Imino Exchange Reaction in Dearomatization

Strategy: Synthesis of N-Acyl Diarylamines and Phenothiazines from Two Anilines

Li Zhang,\textsuperscript{a} Huiqing Wang,\textsuperscript{b} Bo Yang,\textsuperscript{*b} and Renhua Fan\textsuperscript{*a}

\textsuperscript{a}Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China. Fax: 86-21-6510-2412; Tel: 86-21-6564-2019; E-mail: rhfan@fudan.edu.cn

\textsuperscript{b}Department of Urology, Changhai Hospital, 168 Changhai Road, Shanghai 200433, China. E-mail: yangbochanghai@126.com

Supporting Information

1. General information (S2)

2. General experimental procedure and characterization data. (S2- S9)

3. Copies of $^1$H, $^{13}$C NMR of products (S10-S63)
1. General Information

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

2. General Procedure and Spectral Data of Products

1) Synthesis of N-acyl diarylamines from anilines and aldehydes

\[
\begin{align*}
\text{PhI(OAc)}_2 & (0.22 \text{ mmol}) \text{ was added into the solution of } N\text{-sulfonyl protected } \text{para-substituted aniline (0.2 mmol)} \text{ in MeOH (2 mL) at 0 °C. After 5 min, the second aniline (0.22 mmol) and Bi(OTf)}_3 (0.02 \text{ mmol}) \text{ were added. The reaction was stirred at 25 °C until the consumption of } N\text{-sulfonyl cyclohexadienimine determined by TLC,} \\
\text{then was quenched with saturated NaHCO}_3 (20 \text{ mL}), \text{ and extracted by ethyl acetate (25 mL x 3). The organic layer was dried over anhydrous Na}_2\text{SO}_4, \text{ and concentrated in vacuo. The crude product was treated EtOAc (2 mL), TBHP (0.2 mmol), and aldehyde (0.6 mmol). The resulting mixture was stirred at 80 °C until the consumption of } N\text{-aryl cyclohexadienimine determined by TLC. The reaction was quenched with saturated NaHCO}_3 (20 \text{ mL}), \text{ and extracted by ethyl acetate (25 mL x 3). The organic layer was dried over anhydrous Na}_2\text{SO}_4, \text{ and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 10:1) to afford the pure product.}
\end{align*}
\]
**N,N-Di-p-tolyl-4-(trifluoromethyl)benzamide 3:** white solid; m.p. 126-127 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.1$ Hz, 2 H), 7.46 (d, $J = 8.2$ Hz, 2 H), 6.85-7.18 (m, 8 H), 2.30 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.0, 140.7, 139.9, 136.5, 131.6, 131.3, 129.8, 129.3, 124.8, 124.7, 122.3, 20.9; HRMS m/z calcd for C$_{22}$H$_{19}$F$_3$NO ([M+H]$^+$): 370.1413, found 370.1412.

**4-Fluoro-N,N-di-p-tolylenzamide 4:** brown solid; m.p. 165-166 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 - 7.48 (m, 2 H), 7.00 – 7.10 (m, 8 H), 8.85-6.90 (m, 2 H), 2.29 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.4, 164.6, 162.1, 141.3, 136.1, 132.3, 131.5, 131.4, 129.7, 127.0, 20.9; HRMS m/z calcd for C$_{21}$H$_{19}$FNO ([M+H]$^+$): 320.1445, found 320.1439.

**4-Cyano-N,N-di-p-tolylenzamide 5:** white solid; m.p. 180-181 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J = 8.5$ Hz, 2 H), 7.49 (d, $J = 8.5$ Hz, 2 H), 6.82-7.12 (m, 8 H), 2.30 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.6, 140.9, 140.5, 136.8, 131.8, 130.0, 129.2, 127.1, 118.2, 113.4, 21.0; HRMS m/z calcd for C$_{22}$H$_{19}$N$_2$O ([M+H]$^+$): 327.1492, found 327.1501.

**4-Nitro-N,N-di-p-tolylenzamide 6:** brown solid; m.p. 146-147 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06 (d, $J = 8.7$ Hz, 2 H), 7.59 (d, $J = 8.8$ Hz, 2 H), 6.75-7.27 (m, 8 H), 2.31 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.3, 148.1, 142.7, 140.4, 137.0, 130.0, 129.8, 127.2, 123.2, 21.0; HRMS m/z calcd for C$_{21}$H$_{19}$N$_2$O$_3$ ([M+H]$^+$): 347.1390, found 347.1389.

**4-Chloro-N,N-di-p-tolylenzamide 7:** white solid; m.p. 139-140 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.5$ Hz, 2 H), 7.17 (d, $J = 8.5$ Hz, 2 H), 6.90 -7.12 (m, 8 H), 2.29 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.3, 141.1, 136.2, 136.9, 134.6, 130.5, 129.7, 128.0, 127.0, 20.9; HRMS m/z calcd for C$_{21}$H$_{19}$ClNO ([M+H]$^+$): 336.1150, found 336.1162.

**4-Methoxy-N,N-di-p-tolylenzamide 8:** white solid; m.p. 131-132 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.9$ Hz, 2 H), 6.98-7.10 (m, 8 H), 6.70 (d, $J = 8.9$ Hz, 2 H), 3.75 (s, 3 H), 2.30 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 160.9, 141.9, 135.8, 130.5, 129.7, 128.0, 127.0, 20.9; HRMS m/z calcd for C$_{21}$H$_{19}$ClNO ([M+H]$^+$): 336.1150, found 336.1162.

4-Methoxy-N,N-di-p-tolylenzamide 8: white solid; m.p. 131-132 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.9$ Hz, 2 H), 6.98-7.10 (m, 8 H), 6.70 (d, $J = 8.9$ Hz, 2 H), 3.75 (s, 3 H), 2.30 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 160.9, 141.9, 135.8,
131.4, 129.7, 128.3, 127.2, 55.2, 21.0; HRMS m/z calcd for C_{22}H_{22}NO_{2} ([M+H]^+): 332.1645, found 332.1648.

N,N-Di-p-tolylbenzamide 9: yellow solid; m.p. 136-137 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 7.2$ Hz, 2 H), 7.16 - 7.27 (m, 3 H), 6.92-7.10 (m, 8 H), 2.28 (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.6, 141.5, 136.4, 136.1, 130.0, 129.7, 129.2, 127.8, 127.2, 21.0; HRMS m/z calcd for C$_{21}$H$_{20}$NO ([M+H]$^+$): 302.1539, found 302.1540.

N-(4-Ethylphenyl)-4-methoxy-N-(p-tolyl)benzamide 11: brown solid; m.p. 124-125 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41-7.45 (m, 2 H), 6.97 -7.13 (m, 8 H), 6.67-6.74 (m, 2 H), 3.75 (s, 3 H), 2.62 (t, $J = 15.2$ Hz, $J = 7.6$ Hz, 2 H), 2.29 (s, 3 H), 1.20 (t, $J = 7.6$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.1, 160.8, 142.0, 141.9, 141.0, 135.7, 131.3, 129.6, 128.4, 128.2, 127.1, 127.1, 112.8, 55.1, 28.2, 20.9, 15.3; HRMS m/z calcd for C$_{23}$H$_{24}$NO$_2$ ([M+H]$^+$): 346.1802, found 346.1797.

N-(4-Butylphenyl)-4-methoxy-N-(p-tolyl)benzamide 12: yellow solid; m.p. 94-95 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.8$ Hz, 2 H), 6.96 -7.10 (m, 8 H), 6.68 (d, $J = 8.8$ Hz, 2 H), 3.72 (s, 3 H), 2.55 (t, $J = 7.6$ Hz, 2 H), 2.28 (s, 3 H), 1.52-1.59 (m, 2 H), 1.27-1.36 (m, 2 H), 0.90 (t, $J = 7.3$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.0, 160.7, 141.8, 141.9, 140.6, 135.6, 131.2, 129.6, 128.8, 128.1, 127.0, 126.9, 112.8, 55.0, 35.0, 33.3, 22.2, 20.9, 13.8; HRMS m/z calcd for C$_{23}$H$_{28}$NO$_2$ ([M+H]$^+$): 374.2115, found 374.2133.

N-(4-Isopropylphenyl)-4-methoxy-N-(p-tolyl)benzamide 13: yellow solid; m.p. 124-125 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.8$ Hz, 2 H), 6.96-7.15 (m, 8 H), 6.69 (d, $J = 8.8$ Hz, 2 H), 3.74 (s, 3 H), 2.82-2.89 (m, 1 H), 2.29 (s, 3 H), 1.21 (d, $J = 6.9$ Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.1, 160.8, 146.5, 141.9, 141.9, 135.7, 131.2, 129.6, 128.2, 127.2, 126.9, 126.8, 112.9, 55.1, 33.5, 23.8, 20.9; HRMS m/z calcd for C$_{24}$H$_{28}$NO$_2$ ([M+H]$^+$): 360.1958, found 360.1950.
4-Methoxy-N-phenyl-\(N\)-(p-tolyl)benzamide 14: white solid; m.p. 151-152 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 (d, \(J = 8.8\) Hz, 2 H), 7.24 - 7.30 (m, 2 H), 7.05-7.18 (m, 5 H), 7.15 (d, \(J = 8.3\) Hz, 2 H), 6.70 (d, \(J = 8.8\) Hz, 2 H), 3.75 (s, 3 H), 2.30 (s, 3 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 161.0, 144.5, 141.8, 136.0, 131.4, 129.8, 129.1, 128.2, 127.3, 126.0, 113.1, 55.2, 21.0; HRMS m/z calcd for \(\text{C}_{21}\text{H}_{20}\text{NO}_2\) ([M+H])\(^+\): 318.1489, found 318.1484.

\(N\)-(3,5-Dimethylphenyl)-4-methoxy-\(N\)-(p-tolyl)benzamide 15; white solid; m.p. 143-144 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 (d, \(J = 8.8\) Hz, 2 H), 7.06 (d, \(J = 8.2\) Hz, 2 H), 6.99 (d, \(J = 8.2\) Hz, 2 H), 6.81 (s, 1 H), 6.77 (s, 2 H), 6.70 (d, \(J = 8.8\) Hz, 2 H), 3.75 (s, 3 H), 2.29 (s, 3 H), 2.22 (s, 6 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 161.0, 144.2, 142.0, 138.7, 135.8, 131.4, 129.8, 128.4, 128.0, 127.2, 125.1, 113.0, 55.2, 21.2, 21.0; HRMS m/z calcd for \(\text{C}_{23}\text{H}_{24}\text{NO}_2\) ([M+H])\(^+\): 346.1802, found 346.1787.

\(N\)-(3,4-Dimethylphenyl)-4-methoxy-\(N\)-(p-tolyl)benzamide 16: yellow solid; m.p. 140-141 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41-7.46 (m, 2 H), 6.98-7.10 (m, 7 H), 6.64 - 6.72 (m, 2 H), 3.74 (s, 3 H), 2.29 (s, 3 H), 2.20 (s, 3 H), 2.16 (s, 3 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.2, 160.8, 142.0, 141.9, 140.2, 137.3, 135.6, 134.6, 131.2, 130.0, 129.6, 128.2, 127.0, 124.7, 55.1, 20.9, 19.8, 19.2; HRMS m/z calcd for \(\text{C}_{23}\text{H}_{24}\text{NO}_2\) ([M+H])\(^+\): 346.1802, found 346.1798.

4-Methoxy-\(N\)-(4-methoxyphenyl)-\(N\)-(p-tolyl)benzamide 17: white solid; m.p. 112-113 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.7\) Hz, 2 H), 6.96 – 7.10 (m, 6 H), 6.80 (d, \(J = 8.8\) Hz, 2 H), 6.70 (d, \(J = 8.8\) Hz, 2 H), 3.76 (s, 3 H), 3.75 (s, 3 H), 2.29 (s, 3 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 160.9, 157.6, 142.0, 137.4, 135.8, 131.3, 129.7, 128.5, 128.3, 127.0, 114.4, 113.1, 55.2, 55.3, 21.0; HRMS m/z calcd for \(\text{C}_{22}\text{H}_{22}\text{NO}_3\) ([M+H])\(^+\): 348.1594, found 348.1593.

\(N\)-(4-chlorophenyl)-4-methoxy-\(N\)-(p-tolyl)benzamide 18: yellow solid; m.p. 127-128 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.9\) Hz, 2 H), 7.24 (d, \(J = 8.7\) Hz, 2 H), 7.02-7.12 (m, 4 H), 6.98 (d, \(J = 8.3\) Hz, 2 H ), 6.72 (d, \(J = 8.8\) Hz, 2 H), 3.77 (s, 3 H), 2.30 (s, 3 H),...
H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.1, 161.1, 142.9, 141.4, 136.3, 131.3, 129.9, 129.1, 128.2, 127.7, 127.3, 113.1, 55.2, 20.9; HRMS m/z calcd for C$_{21}$H$_{19}$ClNO$_2$ ([M+H]$^+$): 352.1099, found 352.1108.

$N$-(4-Fluorophenyl)-4-methoxy-$N$-(p-tolyl)benzamide 19: yellow solid; m.p. 151-152 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J$ = 8.8 Hz, 2 H), 6.94 -7.15 (m, 8 H), 6.71 (d, $J$ = 8.8 Hz, 2 H), 3.76 (s, 3 H), 2.30 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.2, 161.7, 161.0, 159.2, 141.6, 140.4, 136.1, 131.3, 129.8, 128.7, 128.6, 127.8, 127.1, 116.0, 115.7, 113.1, 55.2, 20.9; HRMS m/z calcd for C$_{21}$H$_{19}$FNO$_2$ ([M+H]$^+$): 336.1394, found 336.1389.

2) Synthesis of phenothiazines

PhI(OAc)$_2$ (0.22 mmol) was added into the solution of $N$-sulfonyl protected para-substituted aniline (0.2 mmol) in MeOH (2 mL) in ice-water bath. After 5 minutes, 2-aminobenzenethiol (0.30 mmol) and CuI (0.02 mmol) were added into the reaction system. Upon completion determined by TLC, the reaction mixture was quenched with saturated NaHCO$_3$ (25 mL), and extracted by ethyl acetate (25 mL x 3). The organic layer was dried over Na$_2$SO$_4$, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 20:1) to afford the pure product.

3-Methyl-10$H$-phenothiazine 23: $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.46 (s, 1 H), 6.96 (t, $J$ = 7.6 Hz, 1 H), 6.89 (d, $J$ = 7.5 Hz, 1 H), 6.78 (d, $J$ = 7.9 Hz, 1 H), 6.70-6.73 (m, 2 H), 6.67 (d, $J$ = 7.9 Hz, 1 H), 6.59 (d, $J$ = 8.0 Hz, 1 H), 2.12 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 142.9, 140.0, 131.1, 128.4, 127.9, 127.0, 126.7, 121.9, 116.8, 116.7, 114.8, 20.4; HRMS m/z calcd for C$_{13}$H$_{12}$NS ([M+H]$^+$): 214.0685, found 214.0669.
3-Ethyl-10H-phenothiazine 24: $^1$H NMR (400 MHz, DMSO-d6) $\delta$
8.47 (s, 1 H), 6.97 (dt, $J = 7.7$, 1.4 Hz, 1 H), 6.89 (dd, $J = 7.6$, 1.2 Hz, 1 H), 6.81 (dd, $J = 8.1$, 1.9 Hz, 1 H), 6.75 (dd, $J = 1.7$, 1 Hz, 1 H), 6.72 (dt, $J = 7.6$, 1.2 Hz, 1 H), 6.67 (dd, $J = 7.9$, 1.1 Hz, 1 H), 6.61 (d, $J = 8.0$ Hz, 1 H), 2.39-2.44 (m, 2 H), 1.09 (t, $J = 7.6$ Hz, 3 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 142.9, 140.3, 137.8, 127.9, 127.3, 126.7, 125.9, 121.9, 116.8, 116.7, 114.8, 114.7, 27.7, 16.2; HRMS m/z calcd for C$_{14}$H$_{14}$NS ([M+H]$^+$): 228.0841, found 228.0852.

3-Isopropyl-10H-phenothiazine 25: $^1$H NMR (400 MHz, DMSO-d6) $\delta$
8.48 (s, 1 H), 6.96 (t, $J = 7.6$ Hz, 1 H), 6.89 (d, $J = 7.6$ Hz, 1 H), 6.85 (dd, $J = 8.1$, 1.8 Hz, 1 H), 6.77 (d, $J = 1.7$ Hz, 1 H), 6.72 (dd, $J = 10.8$, 4.2 Hz, 1 H), 6.67 (d, $J = 7.3$ Hz, 1 H), 6.62 (d, $J = 8.1$ Hz, 1 H), 2.70 (m, 1 H), 1.12 (s, 3 H), 1.10 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 142.9, 142.5, 140.4, 127.9, 126.7, 125.8, 124.4, 121.9, 116.8, 116.7, 114.8, 114.7, 33.0, 24.3; HRMS m/z calcd for C$_{15}$H$_{16}$NS ([M+H]$^+$): 242.0998, found 242.0987.

3-Butyl-10H-phenothiazine 26: $^1$H NMR (400 MHz, DMSO-d6) $\delta$
8.48 (s, 1 H), 6.96 (t, $J = 7.6$ Hz, 1 H), 6.89 (d, $J = 6.9$ Hz, 1 H), 6.79 (dd, $J = 8.0$, 1.3 Hz, 1 H), 6.72 (s, 2 H), 6.67 (d, $J = 7.8$ Hz, 1 H), 6.60 (d, $J = 7.9$ Hz, 1 H), 2.38 (s, 2 H), 1.49-1.39 (m, 2 H), 1.24 (m, 2 H), 0.86 (t, $J = 7.3$ Hz, 3 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 142.8, 140.3, 136.3, 127.9, 126.7, 126.3, 121.9, 116.8, 116.7, 114.8, 34.3, 33.6, 22.1, 14.3; HRMS m/z calcd for C$_{16}$H$_{18}$NS ([M+H]$^+$): 256.1154, found 256.1151.

3-Phenyl-10H-phenothiazine 27: $^1$H NMR (400 MHz, DMSO-d6) $\delta$
8.72 (s, 1 H), 7.56 (d, $J = 7.4$ Hz, 2 H), 7.39 (t, $J = 7.6$ Hz, 2 H), 7.34-7.24 (m, 2 H), 7.22 (s, 1 H), 7.00 (t, $J = 7.4$ Hz, 1 H), 6.93 (d, $J = 7.4$ Hz, 1 H), 6.74-6.77 (m, 2 H), 6.70 (d, $J = 7.8$ Hz, 1 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 142.2, 141.9, 139.6, 134.2, 129.3, 128.1, 127.3, 126.7, 126.3, 126.2, 124.6, 122.3, 117.5, 116.6, 115.2, 115.0; HRMS m/z calcd for C$_{18}$H$_{14}$NS ([M+H]$^+$): 276.0841, found 276.0824.
1,3-Dimethyl-10H-phenothiazine 28: $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 7.54 (s, 1 H), 7.02-6.94 (m, 2 H), 6.90 (d, $J$ = 7.3 Hz, 1 H), 6.74 (dt, $J$ = 7.7, 1.8 Hz, 1 H), 6.68 (s, 1 H), 6.60 (s, 1 H), 2.16 (s, 3 H), 2.09 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 142.9, 138.0, 130.8, 130.3, 127.7, 126.5, 124.9, 122.7, 122.2, 117.6, 116.9, 116.0, 20.3, 18.0; HRMS m/z calcd for C$_{14}$H$_{14}$NS ([M+H]$^+$): 228.0841, found 228.0813.

2,3-Dimethyl-10H-phenothiazine and 3,4-dimethyl-10H-phenothiazine 29: $^1$H NMR (400 MHz, DMSO-d$_6$): I: $\delta$ 8.37 (s, 1 H, NH, peaks of two isomers overlapped), 6.95 (dt, $J$ = 7.8, 1.3 Hz, 1 H, CHar, peaks of two isomers overlapped), 6.88 (d, $J$ = 7.6 Hz, 1 H, CHar), 6.71 (d, $J$ = 7.4 Hz, 1 H, CHar), 6.65-6.68 (m, 2 H, CHar, peaks of two isomers overlapped), 6.48 (s, 1 H, CHar), 2.07 (s, 3 H, CH), 2.04 (s, 3 H, CH); II: $\delta$ 8.37 (s, 1 H, NH, peaks of two isomers overlapped), 6.95 (dt, $J$ = 7.8, 1.3 Hz, 2 H, CHar, peaks of two isomers overlapped), 6.76 (d, $J$ = 8.0 Hz, 1 H, CHar), 6.65-6.68 (m, 2 H, CHar, peaks of two isomers overlapped), 6.44 (d, $J$ = 7.9 Hz, 1H, CHar), (s, 6 H, CH); HRMS m/z calcd for C$_{14}$H$_{14}$NS ([M+H]$^+$): 228.0841, found 228.0832.

3,7-dimethyl-10H-phenothiazine 30: gray oil; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.31 (s, 1 H), 6.76 (d, $J$ = 8.1 Hz, 2 H), 6.72 (s, 2 H), 6.56 (d, $J$ = 8.0 Hz, 2 H), 2.11 (s, 6 H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 140.3, 130.8, 128.3, 126.9, 116.6, 114.6, 20.4; HRMS m/z calcd for C$_{14}$H$_{14}$NS ([M+H]$^+$): 228.0841, found 228.0816.

3-Methoxy-7-methyl-10H-phenothiazine 31: $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.23 (s, 1 H), 6.77 (dd, $J$ = 8.0, 1.2 Hz, 1 H), 6.73 (s, 1H), 6.61 (s, 1 H), 6.60 (d, $J$ = 2.6 Hz, 1 H), 6.57-6.56 (m, 2 H), 3.64 (s, 3 H), 2.12 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ 154.9, 140.7, 136.4, 130.6, 128.4, 126.9, 118.0, 116.1, 115.4, 114.6, 113.5, 112.1, 55.8, 20.4; HRMS m/z calcd for C$_{14}$H$_{14}$NOS ([M+H]$^+$): 244.0791, found 244.0779.

2-Chloro-7-methyl-10H-phenothiazine 32: pale yellow solid; m.p. 229-231 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.64 (s, 1 H), 6.89 (d, $J$ = 8.2 Hz, 1 H), 6.80 (d, $J$ = 8.0 Hz, 1 H), 6.75-6.73 (m, 2 H), 6.67 (d, $J$
$= 2.1$ Hz, 1 H), 6.56 (d, $J = 8.0$ Hz, 1 H), 2.12 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 144.2, 139.0, 132.2, 131.8, 128.6, 127.9, 127.0, 121.3, 116.4, 115.9, 115.0, 114.0, 20.4; HRMS m/z calcd for C$_{13}$H$_{11}$ClNS ([M+H]$^+$): 248.0295, found 248.0264.

3-Phenyl-7-(trifluoromethyl)-10H-phenothiazine 33: pale yellow solid; m.p. 226-228 °C; $^1$H NMR (400 MHz, DMSO-d6) $\delta$ 8.99 (s, 1 H), 7.56 (d, $J = 7.5$ Hz, 2 H), 7.39 (t, $J = 7.6$ Hz, 2 H), 7.35-7.25 (m, 2 H), 7.23 (d, $J = 1.6$ Hz, 1 H), 7.11 (d, $J = 8.0$ Hz, 1 H), 7.03 (d, $J = 8.0$ Hz, 1 H), 6.92 (s, 1 H), 6.73 (d, $J = 8.2$ Hz, 1 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 142.7, 140.6, 139.4, 135.0, 129.3, 128.6 ($J = 31.8$ Hz), 127.4 ($J = 6.9$ Hz), 126.8, 126.3, 124.8, 124.5 ($J = 271.8$ Hz), 122.3, 118.5 ($J = 3.4$ Hz), 116.6, 115.5, 110.6 ($J = 3.4$ Hz); HRMS m/z calcd for C$_{19}$H$_{13}$F$_3$NS ([M+H]$^+$): 344.0715, found 344.0689.

4-Methyl-N-(10H-phenothiazin-3-yl)benzenesulfonamide 35: black solid; m.p. 168-170 °C; $^1$H NMR (400 MHz, DMSO-d6)$\delta$ 9.82 (s, 1 H), 8.53 (s, 1 H), 7.58 (d, $J = 8.2$ Hz, 2 H), 7.33 (d, $J = 8.1$ Hz, 2 H), 6.96 (t, $J = 7.6$ Hz, 1 H), 6.87 (d, $J = 7.3$ Hz, 1 H), 6.68-6.74 (m, 2 H), 6.64 (d, $J = 7.8$ Hz, 1 H), 6.60 (d, $J = 2.1$ Hz, 1 H), 6.53 (d, $J = 8.5$ Hz, 1 H), 2.33 (s, 3 H); $^{13}$C NMR (100 MHz, DMSO-d6) $\delta$ 143.6, 142.5, 139.6, 137.0, 132.1, 130.1, 128.2, 127.2, 126.7, 122.3, 121.5, 119.9, 117.4, 116.0, 115.1, 114.9, 21.5; HRMS m/z calcd for C$_{19}$H$_{17}$N$_2$O$_2$S$_2$ ([M+H]$^+$): 369.0726, found 369.0692.
29-I + 29-II

6.5 : 1

Diagram showing chemical structures and peaks.