SUPPORTING INFORMATION.

Synthetic procedures.

Amines 1; a typical procedure: Solution of 4.56 g (28 mmol) 1,1,1,3,3,3-hexamethyldisilazane in 100 ml of freshly distilled THF was cooled to 0°C and 19.4 ml of *n*-butyllithium (1.6M solution in hexanes, 30 mmol) was added while stirring under N_2 atmosphere. Reaction mixture was stirred at this temperature for 1.5 hr after which 3 g (28 mmol) of benzaldehyde was slowly added and the resulting mixture was stirred at 0°C for 1 hr. Lithiated dithiane was prepared by adding 19.4 mL of 1.6 M n-butyllithium (30 mmol) to a solution of 3.39 g (28 mmol) 1,3-dithiane in 100 mL of freshly distilled THF at -20 to -25°C and stirred at this temperature for 2 hrs. The solution of lithiodithiane was added slowly to the solution of silylated benzaldimine, the cooling bath was removed and the reaction mixture was stirred overnight at room temperature. Resulting red solution was washed with 100ml of saturated NH_4Cl and THF was removed in vacuum producing yellow oil, which was dissolved in 200 ml of EtOAc and extracted 2x100ml of 10% HCl. The acid extracts were combined, pH was adjusted to 12 with 20% NaOH and water layer was extracted with 3x100 ml of EtOAc. Organic extracts where combined and washed with water 3x100ml. Organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuum, furnishing **1a** (Ar = Ph, 6.2 g, 97%) as a yellow oil, which was used without further purification. ^{1}H NMR ($CDCl_3$), δ(ppm) 7.42-7.22 (5H, m), 4.25 (1H, d, J_1 = 6.6 Hz), 4.22 (1H, d, J_1 = 6.6 Hz), 2.92-2.73 (4H, m), 2.12-2.04 (1H, m), 1.82-1.92 (1H, m)

1-([1,3]Dithian-2-yl-phenyl-methyl)-3-phenyl-urea (3a) . Solution of **1** (0.67 g, 3 mmol) in 10 ml of ether was added to the solution of phenylisocyanate 0.38 g (3 mmol) in 25 ml of ether, and reaction mixture was stirred 12 hours at room temperature. Precipitated white powder was filtered and washed two times with ether, and dried in vacuum (3.1g, 86%); m.p. 160-163 °C; H^1 NMR ($CDCl_3$), δ(ppm) 7.37- 7.23 (10H, m), 7.12-7.03 (1H, m), 6.63 (1H, broad s), 5.81(1H, d, J=7.2Hz), 5.30 (1H, dd, J_1=7.2Hz, J_2=1.6Hz), 2.88-2.69 (4H, m), 2.10-2.00 (1H, m), 1.88-1.74 (1H, m).
Calcd. for $C_{18}H_{20}N_2OS_2$,%: C 62.76, H 5.85; Found, %: C 62.94, H 6.01.

Amides, general procedure. Acyl chloride (11 mmol) was added to the solution of **1** (10mmol) and 2 g of Et_3N in 50 ml of methylene chloride. Reaction mixture was stirred 24 hours, than washed with 2x50 ml of saturated aqueous $NaHCO_3$, and the solvent was removed under reduced pressure. Resulting white powder was washed with ether and dried in vacuum.

N-([1,3]Dithian-2-yl-phenyl-methyl)-4-nitro-benzamide (2a) (74%); m.p. 230-232 °C; ^{1}H NMR ($CDCl_3$), δ(ppm) 8.31 (2H, d, J=8.8Hz), 8.00 (2H, J=8.8Hz), 7.45-7.29 (5H, m), 7.067 (1H, broad d, J=7.2Hz), 5.51, (1H, dd, J_1=7.2Hz, J_2=5.6Hz), 4.55 (1H, d, J=5.6), 2.93-2.75 (4H, m), 2.17-2.06 (1H, m), 1.97-1.82 (1H, m).
Calcd. for $C_{18}H_{18}N_2O_3S_2$,%: C, 57.73; H, 4.84; Found, %: C, 57.62; H, 4.48.

N-([1,3]Dithian-2-yl-phenyl-methyl)-benzamide (2b) (77%); m.p. 240-243 °C; H^1 NMR ($CDCl_3$), δ(ppm) 7.84(2H, d, J=5.6Hz), 7.56-7.23 (8H, m), 7.01 (1H, broad d, J=7.5Hz), 5.53 (1H, dd, , J_1=7.5Hz, J_2=7.3Hz), 4.546 (1H, d, J=7.3), 2.92-2.75 (4H, m), 2.15-2.04 (1H, m), 1.96-1.83(1H,m).
Calcd. for $C_{18}H_{19}NOS_2$,%: C, 65.62; H, 5.81. Found,%: C, 65.53; H, 6.03.

N-(Phenyl-[1,3,5]trithian-2-yl-methyl)-benzamide (5) (85%), m.p.=269-273°C; H^1 NMR ($CDCl_3$), δ(ppm) 7.83(2H, d, J=6.9Hz), 7.60-7.28 (8H, m), 6.88 (1H, broad d, J=7.0Hz), 5.62 (1H, dd, , J_1=5.4Hz, J_2=7.0Hz), 4.82 (1H, d, J=5.4), 4.40-4.24 (2H, m), 4.06-3.97 (2H, m)

Crown-urea 3b:
A solution of 1,3-dithiane (312 mg, 2.6 mmol) in 10 ml of freshly distilled THF was cooled to -78°C under nitrogen. Then n-butyllithium (1.6M solution in hexanes, 1.8 ml, 2.88 mmol) was added dropwise upon stirring. The resulting mixture was allowed to stand for 2h at -20°C. A solution of formylcrownbenzaldehyde (445 mg, 1.3 mmol) in 2 ml THF was added to a solution of lithium bis(trimetylsylil)amide (241 mg, 1.44

mmol) at 0° C under nitrogen. The mixture was stirred at 0° C for 30 min. and then the solution of dithiane anion was added. The mixture was stirred overnight and then quenched with saturated solution of ammonium chloride, evaporated and extracted with dichloromethane. The solution was washed twice with water and extracted twice with 6% HCl. The aqueous layer was washed with dichloromethane and basified, then extracted again with dichloromethane, washed with water, dried and evaporated to give 312 mg (52%) of amine, which was used without additional purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01(t, J=7.8 Hz,1H), 6.97(d d, J_1=1.9 Hz, J_2=7.8 Hz, 1H), 6.82(d d, J_1=1.9 Hz, J_2=7.8 Hz, 1H), 4.37-4.48(m, 3H), 4.21-4.26(m, 1H), 4.14(t, J=4.6 Hz, 2H), 3.89-3.99(m, 4H), 3.64-3.77(m, 12H), 2.73-2.92(m,4H), 2.02-2.10(m, 1H), 1.81-1.92(m, 3H). To a solution of thus isolated amine (312 mg, 0.68 mmol) in 10 ml EtOAc/Et_2O mixture (1:1) was added phenylisocyanate (0.09 ml, 0.8 mmol) and the reaction mixture was stirred for 12 hrs. Precipitated compound was filtered, washed with ether and dried to yield 291 mg (74%) of **3b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83-7.37(m, 10H), 5.35(t, J=0.024, 1H), 4.64-4.71 (m, 1H), 4.25-4.44(m, 3H), 4.16(m, 2H), 4.00-4.05(m, 1H), 3.89(m, 2H), 3.74-3.83(m, 4H), 3.60-3.69(m, 8H), 3.04-3.11(m, 1H), 2.90-2.97(m, 1H), 2.61-2.70(m, 2H), 1.90-2.08(m, 2H).

Aminopyridine 4 (Ar = p-EtO-$CH_2CH_2OC_6H_4$-) was obtained by boiling 1:1 mixture of 1 and chloronitropyridine in isopropanole for 48h in the presence of triethylamine, cooling and filtering. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98(d, J=2.7 Hz, 1H), 8.12(d d, J_1=2.7 Hz, J_2=9.2 Hz, 1H), 7.31-7.37(m, 5H), 6.31(d, J=9.2 Hz, 1H), 6.22(s, broad, 1H), 5.27(s, broad, 1H), 4.55(d, J=5 Hz, 1H), 2.76-2.94(m, 4H), 2.10-2.88(m, 1H), 1.81-1.92(m, 1H).

Diamine 7:
A solution of spiro-bis dithiane (417 mg, 1.86 mmol) in 10 ml of freshly distilled THF was cooled to -78°C under nitrogen and n-butyllithium (1.6M solution in hexanes, 2.5 ml, 4 mmol) was added dropwise upon stirring. The resulting mixture was stirred for 2 hrs at -20°C. A solution of 4-(2-ethoxyethoxy)benzaldehyde (759 mg, 3.9 mmol) in 2 ml THF was added to a solution of lithium bis(trimetylsylil)amide (prepared from 0.83 ml of bis-(trimethylsilil)amine and 2.5 ml 1.6M butyllithium) in 10 ml THF at 0° C under nitrogen. The mixture was stirred at 0° C for 30 min. and then the solution of lithiated spiro-bis-dithiane was added. The mixture was stirred overnight and then quenched with saturated solution of ammonium chloride, evaporated and extracted with dichloromethane. The solution was washed twice with water and extracted twice with 6% HCl. The aqueous layer was washed with dichloromethane and basified, then extracted again with dichloromethane, washed with water, dried and evaporated to give 938 mg (83%) of diamine **7**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27(d m, 4H), 6.89(d m, 4H), 4.06-4.19 (m, 8H), 3.77(m, 4H), 3.58-3.62(m, 4H), 3.37-3.42(m, 2H), 2.60-2.76(m, 6H), 1.77(broad s, 4H), 1.23(t m, 6H).

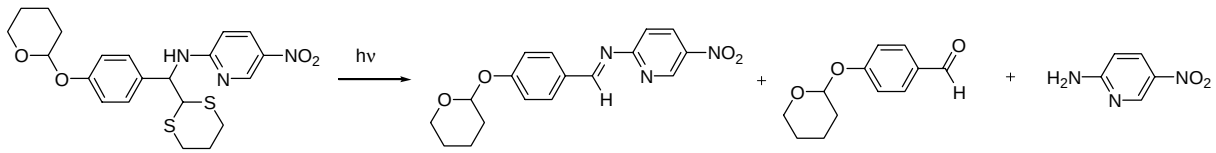
Bis-urea 8:
To a solution of diamine **7** (170 mg, 0.28 mmol) in 10 ml EtOAc was added phenylisocyanate (0.07 ml, 0.64 mmol) and mixture was stirred for 12 hrs. After addition of 10ml of ether precipitated compound was filtered, washed with ether and dried, yielding 150 mg (64%) of **8**. ^{1}H NMR (400 MHz, CD_3CN) δ 7.21-7.37(m, 14H), 6.87-6.97(m, 6H), 5.87(t, J=7.8 Hz, 2H), 5.12-5.16(m, 2H), 4.40-4.43(m, 2H), 4.06-4.09(m, 4H), 3.69-3.72(m, 4H), 3.39-3.55(m, 6H), 2.71-2.86(m, 6H), 1.16(t, J=7.0 Hz, 6H).

Bis-pyridine 11:
A suspension of trithiane (0.4 g, 2.9 mmol) in 15 ml of freshly distilled THF was cooled to -70°C under nitrogen. Then n-butyllithium (1.6M solution in hexanes, 4 ml, 6.4 mmol) was added dropwise upon stirring. The resulting mixture was stirred for 4 hrs at -20°C. A solution of 4-(2-ethoxyethoxy)benzaldehyde (1.3 g, 5.8 mmol) in 3 ml THF was added to a solution of lithium bis-trimetylsylilamide (prepared from 1.22 ml of bis-(trimethylsilil)amine and 3.8 ml 1.6M butyllithium) in 10 ml THF at 0° C under nitrogen. The mixture was stirred at 0° C for 30 min. and then added to the solution of trithiane dianion. The mixture was stirred overnight and then quenched with saturated solution of ammonium chloride, evaporated and extracted with dichloromethane. The solution was washed twice with water and extracted twice with 6% HCl. The aqueous layer was washed with dichloromethane and basified, then extracted again with dichloromethane, washed with water, dried and evaporated to give 0.9 g of amines **9** and **10**. Resulted mixture of amines was boiled with 2-fluoro-5-nitropyridine (0.73 g, 5.14 mmol) in 20 ml of isopropanol for 48 hrs, evaporated and separated

by column chromatography on SiO_2 (chloroform : acetonitrile 10:1), yieldng 462 mg (21%) of **11**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96-9.00(m, 2H), 8.11-8.16(m, 2H), 7.21-7.28(m, 4H), 6.88-6.92(m, 4H), 6.30-6.37(m, 2H), 5.91-6.07(m, broad, 2H), 5.26-5.45(m, broad, 2H), 4.74-4.85(m, 2H), 4.05-4.25(m, 6H), 3.75-3.80(m, 4H), 3.55-3.62(m, 4H), 1.21-1.26(m, 6H).

Direct irradiation of 4b and mass balance.

A solution of {[1,3]Dithian-2-yl-[4-(tetrahydro-pyran-2-yloxy)-phenyl]-methyl}-(5-nitro-pyridin-2-yl)-amine **4b** (98 mg) in 20 ml of acetonitrile in a pyrex tube was degassed by bubbling N_2 for 15 min. The tube was capped and the irradiation was carried out in a carousel Rayonet photoreactor for 4 hrs. The solvent was then removed with a rotary evaporator, and the residue was chromatographed on a silica gel column, eluted with ethyl acetate/hexane (5:1) to give: 21 mg (21%) of starting material **4b**, 12 mg (17%) of (5-nitro-pyridin-2-yl)-[4-(tetrahydro-pyran-2-yloxy)-benzylidene]-amine, 16 mg (35%) of 4-(tetrahydro-pyran-2-yloxy)-benzaldehyde, and 12 mg (39%) of 2-amino-5-nitropyridine:



4b

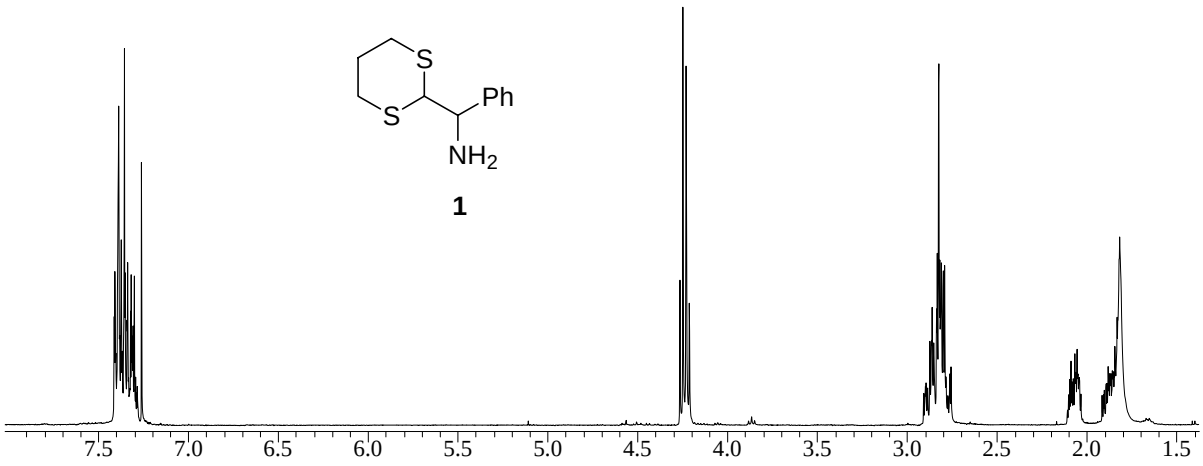
{[1,3]Dithian-2-yl-[4-(tetrahydro-pyran-2-yloxy)-phenyl]-methyl}-(5-nitro-pyridin-2-yl)-amine **4b**:
^{1}H NMR ($CDCl_3$), δ(ppm) 8.98 (1H, d, J=3Hz), 8.10 (1H, dd, J_1=3Hz, J_2=10Hz), 7.27 (2H, d, J=9Hz), 7.02 (2H, d, J=9Hz), 6.33-6.23 (2H, m), 5.43-5.37 (1H, m), 5.20 (s, 1H), 4.52 (1H, dd, J_1=5Hz, J_2=1Hz), 3.92-3.83 (1H, m), 3.63-3.55 (1H, m), 2.93-2.75 (m, 4H), 2.16-2.06 (m, 1H), 2.04-1.92 (m, 1H), 1.90-1.78 (3H, m), 1.72-1.64(m, 3H). ^{13}C NMR ($CDCl_3$), δ(ppm) 160.0, 156.9, 146.5, 136.1, 132.7, 130.4, 127.8, 116.3, 116.2, 96.3, 96.2, 62.1, 59.0, 52.9, 30.4, 30.3, 30.1, 25.5, 25.2, 18.8.

(5-Nitro-pyridin-2-yl)-[4-(tetrahydro-pyran-2-yloxy)-benzylidene]-amine: ^{1}H NMR ($CDCl_3$), δ(ppm) 9.15 (1H, d, J=3Hz), 8.85-8.84 (1H, m), 8.56 (1H, s), 8.54(1H, d, J=3Hz), 7.89 (2H, d, J=9Hz), 7.17 (2H, d, J=9Hz), 5.54 (1H, t, J=3Hz), 3.90-3.82 (1H, m), 3.67-3.60 (1H, m), 2.10-1.96 (1H, m), 1.94-1.86 (2H, m), 1.80-1.60 (3H, m); ^{13}C NMR ($CDCl_3$), δ(ppm) 164.9, 160.8, 155.5, 144.6, 133.9, 129.1, 125.7, 116.4, 112.8, 96.1, 62.1, 30.2, 29.8, 25.1, 18.6; MS (EI): *m/z* (%) 242 ([M–C_5H_9O]$^+$, 2), 121 (100), 93 (20), 65 (25).

4-(Tetrahydro-pyran-2-yloxy)-benzaldehyde: ^{1}H NMR ($CDCl_3$), δ(ppm) 9.88 (1H, s), 7.82 (2H, d, J=9Hz), 7.15 (2H, d, J=9Hz), 5.54 (1H, t, J=3Hz), 3.87-3.81 (1H, m), 3.67-3.60 (1H, m), 2.10-1.95 (1H, m), 1.92-1.88 (2H, m), 1.78-1.56 (3H, m); ^{13}C NMR ($CDCl_3$), δ(ppm) 190.6, 161.9, 131.7, 130.3, 116.3, 96.0, 62.1, 31.1, 30.1, 25.1, 18.5; MS (EI): *m/z* (%) 206 ([M]$^+$, 2), 121 (15), 85 (100), 67 (20), 57 (22).

2-Amino-5-nitropyridine: ^{1}H NMR ($CDCl_3$), δ(ppm) 8.99 (1H, d, J=2Hz), 8.21 (1H, dd, J_1=2Hz, J_2=9Hz), 6.48 (1H, d, J=9Hz), 5.28 (2H, s). Same as the compound purchased from Sigma-Aldrich.
MS (EI): *m/z* (%) 139 ([M]$^+$, 100), 109 (60), 81 (50), 66 (99).

NMR Spectra.



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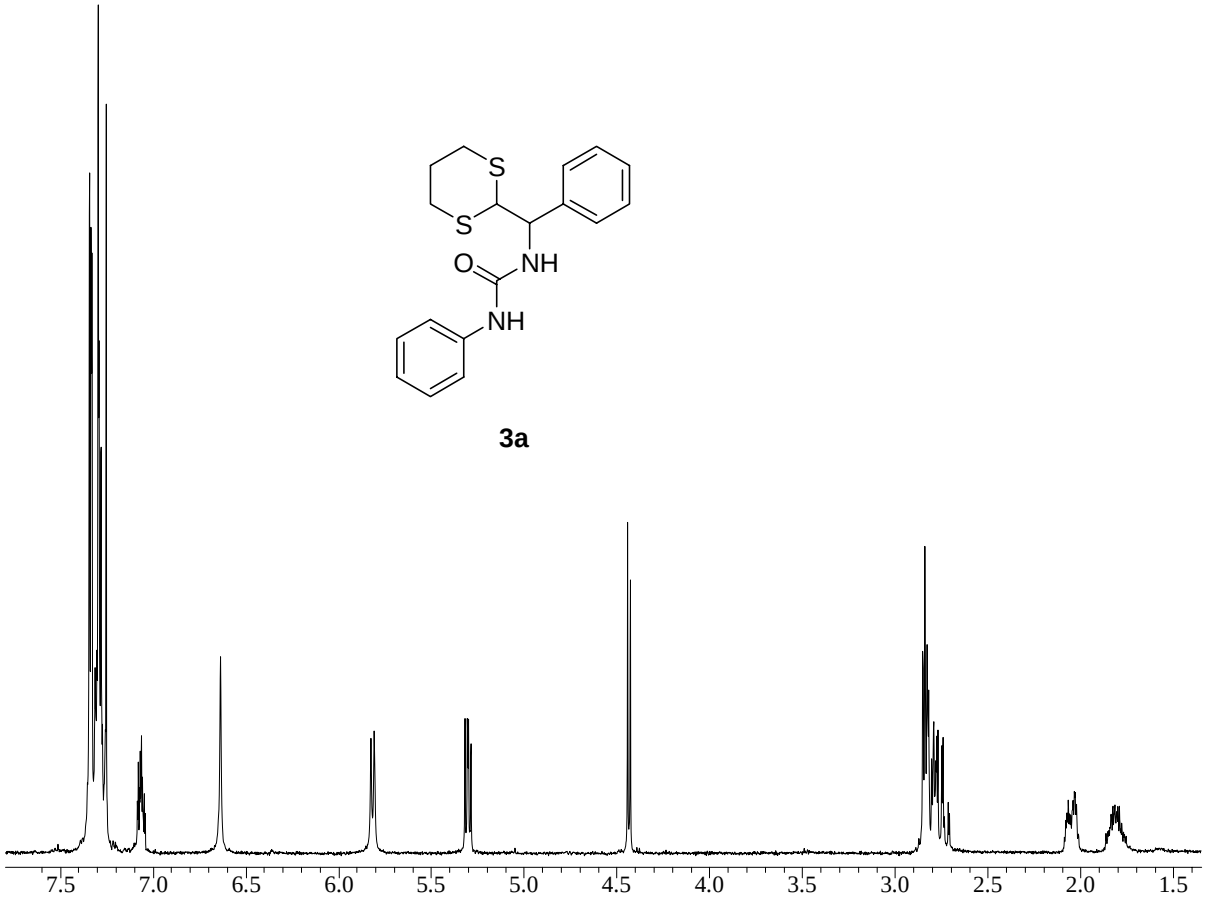

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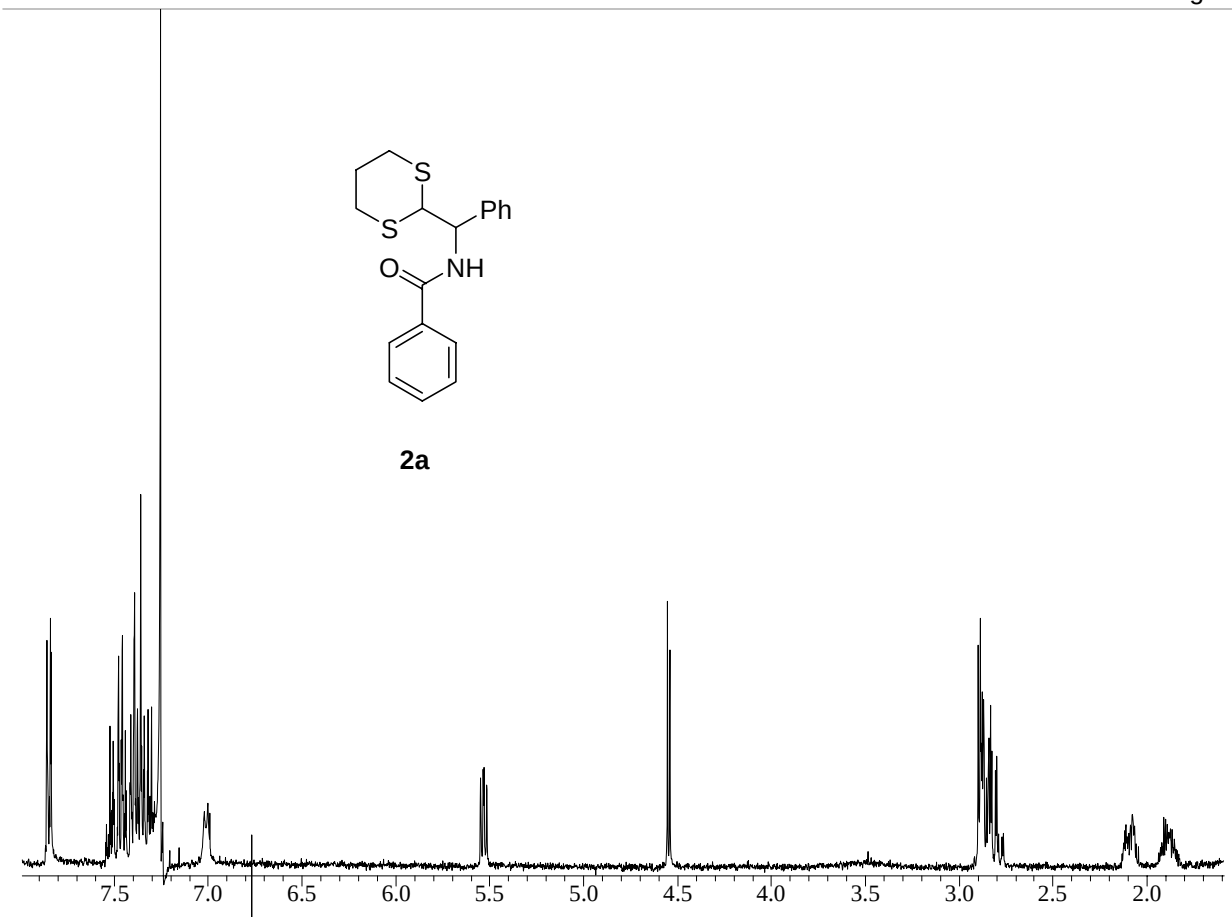
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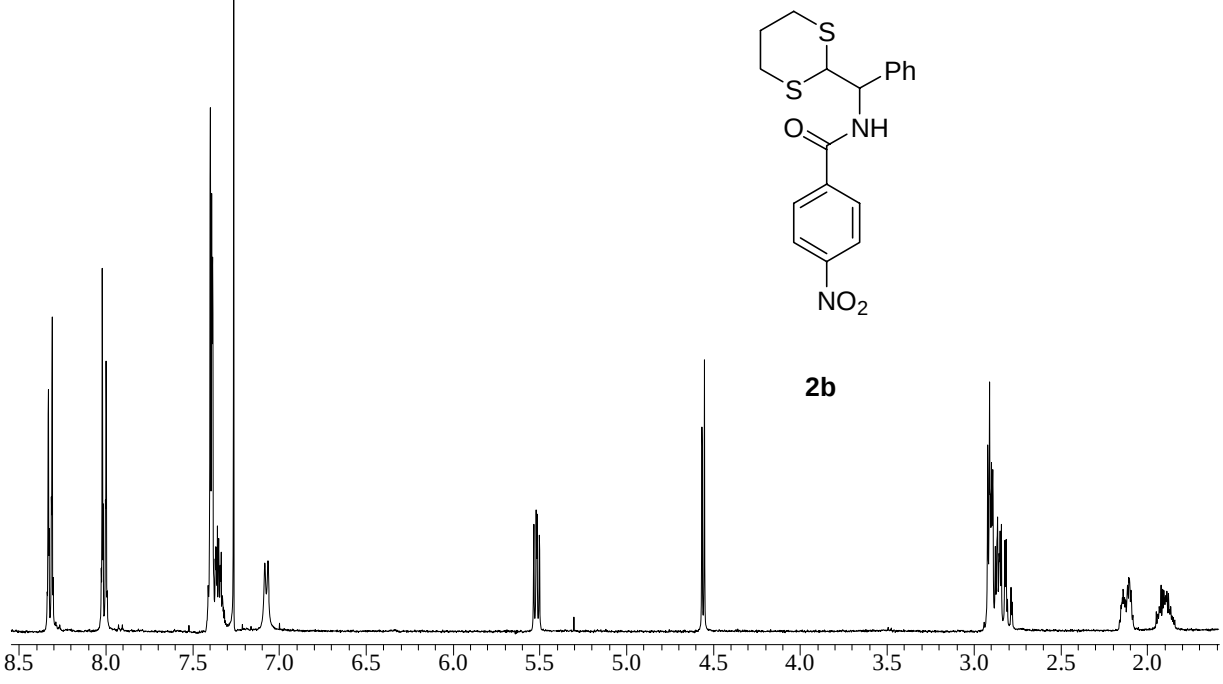
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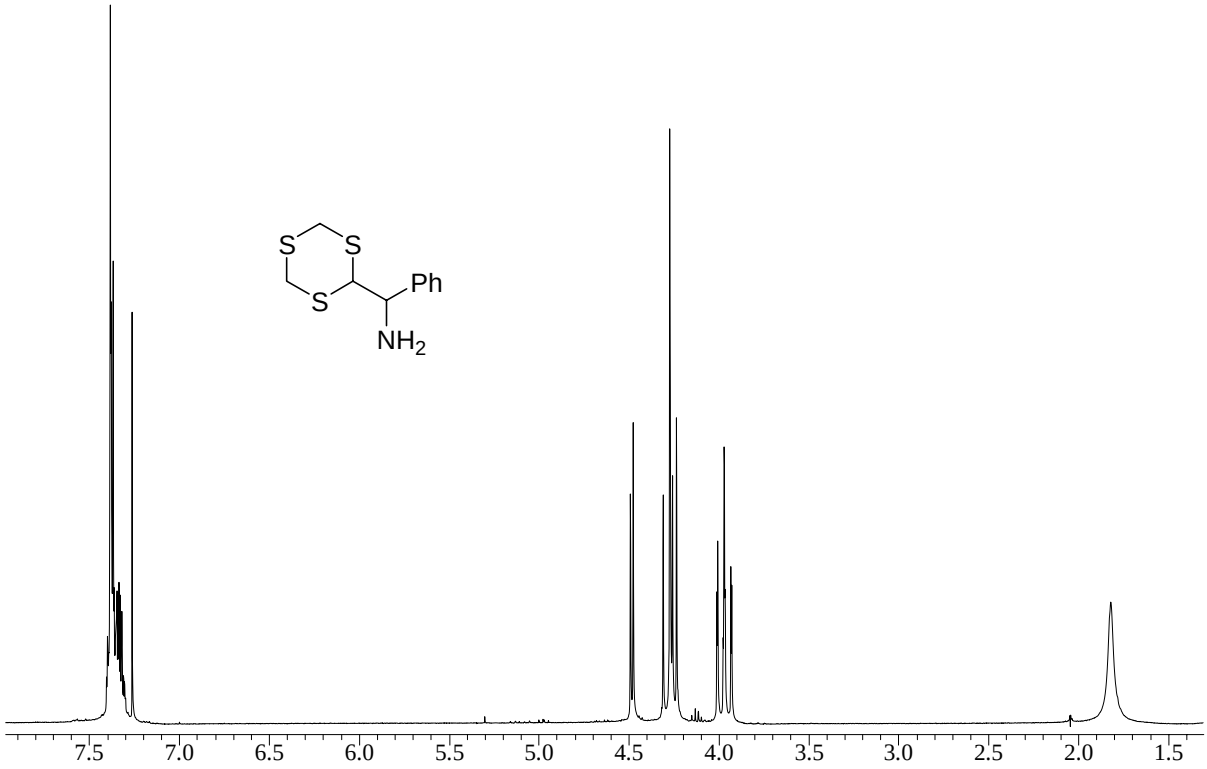
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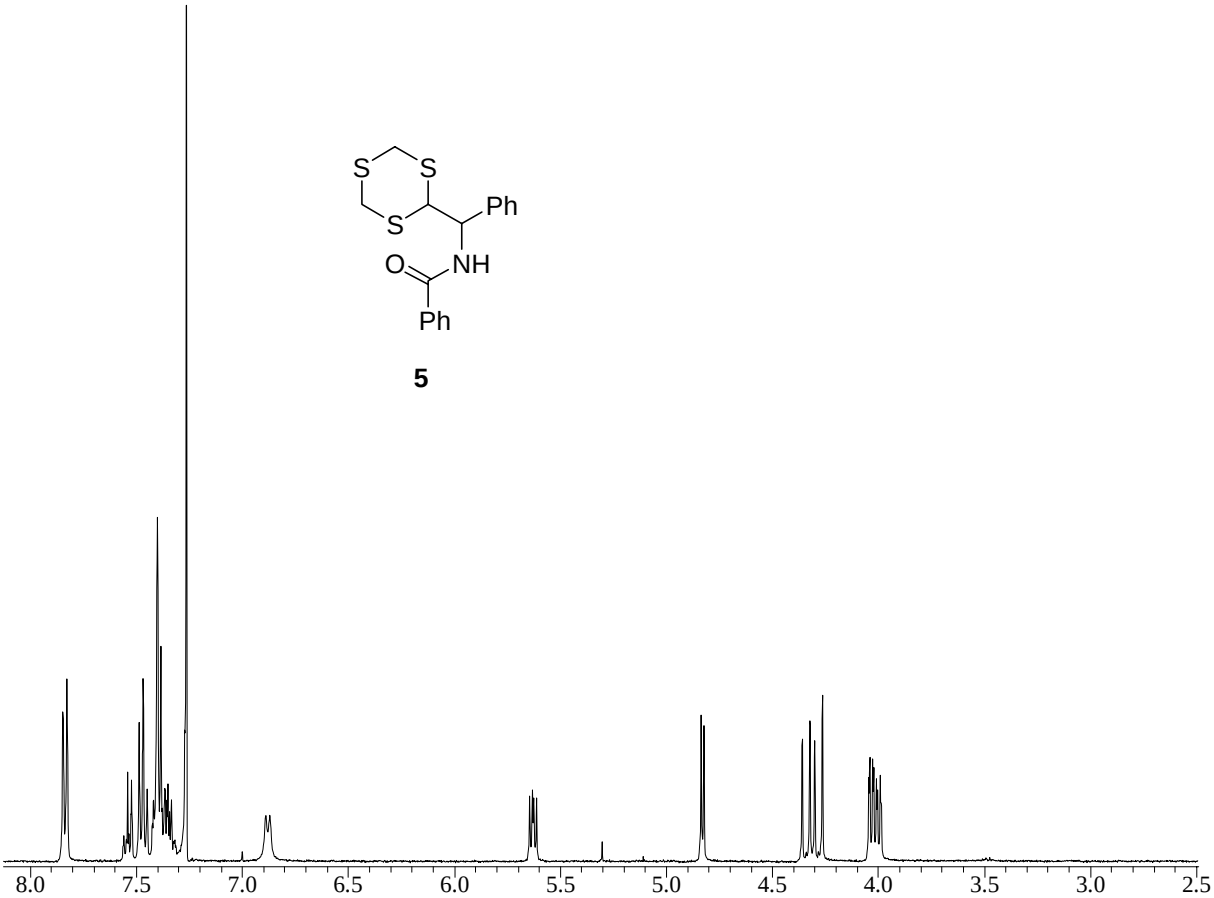
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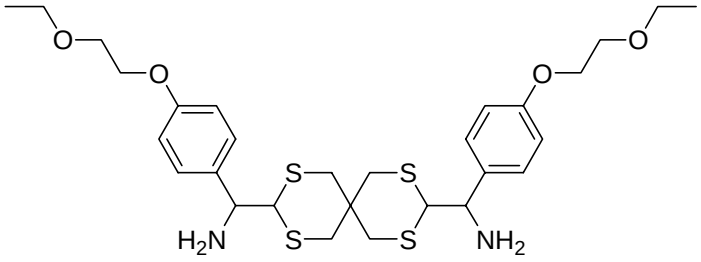
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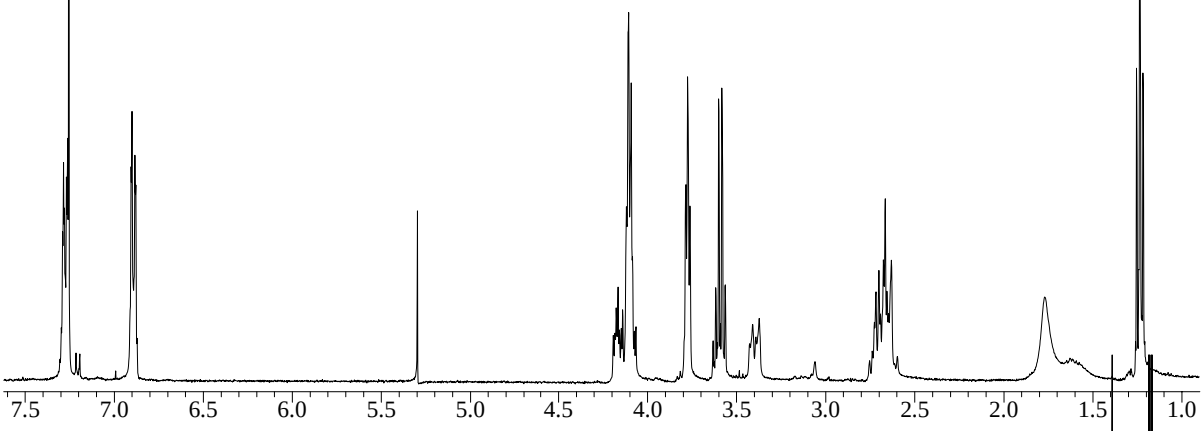
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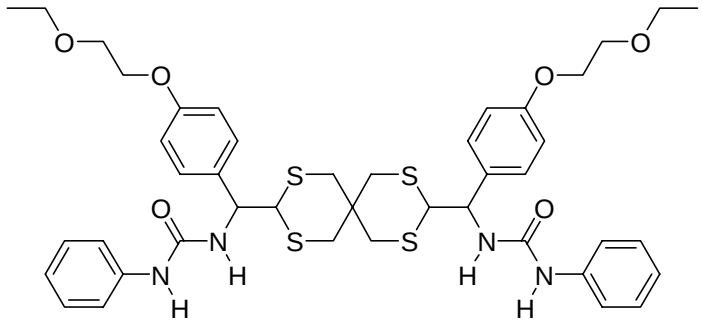
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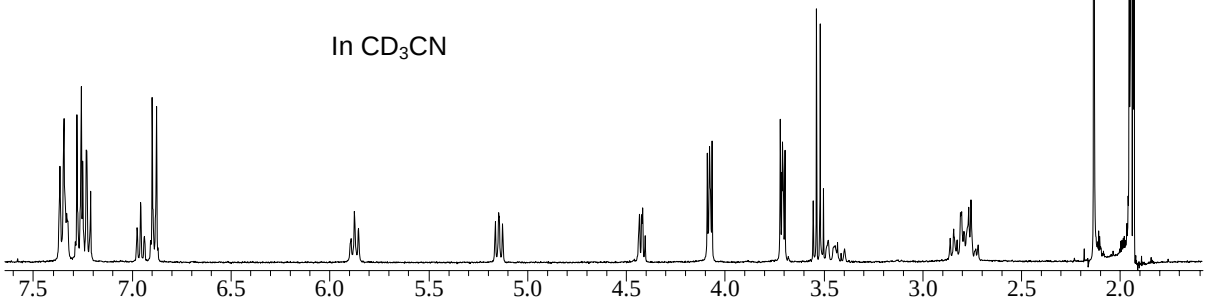
In CD_3CN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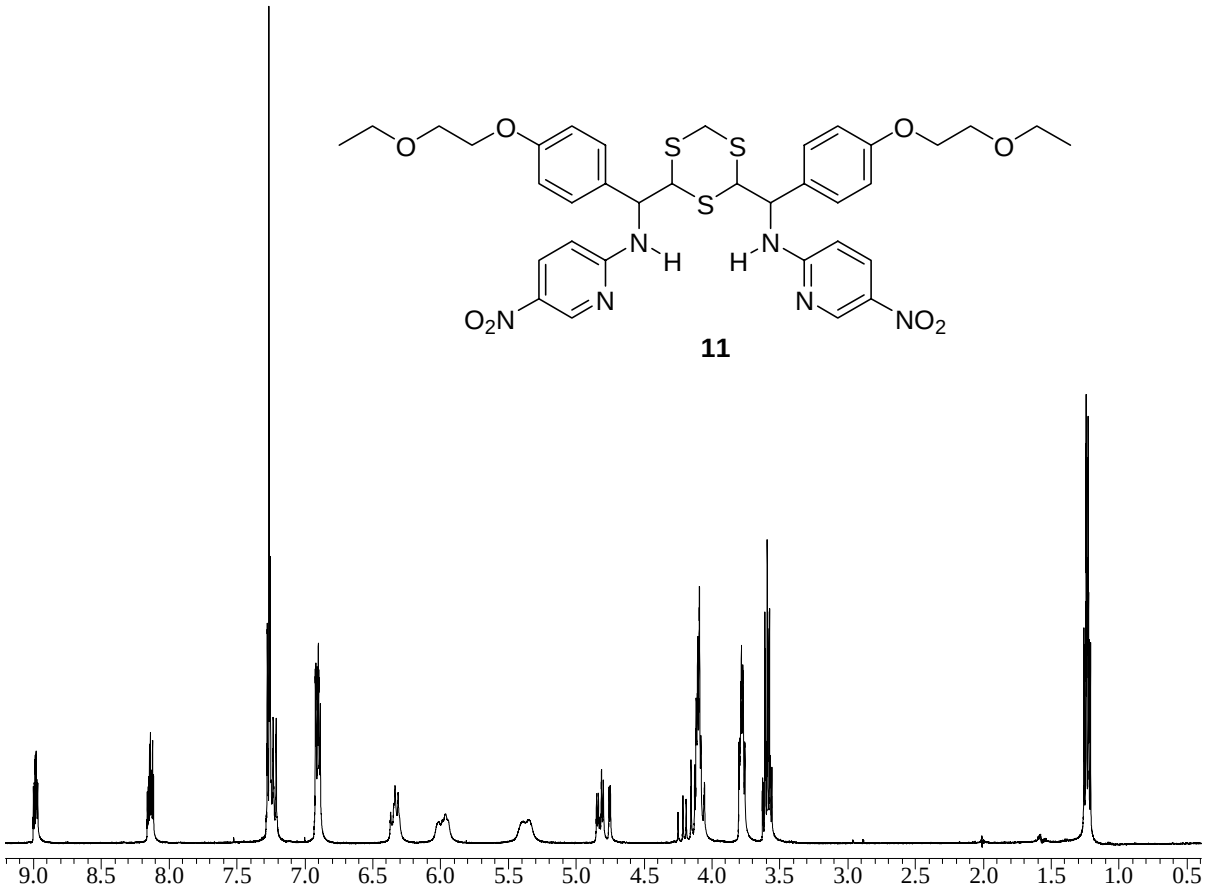

11

A typical NMR titration curve:

x/(1-x) vs free host concentration, [**11**] - *x* [imidazolidone]

K_D = 1000/31.075 = 32.18 mM