Supplementary Material (ESI) for Chemical Communications

Supporting informations

Cylindrical sheet formation of oligo-*meta*-aniline foldamers

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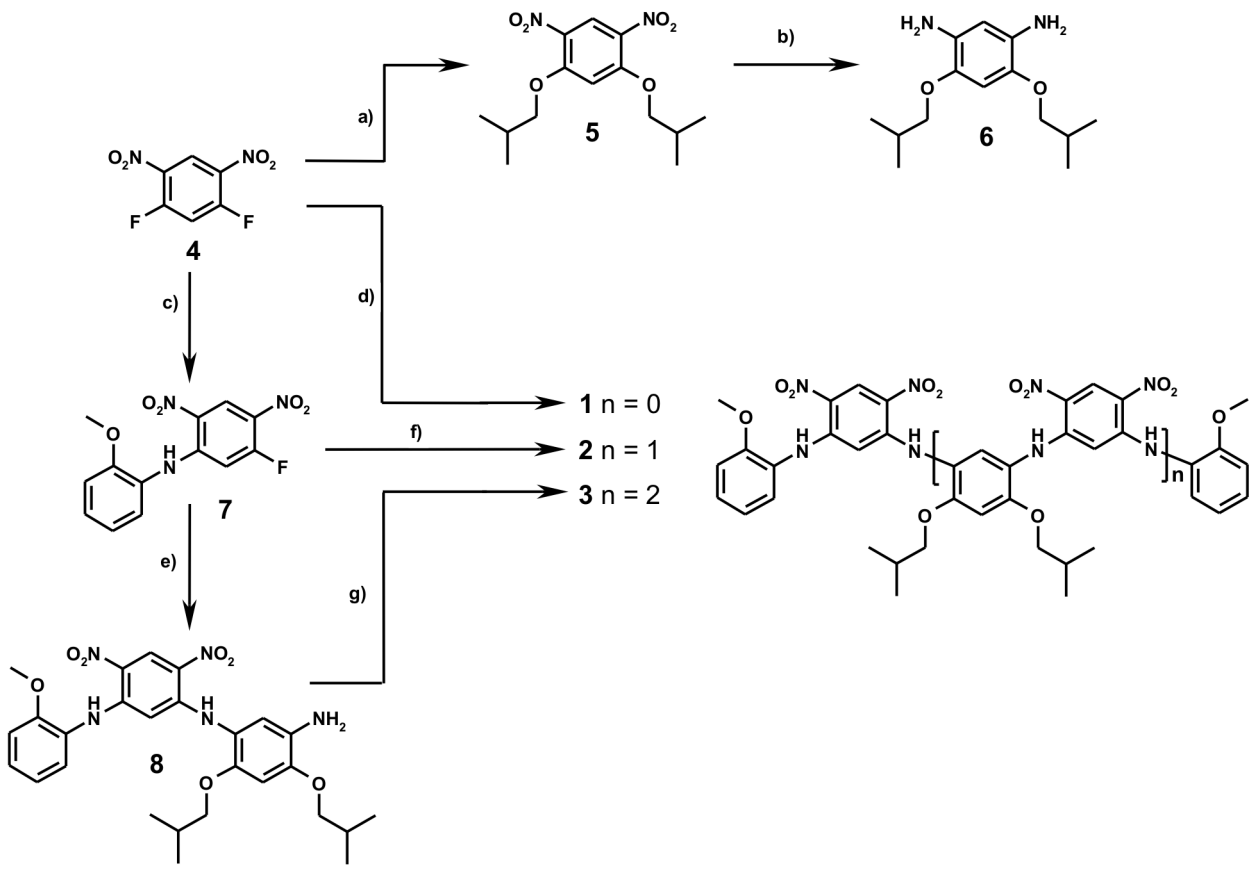
Synthesis



Synthesis of oligomers : a) 2-methylpropanol, K_2CO_3, DMF, RT, 5d, (65%); b) H_2, Pd/C, EtOAc, 24h, (quant.); c) *o*-anisidine, THF, RT, 4h, (96%); d) *o*-anisidine, *i*Pr_2NEt, DMSO, RT, 4h, (97%); e) **6**, DMSO, RT, 4h, (95%); f) **6**, *i*Pr_2NEt, DMSO, 40°C, 24h, (18%); g) **4**, *i*Pr_2NEt, DMSO, 60°C, 24h, (38%)

*Synthesis of **5***

6 g of 1,3-difluoro-4,6-dinitrobenzene (29.4 mmol, 1 eq.) were dissolved in 20 mL of DMF, 14 mL of 2-methylpropanol (150 mmol, 5 eq.) were added to the solution followed by 16 g of K_2CO_3 (90 mmol, 3 eq.). The mixture was stirred at room temperature for 5 days. 200 mL of diethylether was added to the solution and the organic phase was washed with water (4 x 100 mL). The organic phase was then dried over $MgSO_4$ and evaporated to give 6 g of a light brown solid (65%), that could be used without further purification.
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 8.78 (s, 1H, H5), 6.54 (s, 1H, H2), 3.95 (d, *J* = 6.5 Hz, 4H, CH_2), 2.24 (sept, *J* = 6.5 Hz, 2H, CH), 1.11 (d, *J* = 6.5 Hz,12H, CH_3).

^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 158.1, 130.7, 125.7, 98.4, 76.6, 28.2, 18.9.

HR-Mass (ESI) : m/z = 335.1216 Da $[M+Na]^+$ (Calculated $C_{14}H_{20}N_2O_6Na$: m/z = 335.1213)

*Synthesis of **6***

6 g (19.2 mmol) of **5** were dissolved in 100 mL of EtOAc containing 600 mg of 5% Pd/C (10% weight) and stirred under H_2 atmosphere. After 24 h, the solution was filtered and the filtrate was evaporated to give 4.8 g of **6** as a gray solid. *This product decomposed rapidly so this reaction was done just before **6** was needed and used without purification.*
^{1}H-NMR (300 MHz, $CDCl_3$) : δ =6.44 (bs, 1H, H_{ar}), 6.33 (s, 1H, H_{ar}), 3.61 (d, *J* = 6.5 Hz, 4H, CH_2), 2.09 (sept, *J* = 6.5 Hz, 2H, CH), 1.04 (d, *J* = 6.5 Hz, 12H, CH_3).

*Synthesis of **7***

1 g of 1,3-difluoro-4,6-dinitrobenzene (5 mmol, 1 eq.) was dissolved in 20 mL of THF and 570 µL of *o*-anisidine (5 mmol, 1 eq.) was added dropwise. The solution was stirred at room temperature for 4h. THF was then evaporated and the solid was suspended in water. After filtration, the solid was dried under vacuum to give 1.48 g of **7** (96%) as a light orange powder. That could be used without further purification.
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.84 (bs, 1H, NH), 9.17 (d, J_{H-F} = 7.8 Hz, 1H, H5), 7.37(t, *J* = 7.9 Hz, Har), 7.32(d, *J* = 7.9 Hz, Har), 7.07 (t, *J* = 7.9 Hz, Har), 7.04 (d, *J* = 7.9 Hz, Har), 6.75 (d, J_{H-F}= 13.5 Hz, H2), 3.87 (s, 3H, OCH_3).

^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 159.6 (d, J_{C-F} = 270 Hz), 153.4, 148.1, 147.9 129.0, 127.8 (d, J_{C-F} = 27 Hz), 127.6, 125.6, 124.8, 121.2, 112.1, 103.2 (d, J_{C-F} = 27 Hz), 55.8.

*Synthesis of **8***

1.48 g of **7** (4.82 mmol, 1 eq.) were dissolved in 10 mL of DMSO and 1.45 g (5.7 mmol, 1.2 eq) of freshly prepared **6** were added to the solution. The solution was stirred at room temperature for 4h. 10 mL of a saturated solution of $NaHCO_3$ were then added to the mixture. The precipitate was filtered off and washed with water. The brown solid was dried under vacuum and purified through a short plug of silica using DCM / EtOAc (9/1) as eluant to give 2.47 g of **8** (95%) as a dark purple solid.
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.75 (s, 1H), 9.61 (s, 1H), 9.33 (s, 1H), 7.31(d, 1H), 7.14 (t, 1H), 6.95 (t, 1H), 6.92 (d, 1H), 6.81 (bs, 1H, NH), 6.56 (bs, 1H, NH), 6.44 (s, 1H), 3.84 (s, 3H, OCH_3), 3.75 (d, 2H, OCH_2), 3.62 (d, 2H, OCH_2), 2.15 (sept, 1H, CH), 1.99 (sept, 1H, CH), 1.06 (d, 3H, CH_3), 0.93 (d, 3H, CH_3).

^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 152.5, 146.7, 145.8, 145.5, 145.4, 129.9, 129.2, 126.8, 126.5, 125.5, 125.4, 123.6, 120.3, 119.1, 111.6, 111.3, 99.7, 95.6, 76.2, 75.2, 55.7, 28.5, 28.3, 19.3, 19.2.
HR-Mass (ESI) : m/z = 540.2447 Da $[M+H]^+$ (Calculated $C_{27}H_{34}N_5O_7$: m/z = 540.2452)

*Synthesis of **1***

200 mg of 1,3-difluoro-4,6-dinitrobenzene (1 mmol, 1 eq.) were dissolved in 3 mL of DMSO and 250 µL of *o*-anisidine (2.2 mmol, 2.2 eq.) were added followed by 500 µL of *i*Pr_2NEt. The solution was stirred at room temperature for 24 h. Water was added to the solution and the precipitate was filtered, washed with water and dried under vacuum to afford 400 mg of **1** (97%) as an orange solid. *Crystals for X-ray analysis were grown by slow diffusion of MeOH to a nitrobenzene solution of **1**.*
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.75 (bs, 2H, NH), 9.35 (s, 1H, H6), 7.22 (d, *J* = 8 Hz, 2H, H4), 7.18 (t, *J* = 8 Hz, 2H, H2), 6.94 (d, *J* = 8 Hz, 2H, H1), 6.91 (t, *J* = 8 Hz, 2H, H3), 6.61 (s, 1H, H5), 3.84 (s, 6H, OCH_3)

^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 152.6, 146.2, 129.2, 127.0, 126.3, 125.7, 124.0, 120.5, 111.6, 95.6, 55.6.

Synthesis of **2**

40 mg of freshly prepared **6** (0.162 mmol, 1 eq.) were dissolved in 2 mL of DMSO, 100 mg of **7** (0.325 mmol, 2 eq.) and 250 mL of *i*Pr_2NEt (1.44 mmol, 9 eq.) were added to the mixture. The solution was stirred at 40°C for 24 h before EtOAc and water were added to the mixture. The organic phase was then washed extensively with water, dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography (SiO_2) using DCM / Heptane (8/2 → 10/0) to afford 50 mg of **2** (18%) as an orange solid. *Crystals for X-ray analysis were grown by slow diffusion of methanol to a chloroform solution of **2**.*
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.68 (bs, 4H, NH), 9.38 (s, 2H, H6), 7.08 (t, *J* = 8 Hz, 2H, H2), 7.06 (d, *J* = 8 Hz, 2H, H4), 7.05 (s, 2H, H7), 6.86 (d, *J* = 8 Hz, 2H, H1), 6.71 (t, *J* = 8 Hz, 2H, H3), 6.48 (s, 1H, H8), 6.40 (s, 2H, H5), 3.77 s, 6H, OCH_3), 3.70 (d, *J* = 6.5 Hz, 4H, OCH_2), 2.08 (sept, *J* = 6.5 Hz, 2H, CH), 0.99 (d, *J* = 6.5 Hz, 12H, CH_3).

^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 152.8, 151.1, 146.4, 146.0, 129.2, 127.3, 126.1, 125.7, 125.3, 124.1, 120.3, 119.3, 118.8, 111.7, 98.4, 95.2, 75.4, 55.6, 28.2, 19.1.

Synthesis of **3**

1g of **8** (1.85 mmol, 2.5 eq) was dissolved in 5 mL of DMSO. 150 mg of 1,3-difluoro-4,6-dinitrobenzene (0.74 mmol, 1 eq.) and 1mL of *i*Pr_2NEt (5.75 mmol, 7.5 eq.) were added to the mixture and stirred at 60°C for 48 h. EtOAc and water were added to the mixture. The organic phase was then washed extensively with water, dried over $MgSO_4$ and evaporated. The crude product was purified by two successive flash chromatographies (SiO_2) using DCM for the first purification and then toluene / EtOAc (95/5) for the second purification to afford 350 mg of **3** (38%) as an orange solid. *Crystals for X-ray analysis were grown by slow diffusion of Methanol to a chloroform solution of **3**.*
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.66 (s, 2H, NH1, 9.62 (s, 2H, NH2), 9.50 (s, 2H, NH3), 9.38 (s, 1H, H10), 9.30 (s, 2H, H6), 7.08 (t, *J* = 8 Hz, 2H, H2), 7,05 (d, *J* = 8 Hz, 2H, H4), 6.97 (s, 2H, H7), 6.85 (d, *J* = 8 Hz, H1), 6.69 (t, *J* = 8 Hz, H3), 6.48 (s, 2H, H8), 6.37 (s, 2H, H5), 6.01 (s, 1H, H9), 3.74 (s, 6H, OCH_3), 3.69 (d, *J* = 6.5 Hz, 4H, OCH_2), 3.62 (d, *J* = 6.5 Hz, 4H, OCH_2), 2.04 (sept, *J* = 6.5 Hz, 2H, CH), 1.96 (sept, *J* = 6.5 Hz, 2H, CH), 0.96 (d, *J* = 6.5 Hz, 12H, CH_3), 0.88 (d, *J* = 6.5 Hz, 12H, CH_3).

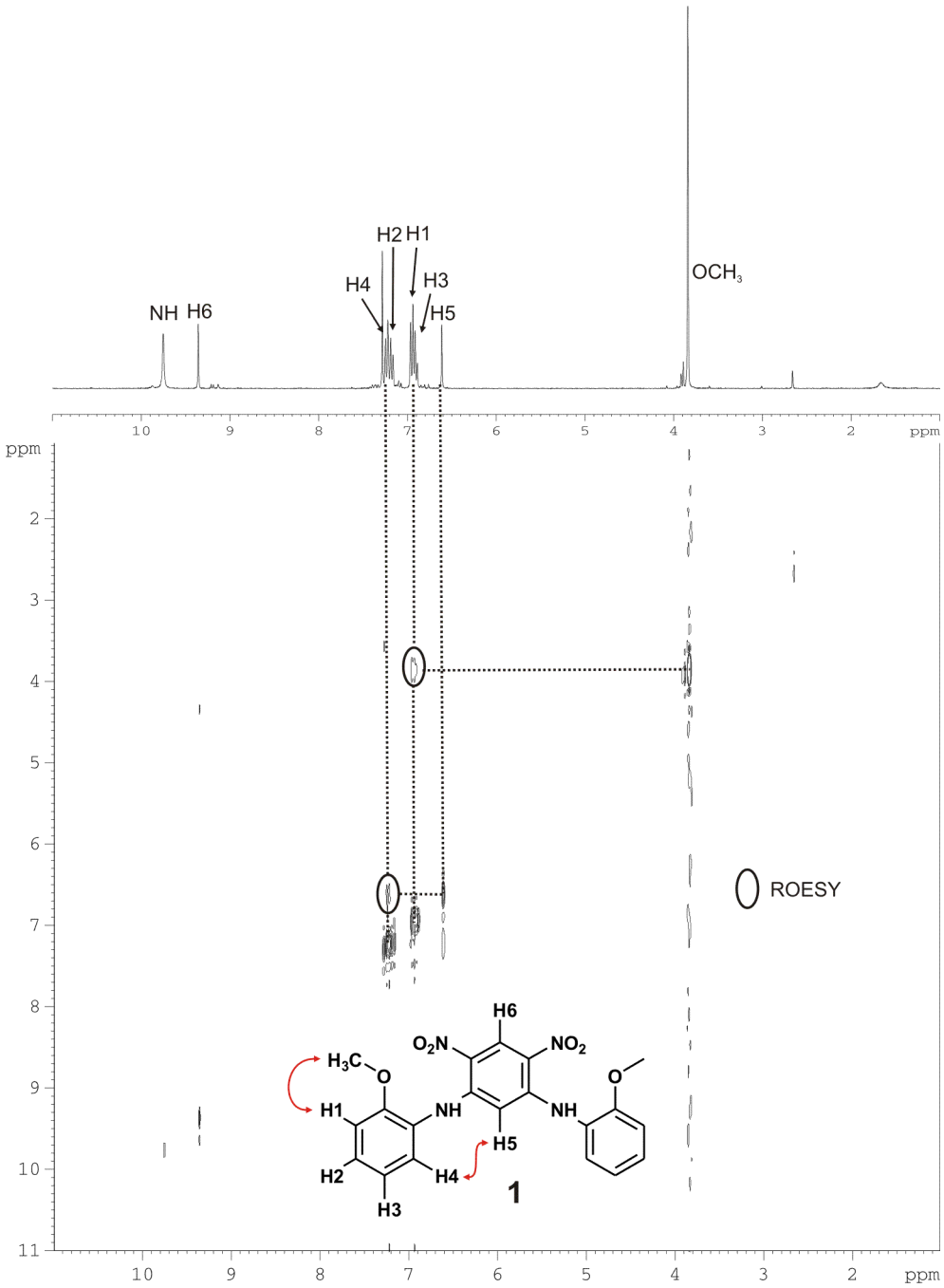
^{13}C-NMR (300 MHz, $CDCl_3$) : δ = 152.7, 151.6, 151.6, 146.3, 146.2, 146.0, 129.2, 127.3, 126.1, 125.7, 125.3, 125.2, 124.0, 120.3, 120.2, 119.2, 118.2, 111.7, 99.9, 98.6, 95.1, 75.7, 75.4, 55.6, 28.3, 28.2, 19.0.

NMR Experiments

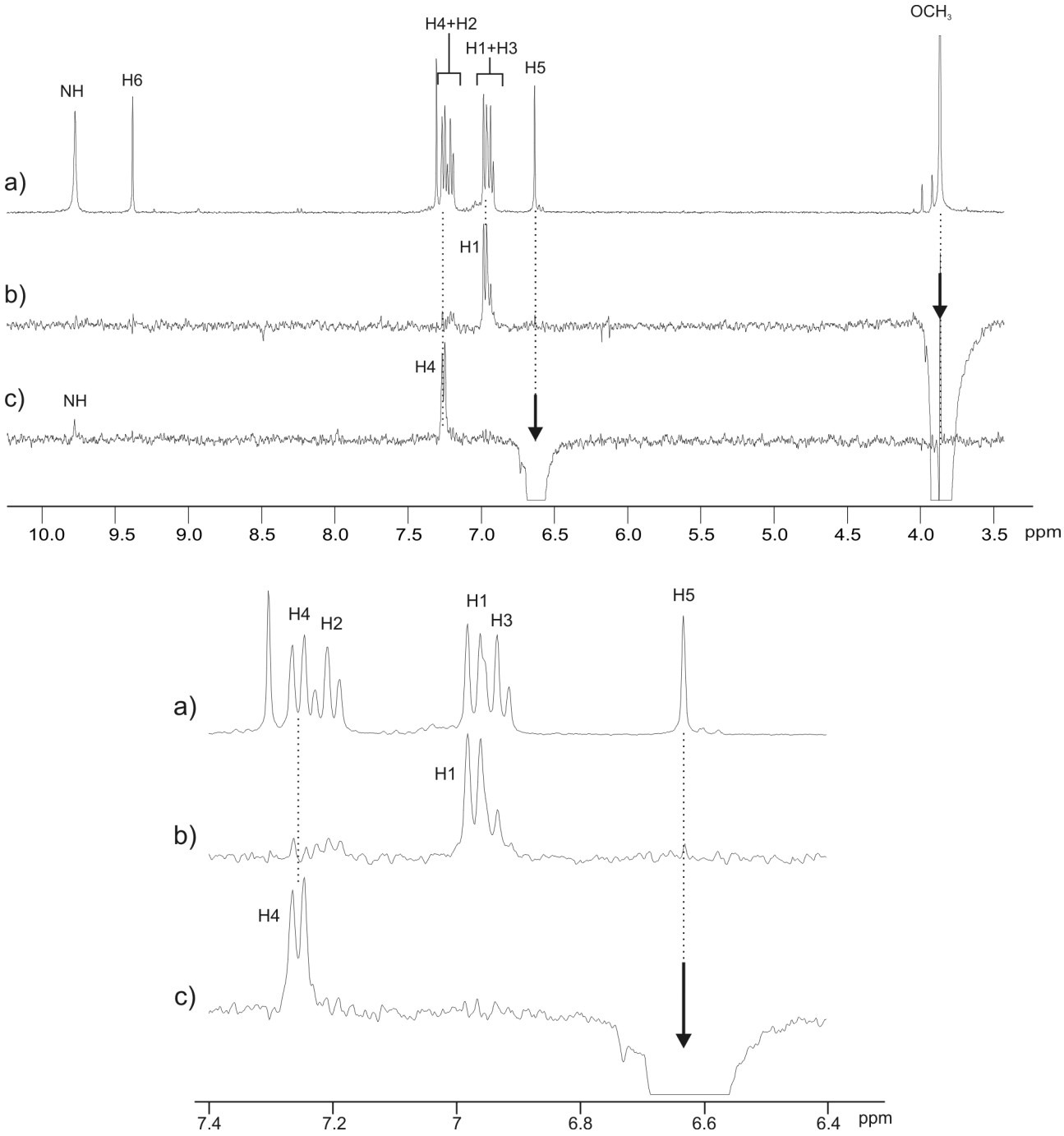
2D Roesy experiment were recorded on a Bruker Avance 300 MHz Spectrometer at 298 K, using a mixing time of 200 µs.

Selective 1D Roesy experiments were recorded on a Avance Bruker 400MHz spectrometer at 300K, using a mixing time of 200 ms. 2D Roesy experiment of **1**

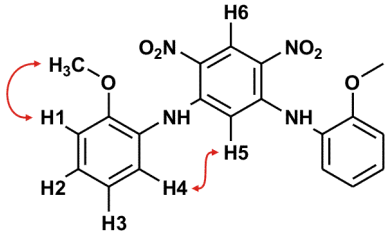
*2D Roesy experiment of **1***



*Selective 1D Roesy experiment of **1***

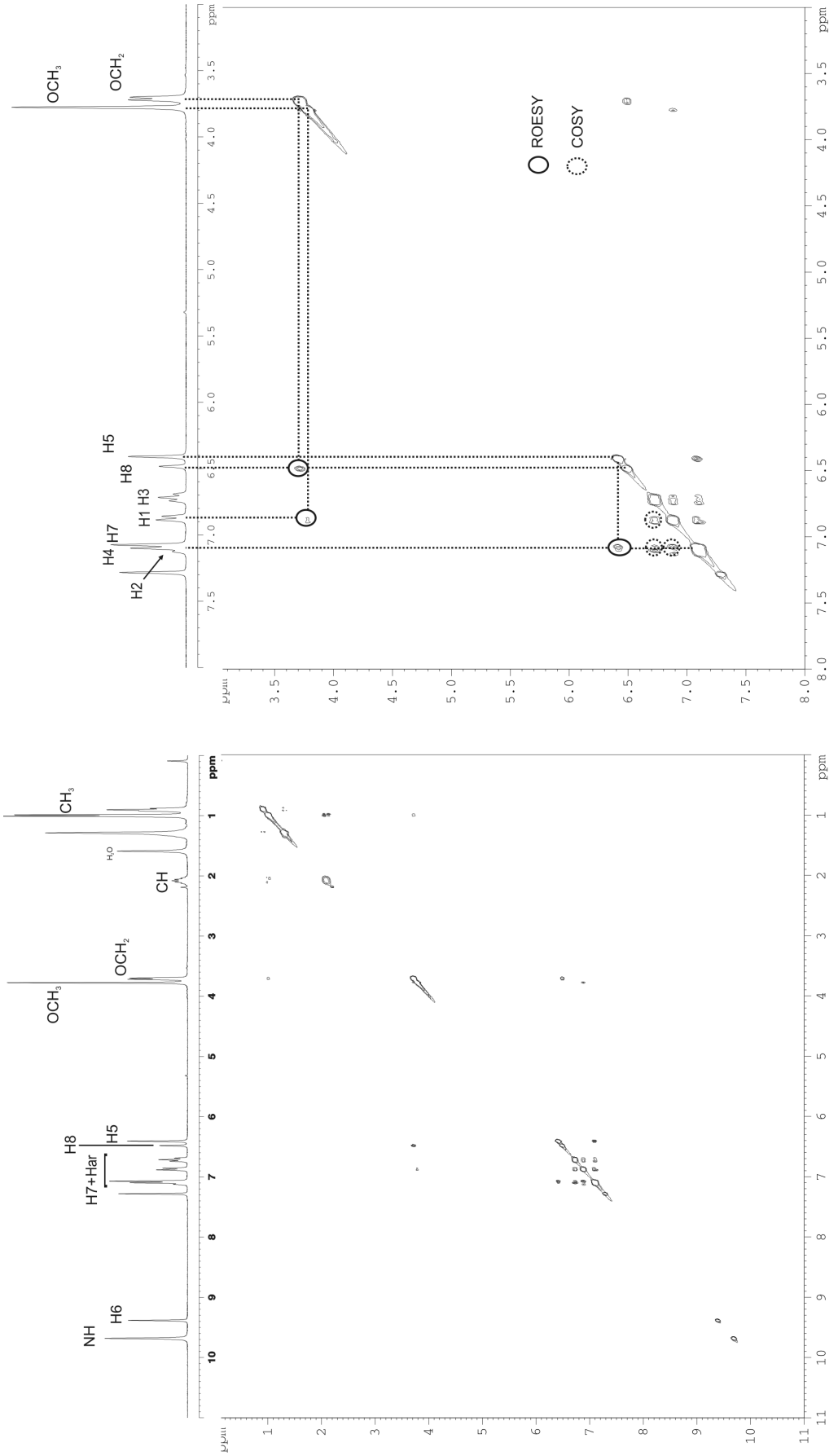


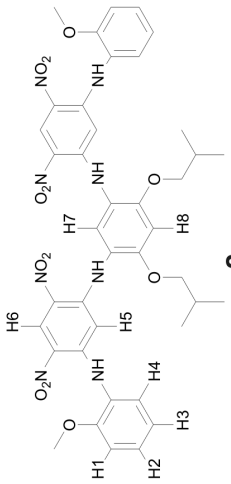
Full spectra (on top) and closed up of the aromatic region (above) : (a) ^{1}H NMR spectrum, (b) Selective irradiation of the methoxy signal, (c) selective irradiation of H5 signal. (arrows indicate the signal that was irradiated)



Representation of the observed ROE correlations

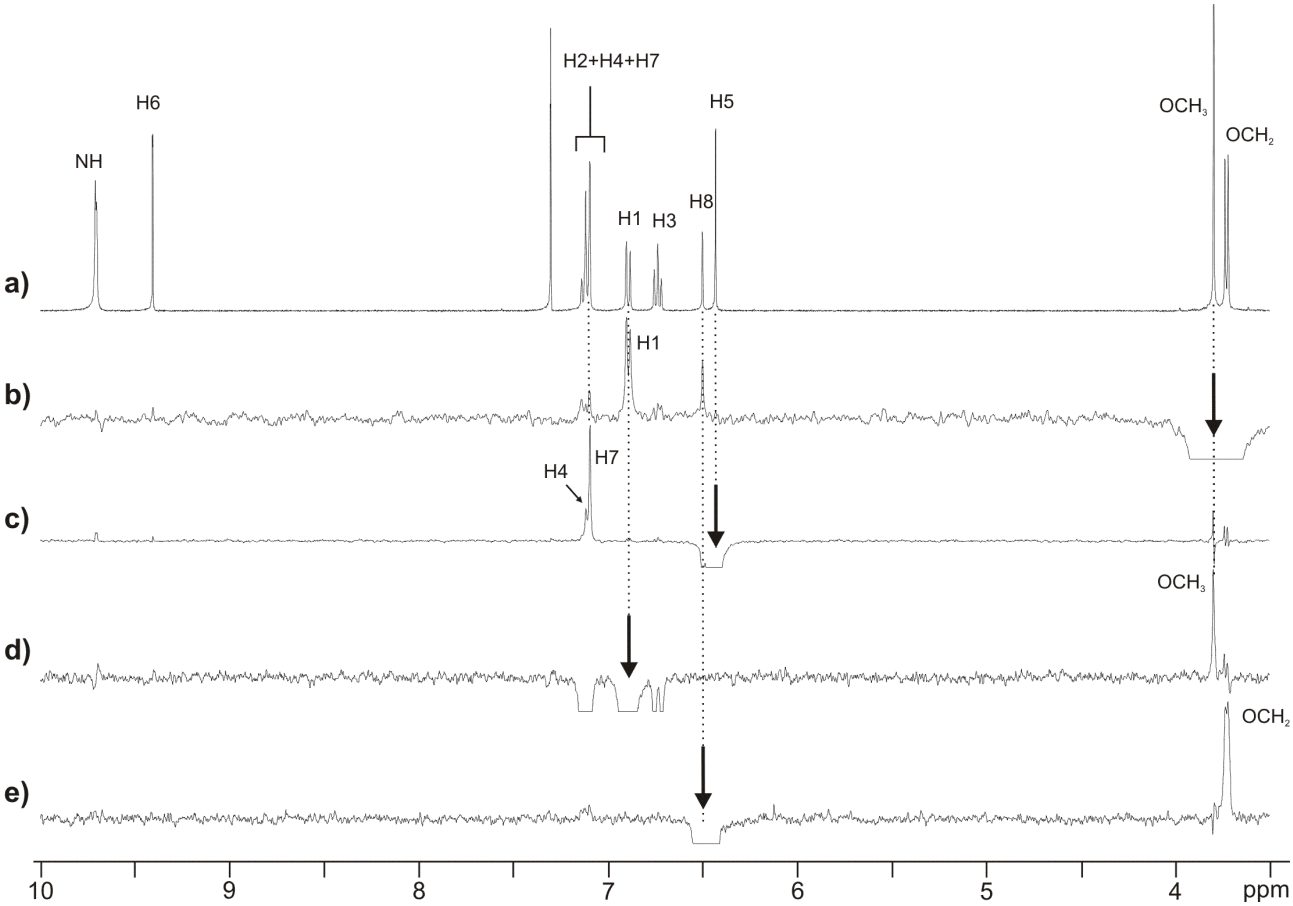
*2D Roesy experiment of **2***



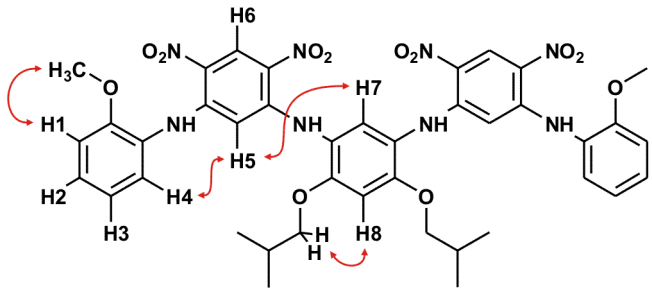


2

*Selective 1D Roesy experiment of **2***

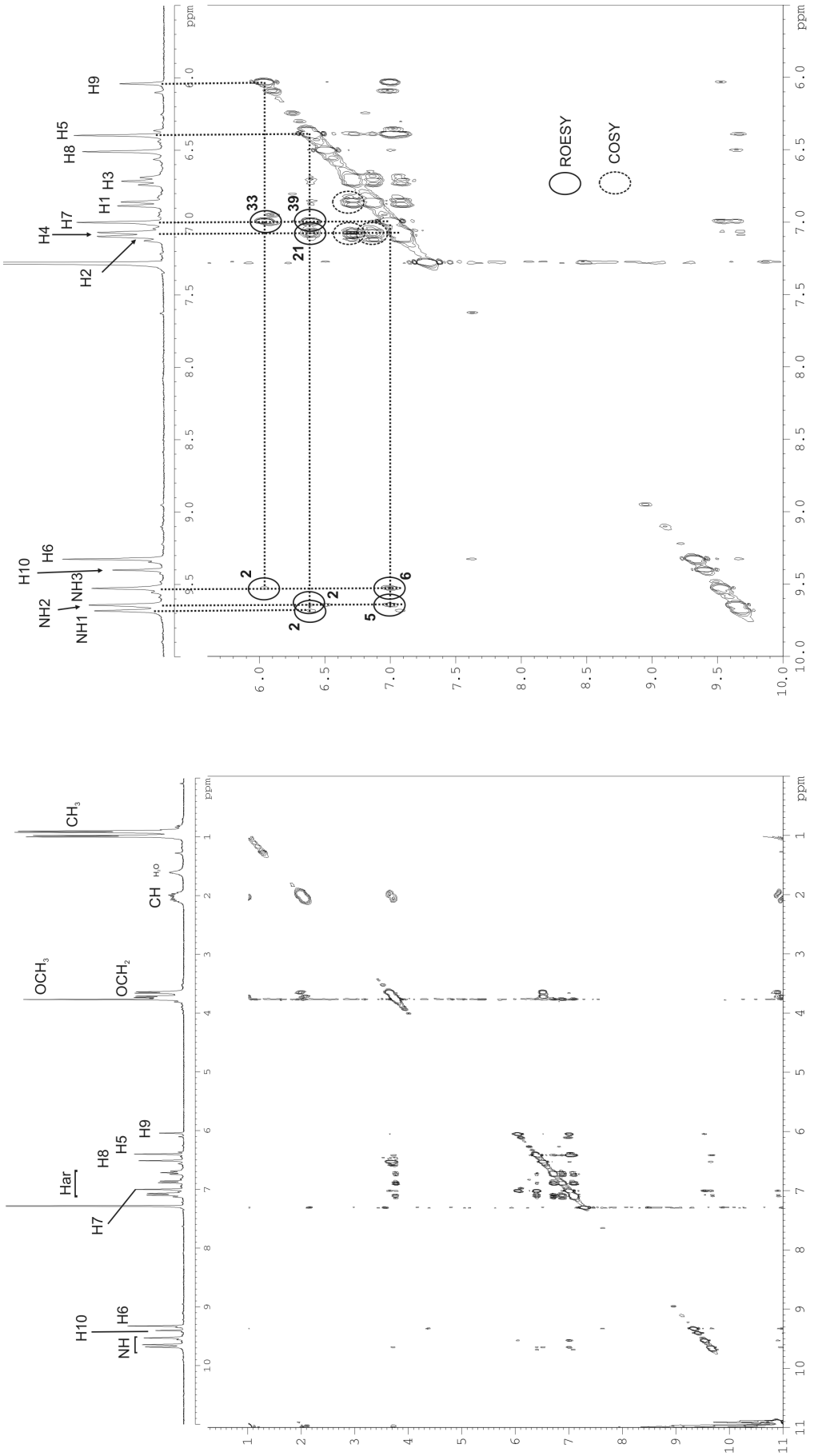


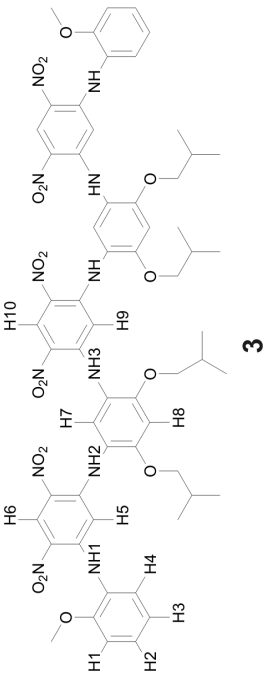
(a) ^{1}H NMR spectrum, (b) Selective irradiation of the methoxy signal, (c) selective irradiation of H5 signal, (d) selective irradiation of H1 signal, (e) selective irradiation of H8 signal. (arrows indicate the signal that was irradiated)



Representation of the observed ROE correlations

*2D Roesy experiment of **3***

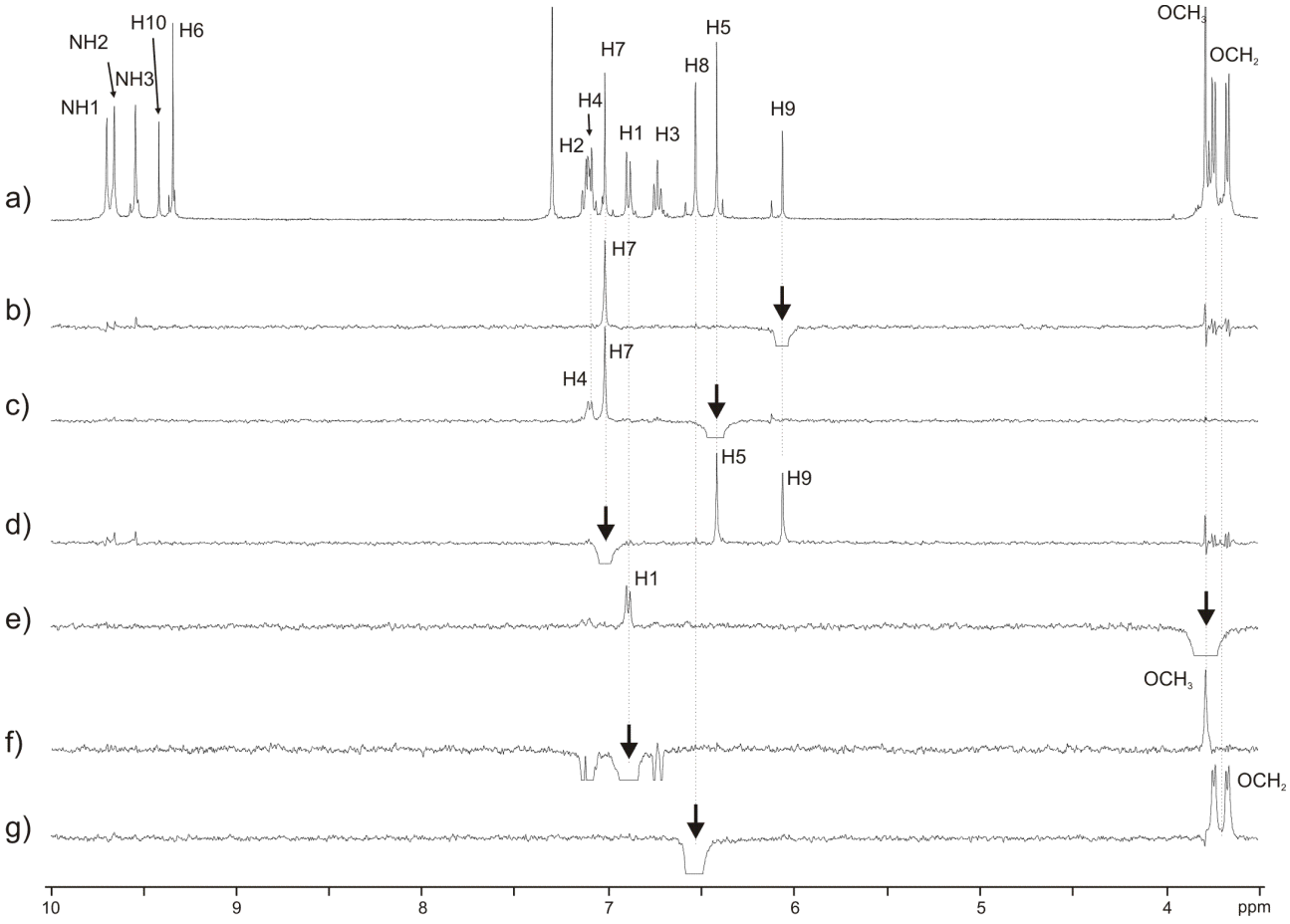




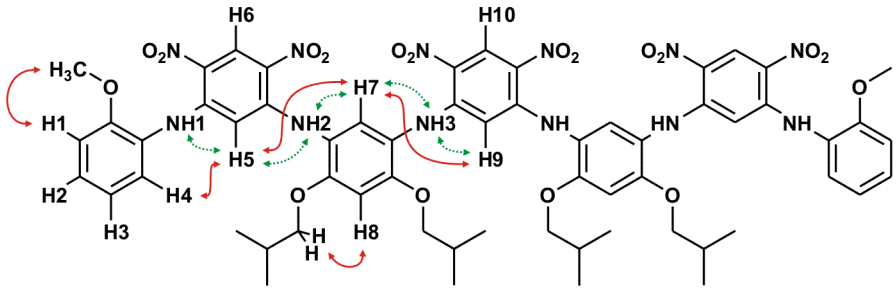
3

Values indicated on the spectrum are integration values of ROESY cross peaks.

*Selective 1D Roesy experiment of **3***



a) ^{1}H NMR spectrum, (b) selective irradiation of H9 signal, (c) selective irradiation of H5 signal, (d) selective irradiation of H7 signal, (e) selective irradiation of the methoxy signal, (f) selective irradiation of H1 signal, (g) selective irradiation of H8 signal. (arrows indicate the signal that was irradiated)



Representation of the observed ROE correlations. Red arrows show strong NOE correlations compatible with a folded organization. Green dashed arrows show very weak NOE correlations compatible with an unfolded conformation

1,3-diaminophenyl-4,6-dinitrobenzene.

Synthesis

100 mg of 1,3-difluoro-4,6-dinitrobenzene (0.5 mmol, 1 eq.) were dissolved in 3 mL of DMSO and 150 µL of aniline (1.5 mmol, 3 eq.) were added followed by 200 µL of *i*Pr_2NEt. The solution was stirred at room temperature for 4 h. Water was added to the solution and the precipitate was filtered, washed with water and dried under vacuum to give 150 mg of the desired product (85%) as an orange solid.

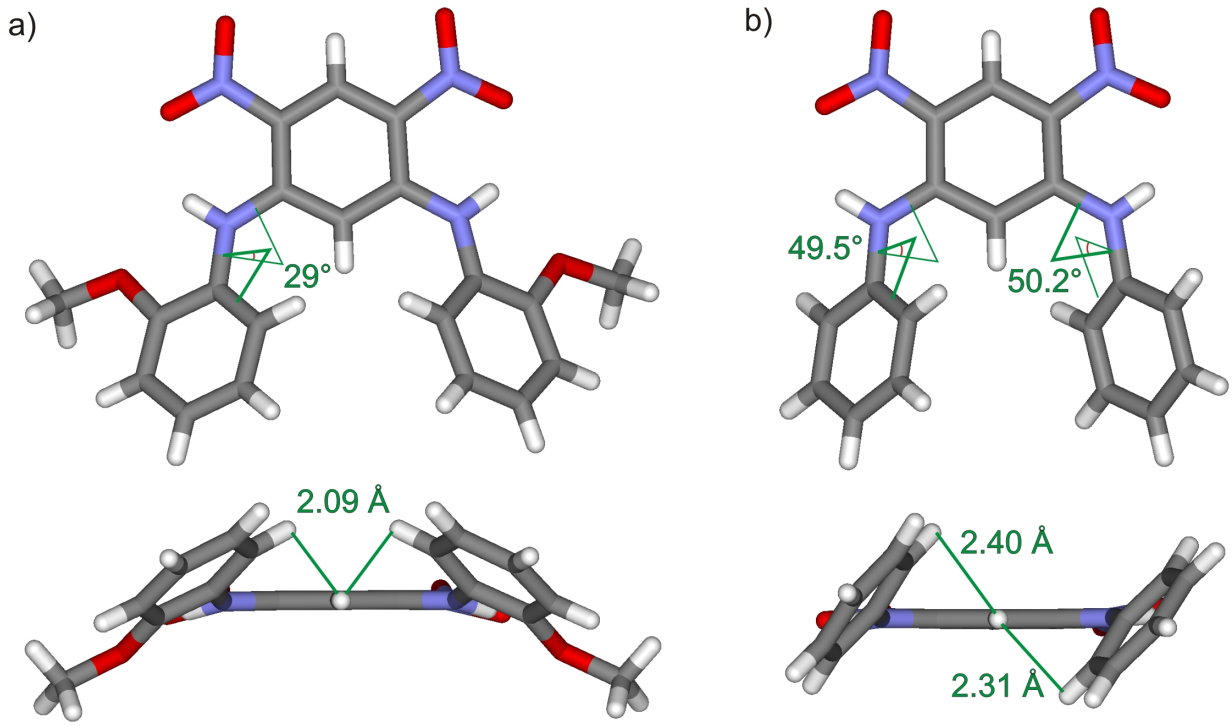
^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 9.75 (bs, 2H, NH), 9.34 (s, 1H, H6), 7.39–7.29 (m, 4H), 7.23–7.11 (m,6H), 6.75 (s,1H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 146.7, 137.0, 129.5, 129.2, 126.6, 125.3, 124.6, 95.2.

Crystal structure

Crystals for X-ray analysis were grown by slow diffusion of MeOH to a nitrobenzene solution of 1,3-diaminophenyl-4,6-dinitrobenzene

$C_{18}H_{14}N_4O_4$, *M = 360.41,* Monoclinic, Space Group *P21/c, a* = 10.952(6) Å, *b* = 11.007(3) Å, *c = 14.*736(5) Å, *α = 90°, β = 109.90(3)°, γ = 90°, V* = 1670.3(12) Å^3, *T* = 293(2) K, *Z* = 4, *Wavelength* = 0.154180 nm, *reflections measured* = 3100, 3100 unique, final R indices were R_1 *(I > 2σ(I))* = 0.0433, *wR2 (all data)* = 0.1224.



X-Ray crystal structures of (a) ***1*** *and (b) 1,3-diaminophenyl-4,6-dinitrobenzene. Torsion angles and distances are mentioned in green in the figure.*