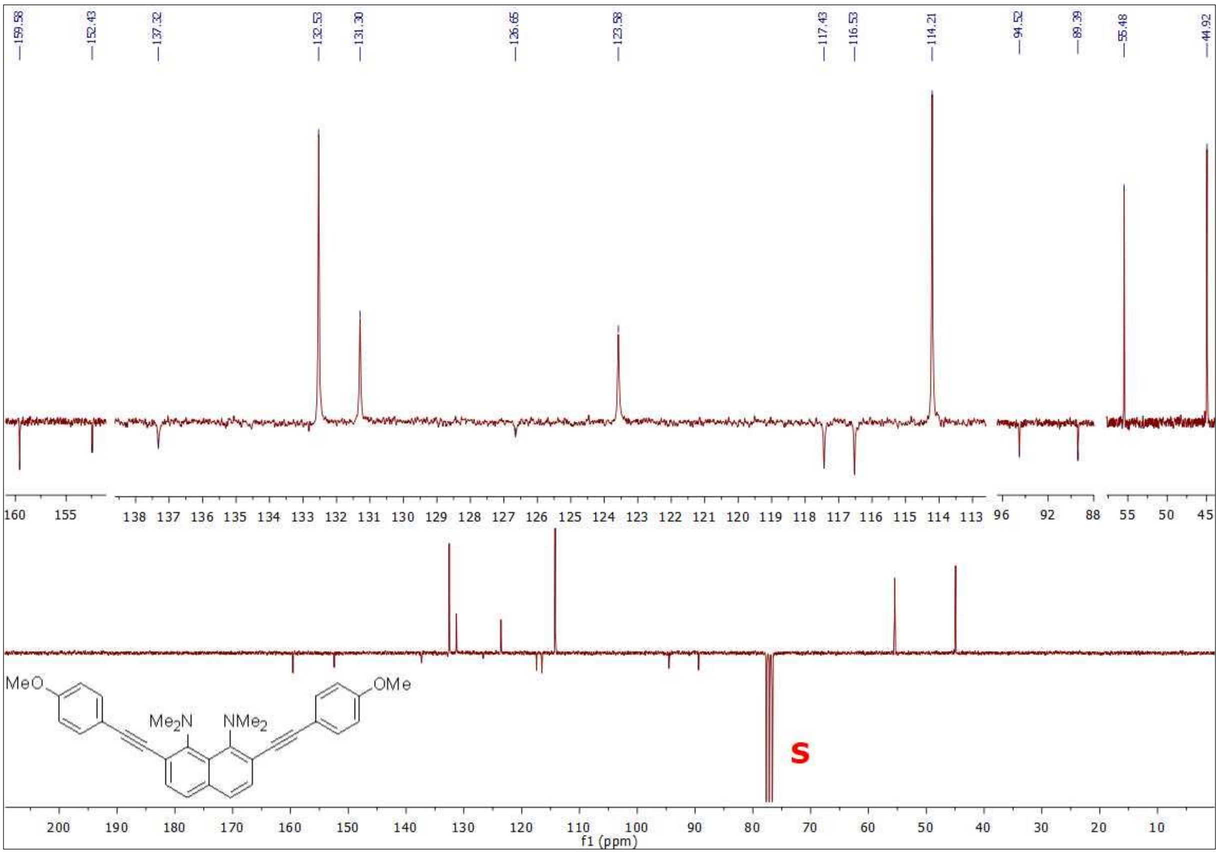

Figure S12. ^{13}C{^{1}H} APT-NMR spectrum of compound **9b** (62.9 MHz, CDCl$_3$).

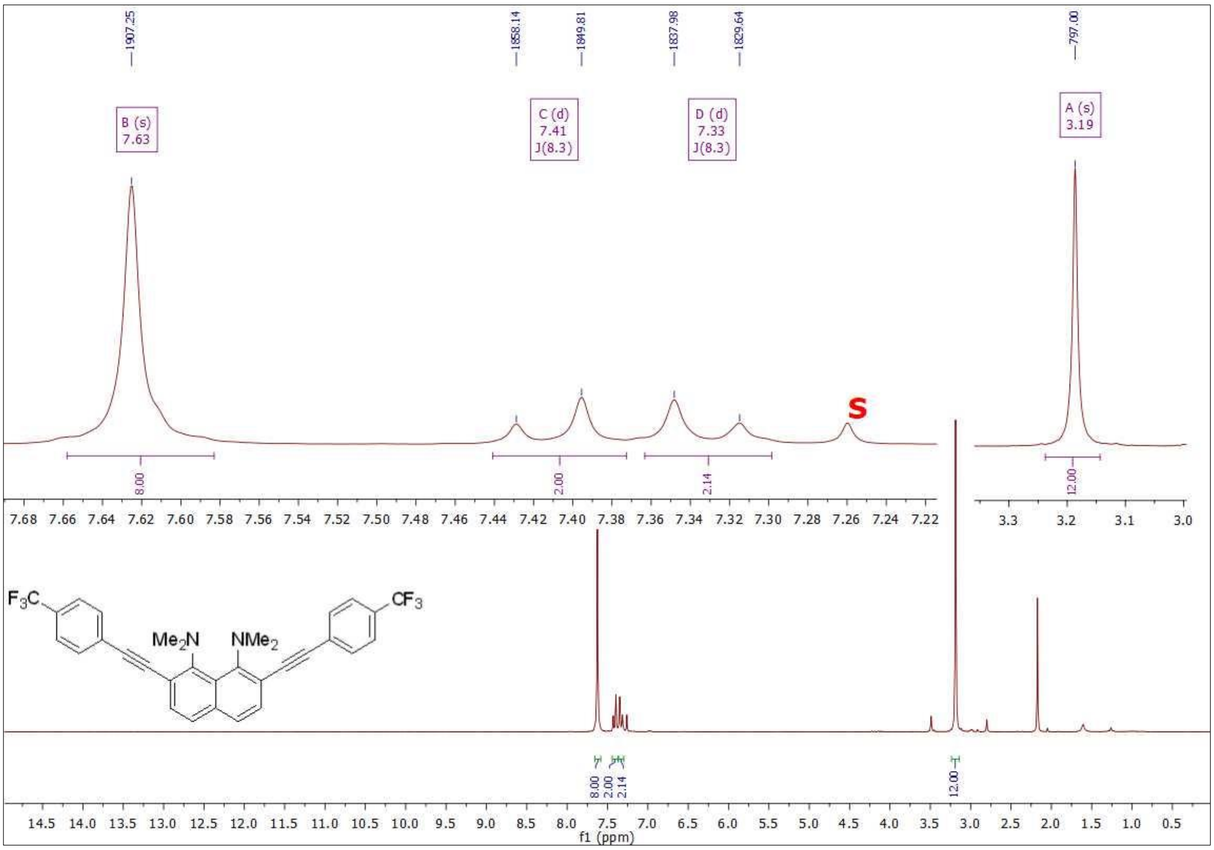

Figure S13. ^{1}H NMR spectrum of compound **9c** (250 MHz, $CDCl_3$).

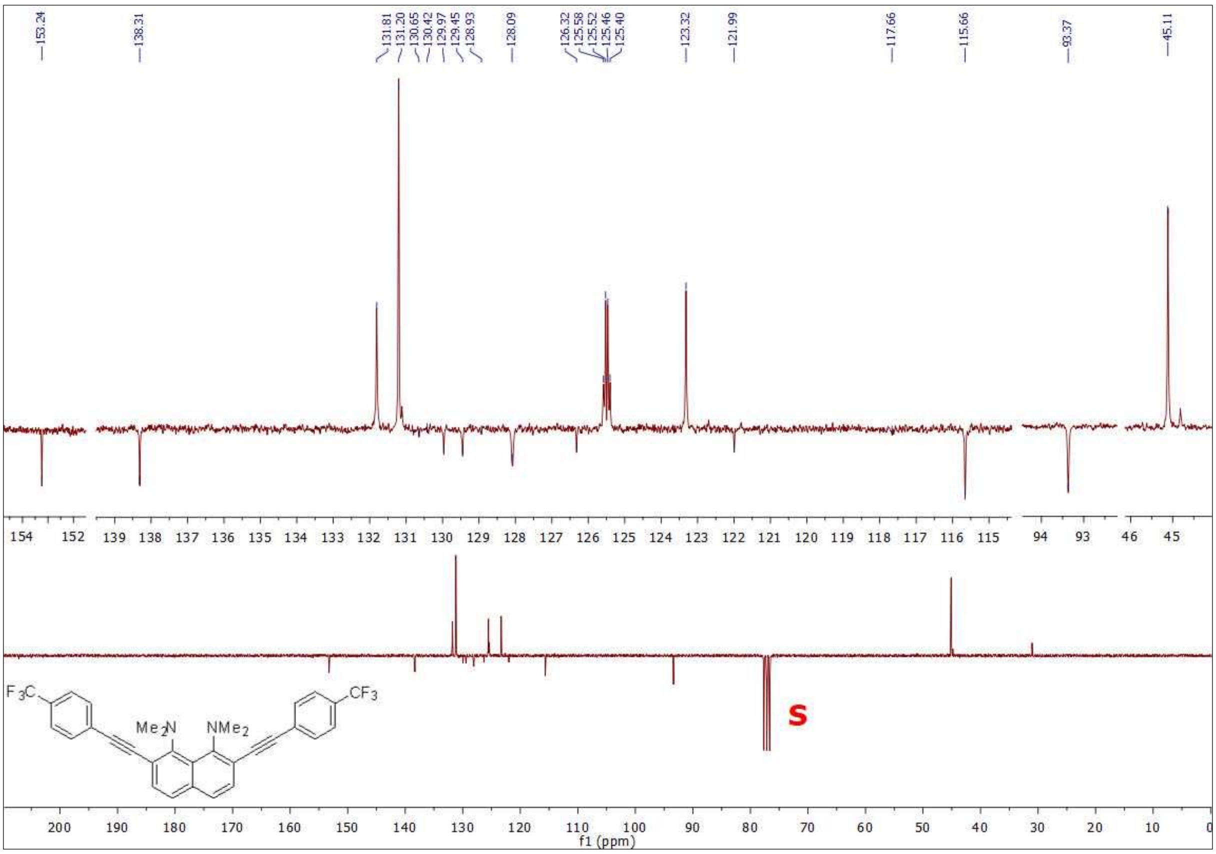

Figure S14. ^{13}C{^{1}H} APT-NMR spectrum of compound **9c** (62.9 MHz, $CDCl_3$).

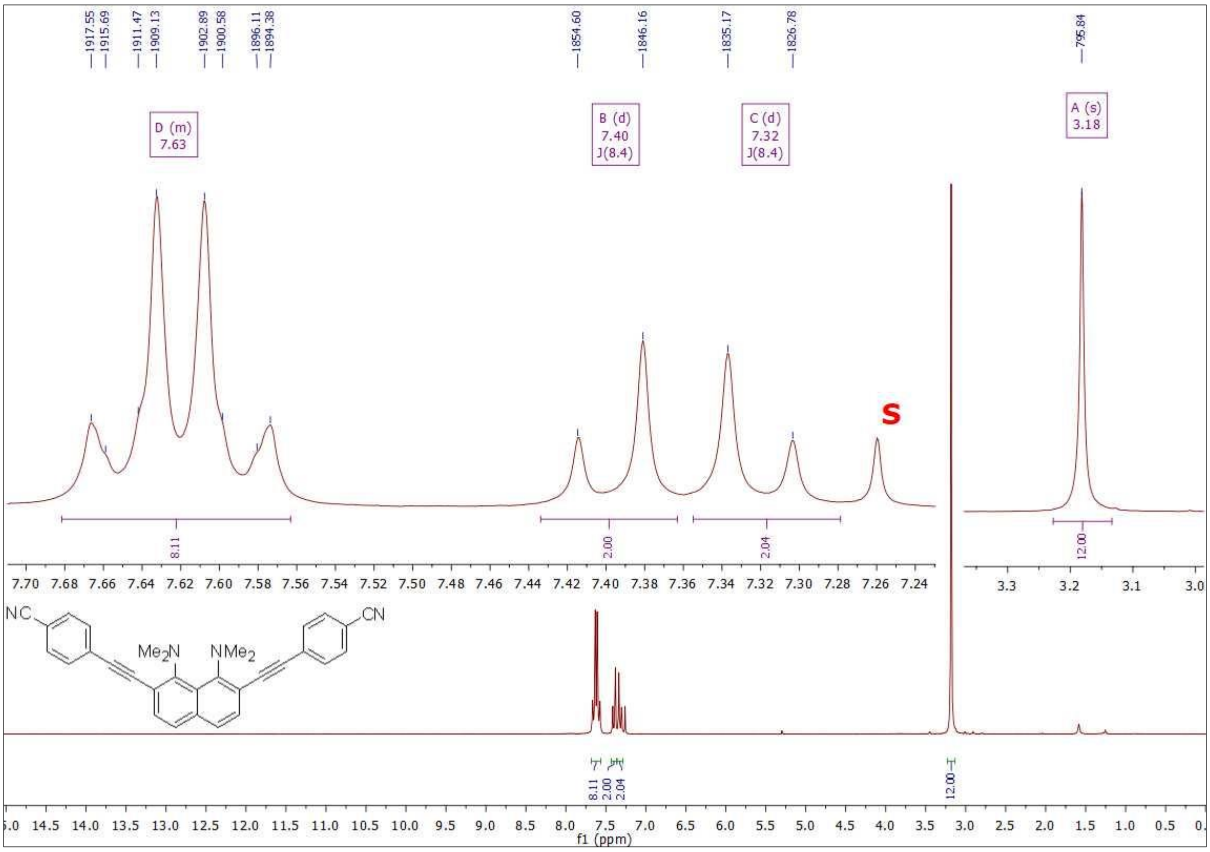

Figure S15. ^{1}H NMR spectrum of compound **9d** (250 MHz, CDCl$_3$).

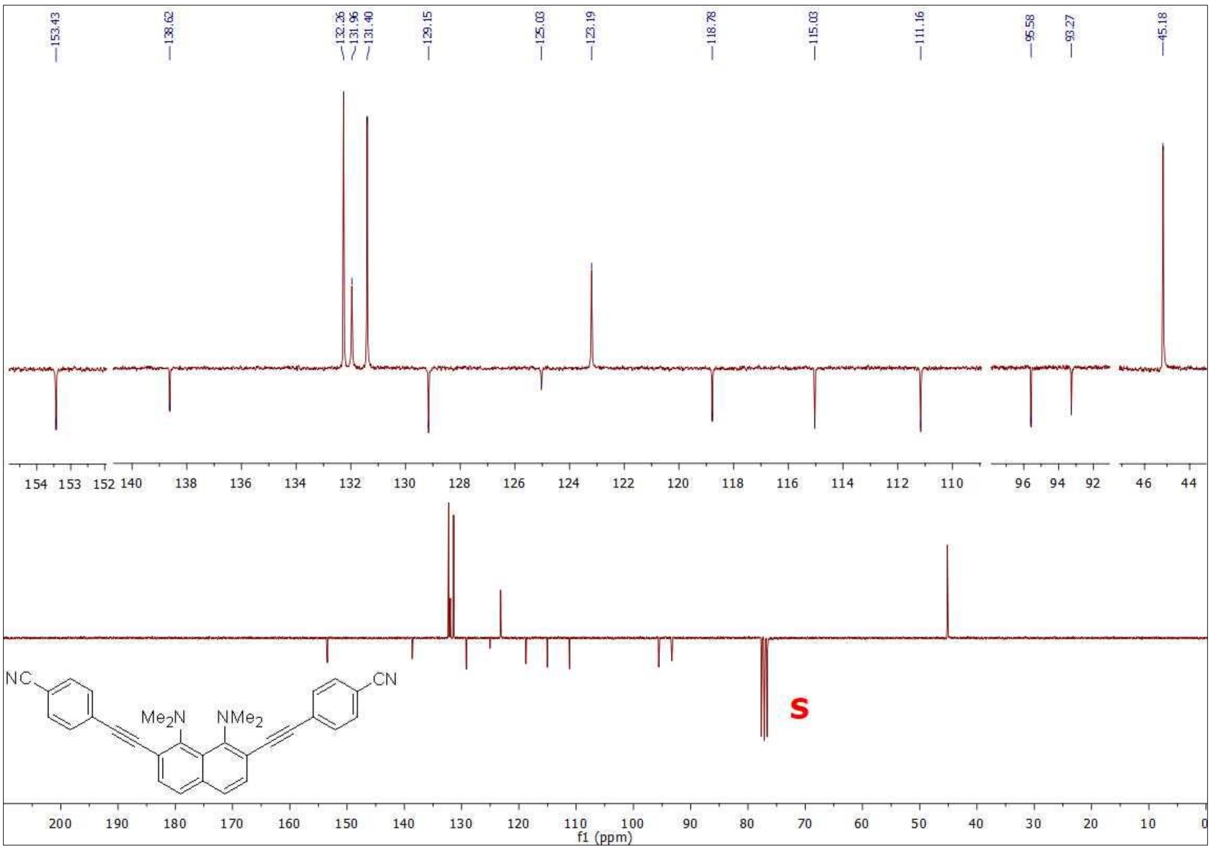

Figure S16. ^{13}C{^{1}H} APT-NMR spectrum of compound **9d** (62.9 MHz, CDCl$_3$).

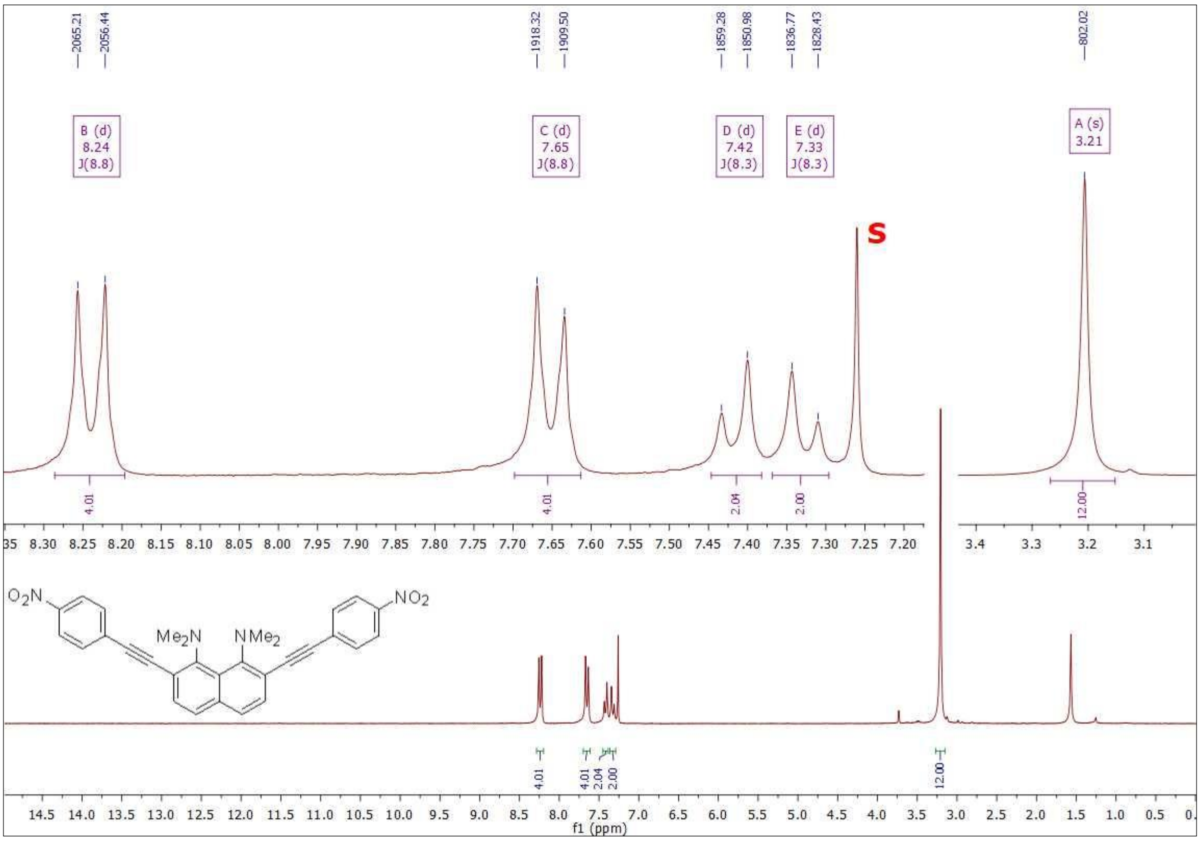

Figure S17. ^{1}H NMR spectrum of compound **9e** (250 MHz, CDCl$_3$).

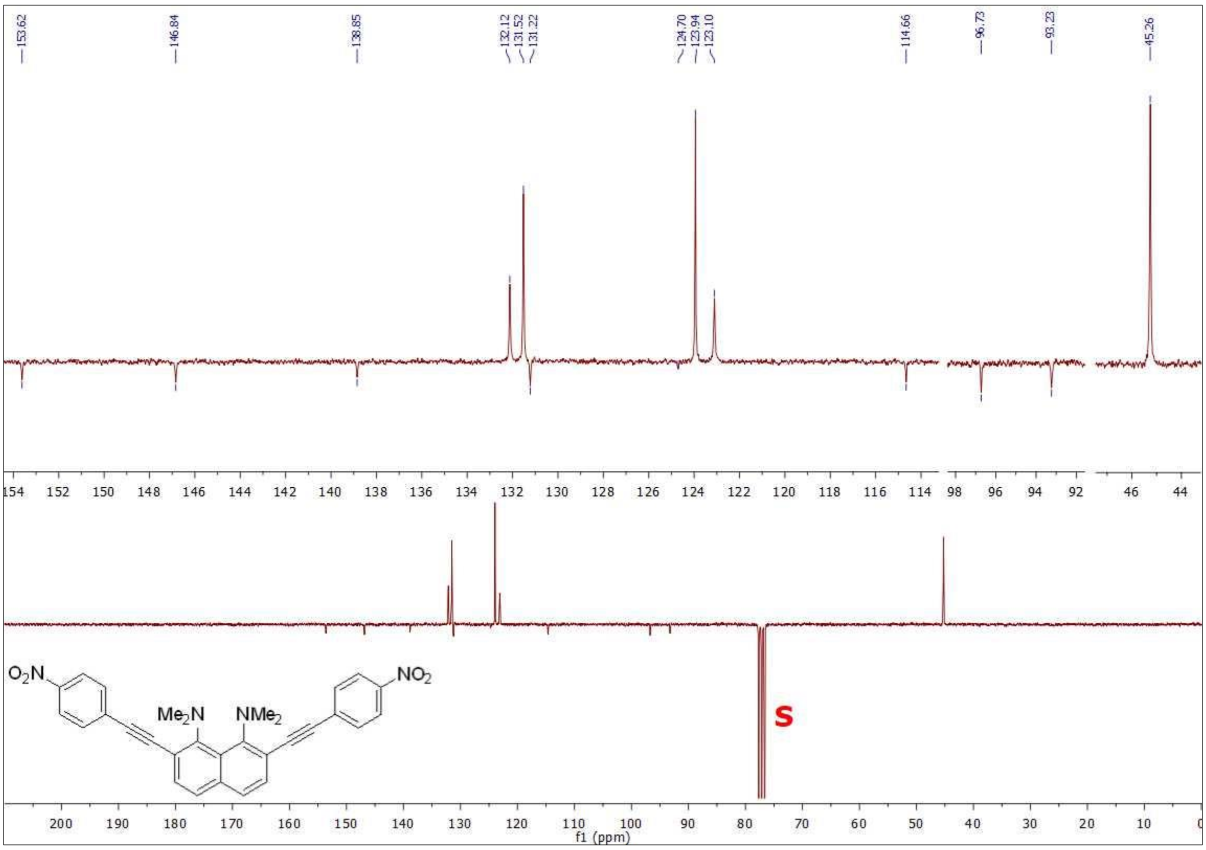

Figure S18. ^{13}C{^{1}H} APT-NMR spectrum of compound **9e** (62.9 MHz, CDCl$_3$).

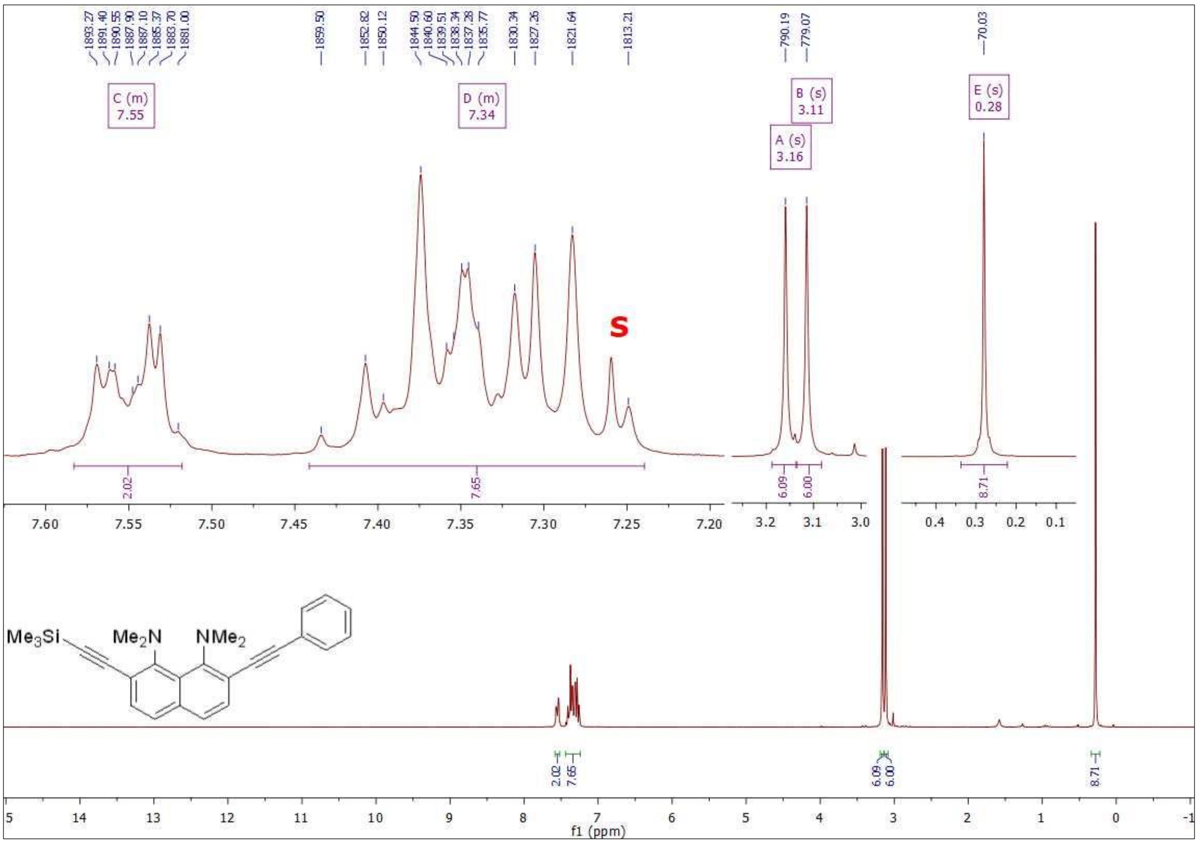

Figure S19. ^{1}H NMR spectrum of compound **10a** (250 MHz, CDCl$_3$).

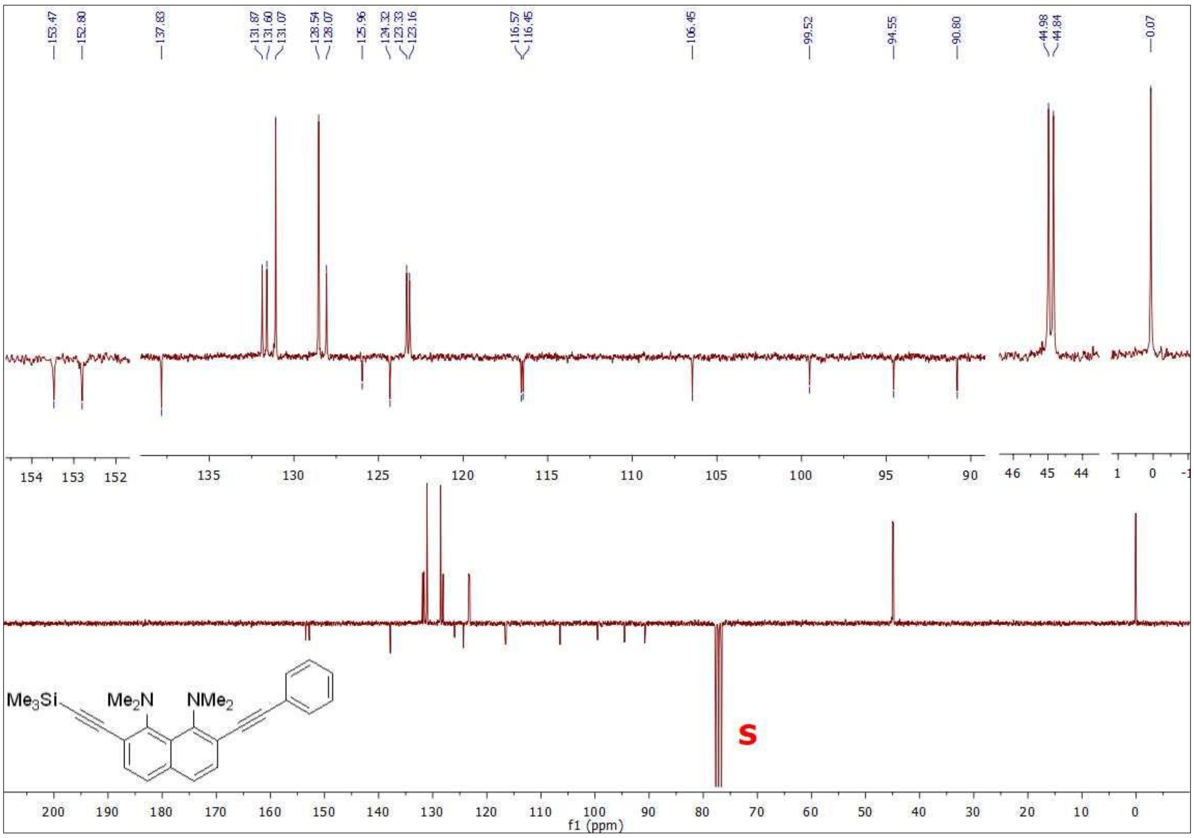

Figure S20. ^{13}C{^{1}H} APT-NMR spectrum of compound **10a** (62.9 MHz, CDCl$_3$).

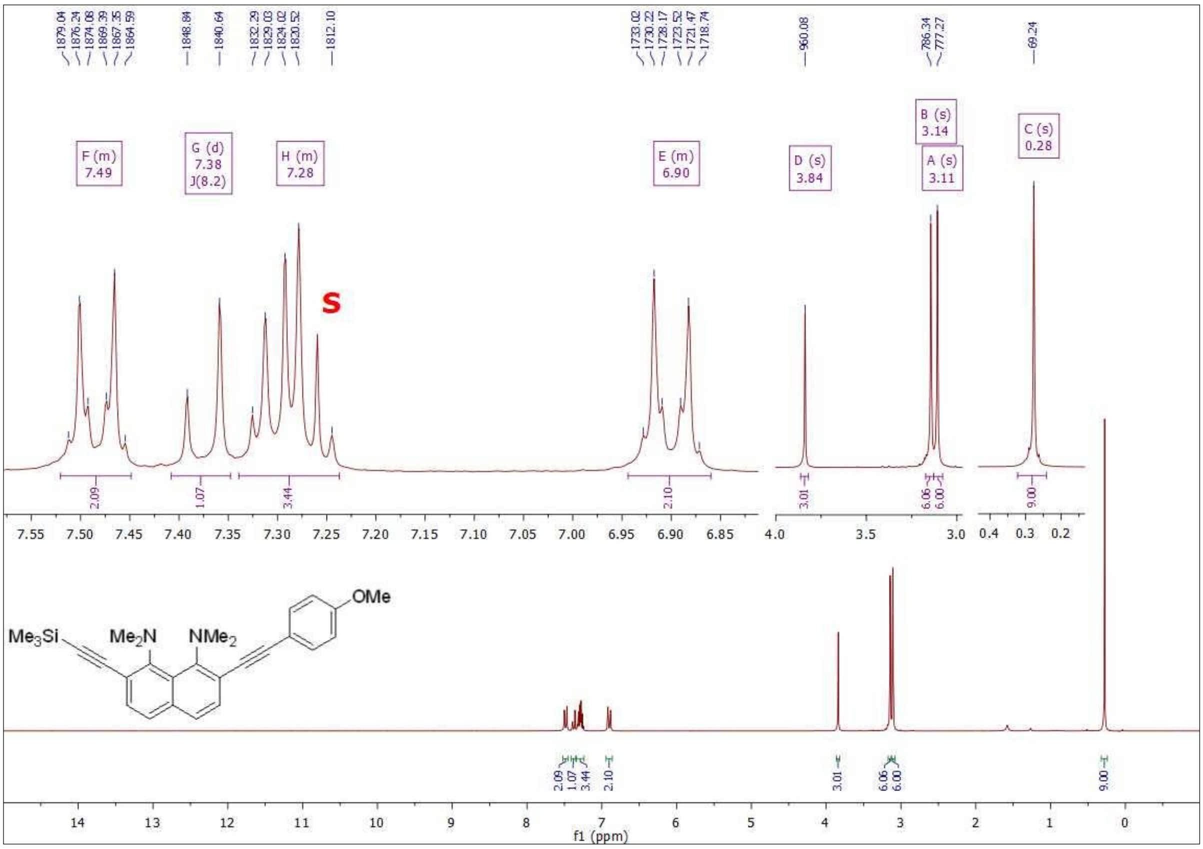

Figure S21. ^{1}H NMR spectrum of compound **10b** (250 MHz, $CDCl_3$).

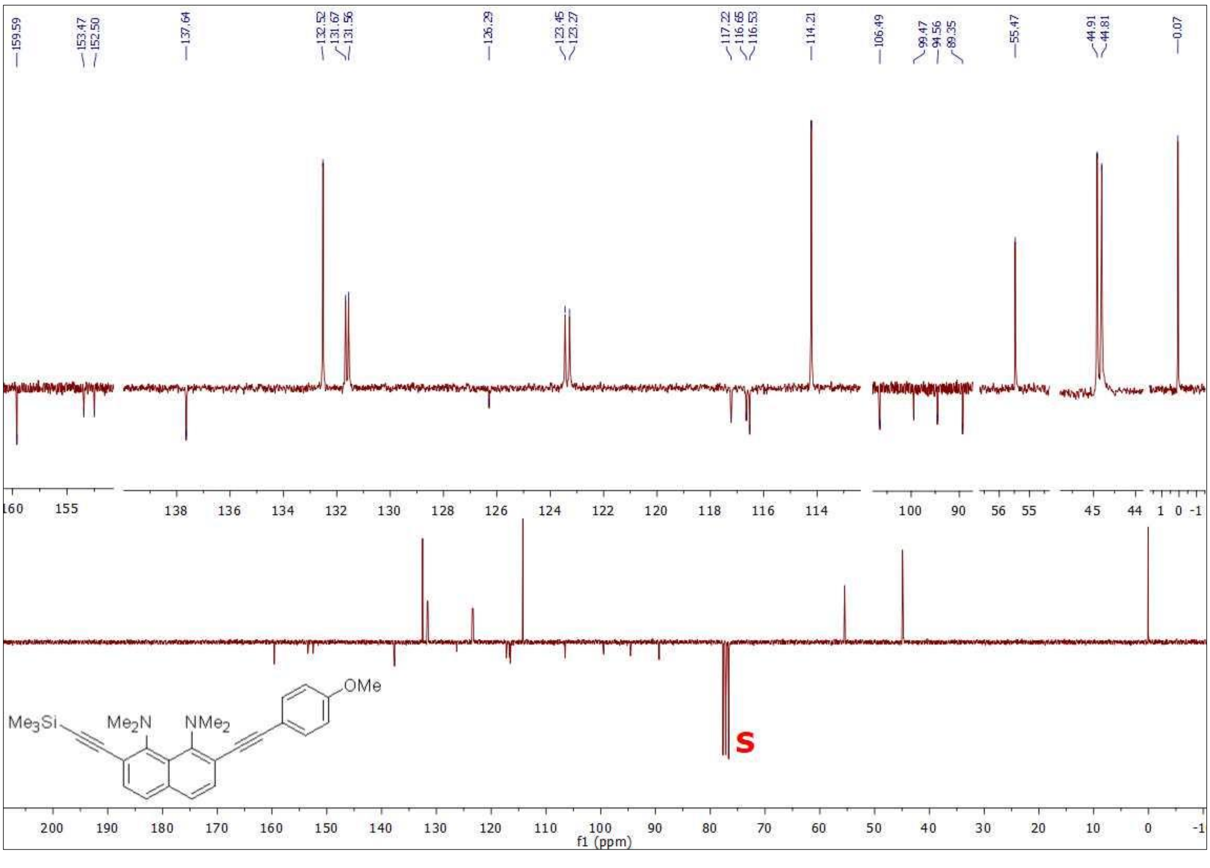

Figure S22. $^{13}C\{^1H\}$ APT-NMR spectrum of compound **10b** (62.9 MHz, $CDCl_3$).

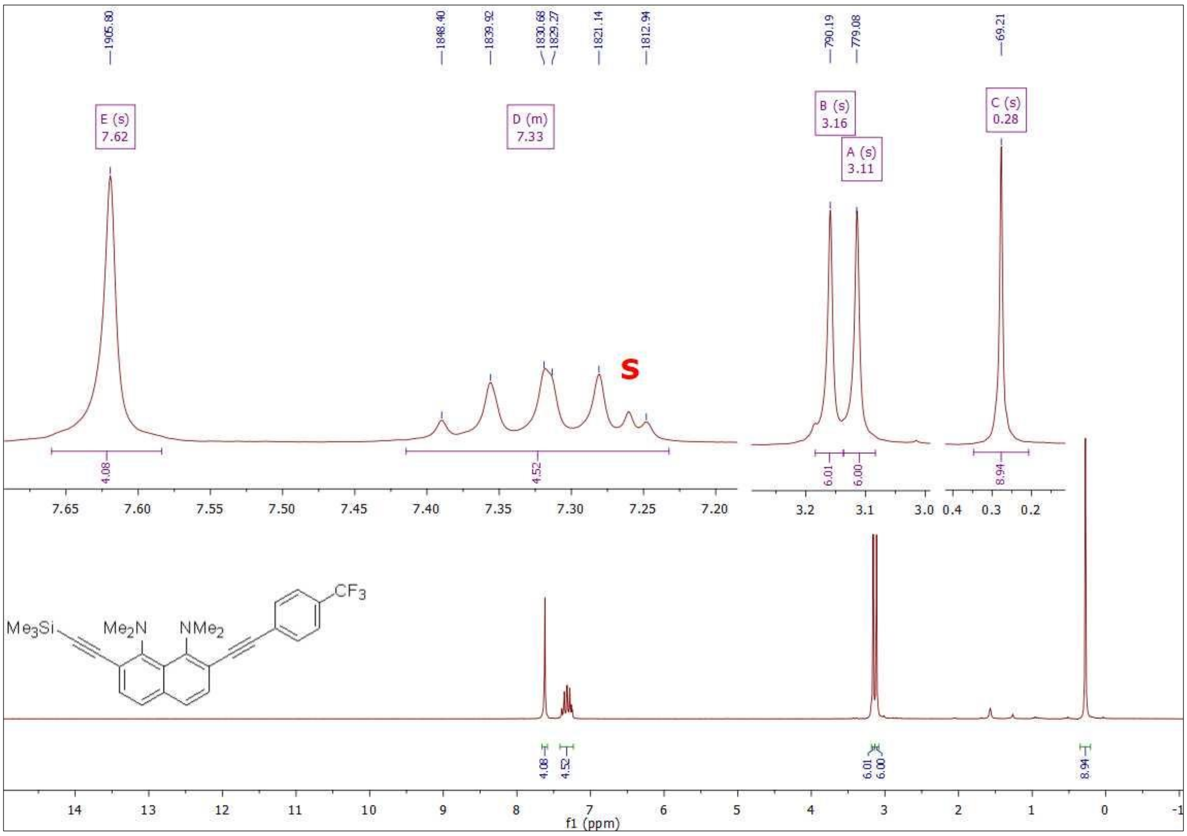

Figure S23. ^{1}H NMR spectrum of compound **10c** (250 MHz, $CDCl_3$).

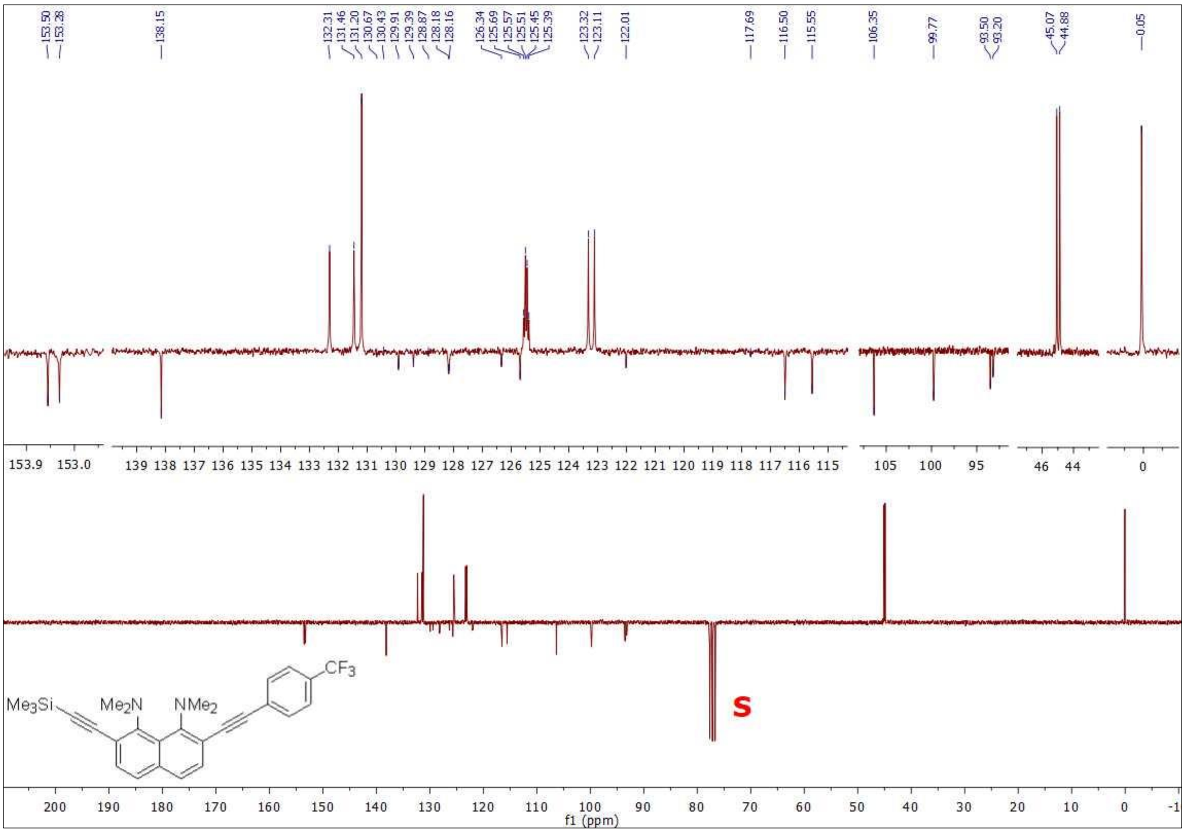

Figure S24. ^{13}C{^{1}H} APT-NMR spectrum of compound **10c** (62.9 MHz, $CDCl_3$).

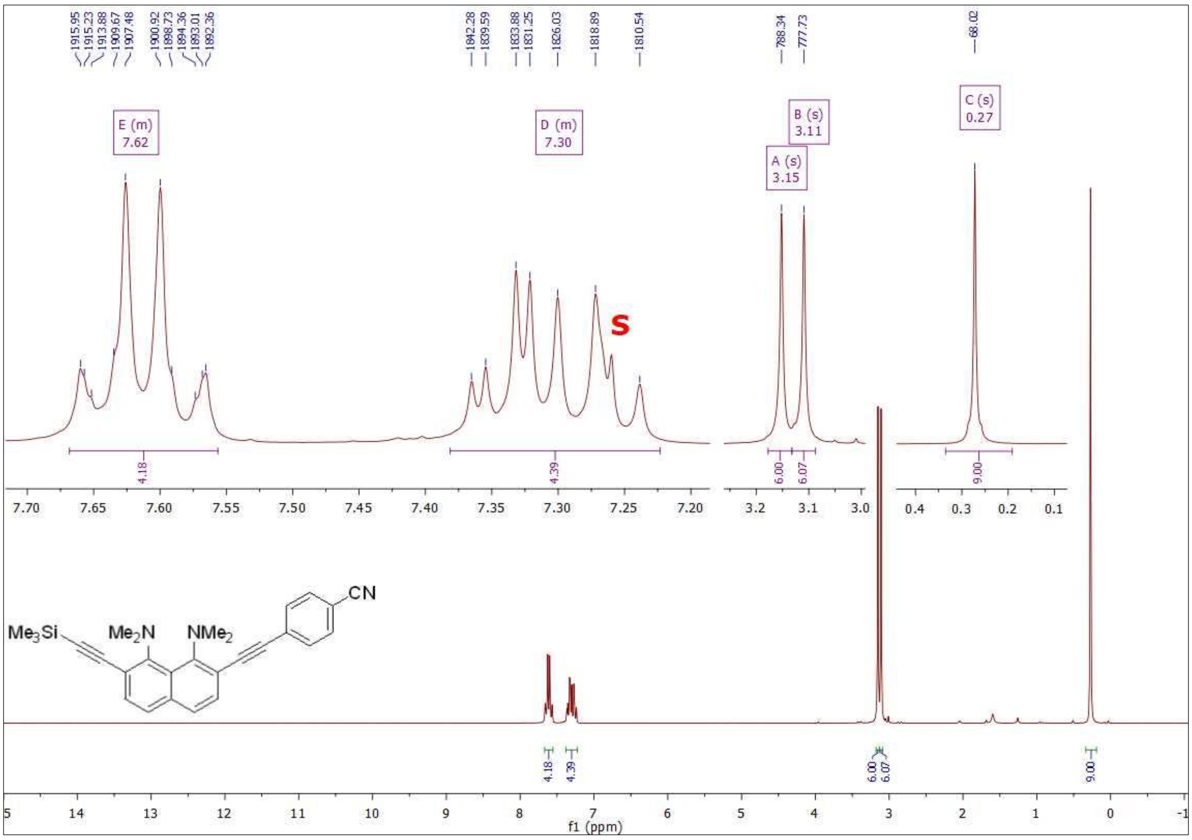

Figure S25. ^{1}H NMR spectrum of compound **10d** (250 MHz, CDCl$_3$).

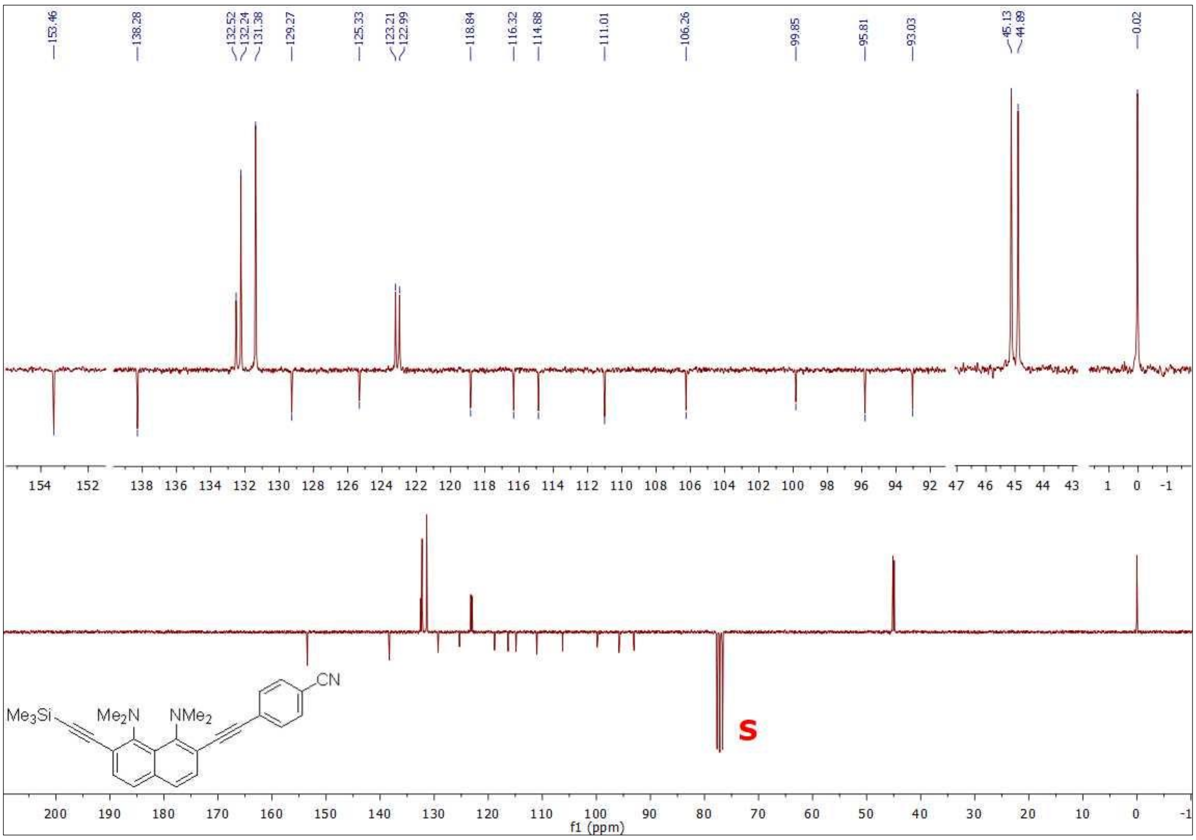

Figure S26. ^{13}C{^{1}H} APT-NMR spectrum of compound **10d** (62.9 MHz, CDCl$_3$).

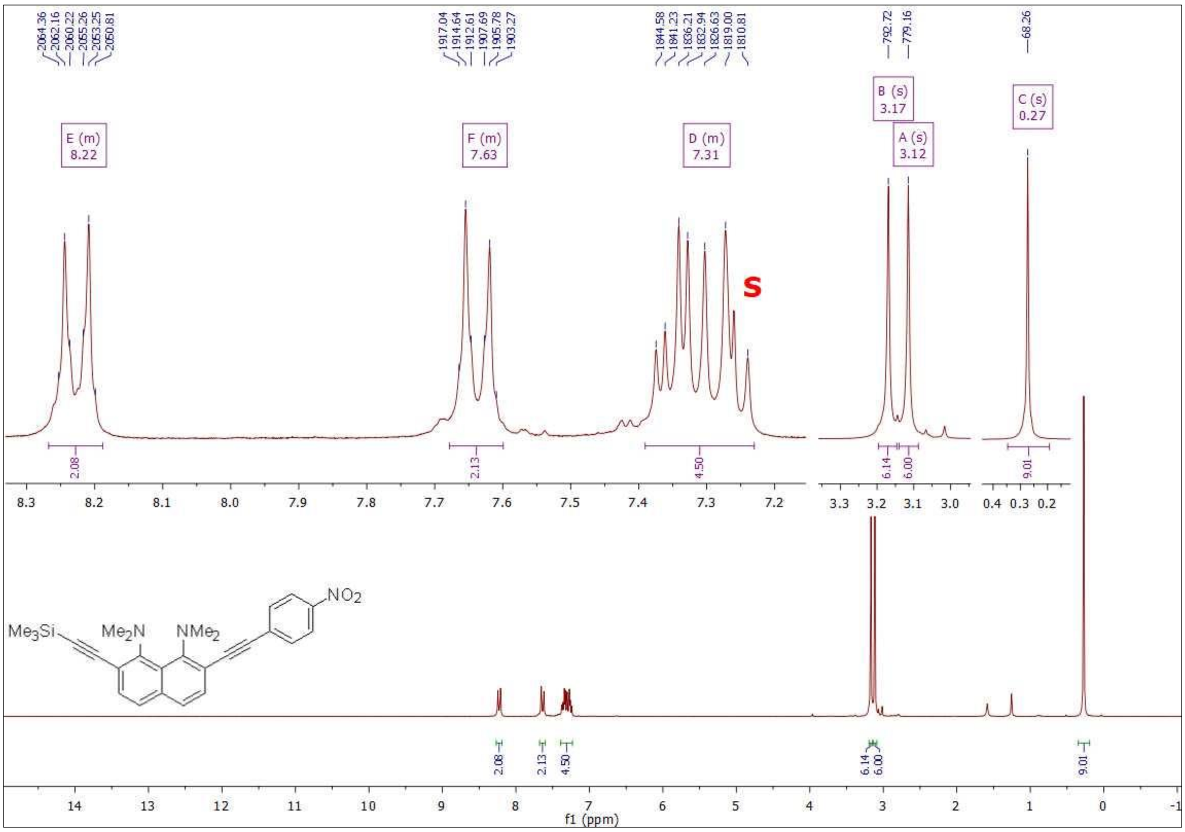

Figure S27. ^{1}H NMR spectrum of compound **10e** (250 MHz, $CDCl_3$).

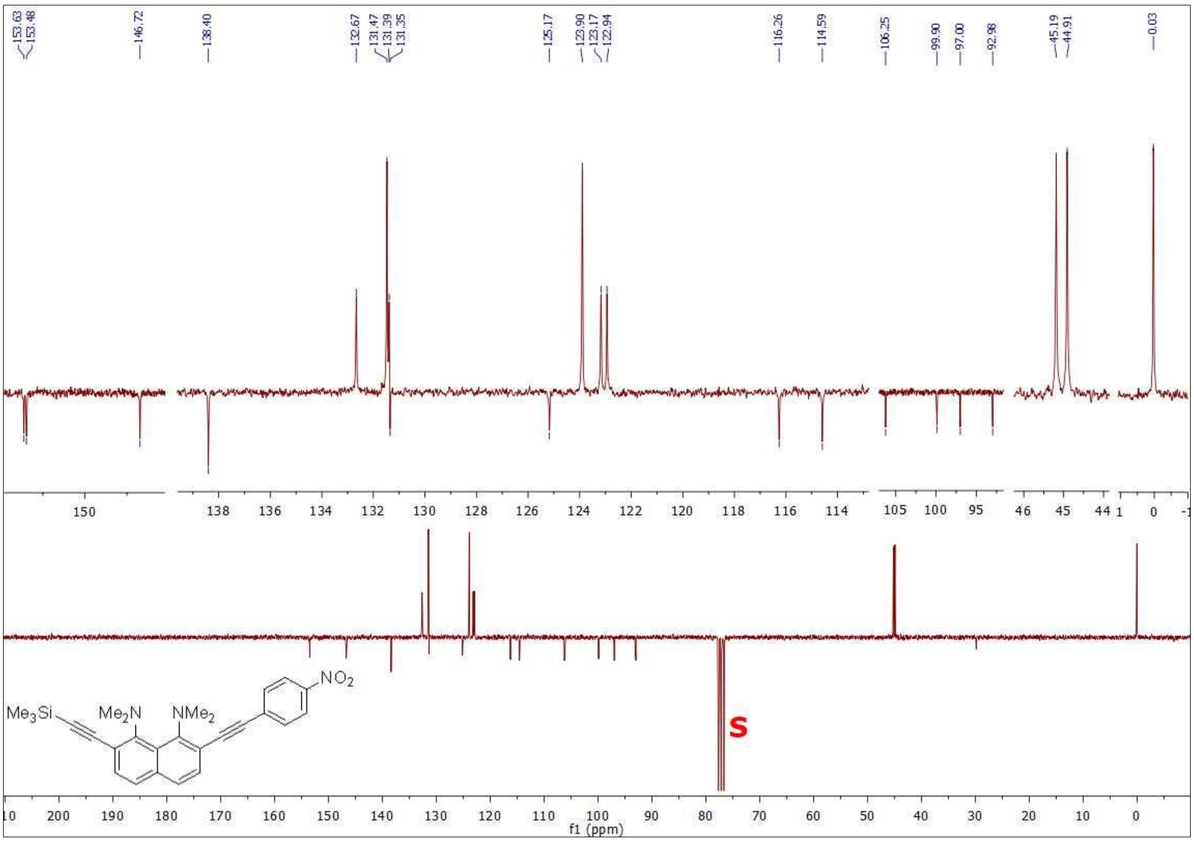

Figure S28. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **10e** (62.9 MHz, $CDCl_3$).

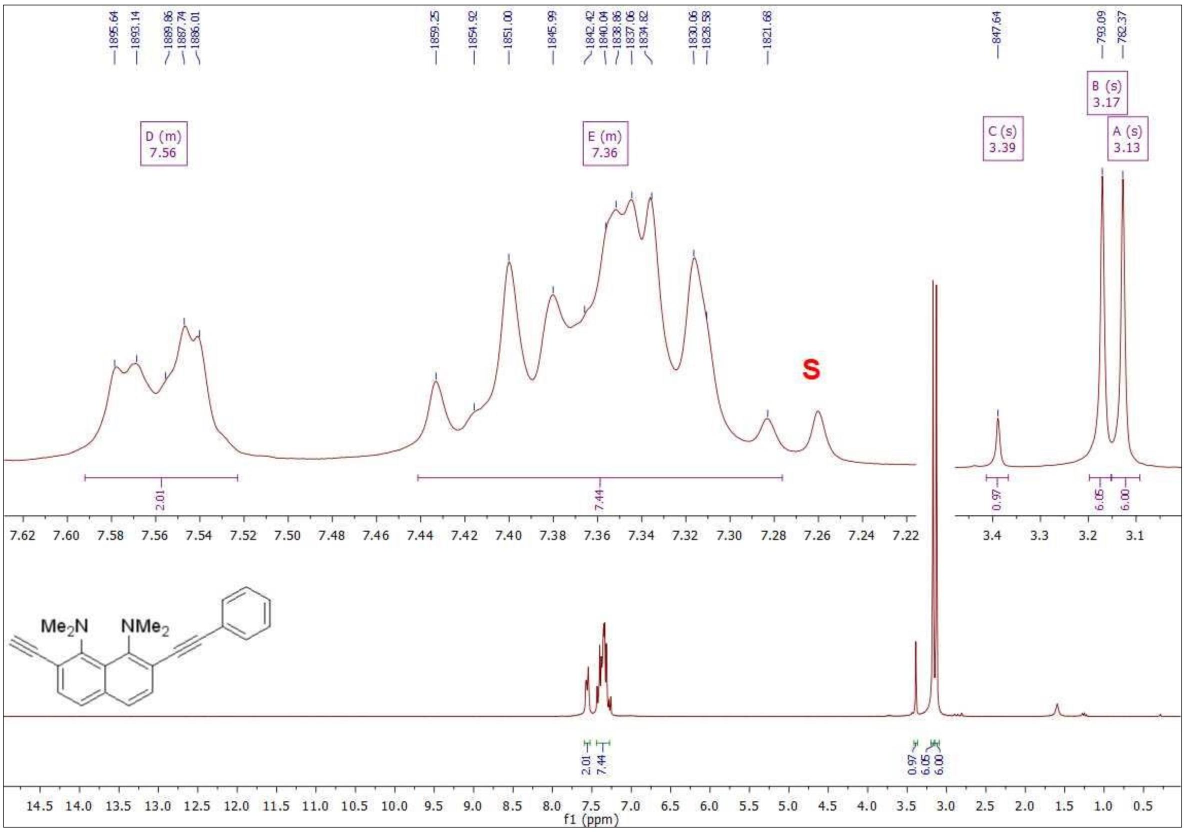

Figure S29. ^{1}H NMR spectrum of compound **6a** (250 MHz, CDCl$_3$).

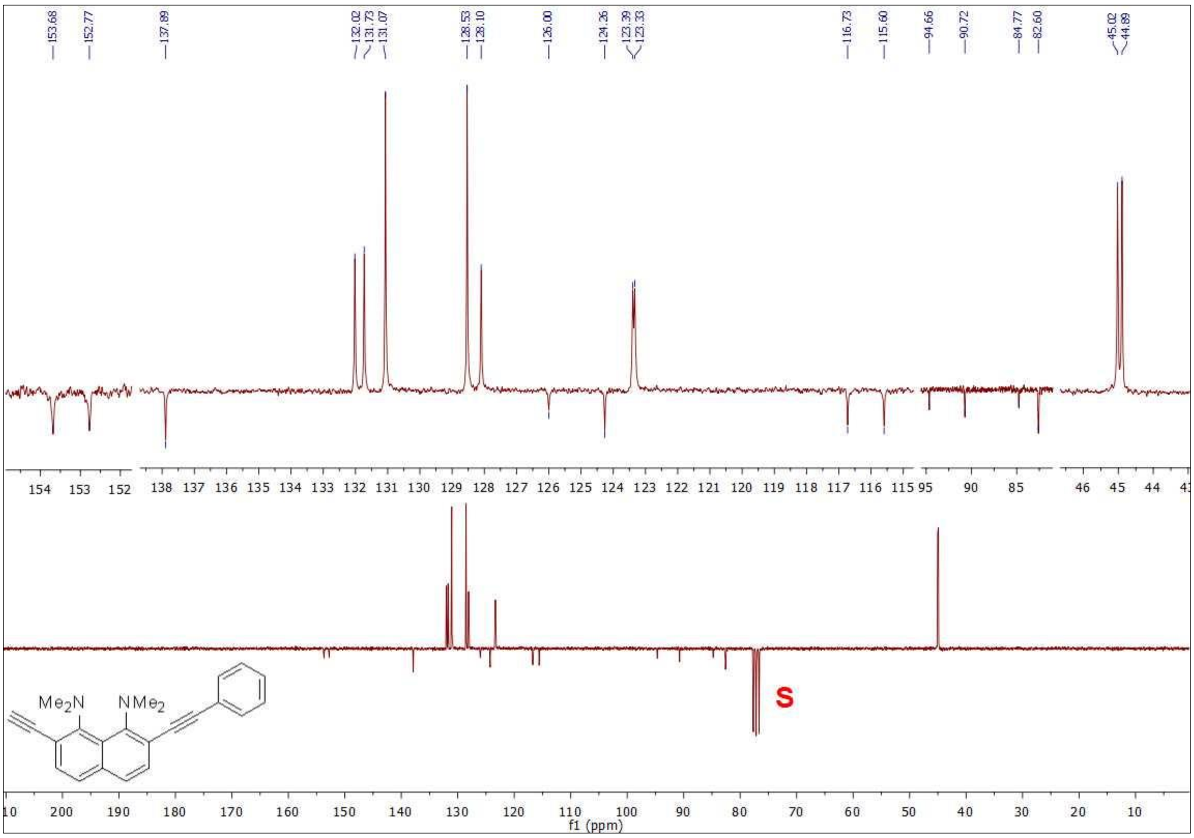

Figure S30. ^{13}C{^{1}H} APT-NMR spectrum of compound **6a** (62.9 MHz, CDCl$_3$).

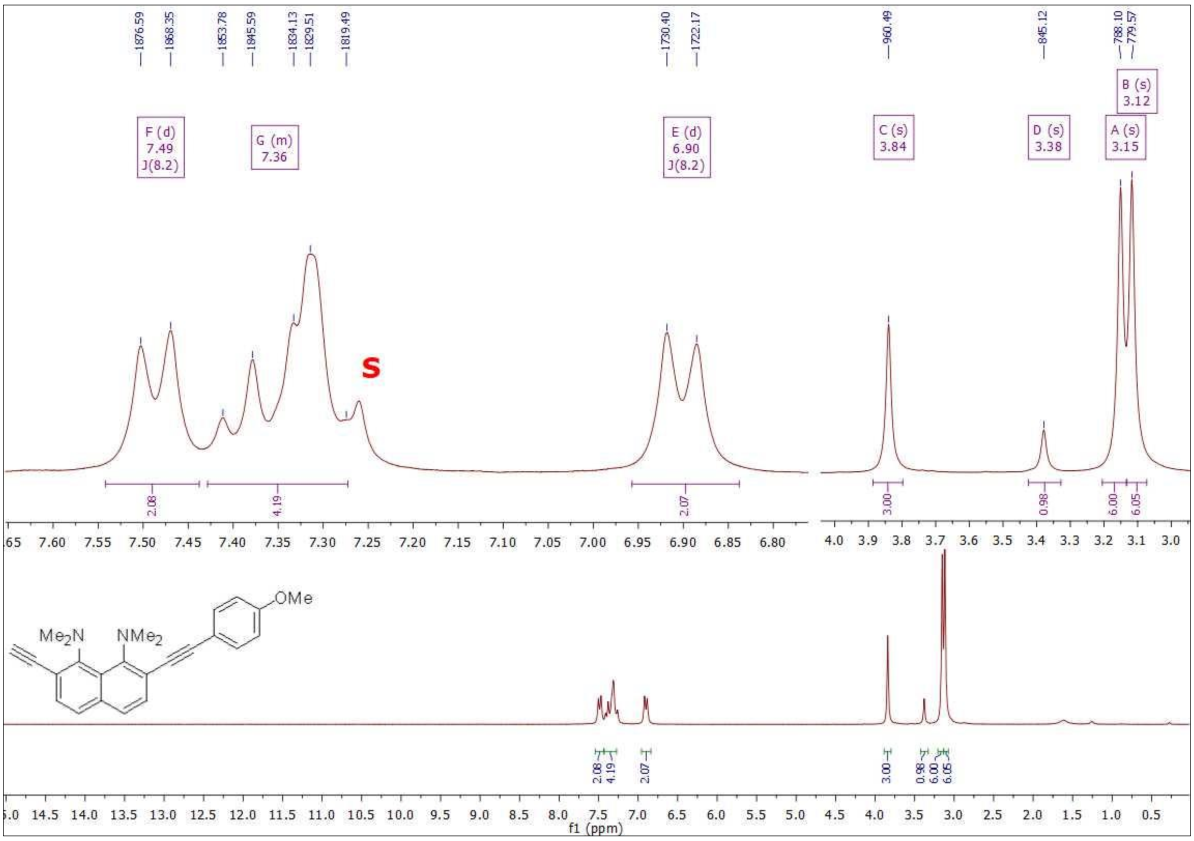

Figure S31. ^{1}H NMR spectrum of compound **6b** (250 MHz, CDCl$_3$).

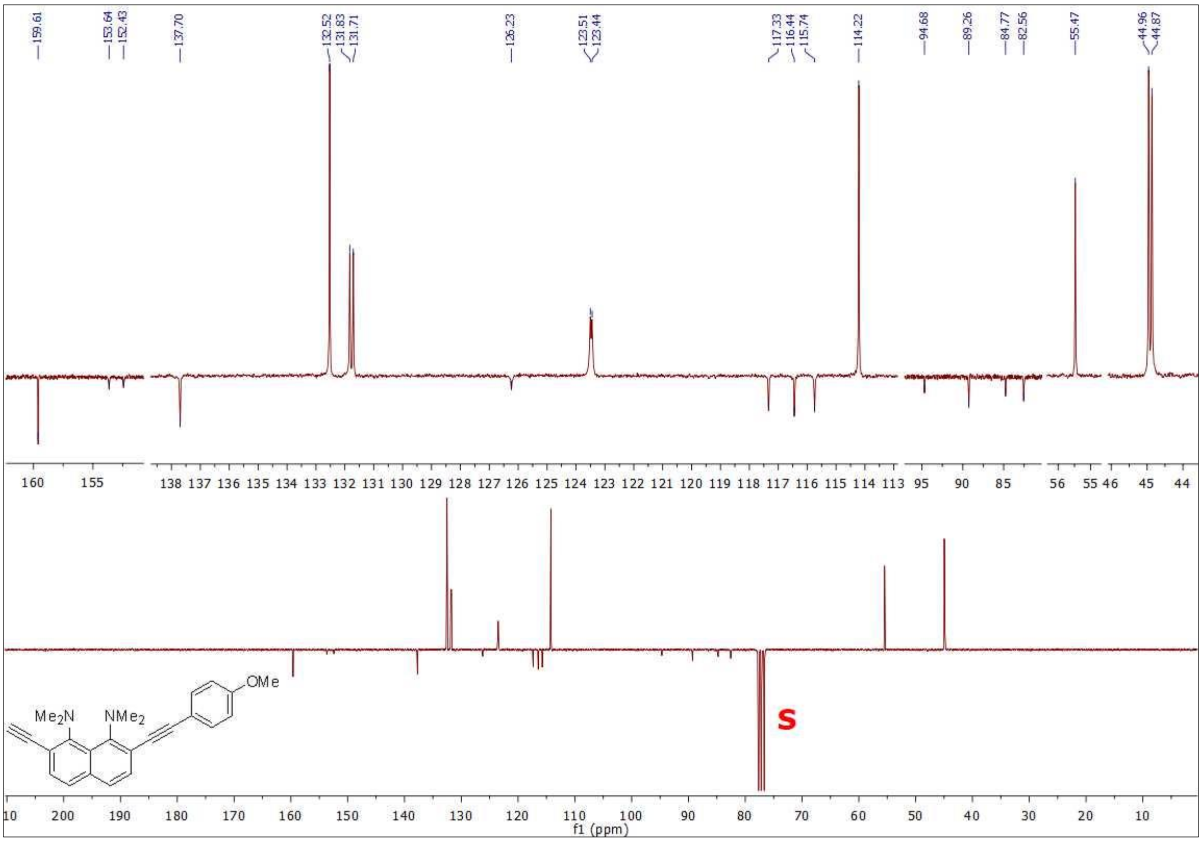

Figure S32. ^{13}C{^{1}H} APT-NMR spectrum of compound **6b** (62.9 MHz, CDCl$_3$).

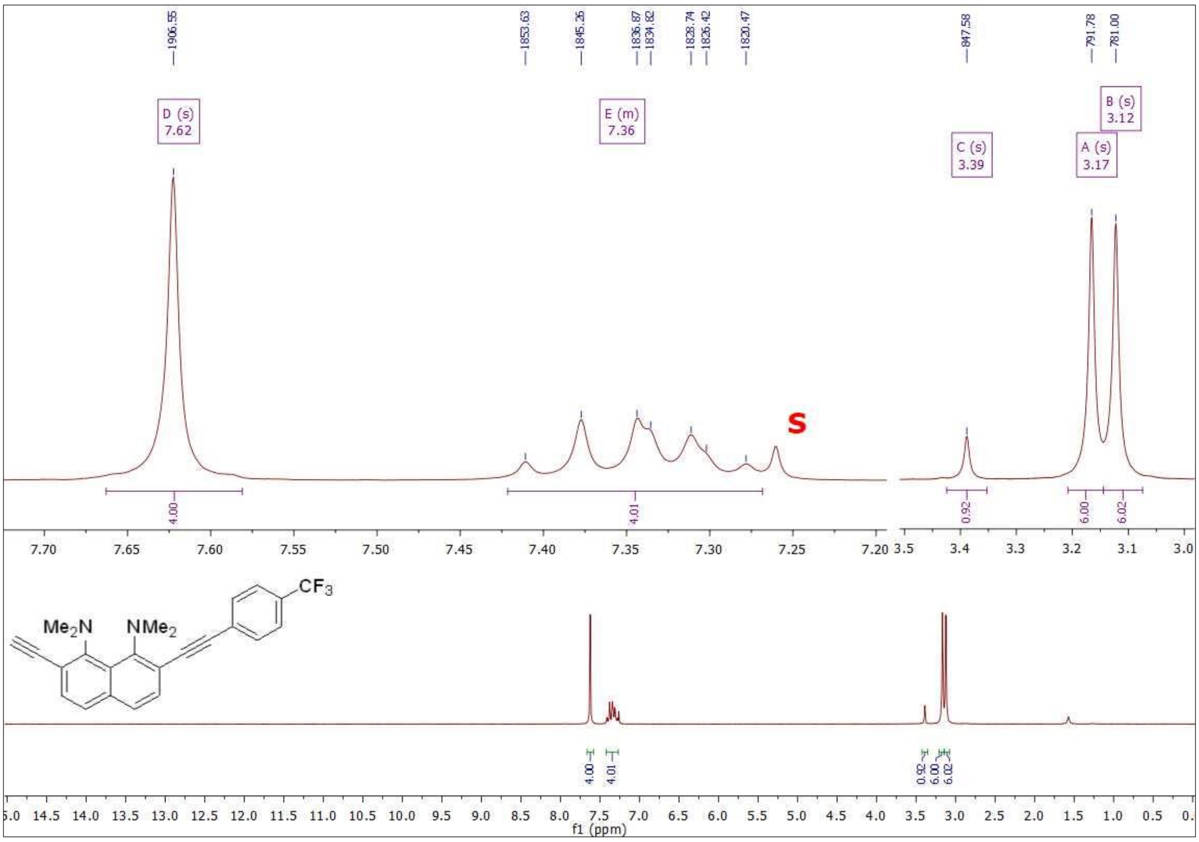

Figure S33. ^{1}H NMR spectrum of compound **6c** (250 MHz, CDCl$_3$).

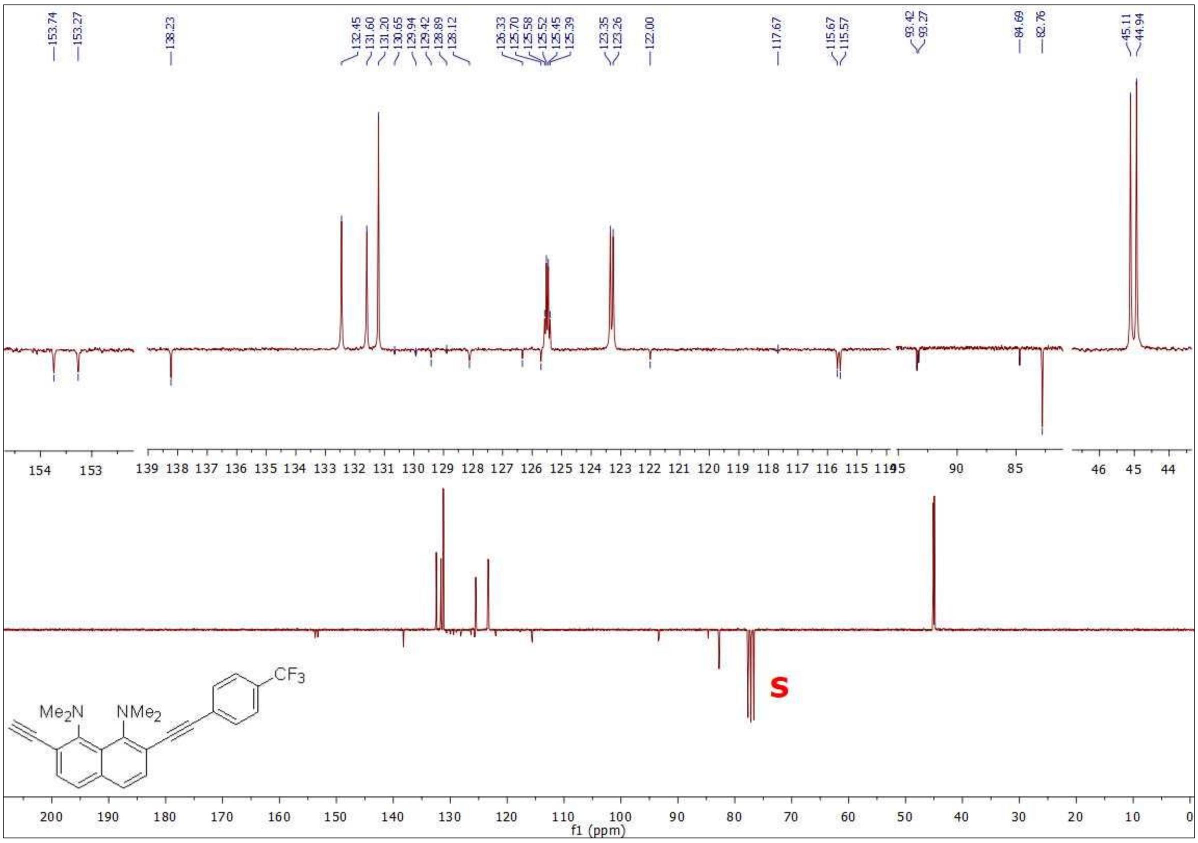

Figure S34. ^{13}C{^{1}H} APT-NMR spectrum of compound **6c** (62.9 MHz, CDCl$_3$).

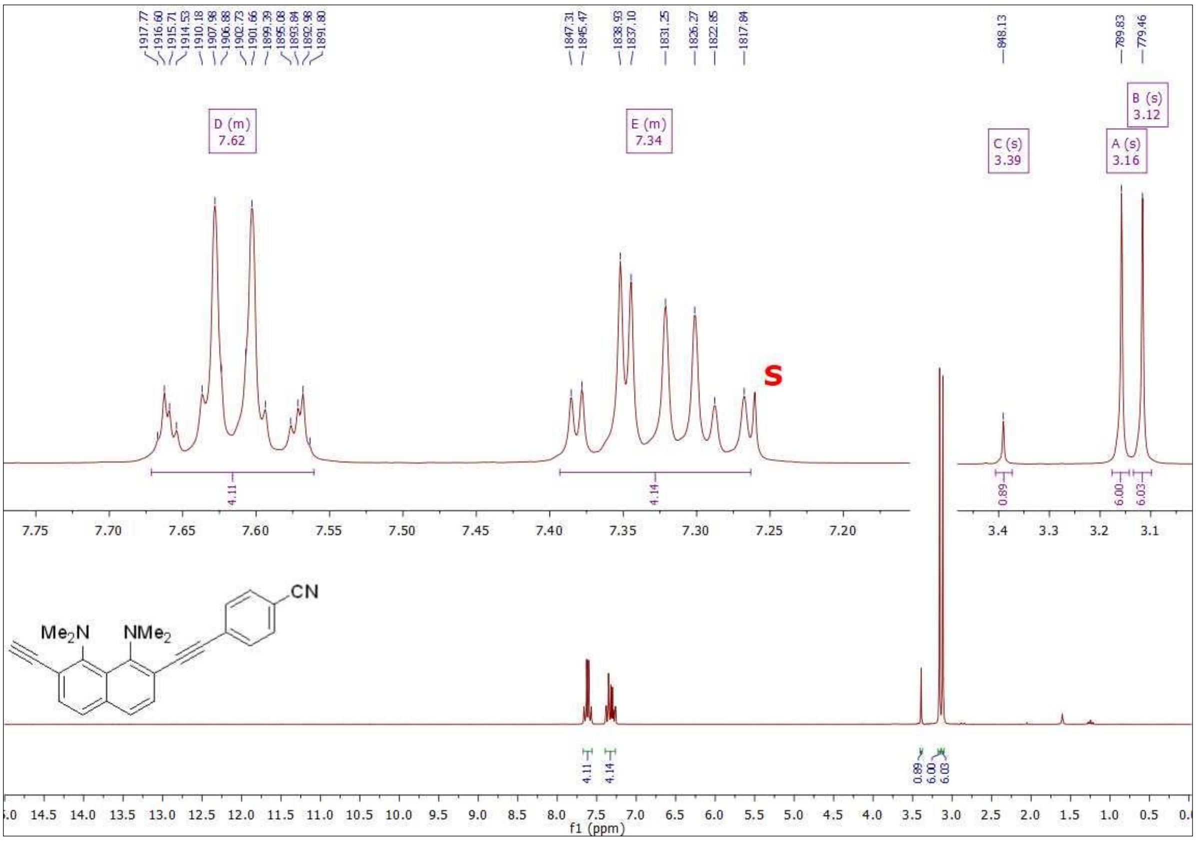

Figure S35. ^{1}H NMR spectrum of compound **6d** (250 MHz, $CDCl_3$).

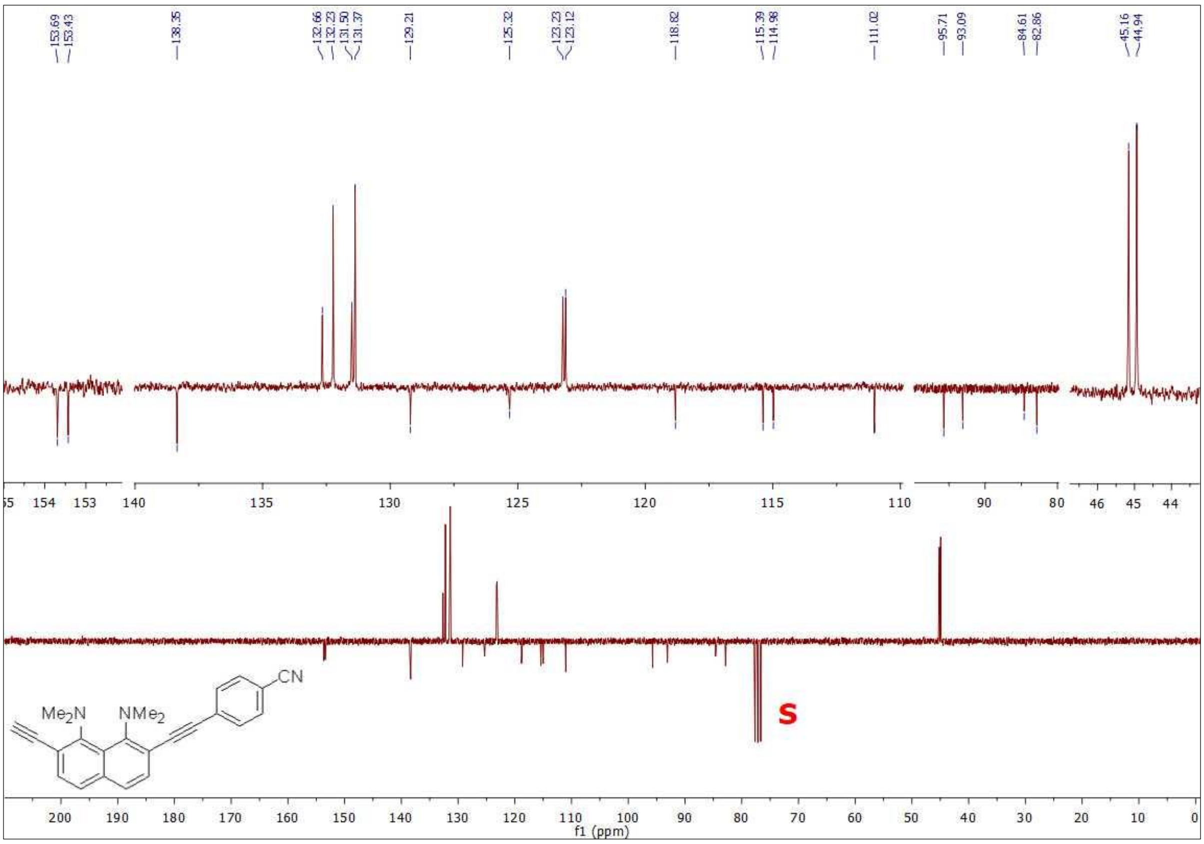

Figure S36. ^{13}C{^{1}H} APT-NMR spectrum of compound **6d** (62.9 MHz, $CDCl_3$).

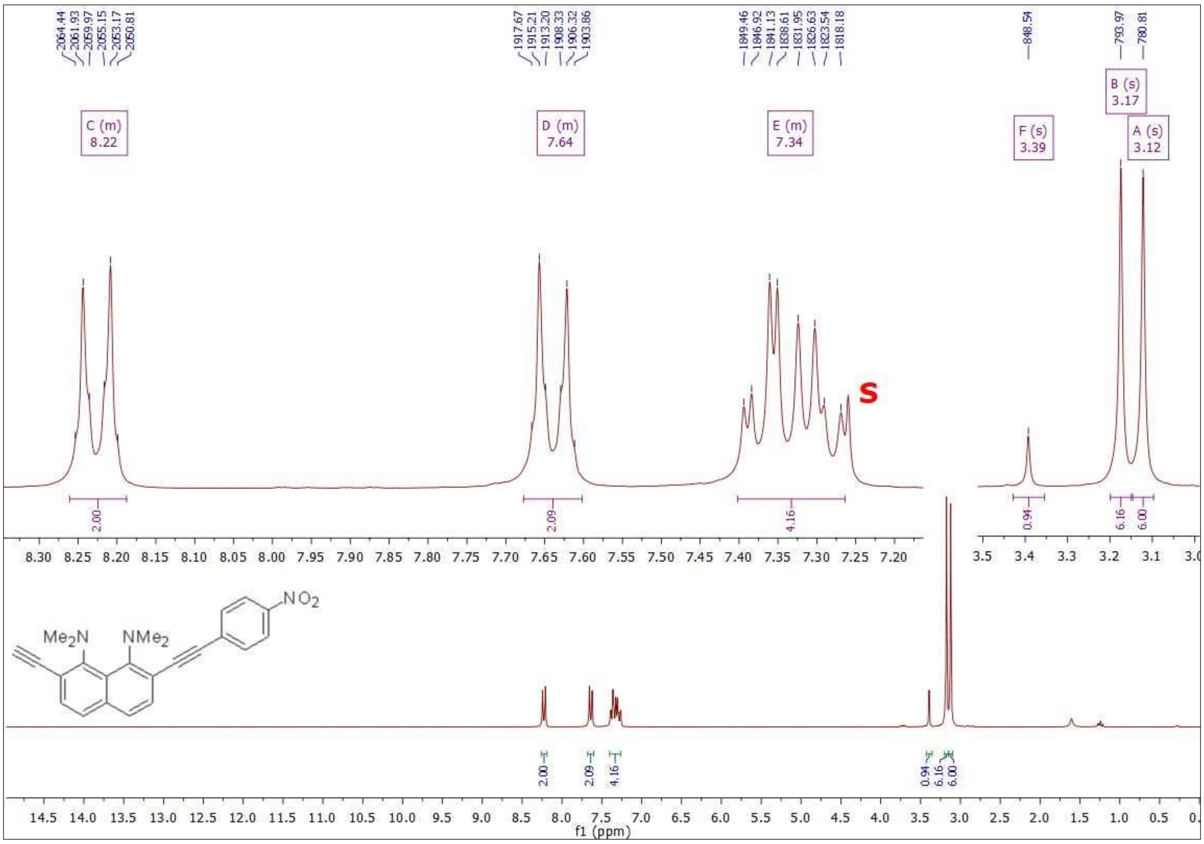

Figure S37. ^{1}H NMR spectrum of compound **6e** (250 MHz, $CDCl_3$).

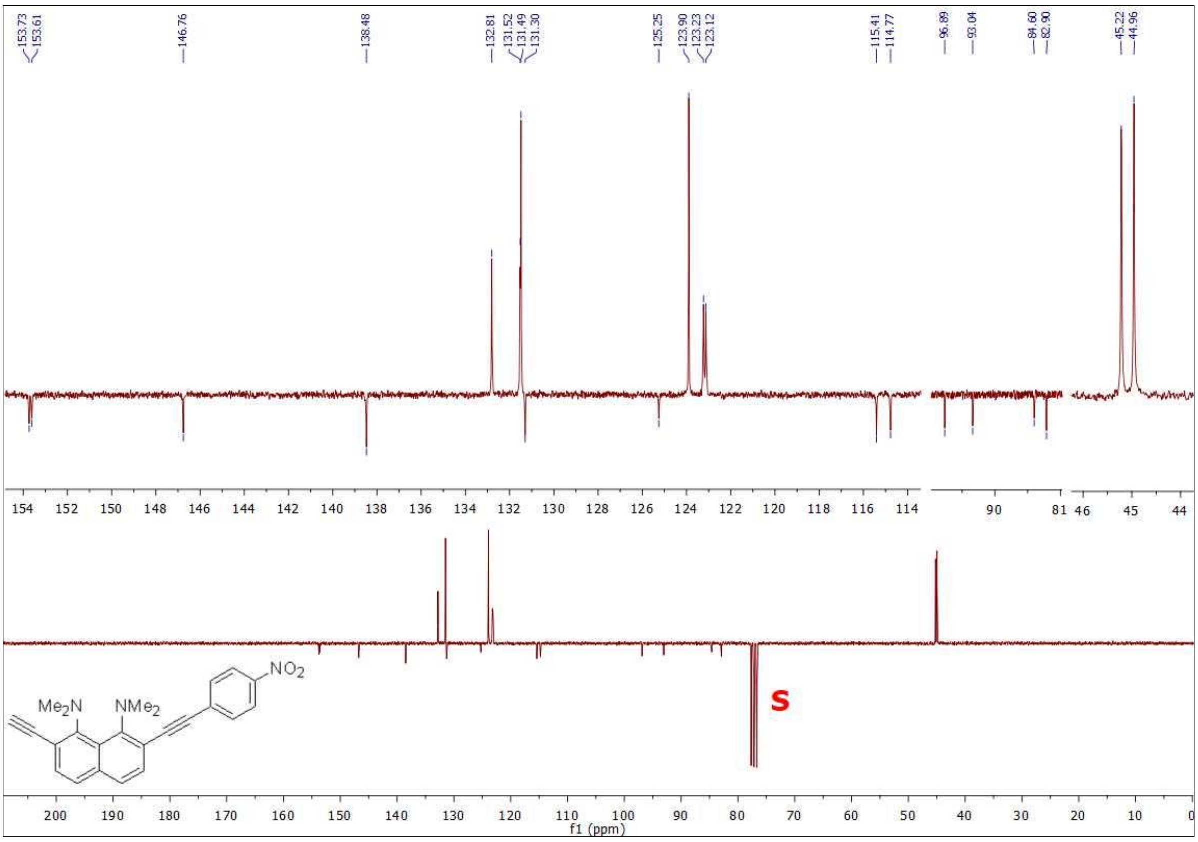

Figure S38. $^{13}C\{^1H\}$ APT-NMR spectrum of compound **6e** (62.9 MHz, $CDCl_3$).

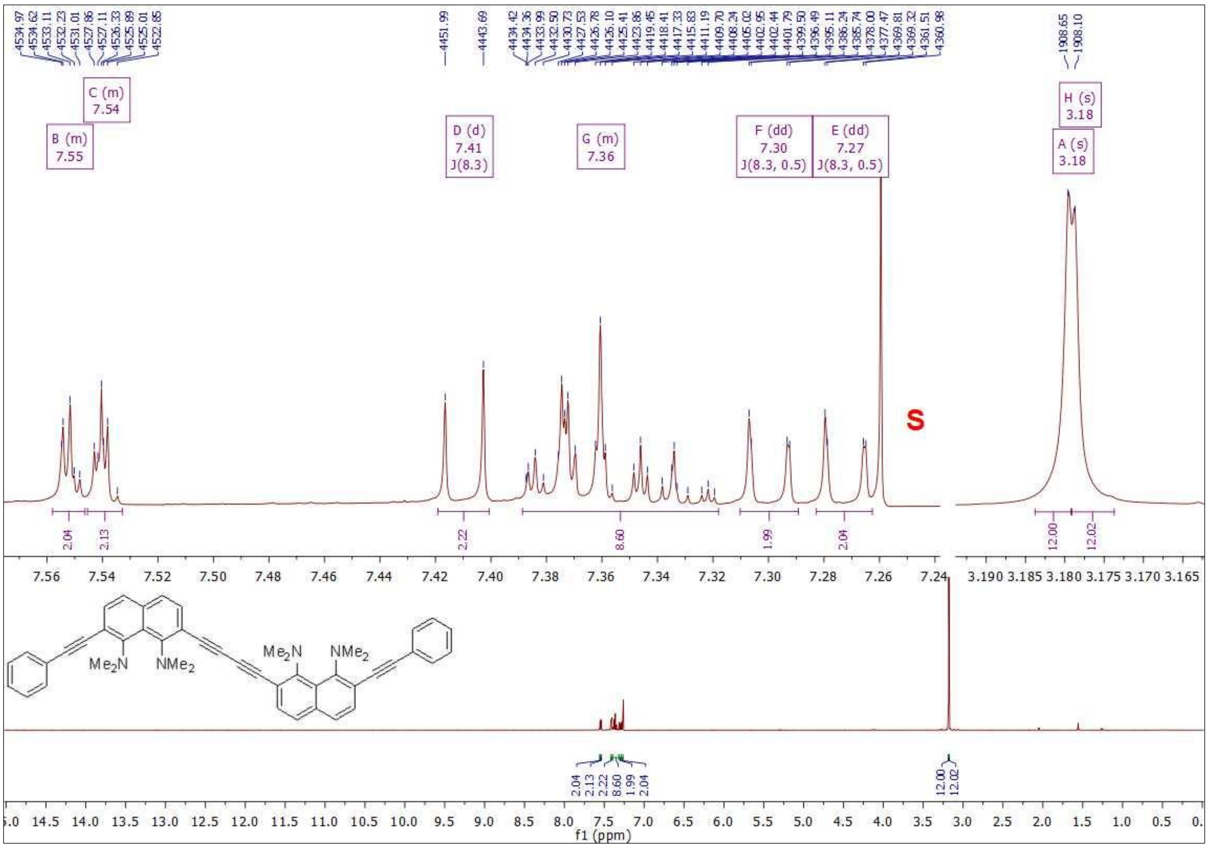

Figure S39. ^{1}H NMR spectrum of compound **5a** (600 MHz, CDCl$_3$).

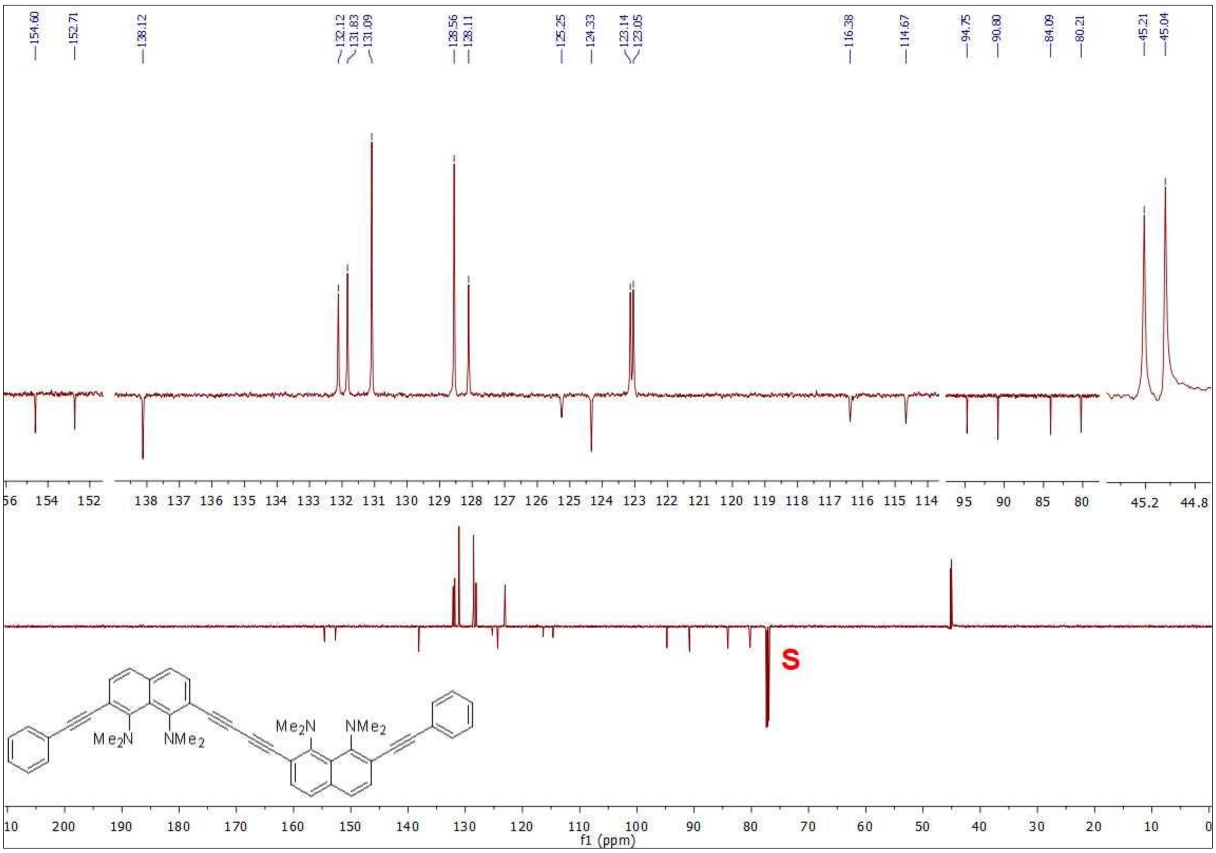

Figure S40. ^{13}C{^{1}H} APT-NMR spectrum of compound **5a** (150 MHz, CDCl$_3$).

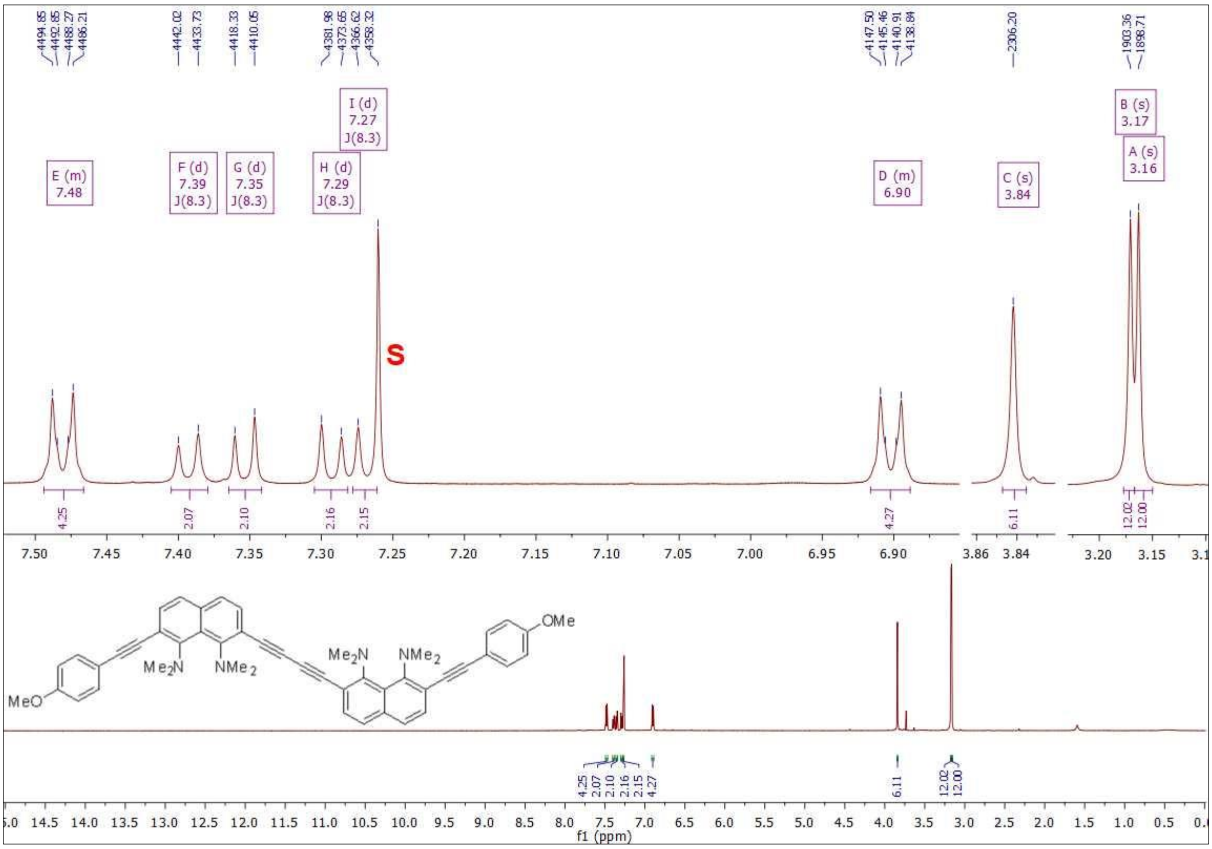

Figure S41. ^{1}H NMR spectrum of compound **5b** (600 MHz, $CDCl_3$).

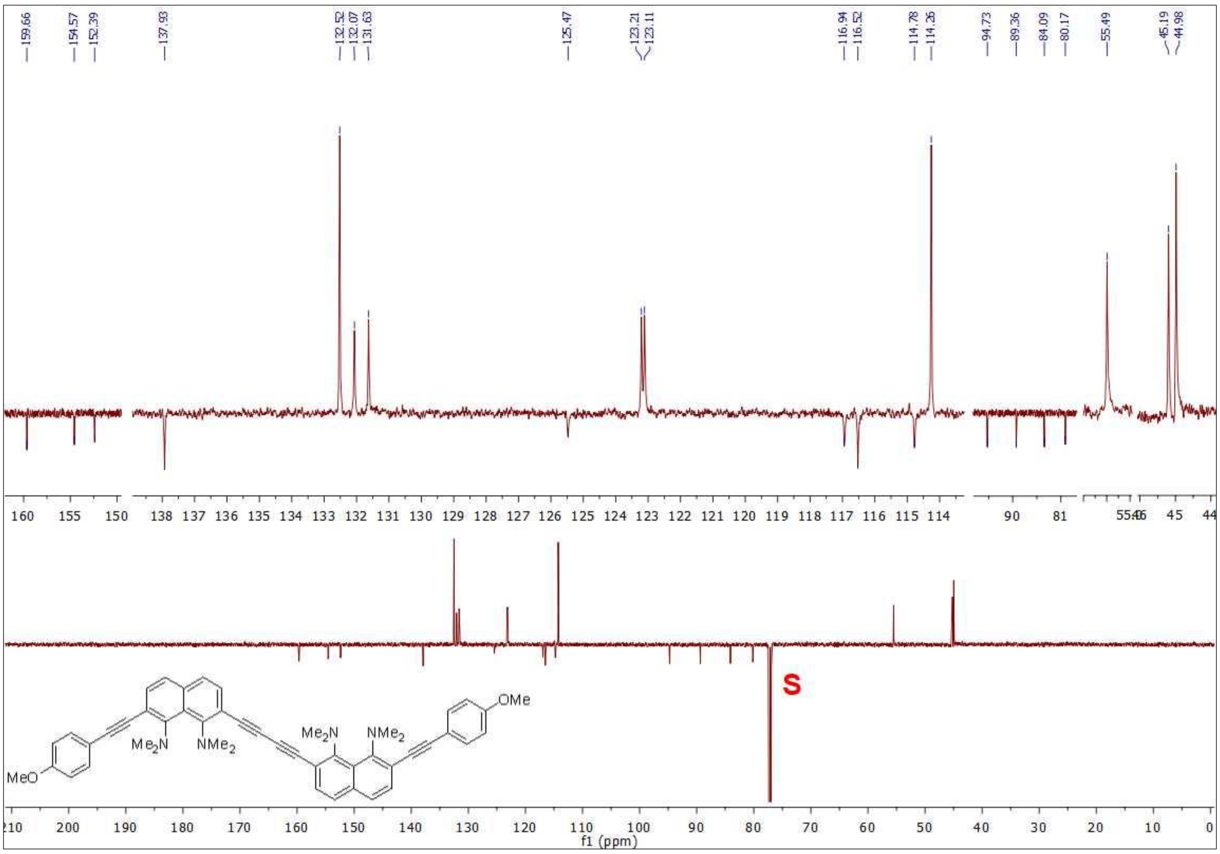

Figure S42. $^{13}C\{^1H\}$ APT-NMR spectrum of compound **5b** (150 MHz, $CDCl_3$).

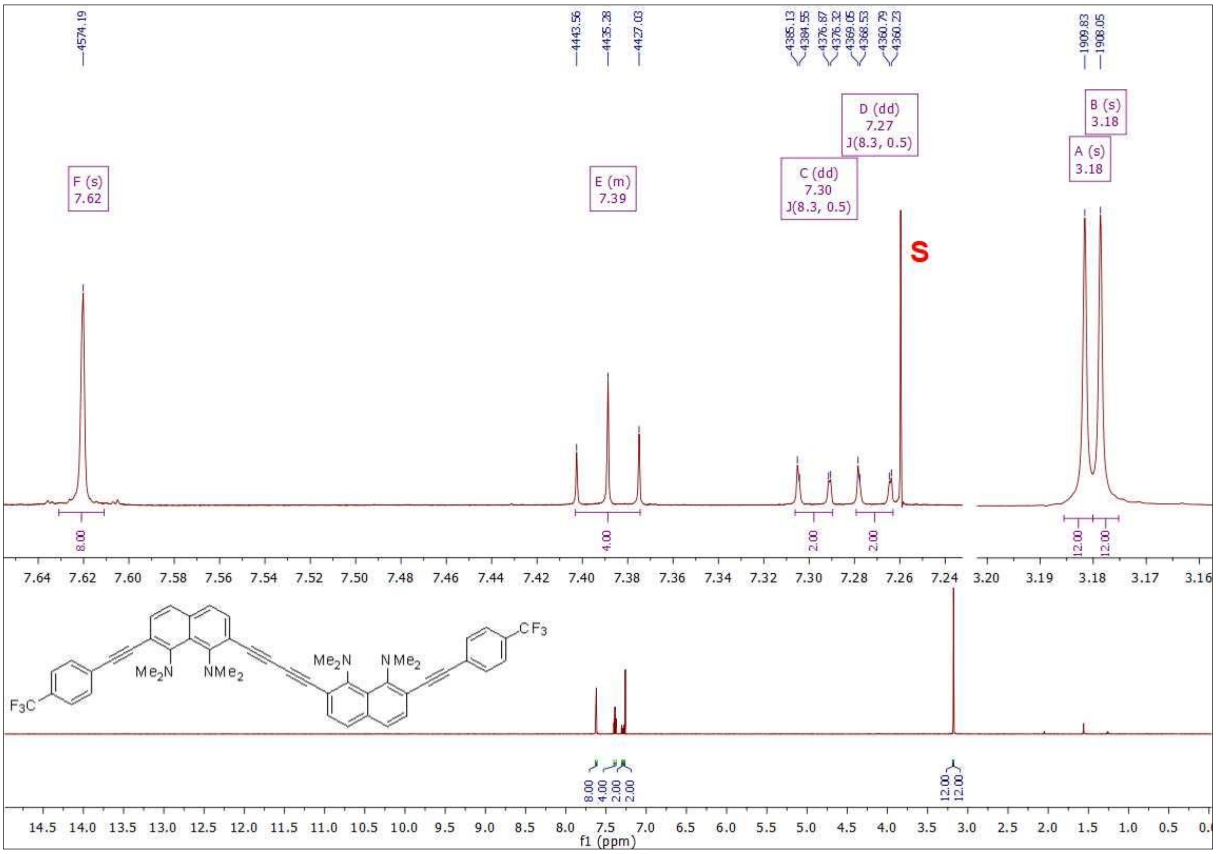

Figure S43. ^{1}H NMR spectrum of compound **5c** (600 MHz, CDCl$_3$).

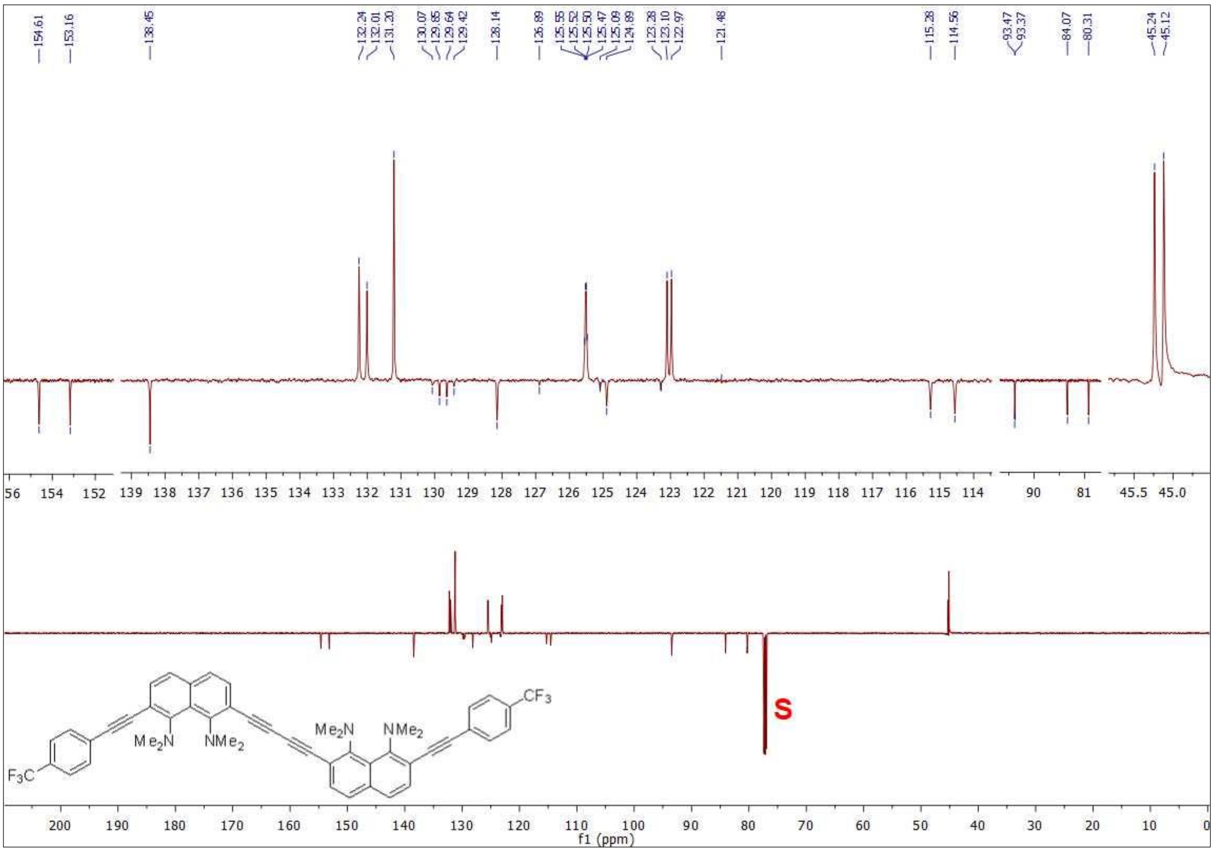

Figure S44. ^{13}C{^{1}H} APT-NMR spectrum of compound **5c** (150 MHz, CDCl$_3$).

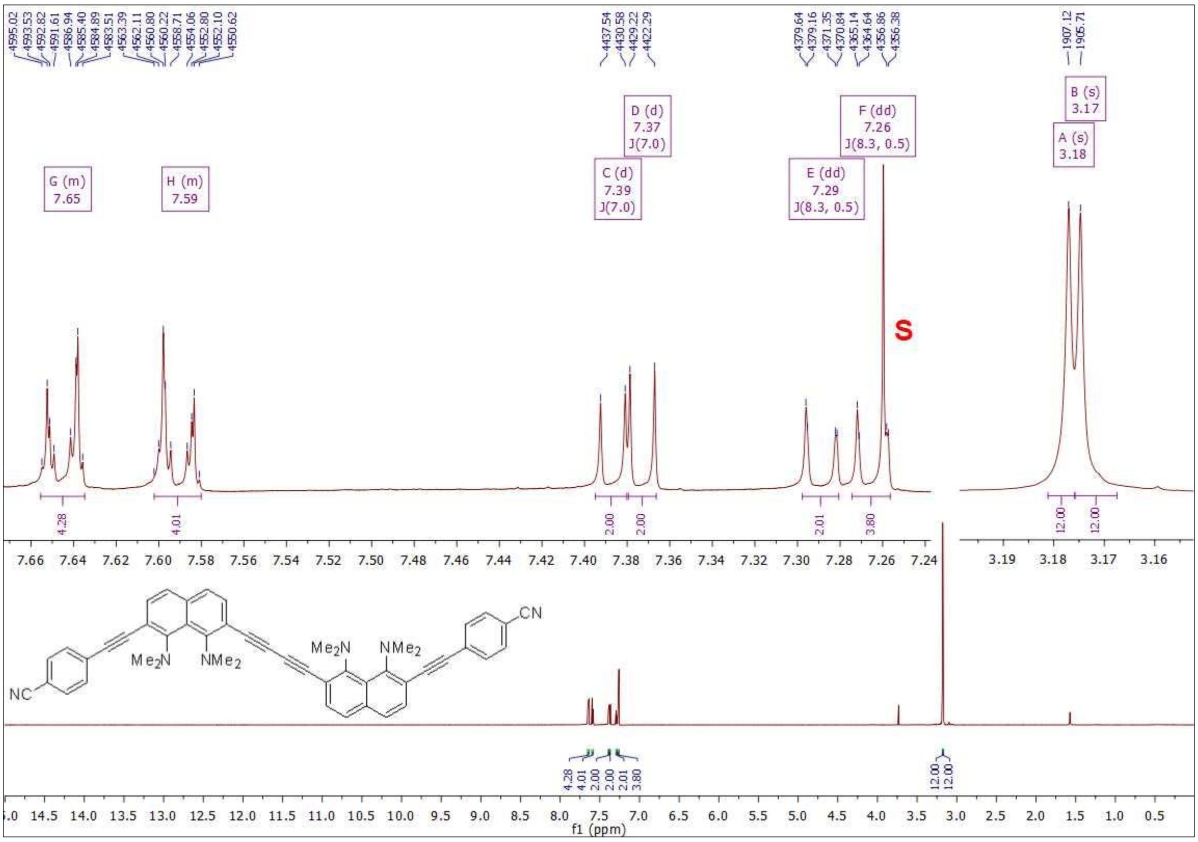

Figure S45. ^{1}H NMR spectrum of compound **5d** (600 MHz, CDCl$_3$).

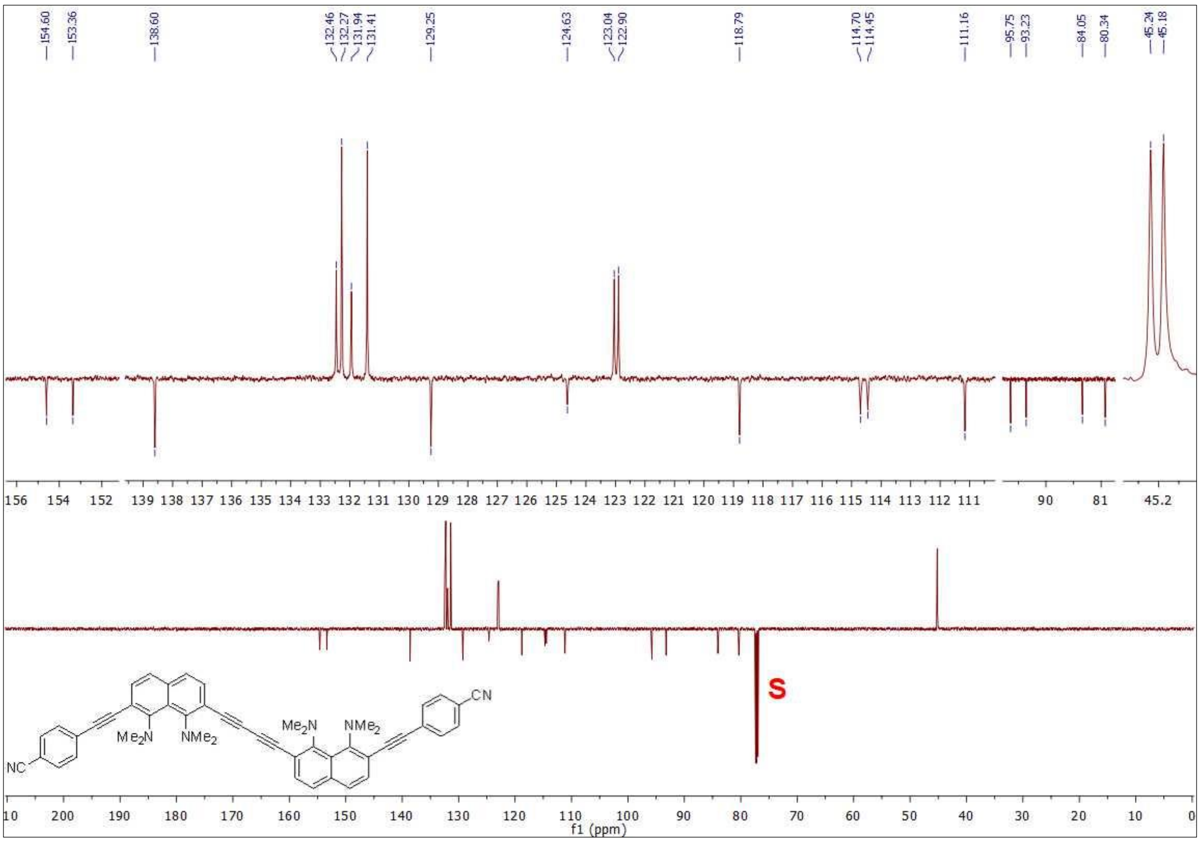

Figure S46. ^{13}C{^{1}H} APT-NMR spectrum of compound **5d** (150 MHz, CDCl$_3$).

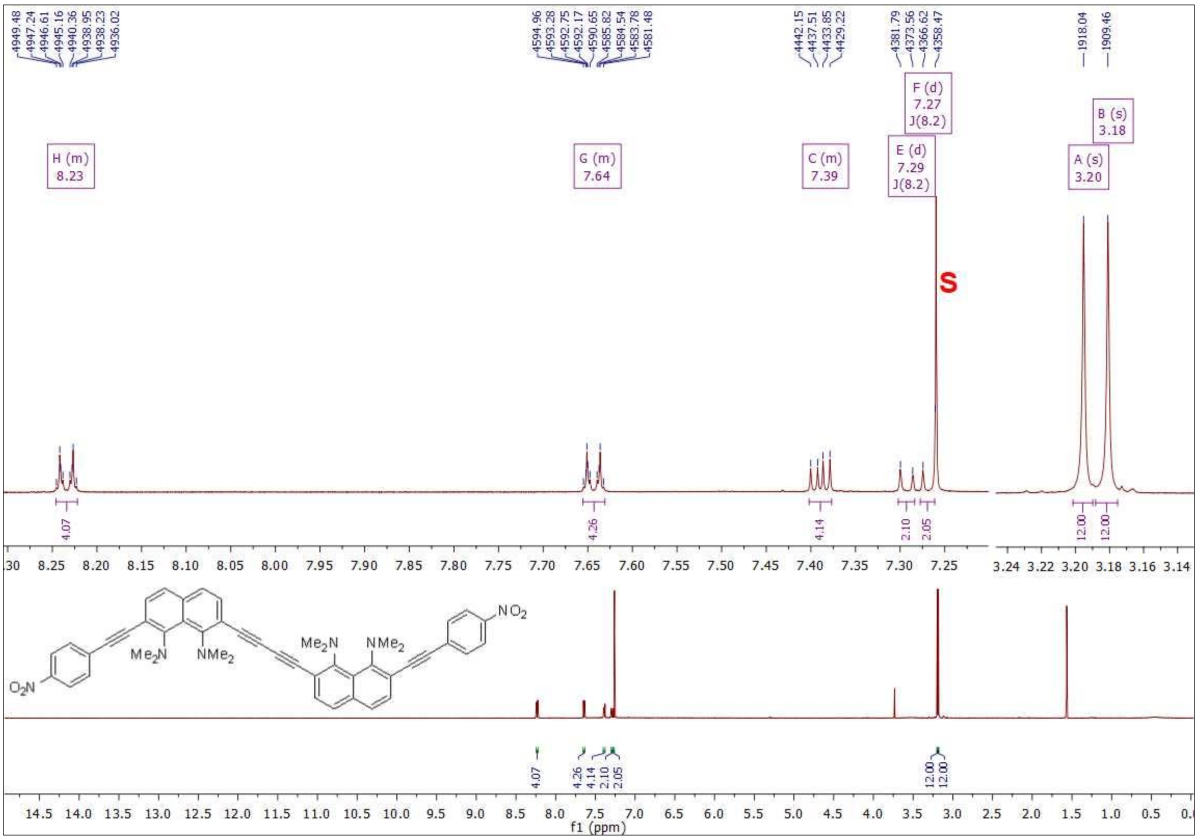

Figure S47. ^{1}H NMR spectrum of compound **5e** (600 MHz, CDCl$_3$).

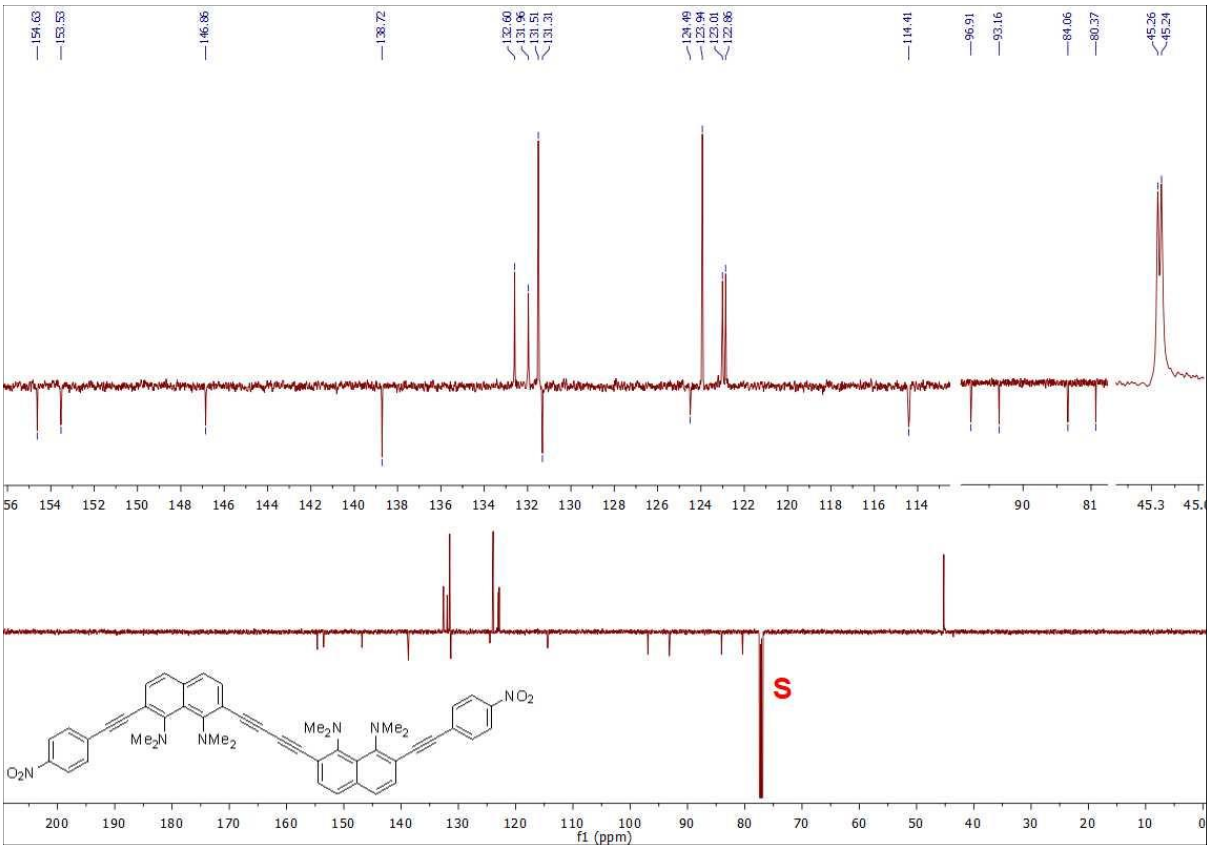

Figure S48. ^{13}C{^{1}H} APT-NMR spectrum of compound **5e** (150 MHz, CDCl$_3$).

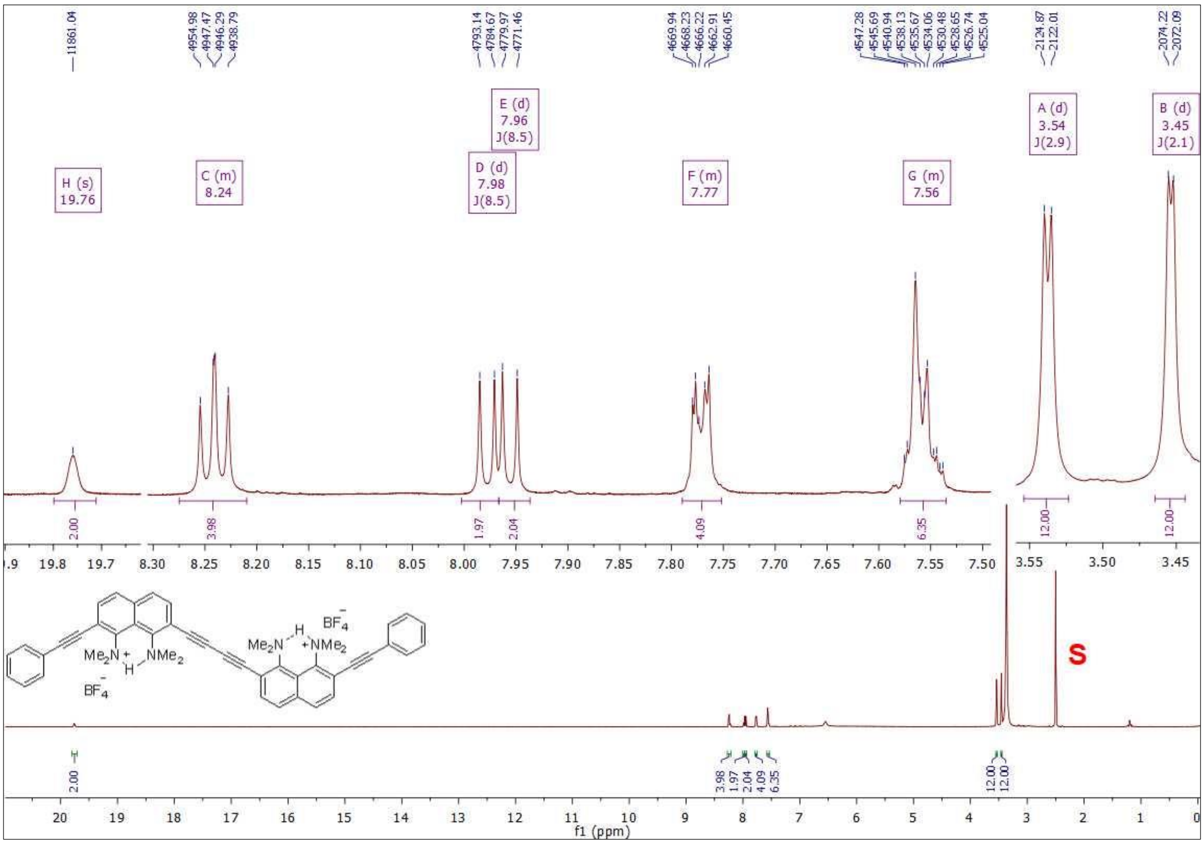

Figure S49. ^{1}H NMR spectrum of compound **11a** (600 MHz, DMSO-d$_6$).

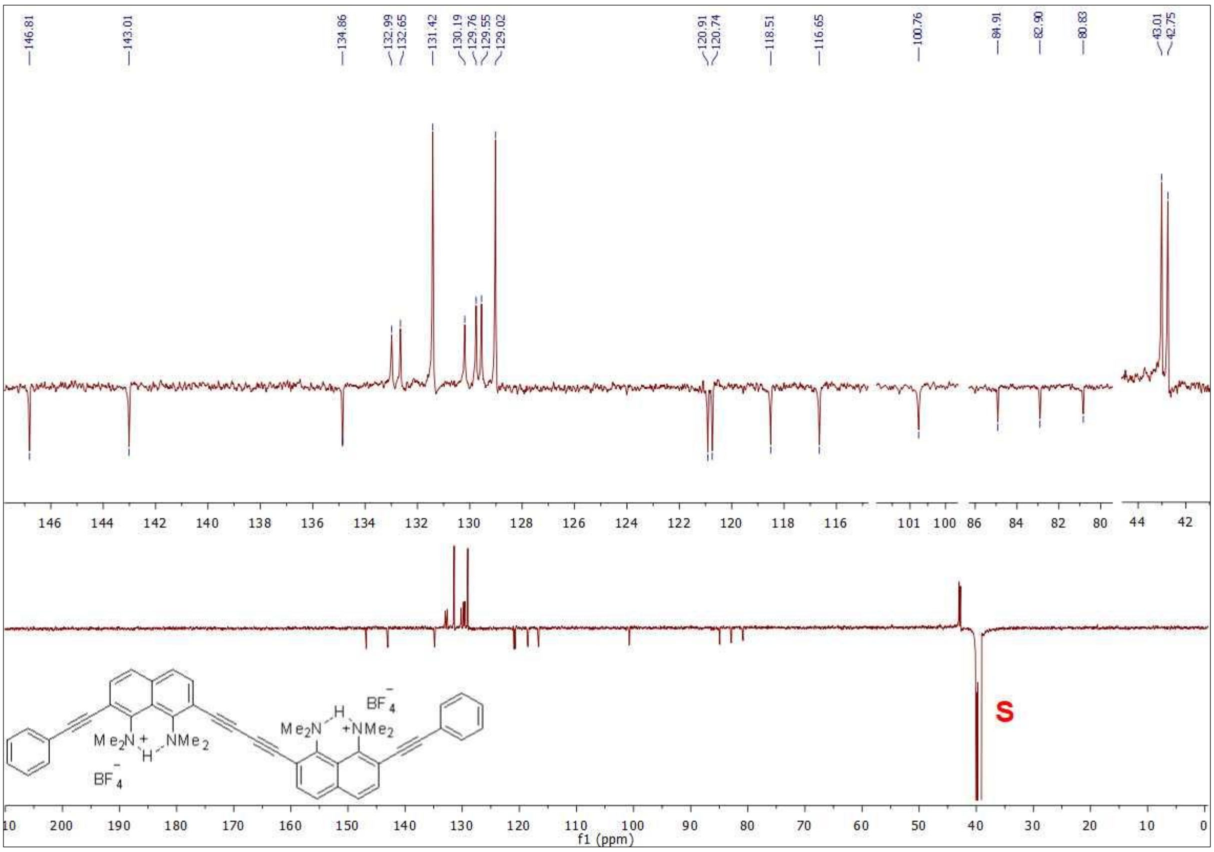

Figure S50. ^{13}C{^{1}H} APT-NMR spectrum of compound **11a** (150 MHz, DMSO-d$_6$).

Figure S51. ^{1}H NMR spectrum of compound **11b** (600 MHz, DMSO-d$_6$).

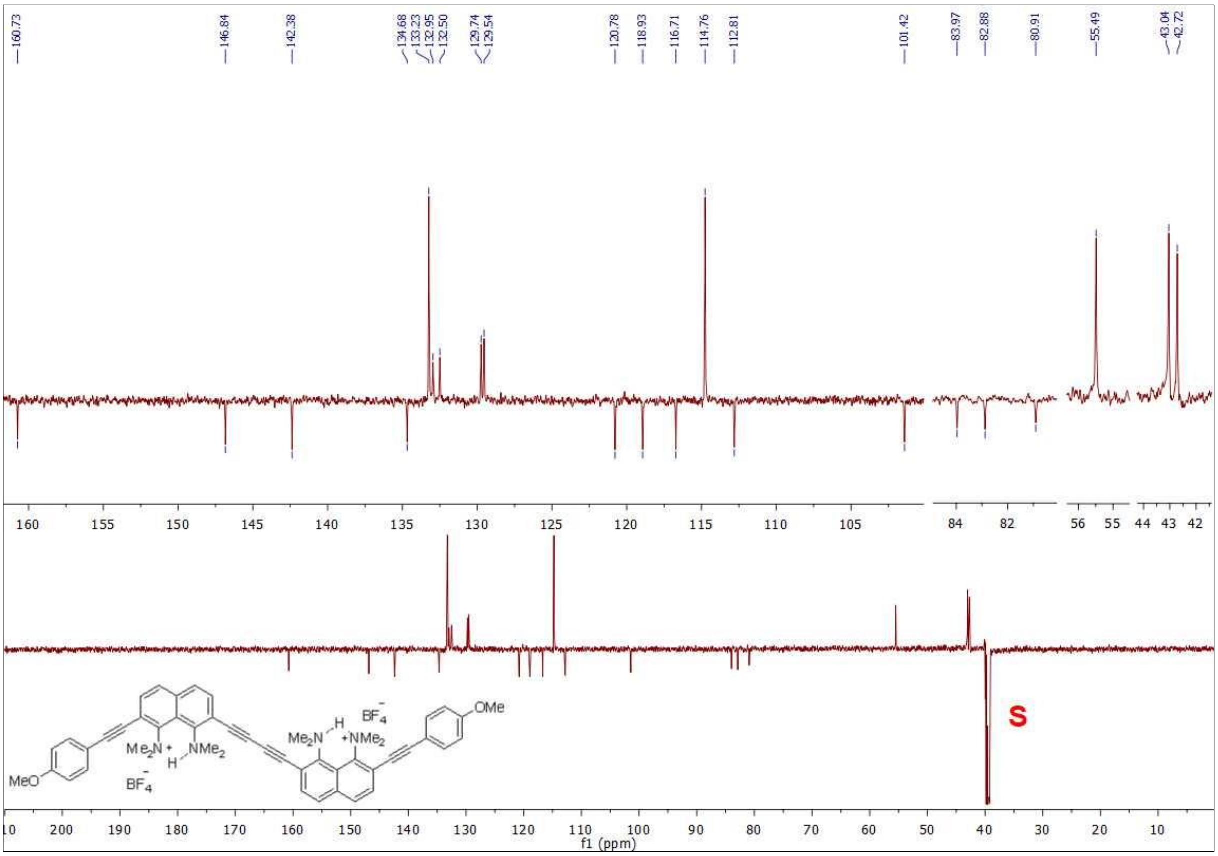

Figure S52. ^{13}C{^{1}H} APT-NMR spectrum of compound **11b** (150 MHz, DMSO-d$_6$).

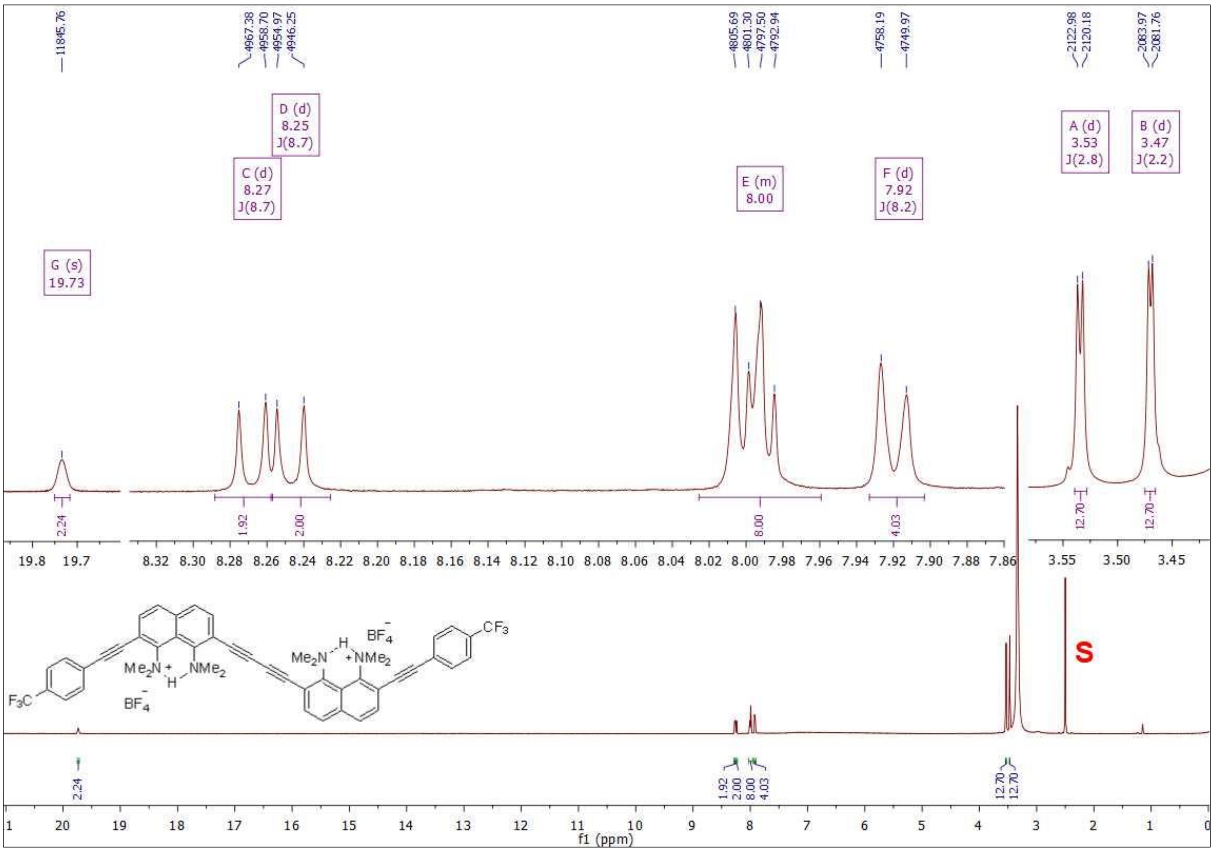

Figure S53. ^{1}H NMR spectrum of compound **11c** (600 MHz, DMSO-d$_6$).

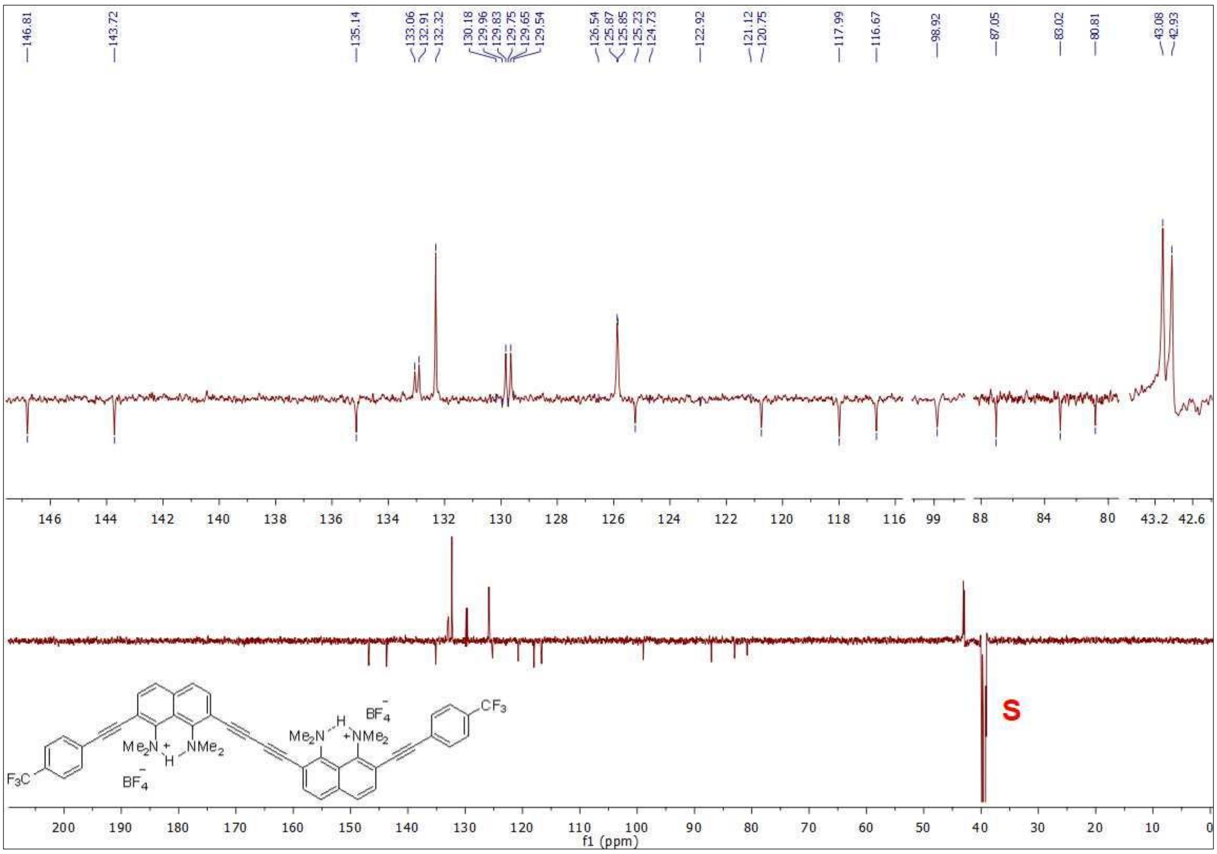

Figure S54. ^{13}C{^{1}H} APT-NMR spectrum of compound **11c** (150 MHz, DMSO-d$_6$).

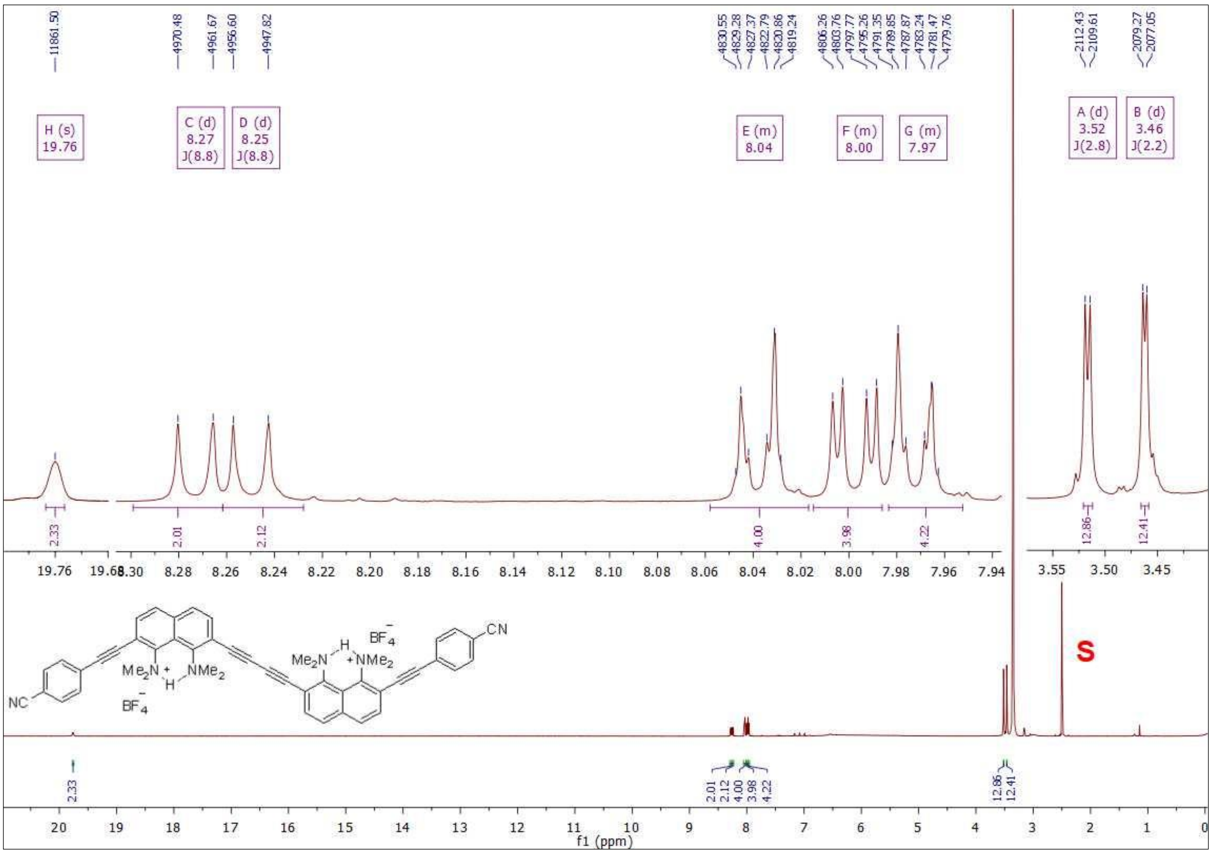

Figure S55. ^{1}H NMR spectrum of compound **11d** (600 MHz, DMSO-d_6).

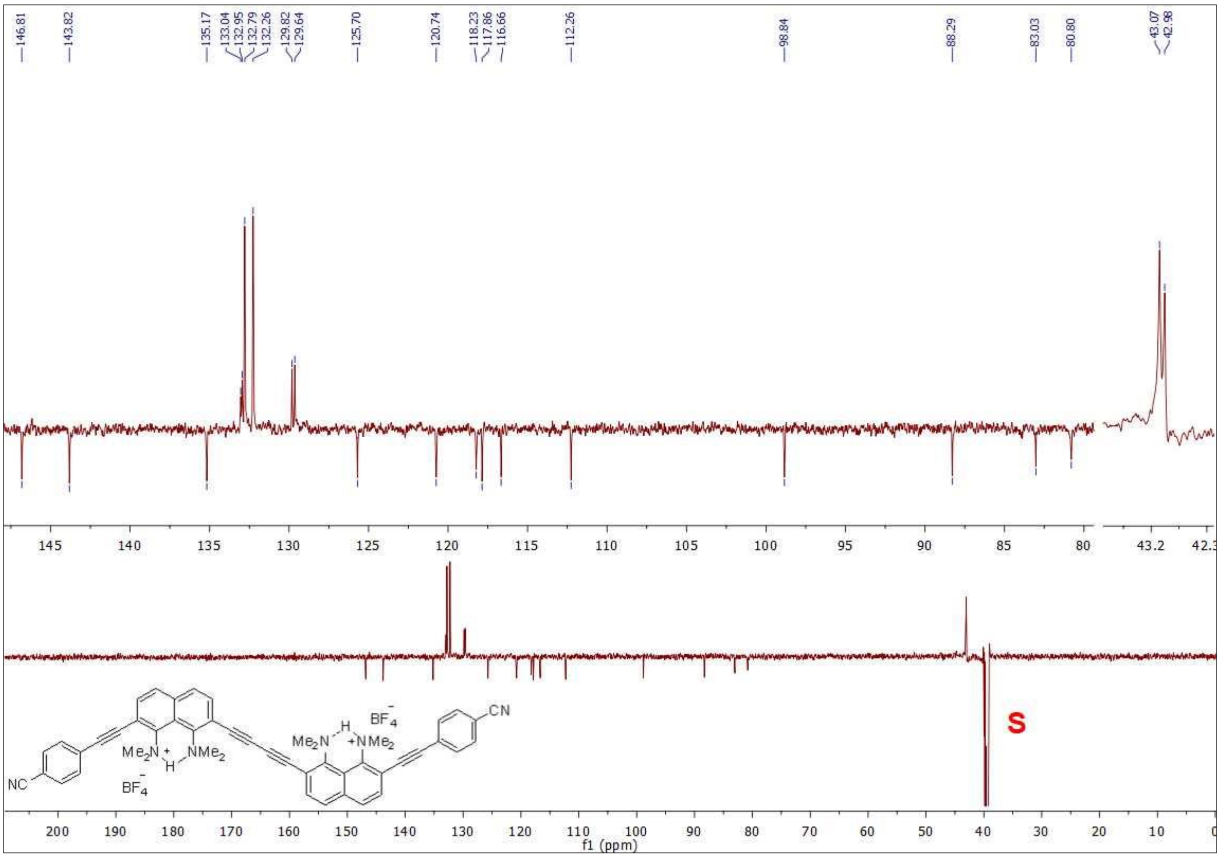

Figure S56. $^{13}C\{^{1}H\}$ APT-NMR spectrum of compound **11d** (150 MHz, DMSO-d_6).

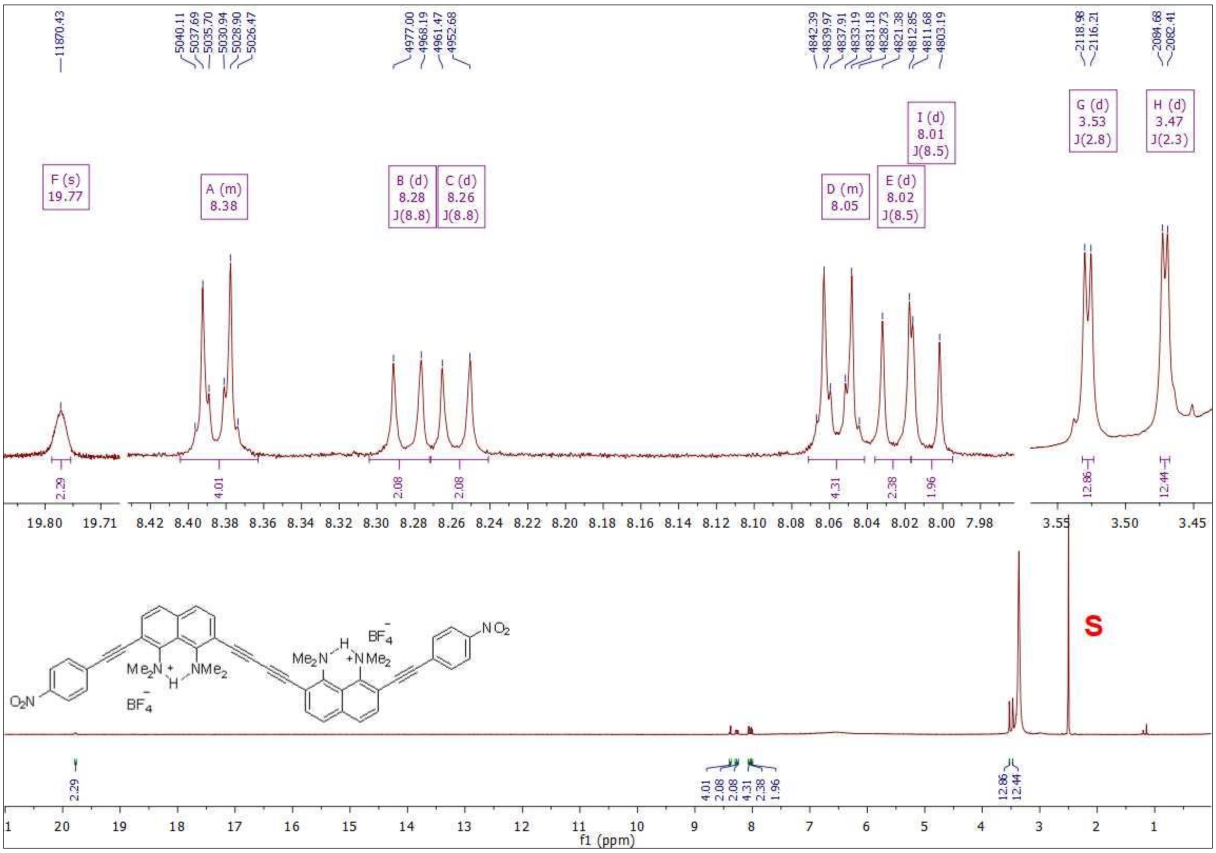

Figure S57. ^{1}H NMR spectrum of compound **11e** (600 MHz, DMSO-d$_6$).

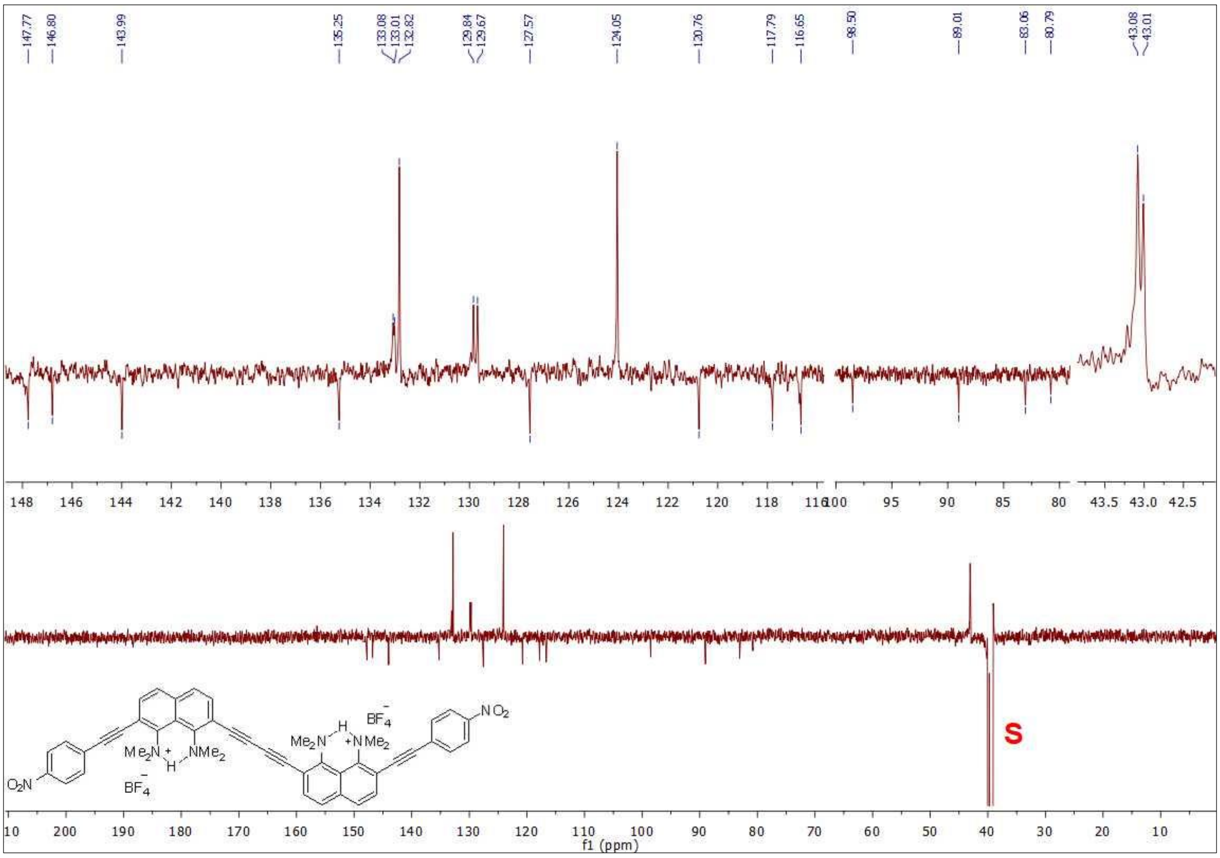

Figure S58. ^{13}C{^{1}H} APT-NMR spectrum of compound **11e** (150 MHz, DMSO-d$_6$).

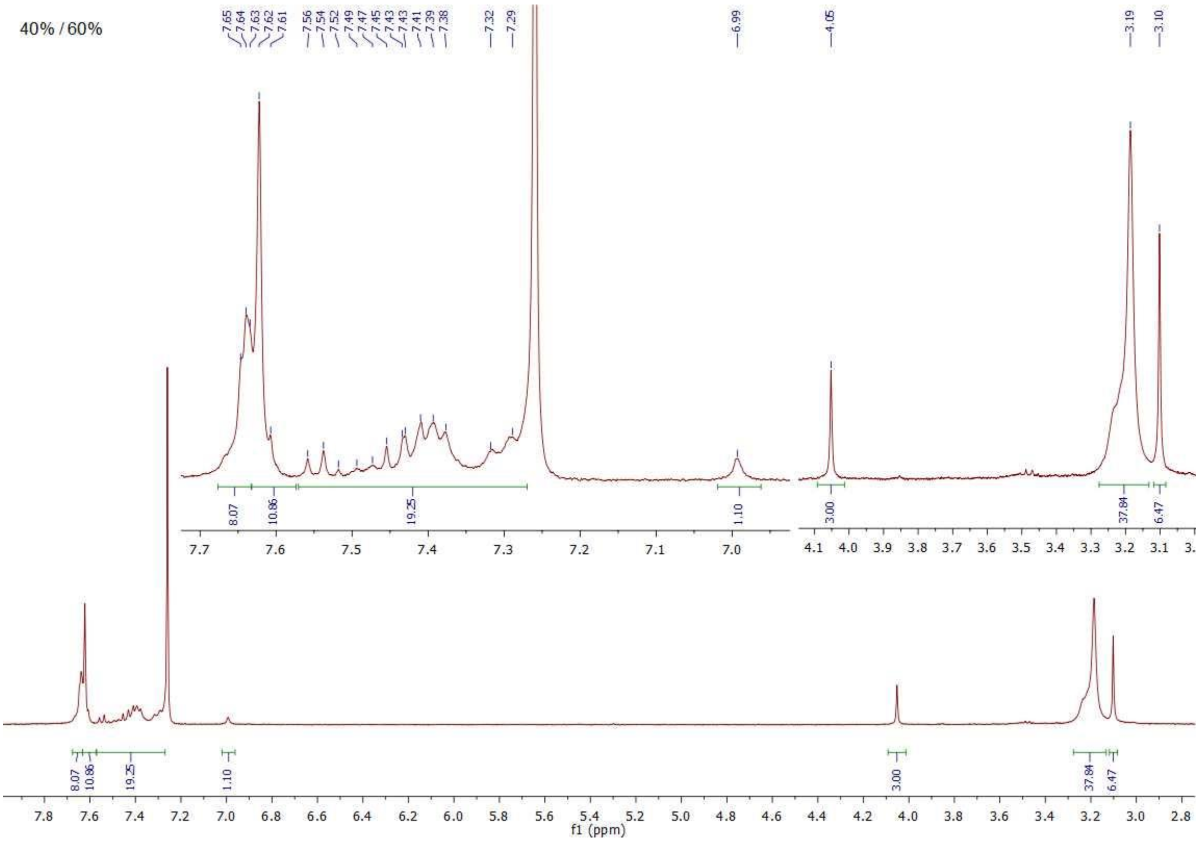

Figure S59. ^{1}H NMR spectrum of a mixture of compounds **5c** and **12** formed after keeping a solution of **5c** in chloroform/ethanol 1:1 for a month (250 MHz, CDCl$_3$).

X-ray data

Crystal structure determination: X-Ray measurements were conducted with four-circle SuperNova and XtaLAB Synergy diffractometers, single source at offset/far, AtlasS2 and HyPix3000 detectors (CuK_α radiation). Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2215907 (**5b**), CCDC 2215905 (**5d**), CCDC 2215904 (**5e**), CCDC 2215908 (**9e**), CCDC 2215909 (**11c**) and CCDC 2215906 (**12**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

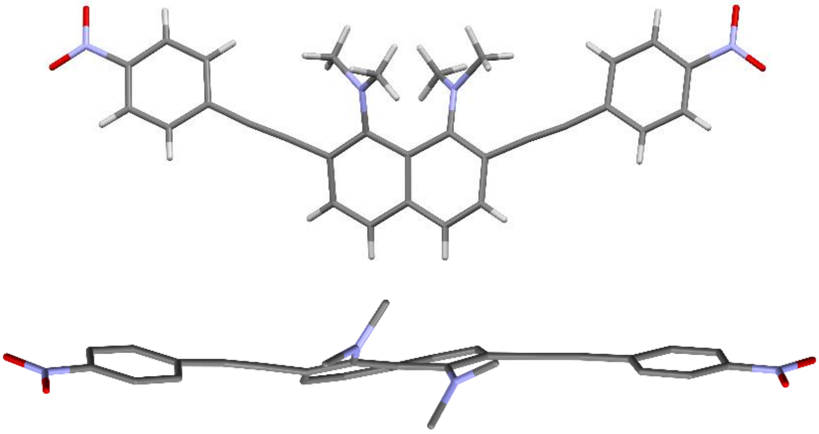

Figure S60. Molecular structure of compound **9e:** frontal (top) and side views (bottom, hydrogen atoms omitted).

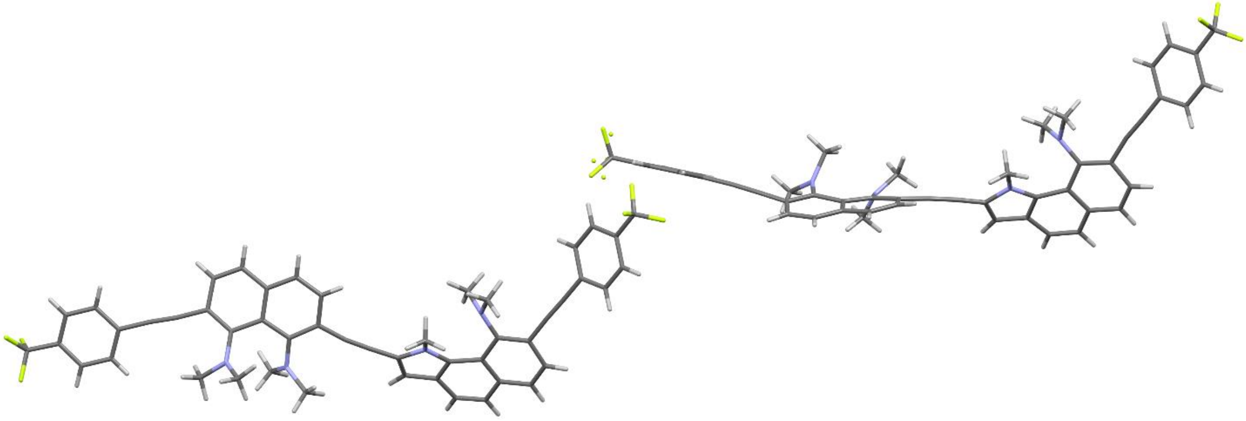

Figure S61. Molecular structure of compound **12** (two independent molecules in the unit cell).

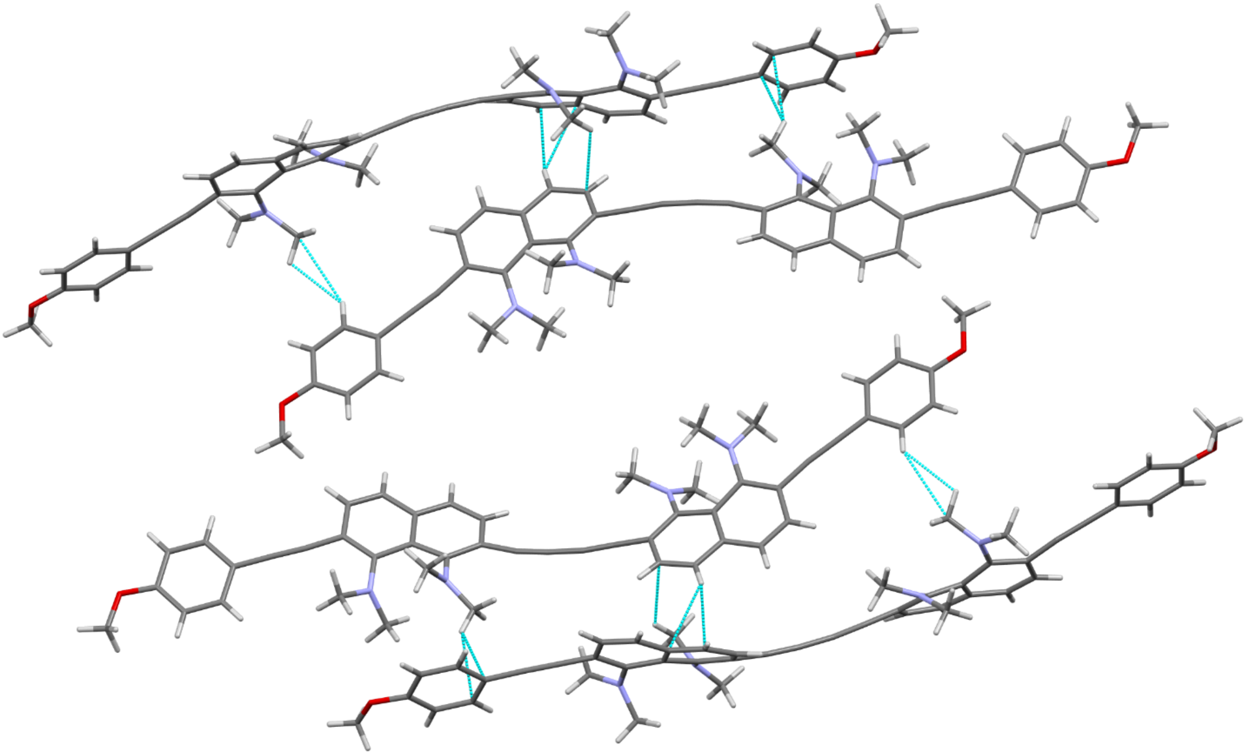

Figure S62. Short contacts in the unit cell of **5b**.

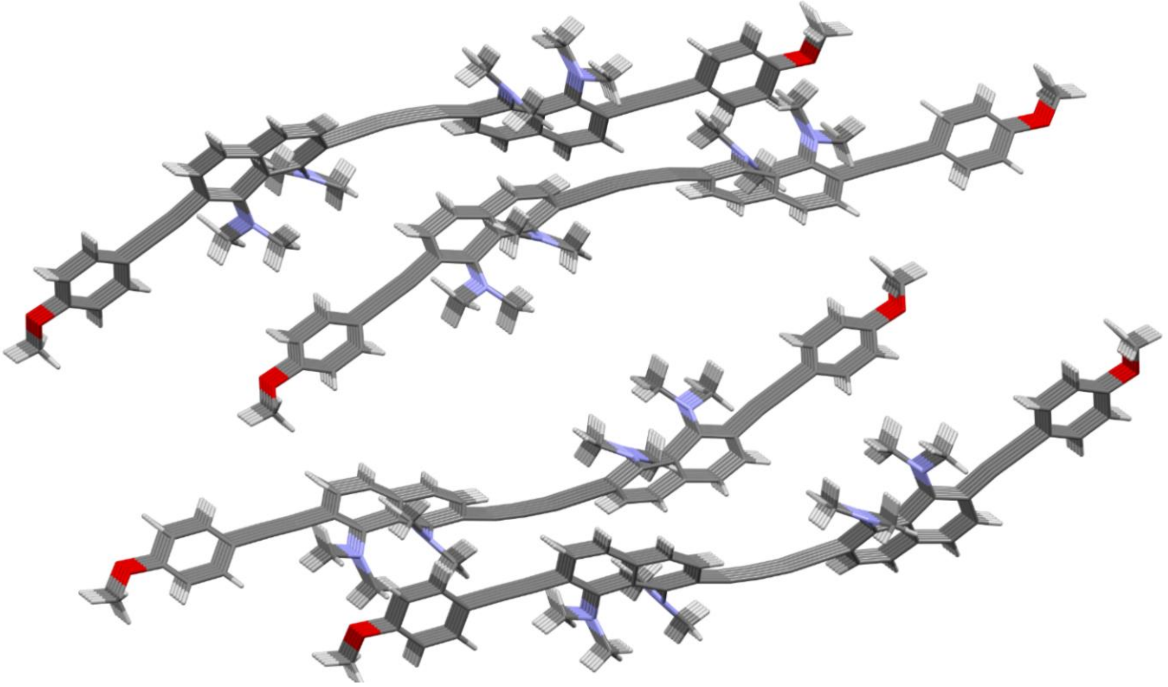

Figure S63. Crystal packing of **5b** (view along *b* axis).

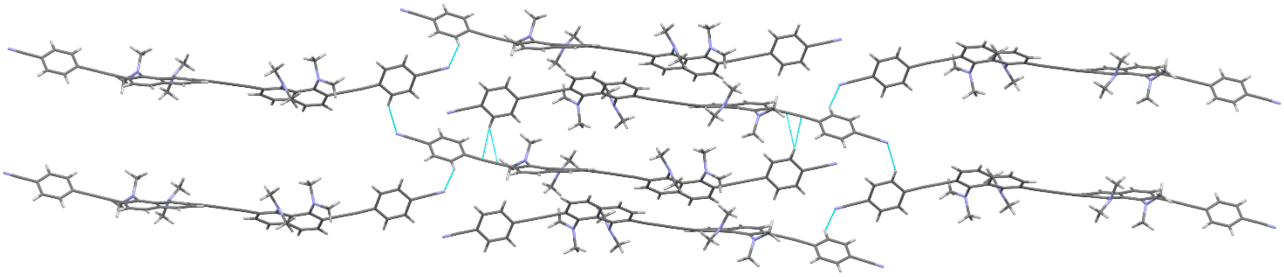

Figure S64. Crystal packing of **5d** (short contacts).

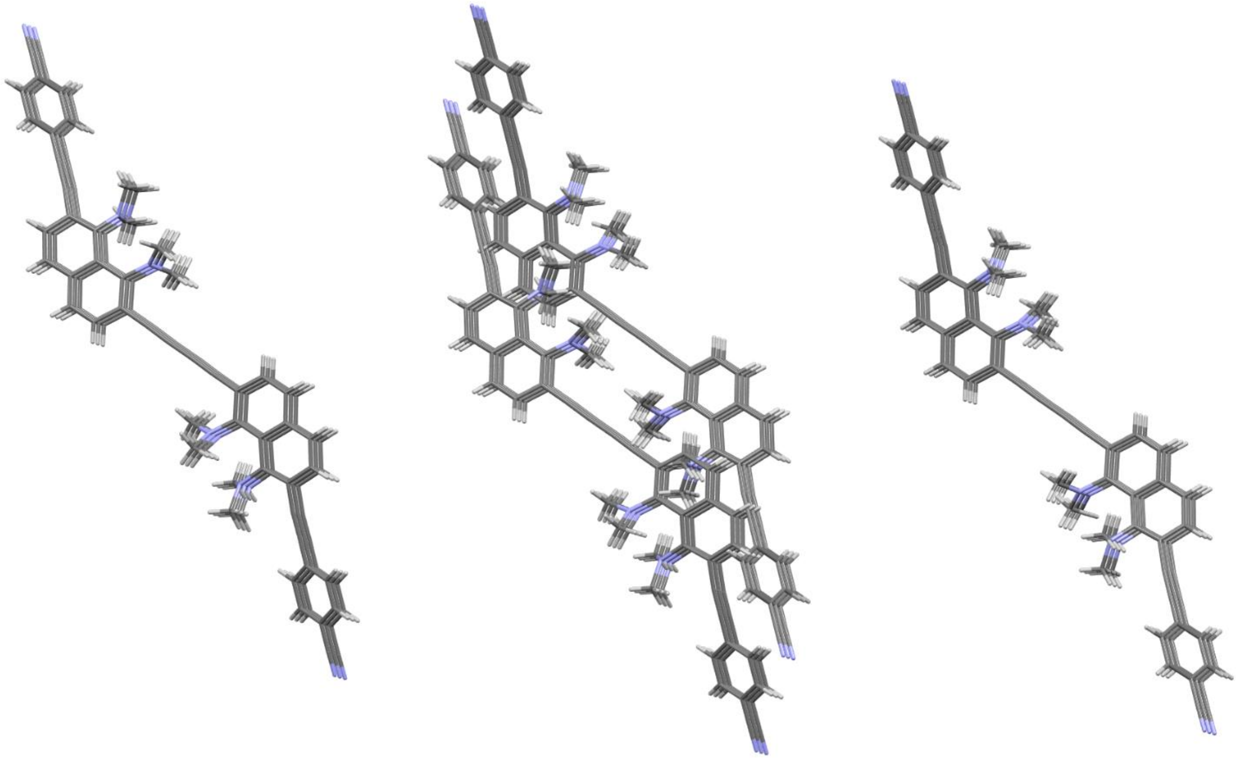

Figure S65. Crystal packing of **5d** (view along *b* axis).

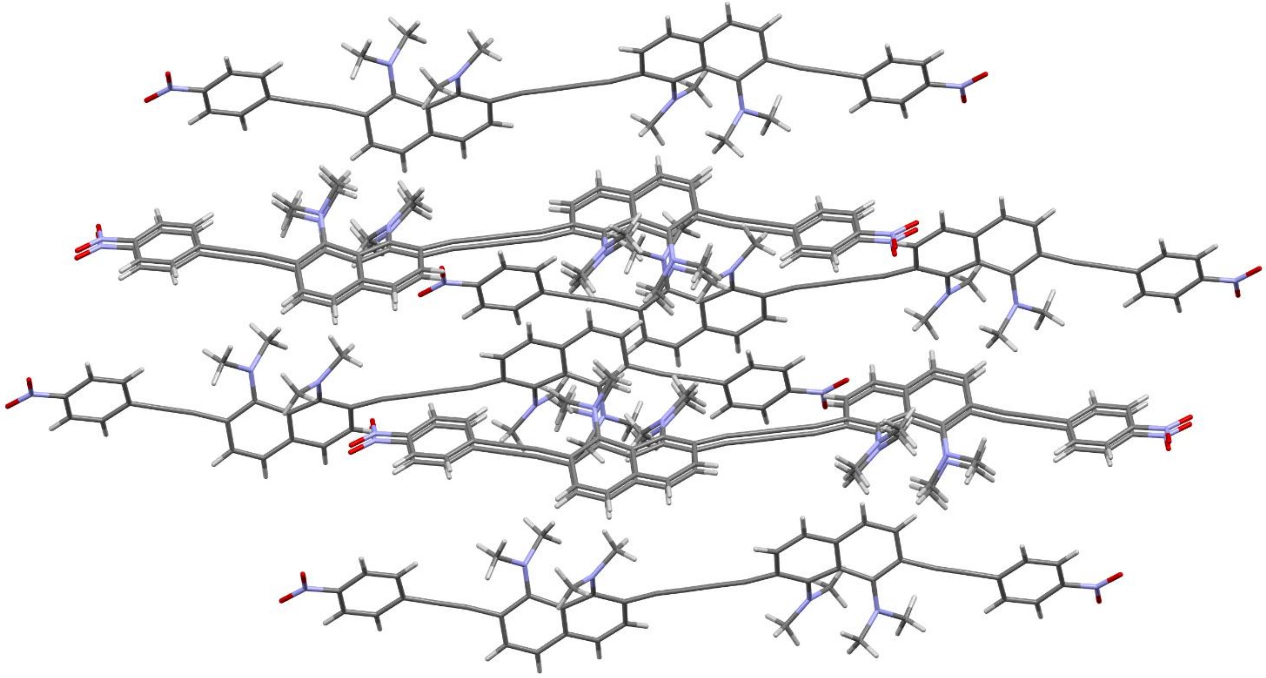

Figure S66. Crystal packing of **5e** (view along *b* axis).

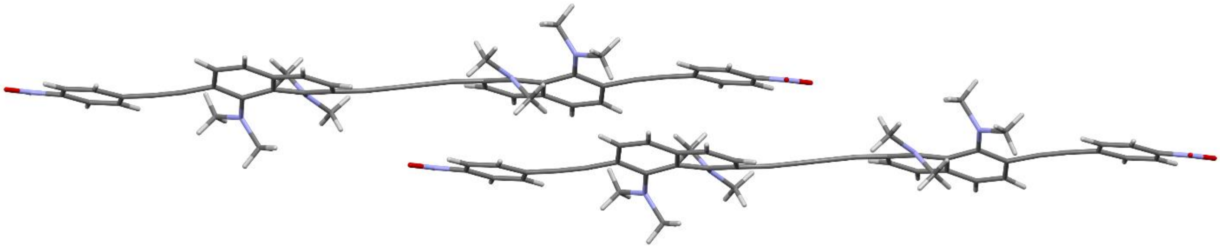

Figure S67. Molecules **5e** tend to approach π-donor DMAN and π-acceptor *p*-nitrophenyl fragments with the shortest distance between the two molecules equal to 2.810 Å.

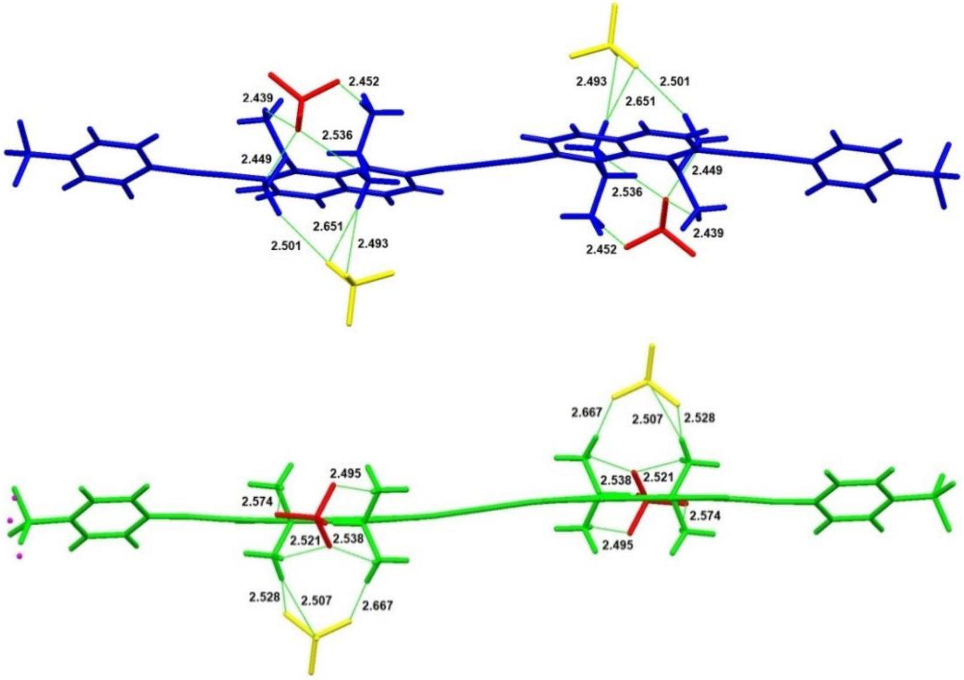

Figure S68. Two types of independent non-equivalent dications, marked in blue and green, and two types of BF_4^- anions, marked in red and yellow, in the crystal structure of salt **11c**.

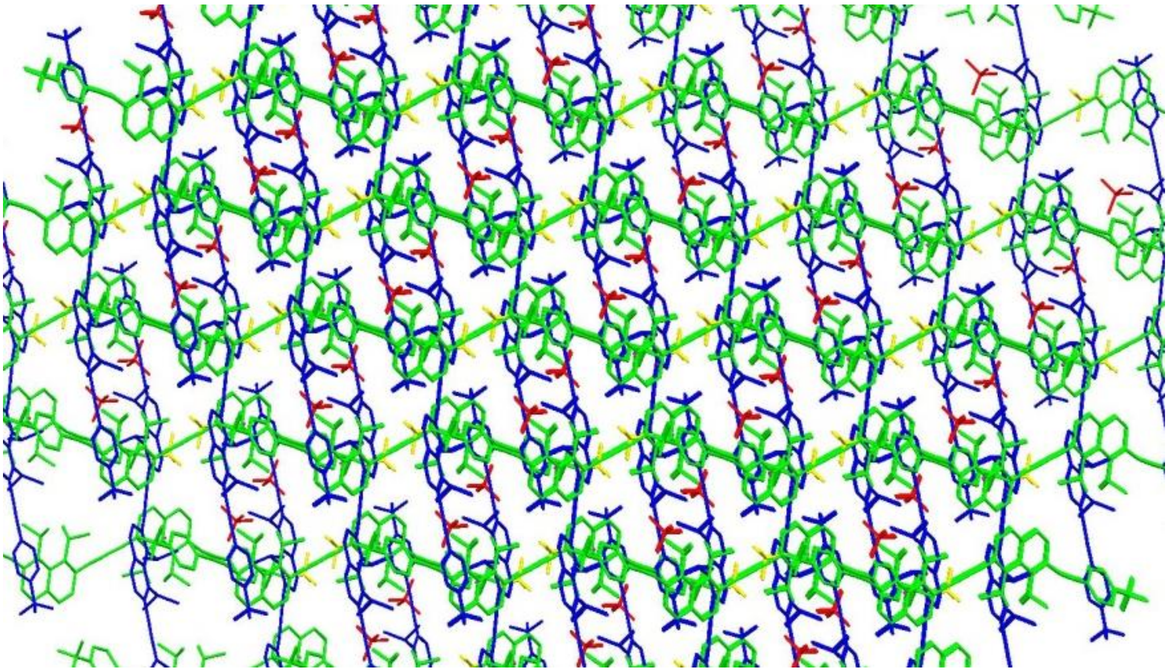

Figure S69. Crystal packing of salt **11c** with perpendicular layers of cations of two types.

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