Supporting Information

For

Pd-catalyzed Double N-arylation of Primary Amines to Synthesize Phenoxazines and Phenothiazines

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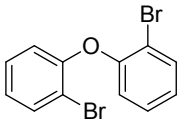
1. Synthesis of Starting Materials and Characterization Data

General Procedure 1: Synthesis of Starting Materials (Compounds 1a-c).

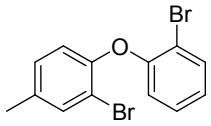
Following a slightly modified literature procedure,[1] 1-bromo-2-iodobenzene (11.3 g, 40 mmol), 2-bromophenol (8.3 g, 48 mmol), CuI (1.5 g, 8.0 mmol), $Fe(acac)_3$ (2.8 g, 8.0 mmol), K_3PO_4 (17.0 g, 80 mmol) and DMSO (30 mL) were added to a 100 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated and refilled with nitrogen three times. The tube was placed in an oil bath at 110 °C with stirring for 18 h. The tube was then cooled to room temperature, diluted with ethyl acetate, washed with brine, dried with Na_2SO_4, and concentrated on a rotovap. The residue was purified using column chromatography to give the product **1a-c**.

General Procedure 2: Synthesis of Starting Materials (Compounds 1d-g).

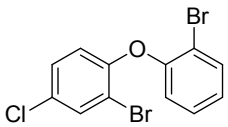
Following a slightly modified literature procedure,[2] a mixture of 2-bromo-1-fluoro-4-nitrobenzene (0.4 g, 2 mmol), 2-bromophenol (0.4 g, 2.4 mmol), K_2CO_3 (0.8 g, 6 mmol) and DMSO (2 mL) was stirred for 12 h at 140 °C. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and concentrated on a rotovap. The residue was purified using column chromatography to give the product **1d-g**.



Bis(2-bromophenyl)ether (1a)[1]: Colorless liquid, isolated yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.59-7.57 (m, 2H), 7.21-7.16 (m, 2H), 6.98-6.94 (m, 2H), 6.81-6.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 153.04, 133.73, 128.54, 124.96, 119.36, 114.04. LRMS (EI): calculated for $C_{12}H_8Br_2O$, 328; observed 328.

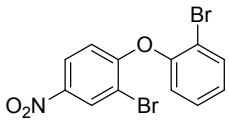


2-Bromo-1-(2-bromophenoxy)-4-methyl-benzene (1b)[1]: Colorless liquid, isolated yield 73%; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.59-7.56 (m, 1H), 7.42 (d, J = 1.62 Hz, 1H), 7.18-7.16 (m, 1H), 7.02-7.00 (m, 1H), 6.95-6.93 (m, 1H), 6.76-6.73 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 153.60, 150.63, 135.25, 134.06, 133.69, 129.21, 128.44, 124.49, 119.88, 118.53, 114.12, 113.57, 20.37. LRMS (EI): calculated for $C_{13}H_{10}Br_2O$, 342; observed 342.

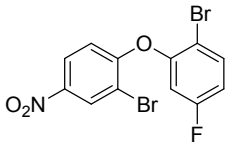


2-Bromo-1-(2-bromophenoxy)-4-chloro-benzene (1c)[1]: Colorless liquid, isolated yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.52-7.51 (m, 2H), 7.16-7.07 (m, 2H), 6.92 (t, J = 7.40 Hz, 1H), 6.75 (d, J = 8.00 Hz, 1H), 6.61 (d, J = 8.72 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 152.74, 152.18, 133.97, 133.28,

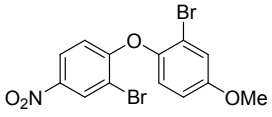
129.21, 128.72, 128.54, 125.51, 119.82, 119.59, 114.44, 114.36. LRMS (EI): calculated for $C_{12}H_7Br_2ClO$, 362; observed 362.



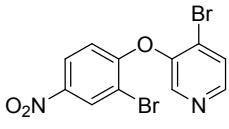
2-Bromo-1-(2-bromophenoxy)-4-nitro-benzene (1d): Colorless liquid, isolated yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 8.54 (d, J = 2.64 Hz, 1H), 8.09-8.06 (m, 1H), 7.71-7.68 (m, 1H), 7.44-7.40 (m, 1H), 7.23-7.15 (m, 2H), 6.65 (d, J = 9.08 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 159.03, 151.01, 142.85, 134.36, 129.53, 129.31, 127.50, 124.23, 122.58, 115.71, 115.28, 112.39. HRMS (ESI): calculated for $C_{12}H_7Br_2NO_3$, 370.8793; observed 370.8795.



2-Bromo-1-(2-bromo-5-fluorophenoxy)-4-nitrobenzene (1e): Colorless liquid, isolated yield 92%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 8.50 (d, J = 2.68 Hz, 1H), 8.14-8.11 (m, 1H), 7.69-7.66 (m, 1H), 7.01-6.91 (m, 2H), 6.83 (d, J = 9.08 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 161.98 (d, J = 248.90 Hz), 157.92, 151.63 (d, J = 10.42 Hz), 143.06, 134.58 (d, J = 9.07 Hz), 129.21, 124.07, 116.08, 114.22 (d, J = 22.05 Hz), 112.67, 109.62 (d, J = 25.07 Hz), 109.62 (d, J = 4.15 Hz). HRMS (ESI): calculated for $C_{12}H_6Br_2FNO_3$, 388.8698; observed 388.8695.



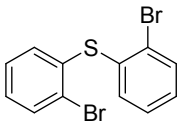
2-Bromo-1-(2-bromo-4-methoxyphenoxy)-4-nitrobenzene (1f): Yellow liquid, isolated yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 8.47 (d, J = 2.72 Hz, 1H), 8.05-8.02 (m, 1H), 7.18-7.13 (m, 2H), 6.95-6.92 (m, 1H), 6.63 (d, J = 9.12 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 159.34, 157.72, 144.40, 142.23, 129.07, 123.97, 123.14, 118.74, 115.88, 114.56, 114.33, 111.54, 55.65. HRMS (ESI): calculated for $C_{13}H_9Br_2NO_4$, 400.8898; observed 400.8894.



4-Bromo-3-(2-bromo-4-nitrophenoxy)pyridine (1g): Yellow liquid, isolated yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 8.57 (d, J = 2.68 Hz, 1H), 8.36-8.35 (m, 1H), 8.16-8.13 (m, 1H), 7.46-7.40 (m, 2H), 6.78-6.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 157.95, 148.67, 146.88, 143.57, 135.70, 129.72, 129.37, 124.31, 124.05, 116.30, 113.23. HRMS (ESI): calculated for $C_{11}H_6Br_2N_2O_3$, 371.8745; observed 371.8748.

General Procedure 3: Synthesis of Starting Materials (Compounds 4).

Following a slightly modified literature procedure[2], $Pd(OAc)_2$ (11 mg, 0.05 mmol), DPEphos (54 mg, 0.10 mmol), and NaO^{t}Bu (192 mg, 2 mmol) were added to a 25 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated and refilled with nitrogen three times before adding dry toluene (2 mL) followed by addition of the 2-Bromo-iodobenzene (339 mg, 1.2 mmol) and 2-bromobenzenethiol (189 mg, 1 mmol). The tube was placed in an oil bath at 110 °C with stirring for 24 h. The tube was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine, dried with Na_2SO_4, and purified using column chromatography to give the product **4**.



Bis(2-bromophenyl)sulfide (4)[3]: white solid, isolated yield 90%; mp 71-72 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.60-7.59 (m, 2H), 7.19 (t, J = 7.62 Hz, 2H), 7.11-7.09 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 135.51, 133.34, 132.28, 128.66, 128.05, 125.65. LRMS (EI): calculated for $C_{12}H_8Br_2S$, 344; observed 344.

2. Synthesis of Target products and Characterization Data

General Procedure 1: Synthesis of Phenoxazine Derivatives (Compounds 3a-s).

Bis(2-bromophenyl)ether **1** (0.2 mmol) and phenylamine **2** (0.22 mmol), NaO^{t}Bu (0.6 mmol), $Pd(OAc)_2$ (0.01 mmol), DPEphos (0.02 mmol), and dry toluene (2 mL) were added to a 25 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated and refilled with nitrogen three times. The tube was kept in an oil bath at 120 °C under stirring for 15 h. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine. The organic phase was collected and dried over Na_2SO_4. The solvent was removed on a rotovap and the residue was purified by column chromatography to give the product **3**. (The reaction time extended to 24 h of compounds **3e** and **3h**. Rac-BINAP was used in place of DPEphos at 100 ^{o}C for 24 h of compounds **3n-p**. $Pd_2(dba)_3$ (5 mol%), Xantphos (10 mol%), Cs_2CO_3 (3.0 equiv.) and dioxane (2 mL) at 100 ^{o}C for 24 h of compound **3q**.)

General Procedure 2: Synthesis of 1,4-Bis(10-phenoxazinyl)benzene (Compound 3t).

Bis(2-bromophenyl)ether **1** (1.2 mmol) and 1,4-benzendiamine **2t** (0.6 mmol), NaO^{t}Bu (3.6 mmol), $Pd(OAc)_2$ (0.06 mmol), DPEphos (0.12 mmol), and dry toluene (2 mL) were added to a 25 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated and refilled with nitrogen three times. The tube was kept in an oil bath at 120 °C under stirring for 3 d. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine. The organic phase was collected and dried over Na_2SO_4. The solvent was removed on a rotovap and the residue was purified by column chromatography to give the product **3t**.

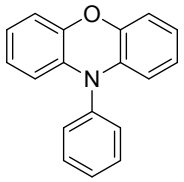
General Procedure 3: Synthesis of Phenothiazine Derivatives (Compounds 5a-b).

Bis(2-bromophenyl)sulfide **4** (0.2 mmol) and phenylamine **2** (0.22 mmol), NaO^{t}Bu (0.6 mmol), $Pd_2(dba)_3$ (0.01 mmol), Rac-BINAP (0.02 mmol), and dry toluene (2 mL) were added to a 25 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated

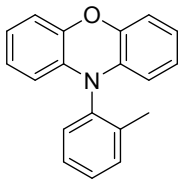
and refilled with nitrogen three times. The tube was kept in an oil bath at 110 °C under stirring for 20 h. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine. The organic phase was collected and dried over Na_2SO_4. The solvent was removed on a rotovap and the residue was purified by column chromatography to give the product **5a-b**.

General Procedure 4: Synthesis of 1,4-Bis(10-phenothiazinyl)benzene (Compound 5c).

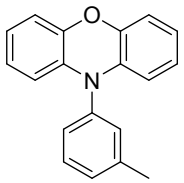
Bis(2-bromophenyl)sulfide **4** (1.2 mmol) and 1,4-benzendiamine **2t** (0.6 mmol), NaO^{t}Bu (3.6 mmol), $Pd_2(dba)_3$ (0.06 mmol), Rac-BINAP (0.12 mmol), and dry toluene (2 mL) were added to a 25 mL Schlenk tube armed with a magnetic stir bar. The tube was evacuated and refilled with nitrogen three times. The tube was kept in an oil bath at 110 °C under stirring for 3 d. The reaction mixture was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine. The organic phase was collected and dried over Na_2SO_4. The solvent was removed on a rotovap and the residue was purified by column chromatography to give the product **5c**.



10-Phenyl-phenoxazine (3a)[4]: Using procedure 1, white solid, isolated yield 99%; mp 142-143 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.53 (t, J = 7.74 Hz, 2H), 7.41 (t, J = 7.38 Hz, 1H), 7.29 (d, J = 7.86 Hz, 2H), 6.66-6.65 (m, 2H), 6.59 (t, J = 7.68 Hz, 2H), 6.54- 6.52 (m, 2H), 5.87 (d, J = 7.98 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.85, 138.90, 134.33, 130.95, 130.72, 128.38, 123.15, 121.19, 115.32, 113.16. LRMS (EI): calculated for $C_{18}H_{13}NO$, 259; observed 259.

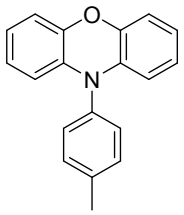


10-(2-Methylphenyl)-phenoxazine (3b)[4]: Using procedure 1, white solid, isolated yield 83%; mp 174-175 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.42-7.40 (m, 1H), 7.38-7.35 (m, 2H), 7.25-7.24 (m, 1H), 6.67-6.54 (m, 6H), 5.76-5.75 (m, 2H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.83, 138.90, 136.76, 133.38, 130.95, 128.82, 128.50, 123.37, 121.07, 115.33, 112.54, 17.51. HRMS (ESI): calculated for $C_{19}H_{15}NO$, 273.1154; observed 273.1152.

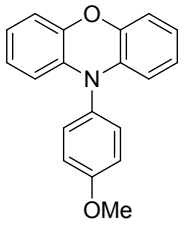


10-(3-Methylphenyl)-phenoxazine (3c)[4]: Using procedure 1, white solid, isolated yield 85%; mp 123-125 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.44-7.42

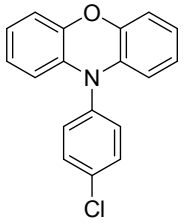
(m, 1H), 7.24 (d, J = 7.62 Hz, 1H), 7.12-7.09 (m, 2H), 6.66-6.53 (m, 6H), 5.91-5.89 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.86, 141.12, 138.79, 134.39, 131.06, 130.70, 129.16, 127.54, 123.13, 121.09, 115.26, 113.21, 21.29. HRMS (ESI): calculated for $C_{19}H_{15}NO$, 273.1154; observed 273.1151.



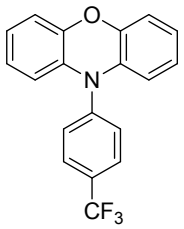
10-(4-Methylphenyl)-phenoxazine (3d)[4]: Using procedure 1, white solid, isolated yield 87%; mp 122-124 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.35 (d, J = 7.98 Hz, 2H), 7.18 (d, J = 8.10 Hz, 2H), 6.66-6.53 (m, 6H), 5.91-5.89 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.92, 138.31, 136.14, 134.52, 131.63, 130.40, 123.15, 121.06, 115.26, 113.18, 21.21. HRMS (ESI): calculated for $C_{19}H_{15}NO$, 273.1154; observed 273.1151.



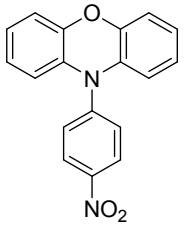
10-(4-Methoxyphenyl)-phenoxazine (3e)[4]: Using procedure 1, white solid, isolated yield 98%; mp 174-175 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.21 (d, J = 8.58 Hz, 2H), 7.06 (d, J = 8.58 Hz, 2H), 6.65-6.55 (m, 6H), 5.91 (d, J = 7.68 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 159.27, 143.93, 134.65, 131.76, 131.21, 123.15, 121.07, 116.14, 115.21, 113.15, 55.43. LRMS (EI): calculated for $C_{19}H_{15}NO_2$, 289; observed 289.



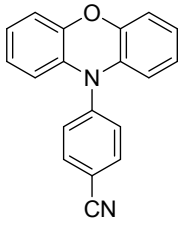
10-(4-Chlorophenyl)-phenoxazine (3f)[4]: Using procedure 1, white solid, isolated yield 69%; mp 177-178 ^{o}C); ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.53 (d, J = 8.40 Hz, 2H), 7.26 (d, J = 8.40 Hz, 2H), 6.68-6.56 (m, 6H), 5.89 (d, J = 7.92 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.87, 137.50, 134.24, 133.98, 132.32, 131.35, 123.23, 121.55, 115.52, 113.11. LRMS (EI): calculated for $C_{18}H_{12}ClNO$, 293; observed 293.



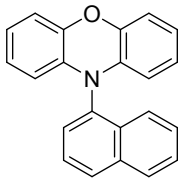
10-(4-Trifluoromethylphenyl)-phenoxazine (3g)[5]: Using procedure 1, light yellow solid, isolated yield 68%; mp 195-196 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.85 (d, J = 8.28 Hz, 2H), 7.48 (d, J = 8.16 Hz, 2H), 6.71-6.58 (m, 6H), 5.89 (d, J = 7.92 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.94, 142.57, 133.66, 131.53, 130.57 (q, J = 32.72 Hz), 128.21 (q, J = 3.45 Hz), 123.79 (q, J = 271.11 Hz), 123.29, 121.89, 115.71, 113.20. LRMS (EI): calculated for $C_{19}H_{12}F_3NO$, 327; observed 327.



10-(4-Nitrophenyl)-phenoxazine (3h)[4]: Using procedure 1, red solid, isolated yield 93%; mp 197-198 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 8.43 (d, J = 8.82 Hz, 2H), 7.55 (d, J = 8.88 Hz, 2H), 6.76-6.72 (m, 4H), 6.66-6.64 (m, 2H), 6.02-6.00 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 146.92, 145.71, 144.35, 133.06, 131.19, 126.34, 123.36, 122.54, 116.05, 113.78. LRMS (EI): calculated for $C_{18}H_{12}N_2O_3$, 304; observed 304.

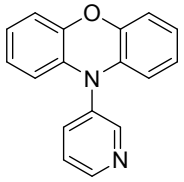


10-(4-Cyanophenyl)-phenoxazine (3i)[4]: Using procedure 1, yellow solid, isolated yield 56%; mp 160-161 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.88-7.87 (m, 2H), 7.50-7.48 (m, 2H), 6.74-6.61 (m, 6H), 5.93-5.92 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.01, 143.70, 134.88, 133.18, 131.69, 123.27, 122.23, 118.02, 115.87, 113.36, 112.11. HRMS (ESI): calculated for $C_{19}H_{12}N_2O$, 284.0950; observed 284.0945.

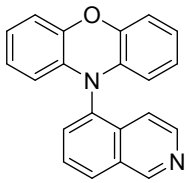


10-(1-Naphthyl)-phenoxazine (3j)[5]: Using procedure 1, yellowish solid, isolated yield 90%; mp 198-199 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 8.06 (d, J = 8.40 Hz, 1H), 7.96-7.94 (m, 2H), 7.61 (t, J = 7.98 Hz, 1H), 7.52-7.49 (m, 2H), 7.43 (t, J =

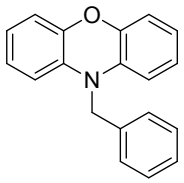
7.32 Hz, 1H), 6.72 (d, J = 7.86 Hz, 2H), 6.61-6.58 (m, 2H), 6.45 (t, J = 7.56 Hz, 2H), 5.68 (d, J = 7.92 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.89, 135.55, 135.06, 134.26, 131.36, 129.11, 128.91, 128.72, 127.26, 126.82 (2C), 123.35, 123.30, 121.25, 115.36, 113.36. HRMS (ESI): calculated for $C_{22}H_{15}NO$, 309.1154; observed 309.1155.



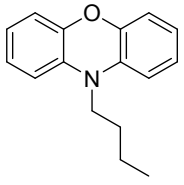
10-(3-Pyridyl)-phenoxazine (3k)[4]: Using procedure 1, white solid, isolated yield 91%; mp 153-155 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 8.72-8.71 (m, 1H), 8.62 (d, J = 2.04 Hz, 1H), 7.72-7.70 (m, 1H), 7.53-7.51 (m, 1H), 6.71-6.57 (m, 6H), 5.87-5.85 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 152.70, 149.40, 143.79, 138.81, 135.65, 133.69, 125.26, 123.20, 121.84, 115.64, 112.99. HRMS (ESI): calculated for $C_{17}H_{12}N_2O$, 260.0950; observed 260.0957.



10-(5-Isoquinolinyl)-phenoxazine (3l): Using procedure 1, yellow solid, isolated yield 86%; mp 219-221 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 9.40 (s, 1H), 8.51 (d, J = 5.46 Hz, 1H), 8.13-8.11 (m, 1H), 7.84 (d, J = 5.64 Hz, 1H), 7.80-7.78 (m, 2H), 6.66-6.48 (m, 6H), 5.66-5.64 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 153.18, 144.25, 143.77, 134.42, 134.38, 133.77, 133.67, 130.53, 128.62, 128.27, 123.34, 121.68, 115.91, 115.60, 113.10. HRMS (ESI): calculated for $[M+H]^+$ $C_{21}H_{15}N_2O$, 311.1179; observed 311.1182.

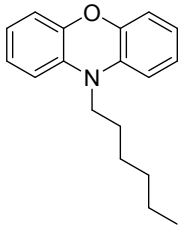


10-Benzyl-phenoxazine (3m)[6]: Using procedure 1, white solid, isolated yield 72%; mp 125-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.31-7.20 (m, 5H), 6.67-6.59 (m, 6H), 6.29-6.27 (m, 2H), 4.69 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 145.08, 136.24, 133.76, 128.86, 127.10, 125.93, 123.64, 121.15, 115.19, 112.13, 49.15. LRMS (EI): calculated for $C_{19}H_{15}NO$, 273; observed 273.

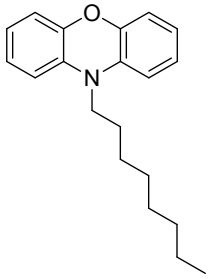


10-Butyl-phenoxazine (3n)[7]: Using procedure 1, colorless liquid, isolated yield 55%; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 6.77-6.75 (m, 2H), 6.60 (d, J = 3.60

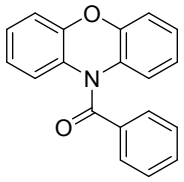
Hz, 4H), 6.44 (d, J = 7.92 Hz, 2H), 3.46 (s, 2H), 1.65-1.60 (m, 2H), 1.46-1.39 (m, 2H), 0.99 (t, J = 7.38 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.99, 133.31, 123.52, 120.62, 115.20, 111.22, 43.70, 27.01, 20.12, 13.86. LRMS (EI): calculated for $C_{16}H_{17}NO$, 239; observed 239.



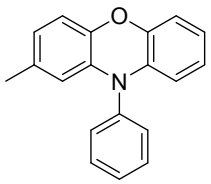
10-Hexyl-phenoxazine (3o)[8]: Using procedure 1, colorless liquid, isolated yield 67%; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 6.79-6.75 (m, 2H), 6.63-6.60 (m, 4H), 6.45 (d, J = 7.98 Hz, 2H), 3.45 (t, J = 8.22 Hz, 2H), 1.67-1.62 (m, 2H), 1.41-1.34 (m, 6H), 0.91 (t, J = 6.78 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.98, 133.40, 123.56, 120.60, 115.26, 111.21, 44.07, 31.56, 26.58, 24.83, 22.65, 14.00. LRMS (EI): calculated for $C_{18}H_{21}NO$, 267; observed 267.



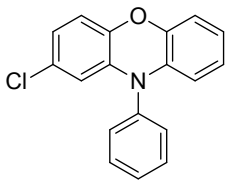
10-Octyl-phenoxazine (3p)[9]: Using procedure 1, colorless liquid, isolated yield 48%; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 6.78-6.76 (m, 2H), 6.64-6.58 (m, 4H), 6.44 (d, J = 7.98 Hz, 2H), 3.44 (t, J = 7.92 Hz, 2H), 1.67-1.61 (m, 2H), 1.39-1.25 (m, 10H), 0.89 (t, J = 6.96 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.99, 133.39, 123.55, 120.60, 115.26, 111.22, 44.06, 31.78, 29.35, 29.27, 26.91, 24.86, 22.62, 14.08. HRMS (ESI): calculated for $C_{20}H_{25}NO$, 295.1936; observed 295.1927.



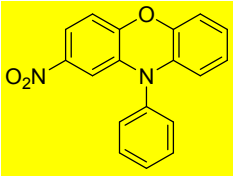
10-Benzoyl-phenoxazine (3q)[10]: Using procedure 1, white solid, isolated yield 79%; mp 155-156 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.42 (d, J = 7.38 Hz, 2H), 7.36-7.33 (m, 3H), 7.24 (t, J = 7.74 Hz, 2H), 7.12-7.09 (m, 4H), 6.93-6.90 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 168.11, 150.21, 134.93, 130.53, 130.03, 128.84, 128.00, 126.40, 124.61, 123.23, 116.58. HRMS (ESI): calculated for $[M+H]^+$ $C_{19}H_{14}NO_2$, 288.1019; observed 288.0980.



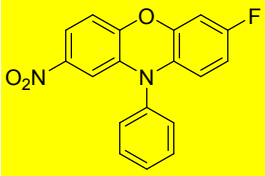
2-Methyl-10-phenyl-phenoxazine (3r)[4]: Using procedure 1, white solid, isolated yield 90%; mp 92-94 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.59 (t, J = 7.80 Hz, 2H), 7.47 (t, J = 7.50 Hz, 1H), 7.32 (d, J = 7.32 Hz, 2H), 6.67-6.54 (m, 4H), 6.42 (d, J = 7.74 Hz, 1H), 5.88-5.86 (m, 1H), 5.70 (d, J = 1.26 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.03, 141.74, 139.01, 134.39, 133.92, 132.69, 130.99, 130.87, 128.41, 122.98, 121.37, 121.16, 115.26, 115.03, 113.91, 113.21, 20.81. HRMS (ESI): calculated for $C_{19}H_{15}NO$, 273.1154; observed 273.1150.



2-Chloro-10-phenyl-phenoxazine (3s)[11]: Using procedure 1, white solid, isolated yield 56%; mp 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.58 (t, J = 7.84 Hz, 2H), 7.46 (t, J = 7.48 Hz, 1H), 7.30-7.28 (m, 2H), 6.67-6.53 (m, 5H), 5.88-5.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 143.61, 142.53, 138.16, 135.37, 133.53, 131.23, 130.47, 128.83, 128.04, 123.38, 121.75, 120.55, 116.11, 115.40, 113.45, 113.02. LRMS (EI): calculated for $C_{18}H_{12}ClNO$, 293; observed 293.

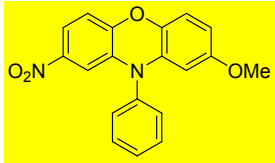


2-Nitro-10-phenyl-phenoxazine (3t): Using procedure 1, Orange solid, isolated yield 85%; mp 136-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.63 (t, J = 7.80 Hz, 2H), 7.55-7.51 (m, 2H), 7.32 (d, J = 7.4 Hz, 2H), 6.69-6.61 (m, 5H), 5.91-5.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 149.26, 143.75, 142.75, 137.36, 134.99, 132.80, 131.60, 130.07, 129.34, 124.38, 122.15, 117.84, 115.67, 115.10, 113.69, 107.64. HRMS (ESI): calculated for $C_{18}H_{12}N_2O_3$, 304.0848; observed 304.0852.

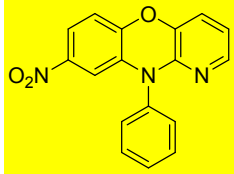


7-Fluoro-2-nitro-10-phenyl-phenoxazine (3u): Using procedure 1, Red solid, isolated yield 72%; mp 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.64 (t, J = 7.84 Hz, 2H), 7.56 (m, 2H), 7.31 (d, J = 7.52 Hz, 2H), 6.71-6.68 (m, 2H), 6.50-6.47 (m, 1H), 6.37-6.32 (m, 1H), 5.85-5.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 157.95 (d, J = 240.10 Hz), 148.26, 144.15, 143.20 (d, J = 11.46 Hz), 137.44, 134.91, 131.71, 130.04, 129.47, 129.32 (d, J = 3.18 Hz), 117.65, 115.28, 113.90 (d, J =

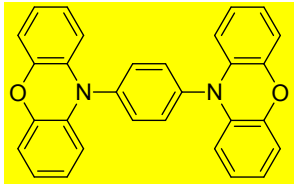
8.73 Hz), 110.01 (d, J = 21.98 Hz), 107.65, 104.14 (d, J = 27.36 Hz). HRMS (ESI): calculated for $C_{18}H_{11}FN_2O_3$, 322.0754; observed 322.0751.



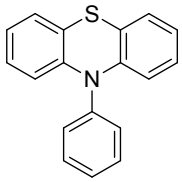
2-Methoxy-8-nitro-10-phenyl-phenoxazine (3v): Using procedure 1, Red solid, isolated yield 78%; mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.62-7.58 (m, 2H), 7.52-7.48 (m, 2H), 7.30-7.28 (m, 2H), 6.68-6.58 (m, 3H), 6.15-6.12 (m, 1H), 5.49 (d, J = 2.80 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 156.36, 149.49, 143.42, 137.23, 136.81, 134.29, 133.45, 131.55, 129.96, 129.37, 118.01, 115.72, 114.95, 107.78, 104.29, 101.67, 55.28. HRMS (ESI): calculated for $C_{19}H_{14}N_2O_4$, 334.0954; observed 334.0954.



8-Nitro-10-phenyl-benzo[b]pyrido[2,3-e][1,4]oxazine (3w): Using procedure 1, Orange solid, isolated yield 81%; mp 232-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.63-7.49 (m, 6H), 7.32 (d, J = 7.20 Hz, 2H), 6.93-6.91 (m, 1H), 6.68-6.65 (m, 1H), 6.01 (d, J = 9.04 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 144.63, 143.01, 142.16, 141.89, 140.18, 139.84, 136.29, 130.75, 129.76, 129.12, 121.72, 120.56, 118.85, 113.13, 111.00. HRMS (ESI): calculated for $C_{17}H_{11}N_3O_3$, 305.0800; observed 305.0806.

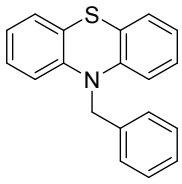


1,4-Bis(10-phenoxazinyl)-benzene (3x)[11]**:** Using procedure 2, light yellow solid, isolated yield 72%; mp 249-250 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.57 (s, 4H), 6.73-6.66 (m, 12H), 6.02-6.00 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 143.99, 139.02, 133.99, 133.66, 123.31, 121.70, 115.66, 113.15. LRMS (EI): calculated for $C_{30}H_{20}N_2O_2$, 440; observed 440.

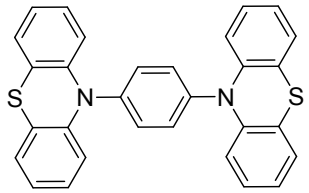


10-Phenyl-phenothiazine (5a)[3]**:** Using procedure 3, white solid, isolated yield 99%; mp 90-91 °C; ^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$): δ = 7.56 (t, J = 7.68 Hz, 2H), 7.44 (t, J = 7.44 Hz, 1H), 7.36 (d, J = 7.62 Hz, 2H), 7.00-6.98 (m, 2H), 6.82-6.76 (m, 4H), 6.18 (d, J = 8.04 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$): δ = 144.17, 140.88,

130.76, 130.66, 128.10, 126.75, 126.63, 122.38, 120.07, 115.95. LRMS (EI): calculated for $C_{18}H_{13}NS$, 275; observed 275.



10-Benzyl-phenothiazine (5b)[3]**:** Using procedure 3, pale brown solid, isolated yield 85%; mp 91-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.32-7.21 (m, 5H), 7.06 (d, J = 7.52 Hz, 2H), 6.94 (t, J = 7.84 Hz, 2H), 6.83 (t, J = 7.40 Hz, 2H), 6.61 (d, J = 8.12 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 144.40, 136.60, 128.67, 127.17, 126.95, 126.77, 126.56, 123.08, 122.45, 115.40, 52.64. LRMS (EI): calculated for $C_{19}H_{15}NS$, 289; observed 289.



1,4-Bis(10-phenothiazinyl)-benzene (5c)[12]**:** Using procedure 4, white solid, isolated yield 61%; mp 254-256 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ = 7.48 (s, 4H), 7.11 (d, J = 7.28 Hz, 4H), 7.01-6.88 (m, 8H), 6.51 (d, J = 8.00 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ = 143.74, 140.35, 130.35, 127.21, 126.98, 123.23, 122.79, 117.86. LRMS (EI): calculated for $C_{30}H_{20}N_2S_2$, 472; observed 472.

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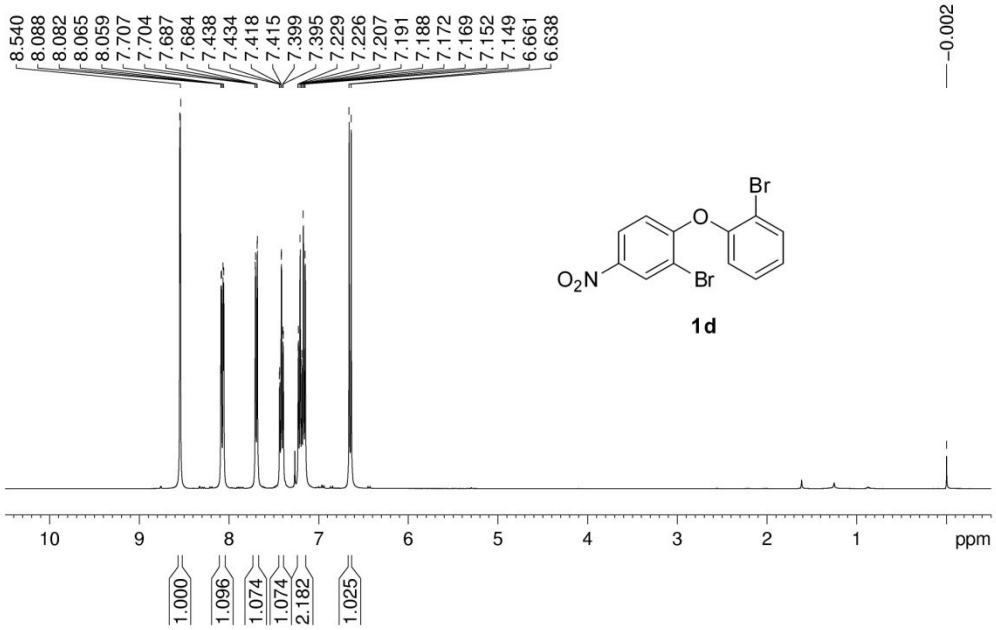
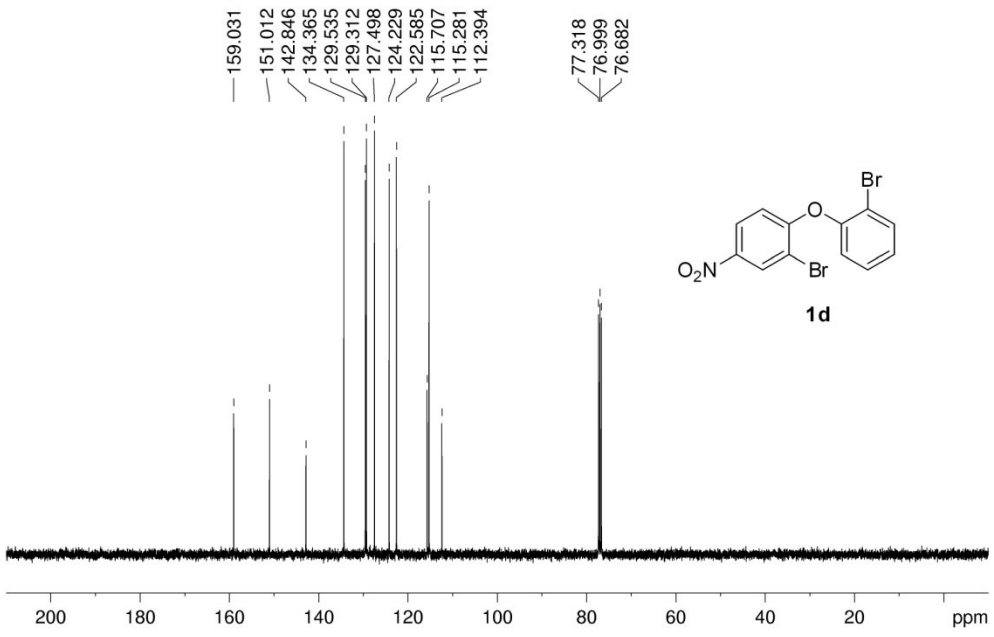
4. Scanned ^{1}H NMR and ^{13}C NMR of compounds 3a to 3t, and 5a to 5c

2-Bromo-1-(2-bromophenoxy)-4-nitro-benzene (1d):

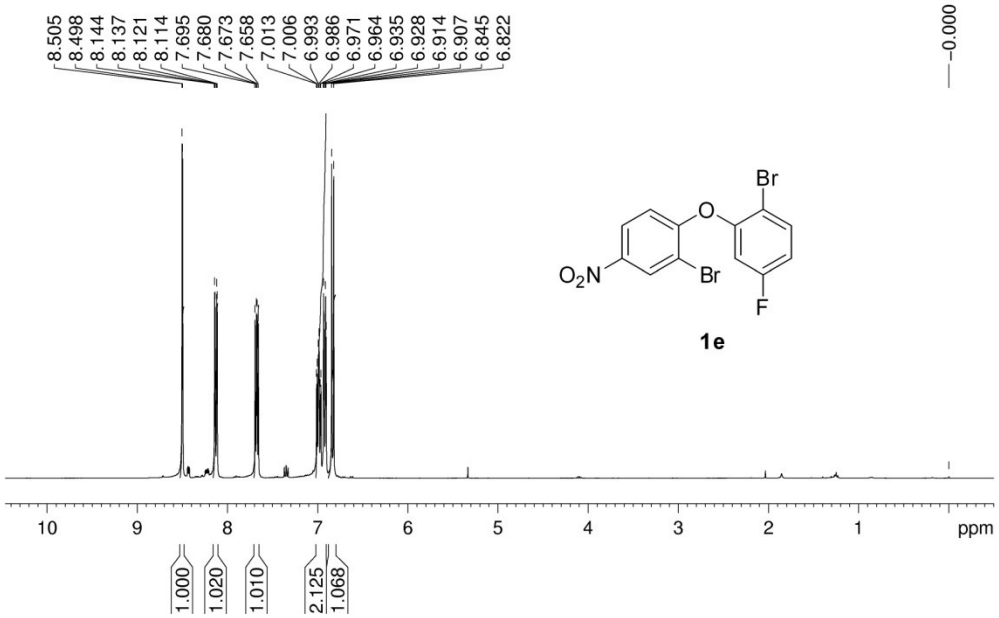
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

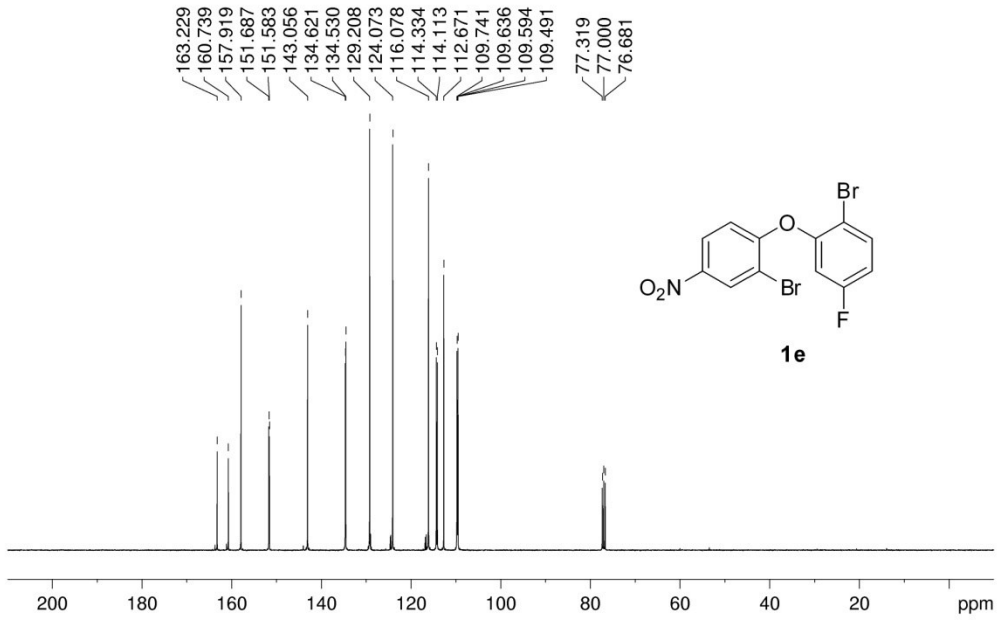




2-Bromo-1-(2-bromo-5-fluorophenoxy)-4-nitrobenzene (1e):

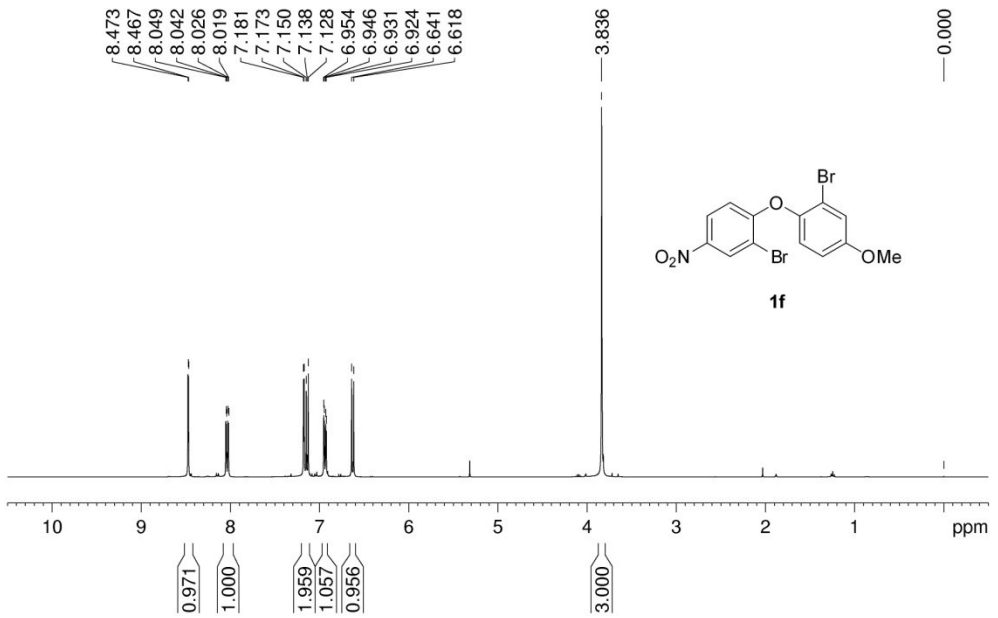
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

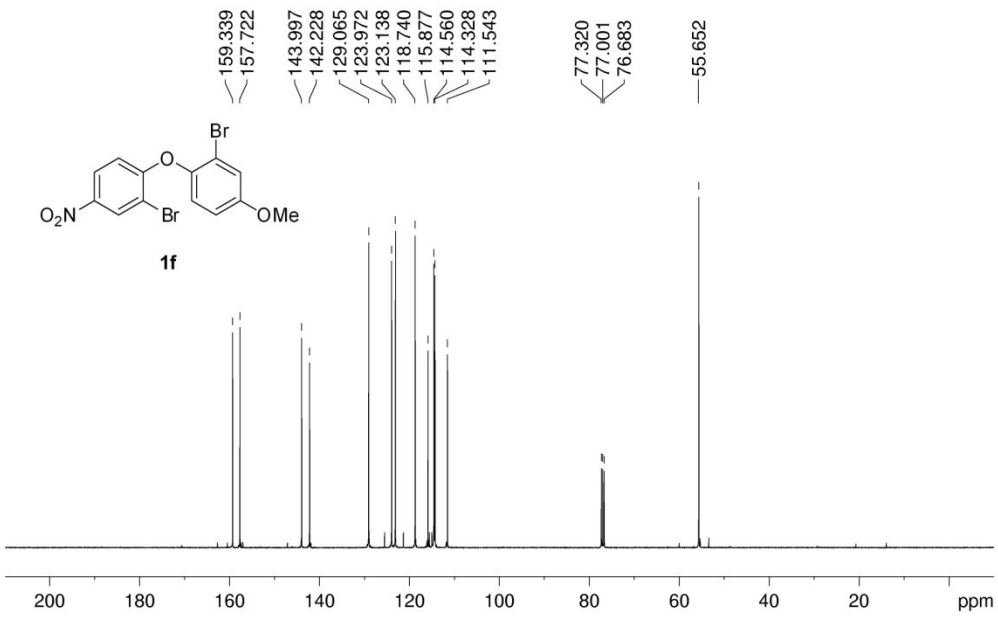




2-Bromo-1-(2-bromo-4-methoxyphenoxy)-4-nitrobenzene (1f):

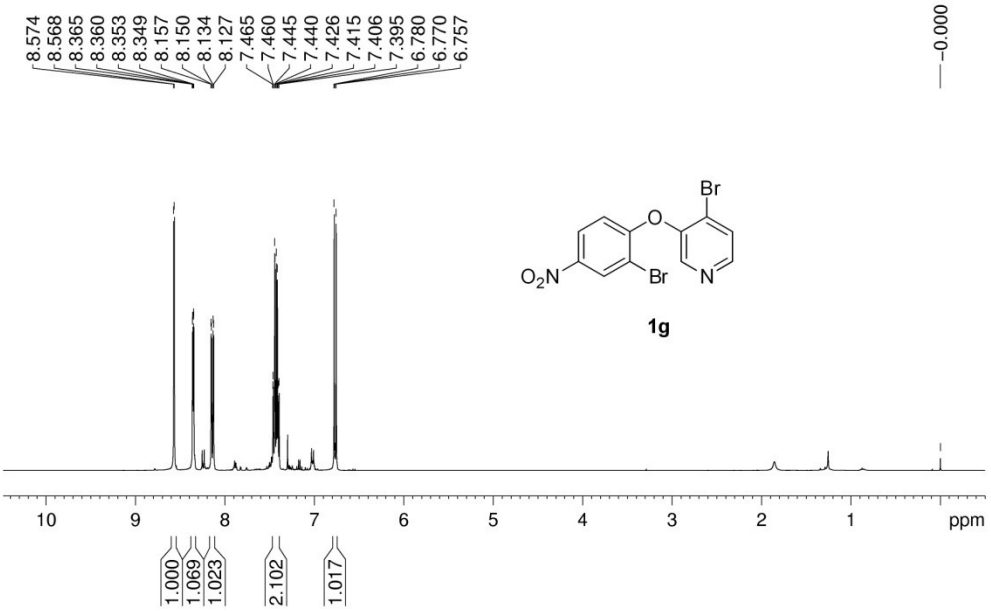
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

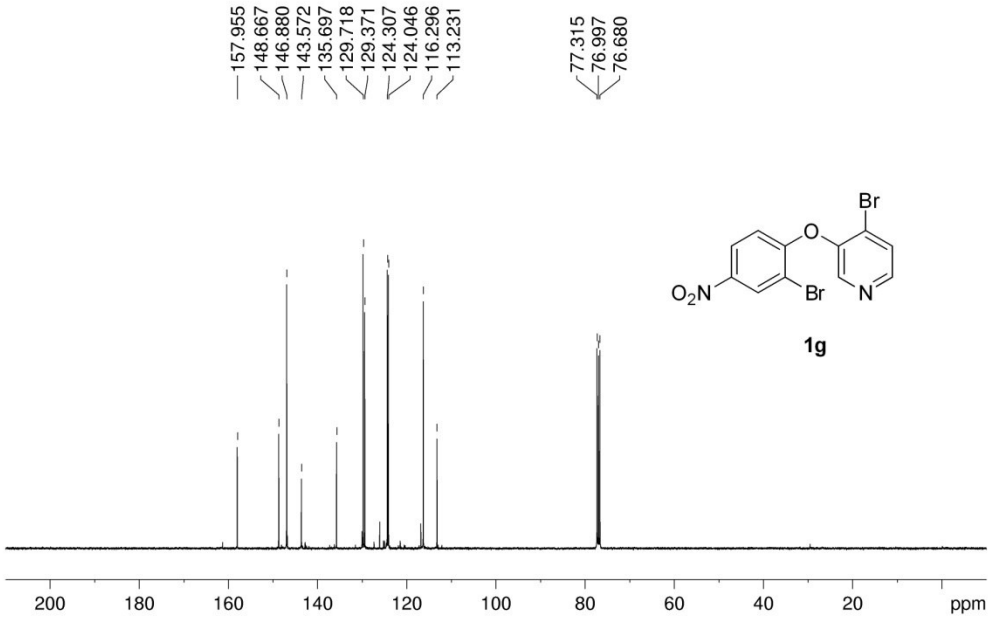




4-Bromo-3-(2-bromo-4-nitrophenoxy)pyridine (1g):

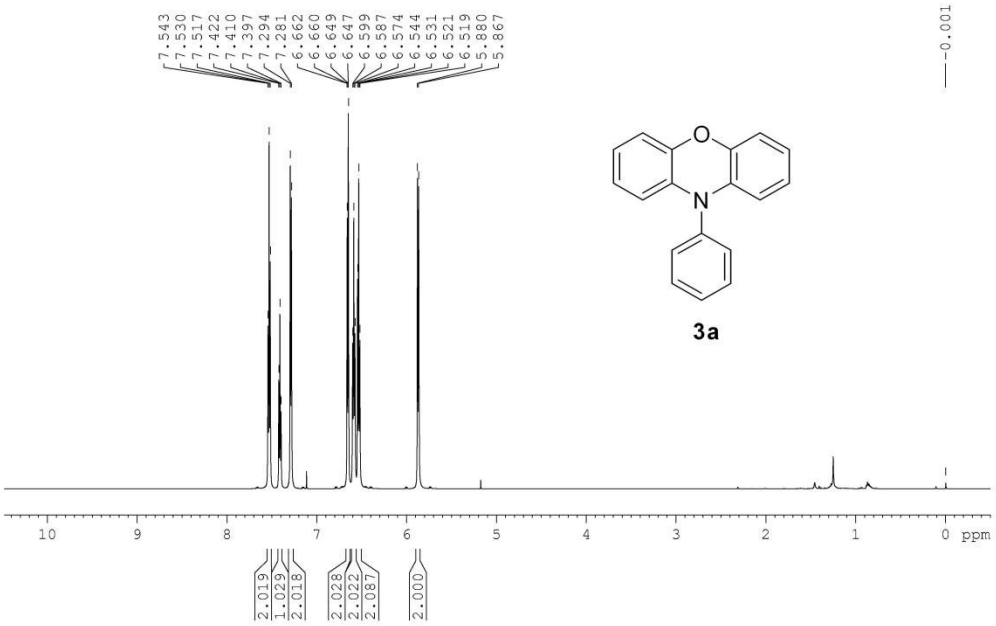
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

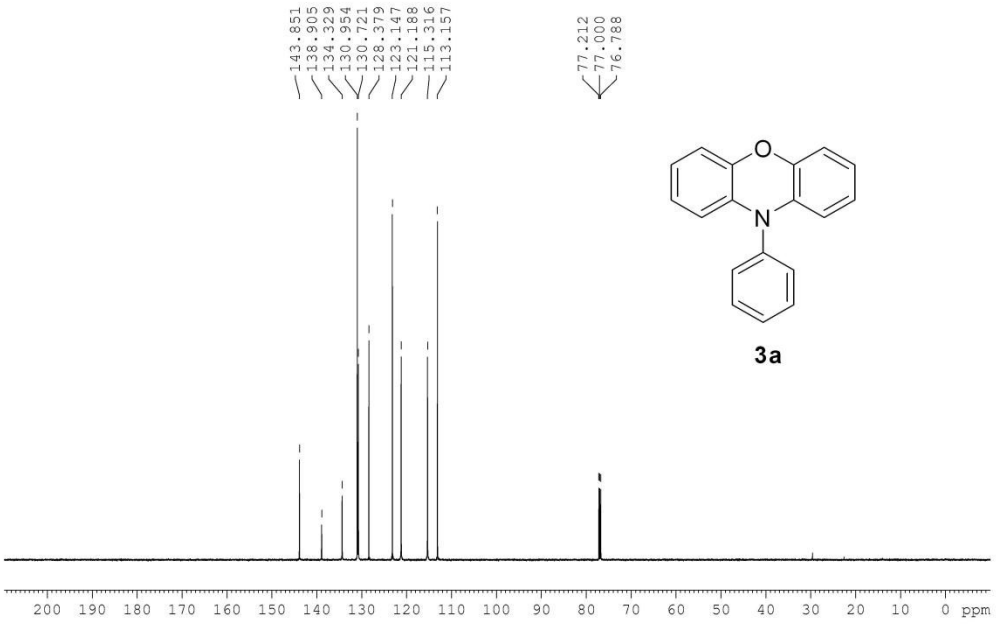




10-Phenyl-phenoxazine (3a):

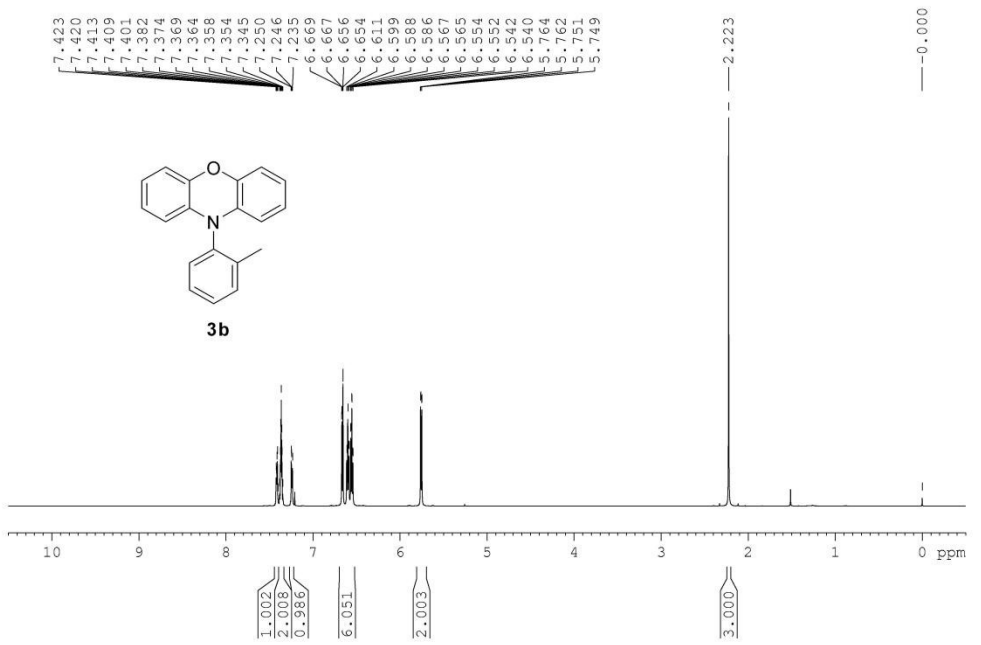
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

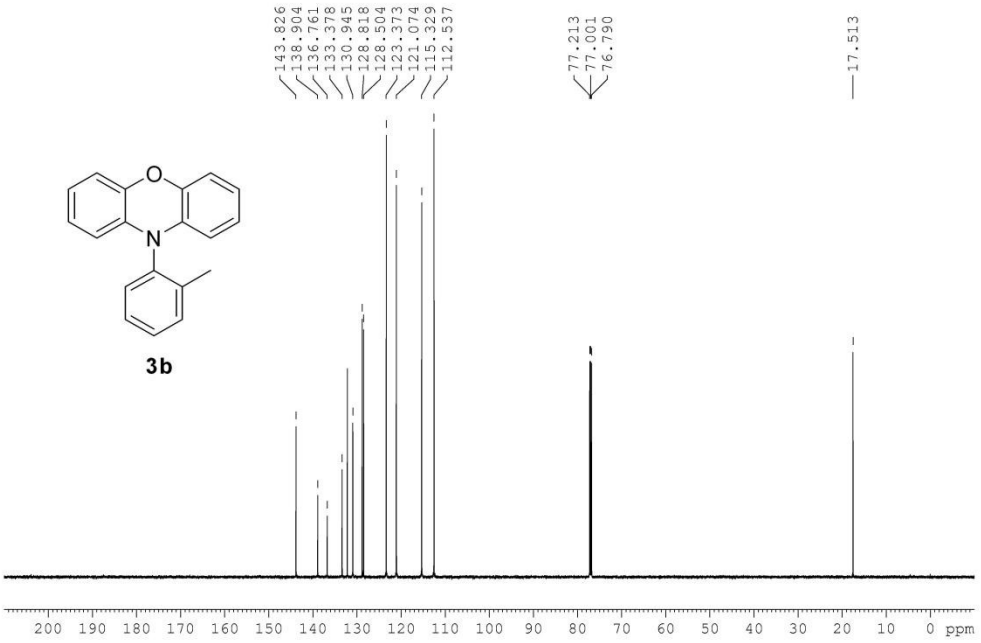




10-(2-Methylphenyl)-phenoxazine (3b):

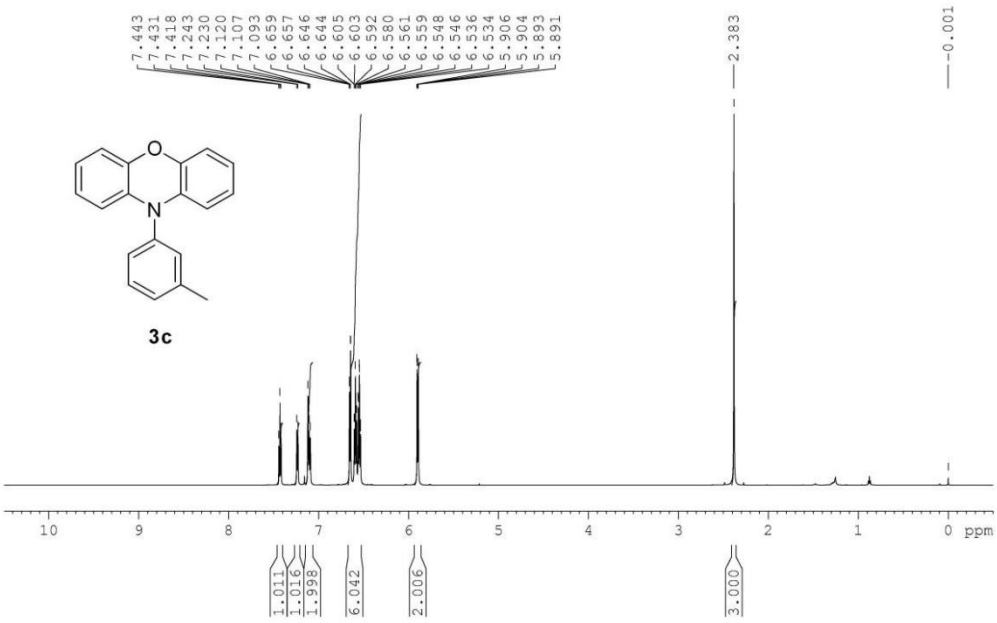
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

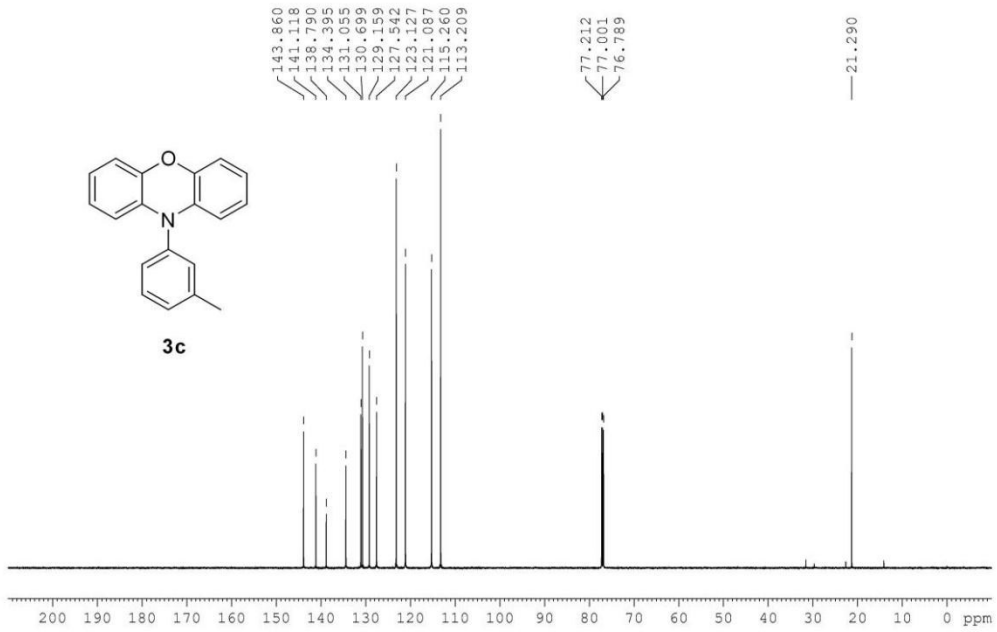




10-(3-Methylphenyl)-phenoxazine (3c):

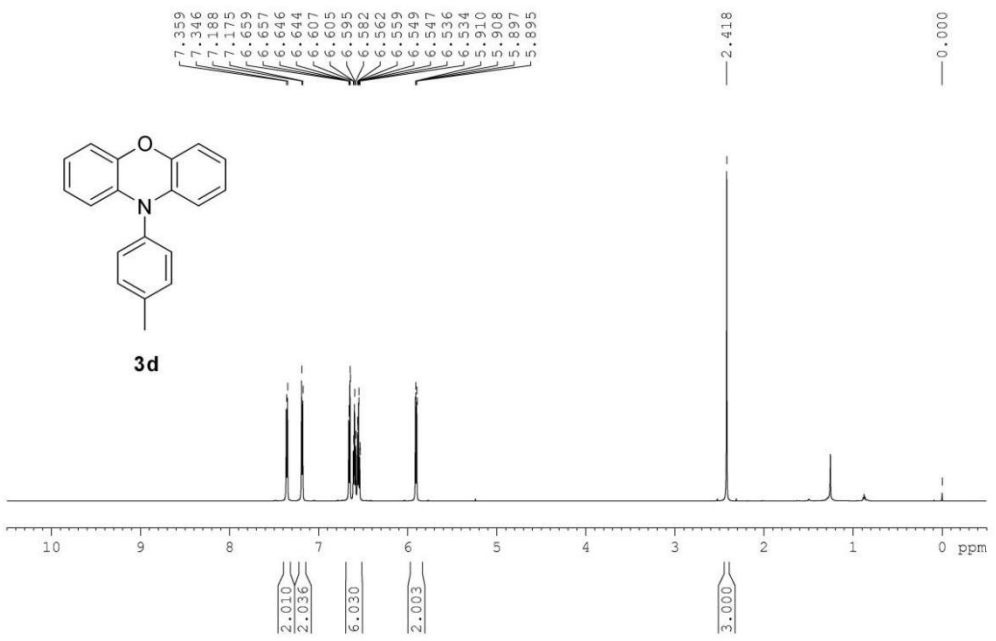
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

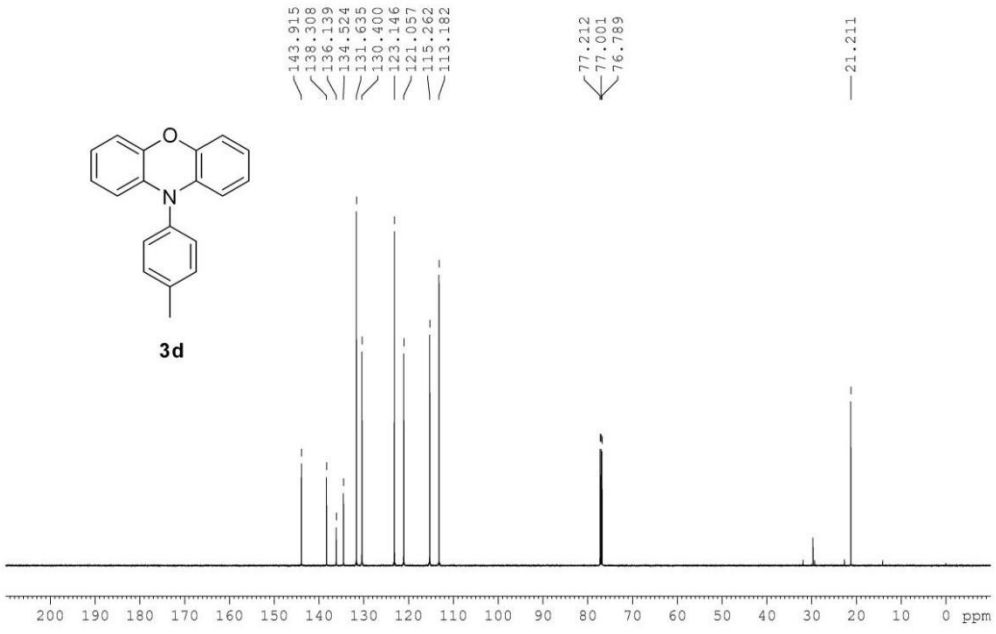




10-(4-Methylphenyl)-phenoxazine (3d):

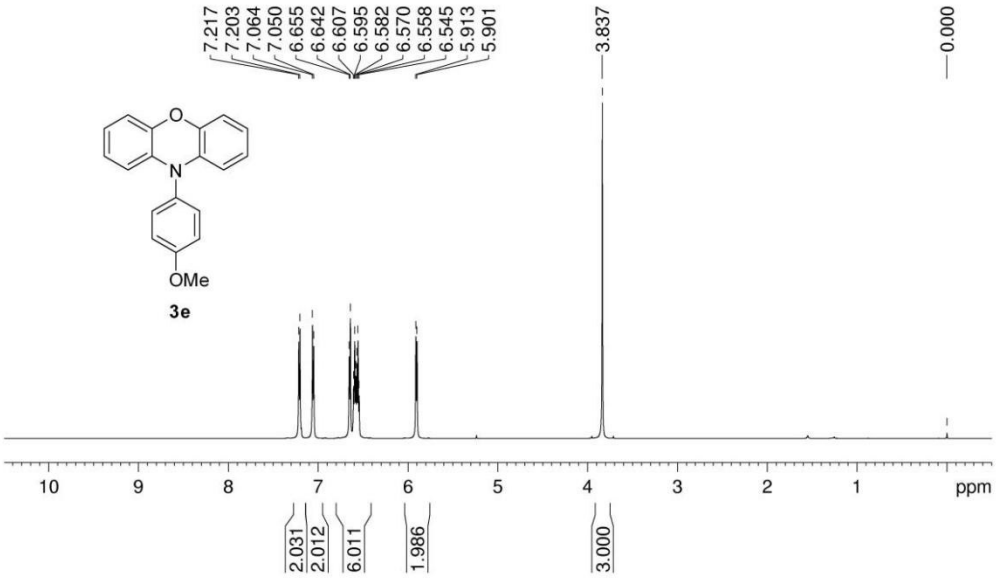
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

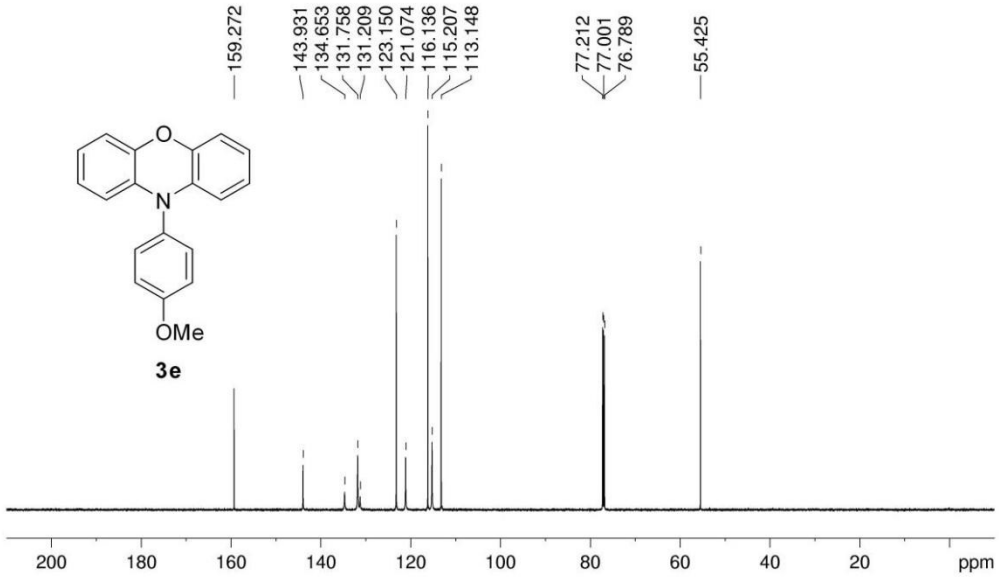




10-(4-Methoxyphenyl)-phenoxazine (3e):

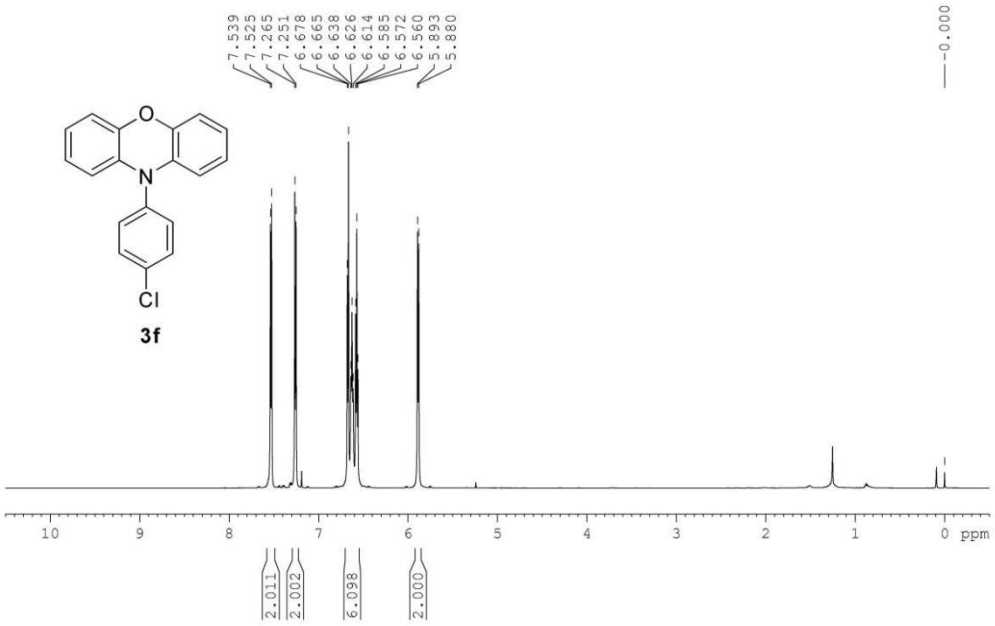
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

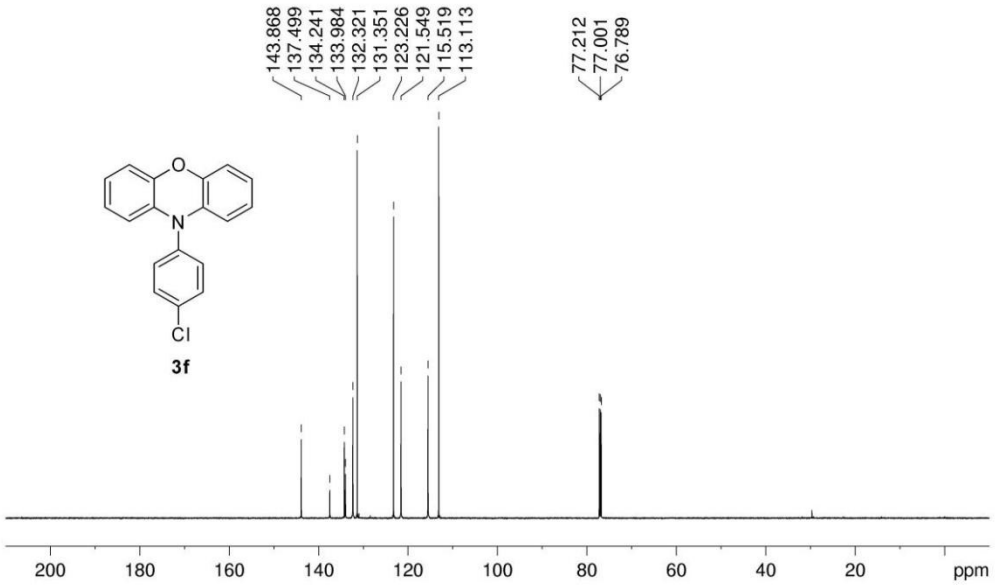




10-(4-Chlorophenyl)-phenoxazine (3f):

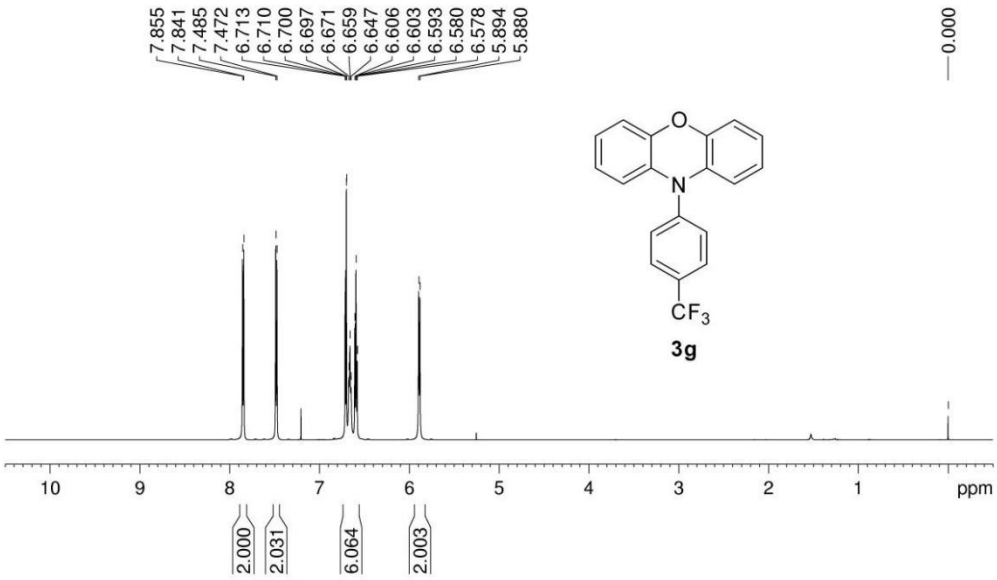
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

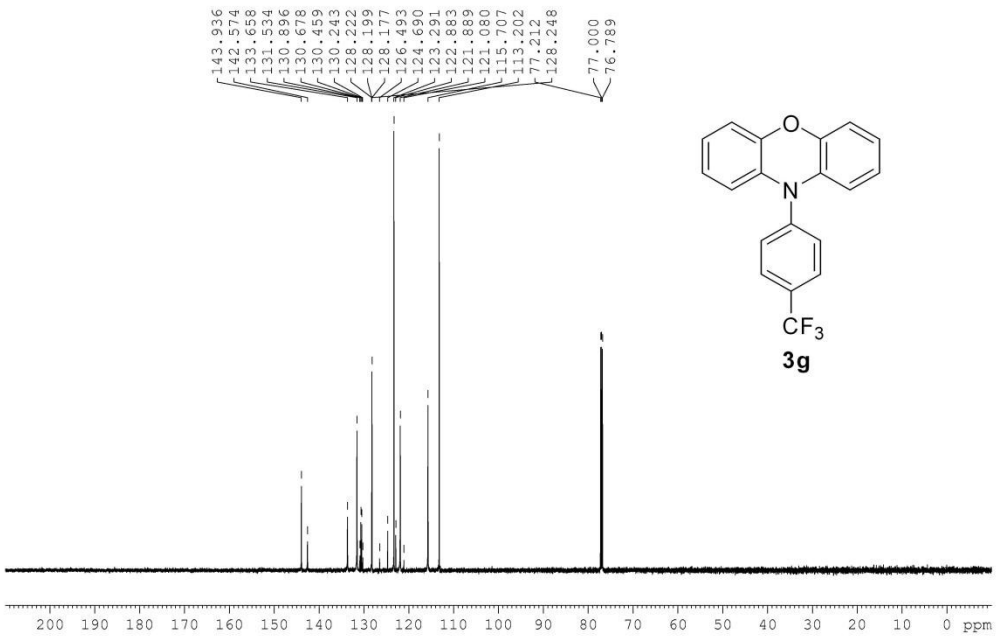




10-(4-Trifluoromethylphenyl)-phenoxazine (3g):

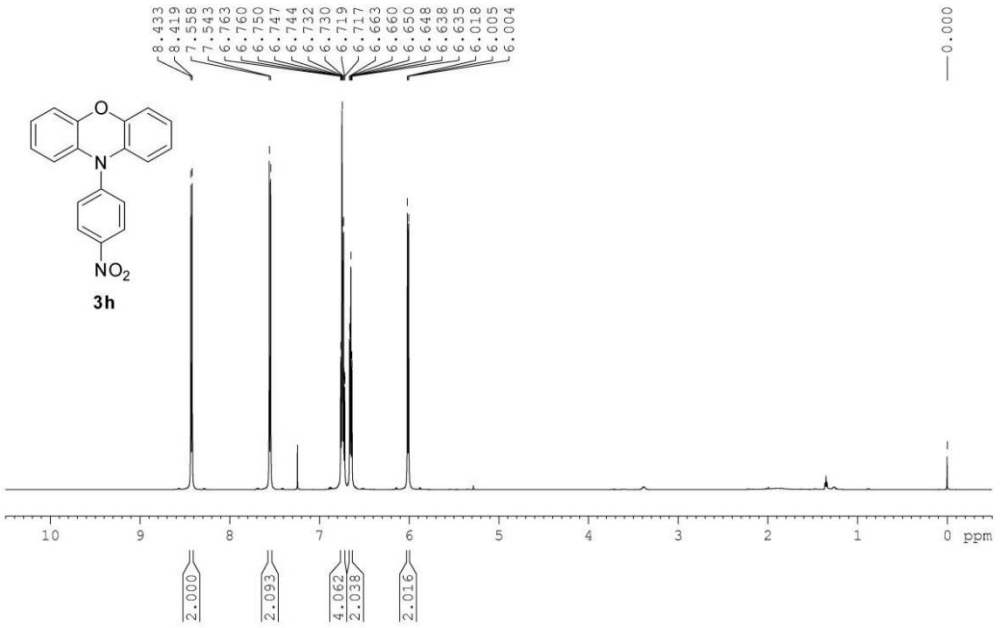
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

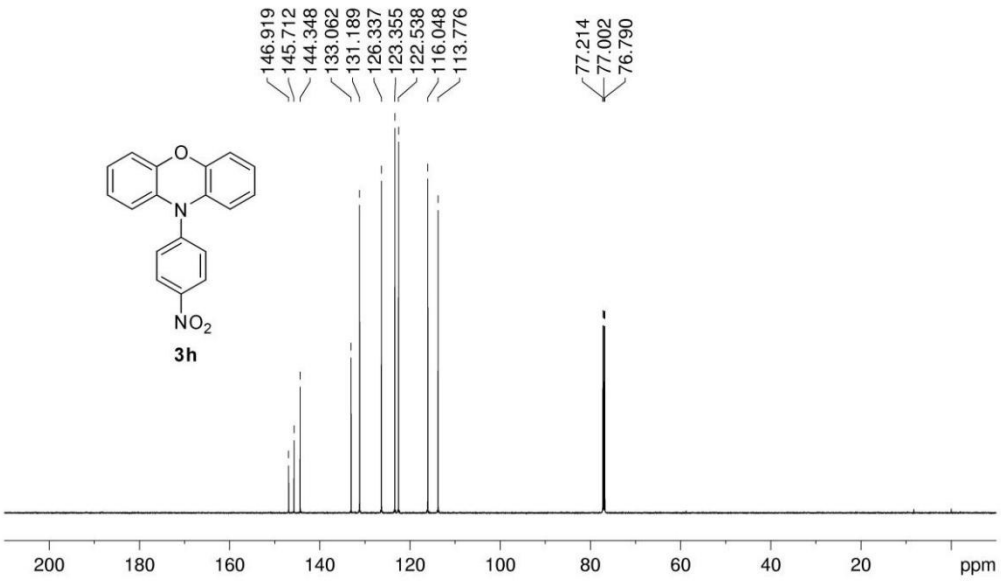




10-(4-Nitrophenyl)-phenoxazine (3h):

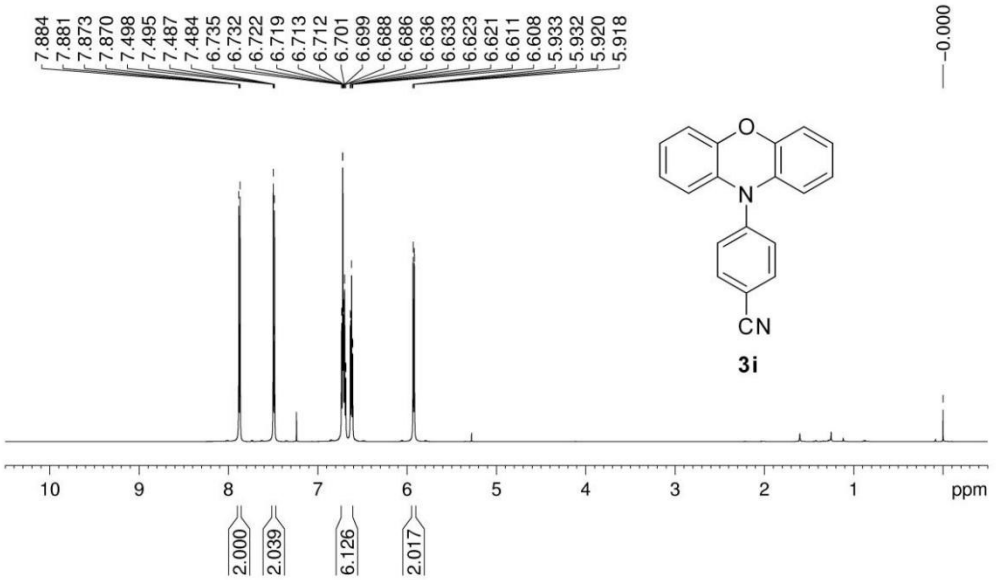
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

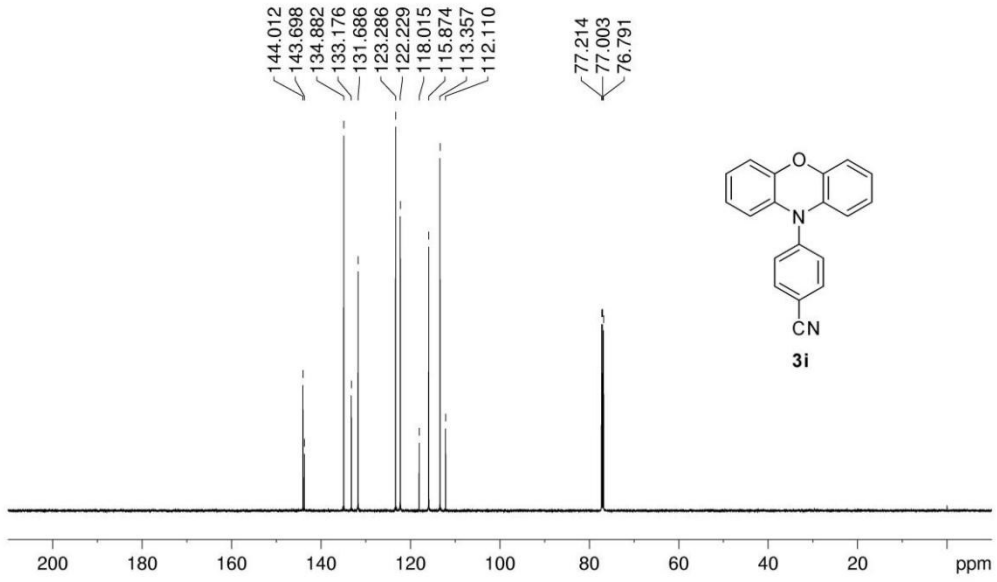




10-(4-Cyanophenyl)-phenoxazine (3i):

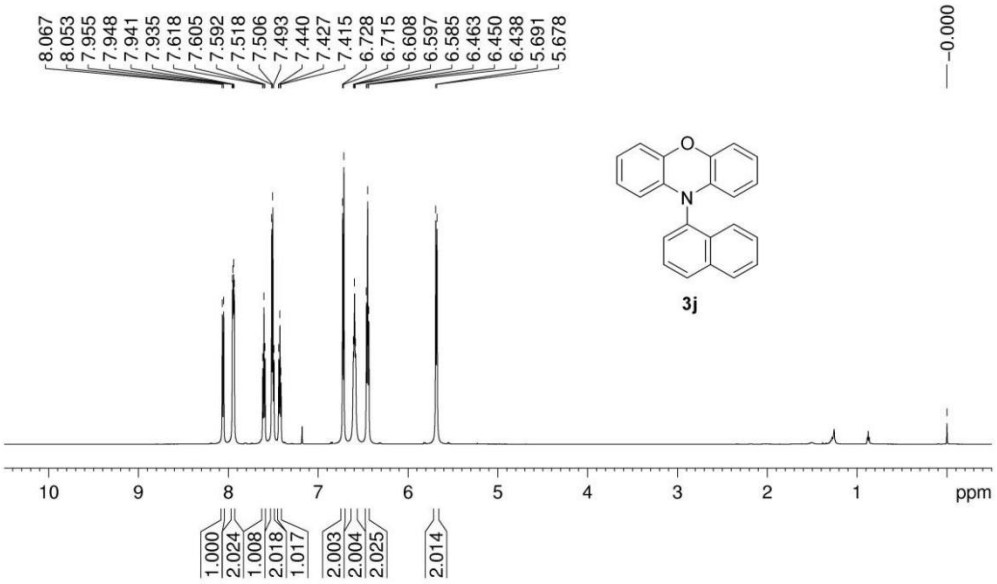
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

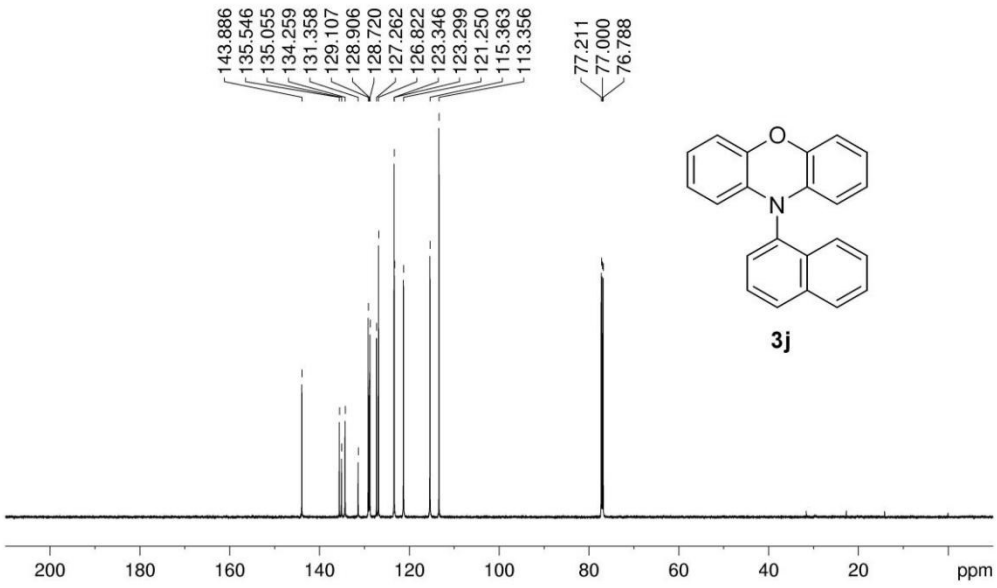




10-(1-Naphthyl)-phenoxazine (3j):

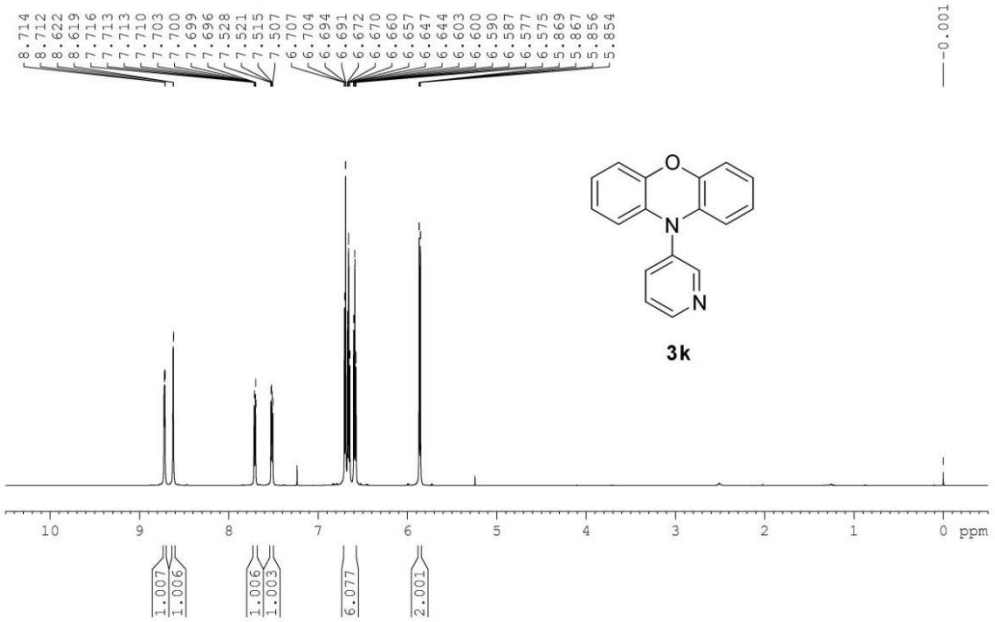
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

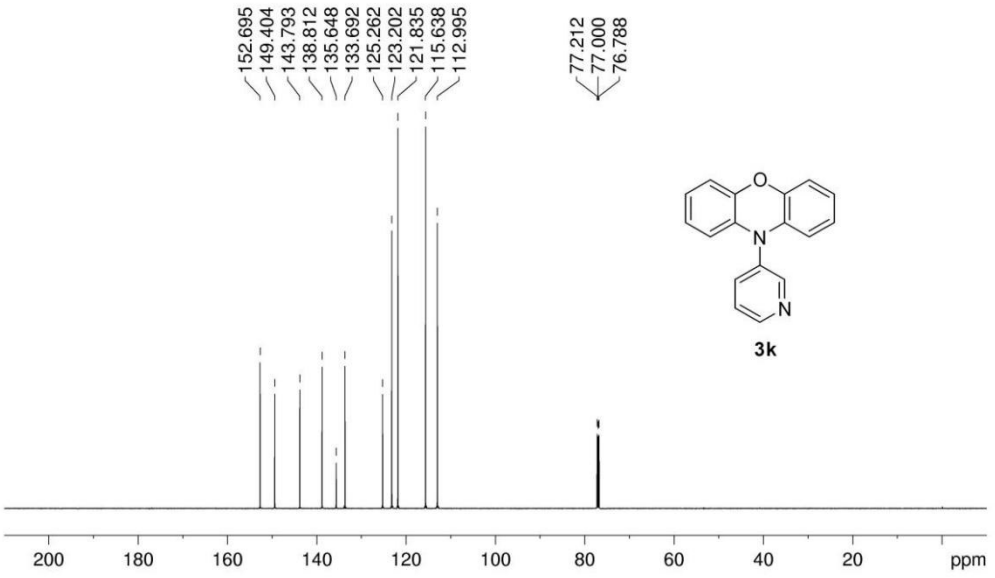




10-(3-Pyridyl)-phenoxazine (3k):

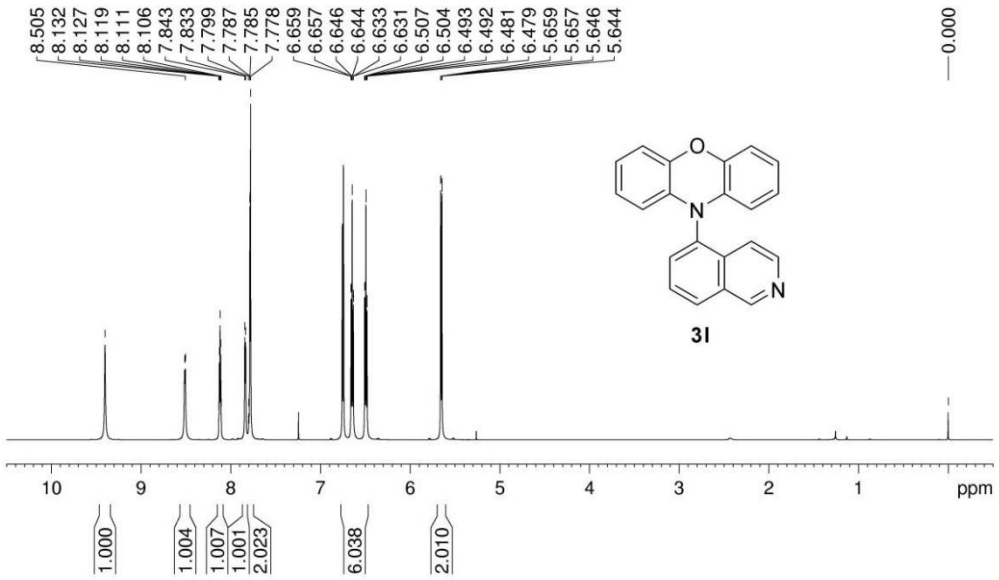
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

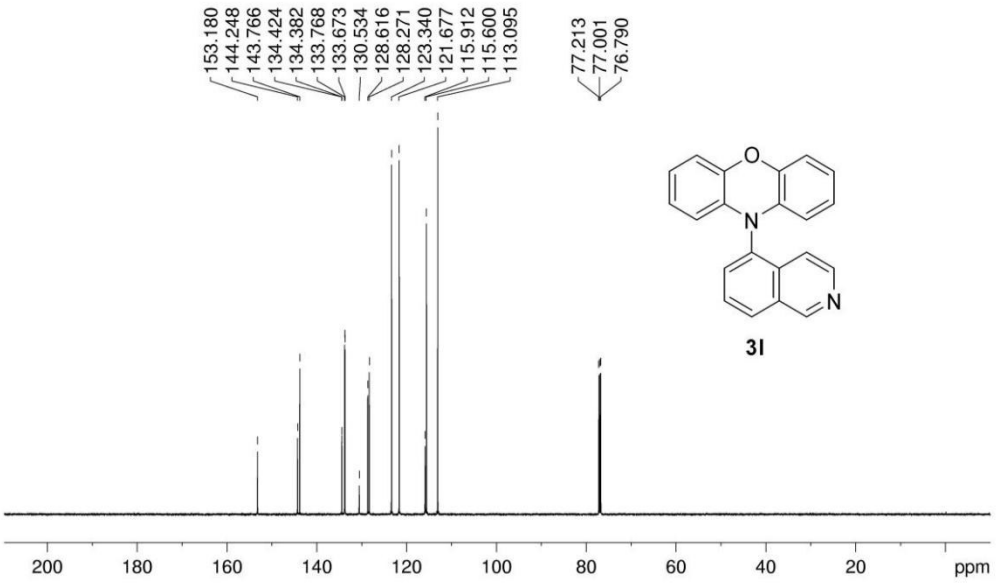




10-(5-Isoquinolinyl)-phenoxazine (3l):

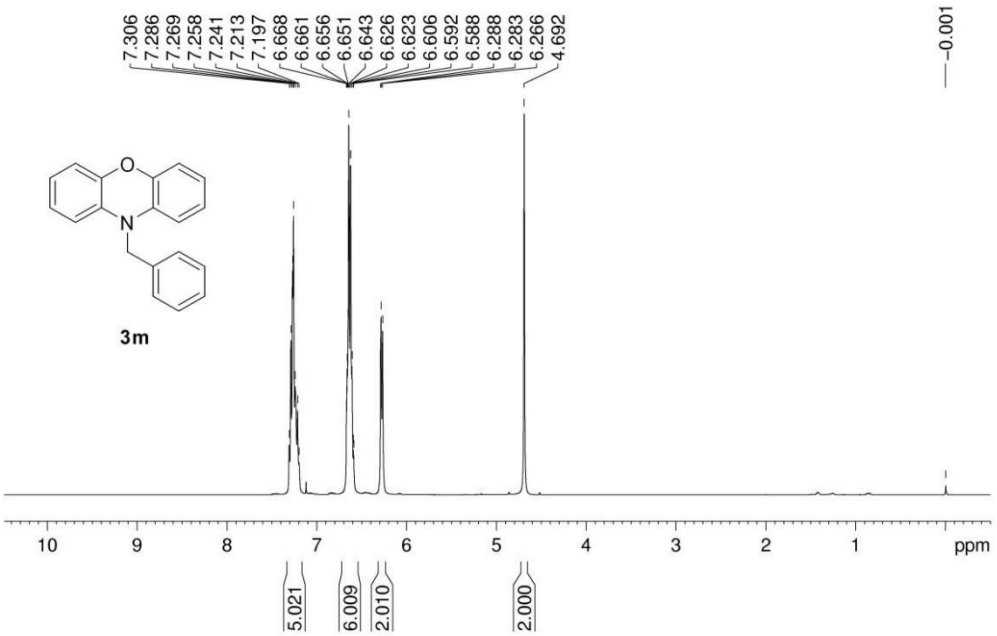
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

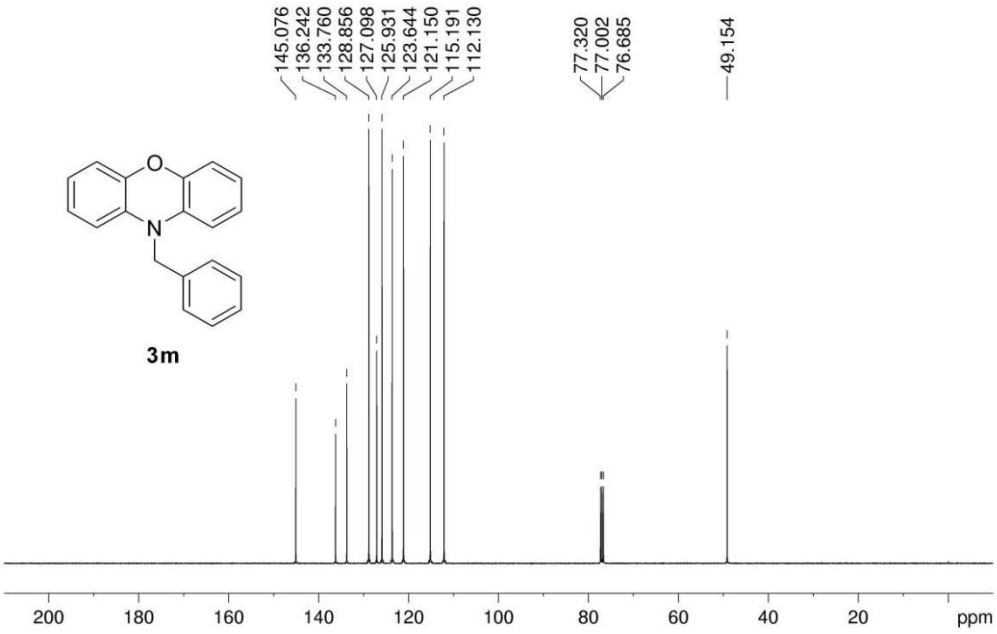




10-Benzyl-phenoxazine (3m):

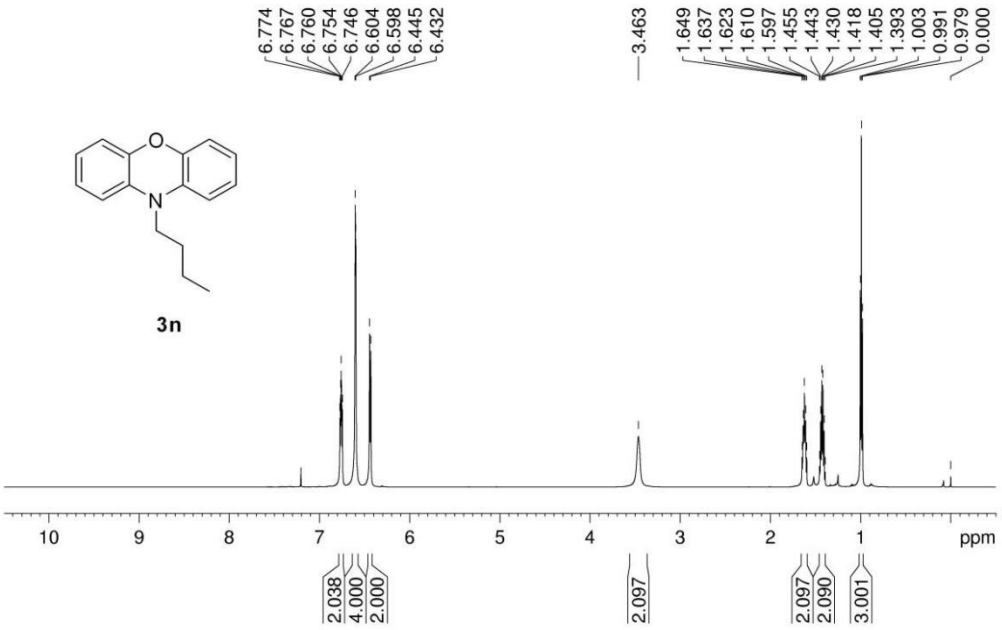
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

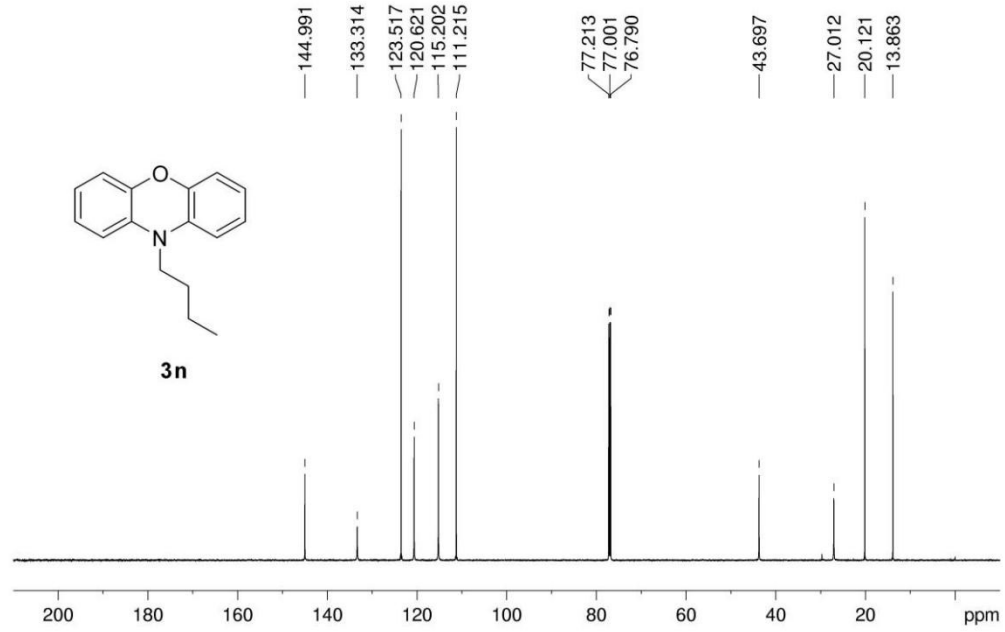




10-Butyl-phenoxazine (3n):

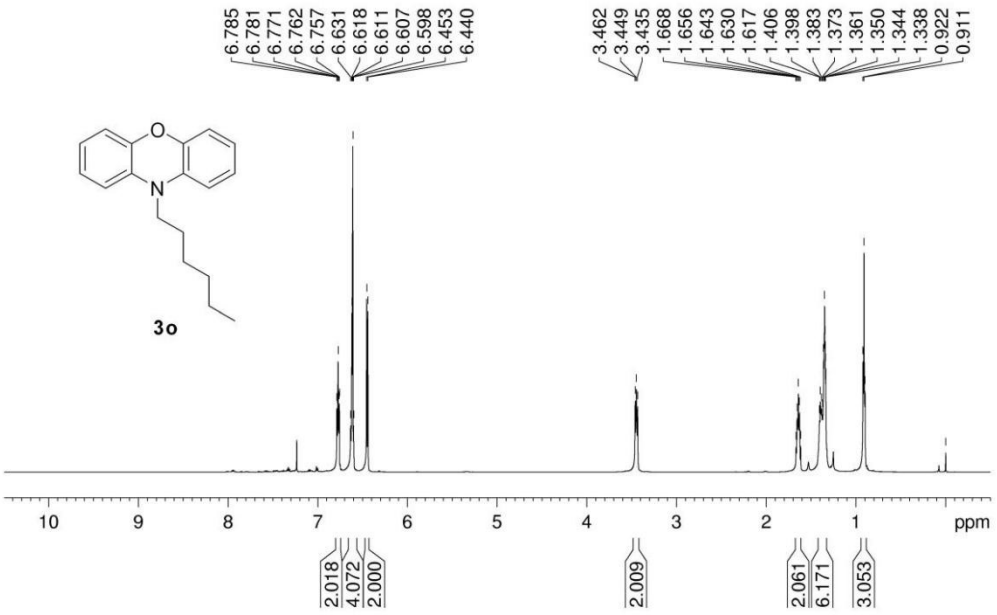
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

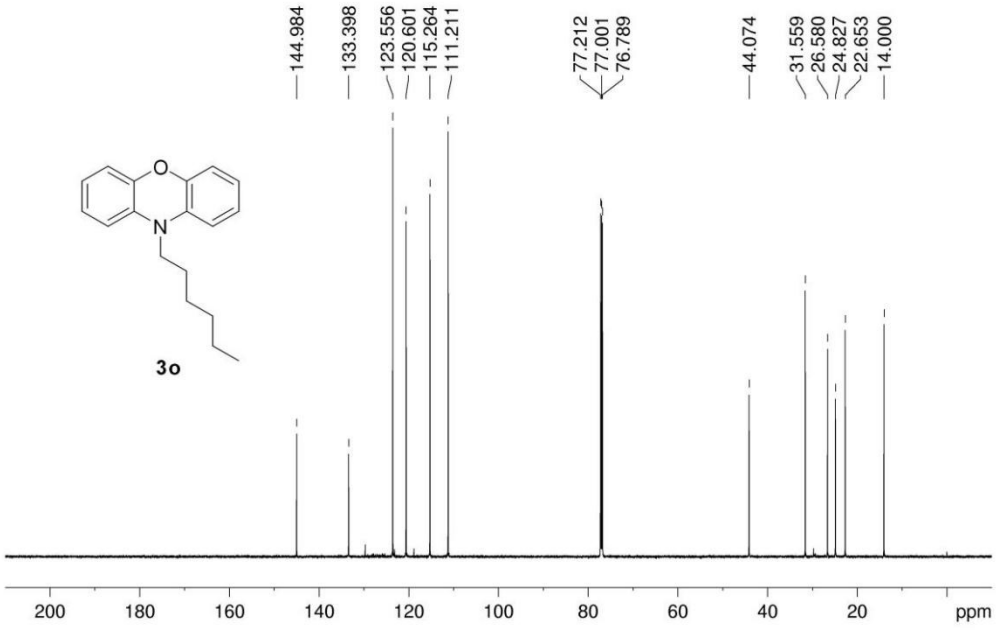




10-Hexyl-phenoxazine (3o):

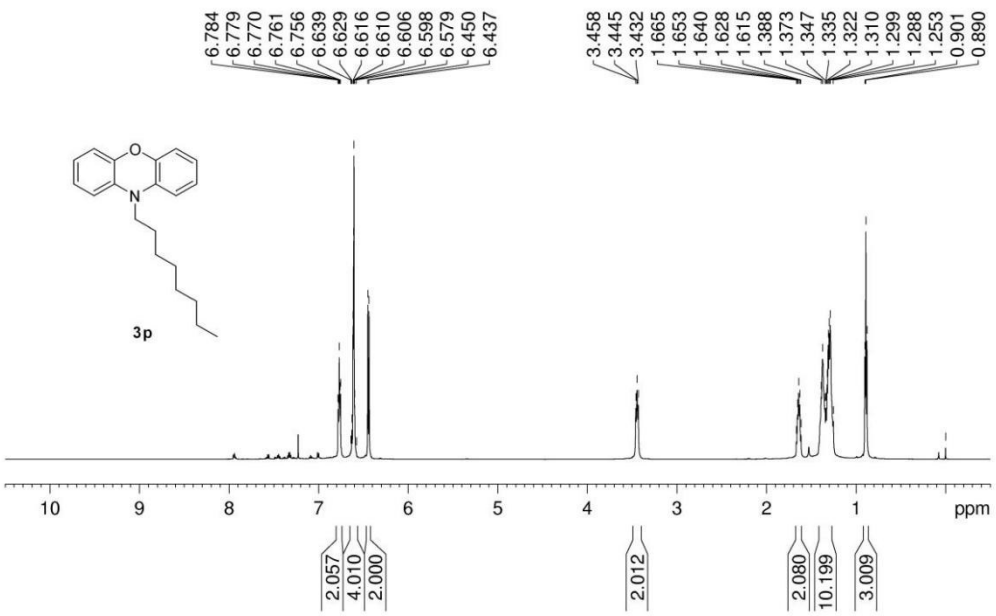
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

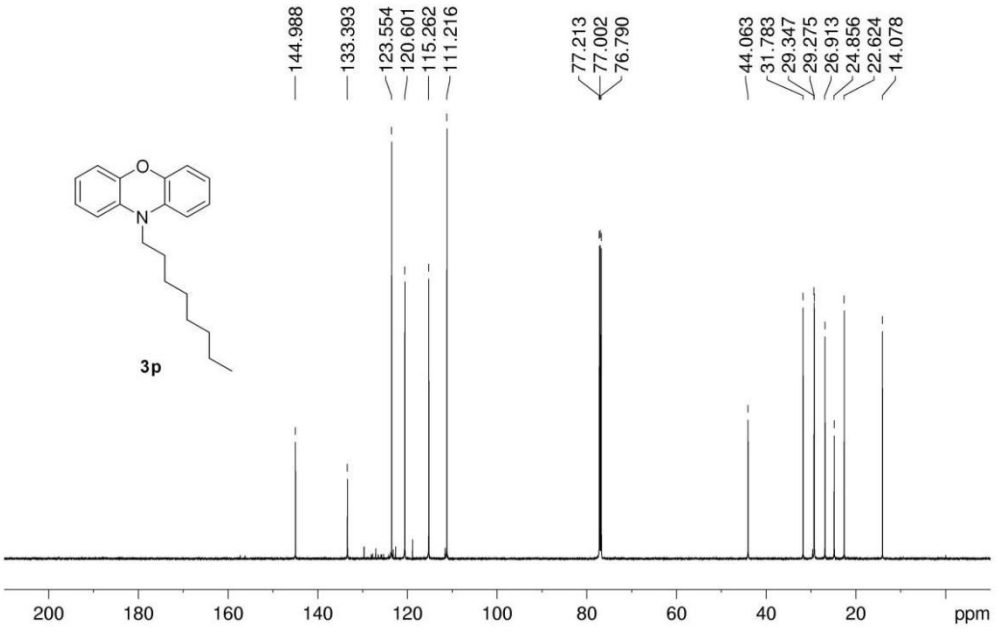




10-Octyl-phenoxazine (3p):

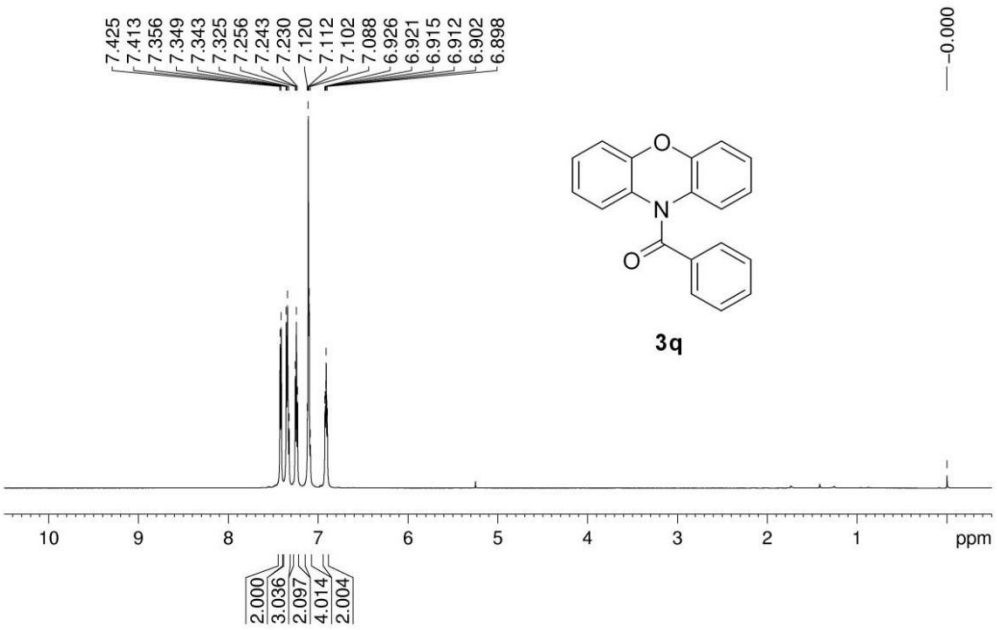
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

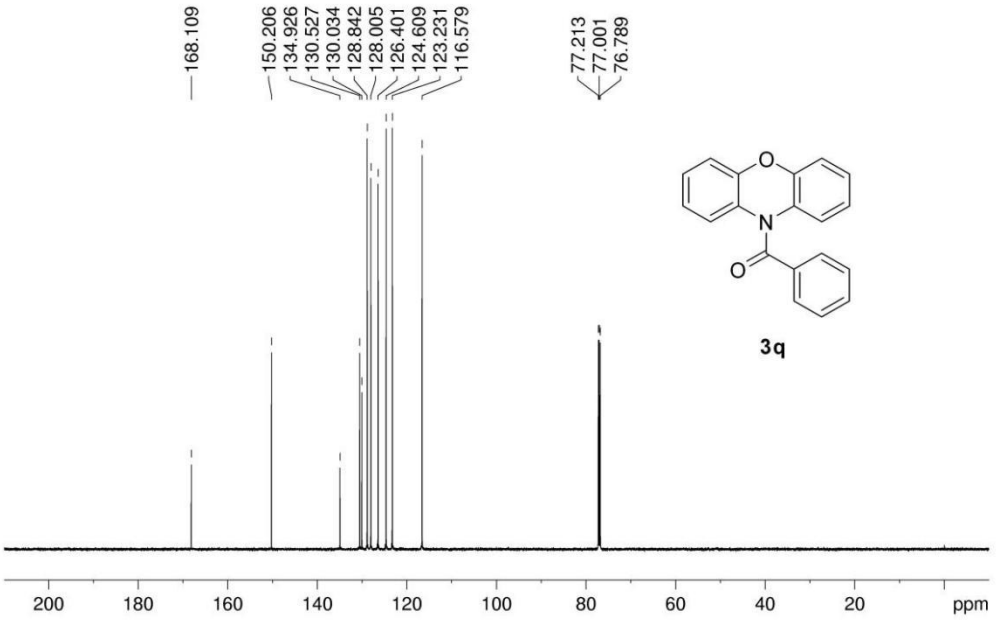




10-Benzoyl-phenoxazine (3q):

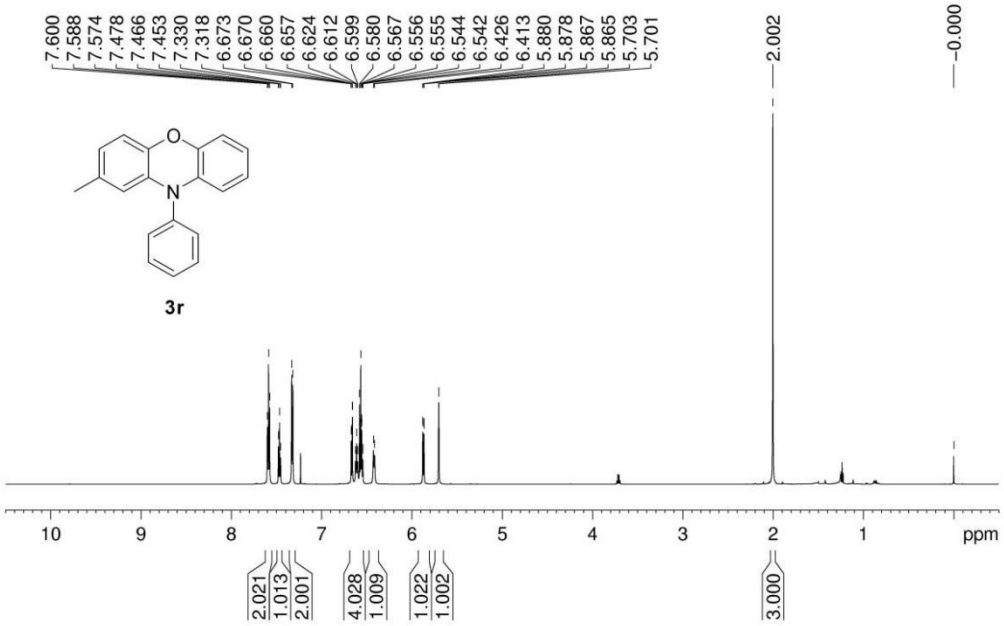
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

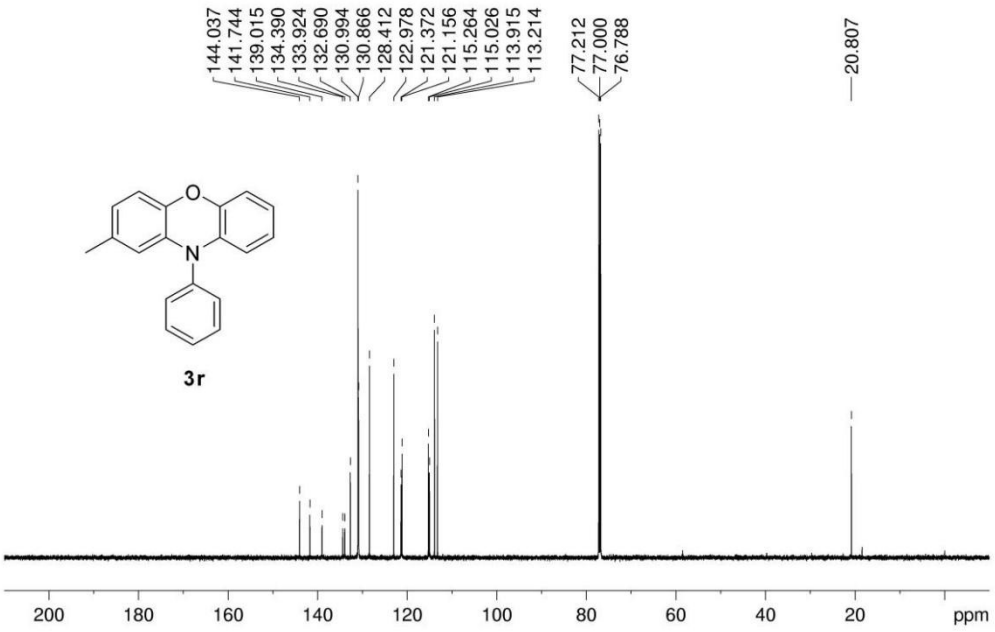




2-Methyl-10-phenyl-phenoxazine (3r):

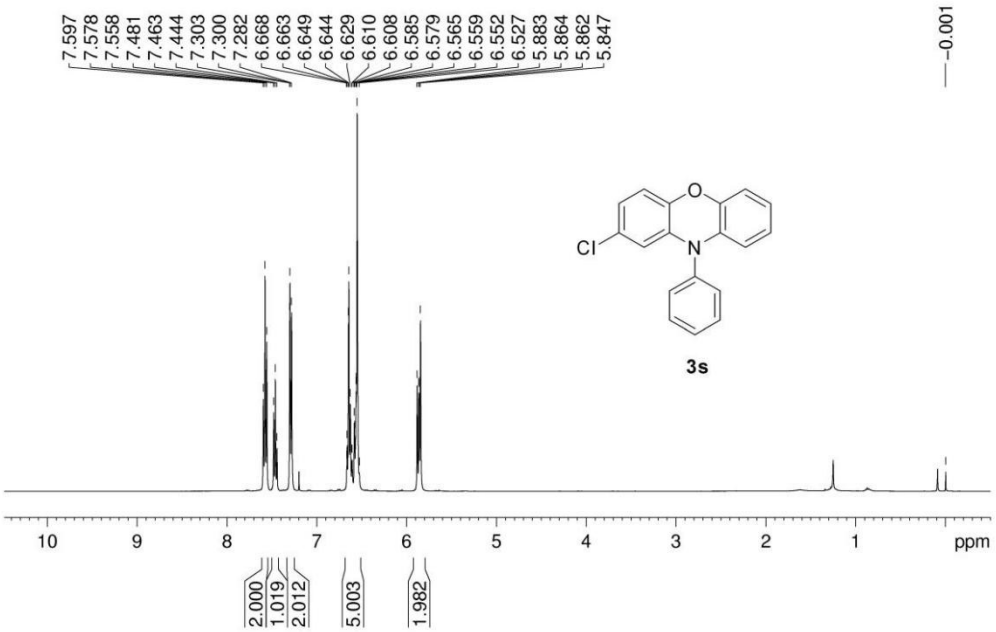
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

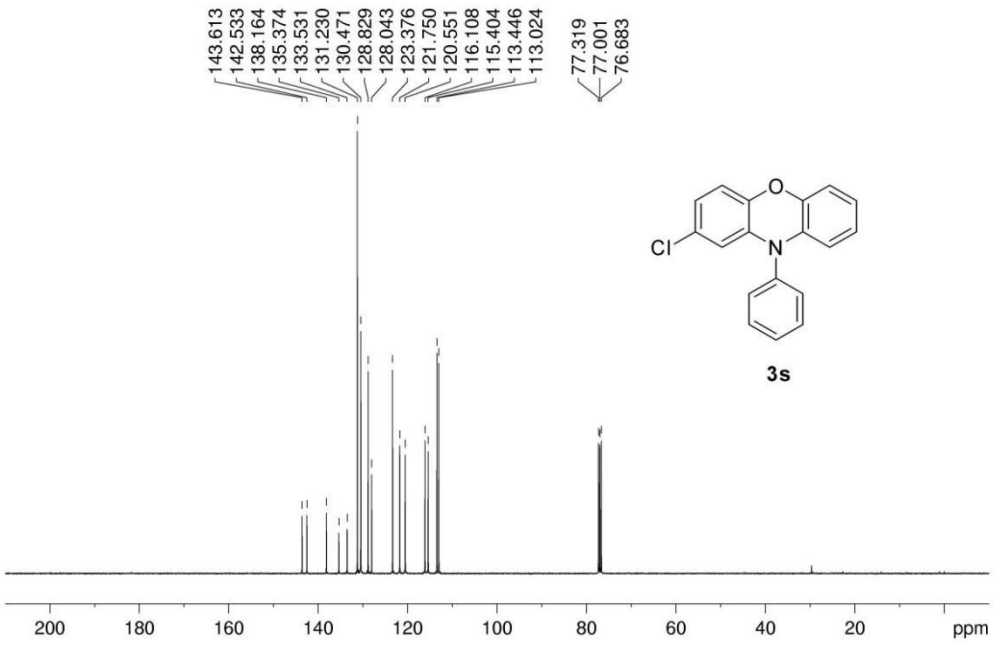




2-Chloro-10-phenyl-phenoxazine (3s):

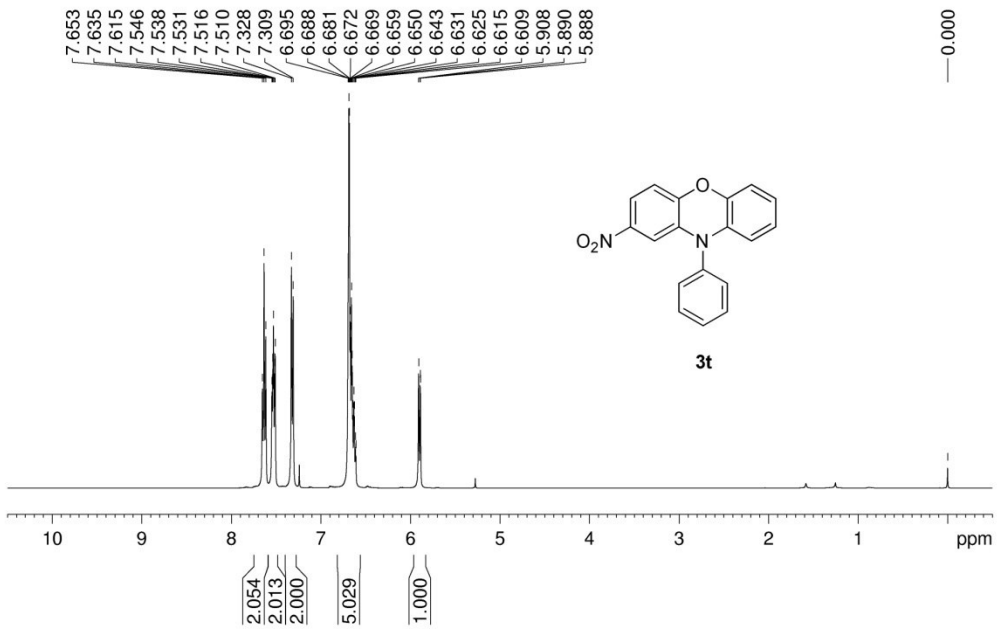
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

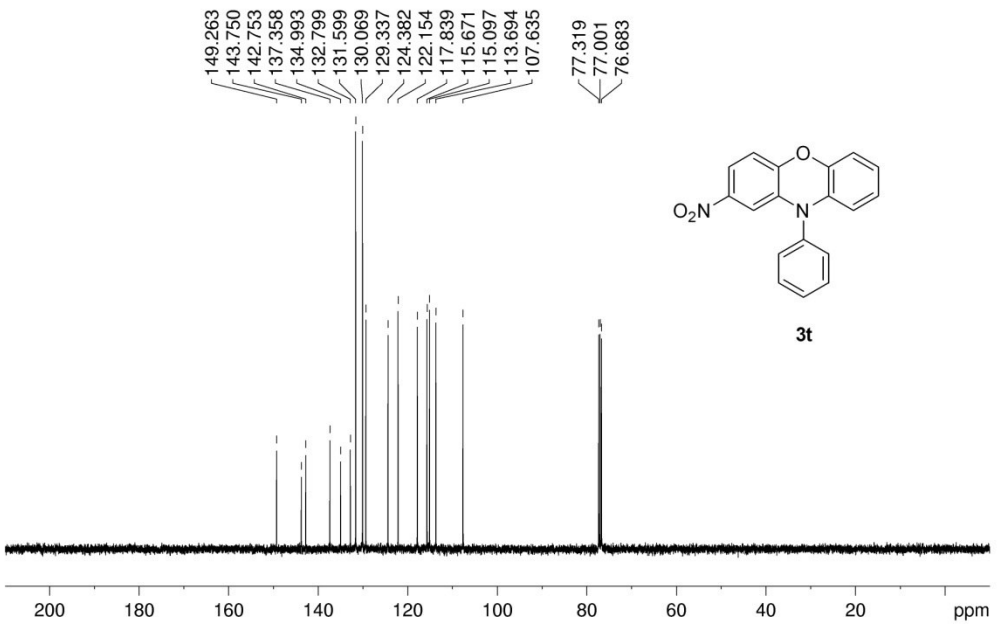




2-Nitro-10-phenyl-phenoxazine (3t):

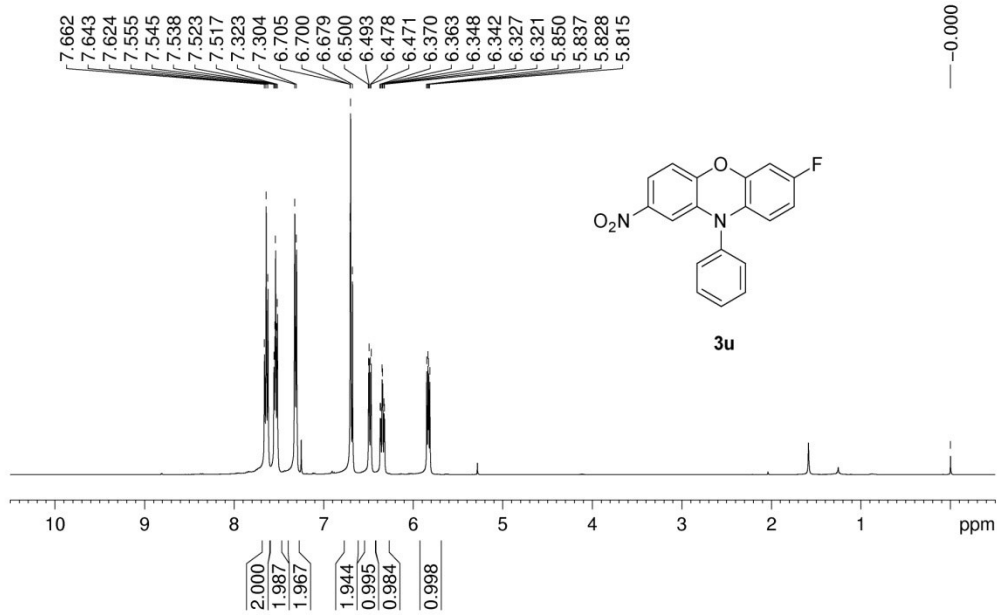
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

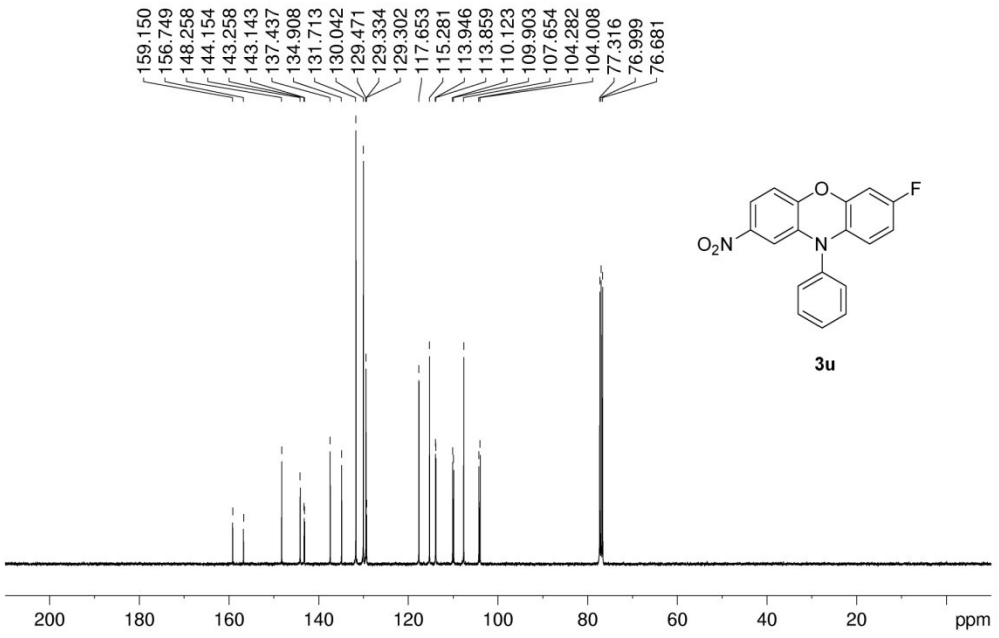




7-Fluoro-2-nitro-10-phenyl-phenoxazine (3u):

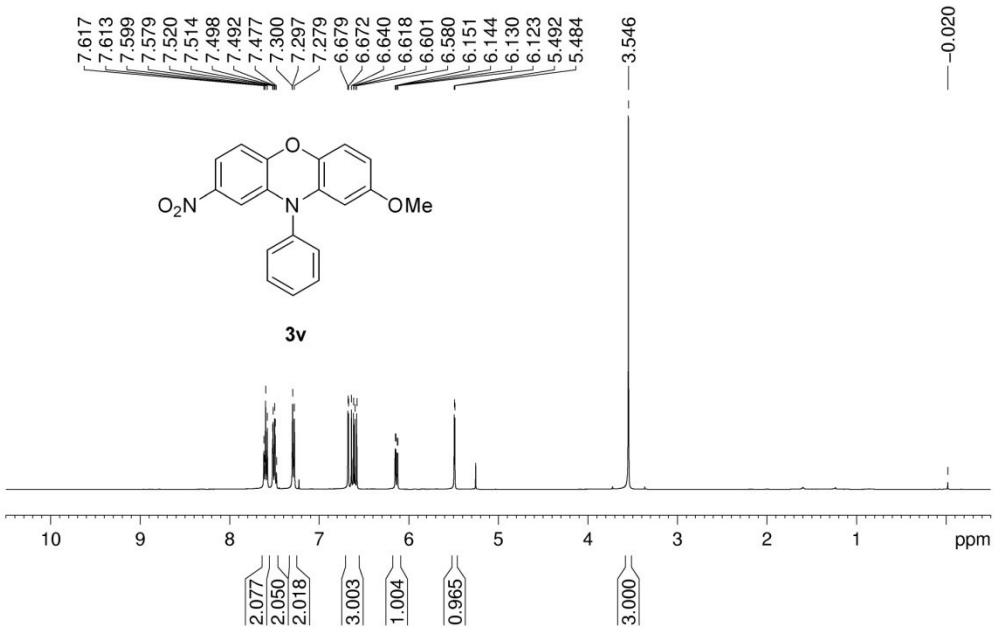
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

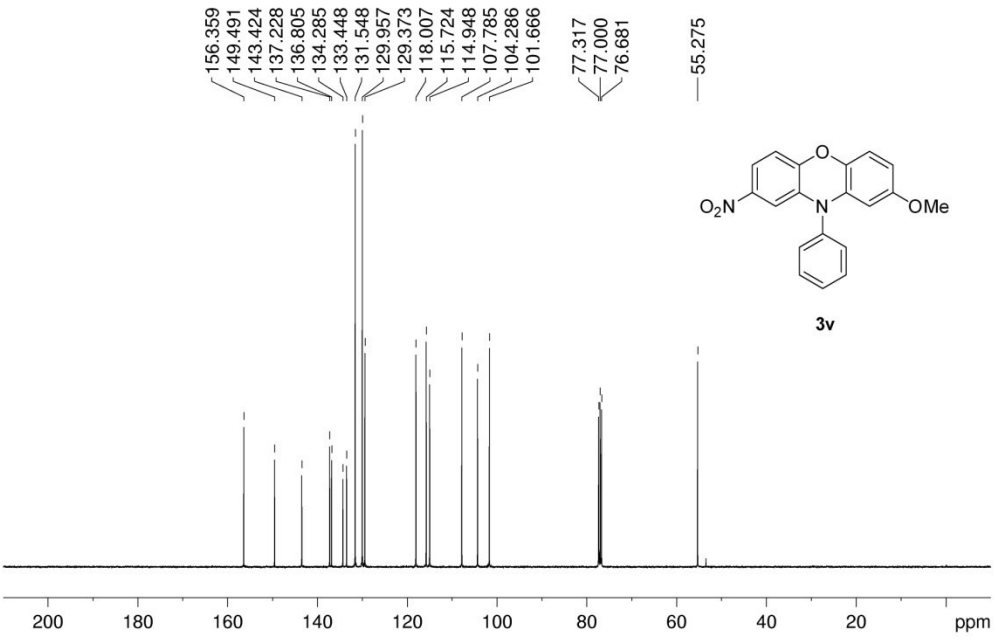




2-Methoxy-8-nitro-10-phenyl-phenoxazine (3v):

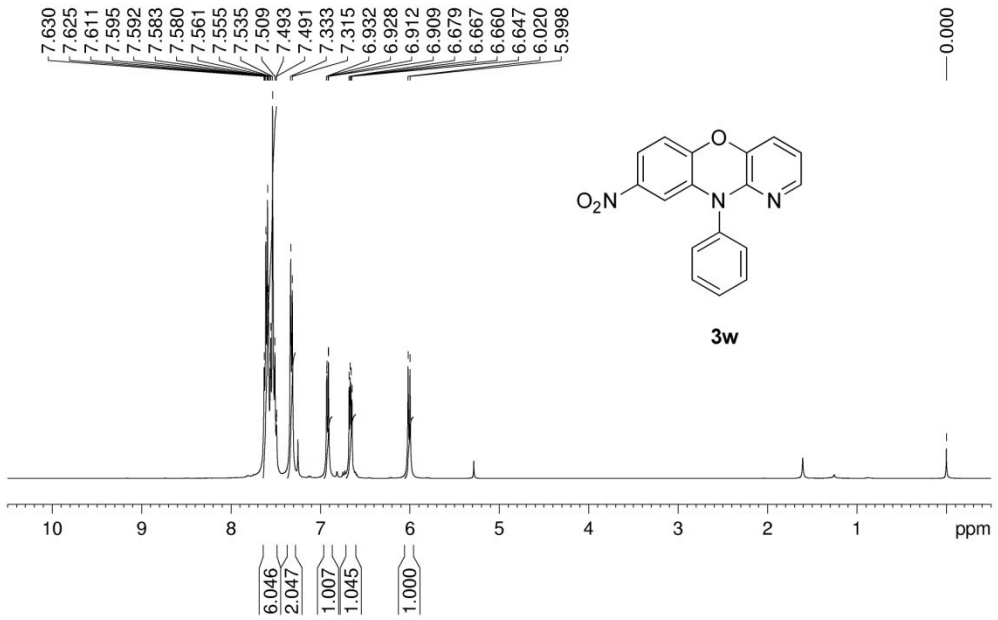
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

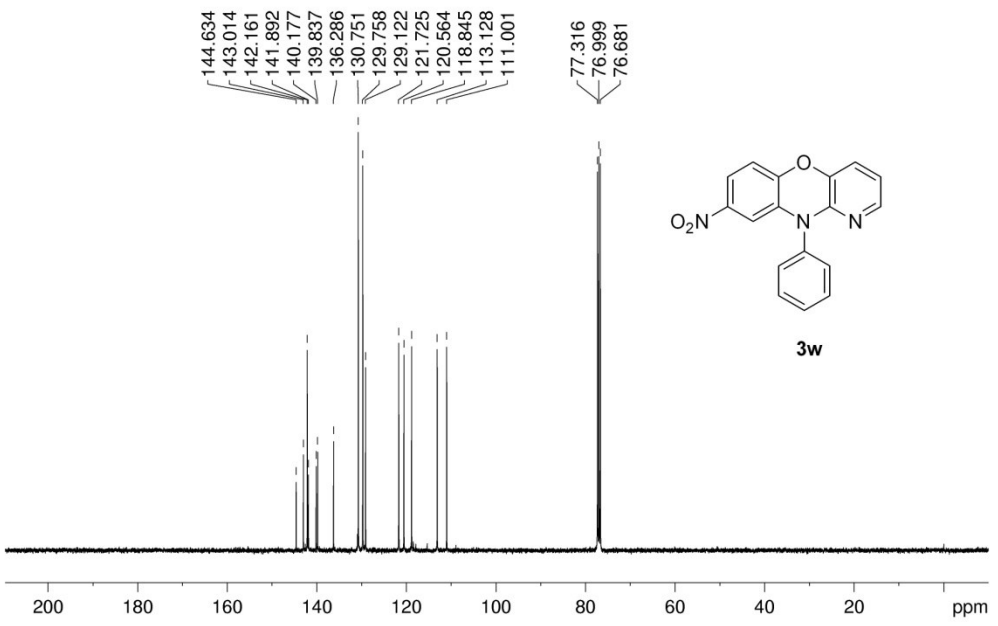




8-Nitro-10-phenyl-benzo[b]pyrido[2,3-e][1,4]oxazine (3w):

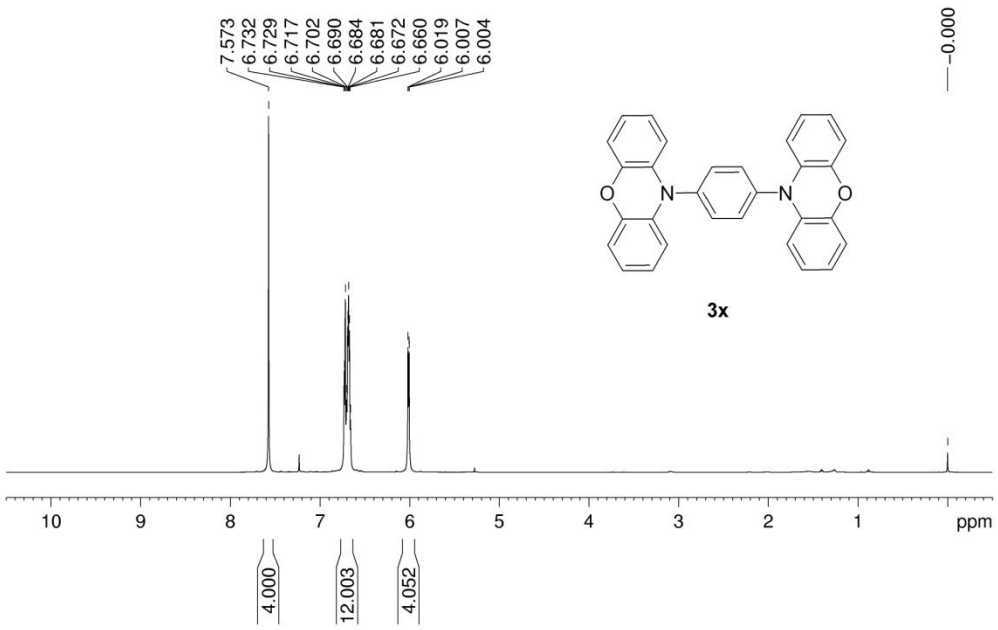
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

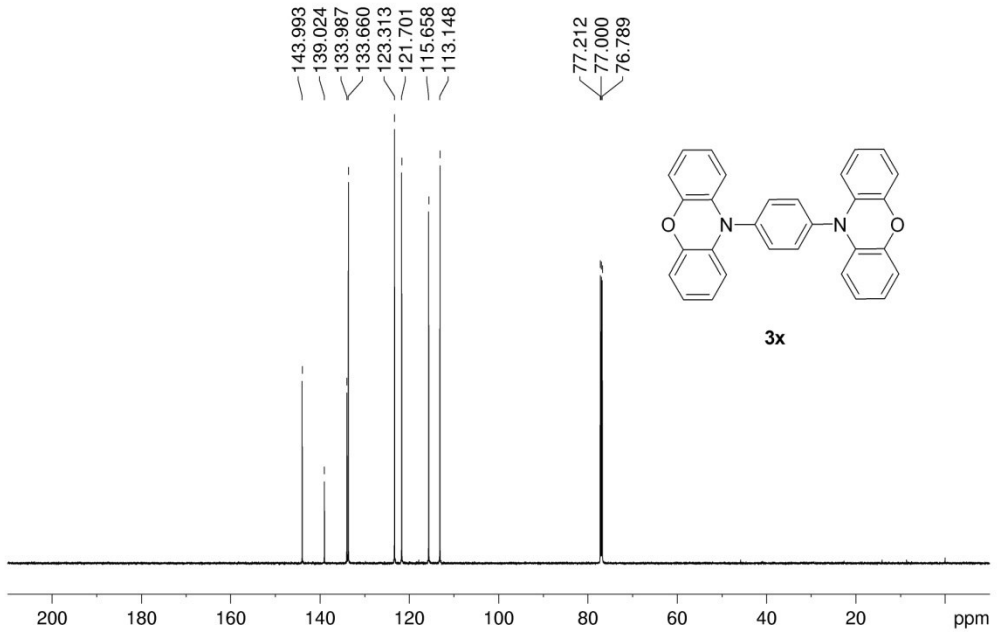




1,4-Bis(10-phenoxazinyl)-benzene (3x):

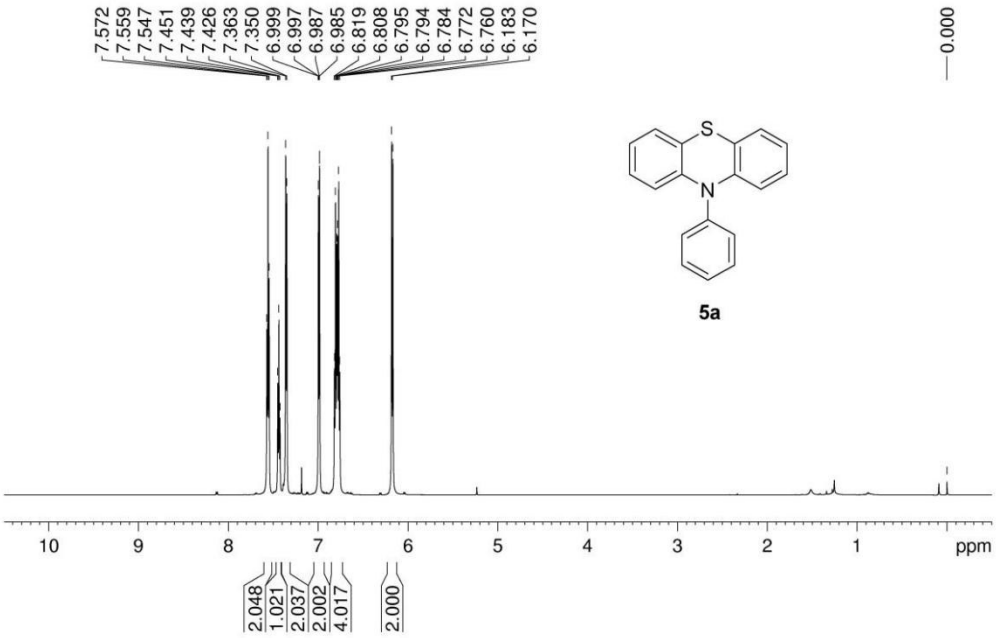
^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)

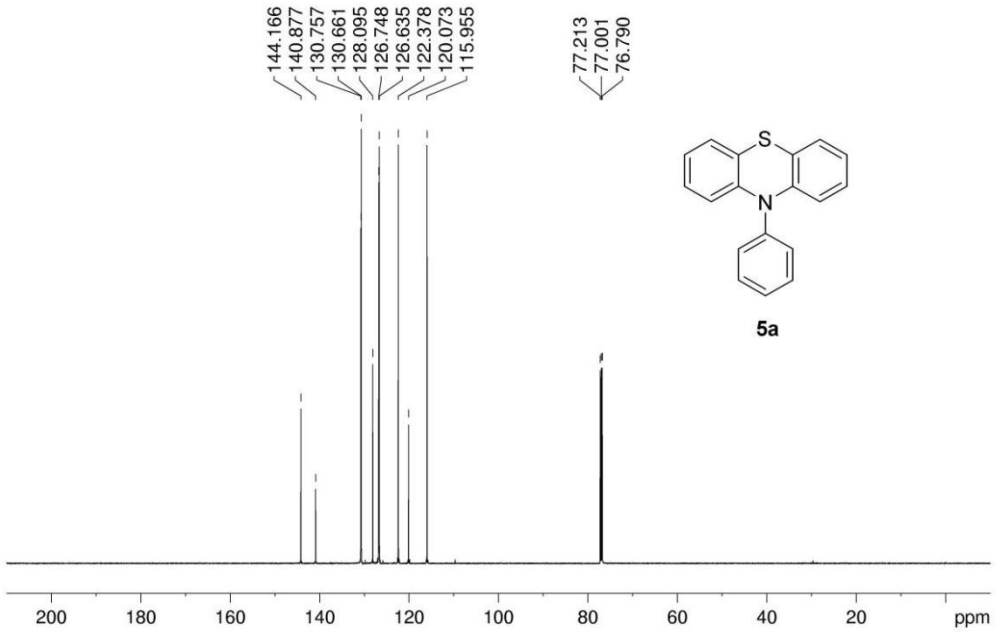




10-Phenyl-phenothiazine (5a):

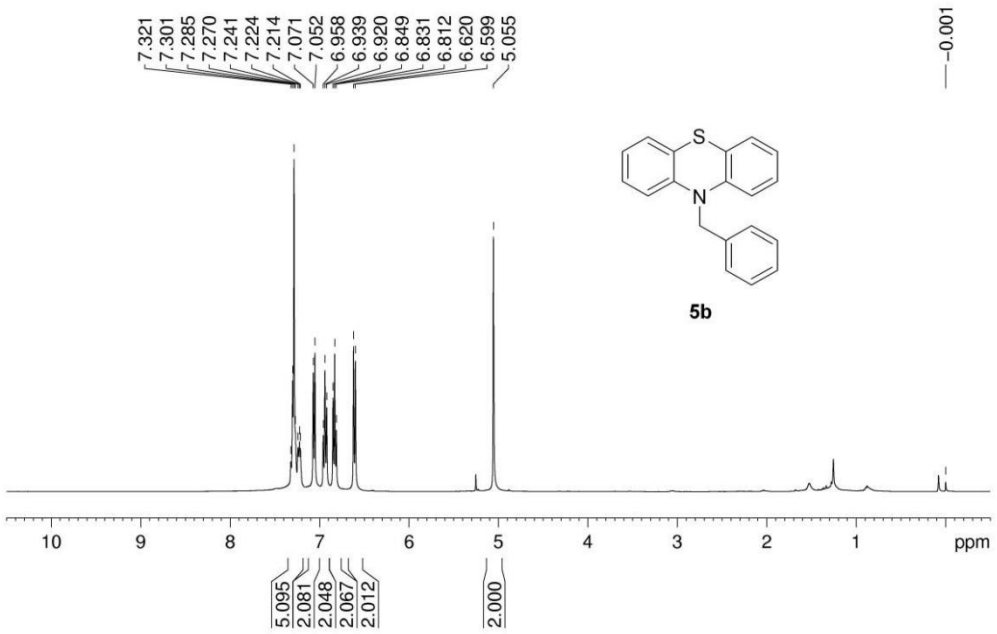
^{1}H NMR (600 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (150 MHz, $CDCl_3$, $SiMe_4$)

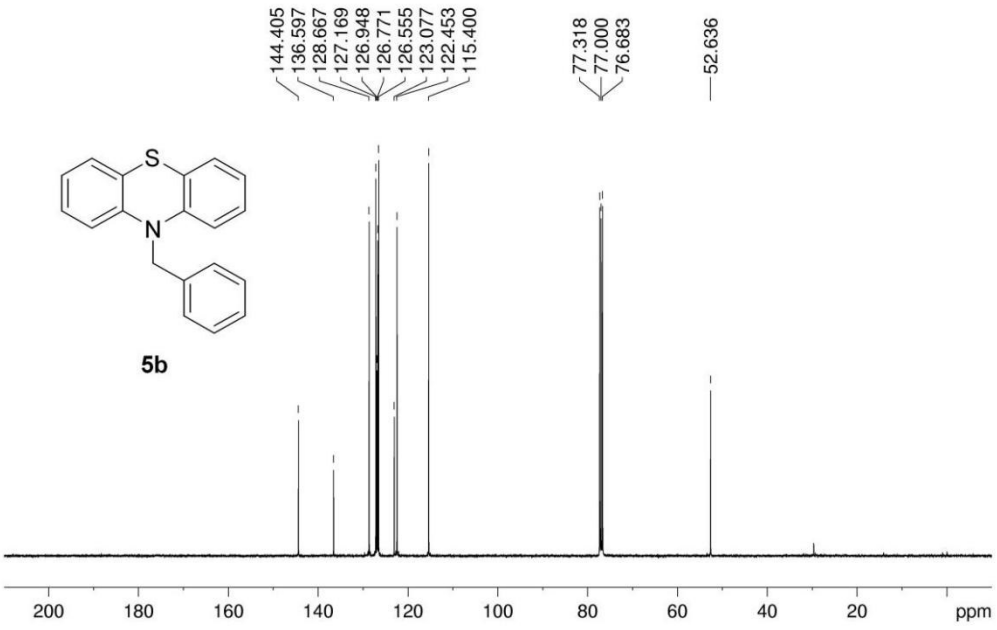




10-Benzyl-phenothiazine (5b):

^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)





1,4-Bis(10-phenothiazinyl)-benzene (5c):

^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$) & ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$)