Supplementary Data

Macrocyclic oligoureas with xanthene and diphenyl ether units

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Experimental details.

All solvents were of analytical quality (p. a.) and were used without additional purification. Deuterated solvents for NMR were purchased from Deutero GmbH. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400 MHz using the solvent signals as internal reference. Mass spectra were recorded with the Finnigan MAT 8230 instrument. The melting points were not corrected.

Diamine 3 (XDX).

A solution of the monoprotected diamine **1** (1.20 g, 0.265 mmol) in chloroform (15 cm^3) was added to the solution of diisocyanate **2** (341 mg, 0.135 mmol) in chloroform (15 cm^3). After 12 h of stirring under nitrogen the solvent was removed under reduced pressure yielding the BOC-protected trimeric diamine as a yellowish oil. The crude product was triturated with acetonitrile (20 cm^3) and a white powder was filtered off. The crude diurea was dissolved in dichloromethane (10 cm^3), cooled in an ice bath and then trifluoroacetic acid (10 cm^3) was added. The mixture was allowed to warm up to room temperature during the next 4 h of stirring. The reaction was stopped by pouring the mixture slowly to a 5 N solution of sodium carbonate (100 cm^3). The pH of the solution was adjusted to 9-10. The organic layer was separated, the aqueous layer was washed with dichloromethane (2x25 cm^3), and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure yielding diamine **3** (1.133 g, 89%) as a brown powder; mp 200-208°C; δ_H (400 MHz, DMSO-d_6): 9.18 (2 H, s, N*H*), 8.93 (2 H, s, N*H*), 8.30 (2 H, dd, ^3J 8.2, ^4J 1.2, ArH_{diph}), 8.10 (2 H, d, *J* 2.0, ArH_{xan}), 7.14 (2 H, t, *J* 8.0, ArH_{diph}), 7.09 (2 H, d, *J* 2.4, ArH_{xan}), 7.01 (2 H, t, *J* 8.2, ArH_{diph}), 6.84 (2 H, d, *J* 7.8, ArH_{diph}), 6.64 (2 H, d, *J* 2.4, ArH_{xan}), 6.48 (2 H, d, *J* 2.0, ArH_{xan}), 5.07 (4 H, s, NH_2), 1.53 (12 H, s, CH_3), 1.26 (18 H, s, *tBu*), 1.20 (18 H, s, *tBu*); *m/z* (ESI) 980.3 ([M + Na]$^+$, 100%).

Diisocyanate 5 (XDX).

A solution of the diamine **3** (102 mg, 0.11 mmol) with di-*i*-propylethylamine (28 mg, 0.22 mmol) in THF/dichloromethane (25 mL, 1:1 vol.) was added dropwise to a solution of triphosgene (32 mg, 0.11 mmol) in acetonitrile (25 mL) with stirring under nitrogen. After 3 h the reaction mixture was filtered through silica gel which subsequently was washed with dichloromethane/ethylacetate (1:1 vol, 3x25 mL.). The solvent was removed under reduced pressure and the crude product was heated on a rotavap for 1 h at 80°C to remove excess triphosgene. After cooling the diisocyanate **5** was isolated as a white solid (99%, 107 mg). m.p. >185-188°C (decomp.). δ_H (400 MHz, DMSO-d_6): 8.73 (2 H, s, N*H*), 8.60 (2 H, s, N*H*), 8.19 (2 H, d, *J* 7.8, ArH_{diph}), 7.66 (2 H, s, ArH_{xan}), 7.66 (2 H, s, ArH_{xan}), 7.33 (2 H, s, ArH_{xan}), 7.10 (2 H, t, *J* 7.8, ArH_{diph}), 6.97 (2 H, t, *J* 7.8, ArH_{diph}), 6.93 (2 H, s, ArH_{xan}), 6.80 (2 H, d, *J* 7.8, ArH_{diph}), 1.57 (12 H, s, CH_3), 1.24 (18 H, s, *tBu*), 1.23 (18 H, s, *tBu*);

Diamine 6 (XXDXX).

A solution of the diamine **3** (800 mg, 0.84 mmol) in chloroform (20 mL) was added to a solution of the isocyanate **4** (800 mg, 0.17 mmol) in chloroform (20 mL) with stirring under nitrogen. After 18 h the solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (10 mL), trifluoroacetic acid (10 mL) was added and the mixture was stirred for the next 3 h. To stop the reaction it was poured slowly to a solution of sodium carbonate (5N, 200 mL). The pH was adjusted to 9-10, the organic layer was separated, and the aqueous layer was washed with dichloromethane (2×25 mL). The combined dichloromethane solutions were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude brown solid was triturated with methanol yielding the dimeric diamine **6** (0.89 g, 62%) as a white powder. m.p. 232-238°C; δ_H (400 MHz, DMSO-d_6): 8.92 (2 H, br s, N*H*), 8.75 (4 H, br s, N*H*), 8.37 (2 H, br s, N*H*), 8.04 (2 H, d, *J* 2.0, ArH_{xan}), 7.91 (2 H, s, ArH_{xan}), 7.87 (2 H, s, ArH_{xan}), 7.81 (2 H, br s, ArH_{diph}), 7.21 (2 H, s, ArH_{xan}), 7.12 (2 H, s, ArH_{xan}), 7.11 (2 H, d, *J* 2.0, ArH_{xan}), 7.07 (2 H, d, *J* 2.0, ArH_{xan}), 6.77 (2 H, br t, *J* 7.8, ArH_{diph}), 6.61 (2 H, s, ArH_{xan}), 6.26-6.18 (4 H, m, *J* 7.8, ArH_{diph}), 6.11 (2 H, s, ArH_{xan}), 4.69 (4 H, br s, NH_2), 1.58 (12 H, s, CH_3), 1.49 (12 H, s, CH_3), 1.27 (18 H, s, *tBu*), 1.22 (18 H, s, *tBu*), 1.20 (18 H, s, *tBu*), 1.13 (18 H, s, *tBu*); *m/z* (ESI) 1737.4 ([M + Na]$^+$, 100%).

Diisocyanate 7 (XXDXX).

A solution of the diamine **6** (103 mg, 0.060 mmol) with di-*i*-propylethylamine (18 mg, 0.12 mmol) in THF (20 mL) was added dropwise to a solution of triphosgene (16 mg, 0.60 mmol) in THF (10 mL) with stirring under nitrogen. After 3 h the reaction mixture was filtered through silica gel which subsequently was washed with ethylacetate (3x15 mL). The solvent was removed under reduced pressure and the crude product was heated on a rotavap for 1 h at 80°C to remove excess triphosgene. After cooling the diisocyanate **7** was isolated as a glass-like solid (95%, 100 mg). The ^{1}H NMR spectrum in $CDCl_3$ is broadened and unclear; m.p. >212-218°C (decomp.).

Cyclic octamer 8 (XXXDXXD).

The diamine **6** (XXDXX, 42 mg, 0.025 mmol) was dissolved in dichloromethane/THF (1:1 vol., 20 mL) and added with stirring under

nitrogen to a solution of the diisocyanate **5** (XDX, 26 mg, 0.026 mmol) in THF (20 mL). Then the reaction mixture was diluted with acetonitrile (30 ml). After 18 h the solvent was removed under reduced pressure. A crude product was dissolved in methanol and the solution was cooled to 0°C for the next 24 h. A white powder of the octamer **8** was filtered off (36%, 24 mg). m.p. > 244-253°C (decomp.). δ_H (400 MHz, THF-d_8): 9.36 (2 H, s), 8.75 (2 H, s), 8.72 (2 H, s), 8.44 (2 H, s), 8.32-8.28 (6 H, m), 7.92 (2 H, s), 7.80 (4 H, s), 7.69 (4 H, s), 7.65 (2 H, s), 7.51 (d, 2 H, *J* 7.8, ArH_{diph}), 7.19 (2 H, s), 7.10 (2 H, s), 7.02-7.00 (4 H, m), 6.97 (2 H, s,), 6.94-6.90 (6 H, m), 6.65-6.61 (6 H, m), 6.31 (d, 2 H, *J* 7.8, ArH_{diph}), 6.02 (t, 2 H, *J* 7.8, ArH_{diph}), 5.92 (d, 2 H, *J* 8.2, ArH_{diph}), 5.45 (t, 2 H, *J* 7.8, ArH_{diph}), 1.80 (6 H, s, CH_3), 1.33 (12 H, s, CH_3), 1.30 (18 H, s, *tBu*), 1.31 (18 H, s, *tBu*), 1.28 (18 H, s, *tBu*), 1.27 (18 H, s, *tBu*), 1.23 (18 H, s, *tBu*) 1.20 (6 H, s, CH_3), 1.01 (18 H, s, *tBu*), 0.65 (18 H, s, *tBu*); *m/z* (ESI) 1384.3 ($[M+2Na]^{2+}$, 77.2%), 2745.6 ($[M+Na]^+$, 100%).

Cyclic decamer 9 (XXXXDXXXXD).

The diamine **6** (XXDXX, 68 mg, 0.04 mmol) was dissolved in THF (10 mL) and added with stirring under nitrogen to a solution of the diisocyanate **7** (XXDXX, 70 mg 0.041 mmol) in chloroform (7 mL). After 18 h the solvent was removed under reduced pressure. A crude product was dissolved in ethanol and the solution was cooled to 0°C for the next 24 h. A white powder of the decamer **9** was filtered off (18%, 25 mg). m.p. 260-267°C. δ_H (400 MHz, DMSO-d_6, in the presence of 10 equivalents of TBA chloride): 9.11 (4 H, br s), 8.86 (4 H, br s), 8.62 (4 H, br s), 8.40 (4 H, br s), 7.96 (4 H, br s), 7.81 (4 H, br s), 7.78 (4 H, br s), 7.59 (4 H, s), 7.18 (4 H, br s), 7.10 (4 H, s), 6.95-6.85 (24 H, m), 6.69 (4 H, br s); alkyl signals are overlapped with signals of the tetrabutylamonium ion; *m/z* (ESI) 1762.9 ($[M+2Na+CH_3OH]^{2+}$, 100%), 3502.9 ($[M+Na+CH_3OH]^+$, 3.1%).

Single-crystal X-ray diffraction

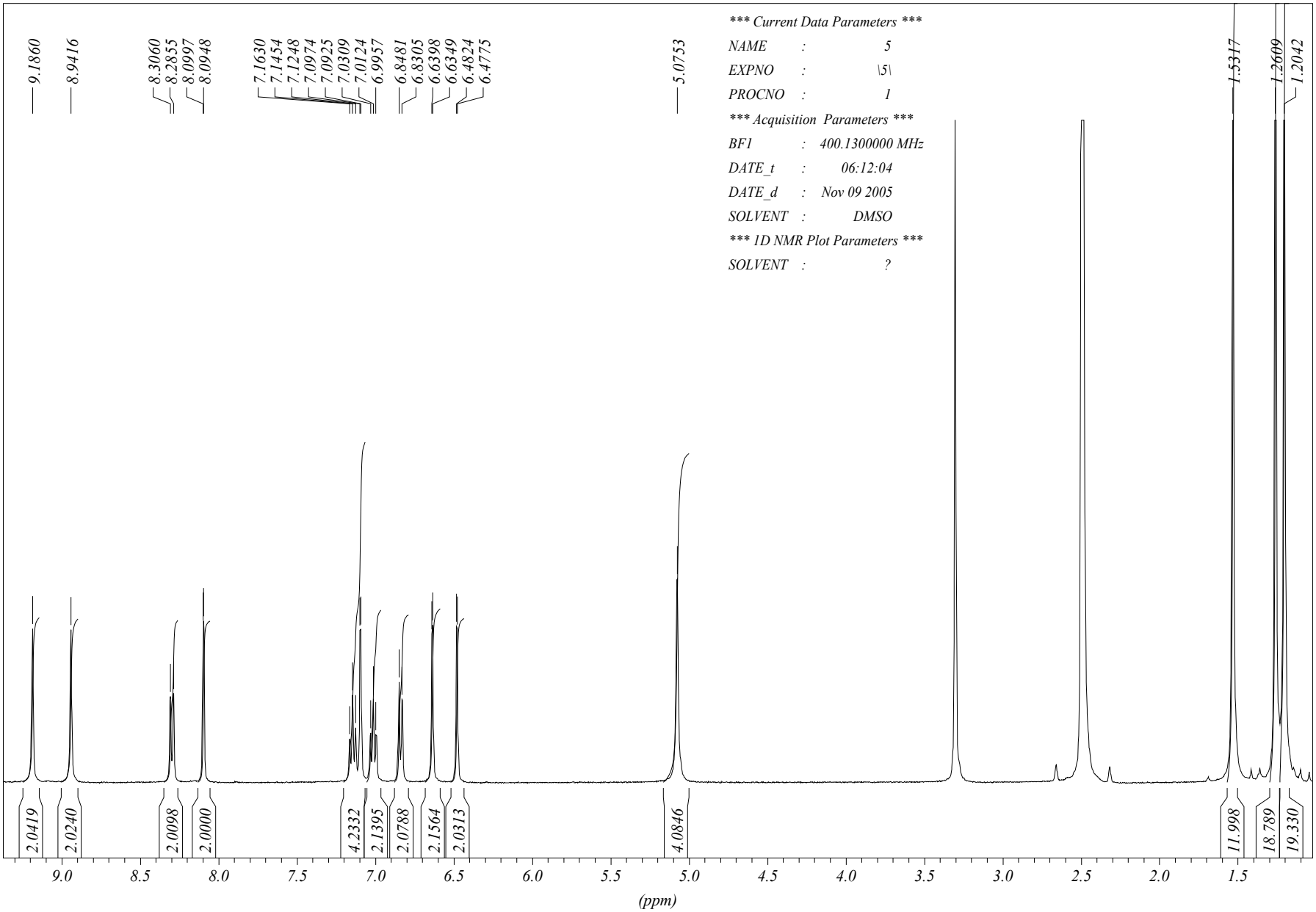
Data were collected on a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo-K_α radiation at 173K. An empirical absorption correction was performed using the program PLATON.[i] The structure was solved by direct methods using the program SHELXS[17] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL.[ii]

Parameters: $C_{170}H_{200}N_{16}O_{16} \bullet 9\ C_2H_6OS \bullet 8\ CH_2Cl_2$, M = 4106.02, colourless block (0.47mm x 0.44mm x 0.43mm), triclinic, space group P-1, a = 15.9483(4) Å, b = 19.0501(5), c = 37.5597(10) Å, α = 93.080(2)°, β = 98.429(2)°, γ = 105.306(2)°, V = 10836.4(5) Å^3, Z = 2, μ = 0.354 mm^{-1}, $\rho_{calculated}$ = 1.258 gcm^{-3}, 301931 reflections, $2\theta_{max}$ = 52.56°, 43376 unique reflections (R_{int} = 0.0804), 2331 parameters, 10 restraints, $R1$ = 0.1395 ($I > 2\sigma(I)$), $wR2$ = 0.4089 (all data), largest maximum/minimum in the final difference densitity map: 2.532/-1.532e$^-$Å^3,

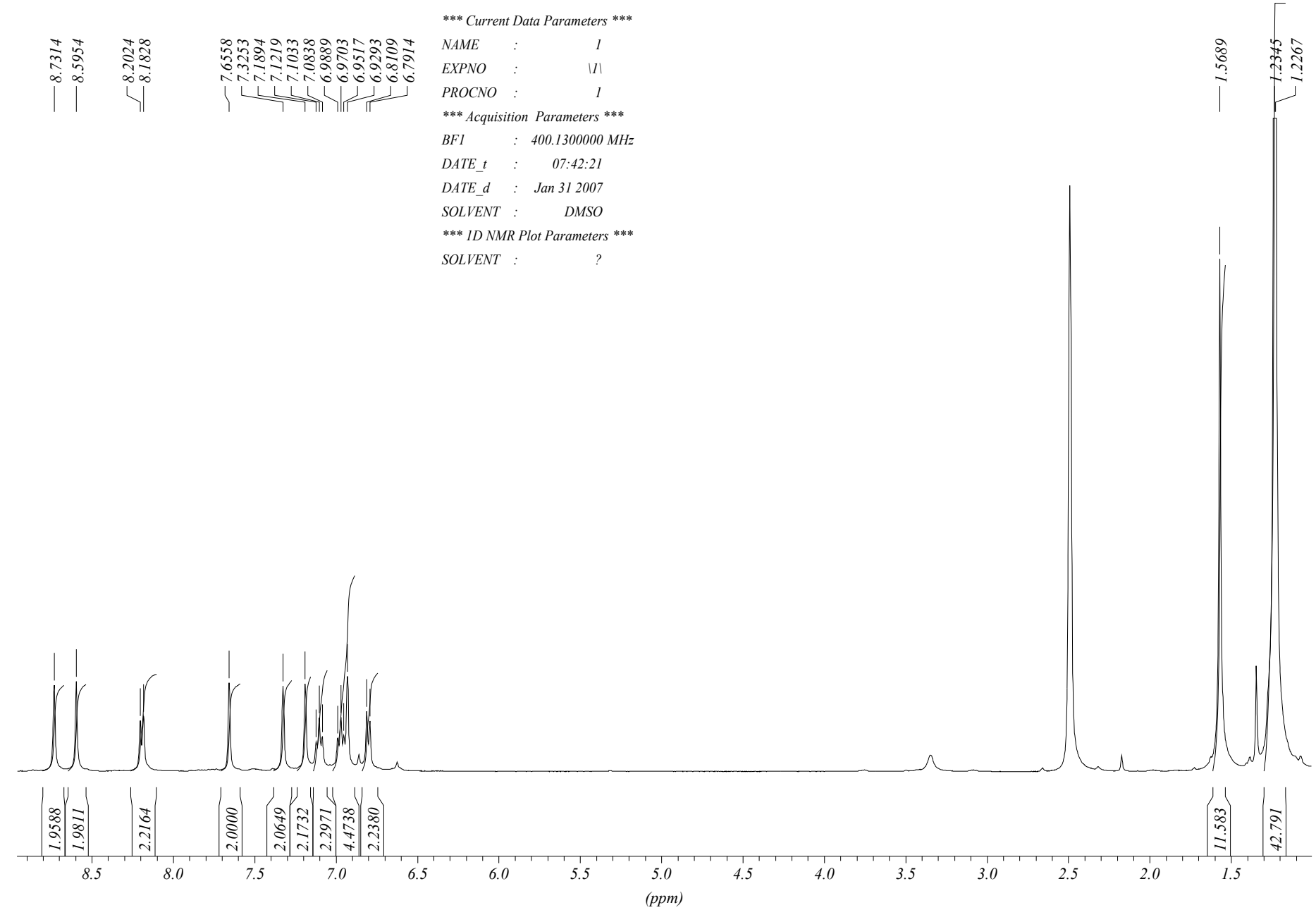
CCDC reference number: XXXXXX

NMR spectra of the compounds.

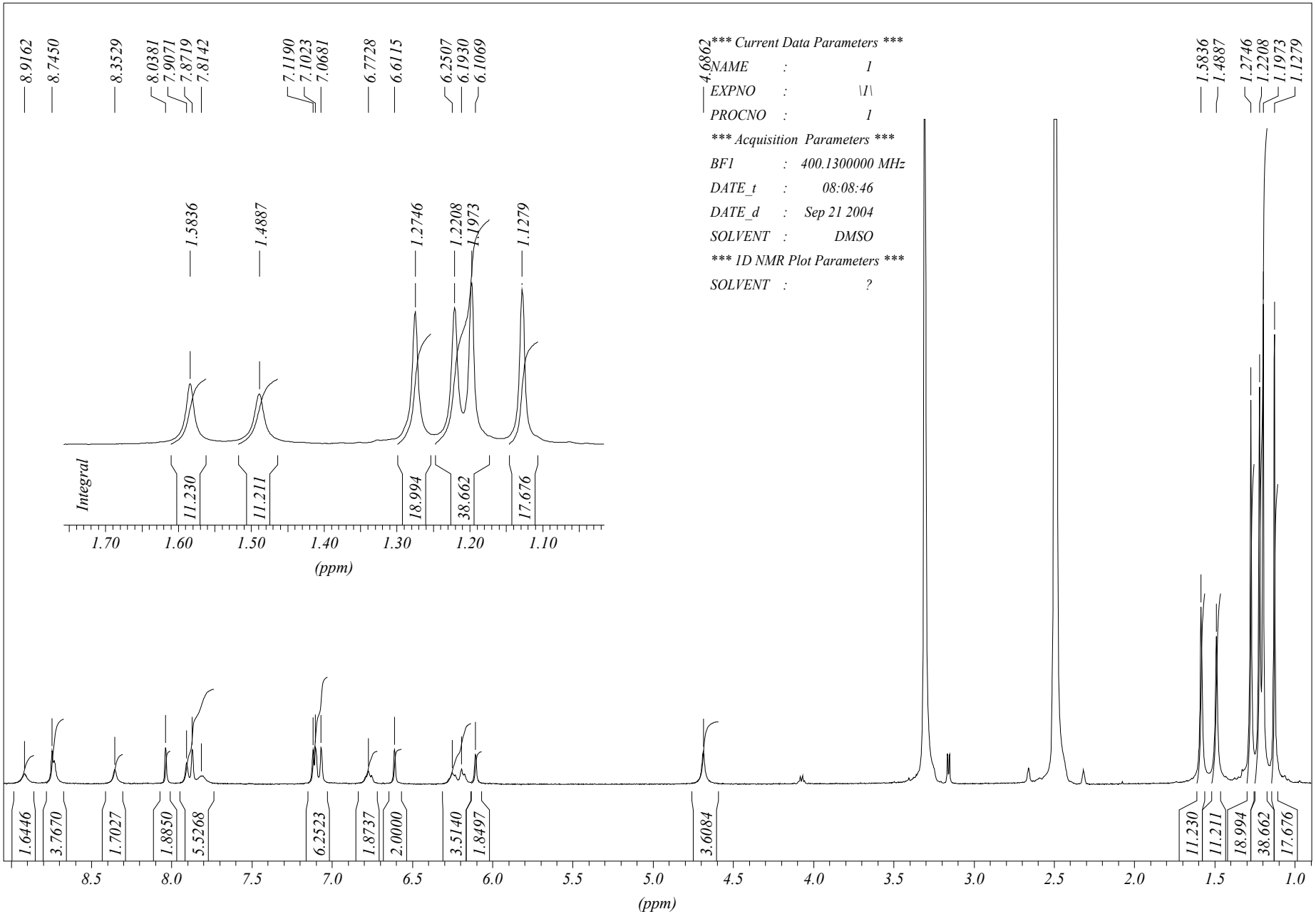
Diamine 3 (XDX) DMSO-d6, 25°C



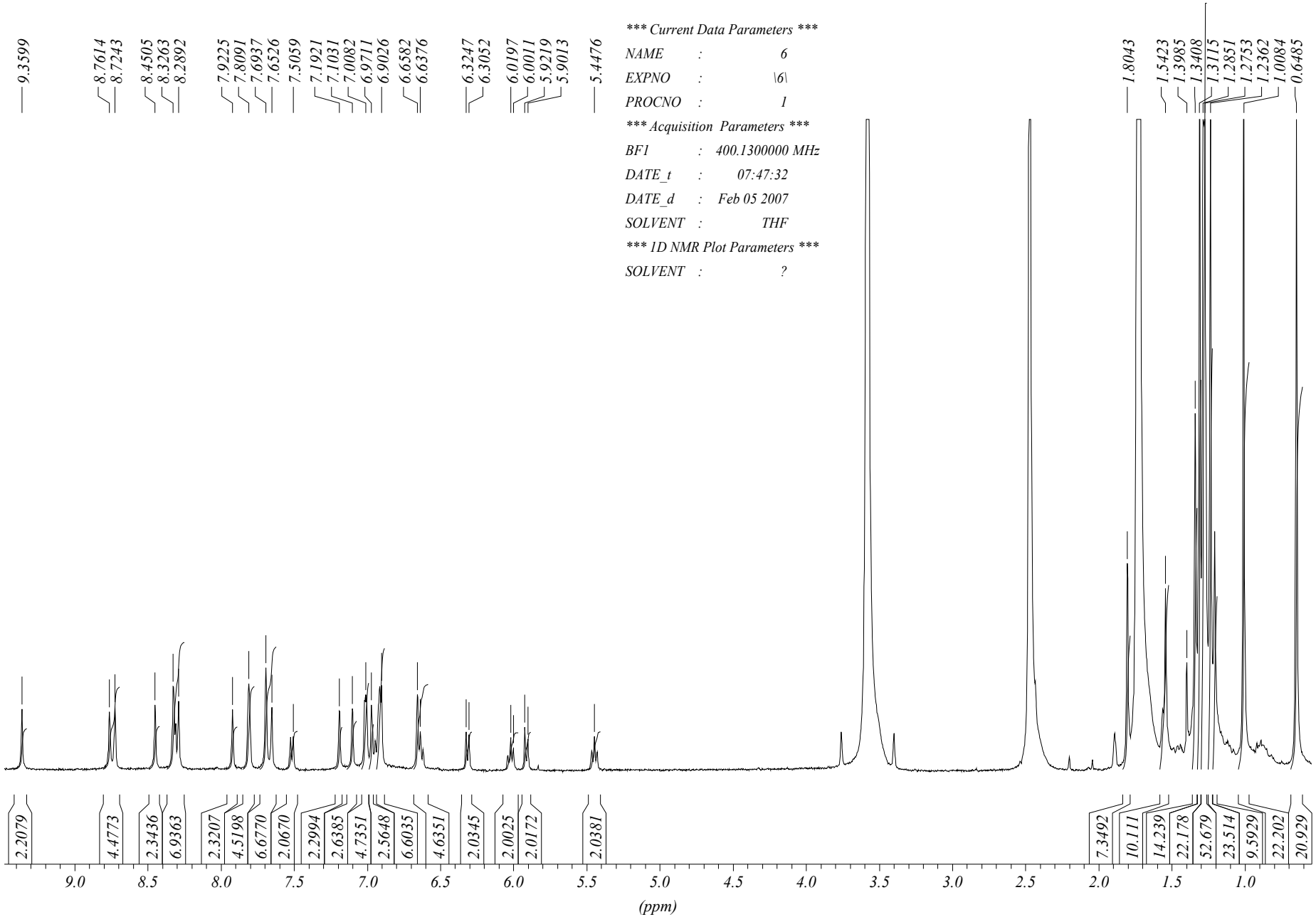
Diisocyanate 5 (XDX), DMSO-d6, 25°C



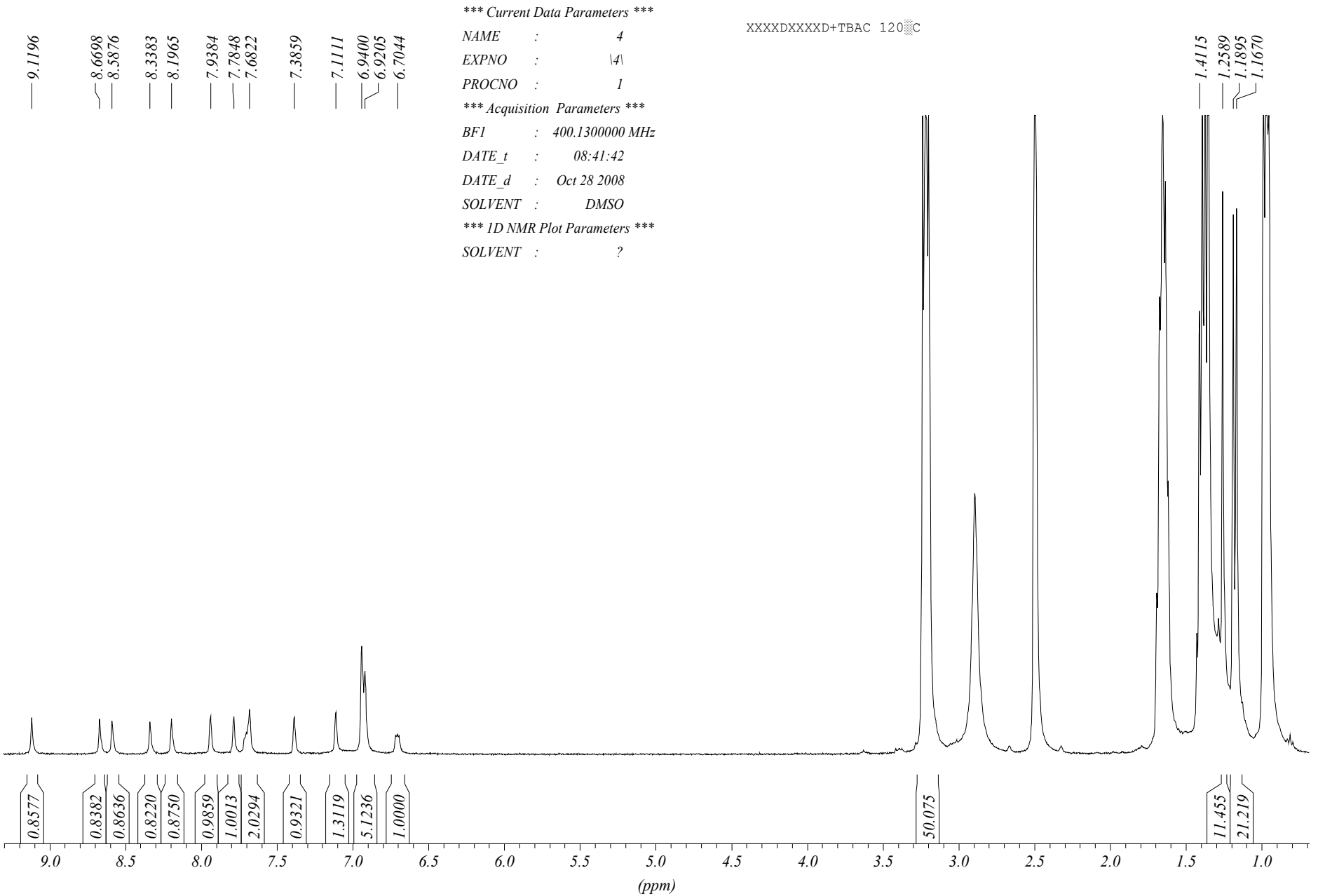
Diamine 6 (XXDXX)



Cyclic octamer 8 (XXXDXXXD) THF-d8, 25°C



Cyclic decamer (XXXXDXXXXD)) DMSO-d6, 120°C, in the presence of TBA chloride



[i] A. L Spek, *J. Appl. Cryst*., 2003, **36**, 7-13.
[ii] G.M. Sheldrick, *Acta Cryst*., 2008, A**64**, 112-122.