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**Supplementary Material**

# TNT Stilbene Derivatives as SERRS Active Species

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*Chemical Synthesis*

**2-Methyl-5-[2-(2,4,6-trinitro-phenyl)-vinyl]-thiophene**
A solution of TNT (0.050 g, 0.22 mmol) and 5-methyl-thiophenecarboxaldehyde (0.025 ml, 0.22 mmol) in dry THF (5 ml) was gently refluxed for three hours with two drops of piperidine. THF was removed *in vacuo* to leave a dark red oily residue, which was dissolved in ethyl acetate (20 ml) and extracted with potassium chloride solution (4 × 20 ml). The organic layer was dried over sodium sulphate and then purified by column chromatography, eluting with methanol (0-10 %) in dichloromethane to afford the stilbene as a red powder. Crystallisation from ethanol gave as small red needles (0.030 g, 41 %). $\lambda_{max}$(MeCN)/nm 408 (ε = 10556). $\nu_{max}$(KBr)/cm$^{-1}$ 1532 ($NO_2$ assym), 1339 ($NO_2$ symm), 812 ($NO_2$ out of plane bend). $^1$H NMR ($CDCl_3$) δ 2.53 (3H, s, $CH_3$), 6.72 (1H, d, *J* = 3.60 Hz, ArH), 6.88 (1H, d, *J* = 16.20 Hz, CH=CH), 6.98 (1H, d, *J* = 16.20 Hz, CH=CH), 6.98 (1H, d, *J* = 3.60 Hz, ArH), 8.79 (2H, s ArH). Anal. Calcd for $C_{12}H_9N_3O_6S$: C, 46.43; H, 2.68; N, 12.50. Found C, 46.60; H, 2.42; N, 12.04.

**3-Methyl-2-[2-(2,4,6-trinitro-phenyl)-vinyl]-thiophene**
As per the procedure above with 3-methyl-thiophenecarboxaldehyde (0.025 ml, 0.22 mmol) to afford the stilbene derivative as a red powder. Crystallisation from ethanol gave the stilbene as very small red needles (0.013 g, 18 %). $\lambda_{max}$(MeCN)/nm 402 (ε = 14758). $\nu_{max}$(KBr)/cm$^{-1}$ 1533 ($NO_2$ assym), 1338 ($NO_2$ symm), 822 ($NO_2$ out of plane bend). $^1$H NMR (Acetone-$\delta_6$) δ 2.26 (3H, s, $CH_3$), 6.95 (1H, d, *J* = 5.00 Hz, ArH), 7.12 (2H, s, CH=CH), 7.48 (1H, d, *J* = 5.00 Hz, ArH), 9.01 (2H, s, ArH). Anal. Calcd for $C_{12}H_9N_3O_6S$: C, 46.43; H, 2.68; N, 12.50. Found C, 47.40; H, 2.78; N, 11.83.

**4-[2-(2,4,6-Trinitro-phenyl)-vinyl]-pyridine**
As per the procedure above with pyridine-4-carbaldehyde (0.20 ml, 2 mmol). Purification by wet flash chromatography, eluting with ethyl acetate (0-50 %) in hexane afforded the stilbene as a pale red powder. Crystallisation from ethanol gave the product as thick yellow needles (0.329 g, 52 %). $\lambda_{max}$(MeOH)/nm 322 (ε = 9752). $^1$H NMR (Acetone-$\delta_6$) δ 6.82 (1H, d, *J* = 16.66 Hz, CH=CH), 7.50 (2H, d, *J* = 4.51 Hz, ArH), 7.76 (1H, d, *J* = 16.64 Hz, CH=CH), 8.60 (2H, d, *J* = 4.46 Hz, ArH), 9.10 (2H, s, ArH). *m/z* (FAB) 317.05266 [$C_{13}H_9N_4O_6$ $(M+H)^+$ < 1.4 ppm]. Anal. Calcd for $C_{13}H_8N_4O_6$: C, 49.36; H, 2.53; N, 17.72. Found C, 49.46; H, 2.34; N, 17.76.

**5-[2-(2,4,6-Trinitro-phenyl)-vinyl]-1*H*-benzotriazole**
As per the procedure above with 1*H*-benzotriazole-5-carbaldehyde (0.147 g, 1 mmol). Purification by wet flash chromatography, eluting with ethyl acetate (0-50 %) in hexane afforded as an orange powder (0.107 g, 30 %). $R_f$ (A) 0.30. $\lambda_{max}$(MeOH)/nm

491 (ε = 443). $^1$H NMR (Acetone-$\delta_6$) δ 7.05 (1H, d, *J* = 16.62 Hz, CH=CH), 7.60 (1H, d, *J* = 16.62 Hz, CH=CH), 7.77 (1H, d, *J* = 8.69 Hz, ArH), 7.93 (1H, d, *J* = 8.67 Hz, ArH), 8.07 (1H, s, ArH), 9.08 (2H, s, ArH). *m/z* (FAB) 357.05724 [$C_{14}H_9N_6O_6$ $(M+H)^+$ < 3.1 ppm].

**8-Hydroxyquinoline-5-carbaldehyde**

A solution of 8-hydroxyquinoline (8.000 g, 55.0 mmol) in chloroform (20 ml) was mixed with a solution of sodium hydroxide (16.500 g) in water (30 ml) and ethanol (60 ml). The contents were refluxed at 100 ˚C for 12 hours. The solution was cooled and then neutralised by addition of 50 % HCl/$H_2O$ to afford a dark precipitate which was filtered through celite and washed with dichloromethane. The collected filtrates were extracted with sodium chloride (3 × 50 ml) and then dried over sodium sulphate. Removal of the solvent *in vacuo* gave an oily solid which was pre-absorbed onto silica and purified by wet flash chromatography eluting with methanol (0-4 %) in dichloromethane to afford the product as white needles (1.180 g, 12.4 $^1$H NMR ($CDCl_3$) δ 7.28 (1H, d, *J* = 9.50 Hz, ArH), 7.65 (1H, dd, *J* = 4.20 and 4.20 Hz, ArH), 8.00 (1H, d, *J* = 7.90 Hz, ArH), 8.86 (1H, d, *J* = 4.20 Hz, ArH), 9.68 (1H, d, *J* = 8.60 Hz, ArH), 10.14 (1H, s, CHO). *m/z* (EI) 173.04778 [$C_{10}H_7NO_2$ $(M)^+$ < 0.6 ppm]. Anal Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.04; N, 8.09. Found: C, 68.97; H, 4.02; N, 8.24.

**1*H*-Benzotriazole-5-carbaldehyde**

Formaldoxime (5.000 g, 37.5 mmol) was made up to 50 ml in distilled water to give a 10 % aqueous solution. To this was added copper sulphate (0.925 g, 3.8 mmol), sodium sulphite (0.15 g, 1.1 mmol) and 4.000 g of sodium acetate in 10 ml of water. The solution was maintained at 10-15 °C by means of a cold water bath and stirred vigorously. The diazonium salt of 5-aminobenzotriazole was neutralised by addition of aqueous sodium acetate solution (1 M) and then slowly introduced below the surface of the formaldoxime solution by siphoning under slight nitrogen pressure. After addition of the diazonium salt was complete, the mixture was stirred for an additional hour. To this stirred solution was added 50 % HCl/$H_2O$ (50 ml), followed by gentle refluxing overnight under an atmosphere of nitrogen. The remaining solution and tan precipitate were neutralised by addition of sodium bicarbonate to pH 7. Removal of water *in vacuo* left a tan coloured solid, which was purified by wet flash chromatography eluting with methanol (0-10 %) in dichloromethane. Trituration of the combined pure fractions with diethyl ether gave the aldehyde as a white powder (1.100 g, 20 %). $R_f$ (A) 0.50. $\nu_{max}/cm^{-1}$ 1695 (CHO) $^1$H NMR (Methanol-$d_4$) δ 7.94 (1H, d, *J* = 8.00 Hz, ArH), 8.02 (1H, d, *J* = 8.70 Hz, ArH), 8.53 (1H, s, ArH), 10.13 (1H, s, CHO). *m/z* (EI) 147.04295 [$C_7H_5N_3O$ $(M)^+$ < 4.5 ppm]. Anal. Calcd for $C_7H_5N_3O$: C, 57.14; H, 3.40; N, 28.57. Found C, 57.02; H, 3.12; N, 30.87.