Supporting Information

For

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

Lu Zhang, Xin Huang, Shan Zhen, Jing Zhao, Heng Li, Bingxin Yuan, and Guanyu Yang

a College of Chemistry and Molecular Engineering, Zhengzhou University, Henan, China 450001
b School of Pharmaceutical Sciences, Guangzhou Medical University, Guangdong, China 510182

*Corresponding author: Bingxin Yuan
E-mail: bx_yuan@163.com
List of Contents

1. Synthesis of Starting Materials and Characterization Data                        S3-S5
2. Synthesis of Target products and Characterization Data                       S5-S13
3. References                                                             S14
4. Scanned $^1$H NMR and $^{13}$C NMR of compounds **1d** to **1g**, **3a** to **3t**, and **5a** to **5c** S15-S45
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), Cul (1.5 g, 8.0 mmol), Fe(acac)\(_3\) (2.8 g, 8.0 mmol), K\(_3\)PO\(_4\) (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\(_2\)SO\(_4\), 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\(_2\)CO\(_3\) (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\(_2\)SO\(_4\), and concentrated on a rotovap. The residue was purified using column chromatography to give the product 1d-g.

**Bis(2-bromophenyl)ether (1a)**: Colorless liquid, isolated yield 85%; \(^1\)H NMR (400 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.59\text{-}7.57\) (m, 2H), 7.21-7.16 (m, 2H), 6.98-6.94 (m, 2H), 6.81-6.78 (m, 2H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 153.04, 133.73, 128.54, 124.96, 119.36, 114.04\). LRMS (EI): calculated for C\(_{12}\)H\(_8\)Br\(_2\)O, 328; observed 328.

**2-Bromo-1-(2-bromophenoxy)-4-methyl-benzene (1b)**: Colorless liquid, isolated yield 73%; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.59\text{-}7.56\) (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); \(^1^3\)C NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 153.60, 150.63, 135.25, 134.06, 133.69, 129.21, 128.44, 124.49, 119.88, 118.53, 114.12, 113.57, 20.37\). LRMS (EI): calculated for C\(_{13}\)H\(_{10}\)Br\(_2\)O, 342; observed 342.

**2-Bromo-1-(2-bromophenoxy)-4-chloro-benzene (1c)**: Colorless liquid, isolated yield 70%; \(^1\)H NMR (400 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.52\text{-}7.51\) (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); \(^1^3\)C NMR (100 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 152.74, 152.18, 133.97, 133.28, 132.75, 130.75, 127.25, 127.00, 125.95, 125.04, 124.45, 124.06, 119.98, 119.36, 118.85, 114.12, 113.57, 20.37\). LRMS (EI): calculated for C\(_{13}\)H\(_{10}\)Br\(_2\)Cl\(_2\)O, 354; observed 354.
2-Bromo-1-(2-bromophenoxy)-4-nitro-benzene (1d): Colorless liquid, isolated yield 90%; $^1$H NMR (400 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 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$_7$Br$_2$ClO, 362; observed 362.

2-Bromo-1-(2-bromo-5-fluorophenoxy)-4-nitrobenzene (1e): Colorless liquid, isolated yield 92%; $^1$H NMR (400 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 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$_6$Br$_2$FNO$_3$, 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$_4$): $\delta$ = 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$_4$): $\delta$ = 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$_9$Br$_2$NO$_4$, 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$_4$): $\delta$ = 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$_4$): $\delta$ = 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$_6$Br$_2$N$_2$O$_3$, 371.8745; observed 371.8748.

General Procedure 3: Synthesis of Starting Materials (Compounds 4).
Following a slightly modified literature procedure, Pd(OAc)$_2$ (11 mg, 0.05 mmol), DPEphos (54 mg, 0.10 mmol), and NaO$\text{t}$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$_2$Cl$_2$, washed with water, brine, dried with Na$_2$SO$_4$, and purified using column chromatography to give the product 4.

\[ \text{Bis-(2-bromophenyl)ether (4)} \] (white solid, isolated yield 90%); mp 71-72 °C; $^1$H NMR (600 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 135.51, 133.34, 132.28, 128.66, 128.05, 125.65. LRMS (EI): calculated for C$_{12}$H$_8$Br$_2$S, 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$\text{t}$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$_2$Cl$_2$, washed with water, brine. The organic phase was collected and dried over Na$_2$SO$_4$. 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 °C for 24 h of compounds 3n-p. Pd$_2$(dba)$_3$ (5 mol%), Xantphos (10 mol%), Cs$_2$CO$_3$ (3.0 equiv.) and dioxane (2 mL) at 100 °C for 24 h of compound 3q.)

General Procedure 2: Synthesis of 1,4-Bis(10-phenoxazinyl)benzene (Compound 3t).
Bis(2-bromophenyl)sulfide 4 (0.2 mmol) and phenylamine 2 (0.22 mmol), NaO$\text{t}$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$_2$Cl$_2$, washed with water, brine. The organic phase was collected and dried over Na$_2$SO$_4$. 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$\text{t}$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 CH₂Cl₂, washed with water, brine. The organic phase was collected and dried over Na₂SO₄. 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'Bu (3.6 mmol), Pd₂(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 CH₂Cl₂, washed with water, brine. The organic phase was collected and dried over Na₂SO₄. The solvent was removed on a rotovap and the residue was purified by column chromatography to give the product 5c.

**10-Phenyl-phenoxazine (3a):** Using procedure 1, white solid, isolated yield 99%; mp 142-143 °C; ¹H NMR (600 MHz, CDCl₃, SiMe₄): 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); ¹³C NMR (150 MHz, CDCl₃, SiMe₄): 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 C₁₈H₁₃NO, 259; observed 259.

**10-(2-Methylphenyl)-phenoxazine (3b):** Using procedure 1, white solid, isolated yield 83%; mp 174-175 °C; ¹H NMR (600 MHz, CDCl₃, SiMe₄): 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); ¹³C NMR (150 MHz, CDCl₃, SiMe₄): 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 C₁₉H₁₅NO, 273.1154; observed 273.1152.

**10-(3-Methylphenyl)-phenoxazine (3c):** Using procedure 1, white solid, isolated yield 85%; mp 123-125 °C; ¹H NMR (600 MHz, CDCl₃, SiMe₄): 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); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 143.86, 141.12, 138.79, 134.39, 131.06, 130.70, 129.16, 127.54, 123.13, 121.09, 115.26, 113.21, 21.29\). HRMS (ESI): calculated for C\(_{19}\)H\(_{15}\)NO, 273.1154; observed 273.1151.

10-(4-Methylphenyl)-phenoxazine (3d): Using procedure 1, white solid, isolated yield 87\%; mp 122-124 °C; \(^1\text{H}\) NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.35\) (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); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 143.92, 138.31, 136.14, 134.52, 131.63, 130.40, 123.15, 121.06, 115.26, 113.18, 21.21\). HRMS (ESI): calculated for C\(_{19}\)H\(_{15}\)NO, 273.1154; observed 273.1151.

10-(4-Methoxyphenyl)-phenoxazine (3e): Using procedure 1, white solid, isolated yield 98\%; mp 174-175 °C; \(^1\text{H}\) NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.21\) (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); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 159.27, 143.93, 134.65, 131.76, 131.21, 123.15, 121.07, 116.14, 115.21, 113.15, 55.43\). LRMS (EI): calculated for C\(_{19}\)H\(_{15}\)NO\(_2\), 289; observed 289.

10-(4-Chlorophenyl)-phenoxazine (3f): Using procedure 1, white solid, isolated yield 69\%; mp 177-178 °C; \(^1\text{H}\) NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.53\) (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); \(^{13}\text{C}\) NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 143.87, 137.50, 134.24, 133.98, 132.32, 131.35, 123.23, 121.55, 115.52, 113.11\). LRMS (EI): calculated for C\(_{18}\)H\(_{12}\)ClNO, 293; observed 293.
10-(4-Trifluoromethylphenyl)-phenoxazine (3g): Using procedure 1, light yellow solid, isolated yield 68%; mp 195-196 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.85\) (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\(_4\)): \(\delta = 143.94, 142.57, 133.66, 131.53, 130.57\) (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\(_3\)NO, 327; observed 327.

10-(4-Nitrophenyl)-phenoxazine (3h): Using procedure 1, red solid, isolated yield 93%; mp 197-198 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 8.43\) (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\(_4\)): \(\delta = 146.92, 145.71, 144.35, 133.06, 131.19, 126.34, 123.36, 122.54, 116.05, 113.78\). LRMS (EI): calculated for C\(_{18}\)H\(_{12}\)N\(_2\)O\(_3\), 304; observed 304.

10-(4-Cyanophenyl)-phenoxazine (3i): Using procedure 1, yellow solid, isolated yield 56%; mp 160-161 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.88-7.87\) (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\(_4\)): \(\delta = 144.01, 143.70, 134.88, 133.18, 131.69, 123.27, 122.23, 118.02, 115.87, 113.36, 112.11\). HRMS (ESI): calculated for C\(_{19}\)H\(_{12}\)N\(_2\)O, 284.0950; observed 284.0945.

10-(1-Naphthyl)-phenoxazine (3j): Using procedure 1, yellowish solid, isolated yield 90%; mp 198-199 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 8.06\) (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, \(J = 7.98\) Hz, 2H).
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\(_4\)): \(\delta = 143.89, 135.55,
135.06, 134.26, 131.36, 129.11, 128.91, 128.72, 127.26, 126.82\) (2C), 123.35, 123.30,
121.25, 115.36, 113.36. HRMS (ESI): calculated for C\(_{22}\)H\(_{18}\)NO, 309.1154; observed
309.1155.

![10-(3-Pyridyl)-phenoxazine (3k)]

10-(3-Pyridyl)-phenoxazine (3k): Using procedure 1, white solid,
isolated yield 91%; mp 153-155 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 8.72-8.71\)
(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\(_4\)): \(\delta = 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\(_2\)O, 260.0950; observed 260.0957.

![10-(5-Isoquinolinyl)-phenoxazine (3l)]

10-(5-Isoquinolinyl)-phenoxazine (3l): Using procedure 1, yellow solid,
isolated yield 86%; mp 219-221 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 9.40\) (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\(_4\)): \(\delta =
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\(_2\)O,
311.1179; observed 311.1182.

![10-Benzyl-phenoxazine (3m)]

10-Benzyl-phenoxazine (3m): Using procedure 1, white solid, isolated
yield 72%; mp 125-126 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.31-7.20\) (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\(_4\)): \(\delta =
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)]

10-Butyl-phenoxazine (3n): Using procedure 1, colorless liquid, isolated
yield 55%; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 6.77-6.75\) (m, 2H), 6.60 (d, J = 3.60
10-Hexyl-phenoxazine (3o): Using procedure 1, colorless liquid, isolated yield 67%; $^1$H NMR (600 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 144.98, 133.56, 123.55, 120.60, 115.26, 111.22, 44.06, 31.78, 29.35, 29.27, 26.91, 24.86, 22.62, 14.08. LRMS (EI): calculated for C$_{18}$H$_{21}$NO, 267; observed 267.

10-Butyl-phenoxazine (3q): Using procedure 1, white solid, isolated yield 79%; mp 155-156 °C; $^1$H NMR (600 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 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): Using procedure 1, white solid, isolated yield 90%; mp 92-94 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.59\) (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\(_4\)): \(\delta = 144.03, 141.74, 139.01, 134.39, 133.92, 132.69, 130.99, 130.87, 128.41, 122.98, 121.37, 121.16, 115.26, 115.03, 113.91, 113.21, 20.81.\) HRMS (ESI): calculated for C\(_{19}\)H\(_{15}\)NO, 273.1154; observed 273.1150.

2-Chloro-10-phenyl-phenoxazine (3s): Using procedure 1, white solid, isolated yield 56%; mp 86-87 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), SiMe\(_4\)): \(\delta = 7.58\) (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\(_4\)): \(\delta = 143.61, 142.53, 138.16, 135.37, 133.53, 131.23, 130.47, 128.83, 128.04, 123.38, 121.75, 120.55, 116.11, 115.40, 113.45, 113.02.\) 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\(_4\)): \(\delta = 7.63\) (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\(_4\)): \(\delta = 149.26, 143.75, 142.75, 137.36, 134.99, 132.80, 131.60, 130.07, 129.34, 124.38, 122.15, 117.84, 115.67, 115.10, 113.69, 107.64.\) HRMS (ESI): calculated for C\(_{18}\)H\(_{12}\)N\(_2\)O\(_3\), 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\(_4\)): \(\delta = 7.64\) (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\(_4\)): \(\delta = 157.95\) (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 =

---

S11
8.73 Hz), 110.01 (d, \( J = 21.98 \) Hz), 107.65, 104.14 (d, \( J = 27.36 \) Hz). HRMS (ESI): calculated for \( \text{C}_{18}\text{H}_{11}\text{FN}_{2}\text{O}_{3} \), 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\(_4\)): \( \delta = 7.62-7.58 \) (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\(_4\)): \( \delta = 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 \( \text{C}_{10}\text{H}_{14}\text{N}_{2}\text{O}_{4} \), 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\(_4\)): \( \delta = 7.63-7.49 \) (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\(_4\)): \( \delta = 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 \( \text{C}_{17}\text{H}_{11}\text{N}_{3}\text{O}_{3} \), 305.0800; observed 305.0806.

1,4-Bis(10-phenoxazinyl)-benzene (3x): Using procedure 2, light yellow solid, isolated yield 72%; mp 249-250 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \( \delta = 7.57 \) (s, 4H), 6.73-6.66 (m, 12H), 6.02-6.00 (m, 4H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\), SiMe\(_4\)): \( \delta = 143.99, 143.02, 133.99, 133.66, 123.31, 121.70, 115.66, 113.15. LRMS (EI): calculated for \( \text{C}_{30}\text{H}_{20}\text{N}_{2}\text{O}_{2} \), 440; observed 440.

10-Phenyl-phenothiazine (5a): Using procedure 3, white solid, isolated yield 99%; mp 90-91 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\), SiMe\(_4\)): \( \delta = 7.56 \) (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\(_4\)): \( \delta = 144.17, 140.88, \ldots \)
130.76, 130.66, 128.10, 126.75, 126.63, 122.38, 120.07, 115.95. LRMS (EI): calculated for C$_{13}$H$_{13}$NS, 275; observed 275.

10-Benzyl-phenothiazine (5b)$^3$: Using procedure 3, pale brown solid, isolated yield 85%; mp 91-92 °C; $^1$H NMR (400 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 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 °C; $^1$H NMR (400 MHz, CDCl$_3$, SiMe$_4$): $\delta$ = 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$_4$): $\delta$ = 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$_2$S$_2$, 472; observed 472.

References

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-Isoquinoliny1)-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):
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):
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$_4$)
$^{1}$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$_4$)