Supporting Information

Three components selective synthesis of phenothiazines and bis-phenothiazines under metal-free conditions

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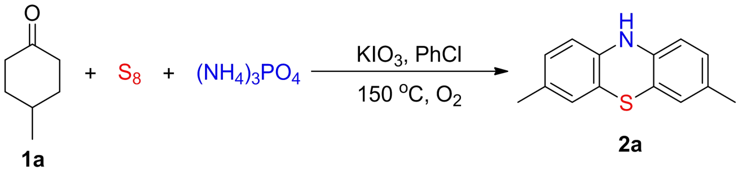
1. General information

Unless otherwise noted, all commercially available reagents and solvents are reagent grade and were used without further purification. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced solvent signals. Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (HRMS) were performed on FTMS ICR MS BRUKER 7T or Agilent 6230 TOF LC/MS. Melting points were measured on BÜCHI B-545 melting point instrument and were uncorrected. X-ray crystal structure data was using collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The structures were solved by direct methods using Olex2 software. The structures of known compounds were further corroborated by comparing their NMR and MS data with those of literature.

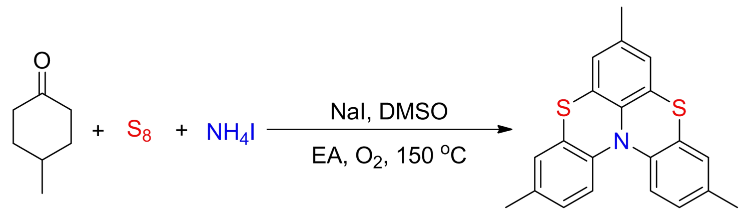
2. General procedure

2.1 General procedure for the synthesis of phenothiazine 2a.



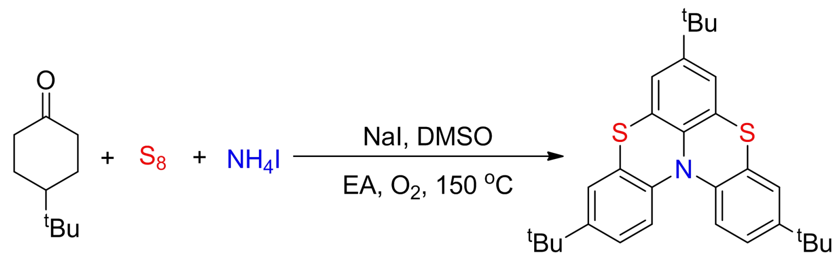
Ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) were added to an oven-dried reaction vessel (10 mL). The reaction vessel was purged with oxygen gas for three times and was added with 4-methylcyclohexan-1-one (52. 0 μL, 0.4 mmol) and chlorobenzene (0.6 mL) by syringe. The reaction vessel was stirred in an oil bath at 150 °C for 12 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2a** as yellow solid (36.1 mg, 80% yield), mp: 243-245 °C.

2.2 General procedure for the synthesis of bis-phenothiazine 3a



Ammonium iodide (73. 0 mg, 0.5 mmol), sodium iodide (9.0 mg, 0.06 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) were added to an oven-dried reaction vessel (10 mL). The reaction vessel was purged with oxygen gas for three times and was added with 4-methylcyclohexan-1-one (78.0 μL, 0.6 mmol), dimethyl sulfoxide (28.0 μL ,0.4 mmol) and ethyl acetate (0.6 mL) by syringe. The reaction vessel was stirred at 150 ^{o}C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3a** as yellow solid (37.9 mg, 55% yield), mp: 174-176 ^{o}C.

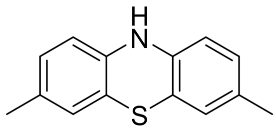
2.3 The synthesis of 3d on 1.0 mmol scale



4-(*tert*-Butyl)cyclohexan-1-one (462.9 mg, 3.0 mmol), ammonium iodide (365.0 mg, 2.5 mmol) and elemental sulfur (256.0 mg, 1.0 mmol) were added to an oven-dried reaction vessel (10 mL). The reaction vessel was purged with oxygen gas for three times and was added with dimethyl sulfoxide (140.0 μL, 2.0 mmol) and ethyl acetate (1.0 mL) by syringe. The reaction vessel was stirred at 150 ^{o}C for 24 h. After cooling to room temperature, the reaction was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3d** as yellow solid (227.0 mg, 48% yield), mp: 282-286 ^{o}C.

3. Characterization data of products

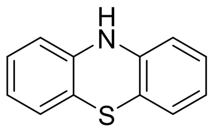
3,7-Dimethyl-10*H*-phenothiazine (2a, CAS: 20751-71-7) [1]



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-methylcyclohexan-1-one (78.0 μL, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2a** as yellow solid (36.1 mg, 80% yield), mp: 243-245 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 1H), 6.77 (d, J = 8.0 Hz, 2H), 6.72 (s, 2H), 6.55 (d, J = 8.0 Hz, 2H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.8, 130.3, 127.9, 126.5, 116.1, 114.1, 19.9.

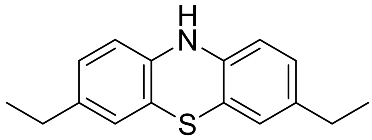
10*H*-Phenothiazine (2b, CAS:92-84-2)[2]



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and cyclohexanone (44.0 μL, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2b** as white solid (23.9 mg, 60% yield), mp:187-189 ^{o}C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.85 (s, 1H), 7.03 - 6.92 (m, 4H), 6.78 (t, J = 7.6 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 143.4, 128.4, 127.3, 123.0, 118.4, 115.4.

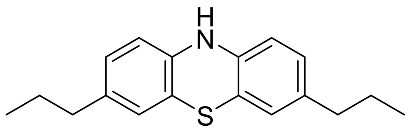
3,7-Diethyl-10*H*-phenothiazine (2c)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-ethylcyclohexan-1-one (56.0 µL, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2c** as yellow solid (33.7 mg, 72% yield), mp: 161-163 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.64 (s, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.79 (s, 2H), 6.61 (d, J = 7.6 Hz, 2H), 2.46 (q, J = 7.5 Hz, 4H), 1.13 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.4, 138.6, 127.6, 126.4, 118.2, 115.2, 28.5, 16.2. HRMS calcd for $C_{16}H_{17}NS$ $[M+H]^+$ 256.1154, found 256.1151.

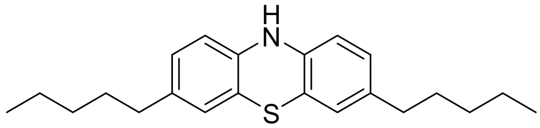
3,7-Dipropyl-10*H*-phenothiazine (2d)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-propylcyclohexan-1-one (65.0 µL, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2d** as yellow solid (36.8 mg, 65% yield), mp: 155-157 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.64 (s, 1H), 6.83-6.75 (m, 4H), 6.61 (d, J = 8.0 Hz, 2H), 2.41 (t, J = 7.6 Hz, 4H), 1.59-1.49 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.4, 137.0, 128.2, 127.0, 118.2, 115.1, 37.6, 25.4, 14.0. HRMS calcd for $C_{18}H_{21}NS$ $[M+H]^+$ 284.1467, found 284.1466.

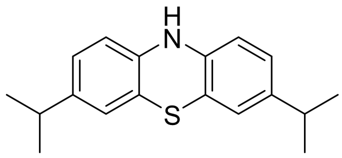
3,7-Dipentyl-10*H*-phenothiazine (2e)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-pentylcyclohexan-1-one (80.0 µl, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2e** as yellow solid (32.1 mg, 50% yield), mp: 149-150 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.64 (s, 1H), 6.81-6.78 (m, 4H), 6.61 (d, J = 8.0 Hz, 2H), 2.44 (t, J = 7.6 Hz, 4H), 1.56-1.49 (d, J = 7.4 Hz, 4H), 1.32-1.25 (m, 8H), 0.87 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.4, 137.2, 128.2, 127.0, 118.2, 115.2, 35.5, 32.1, 23.2, 14.4. HRMS calcd for $C_{22}H_{29}NS$ [M+H]$^+$ 340.2093, found 340.2089.

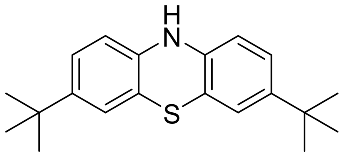
3,7-Diisopropyl-10*H*-phenothiazine (2f)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-isopropylcyclohexan-1-one (62.2 µL, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2f** as yellow solid (33.9 mg, 60% yield), mp: 171-173 °C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.64 (s, 1H), 6.89 - 6.77 (m, 4H), 6.63 (d, J = 8.0 Hz, 2H), 2.78-2.71 (m, 2H), 1.15 (d, J = 6.8 Hz, 12H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 138.7, 136.8, 121.5, 120.4, 113.6, 110.6, 29.3, 19.7. HRMS calcd for $C_{18}H_{21}NS$ [M+H]$^+$ 284.1467, found 284.1464.

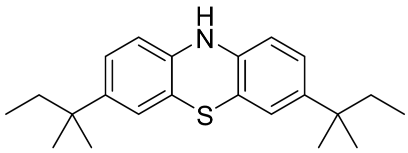
3,7-Di-*tert*-butyl-10*H*-phenothiazine (2g, CAS:27075-55-4)[3]



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-(*tert*-butyl)cyclohexan-1-one (67.3 mg, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2g** as white solid (31.0 mg, 52% yield), mp: 217-219 °C.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.67 (s, 1H), 7.01 (d, J = 8.4 Hz, 2H), 6.98 (s, 2H) 6.64 (d, J = 8.0 Hz, 2H), 1.24 (s, 18H). ^{13}C NMR (100 MHz, Acetone-*d*$_6$) δ 145.6, 141.2, 125.1, 124.1, 118.0, 115.0, 34.6, 31.7.

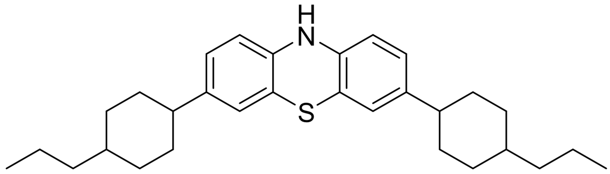
3,7-Di-*tert*-pentyl-10*H*-phenothiazine (2h)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-(*tert*-pentyl)cyclohexan-1-one (77.0 µL, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **2h** as white solid (33.2 mg, 52% yield), mp: 214-215 °C.

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 7.68 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 6.92 (s, 2H), 6.66 (d, J = 8.0 Hz, 2H), 1.62-1.54 (m, 4H), 1.20 (s, 12H), 0.65 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, Acetone-*d*$_6$) δ 143.8, 141,2, 125.8, 124.8, 118.1, 115.0, 38.0, 37.3, 28.9, 9.5. HRMS calcd for $C_{22}H_{29}NS$ [M+H]$^+$ 340.2093, found 340.2100.

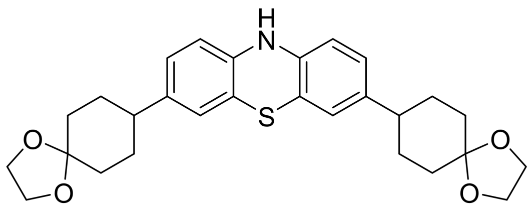
3,7-Bis(4-propylcyclohexyl)-10*H*-phenothiazine (2i)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4'-propyl-[1,1'-bi(cyclohexan)]-4-one (89.0 mg, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2i** as yellow solid (56.4 mg, 63% yield), mp: 258-260 ^{o}C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (s, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.73 (s, 2H), 6.57 (d, J = 8.0 Hz, 2H), 2.33-2.23 (m, 2H), 1.78-1.68 (m, 8H), 1.36-1.27 (m, 10H), 1.18-1.13 (m, 4H), 1.00-0.91 (m, 4H), 0.86 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.8, 140.3, 125.7, 124.3, 116.1, 114.2, 42.9, 36.3, 33.9, 33.1, 19.5, 14.3. HRMS calcd for $C_{30}H_{41}NS$ [M+H]$^+$ 488.3032, found 488.3026.

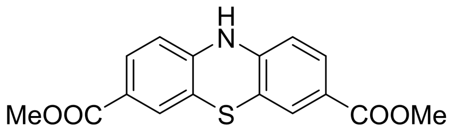
3,7-Di(1,4-dioxaspiro[4.5]decan-8-yl)-10*H*-phenothiazine (2j)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-(1,4-dioxaspiro[4.5]decan-8-yl)cyclohexan-1-one (97.0 mg, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2j** as white solid (42.2 mg, 44% yield), mp: 262-265 ^{o}C.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.68 (s, 1H), 6.85 (d, J = 8.0 Hz, 2H), 6.82 (s, 2H), 6.63 (d, J = 7.6 Hz, 2H), 3.94-3.86 (m, 8H), 2.50-2.44 (m, 2H), 1.79-1.59 (m, 16H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 141.7, 141.5, 126.5,125.5 115.3, 108.8, 64.9, 64.8, 43.0, 35.8, 32.4. HRMS calcd for $C_{28}H_{33}NS$ [M+H]$^+$ 480.2203, found 480.2204.

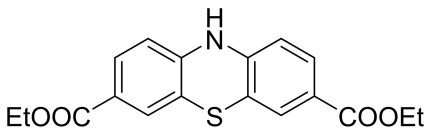
3,7-Dimethoxy-10*H*-phenothiazine (2l)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-phenylcyclohexan-1-one (60.0 μL , 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2l** as yellow solid (43.0 mg, 83% yield), mp: 278-280 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 7.57 (d, J = 8.4, 2H), 7.39 (s, 2H), 6.70 (d, J = 8.4 Hz, 2H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2, 144.5, 129.7, 127.0, 123.6, 116.1, 114.4. HRMS calcd for $C_{16}H_{13}NO_2S$ [M+H]$^+$ 259.0667, found 259.0665.

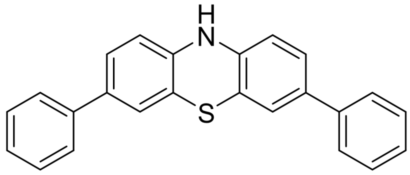
3,7-Diethoxy-10*H*-phenothiazine (2m)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-ethoxycyclohexan-1-one (64.0 μL , 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2m** as yellow solid (48.8 mg, 85% yield), mp: 240-242 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.50 (s, 1H), 7.57 (d, J = 8.4, 2H), 7.39 (s, 2H), 6.70 (d, J = 8.4 Hz, 2H), 4.23 (q, J = 7.2 Hz, 4H), 1.28 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 144.4, 129.6, 126.9, 123.8, 116.0, 114.4, 60.4, 14.2. HRMS calcd for $C_{18}H_{17}NO_2S$ [M+H]$^+$ 287.0980, found 287.0983.

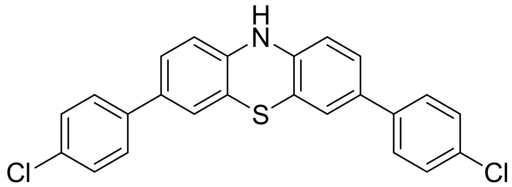
3,7-Diphenyl-10*H*-phenothiazine (2n)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-phenylcyclohexan-1-one (74.0 mg, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2n** as yellow solid (109.9 mg, 85% yield), mp: 287-289 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.86 (s, 1H), 7.58 (d, J = 7.6 Hz, 4H), 7.40 (t, J = 7.4 Hz, 4H), 7.36-7.22 (m, 6H), 6.76 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.0, 139.1, 133.8, 128.9, 126.9, 126.0, 125.8, 124.2, 116.9, 114.8. HRMS calcd for $C_{24}H_{17}ONS$ $[M+H]^+$ 352.1154, found 352.1146.

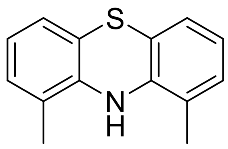
3,7-Bis(4-chlorophenyl)-10*H*-phenothiazine (2o)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 4-(4-chlorophenyl)cyclohexan-1-one (83.5 mg, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2o** as yellow solid (52.1 mg, 62% yield), mp: 290-291 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 7.61 (d, J = 8.8 Hz, 4H), 7.44 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 8.2, 2H), 7.26 (s, 2H), 6.75 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 141.1, 137.9, 132.4, 131.6, 128.8, 127.5, 125.9, 124.1, 116.9, 114.8. HRMS calcd for $C_{24}H_{15}Cl_2NS$ $[M+H]^+$ 420.0375, found 420.0377

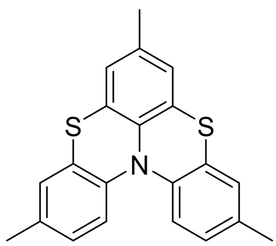
1,9-Dimethyl-10H-phenothiazine (2q)



The reaction was conducted with ammonium phosphate trihydrate (60.9 mg, 0.3 mmol), elemental sulfur (25.6 mg, 0.1 mmol), potassium iodate (8.5 mg. 0.04 mmol) and 2-methylcyclohexan-1-one (52.0 µl, 0.4 mmol). The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 20/1) to yield the desired product **2q** as yellow oil (29.1 mg, 64% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 6.95 (d, J = 7.45 Hz, 2H), 6.87 (d, J = 7.62 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 6.27 (s, 1H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, Acetone-*d*$_6$) δ141.2, 129.9, 125.3, 123.5, 123.0, 119.0, 17.0. HRMS calcd for $C_{14}H_{13}NS$ $[M+H]^+$ 228.0841, found 228.0840.

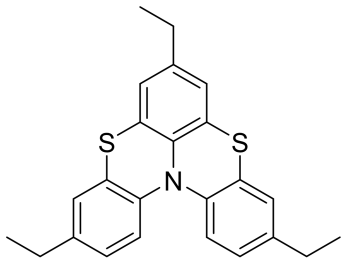
3,7,11-Trimethylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3a, CAS: 1051398-72-1)[4]



The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 µL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-methylcyclohexan-1-one (78.0 µL, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3a** as yellow solid (37.9 mg, 55% yield), mp: 174-176 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 (d, J = 8.0 Hz, 2H), 7.00 (s, 2H), 6.90 (d, J = 8. 0 Hz, 2H), 6.77 (s, 2H), 2.28 (s, 6H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.3, 137.4, 134.5, 134.1, 128.2, 128.1, 126.6, 126.1, 125.4, 120.2, 20.7, 20.5.

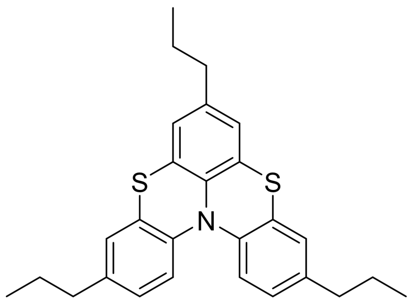
3,7,11-Triethylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3b)



The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 μL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-ethylcyclohexan-1-one (84.6 μL, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3b** as yellow oil (33.1 mg, 42% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.08 (d, J = 8.4 Hz, 2H), 7.03 (s, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.81 (s, 2H), 2.58 (q, J = 7.5 Hz, 4H), 2.51 (q, J = 7.6 Hz, 2H), 1.22 (t, J = 7.6 Hz, 6H), 1.16 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.0, 140.7, 137.6, 127.1, 127.0, 126.7, 125.6, 125.0, 120.4, 117.6, 28.2, 28.0, 15.7, 15.6. HRMS calcd. for $C_{24}H_{23}NS_2$ $[M+H]^+$ 390.1345, found 390.1346

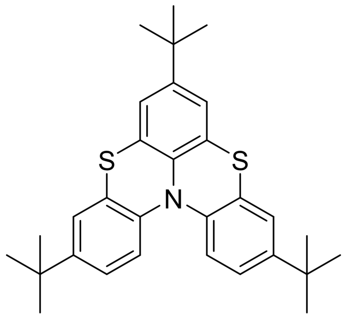
3,7,11-Tripropylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3c)



The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 μL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-propylcyclohexan-1-one (94 μL, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3c** as yellow oil (40,2 mg, 46% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, J = 8.4 Hz, 2H), 7.02 (s, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.79 (s, 2H), 2.54-2.44 (m, 6H), 1.65-1.54 (m, 6H), 0.94-0.89 (m, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 140.6, 139.4, 139.1, 137.6, 127.7, 127.6, 126.6, 125.6, 125.5, 120.3, 37.3, 37.0, 24.6, 24.4, 13.9, 13.8. HRMS calcd. for $C_{27}H_{29}NS_2$ $[M+H]^+$ 432.1814, found 432.1815.

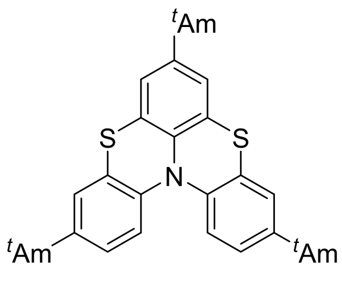
3,7,11-Tri-*tert*-butylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3d)



The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 μL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-(tert-butyl)cyclohexan-1-one (101.0 mg, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3d** as yellow solid (55.8 mg, 59% yield), mp: 282-286 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.21 (s, 2H), 7.14-7.10 (m, 4H), 6.98 (s, 2H), 1.30 (s, 18H), 1.25 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 148.2, 147.8, 140.2, 126.1, 125.2, 124.8, 124.6, 122.8, 120.0, 34.5, 34.5, 31.4, 31.3. HRMS calcd for $C_{30}H_{35}NS_2$ $[M+H]^+$ 474.2284, found 474.2284.

3,7,11-Tri-*tert*-pentylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3e)

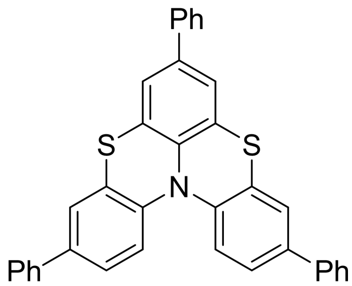


The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 μL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-(tert-pentyl)cyclohexan-1-one (112.0 μL, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3g** as yellow solid

(32.4 mg, 31% yield), mp:186-188 °C.

[1]H NMR (400 MHz, Chloroform-*d*) δ 7.15-7.13 (m, 3H), 7.08-7.05 (m, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 1.63-1.58 (m, 6H), 1.26-1.21 (m, 18H), 0.73-0.67 (m, 9H). [13]C NMR (100 MHz, Chloroform-*d*) δ 150.2, 146.4, 146.1, 145.9, 140.0, 137.2, 126.0, 125.5, 125.4, 125.2, 125.2, 124.5, 123.4, 119.9, 119.6, 117.2, 37.8, 37.8, 36.9, 36.8, 28.6, 28.5, 9.3, 9.2. HRMS calcd. for $C_{33}H_{41}NS_2$ $[M+H]^+$ 516.2753, found 516.2737.

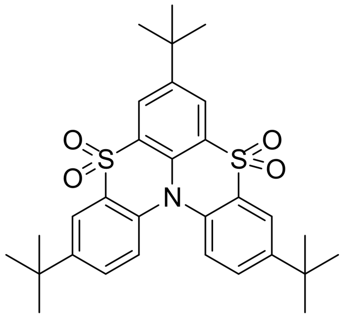
3,7,11-triphenylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (3f)



The reaction was conducted with ammonium iodide (73.0 mg, 0.5 mmol) and elemental sulfur (51.2 mg, 0.2 mmol) and dimethyl sulfoxide (28.0 μL ,0.4mmol) and ethyl acetate (0.6 mL) and 4-phenylcyclohexan-1-one (105.0 mg, 0.6 mmol). The residue was purified by column chromatography on silica gel (petroleum ether) to yield the desired product **3f** as yellow solid (27.2 mg, 25% yield), mp: 220-222 °C.

[1]H NMR (400 MHz, Chloroform-*d*) δ 7.58-7.55 (m, 3H), 7.53-7.30 (m, 20H). [13]C NMR (100 MHz, Chloroform-*d*) δ 141.7, 139.9, 139.3, 138.7, 138.6, 138.2, 129.0, 128.9, 127.8, 127.6, 127.4, 126.8, 126.8, 126.5, 126.5, 126.1, 124.5, 121.0. HRMS calcd. for $C_{36}H_{23}NS_2$ $[M+H]^+$ 534.1345, found 534.1311.

3,7,11-Tri-*tert*-butylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine 5,5,9,9-tetraoxide (4a)



3,7,11-Tri-*tert*-butylbenzo[5,6][1,4]thiazino[2,3,4-*kl*]phenothiazine (47.3 mg, 0.1 mmol) and 3-chloroperbenzoic acid (86.7 mg, 0.5 mmol) and CH_2Cl_2 (0.5 mL) were added to an oven-dried reaction vessel (10 mL). The reaction vessel was stirred at room temperaturefor 24 h**.** After the reaction finished, it was diluted with ethyl acetate (20 mL) and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether：ethyl acetate=3:1) to yield the desired product **A** as white solid (52,6 mg, 98% yield), mp:340-343 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.33 (s, 2H), 8.14 (s, 2H), 7.62-7.61 (m, 4H), 1.42 (s, 9H), 1.39 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*): δ 150.0, 149.0, 137.1, 134.9, 131.0, 128.9, 128.6, 124.6, 121.9, 120.5, 35.6, 35.2, 31.3, 31.2. HRMS calcd. for $C_{30}H_{35}NO_4S_2$ $[M+H]^+$ 538.2080, found 538.2085.

4. References

[1] Chen, S.; Li, Y.; Xiang, S.; Li, S.; Tan, B. *Chem. Commun.*, **2021**, *57*. 8512-8515.

[2] Dai, C.; Sun, X.; Tu, X.; Wu, L.; Zhan, D.; Zeng, Q. *Chem. Commun.,* **2012**, *48*, 5367-5369.

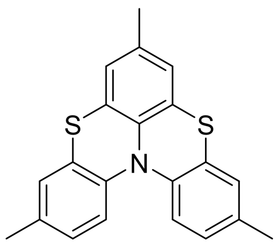
[3] Levitskiy, O. A.; Dulov, D. A.; Bogdanov, A.V.; Magdesieva, T. V. *Eur. J. Org. Chem.,* **2019**, **2019**, 6225-6231.

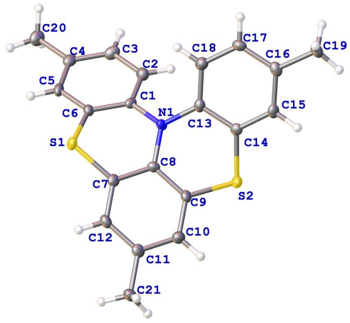
[4] Lamanna, G.; Faggi,.; Gasparrini, F.; Ciogli, A.; Villani, C.; Stephens, P. J.; Devlin, F. J.; Menichetti, S. Chem. Eur. J. 2008, 14, 5747 - 5750.

5. Crystal data and structure refinement for 3a.

The product **3a** (20.0 mg) were complete dissolved in DCM (0.5 mL) in a test tube. Then *n*-hexane (2.0 mL) were added dropwise, slow volatilized at room temperature. A few days later, the crystal was grown at room temperature.

A suitable crystal was collected, on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The data were collected and processed using CrysAlisPro. The structures were solved by direct methods using Olex2 software. The crystal was kept at 150.0(10) K during data collection.





3a **CCDC:** 2112855

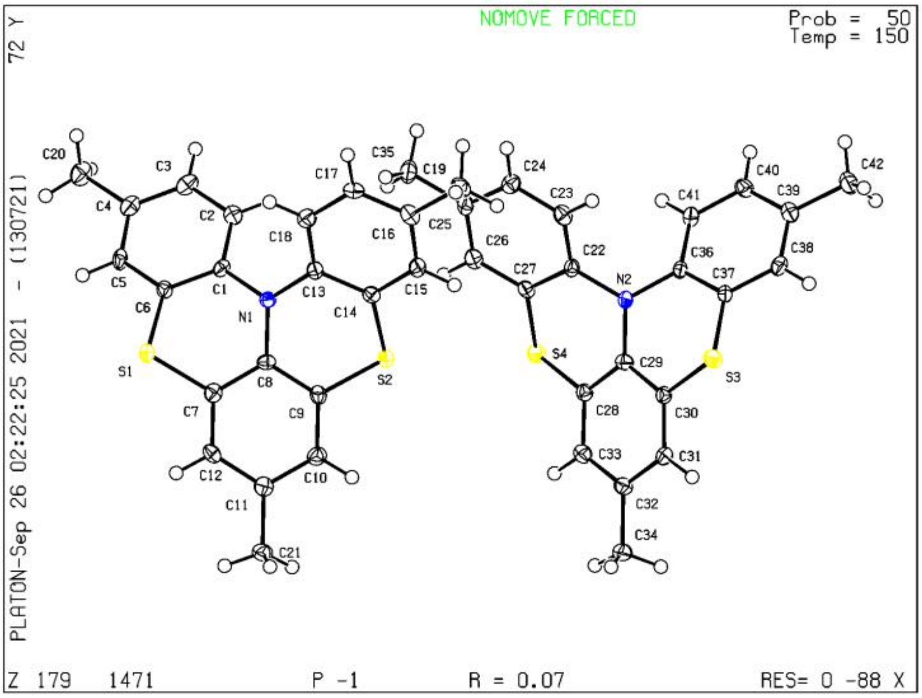


Figure S1. Ellipsoid plot of **3a** (shown at 50% probability levels)

Table 1. Crystal data and structure refinement for **3a.**

Identification code	**3a**
Empirical formula	$C_{21}H_{17}NS_2$
Formula weight	347.48
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.6322(5)
b/Å	14.8230(11)
c/Å	15.0281(12)
α/°	83.056(7)
β/°	82.898(6)
γ/°	89.355(6)
Volume/Å^3	1674.7(2)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	0.319
F(000)	728.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.132 to 49.998
Index ranges	$-9 \leq h \leq 9$, $-17 \leq k \leq 17$, $-6 \leq l \leq 17$
Reflections collected	5879
Independent reflections	5879 [R_{int} = 0.0386, R_{sigma} = 0.0606]
Data/restraints/parameters	5879/0/440
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0687, wR_2 = 0.1862
Final R indexes [all data]	R_1 = 0.0819, wR_2 = 0.1993
Largest diff. peak/hole / e Å^{-3}	1.17/-0.77

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	8728.9(12)	3180.9(6)	6234.1(6)	19.4(3)
S2	5609.9(12)	6540.2(6)	6199.1(6)	18.7(3)
N1	6973(4)	4770(2)	7079.3(19)	16.8(6)
C1	6515(5)	3894(2)	7549(2)	14.5(8)
C2	5371(5)	3808(3)	8362(2)	19.0(8)
C3	4933(5)	2946(3)	8817(3)	20.7(8)
C4	5564(5)	2159(3)	8478(3)	19.3(8)
C5	6672(5)	2259(2)	7661(2)	17.9(8)
C6	7171(4)	3110(2)	7210(2)	14.9(8)
C7	7968(4)	4186(2)	5637(2)	16.4(8)
C8	7210(4)	4874(2)	6119(2)	14.3(7)
C9	6695(5)	5677(2)	5625(2)	15.7(8)
C10	6968(5)	5789(3)	4683(2)	19.2(8)
C11	7699(5)	5094(3)	4208(2)	18.2(8)
C12	8179(5)	4289(3)	4704(2)	17.8(8)
C13	7187(4)	5530(2)	7544(2)	15.7(8)
C14	6682(4)	6396(2)	7180(2)	14.8(8)
C15	6956(5)	7150(2)	7611(2)	16.7(8)
C16	7677(5)	7077(3)	8422(2)	18.1(8)
C17	8156(5)	6210(3)	8787(2)	18.1(8)
C18	7943(5)	5452(3)	8345(2)	19.1(8)
C19	7986(5)	7917(3)	8863(3)	21.1(8)
C20	5067(5)	1232(3)	8960(3)	25.0(9)
C21	7966(6)	5213(3)	3195(2)	23.1(8)
S3	3664.6(12)	11521.0(6)	6261.8(6)	19.0(3)
S4	756.4(12)	8148.8(6)	6284.2(6)	18.8(3)
N2	2020(4)	9733(2)	7142.7(19)	16.4(6)
C22	2281(4)	8859(2)	7618(2)	14.8(7)
C23	3014(5)	8765(3)	8431(2)	18.9(8)
C24	3209(5)	7912(3)	8898(3)	18.5(8)
C25	2749(5)	7122(3)	8559(2)	17.5(8)
C26	2078(5)	7221(3)	7731(2)	19.0(8)
C27	1822(4)	8073(2)	7273(2)	15.0(8)
C28	1754(4)	9156(2)	5703(2)	15.0(8)
C29	2237(4)	9842(2)	6182(2)	14.6(7)
C30	2928(4)	10648(2)	5689(2)	14.7(7)

C31	3099(5)	10772(3)	4751(2)	18.6(8)
C32	2650(5)	10072(3)	4275(2)	18.1(8)
C33	2006(5)	9259(3)	4758(2)	18.8(8)
C34	2881(6)	10192(3)	3259(2)	23.9(9)
C35	3009(5)	6194(3)	9060(3)	24.3(9)
C36	1514(4)	10491(2)	7613(2)	14.1(7)
C37	2131(4)	11359(2)	7253(2)	13.8(7)
C38	1613(5)	12112(3)	7696(2)	17.5(8)
C39	537(5)	12023(3)	8516(2)	17.9(8)
C40	-59(5)	11148(3)	8876(3)	18.4(8)
C41	395(5)	10398(3)	8423(2)	16.7(8)
C42	-16(5)	12846(3)	8979(3)	23.8(9)

Table 3. Anisotropic Displacement Parameters (Å^2×10^3) for **3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S1	25.4(5)	13.4(5)	18.8(5)	-1.8(4)	-1.1(4)	5.0(4)
S2	24.4(5)	15.0(5)	17.5(5)	-3.3(4)	-4.2(4)	5.2(4)
N1	26.7(17)	10.9(16)	12.8(15)	-1.6(13)	-2.4(12)	-2.8(12)
C1	17.4(18)	11.0(19)	15.8(18)	0.2(14)	-6.1(14)	-4.5(14)
C2	19.2(19)	19(2)	20(2)	-3.8(16)	-2.5(15)	0.8(15)
C3	15.2(18)	22(2)	23(2)	4.2(16)	-2.7(15)	-4.7(15)
C4	20.4(19)	17(2)	22(2)	0.4(16)	-9.8(15)	-4.3(15)
C5	21.9(19)	10.1(19)	24(2)	-3.9(15)	-9.8(15)	0.1(15)
C6	17.1(18)	12.6(19)	16.2(18)	-3.8(15)	-4.6(14)	-0.4(14)
C7	16.2(18)	13.9(19)	19.7(19)	-2.3(15)	-3.9(14)	-4.0(14)
C8	14.2(17)	16.2(19)	12.3(17)	-0.7(15)	-0.7(14)	-4.1(14)
C9	16.8(18)	12.8(19)	18.6(19)	-4.2(15)	-3.6(14)	-1.5(14)
C10	23(2)	17(2)	17.6(19)	-0.6(15)	-3.6(15)	-2.9(15)
C11	18.9(18)	15.8(19)	20.0(19)	-2.7(16)	-1.4(15)	-6.0(14)
C12	18.4(19)	17(2)	18.5(19)	-7.1(15)	-1.1(14)	-1.2(15)
C13	15.1(18)	13.2(19)	17.7(19)	-1.4(15)	2.1(14)	-1.2(14)
C14	12.2(17)	17(2)	15.0(18)	-1.9(15)	1.1(13)	-0.6(14)
C15	17.1(18)	12.0(19)	19.5(19)	-0.7(15)	3.0(14)	-4.0(14)
C16	14.7(18)	18(2)	22(2)	-5.8(16)	2.5(14)	-4.2(14)
C17	18.1(18)	23(2)	13.3(18)	-2.6(16)	-2.2(14)	-1.6(15)
C18	19.6(19)	19(2)	18.8(19)	-0.9(16)	-2.1(15)	0.0(15)
C19	25(2)	19(2)	20(2)	-7.9(16)	-0.8(15)	-1.8(16)

C20	26(2)	19(2)	31(2)	-0.2(17)	-6.5(17)	-7.7(16)
C21	35(2)	19(2)	15.9(19)	-4.0(17)	-2.6(16)	-3.4(16)
S3	25.4(5)	13.7(5)	17.7(5)	-3.3(4)	-0.3(4)	-6.4(4)
S4	26.4(5)	12.9(5)	17.7(5)	-2.6(4)	-3.3(4)	-6.4(4)
N2	23.5(16)	9.4(15)	15.6(15)	-1.2(13)	-0.5(13)	-1.0(12)
C22	13.7(17)	11.8(18)	17.6(18)	-0.3(14)	1.6(13)	0.5(13)
C23	18.1(19)	17(2)	22(2)	-5.3(16)	-1.2(15)	-3.3(15)
C24	15.3(18)	20(2)	20(2)	-0.2(16)	-2.6(14)	1.4(15)
C25	12.8(17)	15(2)	22(2)	-0.2(15)	5.2(14)	2.6(14)
C26	18.0(18)	16(2)	21.4(19)	-3.3(16)	3.8(15)	-2.4(14)
C27	14.7(18)	13.3(19)	15.9(18)	-3.0(14)	4.2(13)	-3.3(14)
C28	14.3(18)	14.6(19)	15.9(18)	-2.2(15)	-0.7(13)	0.0(14)
C29	10.2(17)	20(2)	13.2(17)	-2.4(16)	-0.9(13)	2.0(14)
C30	16.0(18)	12.6(19)	15.8(18)	-1.8(14)	-2.7(14)	-0.3(14)
C31	24(2)	13.1(19)	17.3(19)	0.7(15)	0.1(15)	-0.4(15)
C32	18.8(19)	20(2)	15.6(18)	-3.1(16)	-0.5(14)	1.3(14)
C33	19.5(19)	19(2)	18.4(19)	-5.0(16)	-2.8(15)	0.4(15)
C34	38(2)	18(2)	15.4(19)	-2.7(16)	-3.1(17)	-0.4(16)
C35	28(2)	15(2)	29(2)	-0.7(17)	-1.7(17)	3.6(16)
C36	15.8(18)	11.0(18)	16.2(18)	-1.8(14)	-4.8(14)	2.1(13)
C37	14.4(17)	11.6(18)	16.2(18)	-2.7(14)	-4.0(13)	1.7(14)
C38	18.9(18)	14.2(19)	20.2(19)	-0.2(15)	-7.2(15)	0.9(14)
C39	14.5(18)	20(2)	21.5(19)	-7.6(16)	-8.8(14)	4.7(14)
C40	16.3(18)	20(2)	17.9(19)	-4.0(16)	1.2(14)	1.4(15)
C41	16.3(18)	12.8(19)	20.8(19)	-1.6(15)	-1.5(14)	0.7(14)
C42	26(2)	22(2)	26(2)	-9.6(17)	-6.8(16)	5.6(16)

Table 4. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C6	1.764(4)	S3	C30	1.771(4)
S1	C7	1.774(4)	S3	C37	1.771(4)
S2	C9	1.769(4)	S4	C27	1.772(4)
S2	C14	1.763(4)	S4	C28	1.766(4)
N1	C1	1.425(4)	N2	C22	1.426(5)
N1	C8	1.422(4)	N2	C29	1.422(4)
N1	C13	1.417(5)	N2	C36	1.424(5)
C1	C2	1.405(5)	C22	C23	1.397(5)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C6	1.388(5)	C22	C27	1.397(5)
C2	C3	1.397(5)	C23	C24	1.385(5)
C3	C4	1.388(6)	C24	C25	1.397(5)
C4	C5	1.395(5)	C25	C26	1.395(5)
C4	C20	1.504(5)	C25	C35	1.510(5)
C5	C6	1.391(5)	C26	C27	1.387(5)
C7	C8	1.402(5)	C28	C29	1.393(5)
C7	C12	1.380(5)	C28	C33	1.399(5)
C8	C9	1.403(5)	C29	C30	1.400(5)
C9	C10	1.395(5)	C30	C31	1.389(5)
C10	C11	1.397(6)	C31	C32	1.397(5)
C11	C12	1.399(5)	C32	C33	1.391(5)
C11	C21	1.499(5)	C32	C34	1.504(5)
C13	C14	1.402(5)	C36	C37	1.397(5)
C13	C18	1.390(5)	C36	C41	1.391(5)
C14	C15	1.388(5)	C37	C38	1.397(5)
C15	C16	1.390(5)	C38	C39	1.386(5)
C16	C17	1.399(5)	C39	C40	1.402(5)
C16	C19	1.513(5)	C39	C42	1.507(5)
C17	C18	1.394(5)	C40	C41	1.390(5)

Table 5. Bond Angles for **3a**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C6	S1	C7	99.18(17)	C37	S3	C30	98.86(16)
C14	S2	C9	98.78(17)	C28	S4	C27	99.25(16)
C8	N1	C1	118.5(3)	C29	N2	C22	119.2(3)
C13	N1	C1	121.8(3)	C29	N2	C36	119.6(3)
C13	N1	C8	119.7(3)	C36	N2	C22	121.1(3)
C2	C1	N1	120.5(3)	C23	C22	N2	121.3(3)
C6	C1	N1	121.0(3)	C23	C22	C27	118.3(3)
C6	C1	C2	118.6(3)	C27	C22	N2	120.5(3)
C3	C2	C1	120.0(4)	C24	C23	C22	120.5(3)
C4	C3	C2	121.8(4)	C23	C24	C25	121.5(4)
C3	C4	C5	117.3(3)	C24	C25	C35	121.3(3)
C3	C4	C20	121.8(4)	C26	C25	C24	117.6(3)
C5	C4	C20	120.9(4)	C26	C25	C35	121.1(3)
C6	C5	C4	121.9(3)	C27	C26	C25	121.3(3)

C1	C6	S1	120.4(3)	C22	C27	S4	120.4(3)
C1	C6	C5	120.4(3)	C26	C27	S4	118.7(3)
C5	C6	S1	119.1(3)	C26	C27	C22	120.7(3)
C8	C7	S1	119.4(3)	C29	C28	S4	120.1(3)
C12	C7	S1	119.5(3)	C29	C28	C33	121.0(3)
C12	C7	C8	121.0(3)	C33	C28	S4	118.9(3)
C7	C8	N1	121.3(3)	C28	C29	N2	121.2(3)
C7	C8	C9	118.0(3)	C28	C29	C30	117.9(3)
C9	C8	N1	120.7(3)	C30	C29	N2	120.9(3)
C8	C9	S2	119.8(3)	C29	C30	S3	119.8(3)
C10	C9	S2	119.4(3)	C31	C30	S3	118.8(3)
C10	C9	C8	120.7(3)	C31	C30	C29	121.4(3)
C9	C10	C11	120.9(3)	C30	C31	C32	120.3(3)
C10	C11	C12	118.1(3)	C31	C32	C34	120.6(3)
C10	C11	C21	120.6(4)	C33	C32	C31	118.8(3)
C12	C11	C21	121.2(4)	C33	C32	C34	120.6(3)
C7	C12	C11	121.2(3)	C32	C33	C28	120.5(3)
C14	C13	N1	119.9(3)	C37	C36	N2	119.7(3)
C18	C13	N1	121.8(3)	C41	C36	N2	121.9(3)
C18	C13	C14	118.3(3)	C41	C36	C37	118.4(3)
C13	C14	S2	120.8(3)	C36	C37	S3	120.9(3)
C15	C14	S2	118.9(3)	C38	C37	S3	118.7(3)
C15	C14	C13	120.2(3)	C38	C37	C36	120.3(3)
C14	C15	C16	122.0(3)	C39	C38	C37	121.7(3)
C15	C16	C17	117.5(3)	C38	C39	C40	117.4(3)
C15	C16	C19	120.4(3)	C38	C39	C42	120.7(3)
C17	C16	C19	122.1(3)	C40	C39	C42	121.8(3)
C18	C17	C16	121.1(3)	C41	C40	C39	121.3(3)
C13	C18	C17	120.9(3)	C40	C41	C36	120.8(3)

Table 6. Torsion Angles for **3a.**

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
S1	C7	C8	N1	-2.5(4)	S3	C30	C31	C32	175.4(3)
S1	C7	C8	C9	177.1(2)	S3	C37	C38	C39	-174.4(3)
S1	C7	C12	C11	-175.9(3)	S4	C28	C29	N2	3.0(5)
S2	C9	C10	C11	-175.1(3)	S4	C28	C29	C30	-176.3(3)
S2	C14	C15	C16	175.3(3)	S4	C28	C33	C32	174.6(3)
N1	C1	C2	C3	-179.9(3)	N2	C22	C23	C24	178.0(3)
N1	C1	C6	S1	5.1(5)	N2	C22	C27	S4	-4.7(5)

N1	C1	C6	C5	-178.1(3)	N2	C22	C27	C26	179.8(3)
N1	C8	C9	S2	-4.2(4)	N2	C29	C30	S3	3.7(5)
N1	C8	C9	C10	178.4(3)	N2	C29	C30	C31	-178.1(3)
N1	C13	C14	S2	5.4(4)	N2	C36	C37	S3	-4.7(5)
N1	C13	C14	C15	-177.3(3)	N2	C36	C37	C38	178.5(3)
N1	C13	C18	C17	179.4(3)	N2	C36	C41	C40	179.1(3)
C1	N1	C8	C7	-36.1(5)	C22	N2	C29	C28	35.4(5)
C1	N1	C8	C9	144.3(3)	C22	N2	C29	C30	-145.3(3)
C1	N1	C13	C14	-145.0(3)	C22	N2	C36	C37	146.0(3)
C1	N1	C13	C18	37.2(5)	C22	N2	C36	C41	-34.8(5)
C1	C2	C3	C4	-1.6(5)	C22	C23	C24	C25	2.5(5)
C2	C1	C6	S1	-175.6(3)	C23	C22	C27	S4	175.9(3)
C2	C1	C6	C5	1.2(5)	C23	C22	C27	C26	0.4(5)
C2	C3	C4	C5	0.5(5)	C23	C24	C25	C26	-0.2(5)
C2	C3	C4	C20	-178.9(3)	C23	C24	C25	C35	178.4(3)
C3	C4	C5	C6	1.6(5)	C24	C25	C26	C27	-2.0(5)
C4	C5	C6	S1	174.4(3)	C25	C26	C27	S4	-173.6(3)
C4	C5	C6	C1	-2.5(5)	C25	C26	C27	C22	1.9(5)
C6	S1	C7	C8	32.9(3)	C27	S4	C28	C29	-32.5(3)
C6	S1	C7	C12	-149.1(3)	C27	S4	C28	C33	149.1(3)
C6	C1	C2	C3	0.8(5)	C27	C22	C23	C24	-2.6(5)
C7	S1	C6	C1	-34.3(3)	C28	S4	C27	C22	33.4(3)
C7	S1	C6	C5	148.8(3)	C28	S4	C27	C26	-151.0(3)
C7	C8	C9	S2	176.2(2)	C28	C29	C30	S3	-176.9(3)
C7	C8	C9	C10	-1.3(5)	C28	C29	C30	C31	1.2(5)
C8	N1	C1	C2	-144.5(3)	C29	N2	C22	C23	145.1(3)
C8	N1	C1	C6	34.8(5)	C29	N2	C22	C27	-34.2(5)
C8	N1	C13	C14	34.7(5)	C29	N2	C36	C37	-35.1(5)
C8	N1	C13	C18	-143.2(3)	C29	N2	C36	C41	144.0(3)
C8	C7	C12	C11	2.1(5)	C29	C28	C33	C32	-3.9(5)
C8	C9	C10	C11	2.3(5)	C29	C30	C31	C32	-2.8(6)
C9	S2	C14	C13	-34.8(3)	C30	S3	C37	C36	34.2(3)
C9	S2	C14	C15	147.8(3)	C30	S3	C37	C38	-149.1(3)
C9	C10	C11	C12	-1.2(5)	C30	C31	C32	C33	1.0(6)
C9	C10	C11	C21	179.2(3)	C30	C31	C32	C34	-178.2(4)
C10	C11	C12	C7	-1.0(5)	C31	C32	C33	C28	2.3(5)
C12	C7	C8	N1	179.4(3)	C33	C28	C29	N2	-178.6(3)
C12	C7	C8	C9	-0.9(5)	C33	C28	C29	C30	2.1(5)
C13	N1	C1	C2	35.2(5)	C34	C32	C33	C28	-178.5(4)
C13	N1	C1	C6	-145.5(3)	C35	C25	C26	C27	179.4(3)

C13	N1	C8	C7	144.2(3)	C36	N2	C22	C23	-36.1(5)
C13	N1	C8	C9	-35.4(5)	C36	N2	C22	C27	144.6(3)
C13	C14	C15	C16	-2.1(5)	C36	N2	C29	C28	-143.5(3)
C14	S2	C9	C8	33.9(3)	C36	N2	C29	C30	35.8(5)
C14	S2	C9	C10	-148.6(3)	C36	C37	C38	C39	2.4(5)
C14	C13	C18	C17	1.5(5)	C37	S3	C30	C29	-33.4(3)
C14	C15	C16	C17	1.2(5)	C37	S3	C30	C31	148.4(3)
C14	C15	C16	C19	178.9(3)	C37	C36	C41	C40	-1.8(5)
C15	C16	C17	C18	1.0(5)	C37	C38	C39	C40	-1.7(5)
C16	C17	C18	C13	-2.4(5)	C37	C38	C39	C42	-179.5(3)
C18	C13	C14	S2	-176.6(3)	C38	C39	C40	C41	-0.7(5)
C18	C13	C14	C15	0.7(5)	C39	C40	C41	C36	2.5(5)
C19	C16	C17	C18	-176.6(3)	C41	C36	C37	S3	176.1(3)
C20	C4	C5	C6	-179.0(3)	C41	C36	C37	C38	-0.6(5)
C21	C11	C12	C7	178.6(3)	C42	C39	C40	C41	177.1(3)

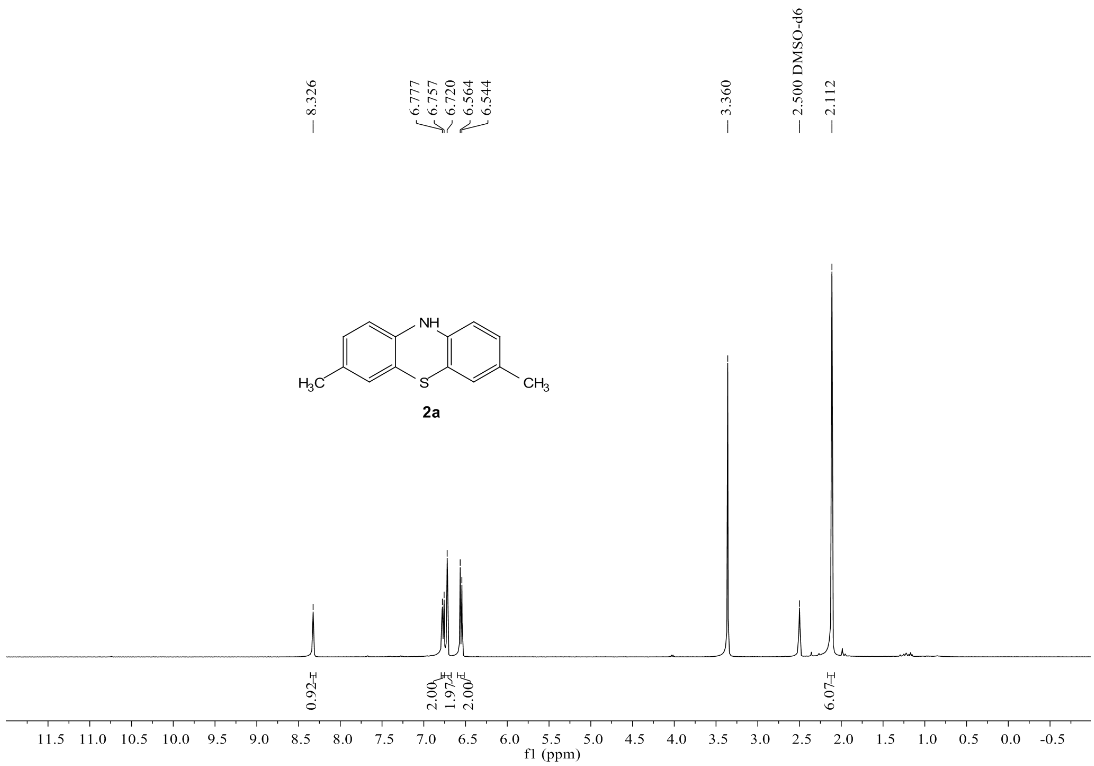
Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

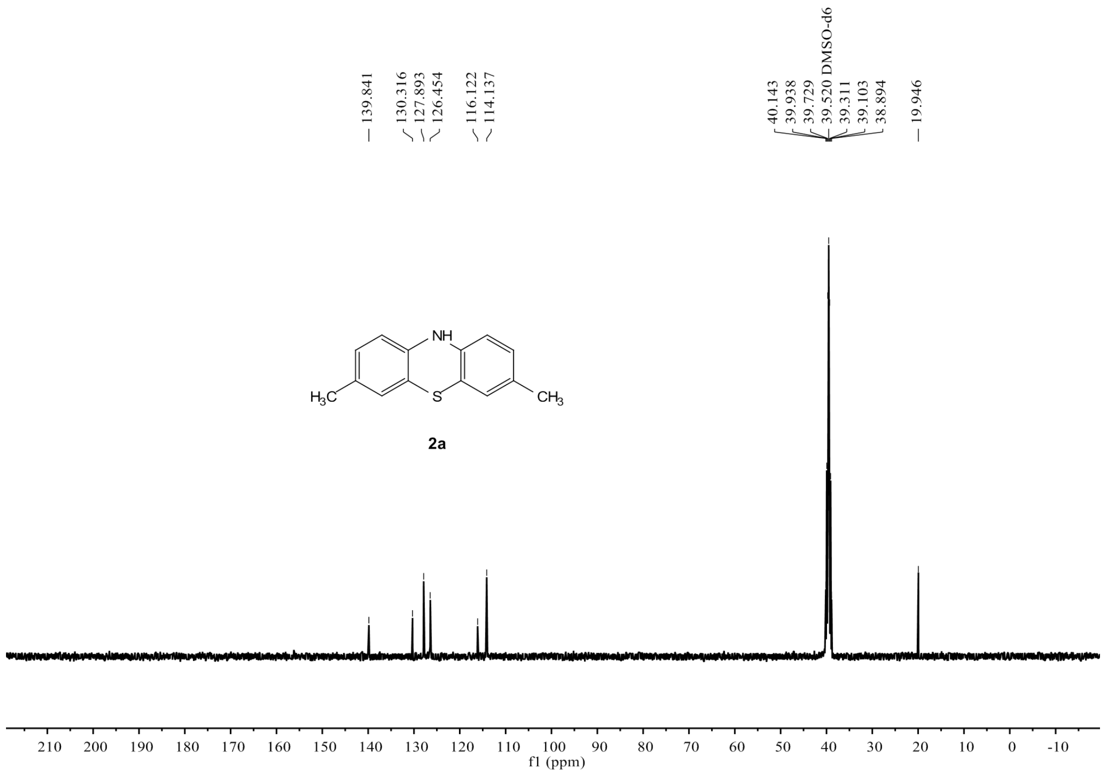
Atom	***x***	***y***	***z***	**U(eq)**
H2	4905.64	4324.13	8597.6	23
H3	4198.46	2899.56	9363.02	25
H5	7090.21	1742.42	7410.46	21
H10	6658.48	6334.59	4367.44	23
H12	8650.49	3813.88	4399.97	21
H15	6648.21	7721.56	7349.46	20
H17	8624.81	6138.11	9333.94	22
H18	8312.41	4885.32	8589.5	23
H19A	9226.8	8050.34	8789.81	32
H19B	7555.94	7812.18	9494.28	32
H19C	7370.16	8421.88	8583.16	32
H20A	3807.09	1160.28	9026.53	37
H20B	5466.58	1166.68	9545.06	37
H20C	5609.93	775.83	8615.04	37
H21A	6995.5	5549.29	2972.21	35
H21B	8026.27	4628.11	2981.08	35
H21C	9046.5	5539.43	2984.67	35
H23	3373.89	9277.86	8660.46	23
H24	3657.21	7864.91	9449.38	22
H26	1796.78	6704.97	7480.65	23

H31	3513.02	11323.67	4438	22
H33	1742.23	8779.61	4450.43	23
H34A	4115.4	10239.55	3038.98	36
H34B	2289.37	10735.09	3043.85	36
H34C	2384.34	9677.69	3047.13	36
H35A	2331.51	5753.46	8828.76	36
H35B	2622.57	6202.44	9691.77	36
H35C	4236.47	6036.31	8978.42	36
H38	1999.9	12687.69	7435.39	21
H40	-771.47	11066.37	9427.78	22
H41	-54.49	9828.3	8664.09	20
H42A	959.72	13262.25	8912.83	36
H42B	-376.6	12662.07	9608.93	36
H42C	-983.54	13139.34	8709.68	36

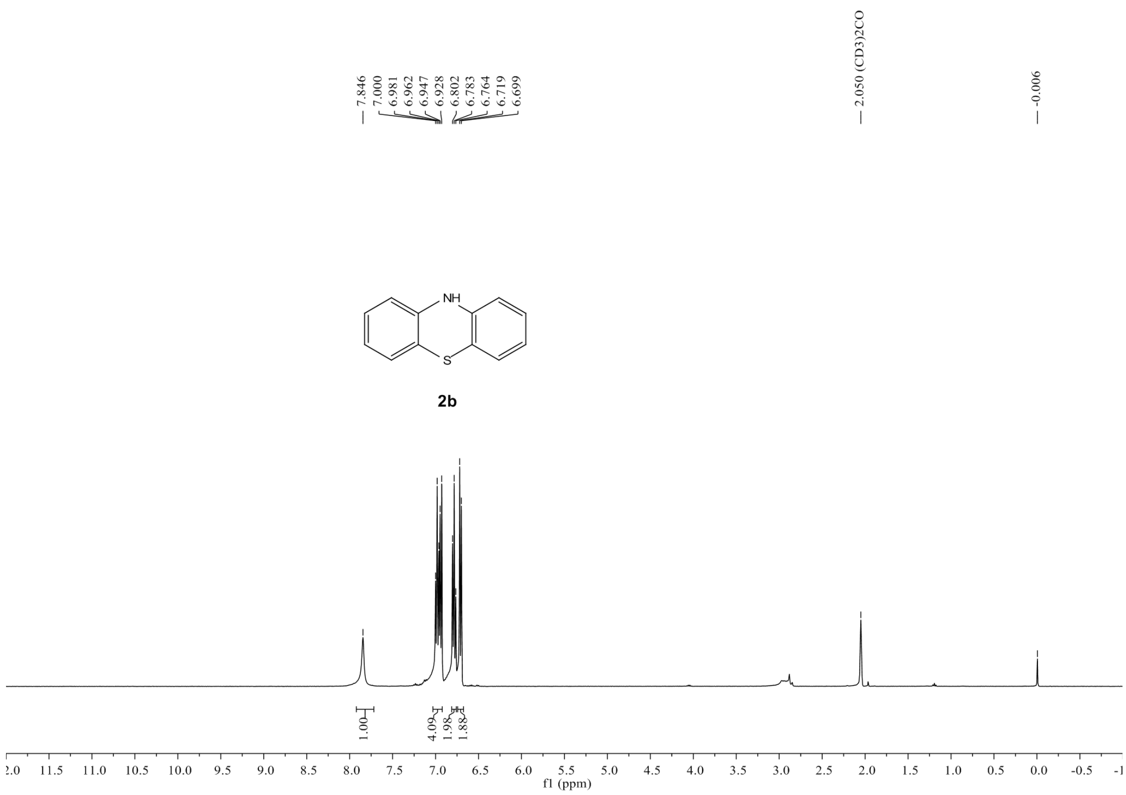
6. Copies of ^{1}H and ^{13}C NMR spectra of all products

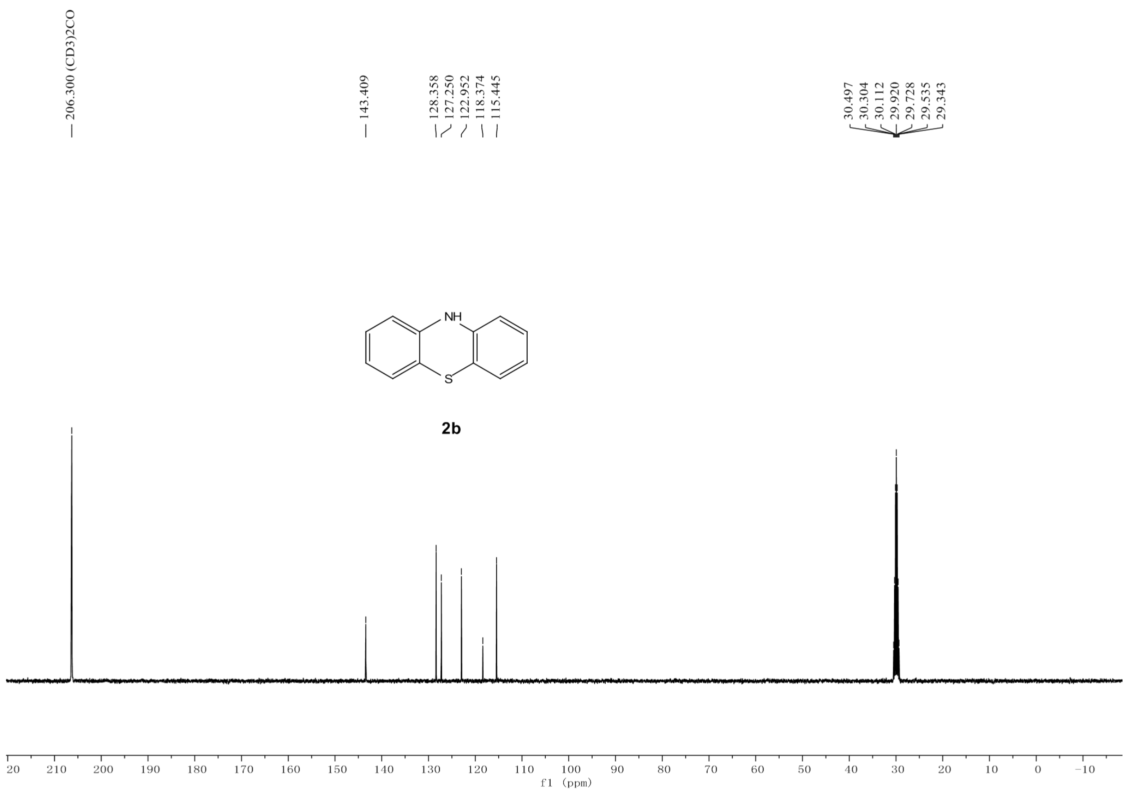
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2a** (**DMSO-*d*$_6$**)



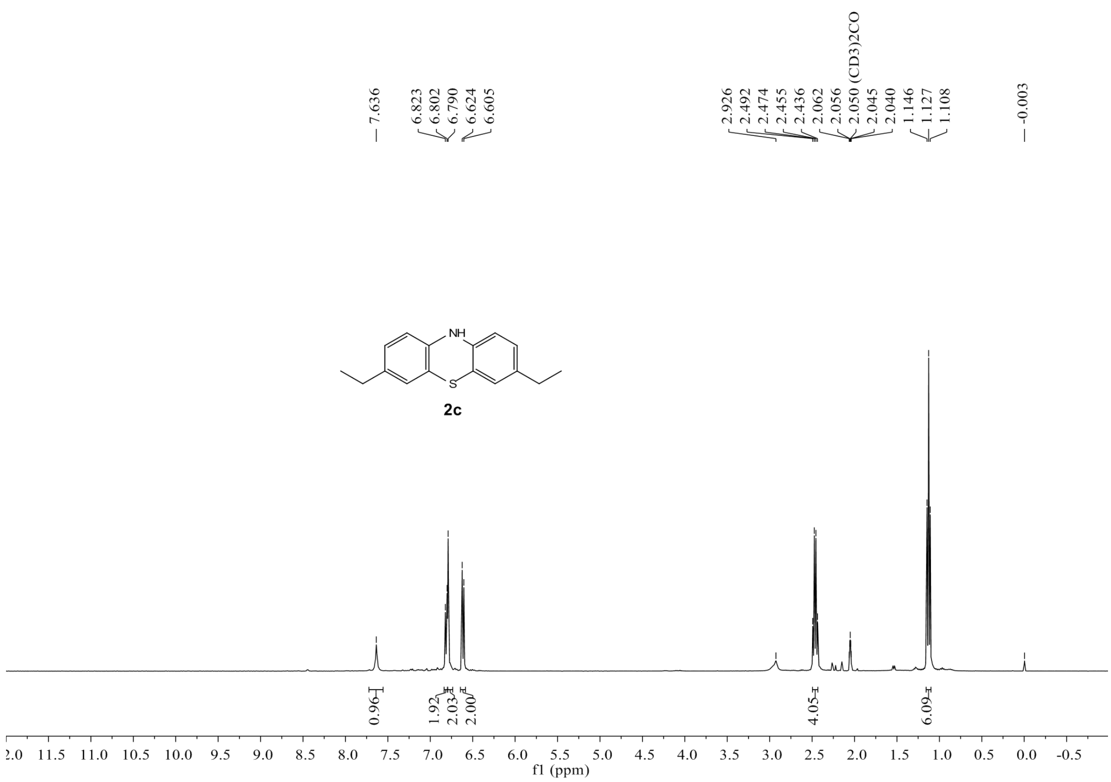


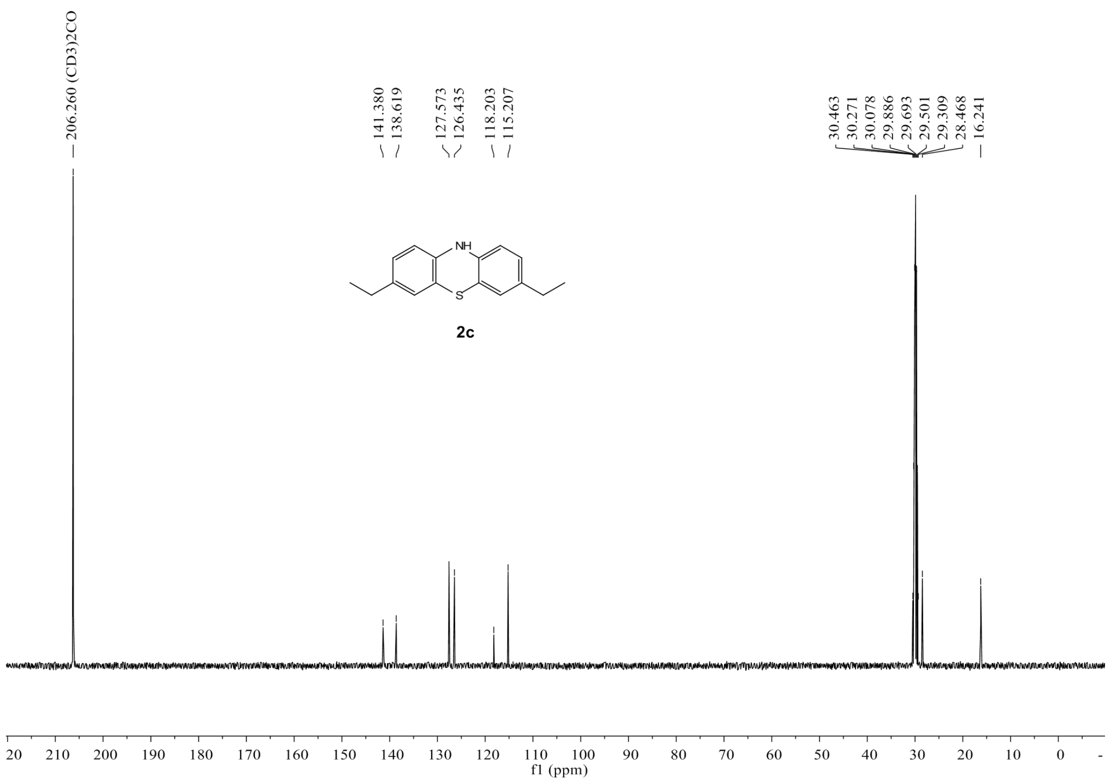
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2b** (**Acetone-*d$_6$***)



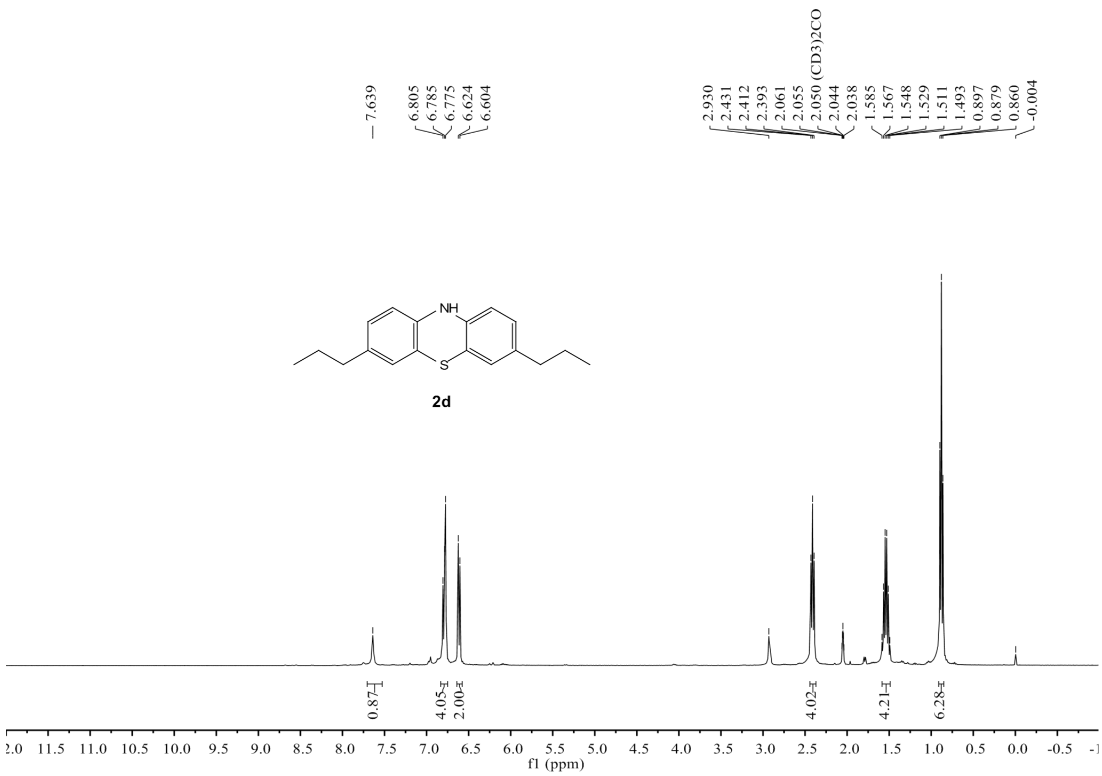


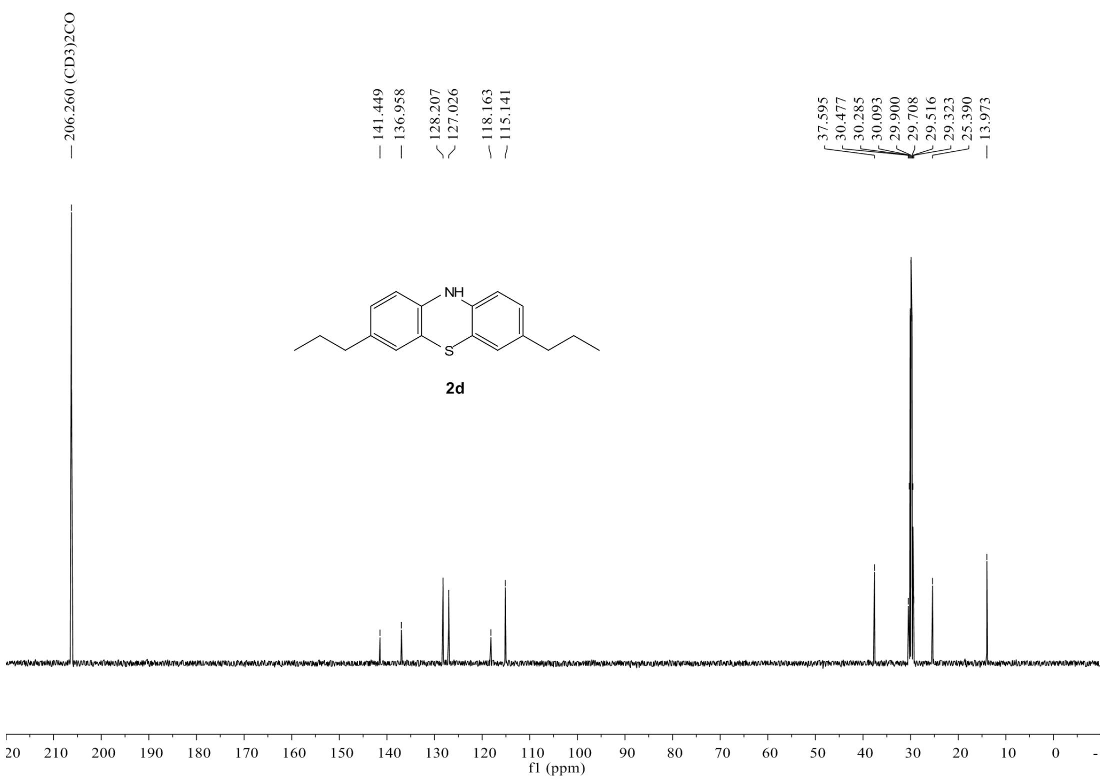
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2c** (**Acetone-*d_6***)



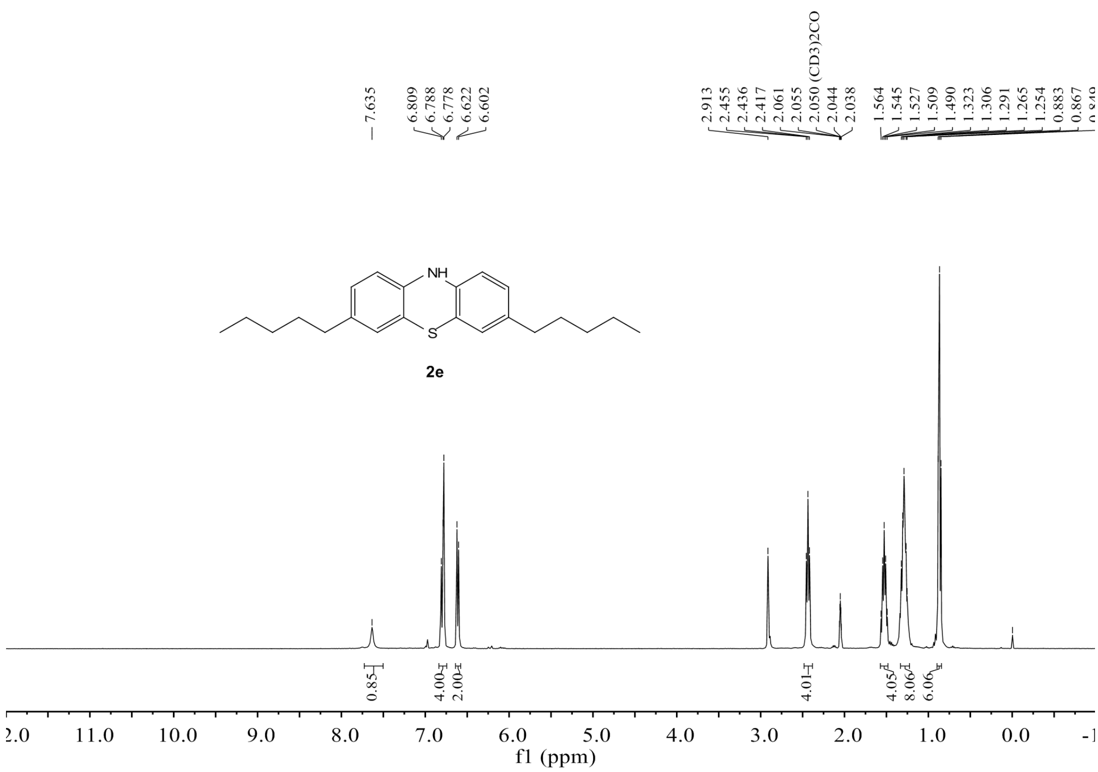


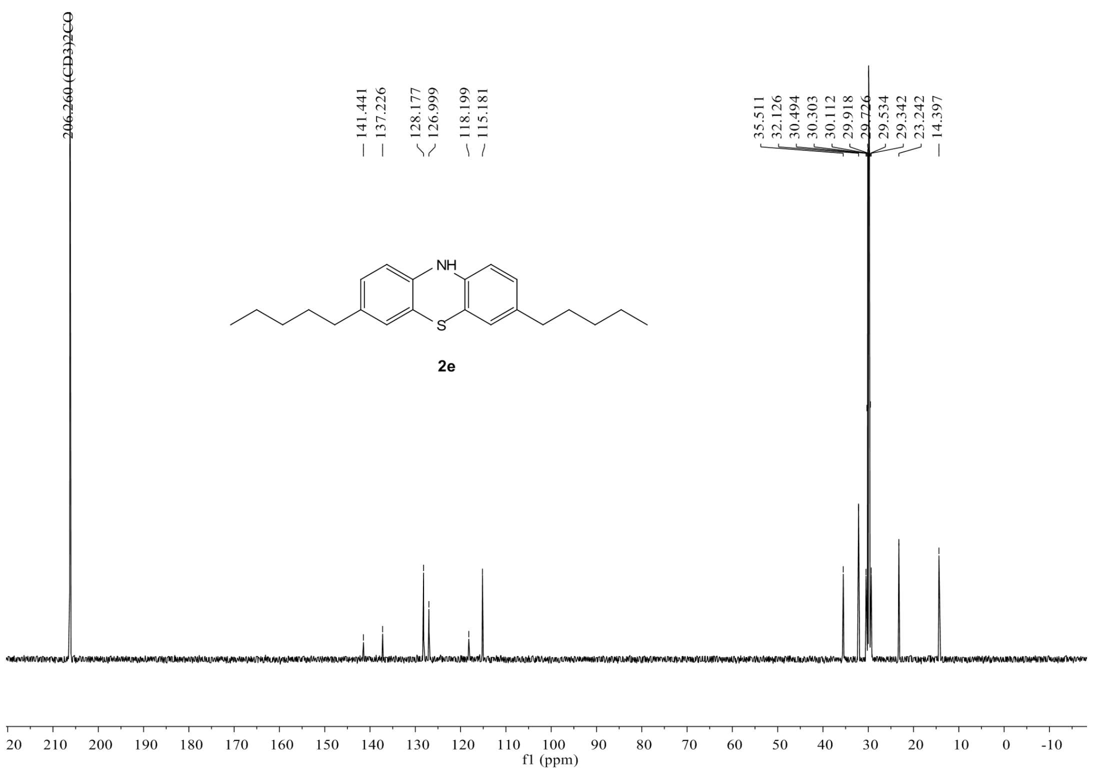
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2d** (**Acetone-*d*$_6$**)



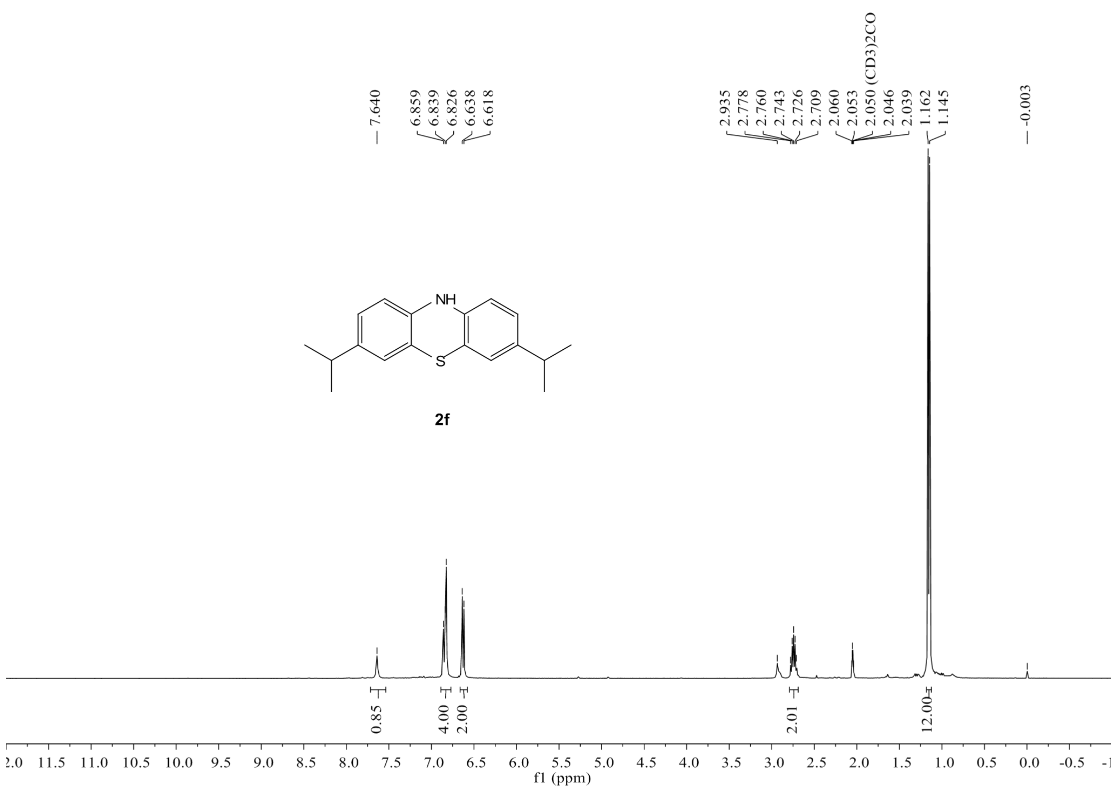


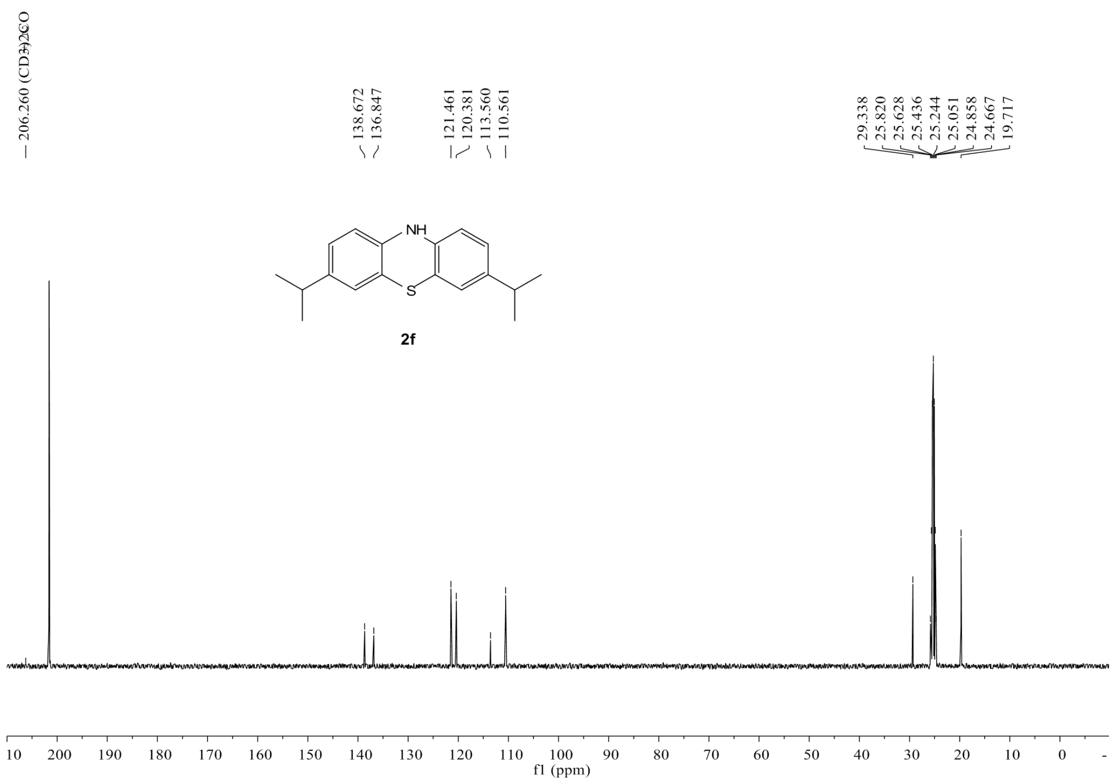
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2e** (**Acetone-*d*$_6$**)



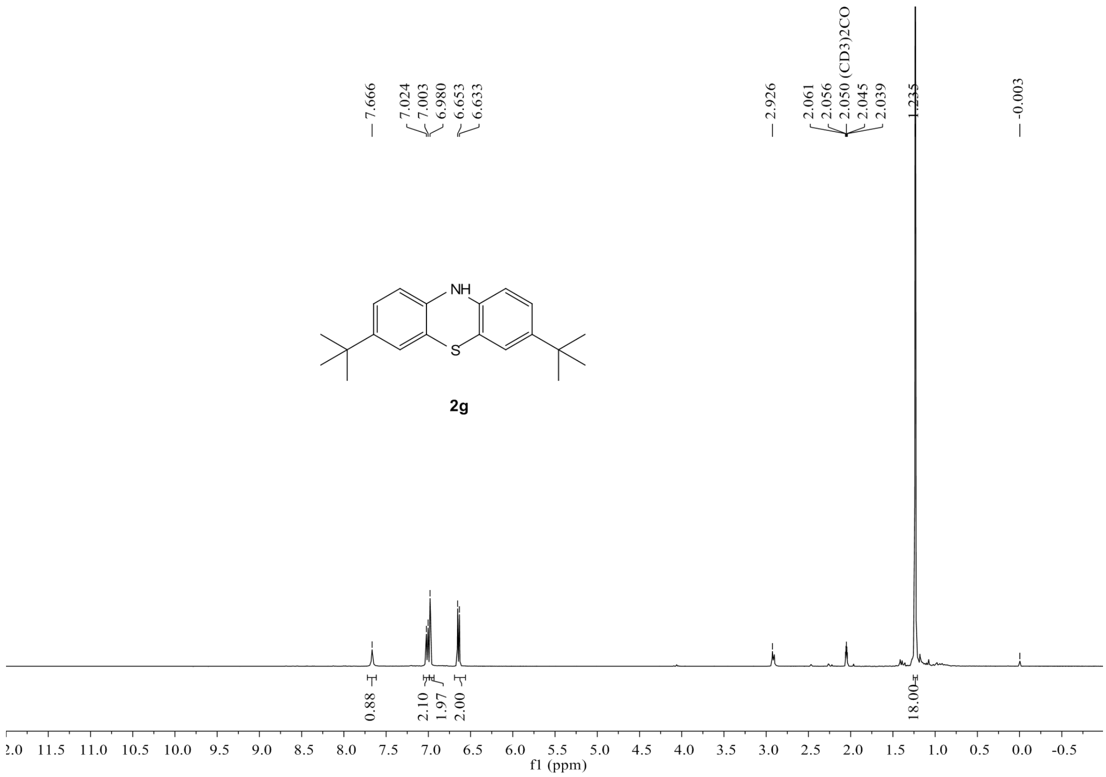


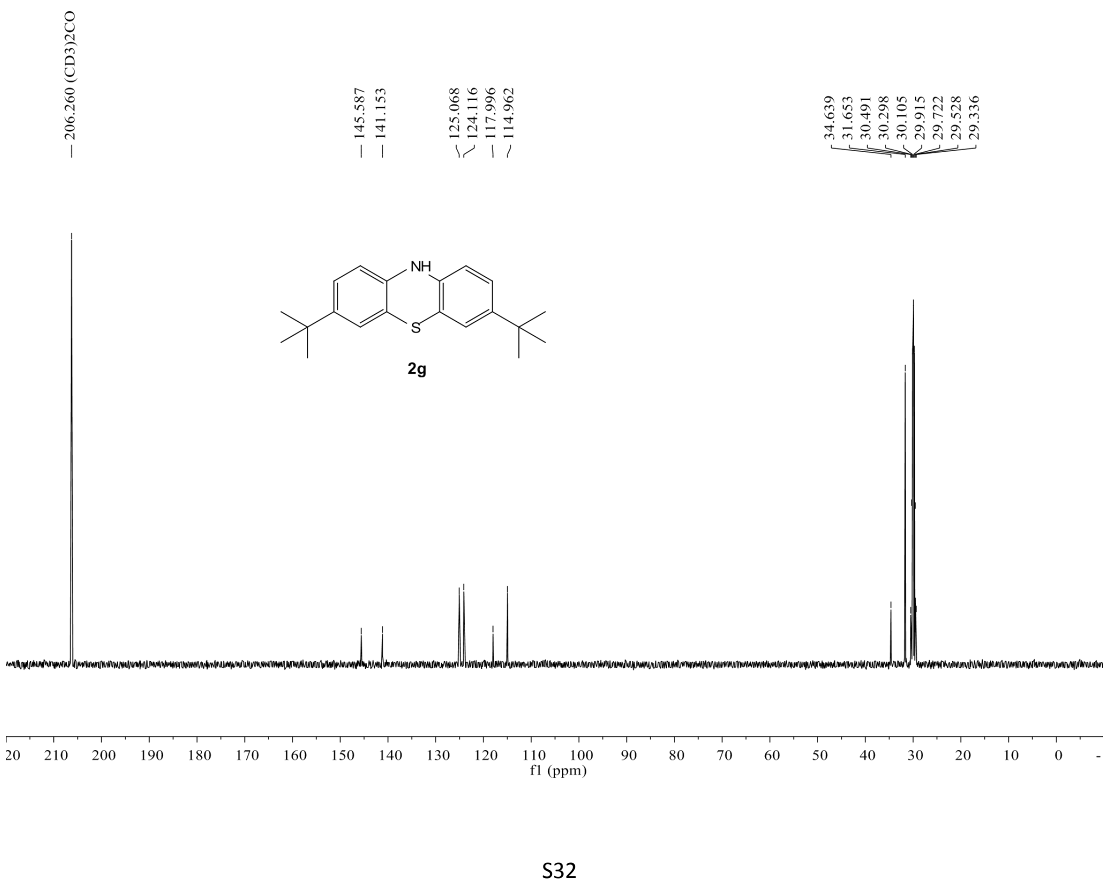
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **2f** (**Acetone-d_6**)



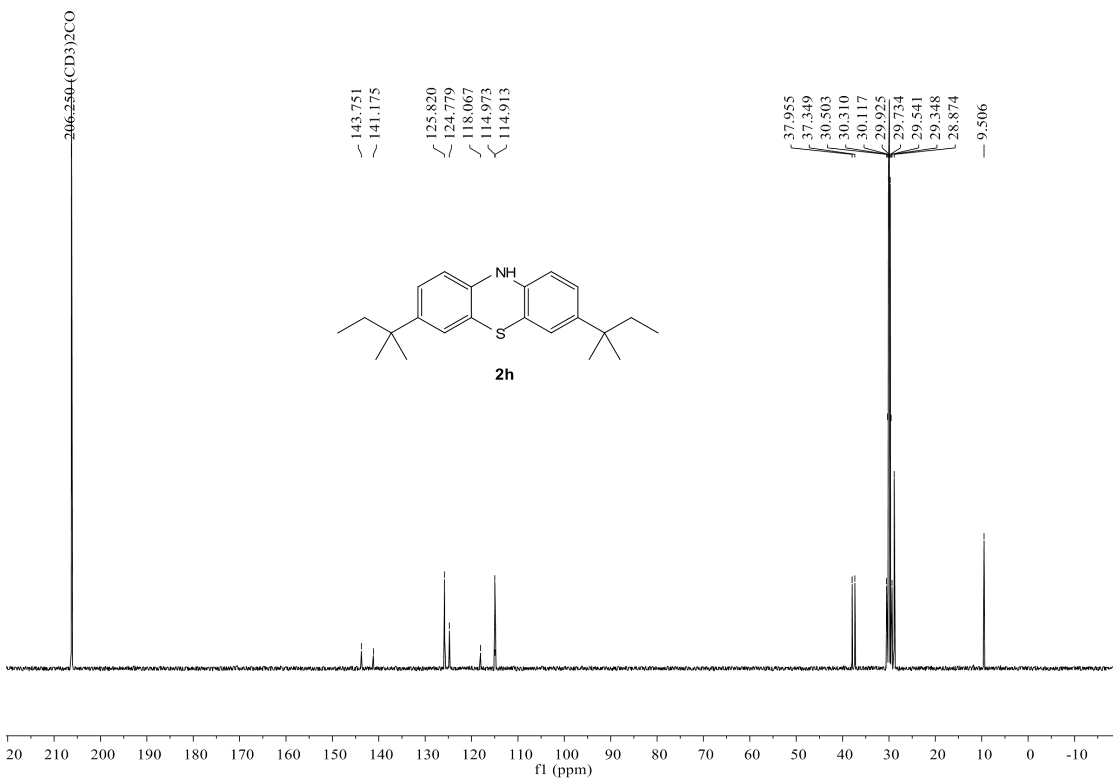


^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2g** (**Acetone-*d*$_6$**)

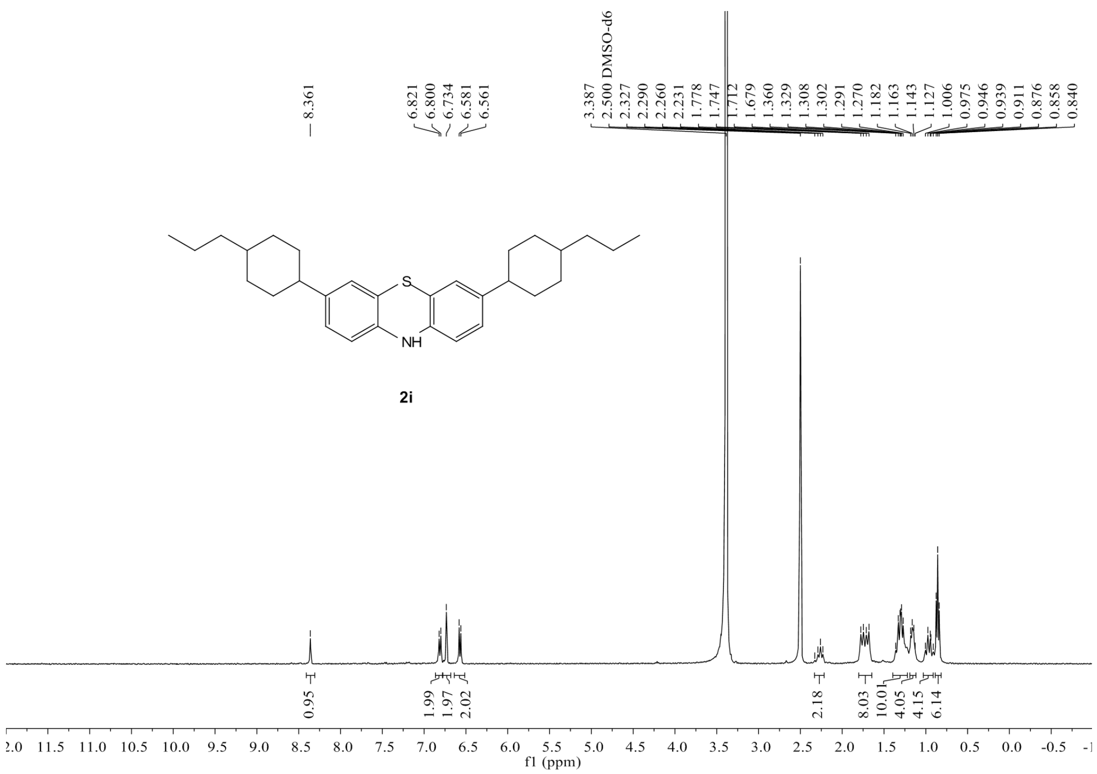


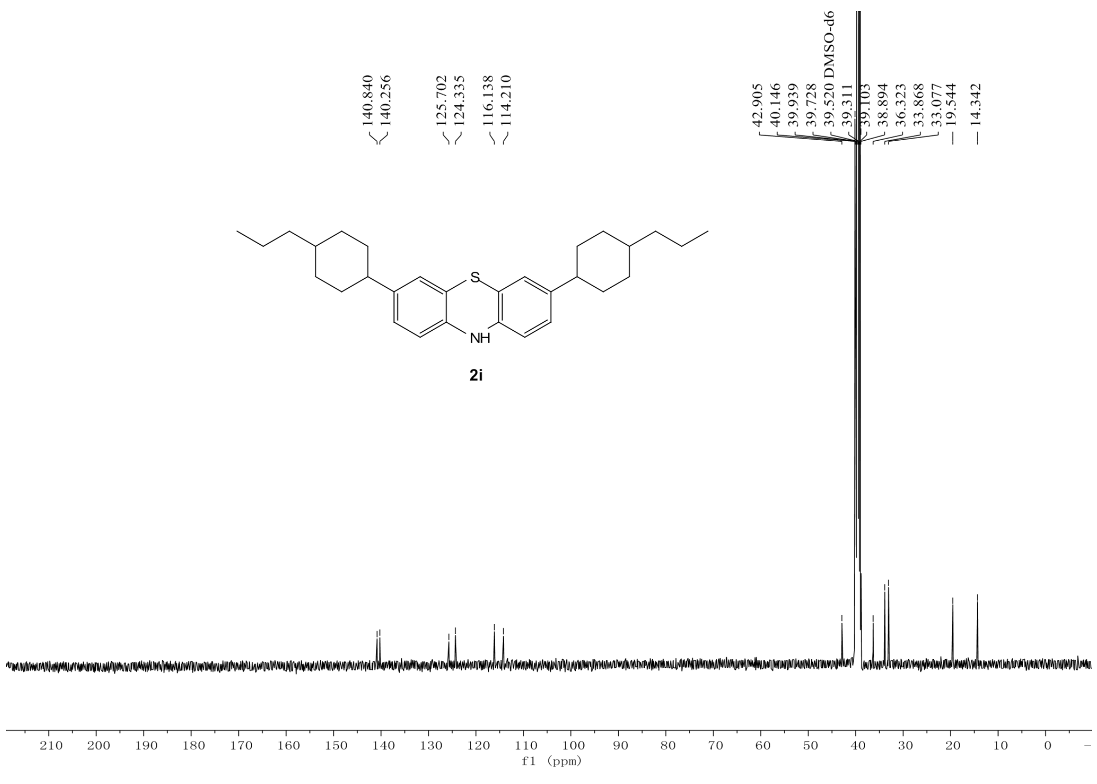


^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2h** (**Acetone-*d*$_6$**)

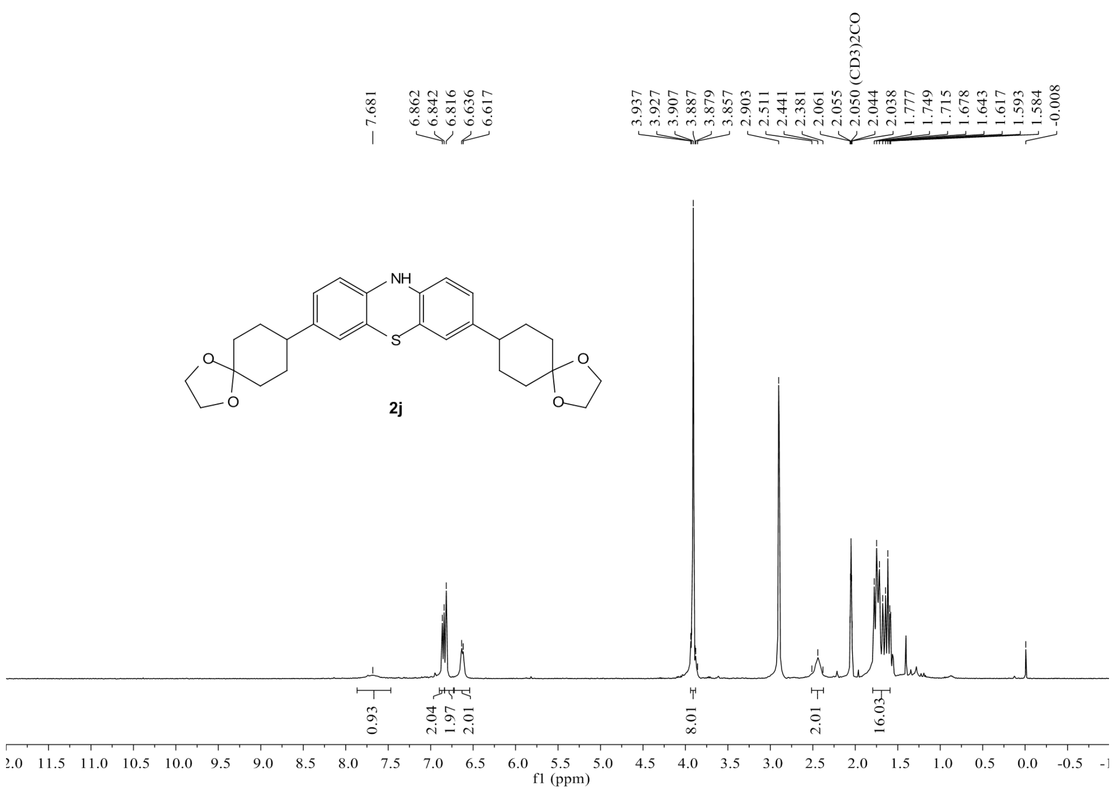


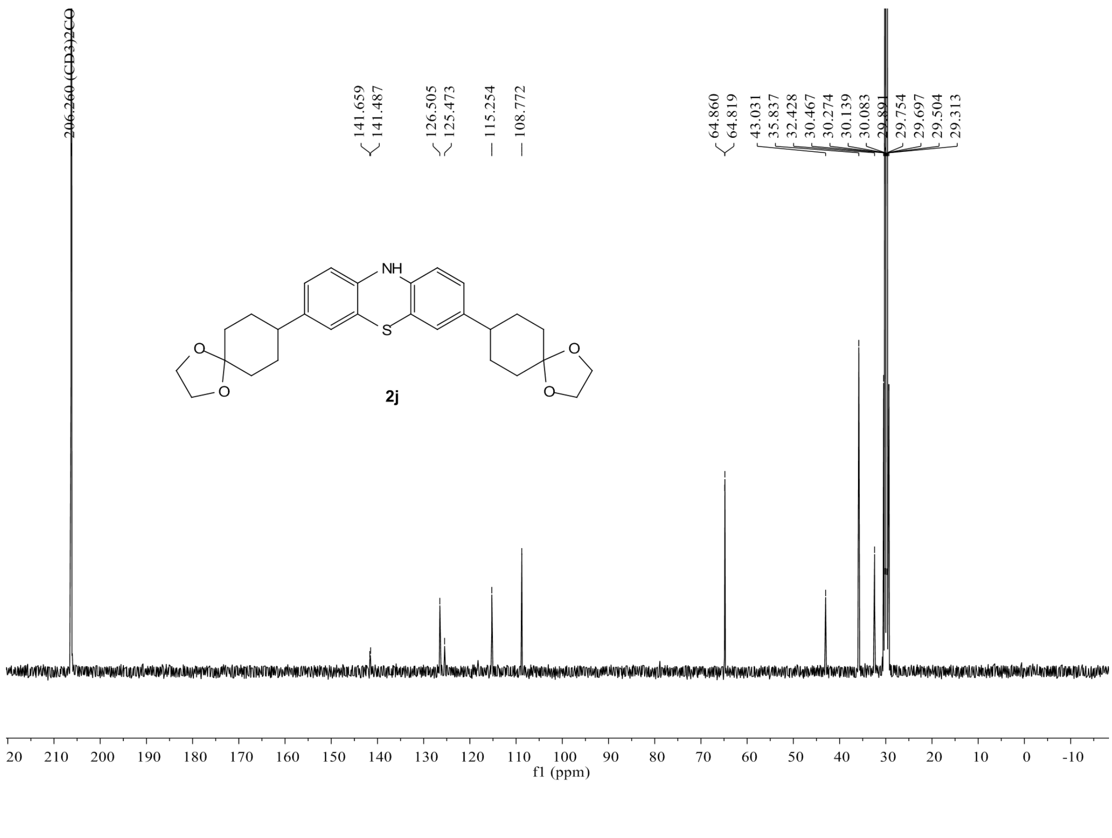
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **2i** (**DMSO-d_6**)



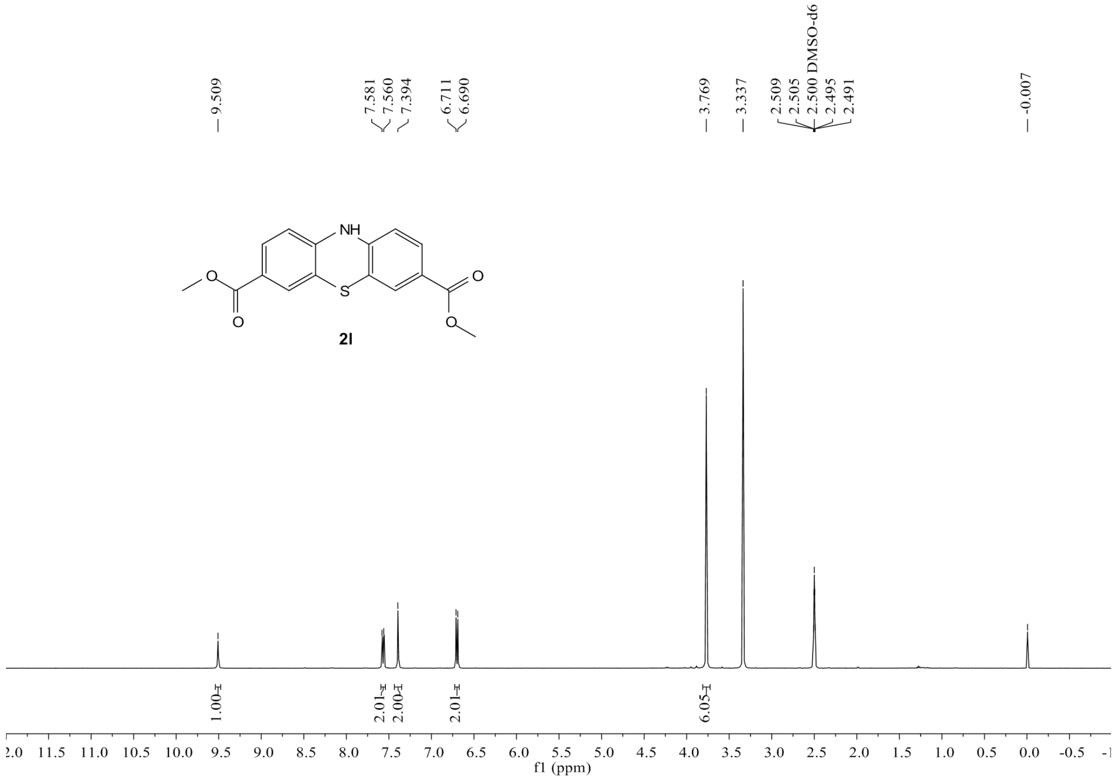


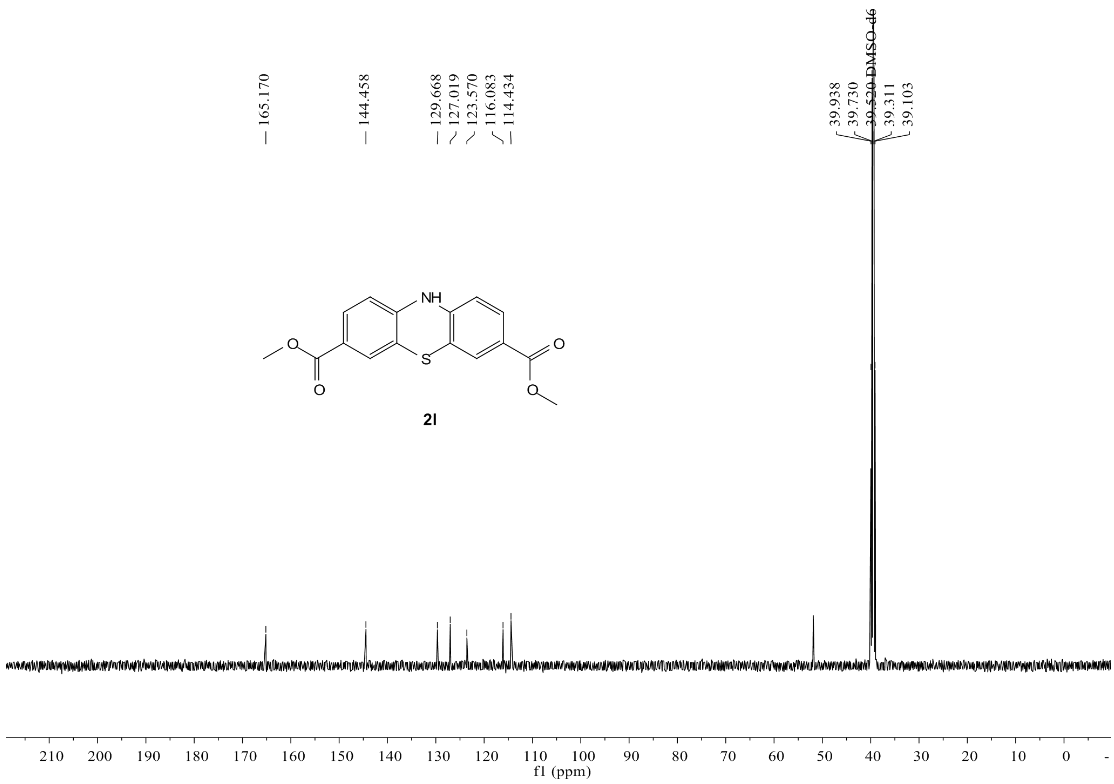
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2j** (**Acetone-*d$_6$***)



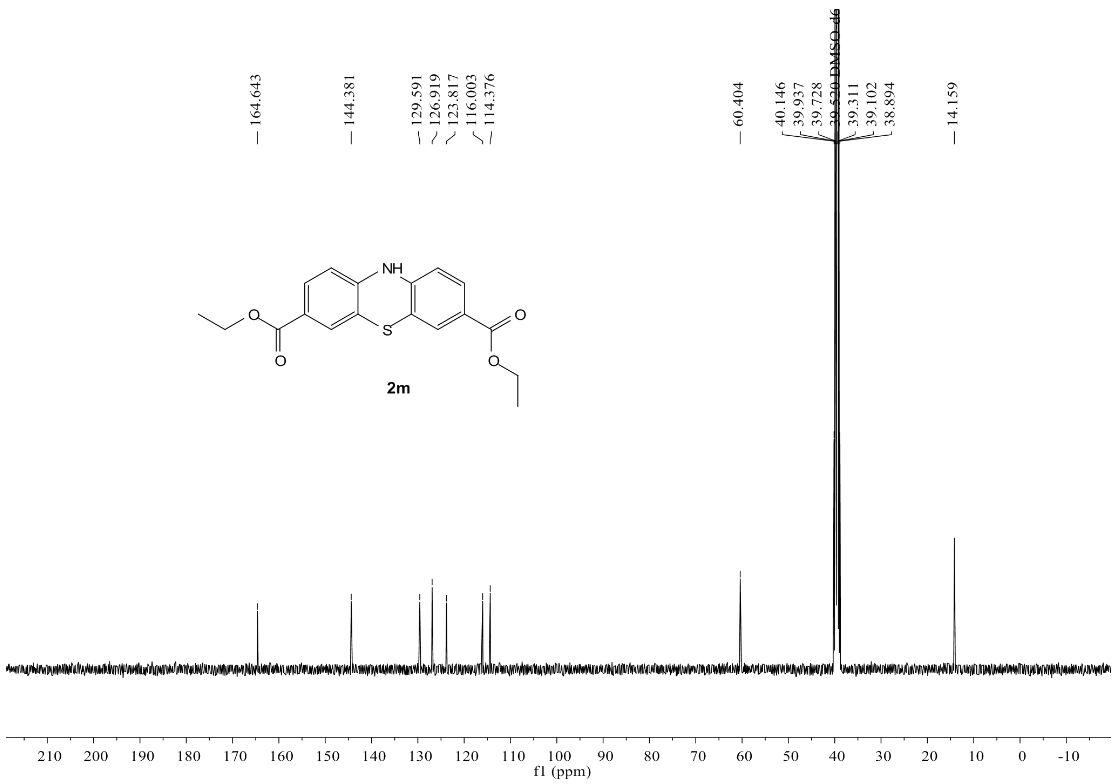


^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2l** (**DMSO-*d*$_6$**)

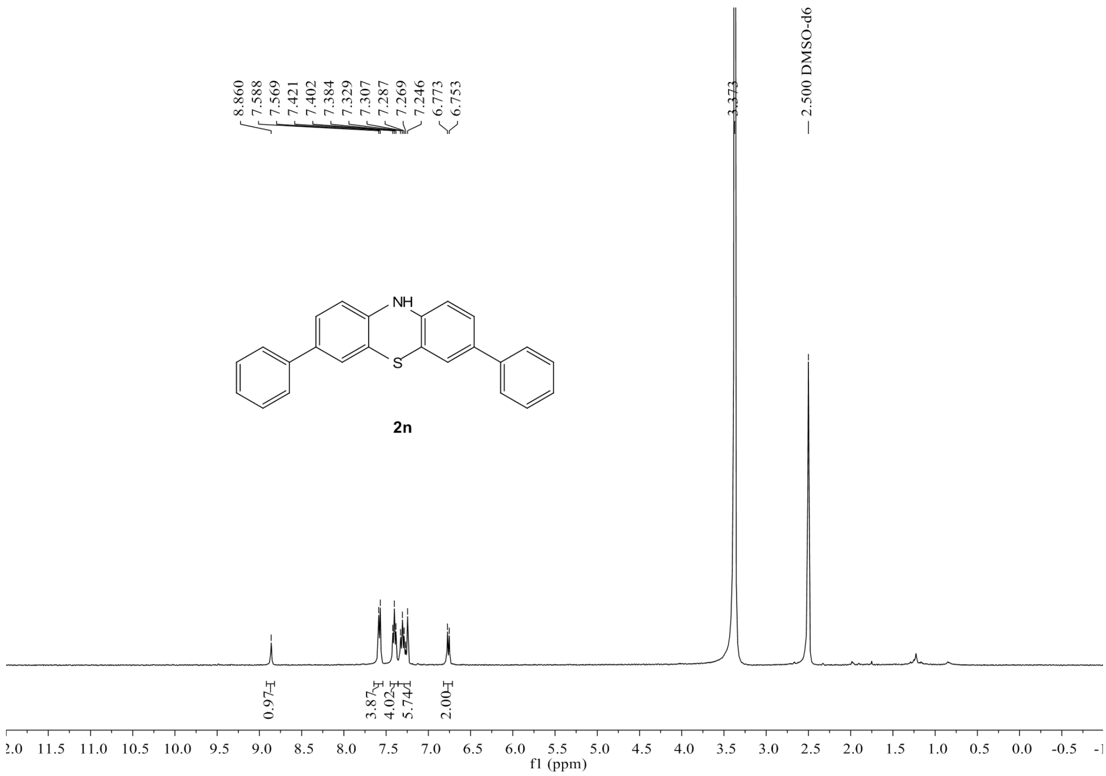


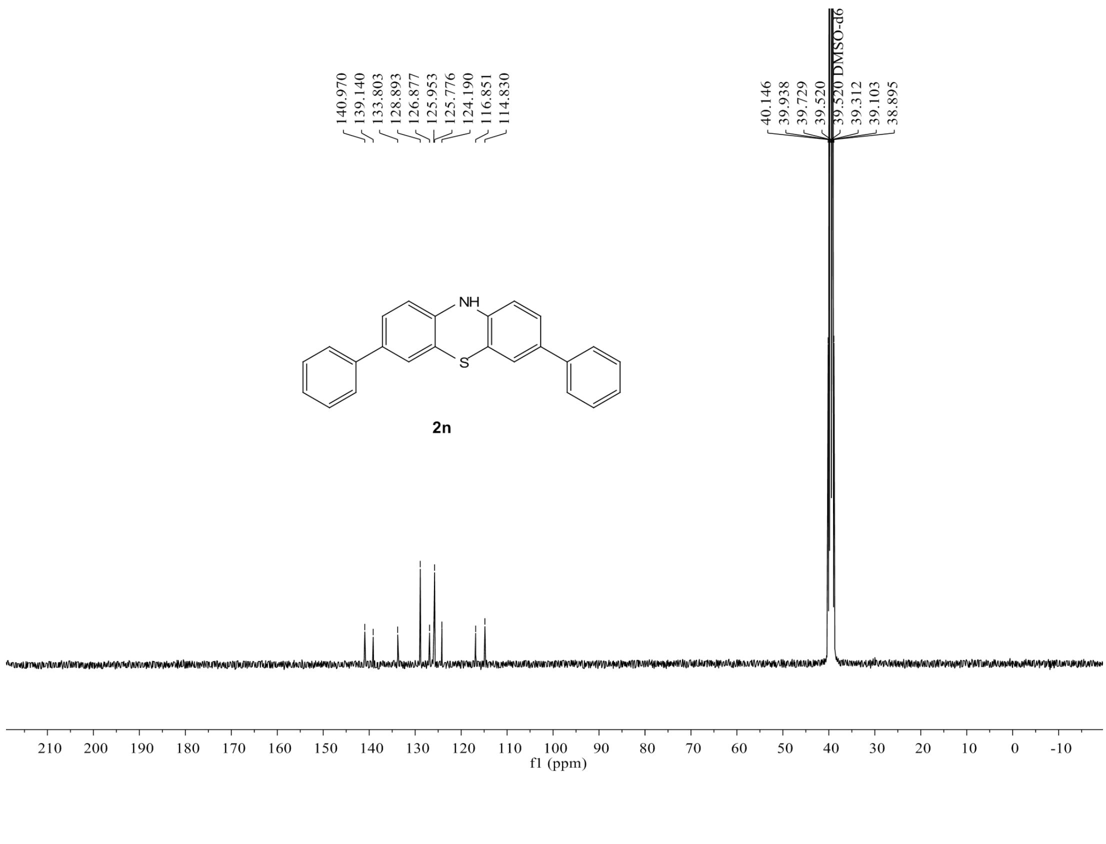


[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **2m** (**DMSO-d_6**)

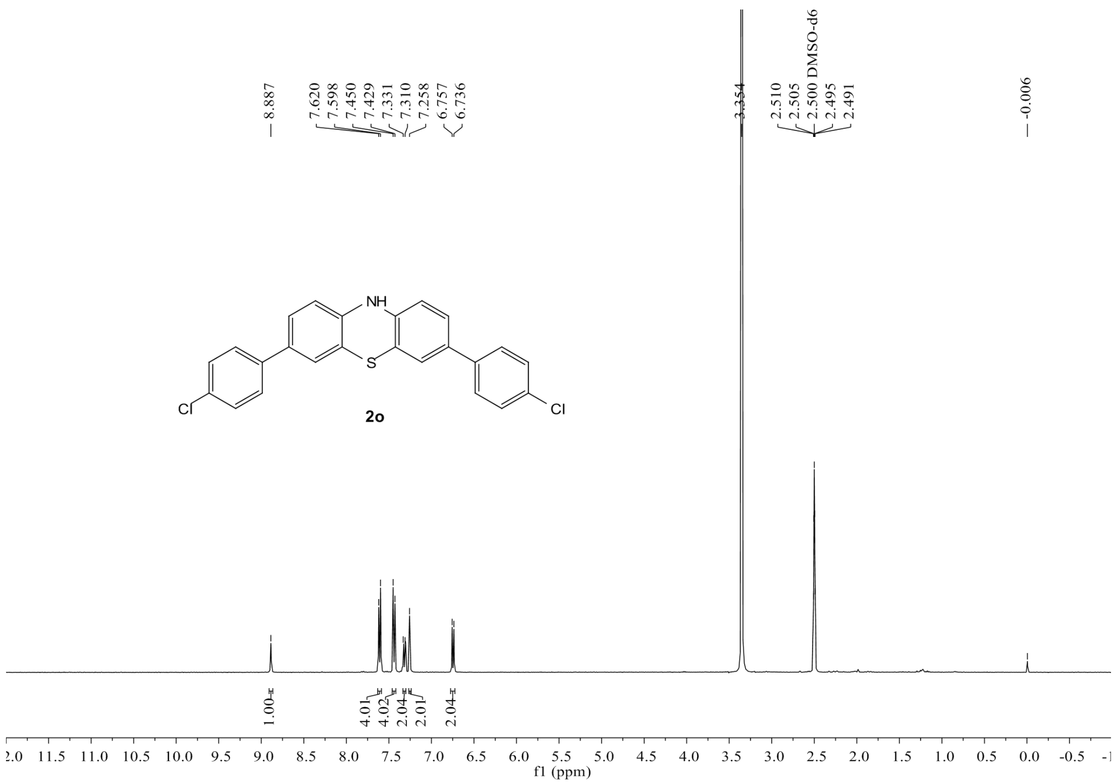


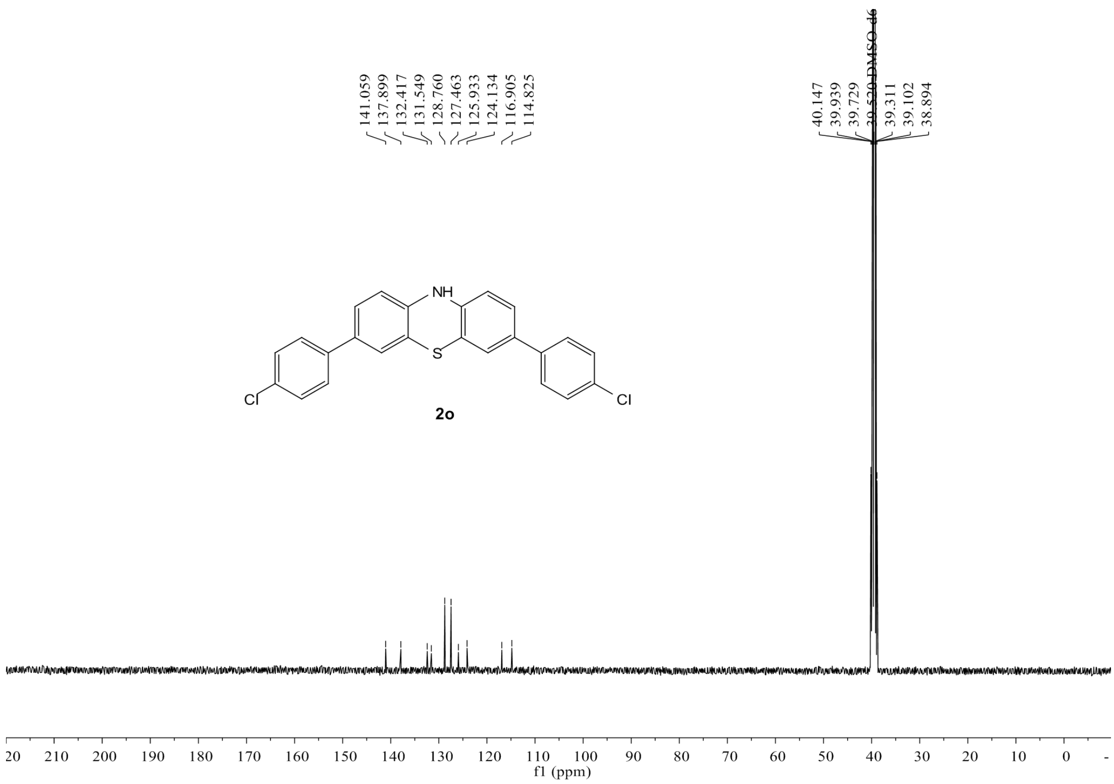
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **2n** (**DMSO-*d$_6$***)



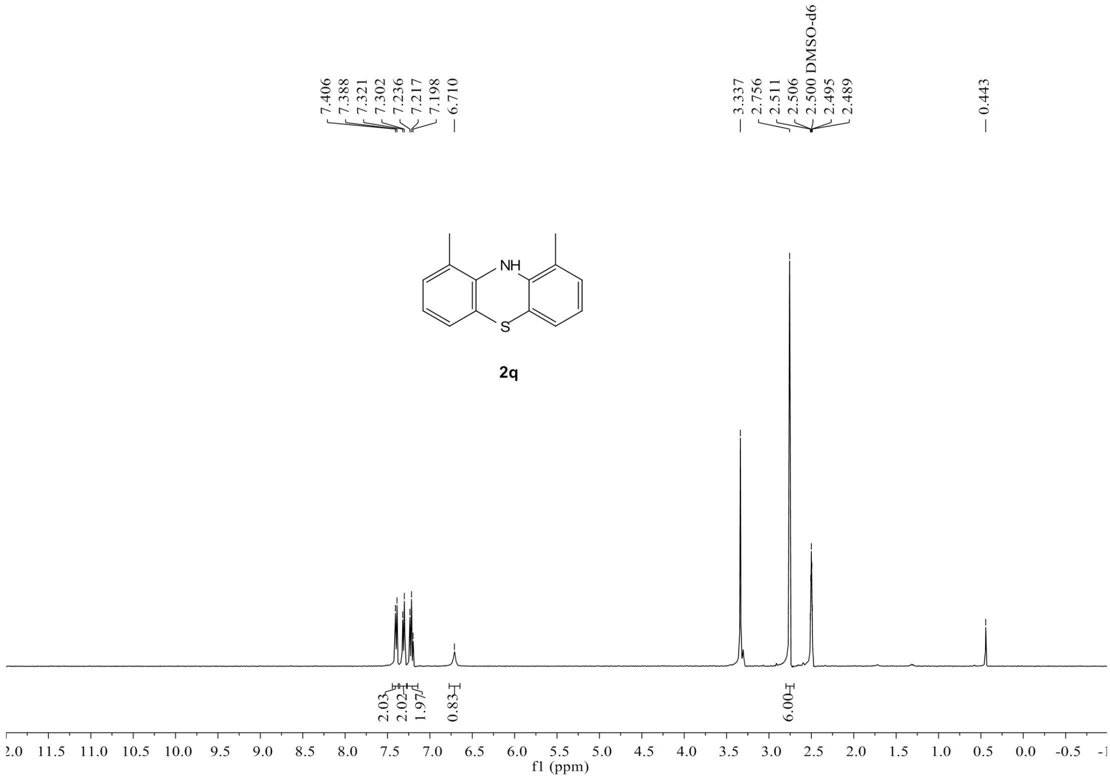


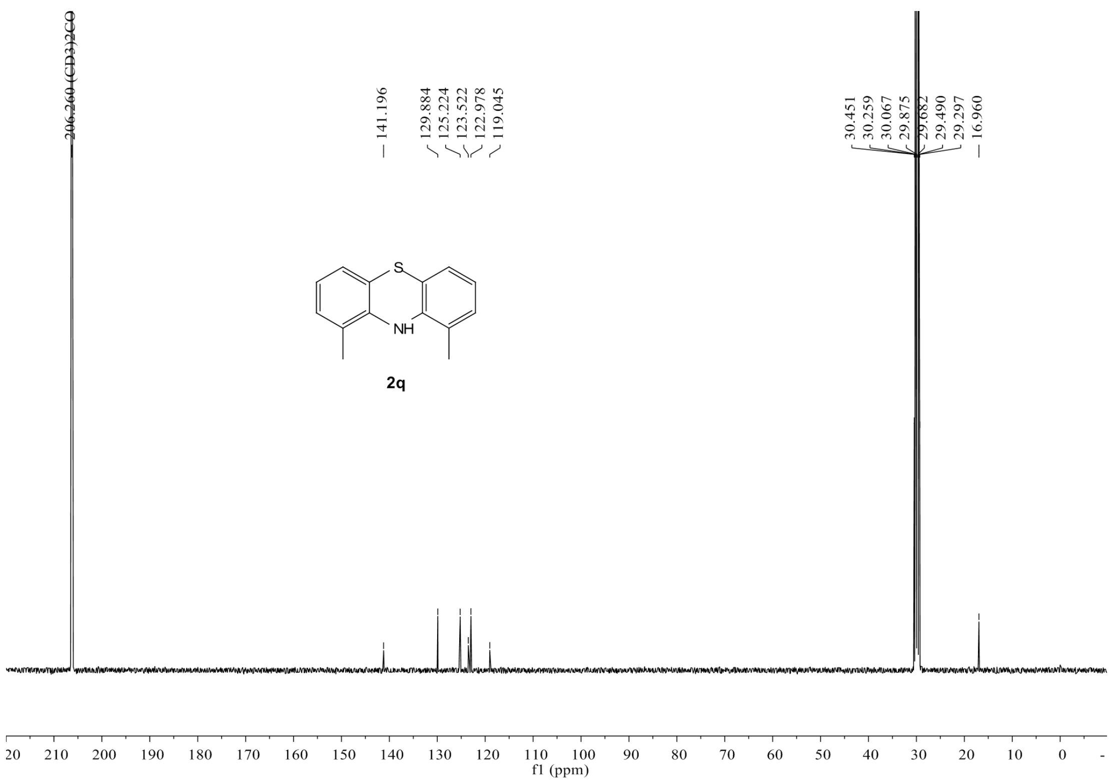
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **2o** (**DMSO-*d*$_6$**)



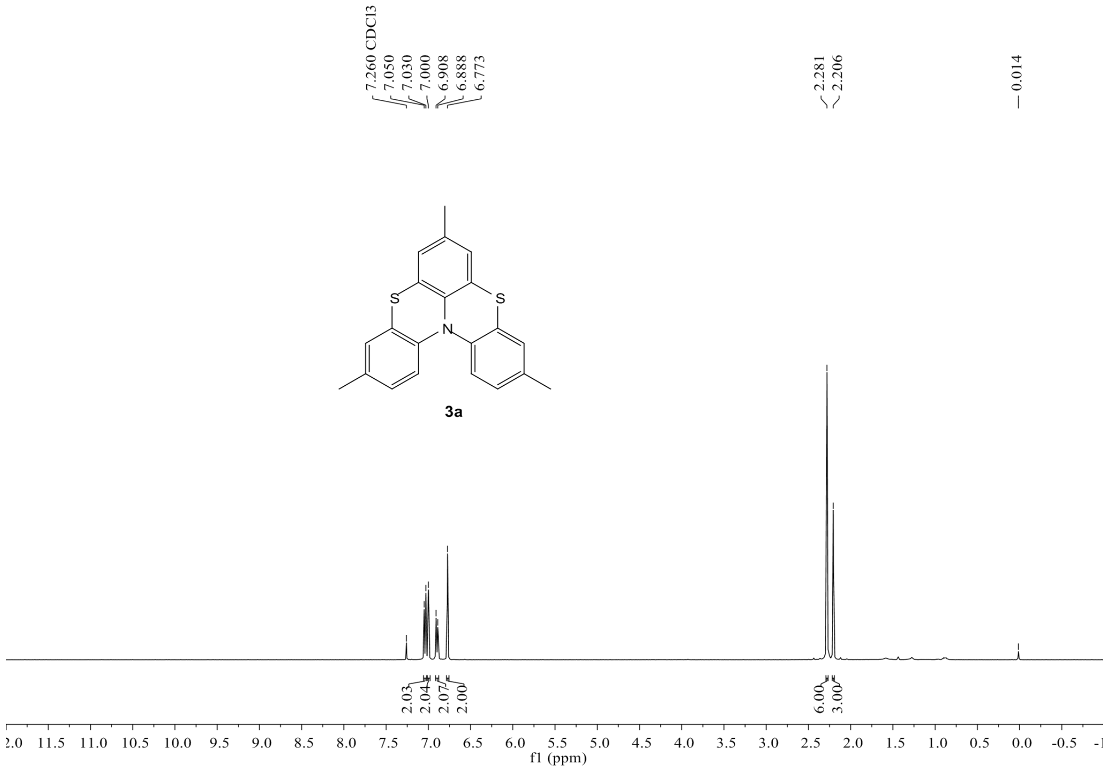


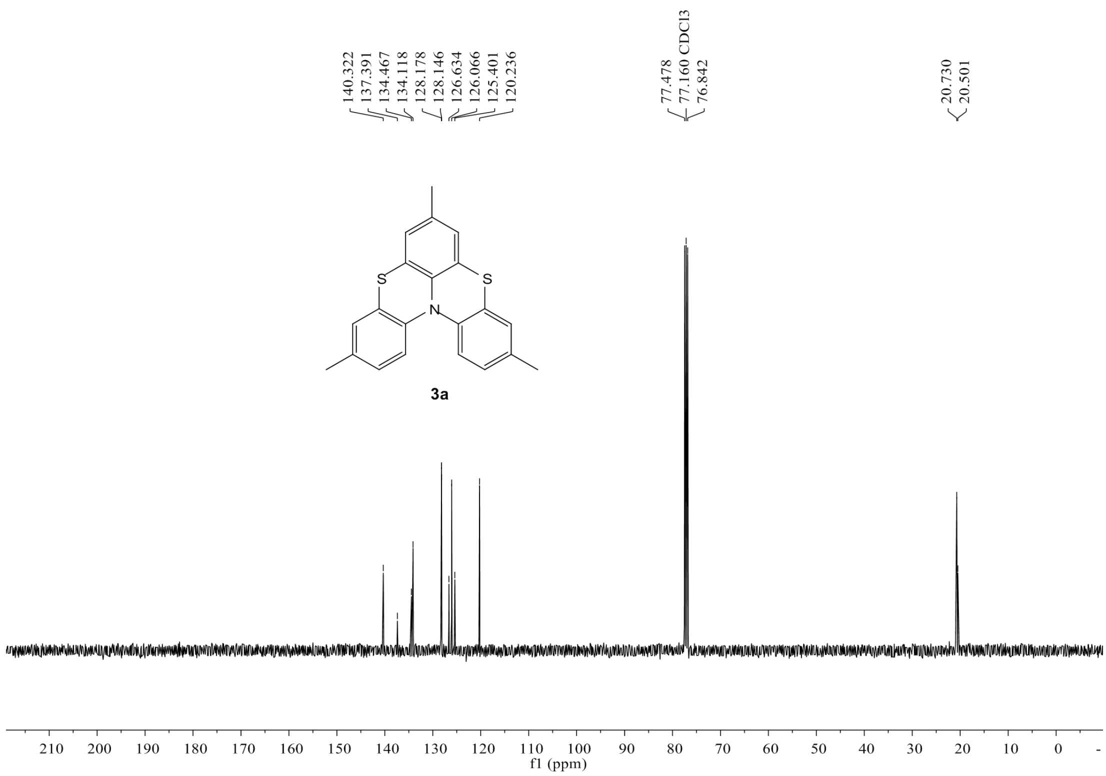
^{1}H **NMR** (400 MHz, **DMSO-d_6**) and ^{13}C **NMR** (100 MHz, **Acetone-d_6**) spectra of **2q**



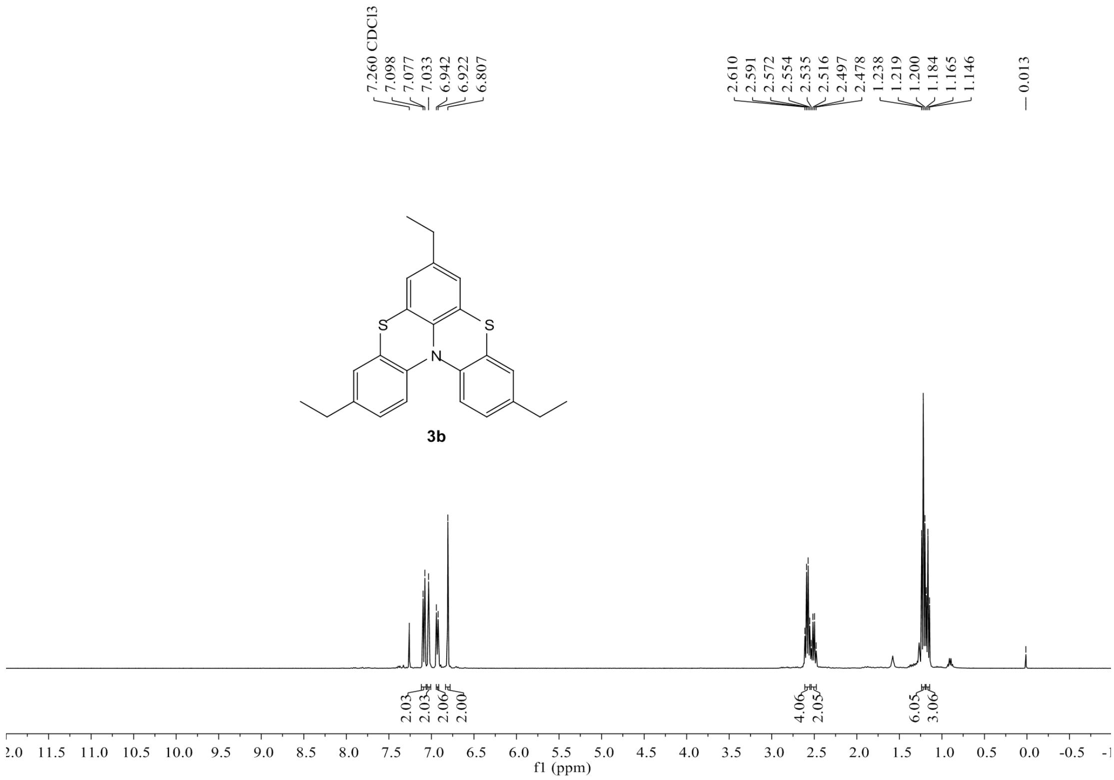


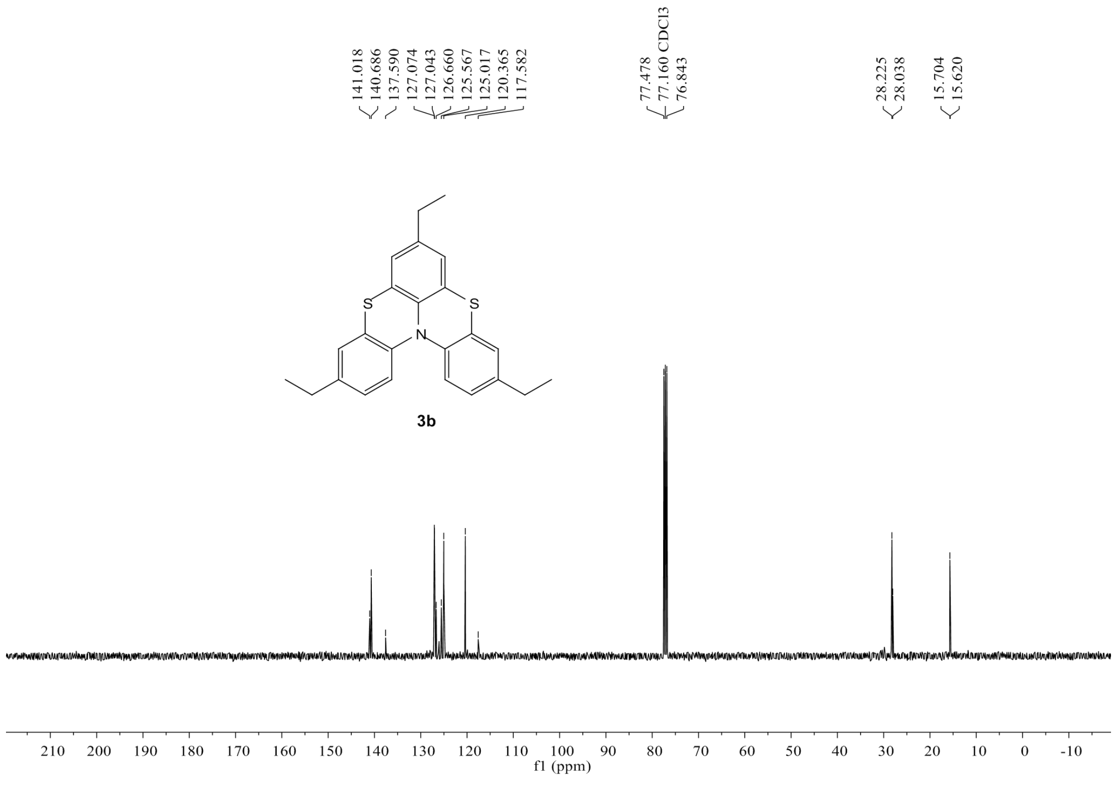
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **3a** (**$CDCl_3$**)



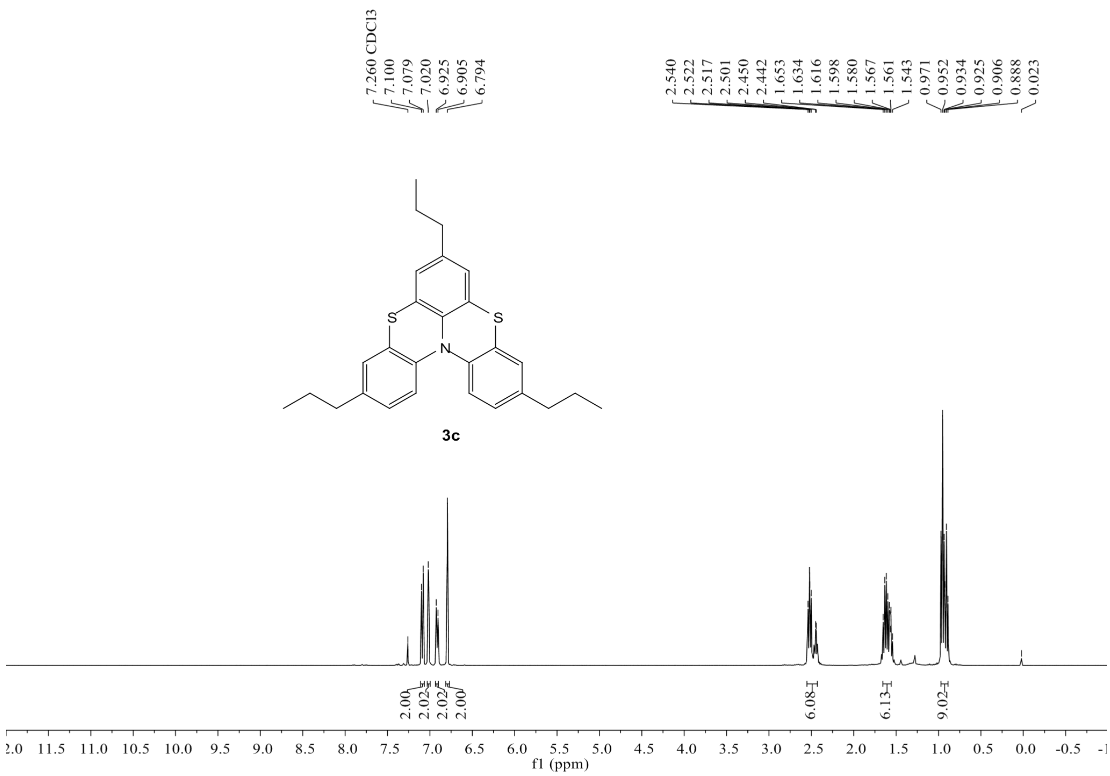


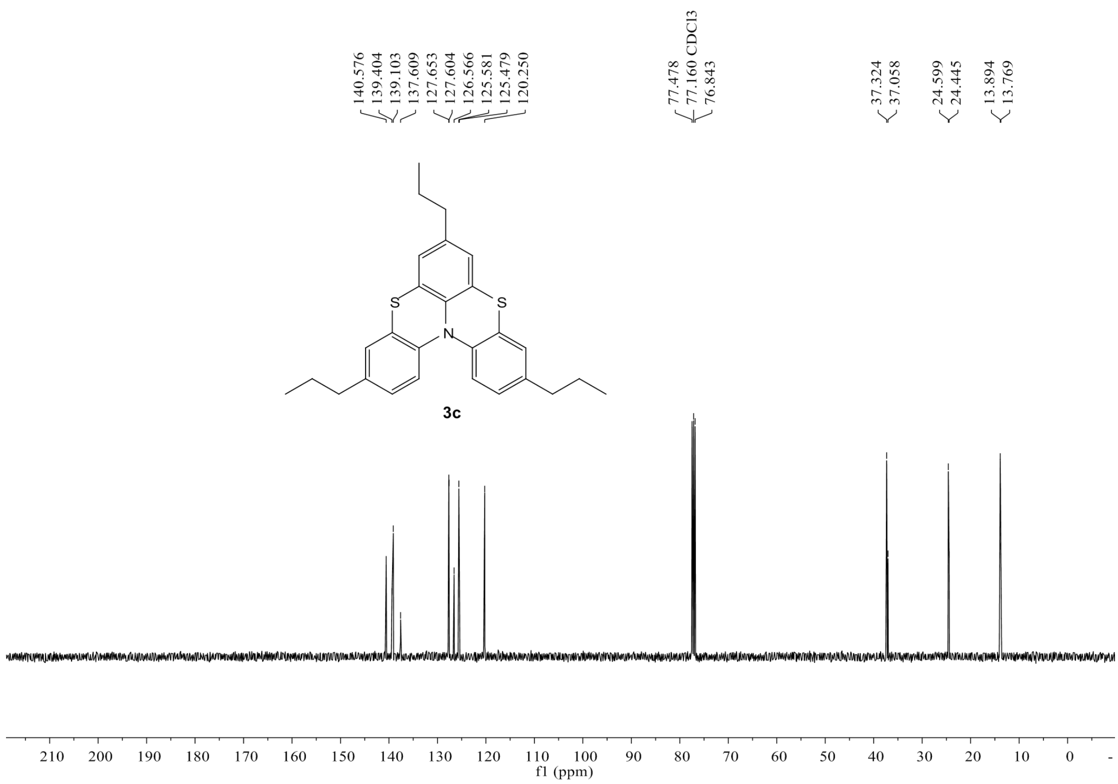
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **3b** (**CDCl₃**)



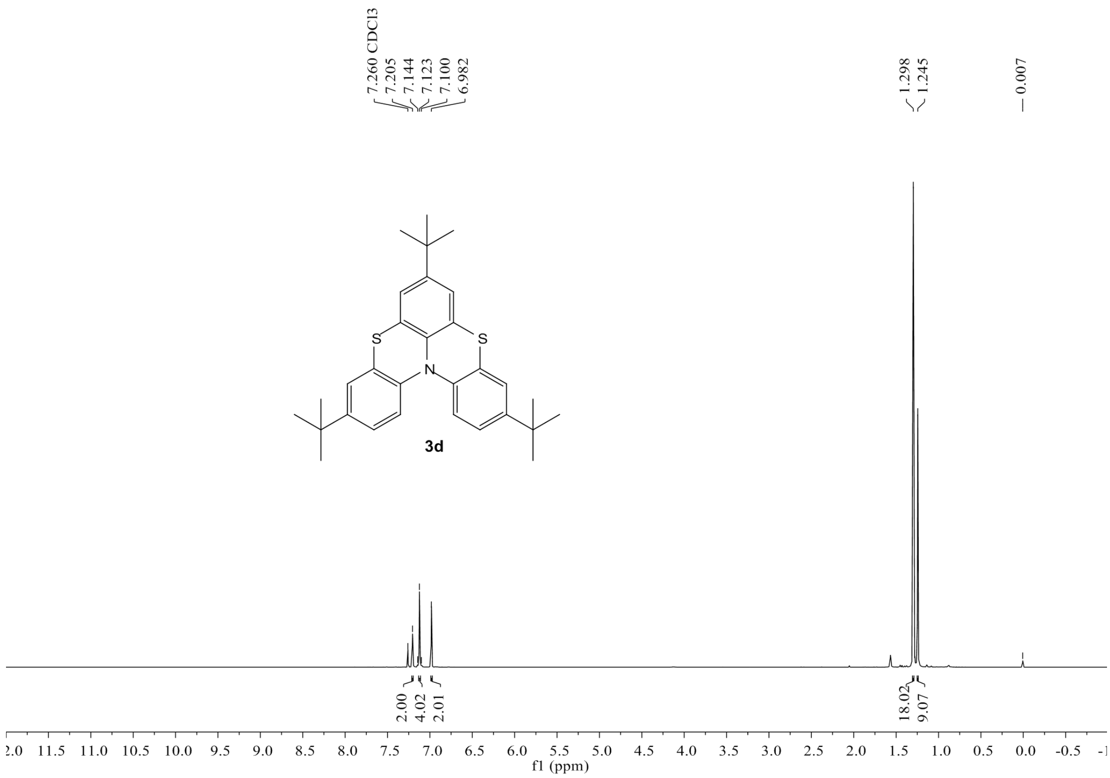


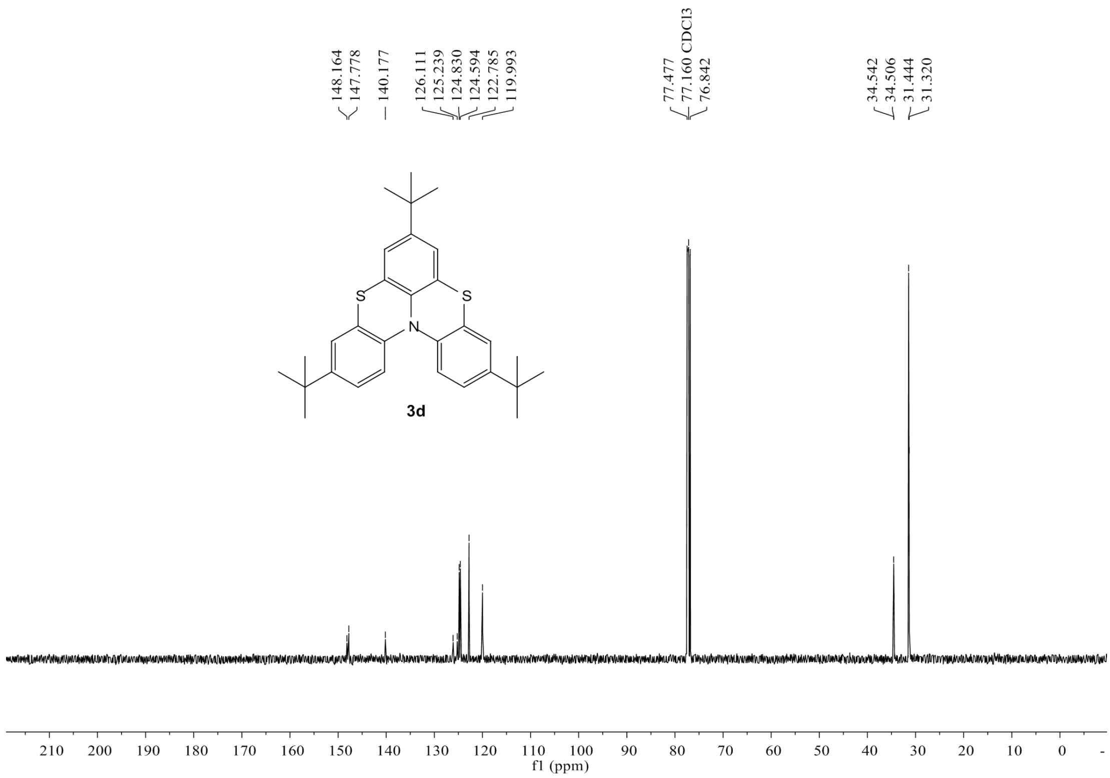
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **3c** (**$CDCl_3$**)



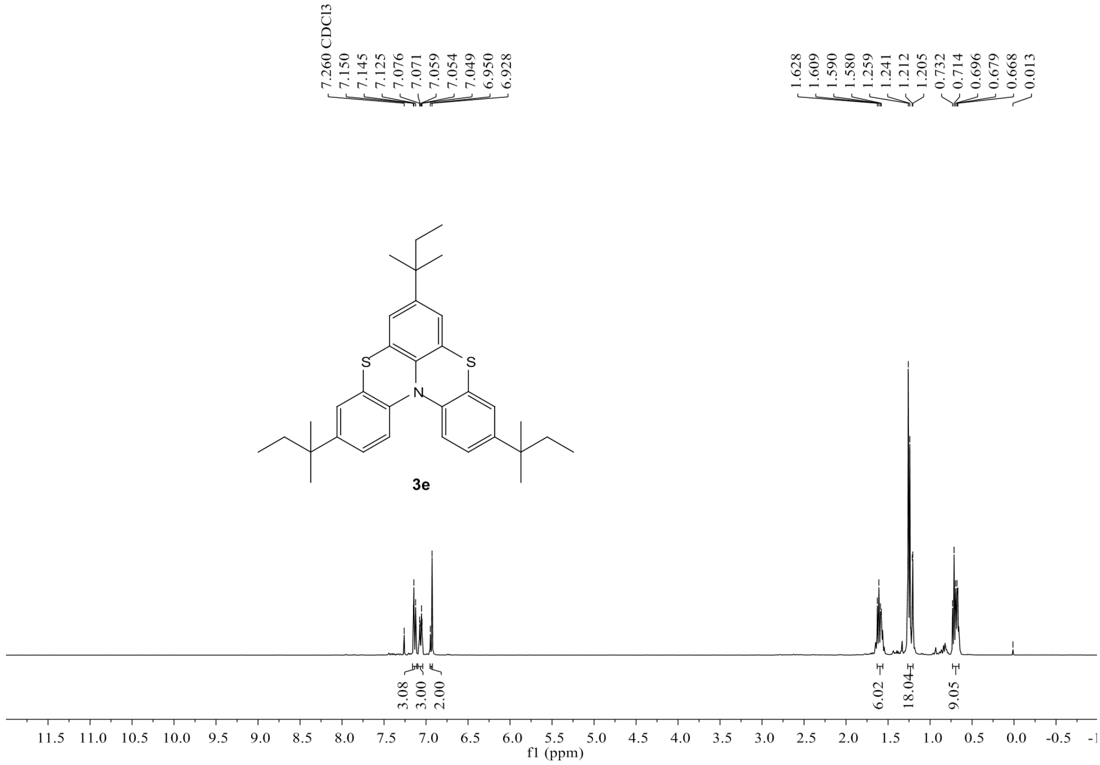


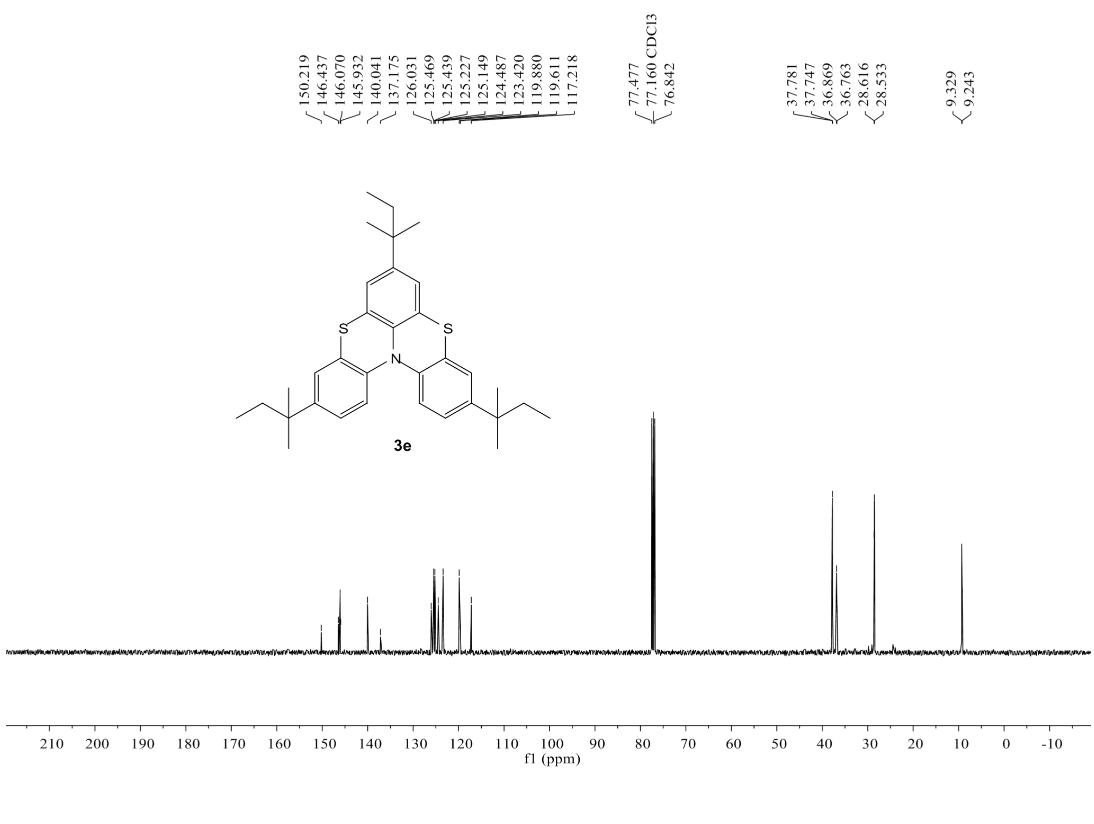
^{1}H **NMR** (400 MHz) and ^{13}C **NMR** (100 MHz) spectra of **3d** (**$CDCl_3$-d_6**)



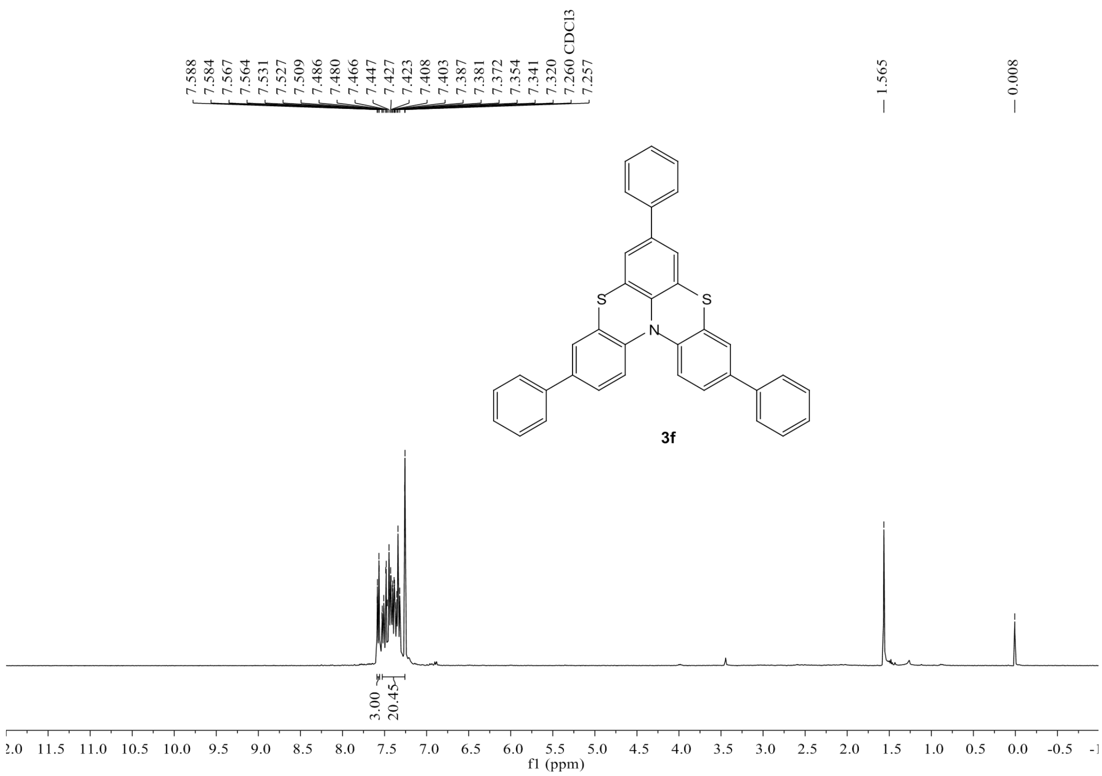


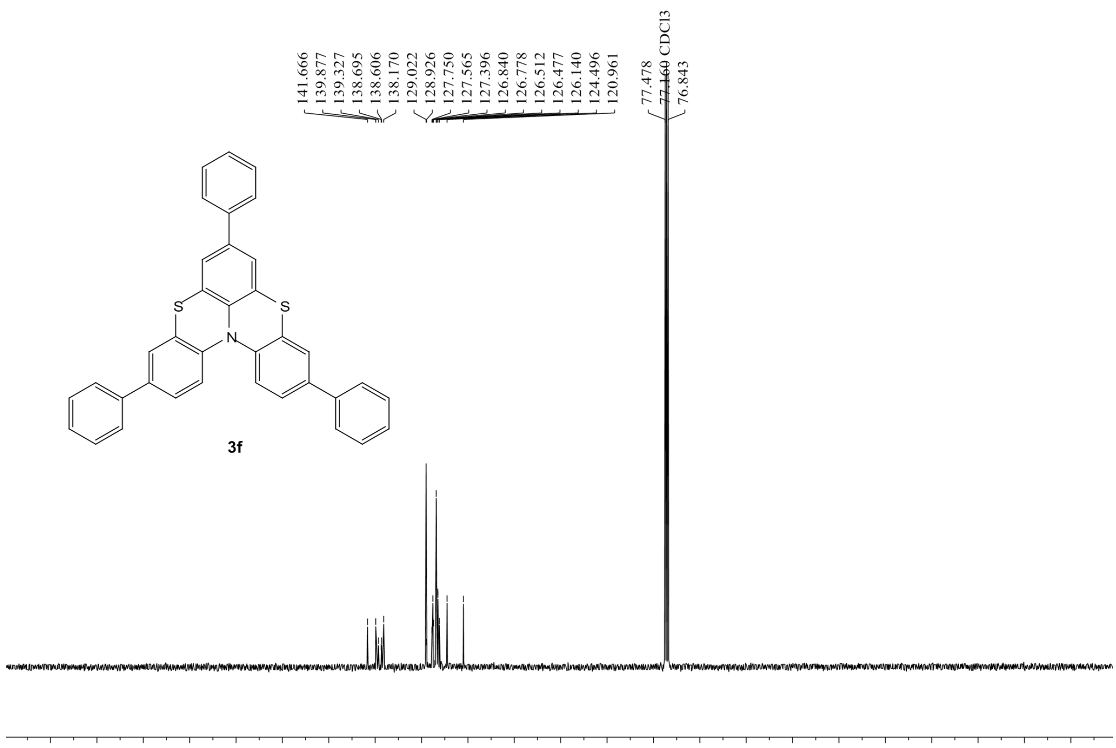
[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **3e** (**$CDCl_3$**)





[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **3f** (**CDCl$_3$**)





[1]H **NMR** (400 MHz) and [13]C **NMR** (100 MHz) spectra of **4a** (**$CDCl_3$**)