

Synthesis of tris-pillar[5]arene and its association with phenothiazine dye: colorimetric recognition of anions

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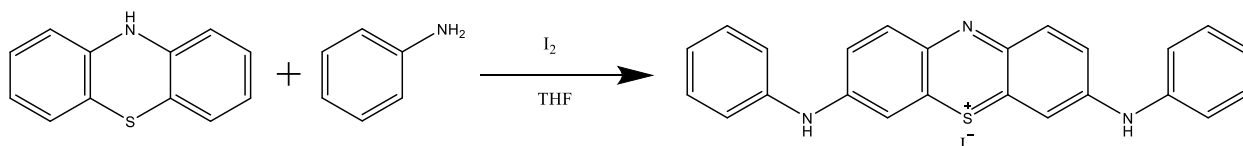
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Synthesis of 3,7-bis(phenylamino)phenothiazin-5-ium iodide

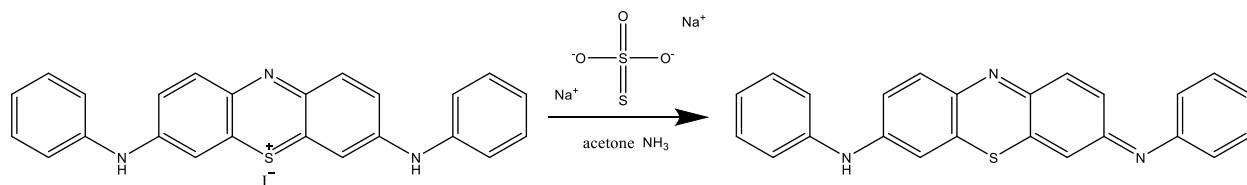


Phenothiazine (1 g, 5.0 mmol) was dissolved in 50 ml of THF at 0°C. Iodine solution in THF was dropwise added to the reaction mixture within 30 min. Then, aniline solution (4.6 g, 50.0 mmol in THF) was dropwise added to the reaction mixture within 15 min. The reaction mixture was stirred for 24 h. The sedimented product was separated by filtration and washed with diethyl ether. The dark blue powder was collected and dried overnight in a vacuum desiccator over P₂O₅ (yield 80%).

¹H NMR (400 MHz, DMSO-d₆): δ 11.06 (s, 2H), 8.12 (d, *J* = 9.3 Hz, 2H), 7.62 – 7.51 (m, 8H), 7.47 (d, *J* = 7.5 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 2H).

Elemental analysis: calculated for C₂₄H₁₈N₃S⁺: C, 75.76; H, 4.77; N, 11.04; S, 8.43, found: C, 75.70; H, 4.81; N, 11.02; S, 8.42.

Synthesis of N-phenyl-3-(phenylimino)-3H-phenothiazin-7-amine



3,7-bis(phenylamino)phenothiazin-5-ium iodide (1 g, 20 mmol) was dissolved in 50 ml of acetone. Then, sodium thiosulfate (6.32 g, 40.0 mmol) and 2% aqueous ammonia were added to the reaction mixture. The reaction mixture was stirred for 12 h. Purple powder was collected and dried overnight in vacuum desiccator over P₄O₁₀ (yield 70%).

¹H NMR (400 MHz, (CD₃)₂SO): δ 9.08 (d, *J* = 8.6 Hz, 1H), 7.54-7.46 (m, 1H), 7.41-7.33 (m, 4H), 7.26-7.18 (m, 3H), 7.12 (t, *J* = 7.9 Hz, 1.5H), 7.09 – 7.01 (m, 2.5H), 7.01 – 6.93 (m, 1H), 6.93-6.79 (m, 2.5H), 6.53 (d, *J* = 1.9 Hz, 0.5H).

Elemental analysis: calculated for C₂₄H₁₇N₃S: C, 75.96; H, 4.52; N, 11.07; S, 8.45, found: C, 75.87; H, 4.50; N, 11.04; S, 8.42.

Melting point: 215-217°C (literature 215-216°C) [28].

Figure 1S. MALDI mass-spectrum (matrix: 2,5-dihydroxybenzoic acid) of 4

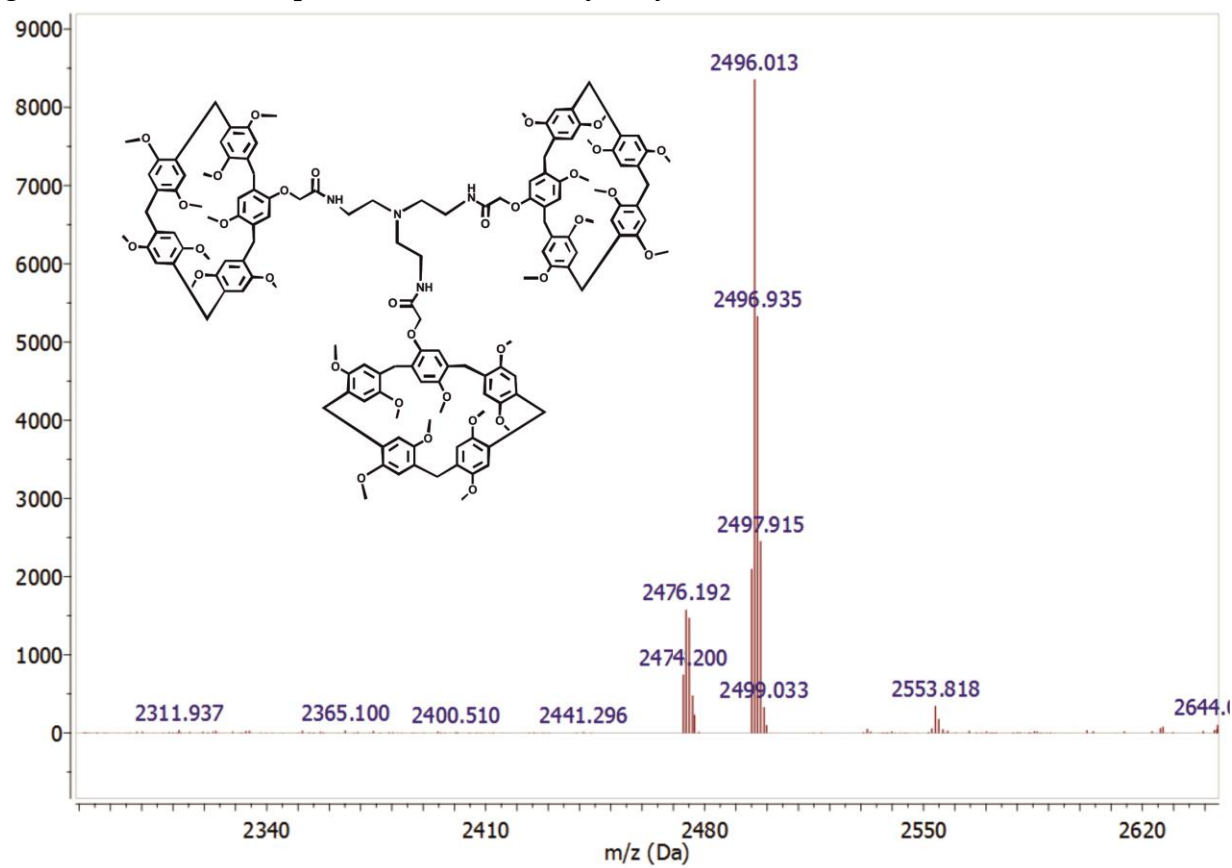


Figure 2S. FTIR-ATR spectrum of 4

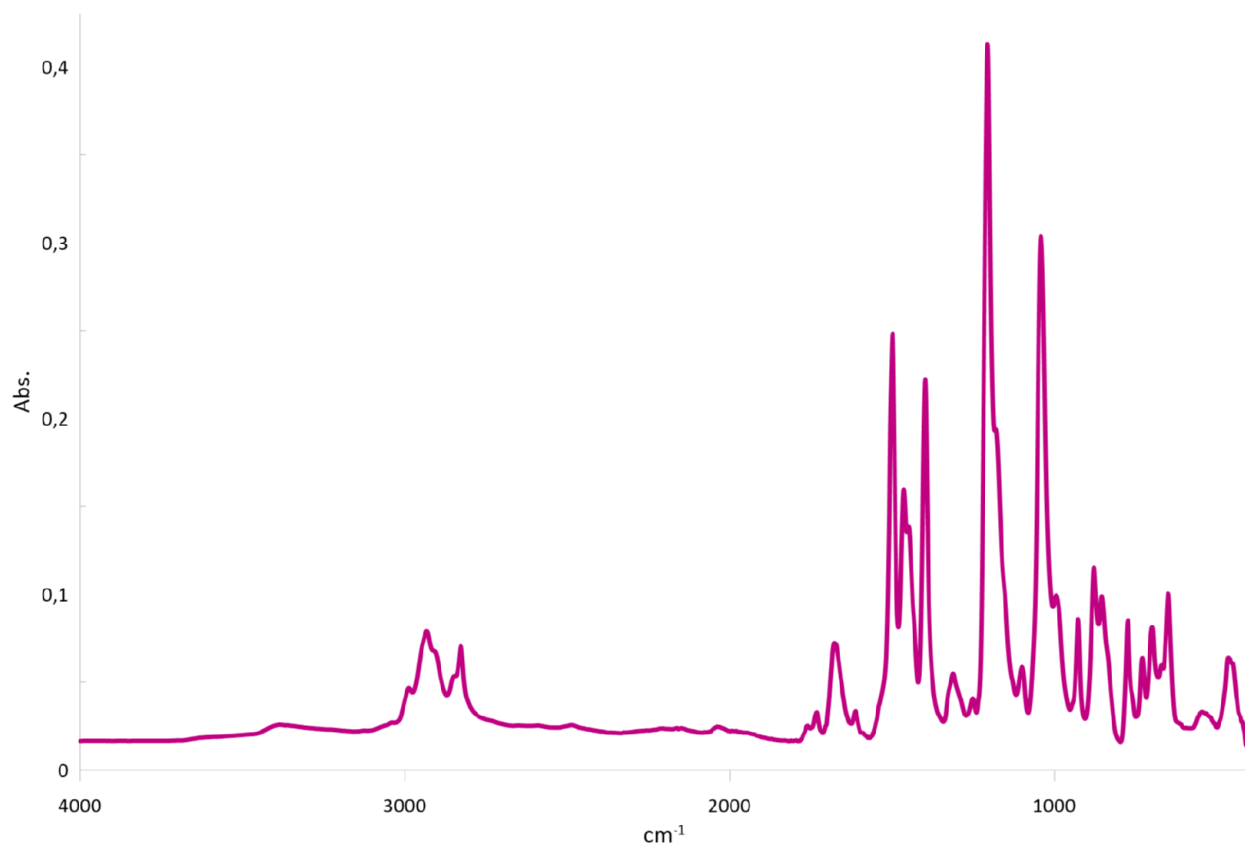


Figure 3S. ^1H NMR ($\text{DMSO-}d_6$) spectrum of 4

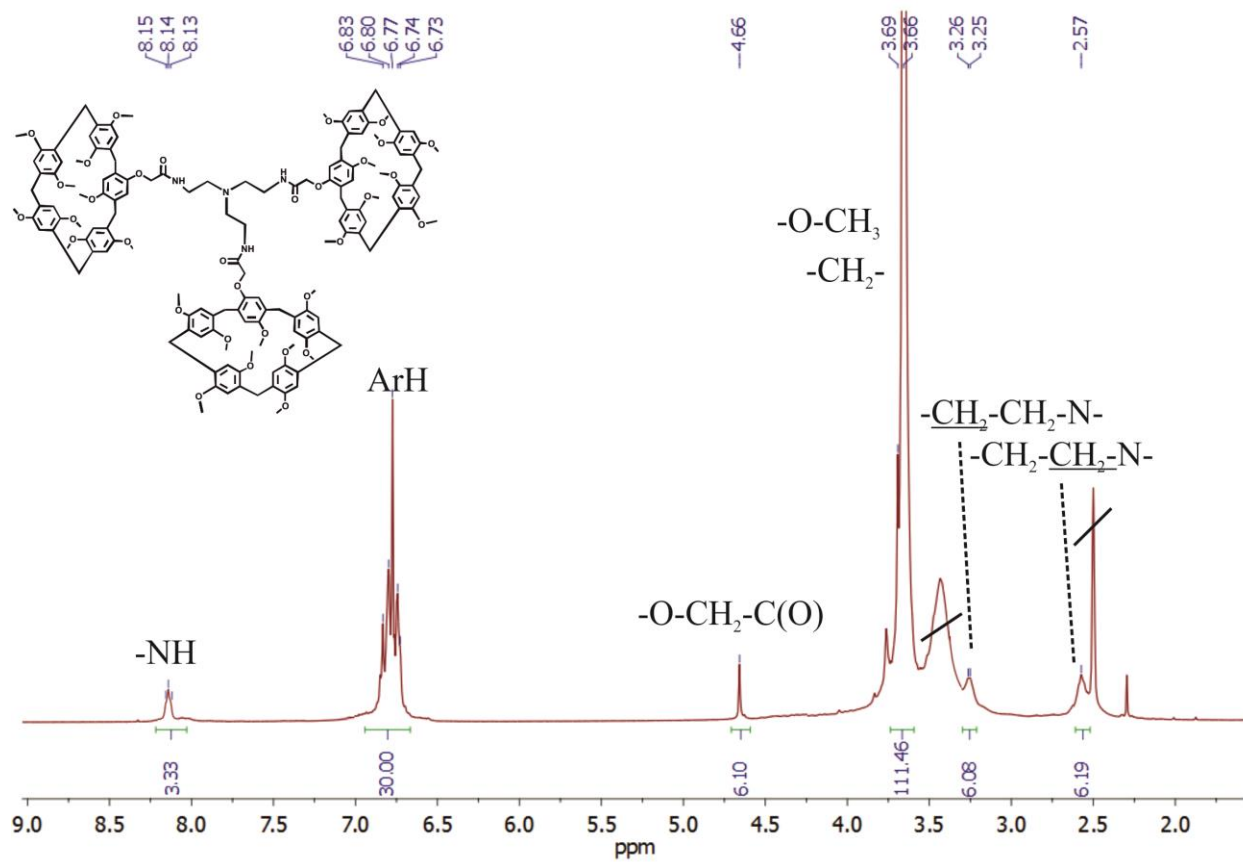


Figure 4S. ^{13}C NMR (DMSO d_6) spectrum of 4

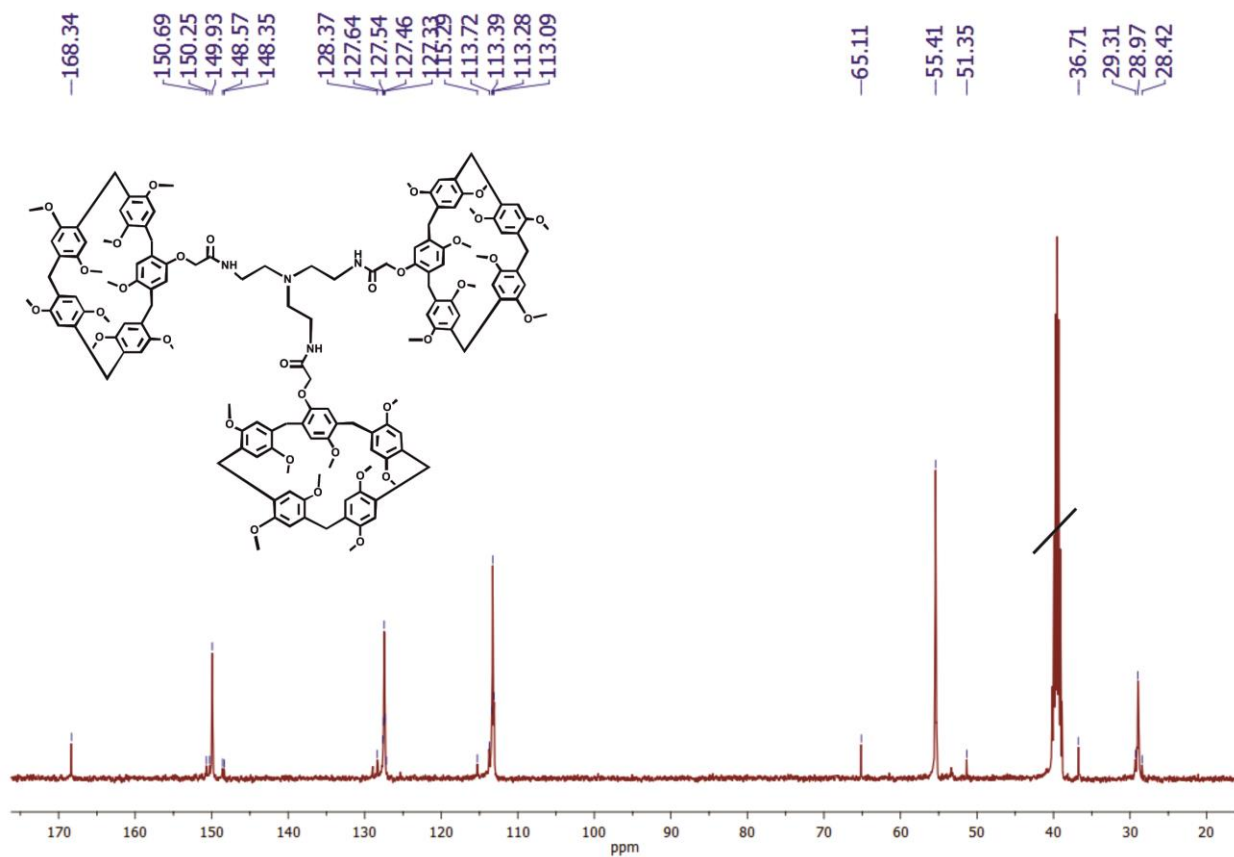


Figure 5S. ^1H NMR (CDCl_3) spectra of PhTz (red), 4:PhTz complex (blue) and 4 (black).

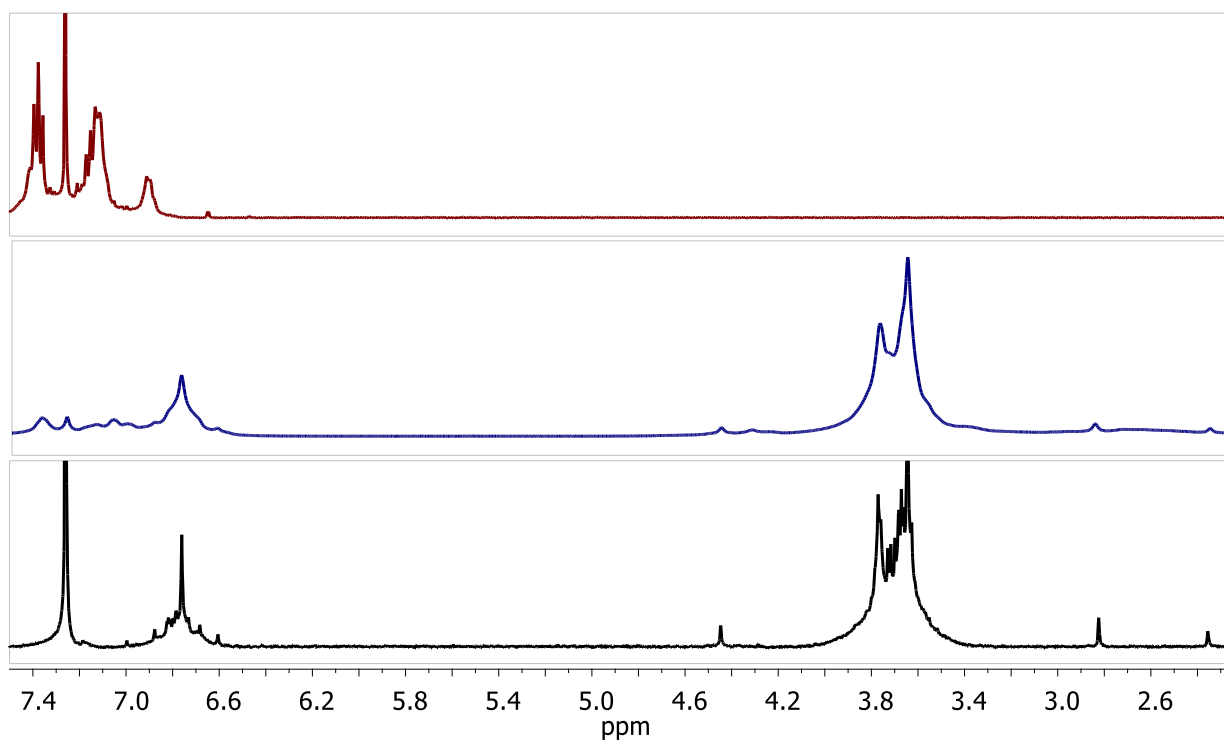


Figure 6S. Fragments of the ^1H NMR (CDCl_3) spectra of PhTz (red), 4:PhTz complex (blue) and 4 (black), sections corresponding to signal of aromatic protons (left), $\sim\text{OCH}_2\text{CONH}\sim$ fragment connecting pillar[5]arene to TREN (center) and $\text{N}(\text{CH}_2\text{CH}_2\text{NH})$ protons (right).

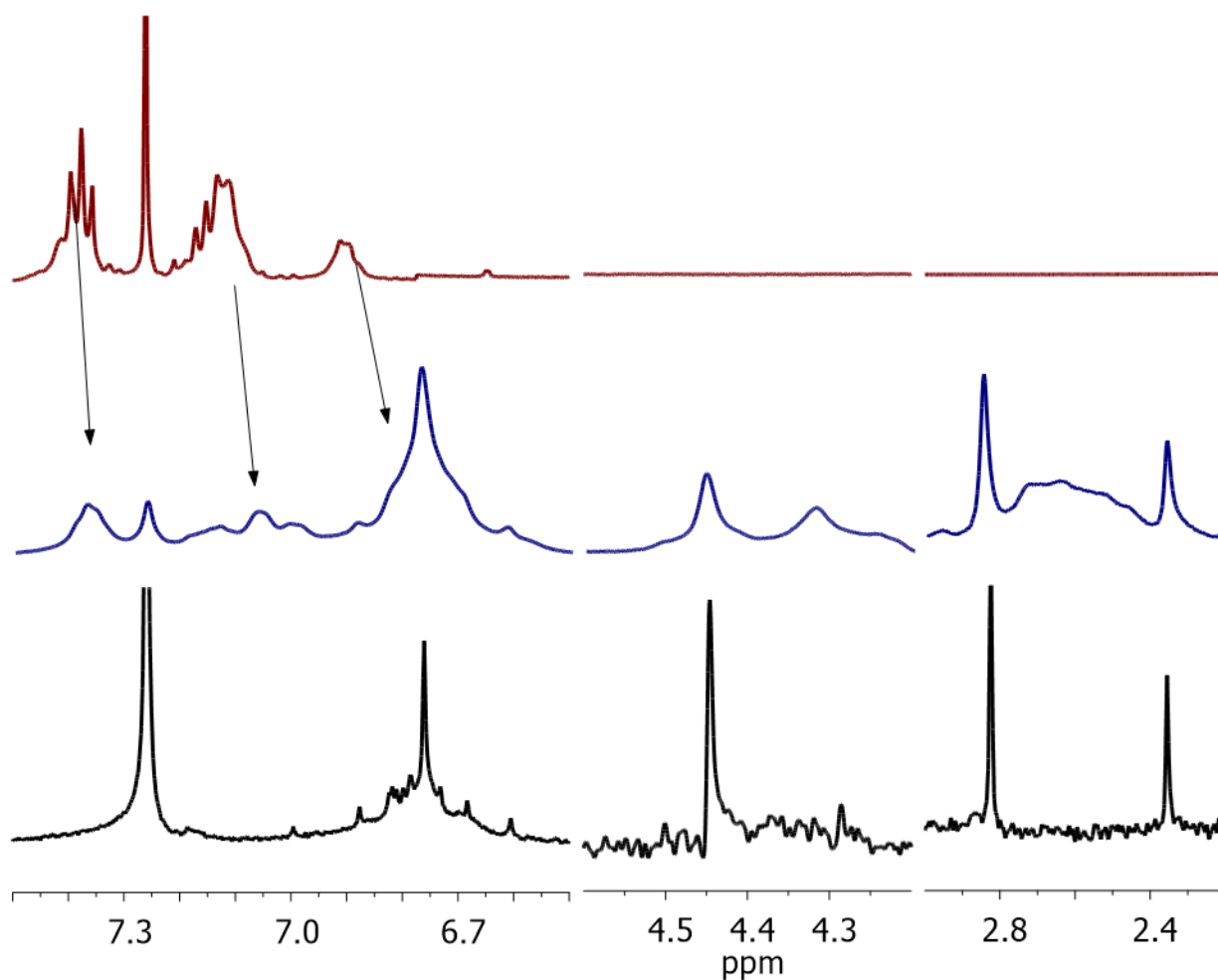


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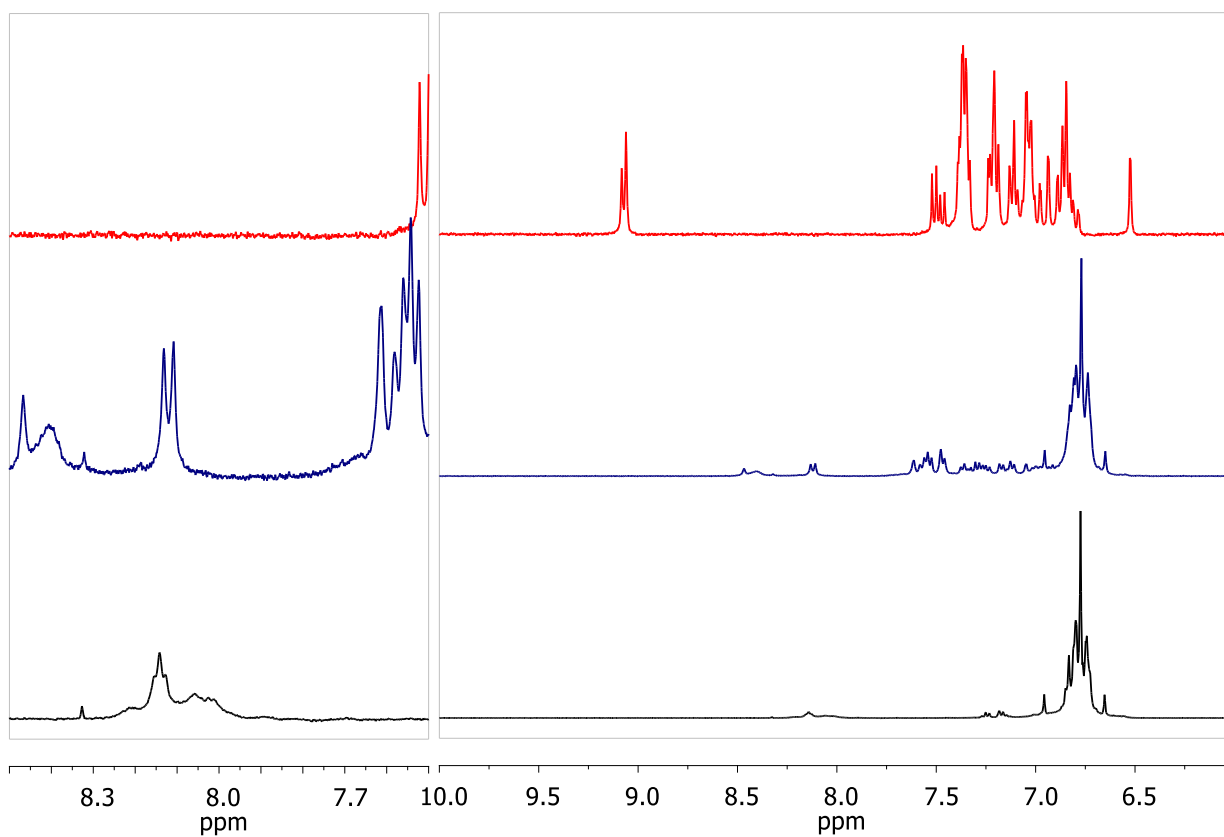


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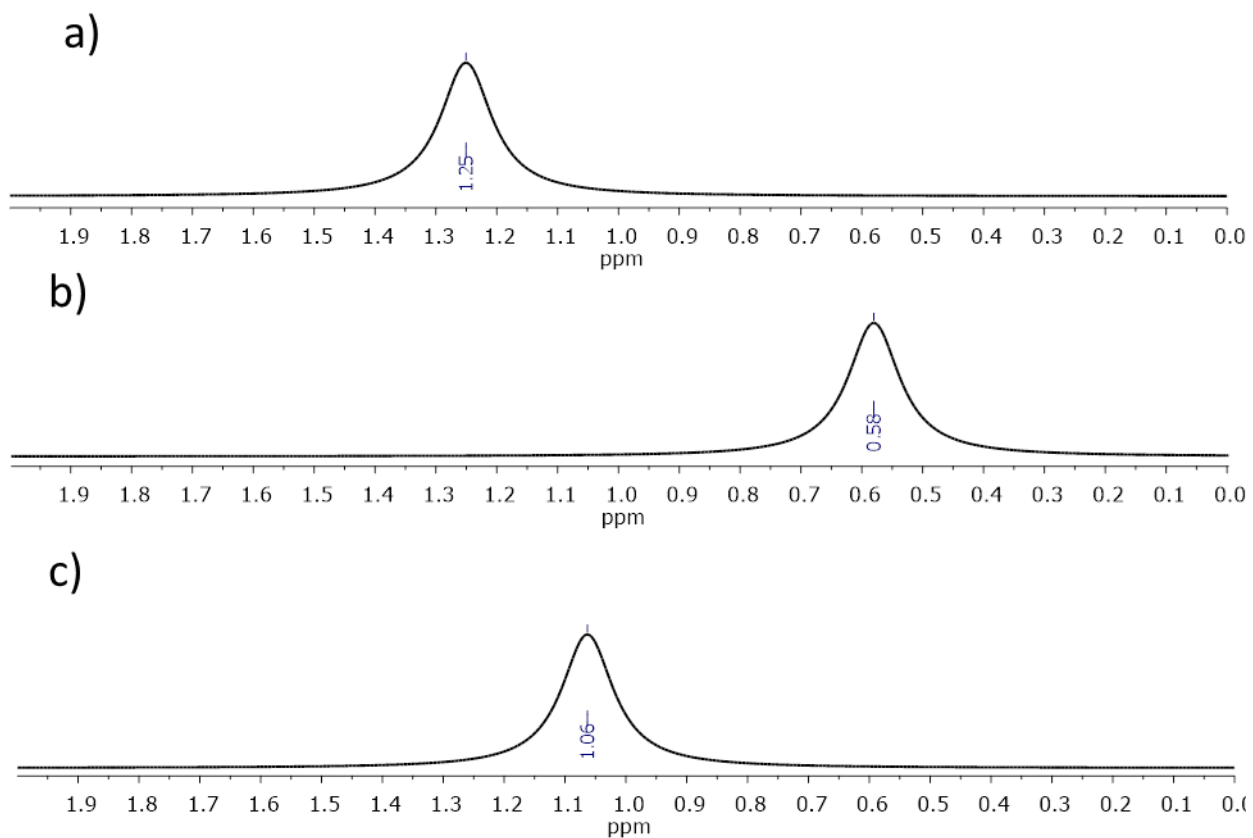


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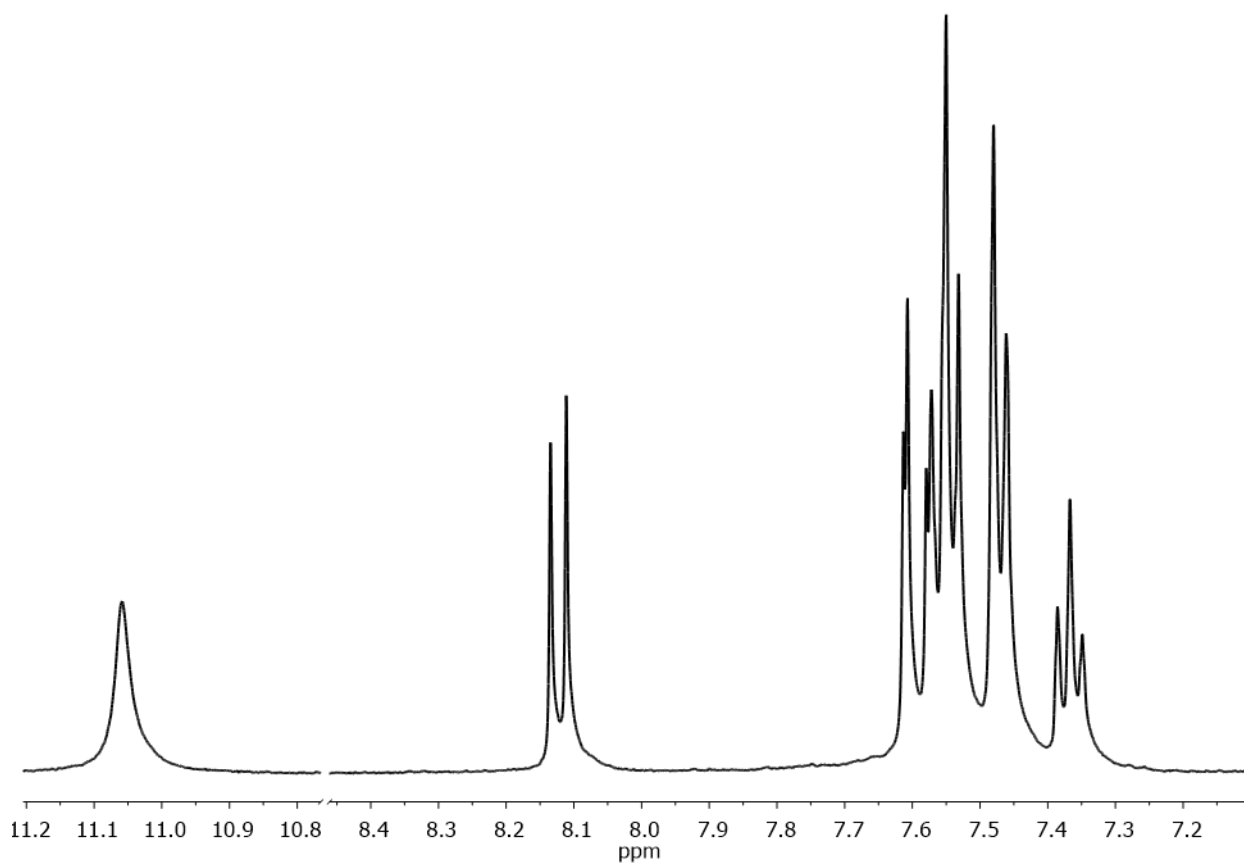


Figure 10S. ^1H NMR ($\text{DMSO}-d_6$) spectrum of N-phenyl-3-(phenylimino)-3H-phenothiazin-7-amine (PhTz)

