Supporting Information

Cyclic ureas as novel building blocks for bent-core liquid crystals

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1. Additional figures

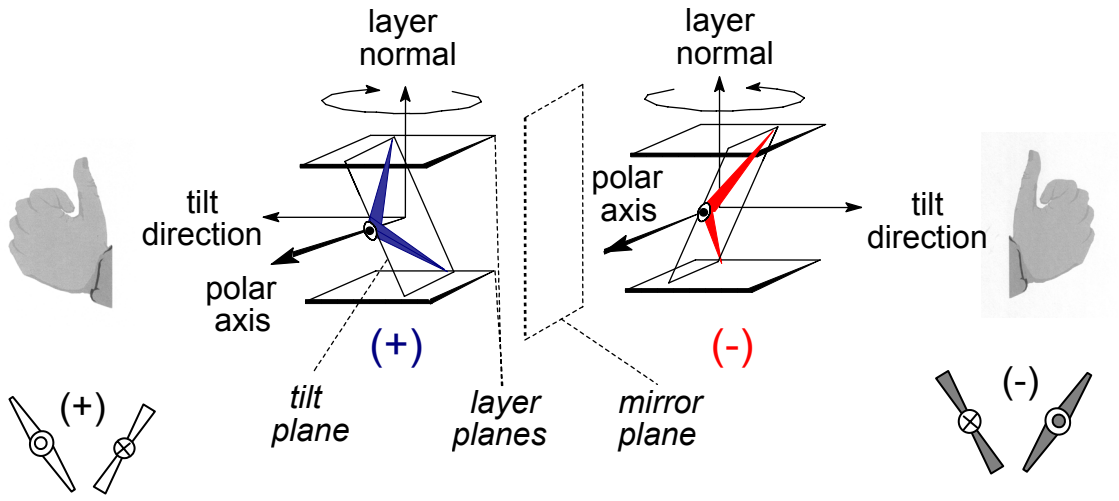


Fig. S1. (a) Origin of the chirality within the smectic phases of bent-core molecules.[4] Owing to the bend shape each molecule possesses a dipole moment in the molecular plane and perpendicular to the long axis of the molecules. Layer normal, tilt direction and the polar axis define either a right handed coordinate system (+), whereas in the mirror image these vectors define a left handed system (-). Changing either polarisation direction or tilt direction changes the chirality sense of the layer (indicated by blue/red colour). Changing both, polarisation direction and tilt direction retains the chirality sense.

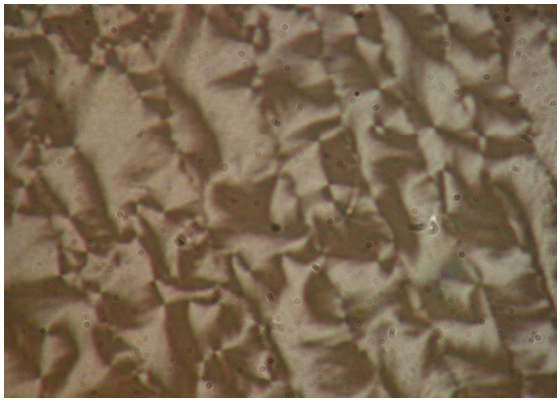


Fig. S2. Texture of a homeotropically aligned sample of the $SmAP_A$ phase of compound **6/2** (crossed polarizers) at 95 °C.

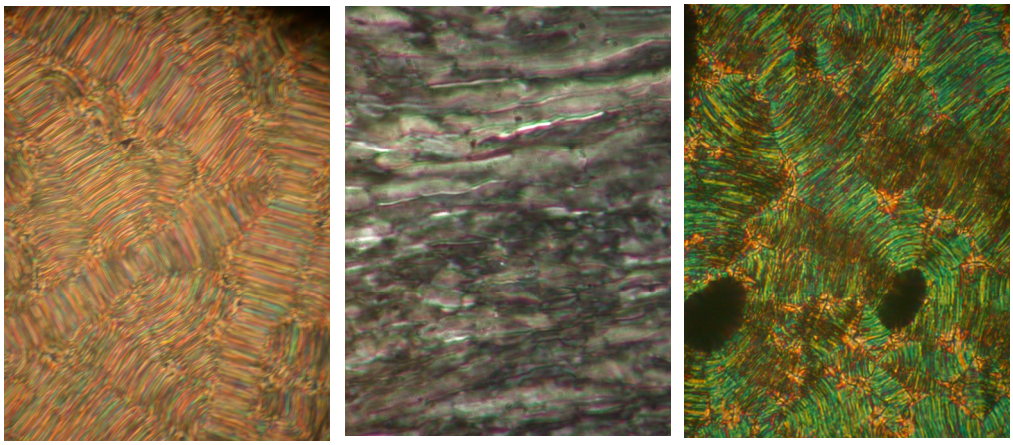


Fig. S3. (a) Textures of the mesophases of compound **7/1** between crossed polarizers: a) $SmCP_A$ phase at 148 °C; b) $SmCP_A$ phase at 148 °C after shearing (the birefringence is much larger than in the $SmAP_A$ phase shown in Fig S2); c) M_2 phase at 124°C.

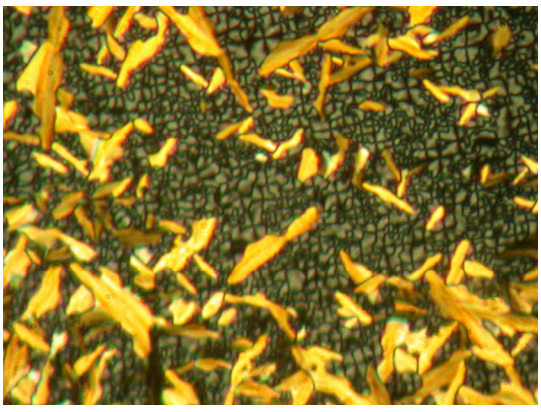


Fig. S4. Texture of the USmC phase of compound **8/1** (crossed polarizers) at 180°C.

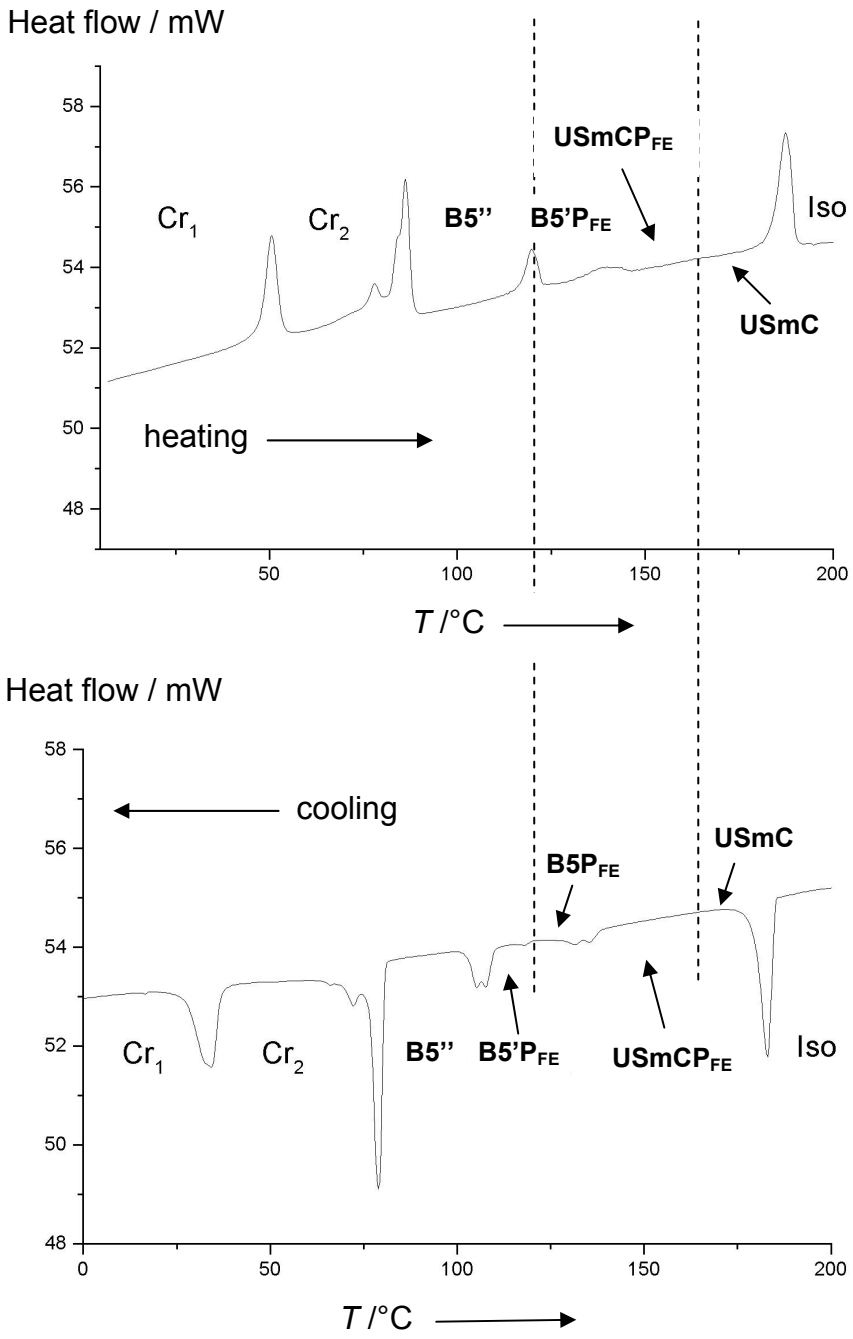


Fig. S5. DSC heating and cooling curves (10 K min^{-1}) of **8/1.**

3. Experimental Methods

The mesophase behaviour of all the compounds was examined under a polarized light optical microscope (Optiphot-2, Nikon) attached with a hot stage (FP-82 HT, Mettler) by sandwiching the sample between a glass slide and a cover-slip. The transition temperatures and the associated enthalpies were obtained from thermograms recorded on a Perkin-Elmer DSC-7, differential scanning calorimeter. The cooling and heating rates were 10 °C min^{-1}. The electro-optical switching characteristics were examined with a home-built setup for electrooptical investigations using ITO cells as specified (EHC Japan). The triangular-wave method was used for determination of the P_s-values by integration of the peak areas. Optical investigation of the switching process was made in the same setup under a polarizing

microscope between crossed polarizers using a DC field or a low frequency (<1 Hz) triangular wave field.
Powder X-ray diffraction measurements were carried out with a Guinier film camera (Huber) with samples in glass capillaries (1 mm) in a temperature-controlled heating stage using quartz-monochromatized CuKα radiation (1.54 Å; 30 to 60 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$). 2D patterns for aligned samples on a glass plate on a temperature controlled heating stage (alignment at the sample – glass or at the sample – air interface) were recorded with a 2D detector (HI-STAR, Siemens).

4. Synthesis and analytical data

N,*N*'-Bis(4-ethoxycarbonylphenyl)-*N*,*N*'-alkyleneureas 2/*n*

2/0: Under an argon atmosphere, a mixture of ethyl 4-bromobenzoate (19.2 g, 84 mmol), **1/0** (2.6 g, 30 mmol), Cs_2CO_3 (27.3 g, 84 mmol), $Pd_2(dba)_3$ (366 mg, 0.5 mol-%) and Xanthphos® (36 mg, 1.5 mol-%) are suspended in dry dioxane (100 ml) and heated under reflux for 30 hours. After cooling to room temperature CH_2Cl_2 (75 ml) is added and the mixture is filtered. The solvent of the filtrate is evaporated and the residue is crystallized twice from MeOH. In case of compound **2/0** the residue contains most of the product. The residue is treated with diluted hydrochloric acid and the mixture is filtered again. The residue is combined with the filtrate from the first filtration. The solvent is evaporated and the residue is suspended in hot MeOH (50 ml) and filtered. The residue is crystallized from $CHCl_3$. Yield:10.4 g (27 mmol, 90.7%); white needles, mp. 213-214 °C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.05 (d, ^3J = 8.9 Hz, 4H, Ar-H), 7.67 (d, ^3J = 9.1 Hz, 4H, Ar-H), 4.35 (q, ^3J = 7.1 Hz, 4H, CH_2), 4.03 (s, 4H, $(CH_2)_2$), 1.38 (t, ^3J = 7.2 Hz, 6H, CH_3).

2/1: Yield:10.9 g (27 mmol, 91.7%); white needles, mp. 161 °C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.00 (d, ^3J = 8.5 Hz, 4H, Ar-H), 7.31 (d, ^3J = 8.5 Hz, 4H, Ar-H), 4.35 (q, ^3J = 7.1 Hz, 4H, CH_2), 3.86 (t, ^3J = 5.9 Hz, 4H, CH_2), 2.31 (quin, 2H, CH_2),1.37 (t, ^3J = 7.2 Hz, 6H, CH_3).

2/2: Yield: 1.93 g (4.7 mmol, 88.7%): colourless plates, mp. 117-118 °C; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.99-8.02 (m, 4H, Ar-H), 7.34-7.36 (m, 4H, Ar-H), 4.35 (q, ^3J = 7.1 Hz, 4H, CH_2), 3.86 (m, 4H, CH_2), 1.91 (m, 4H, CH_2-CH_2), 1.37 (t, ^3J = 7.2 Hz, 6H, CH_3).

N,*N*'-Bis(4-carboxyphenyl)-*N*,*N*'-alkyleneureas (4/*n*)

4/0: 2/0 (1.0 g, 2.6 mmol) is suspended in EtOH (50 ml) and treated with a solution of KOH (0.6 g, 11.7 mmol) in water (50 ml). The reaction mixture is heated at 60 °C for 4 hours. The clear solution is then made acidic with diluted HCl. After cooling to room temperature the mixture is filtered and the precipitate is washed with MeOH. Yield: 840 mg (2.6 mmol, 98.4%); white solid; mp. 402-404 °C (dec.); ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 7.94 (d, ^3J = 8.9 Hz, 4H, Ar-H), 7.75 (d, ^3J = 8.9 Hz, 4H, Ar-H), 4.03 (s, 4H, $(CH_2)_2$).

4/1: Yield: 3.2 g (9.4 mmol, 74.6%); white solid, mp. 346-348 °C; ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 8.19 (d, ^3J = 8.5 Hz, 4H, Ar-H), 7.77 (d, ^3J = 8.5 Hz, 4H, Ar-H), 4.12 (t, ^3J = 5.8 Hz, 4H, CH_2), 2.79 (quin, ^3J = 1.8 Hz, 2H, CH_2).

4/2: Yield: 850 mg (9.4 mmol, 65.6%); white solid, mp. 310-312 °C; ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 7.87-7.90 (m, 4H, Ar-H), 7.39-7.42 (m, 4H, Ar-H), 3.83 (m, 4H, CH_2), 1.78 (m, 4H, CH_2-CH_2).

General procedure for the esterification of 4/*n*

6/0: 4/0 (360 mg, 1.1 mmol) is suspended in $SOCl_2$ (50 ml) and stirred and heated until the reaction mixture became clear. The excess of $SOCl_2$ is distilled off and traces were evaporated under reduced pressure (100 °C bath temperature). To the white residue of the acid chloride there is added 4-tetradecyloxyphenol (676 mg, 2.2 mmol), DMAP (10 mg), Et_3N (1 ml) and dry DMF (100 ml) and the mixture is heated for 4 hours under reflux and exclusion of moisture (in cases of **6/1** and **6/2** dry CH_2Cl_2 (50 ml) was used instead of DMF). After cooling to room temperature a white precipitate is formed which was filtered and washed with CH_2Cl_2 (50 ml). The crude product is then crystallized from $CHCl_3$/MeOH. Yield: 610 mg (0.68 mmol, 61,2%); white solid; ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.20 (d, ^3J = 8.9 Hz, 4H, Ar-H), 7.76 (d, ^3J = 8.9 Hz, 4H, Ar-H), 7.10 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.91 (d, ^3J = 8.7 Hz, 4H, Ar-H), 4.10 (s, 4H, $(CH_2)_2$), 3.94 (t, ^3J = 6.6 Hz, 4H, OCH_2), 1.77 (quin, ^3J = 7.2 Hz, 4H, CH_2), 1.24-1.50 (m, 44H, $(CH_2)_{11}$), 0.86 (t, ^3J = 6.74 Hz, 6H, CH_3); calc. for $C_{57}H_{78}N_2O_7$: C 75.79, H 8.71, N = 3.10; found C 75.4, H 8.67, N = 3.02 %.

6/1: Yield: 460 mg (0.50 mmol, 85.3%); ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.16 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.50 (d, ^3J = 8.7 Hz, 4H, Ar-H), 7.08 (d, ^3J = 9.1 Hz, 4H, Ar-H), 6.90 (d, ^3J = 6.9 Hz, 4H, Ar-H), 3.91 (t, 4H, CH_2), 3.94 (t, 4H, OCH_2), 2.35 (quin, 2H, CH_2), 0.86 (t, ^3J = 6.3 Hz, 6H, CH_3), 1.77 (quin, ^3J = 7.2 Hz, 4H, CH_2), 1.24-1.50 (m, 44H, $(CH_2)_{11}$); calc. for $C_{58}H_{80}N_2O_7$: C 75.94, H 8.79, N 3.05; found: C 76.07, H 8.65, N = 3.19 %.

6/2: Yield: 310 mg (0.33 mmol, 78.6%); ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 8.19-8.21 (m, 4H, Ar-H) 7.75-7.77 (m, 4H, Ar-H), 7.09-7.11 (m, 4H, Ar-H), 6.90-6.92 (m, 4H, Ar-H), 3.94 (t, ^3J = 6.5 Hz, 4H, OCH_2), 3.91 (m, 4H, CH_2), 1.95 (m, 4H, CH_2CH_2), 1.77 (quin, 4H, CH_2), 1.20-1.50 (m, 44H, $(CH_2)_{11}$), 0.86 (t, ^3J = 6.8 Hz, 6H, CH_3); calc. for $C_{59}H_{82}N_2O_7$: C 76.09, H 8.88, N 3.01; found: C 76.11, H 8.64, N = 3.22 %.

N,*N*'-Bis(4-formylphenyl)-*N*,*N*'-alkyleneureas 3/1

Under inert conditions 4-bromobenzaldehyde (5.15 g, 26.9 mmol), N,N'-propyleneurea (5.42 g, 53.4 mmol), Cs_2CO_3 (12.88 g, 38 mmol) $Pd_2(dba)_3$ (127 mg, 0.5 mol-%) and Xanthphos® (255 mg, 1.5 mol-%) are suspended in dry 1,4-dioxane (150 ml). After 35 h heating under reflux the solution is cooled down and filtered. The filter cake is washed with CH_2Cl_2. The solvent of the organic phases is removed by distillation. The crude product is washed with MeOH and crystallized from $CHCl_3$/MeOH. The MeOH solution is purified by a flash column chromatography and crystallized from $CHCl_3$/MeOH to give additional product. Yield: 5.4 g (18.2 mmol, 67%); mp. 162 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 2H, CHO), 7.87 (dt, ^3J = 8.7 Hz, ^3J = 2.32 Hz, 4H, Ar-H), 7.54 (dt, ^3J = 8.6 Hz, ^3J = 2.2 Hz, 4H, Ar-H), 3.91 (t, ^3J = 6.0 Hz, 4H, CH_2N), 2.35 (t, ^{3}J(H, H) = 6.0 Hz, 2H, CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 191.0, 153.4, 148.9, 133.3, 130.2, 125.2, 48.6, 23.0.

N,*N*'-Bis(4-hydroxyphenyl)-*N*,*N*'-alkyleneureas 5/1

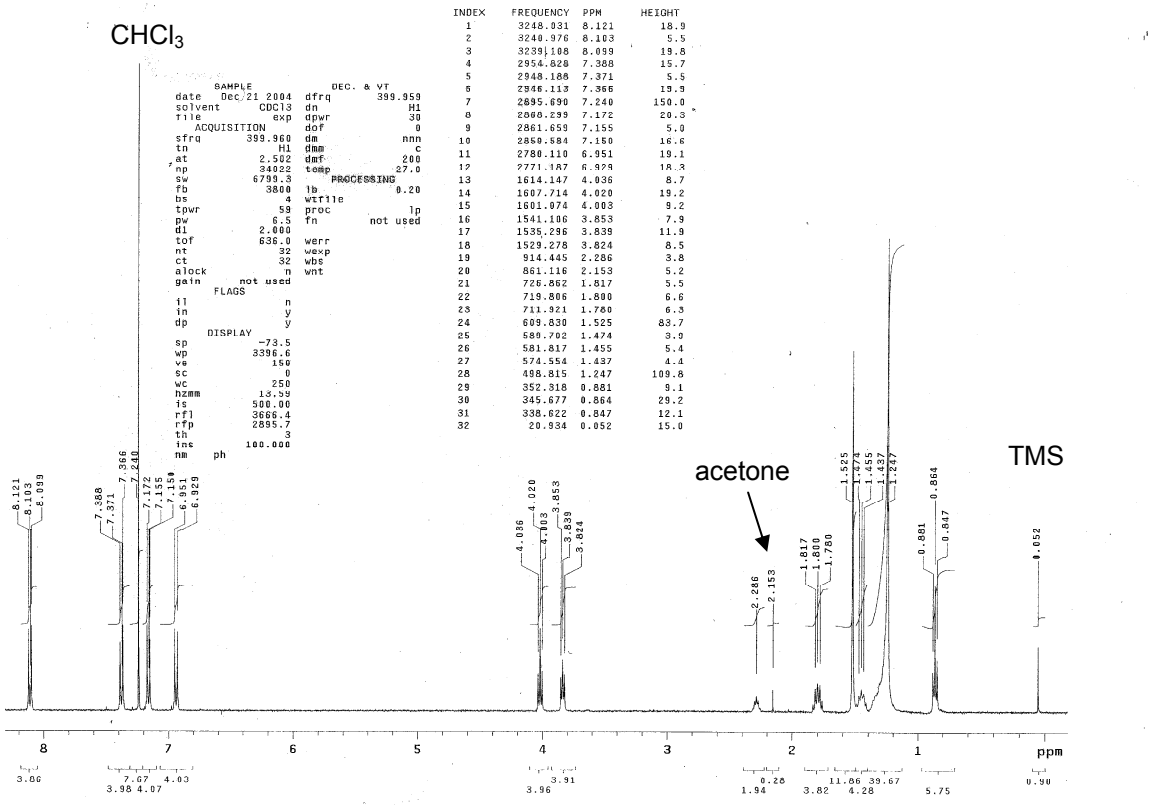
3/1 (5.3 g, 18 mmol) and *m*-Chloroperoxybenzoic acid (5.25 g, 30 mmol) are dissolved under inert conditions in $CHCl_3$ (100 ml) and stirred for 3 h. The solution is washed twice with saturated Na_2SO_3 solution (70 ml), twice with water (70 ml) and after that with brine (50 ml). The absence of peroxide is tested by KI-paper (acidified by AcOH). The solution is dried over Na_2SO_4 and the solvent is removed in vacuum by distillation. The product is crystallized from $CHCl_3$/MeOH. Yield: 0.93 g (3.3 mmol, 18%); white solid; mp. 318- 331°C (dec.); ^{1}H-NMR

(400MHz, CD_3OD): δ = 7.08 (d, ^3J = 8.9 Hz, 4H, Ar-H), 6.75 (d, ^3J = 8.9 Hz, 4H, Ar-H), 3.73 (t, ^3J = 5.8 Hz, 4H, CH_2N), 2.14 (m, 2H, CH_2).

Esterification of 5/1

7/1: 4-Tetradecyloxybenzoic acid (0.530 g, 0.71 mmol) is dissolved in $SOCl_2$ (10 ml) and the mixture is stirred for 5 min at room temperature (hood). The excess of $SOCl_2$ is distilled off and traces were removed under reduced pressure (100 °C bath temperature). The residue is dissolved in dry CH_2Cl_2 (50 ml), a solution of with **5/1** (0.205 g, 0.31 mmol) and DMAP (20 mg) and then. Et_3N (0.8 ml) is dropped to the solution with stirring. After 6 h stirring and heating under reflux the solution is cooled to room temperature. The solution is washed twice with (70 ml) and with brine (50 ml). The solution is dried over Na_2SO_4 and the solvent is removed in vacuum by distillation. The solvent is removed in vacuum by distillation and the residue was purified by repeated crystallization from $CHCl_3$/MeOH. Yield: 0.64 g (0.7 mmol, 99%); ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, ^3J = 8.9 Hz, 4H, Ar-H), 7.34 (d, ^3J = 8.92 Hz, 4H, Ar-H), 7.16 (d, ^3J = 8.7 Hz, 4H, Ar-H), 6.95 (d. ^3J = 8.9 Hz, 4H, Ar-H), 4.02 (t, ^3J = 6.5 Hz, 4H, CH_2O), 3.83 (s, 4H, CH_2N), 1.90 (s, 2H, C*H*$_2$$CH_2N$), 1.82 (t, ^3J = 6.8 Hz, 4H, C*H*$_2$$CH_2O$), 1.54 (s, 4H, C*H*$_2$$CH_2CH_2O$), 1.45 (m, 4H, C*H*$_2$$CH_2CH_2CH_2O$), 1.25 (m, 38H, CH_2), 0.86 (t, ^3J = 6.8 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, $CHCl_3$): δ = 164.8, 163.5, 154.3, 148.4, 141.3, 132.2, 126.8, 121.8, 121.6, 114.3, 68.4, 49.5, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.1, 23.3, 22.8, 14.2.

^{1}H-NMR:



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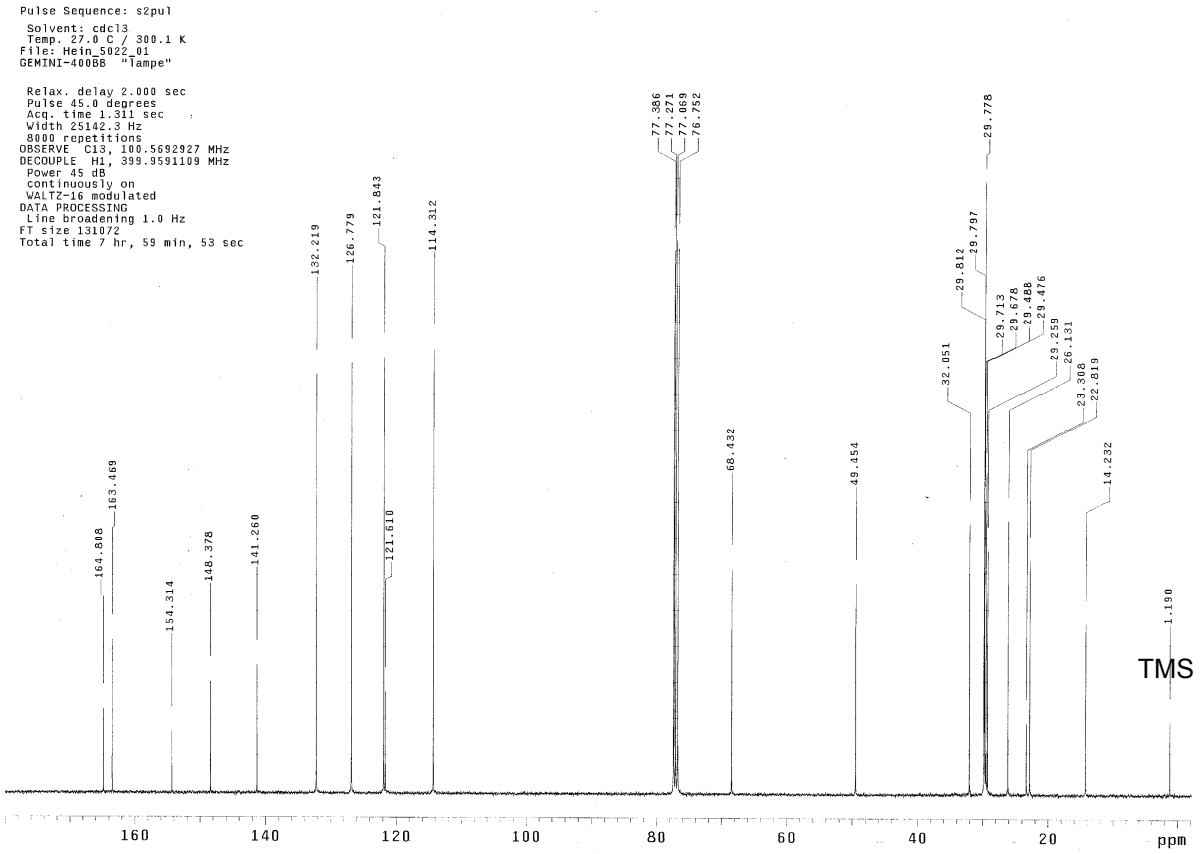
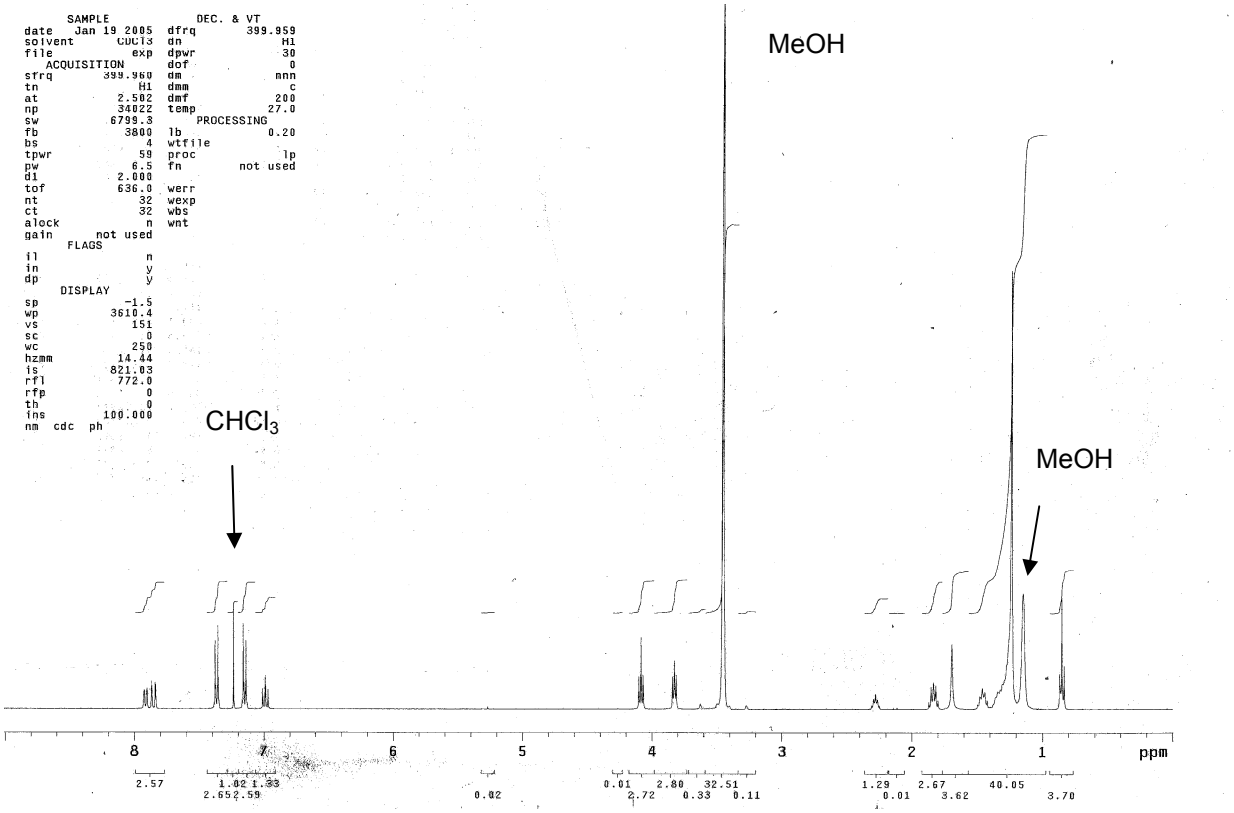


8/1: Yield: 0.29 g (0.30 mmol, 96 %); ^{1}H-NMR ($CHCl_3$, 400 MHz): δ = 7.93 (m, 2H, Ar-H), 7.87 (d, ^{3}J = 11.4 Hz, 2H, Ar-H), 7.35 (d, ^{3}J = 8.9 Hz, 4H, Ar-H), 7.15 (d, ^{3}J = 9.1 Hz, 4H, Ar-H), 7.00 (t, ^{3}J = 8.4 Hz, 2H, Ar-H), 4.20 (t, ^{3}J = 6.6 Hz, 4H, CH_2O), 3.85 (s, 4H, CH_2N), 1.9 (s, 2H, C$H_2$$CH_2O$), 1.84 (m, C$H_2$$CH_2O$), 1.46 (dd, ^{3}J = 7.7 Hz, ^{3}J = 7.5 Hz, 4H, C$H_2$$CH_2CH_2O$), 1.32 (m, 4H, C$H_2$$CH_2CH_2CH_2O$), 1.24 (m, H, CH_2), 0.86 (t, ^{3}J = 6.9 Hz, 6H, CH_3); ^{13}C-NMR (100 MHz, $CHCl_3$): δ = 163.9 (d), 154.3, 151.9 (d), (153.2 +150.7), 148.2, 141.4, 127.3 (d), 126.8, 122.0 (d), 121.7, 117.9, 117.7, 113.6, 69.6, 49.4, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 26.0, 23.3, 22.8, 14.2.

^{1}H-NMR:



^{13}C-NMR: