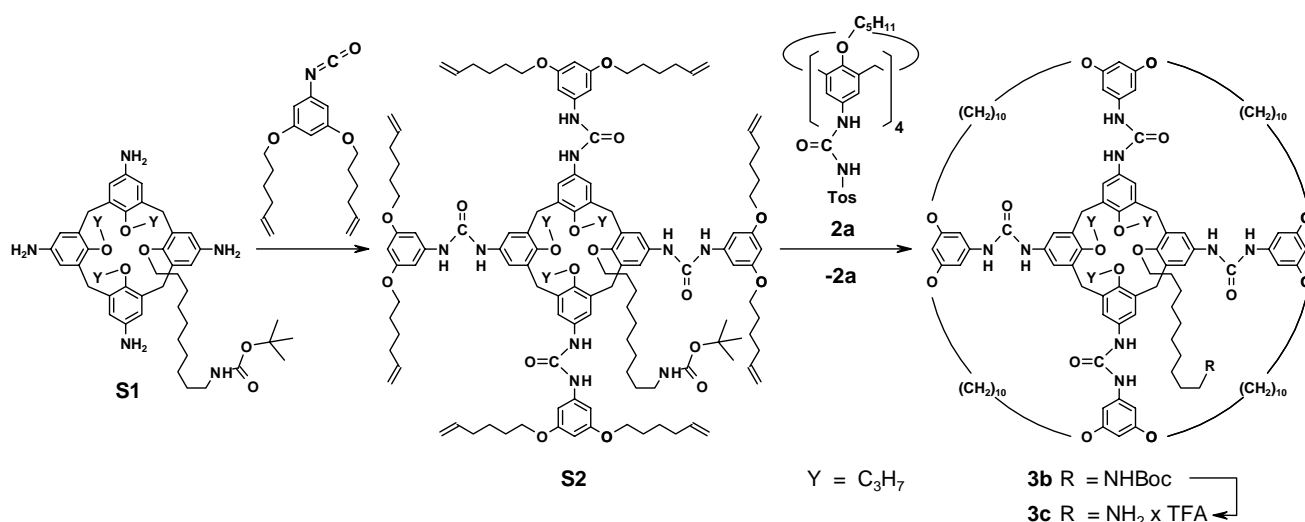


## Self-assembled dendrimers with uniform structure

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**Scheme S1.** Synthesis of the tetra-loop calix[4]arene **3c**.

**Tetra-loop calix[4]arene 3c.** *Step 1.* A solution of 3,5-di-(hexenyloxy)benzoic acid (1.50 g, 4.70 mmol), DPPA (diphenylphosphoryl azide) (1.41 g, 5.18 mmol) and Et<sub>3</sub>N (0.52 g, 5.18 mmol) in toluene (100 mL) was stirred at 70°C for 6 h under nitrogen atmosphere. After that tetraamine **S1** (0.68 g, 0.79 mmol) was added to the solution and stirring was continued during 4 h. The solvent was evaporated and the residue was triturated with MeOH (20 mL). The formed precipitate was filtered off and purified by column chromatography (ethyl acetate/hexane, 1:8). Calix[4]arene **S2** (1.15 g, 68%) was obtained as a white powder; mp >230 °C (decomposition); <sup>1</sup>H NMR (400MHz, THF-*d*<sub>8</sub>): δ = 1.02 (t, <sup>3</sup>J = 7.4 Hz, 9H, CH<sub>3</sub>), 1.40 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29-1.44 (m, 14H, CH<sub>2</sub>), 1.49-1.56 (m, 16H, CH<sub>2</sub>), 1.68-1.74 (m, 16H, CH<sub>2</sub>), 1.92-1.98 (m, 8H, CH<sub>2</sub>), 2.06-2.12 (m, 16H, CH<sub>2</sub>), 3.02 (q, 2H, <sup>3</sup>J = 6.5 Hz, NHCH<sub>2</sub>), 3.08 (d, 4H, <sup>2</sup>J = 13.3 Hz, ArCH<sub>2</sub>Ar), 3.80-3.85 (m, 24H, OCH<sub>2</sub>), 4.44 (d, 4H, <sup>2</sup>J = 13.3 Hz, ArCH<sub>2</sub>Ar), 4.90-5.02 (m, 8H, CH=CH<sub>2</sub>), 5.76-5.86 (m, 8H, CH=CH<sub>2</sub>), 5.93 (s, 1H, NHBoc), 6.03 (s, 4H, ArH), 6.58 (s, 8H, ArH), 6.80 (s, 4H, ArH), 6.82 (s, 4H, ArH), 7.45 (s, 4H, NH), 7.51 (s, 2H, NH), 7.52 (s, 2H, NH); MS(ESI) *m/z* (%): 2150.4 (100) [M<sup>+</sup> + Na].

*Step 2.* The mixture of tetraurea **S2** (0.20 g, 0.094 mmol) and tetratosylurea **2a** (0.15 g, 0.094 mmol) in benzene (25 mL) was stirred for 12 h at room temperature and then diluted with dichloromethane (1 L). The nitrogen was blown through the solution during 2 h, Grubbs catalyst 1<sup>st</sup> generation (0.015 g, 0.019 mmol) was added and the reaction mixture was stirred during 2 days. The solvents were evaporated and the residue was passed through the short column (THF/hexane, 2:3). The obtained white solid was dissolved in THF (25 mL) and hydrogenated during 6 h at room temperature in the presence of the Pt<sub>2</sub>O (0.04 g). The catalyst was filtered off and the solvent was evaporated. The product was purified by column chromatography (THF/hexane, 1:3) to give the calix[4]arene **3b** (0.13 g, 68%) as a white

powder; mp >260 °C (decomposition); <sup>1</sup>H NMR (400MHz, THF-*d*<sub>8</sub>): δ = 0.95-1.01 (m, 9H, CH<sub>3</sub>), 1.30-1.42 (m, 71H, CH<sub>2</sub> and C(CH<sub>3</sub>)<sub>3</sub>), 1.66-1.72 (m, 16H, CH<sub>2</sub>), 1.97-2.03 (m, 8H, CH<sub>2</sub>), 3.02 (q, 2H, <sup>3</sup>J = 6.5 Hz, NHCH<sub>2</sub>), 3.09 (d, 4H, <sup>2</sup>J = 12.5 Hz, ArCH<sub>2</sub>Ar), 3.82-3.88 (m, 24H, OCH<sub>2</sub>), 4.45 (d, 4H, <sup>2</sup>J = 12.5 Hz, ArCH<sub>2</sub>Ar), 5.94 (s, 1H, NHBoc), 6.01 (s, 4H, ArH), 6.58 (s, 8H, ArH), 6.90 (s, 4H, ArH), 6.91 (s, 4H, ArH), 7.53 (s, 8H, NH); MS(ESI) *m/z* (%): 2046.1 (100) [M<sup>+</sup> + Na].

*Step 3.* Trifluoroacetic acid (10 mL) was added to the solution of calix[4]arene **3b** (0.33 g, 0.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated and the residue was triturated with Et<sub>2</sub>O (20 mL). The formed precipitate was filtered off and dried on the air. The calix[4]arene **3c** (0.32 g, 97%) was obtained as a light-grey powder; mp >270 °C (decomposition); <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ = 0.95-1.01 (m, 9H, CH<sub>3</sub>), 1.26-1.64 (m, 78H, CH<sub>2</sub>), 1.92-1.97 (m, 8H, CH<sub>2</sub>), 2.76 (q, 2H, <sup>3</sup>J = 6.5 Hz, NHCH<sub>2</sub>), 3.11 (d, 4H, <sup>2</sup>J = 11.7 Hz, ArCH<sub>2</sub>Ar), 3.74-3.83 (m, 24H, OCH<sub>2</sub>), 4.32 (d, 4H, <sup>2</sup>J = 11.7 Hz, ArCH<sub>2</sub>Ar), 6.04 (s, 4H, ArH), 6.49-6.51 (m, 4H, ArH), 6.52 (s, 4H, ArH), 6.86 (m, 4H, ArH), 6.92 (s, 4H, ArH), 7.63 (br s, 3H, NH<sub>3</sub><sup>+</sup>), 8.17 (s, 2H, NH), 8.22 (s, 2H, NH), 8.41 (s, 2H, NH), 8.43 (s, 2H, NH); MS(ESI) *m/z* (%): 1924.3 (100) [M<sup>+</sup> + Na].

**Tri-urea monoacetamide calix[4]arene 5f.** The solution of acid **5b** (0.094 g, 0.085 mmol), PyBOP (0.046 g, 0.102 mmol), 11-aminoundecanoic acid ethyl ester (0.023 g, 0.102 mmol) and Et<sub>3</sub>N (0.5 mL) in DMF (for peptide synthesis grade, 10 mL) was stirred during 2 days at room temperature. Water (20 mL) was added and the product was extracted with CHCl<sub>3</sub>. The organic layer was washed with water and dried (MgSO<sub>4</sub>). The solvent was evaporated and the product was precipitated from CH<sub>2</sub>Cl<sub>2</sub> solution with Et<sub>2</sub>O. Compound **5f** (0.09 g, 80%) was obtained as a white powder; mp >180 °C (decomposition); <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>): δ = 0.91 (t, 9H, <sup>3</sup>J = 7.4 Hz, CH<sub>3</sub>), 1.16 (t, 3H, <sup>3</sup>J = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.24-1.29 (m, 12H, CH<sub>2</sub>), 1.50 (m, 6H, CH<sub>2</sub>), 1.77-1.86 (m, 6H, CH<sub>2</sub>), 1.90 (s, 3H, C(O)CH<sub>3</sub>), 2.21 (m, 11H, ArCH<sub>3</sub> and C(O)CH<sub>2</sub>), 3.12 (m, 8H, ArCH<sub>2</sub>Ar), 3.23 (br s, 2H, NHCH<sub>2</sub>), 3.70-3.80 (m, 6H, OCH<sub>2</sub>), 4.03 (q, 2H, <sup>3</sup>J = 7.2 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 4.30-4.40 (m, 6H, OCH<sub>2</sub> and ArCH<sub>2</sub>Ar), 6.70 (s, 2H, ArH), 6.72 (s, 2H, ArH), 6.87 (s, 2H, ArH), 6.99-7.04 (m, 8H, ArH<sub>Tol</sub> and ArH), 7.21 (d, 4H, <sup>3</sup>J = 8.3 Hz, ArH<sub>Tol</sub>), 7.28 (d, 2H, <sup>3</sup>J = 8.3 Hz, ArH<sub>Tol</sub>), 8.10-8.43 (m, 7H, NH<sub>urea</sub> and CH<sub>2</sub>C(O)NH), 9.57 (s, 1H, NHC(O)CH<sub>3</sub>); MS(ESI) *m/z* (%): 1321.8 (100) [M<sup>+</sup>].

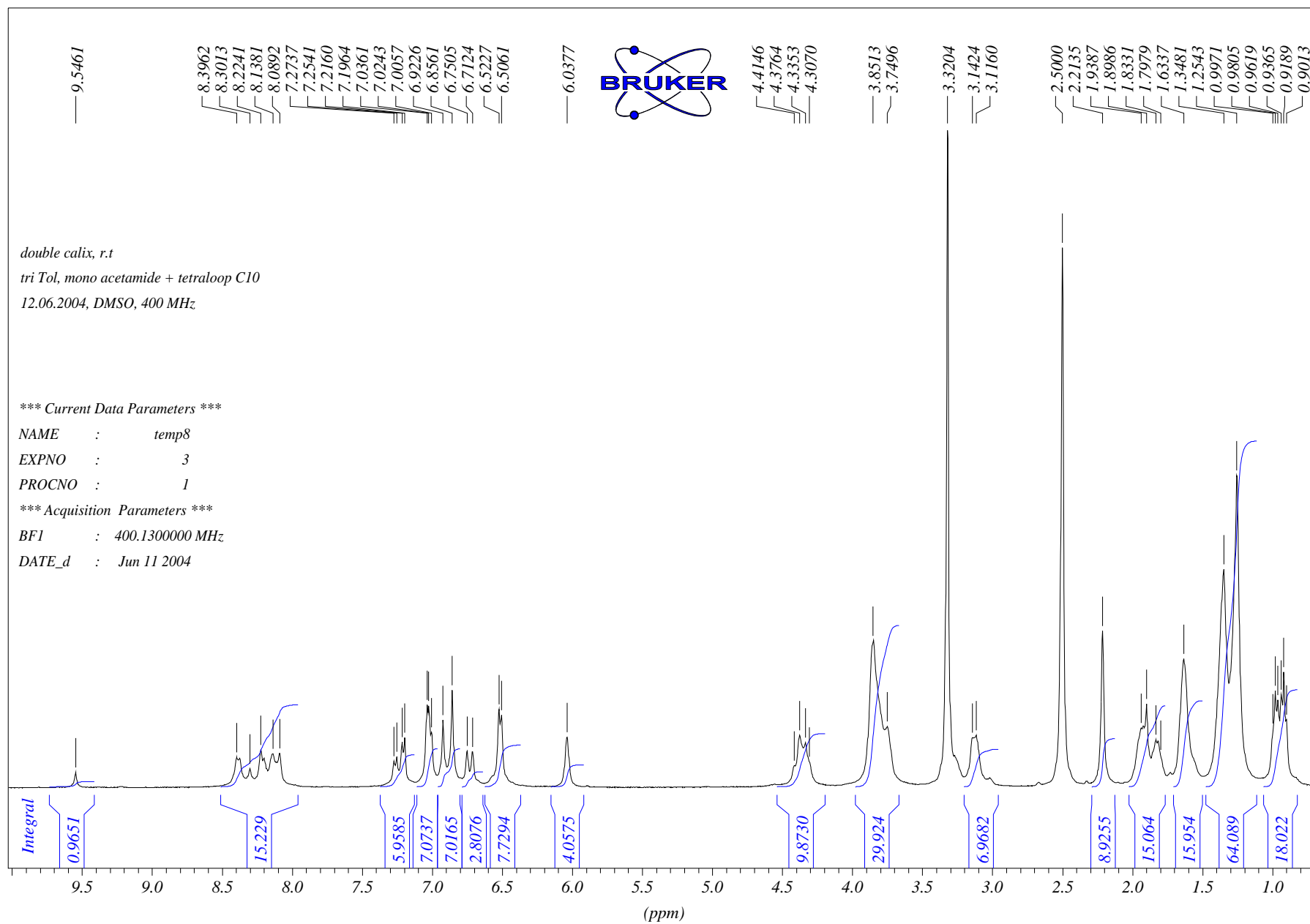
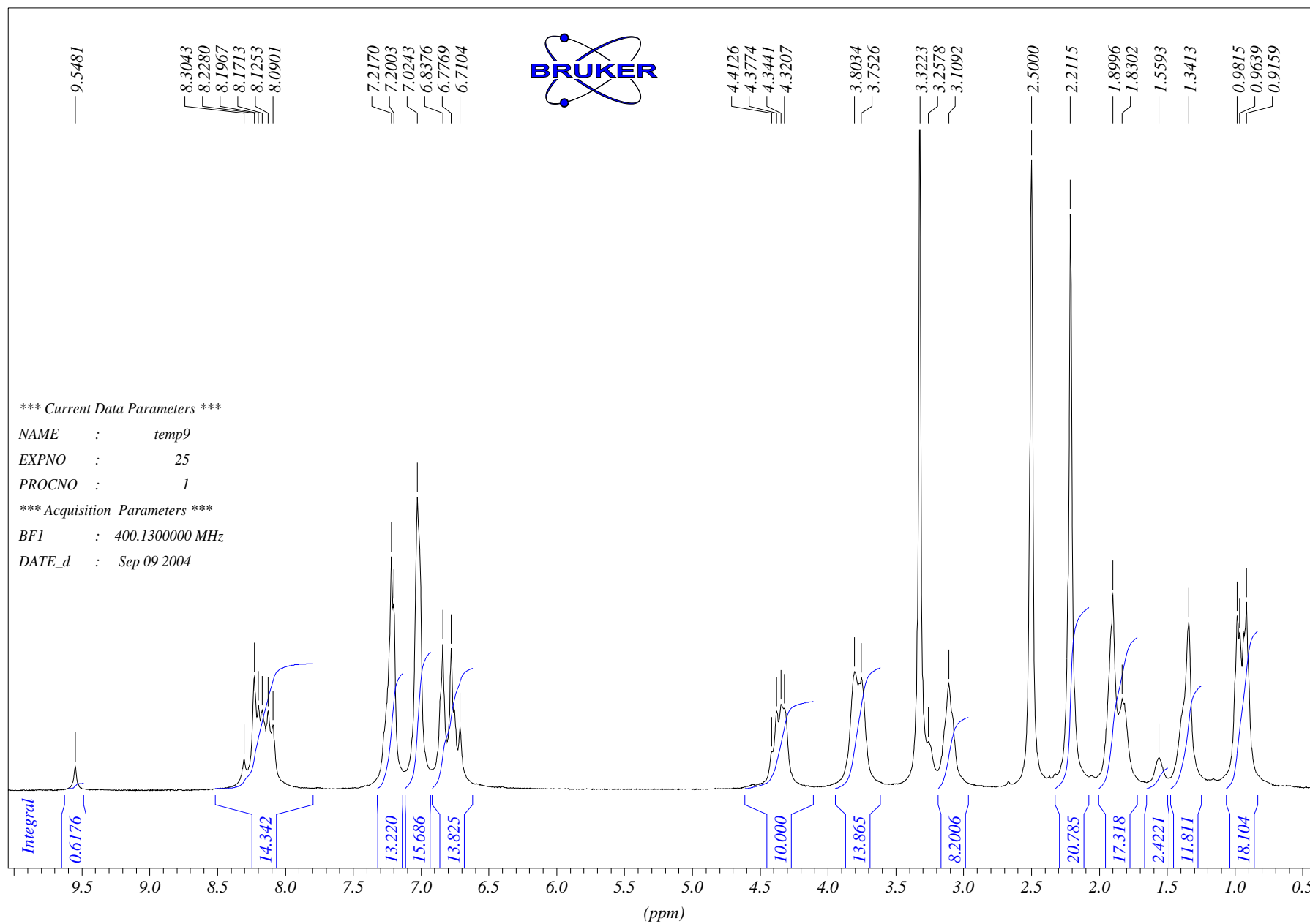
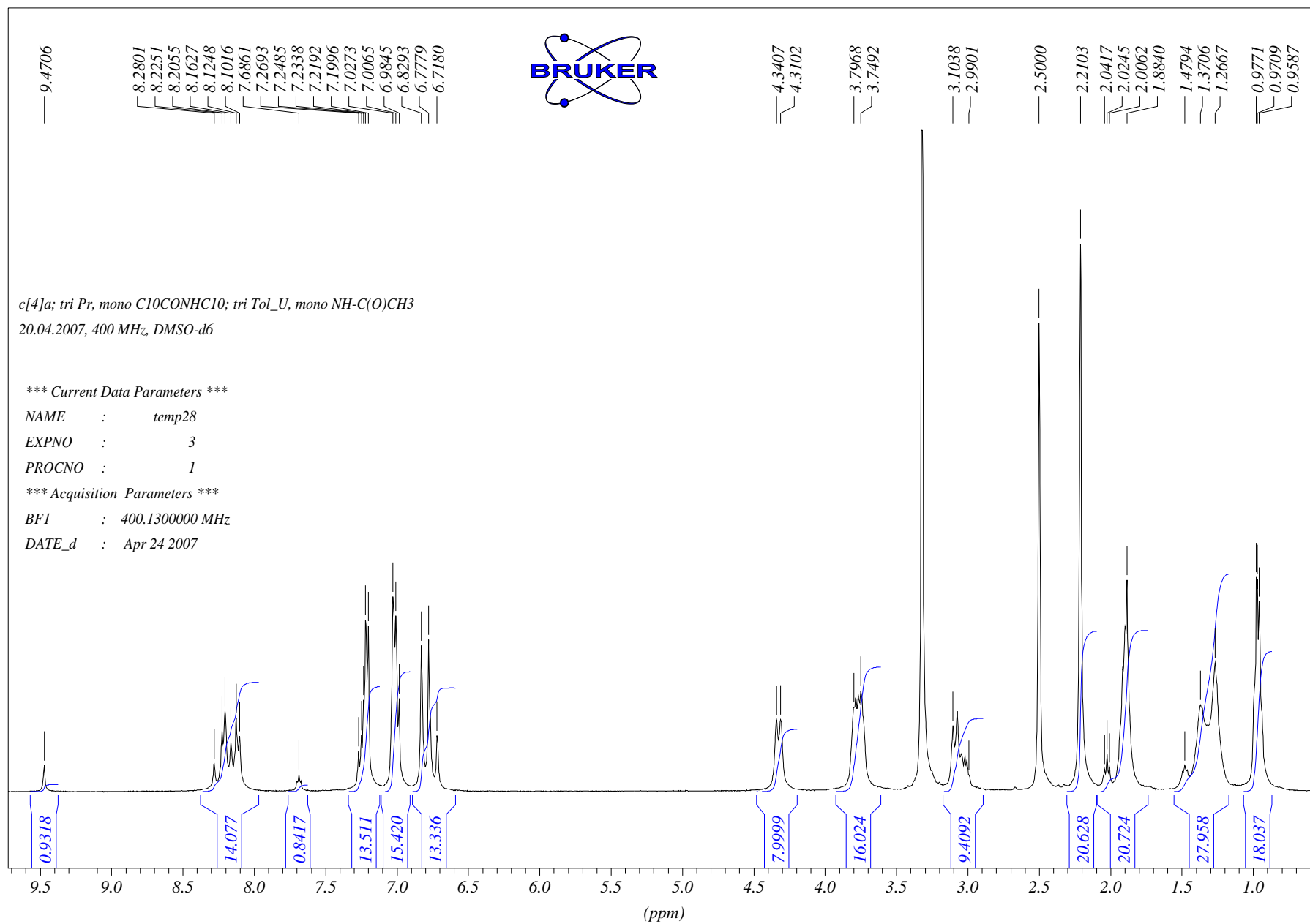


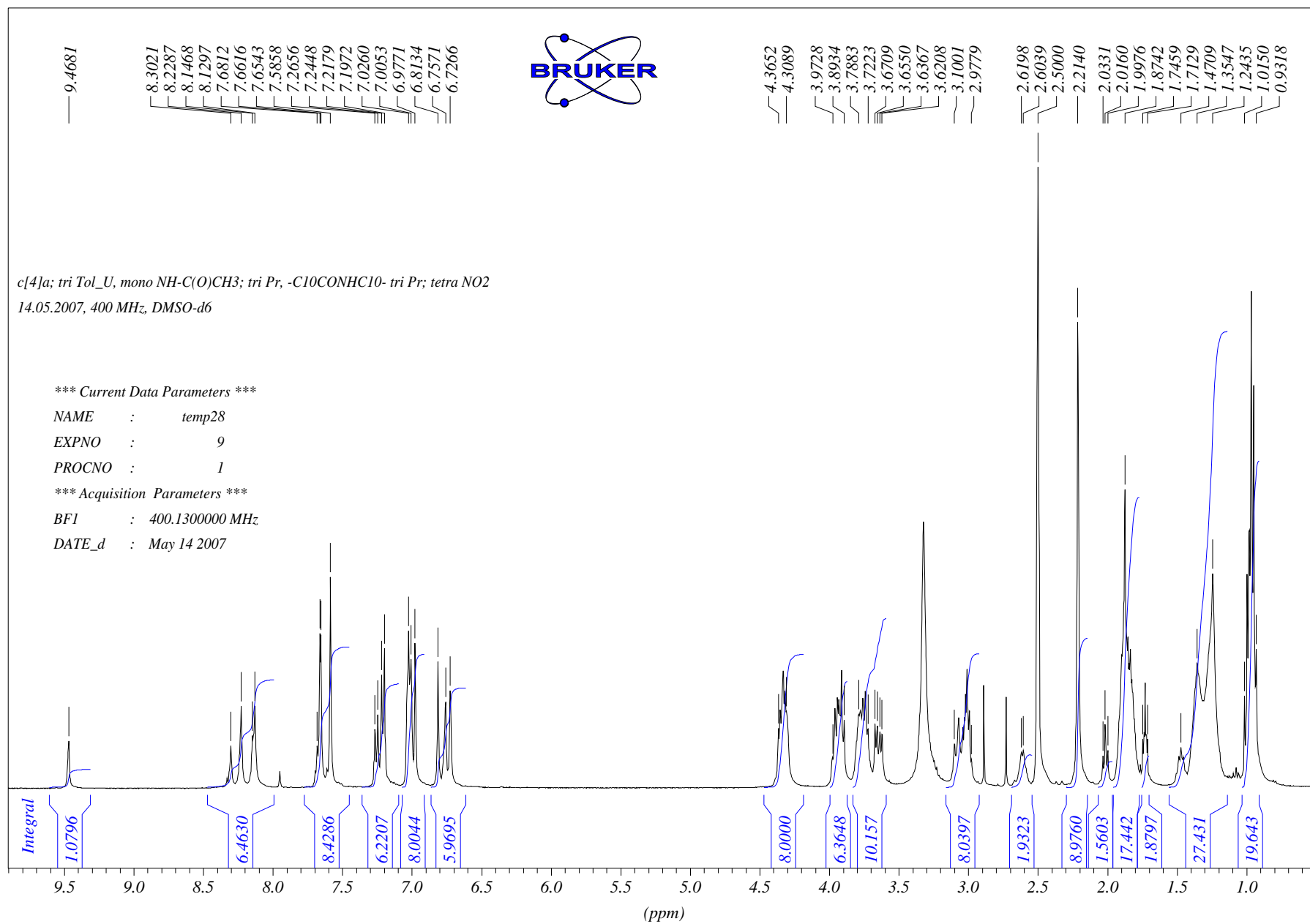
Figure S1. <sup>1</sup>H NMR spectrum of **6** in DMSO-*d*<sub>6</sub>.



**Figure S2.**  $^1\text{H}$  NMR spectrum of **7a** in  $\text{DMSO-}d_6$ .



**Figure S3.** <sup>1</sup>H NMR spectrum of **7b** in DMSO-d<sub>6</sub>.



**Figure S4.** <sup>1</sup>H NMR spectrum of **8** in DMSO-d<sub>6</sub>.

**Diffusion-ordered NMR spectroscopy.** DOSY experiments were performed on a Bruker AVANCE 700 NMR spectrometer equipped with dual z-gradient probehead with  $55.2 \text{ G cm}^{-1}$  gradient strength. Stimulated-echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (BPP-LED) was used. The gradient strength was incremented in 32 steps from 2% up to 95% of the maximum gradient strength. Typical diffusion time and diffusion gradient pulse were 200ms and 2.5ms respectively.