Supplementary Material (ESI) for Soft Matter

Supporting Information

Siloxanes and carbosilanes as new building blocks for T-shaped bolaamphiphilic LC molecules

Robert Kieffer,[a] Marko Prehm,[a,b] Karsten Pelz,[b] Ute Baumeister,[b] Feng Liu,[c] Harald Hahn, [d] Heinrich Lang,[d] Goran Ungar,*[c] Carsten Tschierske *[a]

[a] *Organic Chemistry, Institute of Chemistry, Martin Luther University Halle-Wittenberg, Kurt Mothes Str. 2, D-06120 Halle, Germany; Fax: +49 345 552 7346; Tel: +49 345 552 5664; E-mail: carsten.tschierske@chemie.uni-halle.de*

[b] *Physical Chemistry, Institute of Chemistry, Martin Luther University Halle-Wittenberg, Mühlpforte, D-06108 Halle, Germany*

[c] *Department of Engineering Materials, University of Sheffield, Mappin Street, Sheffield S13JD, UK, E-mail: g.ungar@sheffield.ac.uk*

[d] *Department of Chemistry, Institute of Inorganic Chemistry, TU Chemnitz, Str. der Nationen 62, D-09111 Chemnitz, Germany*

1. Additional Figures and Tables

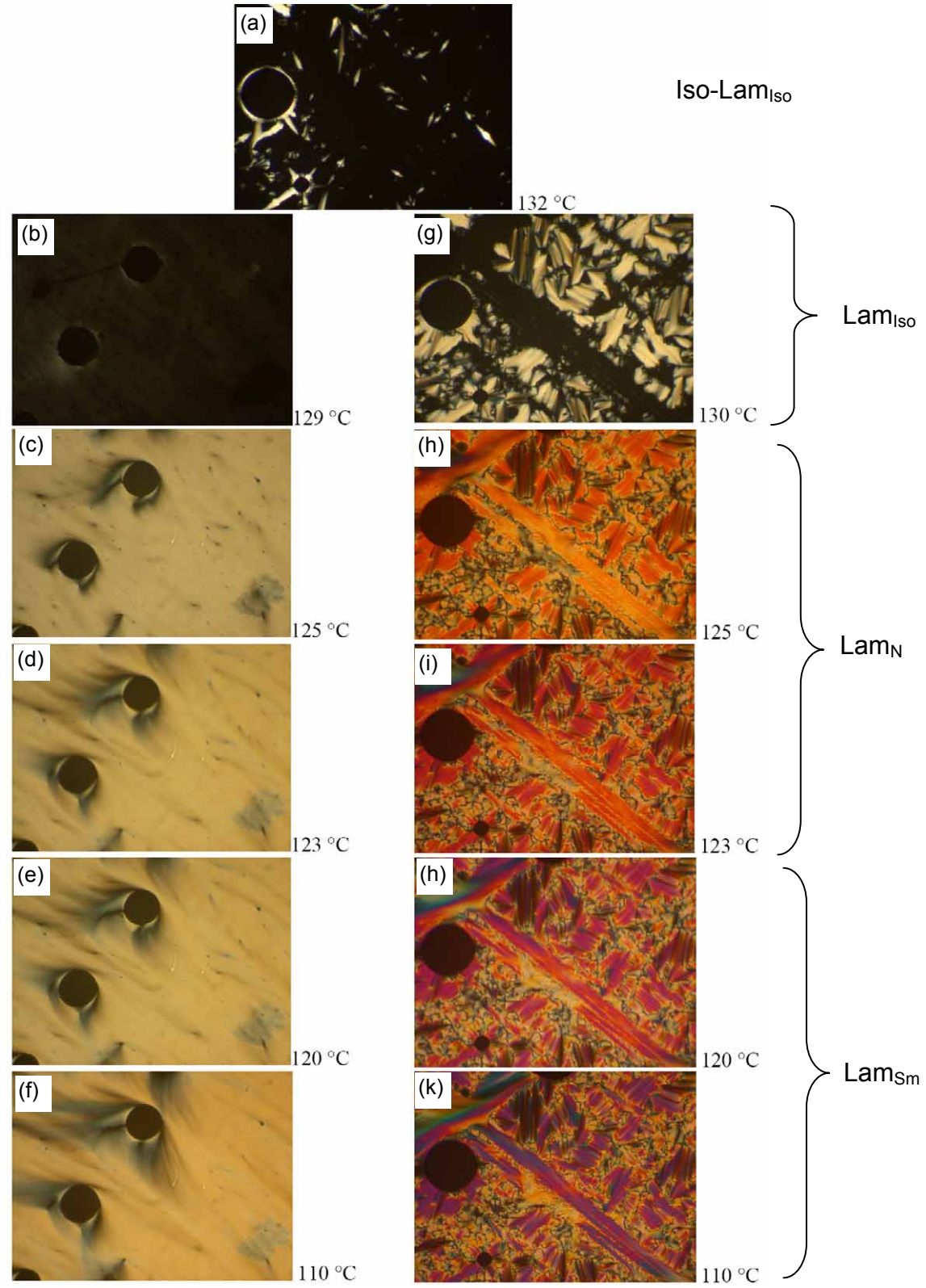

Figure S1. Textures of **C3** at different temperatures: left, homeotropic alignment; right defect texture in the predominately homogeneously aligned region.

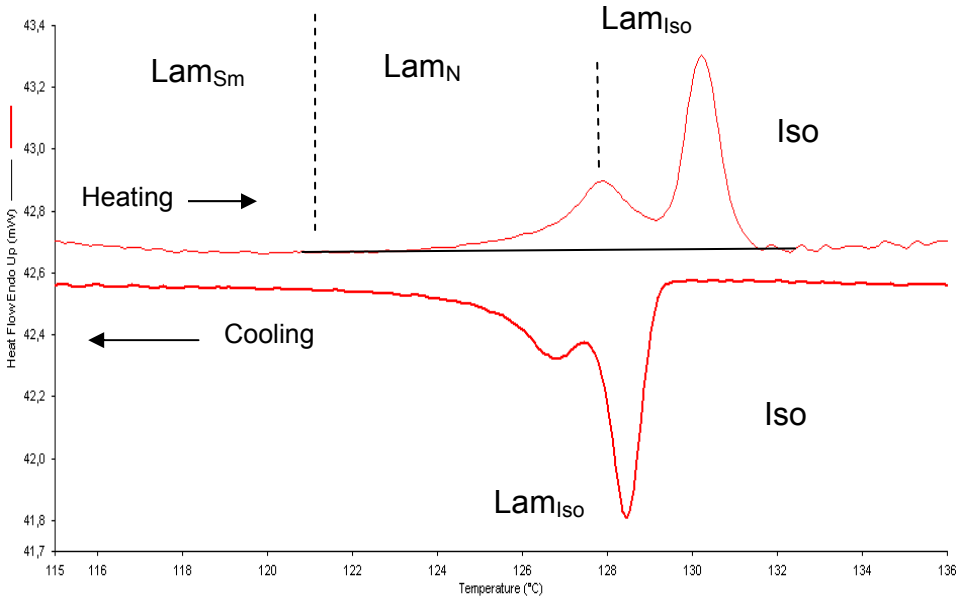

Figure S2. DSC heating ans cooling curves of compound **C3** (5 K min^{-1}).

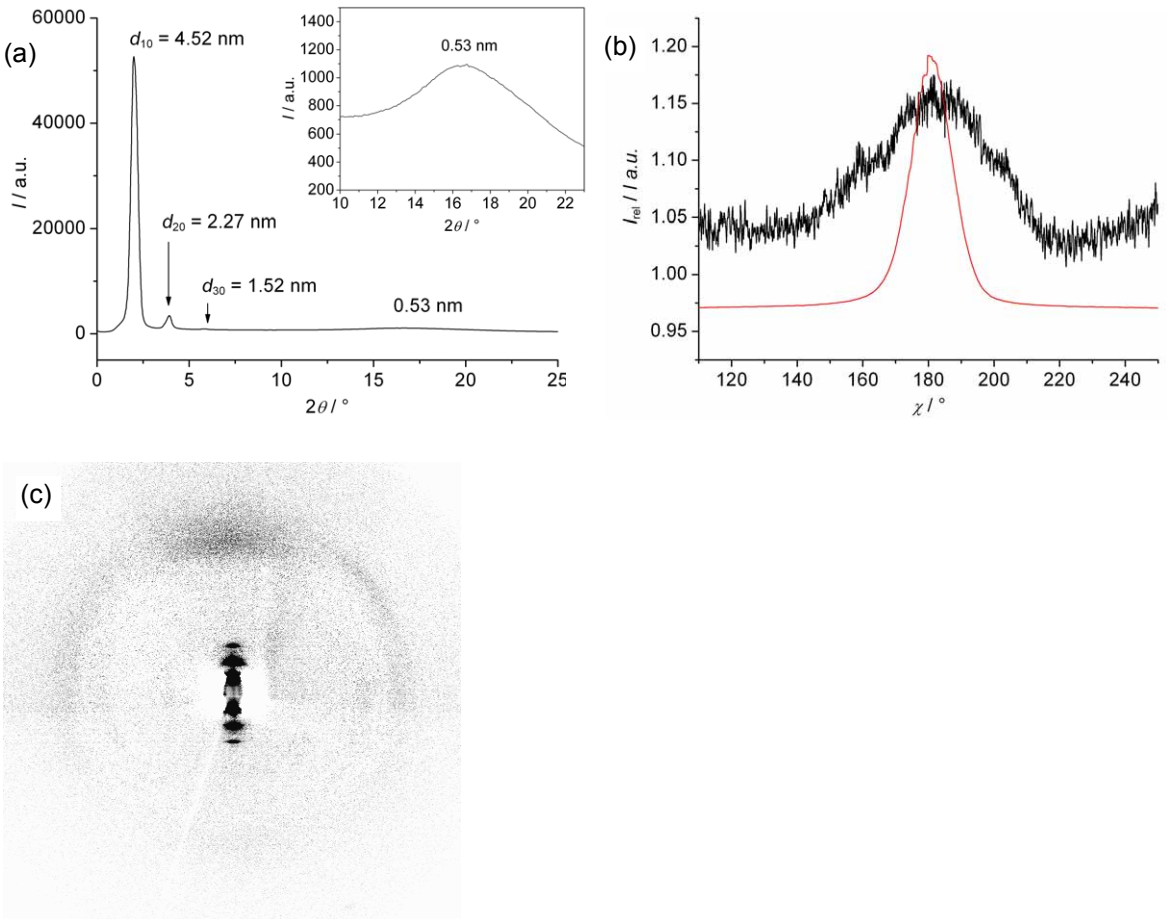

Figure S3. X-ray scattering of the Lam$_N$ phase of **C7**: (a) powder diffraction pattern at 129 °C with *d*-values for the observed reflections and for the maximum of the diffuse scattering (inset); (b) azimuthal distribution of the wide-angle scattering $I_{rel}(\chi)$ at 2θ = 14-22° (black line) with maxima at 180° [I_{rel} = I(129 °C) / I(150 °C, Iso)]. The χ distribution of the 0*k*-reflections at 2θ = 0-7° is shown for comparison (red line); (c) pattern after subtraction of the isotropic phase I_{rel} = I(T)–I(Iso).

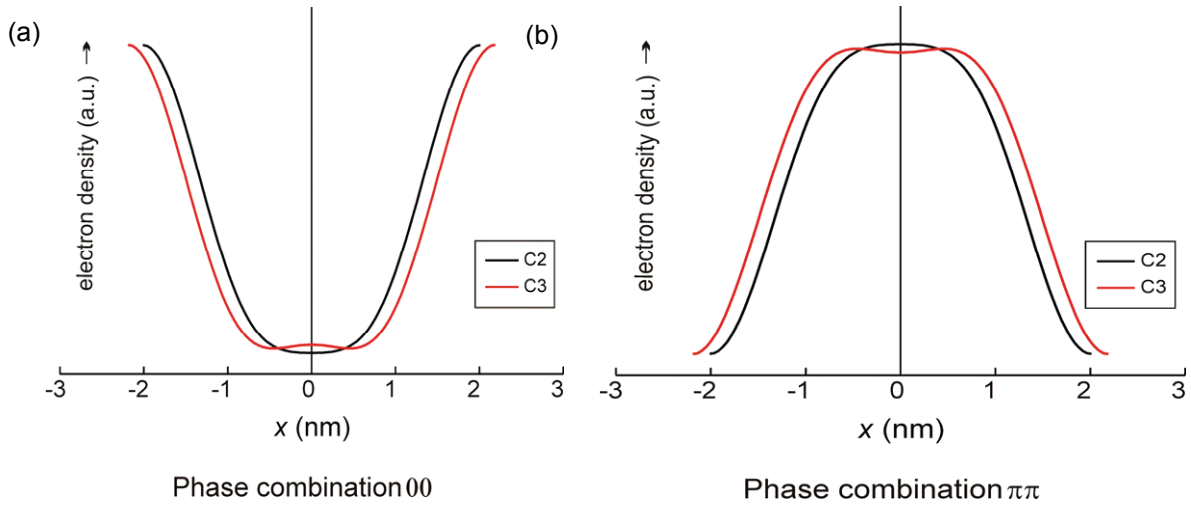

Figure S4. Comparison of the electron density profiles of the Lam_{Sm} phase of compounds **C2** and **C3** for two alternative phase angle (ϕ) combinations of the first two layer X-ray reflection orders: (a) 0,0 and (b) π,π. For the other two phase combinations, (0,π) and (π,0), the profiles differ from those shown only in the position of the origin.

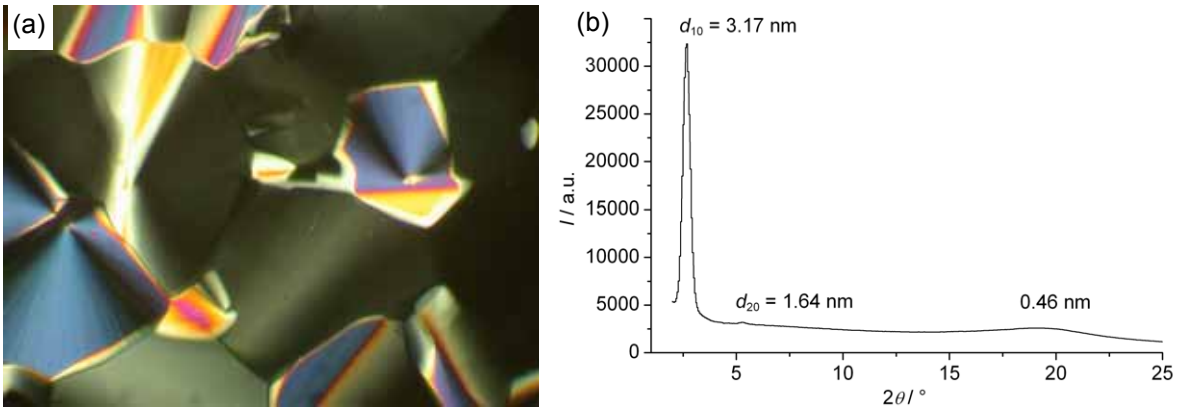

Figure S5. (a) Texture of the Col_{hex}-phase of **H6** at T = 116 °C; (b) powder diffraction pattern of the Col_{hex}-phase of **H4** at T = 110 °C with d-values for the layer reflections and for the maximum of the diffuse outer scattering.

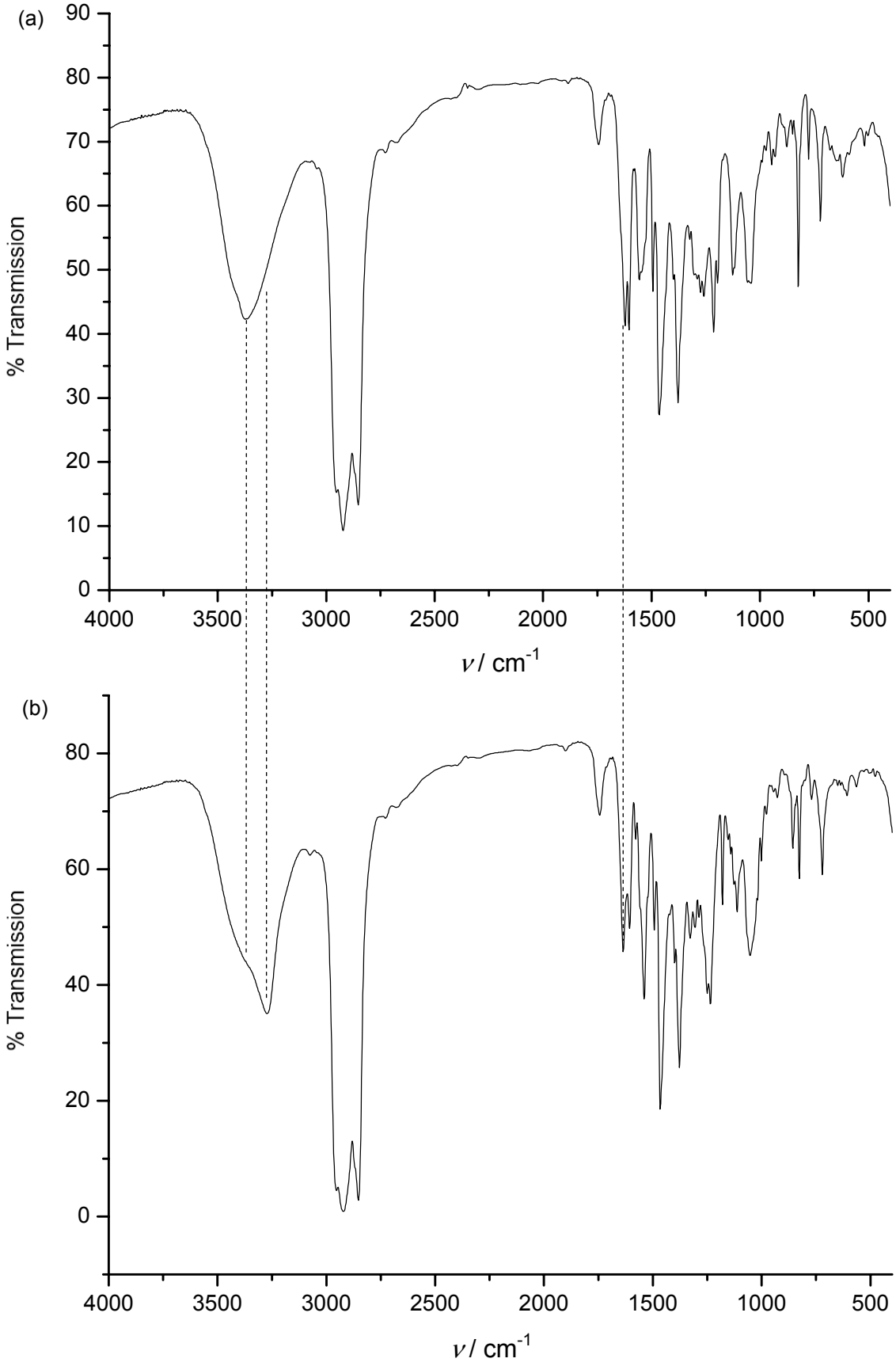

Figure S6. FT-IR spectra of a) compound **H3** and b) compound **H6** in nujol at $T = 20°$ C ($T =$ transmission.

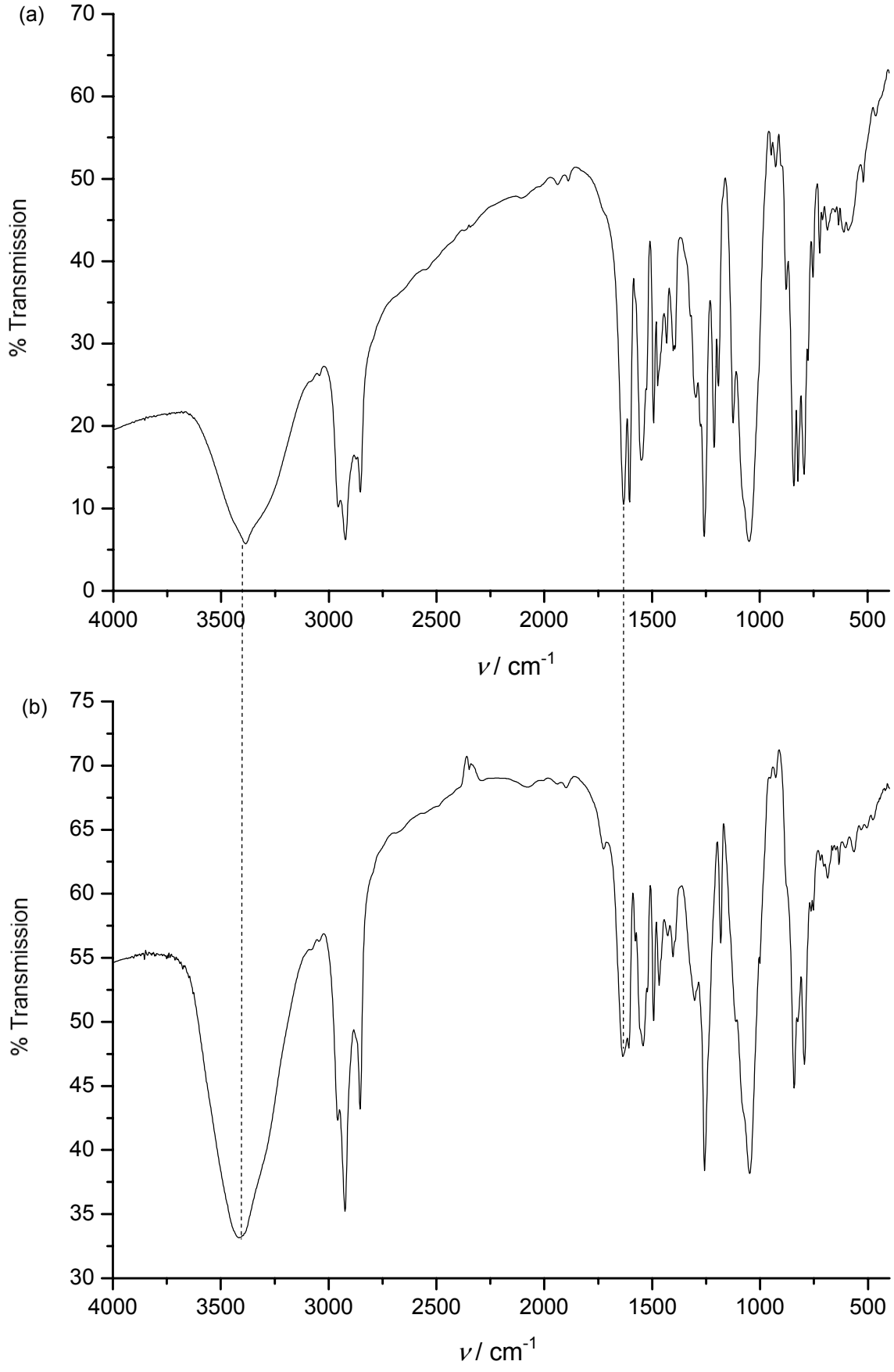

Figure S7. FT-IR spectra of a) compound **Si1** and b) compound **Si4** in KBr at T = 20° C (T = transmission.

Table S1. Crystallographic data (θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated *d* spacing; *hk*/*n*: assigned indices for Col_{hex} phases/ order of reflection for Lam phases, Parameter used: Lattice parameters or *d* values used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm)

Comp.	*T*/°C	Phase	θ_{obs}	d_{obs}	*hk*/*n*	d_{calc}	d_{obs}- d_{calc}	Parameter used/nm
Si1	104	Col_{hex}	1.361	3.25	10	3.25	0.00	*a* = 3.75
			2.378	1.86	11	1.88	-0.02	
			2.741	1.61	20	1.63	-0.02	
Si2	102	Lam_{Sm}	1.188	3.72	1	3.72	0.00	*d* = 3.72
			2.366	1.88	2	1.86	0.02	
Si3	108	Lam_{Sm}	2.344	3.77	1	3.77	0.00	*d* = 3.77
			4.676	1.89	2	1.89	0.00	
C1	100	Col_{hex}	1.401	3.15	10	3.15	0.00	*a* = 3.64
			2.402	1.84	11	1.82	0.02	
			2.739	1.61	20	1.58	0.03	
C4	105	Col_{hex}	1.424	3.10	10	3.10	0.00	*a* = 3.58
			2.813	1.57	20	1.55	0.02	
C5		Lam_{Sm}	1.354	3.26	1	3.26	0.00	*d* = 3.26
			2.674	1.65	2	1.63	0.02	
C6	105	Lam_{Sm}	1.254	3.52	1	3.52	0.00	*d* = 3.52
			2.492	1.77	2	1.76	0.01	
C7	129	Lam_{N}	1.013	4.52	1	4.52	0.00	*d* = 4.52
			1.948	2.27	2	2.26	0.01	
			2.904	1.52	3	1.51	0.01	
H4	110	Col_{hex}	1.390	3.17	10	3.17	0.00	*a* = 3.66
			2.689	1.64	20	1.59	0.05	
H5	100	Col_{hex}	1.340	3.29	10	3.29	0.00	*a* = 3.80
			2.325	1.90	11	1.90	0.00	
H6	110	Col_{hex}	1.290	3.42	10	3.42	0.00	*a* = 3.95
			2.235	1.98	11	1.98	0.00	
			2.580	1.71	20	1.71	0.00	

Table S2. Calculations of molecular volume (V_{mol}), volume of the hypothetical unit cells (V_{cell}) the number of molecules in these unit cells (n_{cell}) and the average thickness of the cylinder walls and aromatic layers (n_{wall}).[a]

Comp.	Phase	V_{cell}/nm^3	V_{mol} /nm^3	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}	n_{wall}
Si1	Col_{hex}	5.48	0.93	5.9	4.6	5.3	1.8
Si2	Lam_{Sm}	3.18	1.03	3.1	2.5	2.8	2.8
Si3	Lam_{Sm}	3.22	1.03	3.1	2.5	2.8	2.8
C1	Col_{hex}	5.16	0.86	6.0	4.7	5.4	1.8
C2	Lam_{Sm}	3.44	1.16	3.0	2.4	2.7	2.7
C3	Lam_{Sm}	3.55	1.32	2.7	2.1	2.4	2.4
C4	Col_{hex}	5.00	0.77	6.5	5.1	5.8	1.9
C5	Lam_{Sm}	2.64	0.93	2.8	2.2	2.5	2.5
C6	Lam_{Sm}	2.85	1.09	2.6	2.0	2.3	2.3
C7	Lam_{N}	3.66	1.29	2.8	2.2	2.5	2.5
H4	Col_{hex}	5.22	0.80	6.5	5.1	5.8	1.9
H5	Col_{hex}	5.63	0.85	6.6	5.2	5.9	2.0
H6	Col_{hex}	6.08	0.90	6.8	5.3	6.1	2.0

[a] V_{cell} = volume of the unit cell defined by the dimensions a^2 x sin(60°) x 0.45 nm for the Col_{hex} phases and by the dimensions d x 0.45 nm x L, where L is the length of the bolaamphiphilic core which is 1.8 nm for compounds **Si*n*** and **C1-3** having two glycerol groups (value corresponds to the periodicity parallel to the layers planes as measured for the correlated Lam phases with *p2mm* lattice[S12]) and L = 1.9 nm is used for the amides **C5-C7** (length of the bolaamphiphilic core in the most compact form as measured with CPK models); V_{mol} = volume for a single molecule as calculated using the crystal volume increments;[S1] a volume of 0.023 nm^3 was assumed for Si; $n_{cell,cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is k = 0.7;[S2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient k = 0.55, calculated according to $n_{cell,liq} = 0.55/0.7$ x $n_{cell,cryst}$; n_{cell} = in the LC phase estimated as the average of that in the $n_{cell,cryst}$ and $n_{cell,liq}$; n_{wall} = average number of molecules organized side-by-side in the cross section of the cylinder walls; for the Lam phases this number indicates the number of molecules organized in the cross section of the aromatic sublayers.

2. Conditions for X-ray scattering

2.1 X-ray scattering on powder-like and aligned samples

X-ray investigations on powder-like samples were carried out with a Guinier film camera (Huber), samples in glass capillaries (∅ 1 mm) in a temperature-controlled heating stage, quartz-monochromatized CuK_α radiation, 30 to 60 min exposure time, calibration with the powder pattern of $Pb(NO_3)_2$. Aligned samples were obtained on a glass plate. Alignment was achieved upon slow cooling (rate: 1 $K \cdot min^{-1}$ – 0.01 $K \cdot min^{-1}$) of a small droplet of the sample and takes place at the sample–glass or at the sample–air interface, with domains fiber-like disordered around an axis perpendicular to the interface. The aligned samples were held on a temperature-controlled heating stage and the diffraction patterns were recorded with a 2D detector (HI-STAR, Siemens).

2.2 Synchrotron X-ray diffraction and electron density reconstruction

High-resolution small-angle powder diffraction experiments were recorded at Station I22 of the Diamond Light Source, U.K. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage was used, with a hole for the capillary drilled through the silver heating block and with mica windows attached to it on each side. A RAPID2 area detector was used. q calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of n-alkanes. Diffraction intensities were Lorentz corrected. From the corrected intensities I_n of the diffraction orders n we have reconstructed the differential one-dimensional electron density profiles $\Delta\eta\,(x)$ along the layer normal, using:

$$\Delta\eta_{\mathrm{exp}}(x) \approx \sum_{n=1}^{N} \sqrt{I_n}\,\cos(q_n x + \phi),\ \phi = 0, \pi.$$

Here $\Delta\eta(x) = \eta(x) - \langle\eta\rangle$, where $\eta(x)$ and $\langle\eta\rangle$ are local and average electron densities, q is the wavevector and N is the number of diffraction orders analysed, $N = 2$ in the present case..

Table S3a. Experimental and calculated d-spacings and Lorentz corrected intensities of SAXS reflections of the Lam_{Sm} phase of compound **C2** at 110 ºC; d = 4.02 nm.

(hk)	$d_{obs.}$ –spacing/nm	$d_{cal.}$ –spacing/nm	intensity
(10)	4.02	4.02	100.0
(20)	2.01	2.01	5.3

Table S3b. Experimental and calculated d-spacings and Lorentz corrected intensities of SAXS reflections of the Lam_{Sm} phase of compound **C3** at 110 ºC; d = 4.38 nm.

(hk)	$d_{obs.}$ –spacing/nm	$d_{cal.}$ –spacing/nm	intensity
(10)	4.38	4.38	100.0
(20)	2.19	2.19	9.8
(30)	1.47	1.47	0.6

3. Molecular dynamics simulation

Annealing dynamics runs for compound **C3** were carried out using the Forcite Plus module of Material Studio (Accelrys). Universal Force Field was used. The structures in Figure 10 were obtained with 12 molecules in a box 9.1 x 0.45 x 4.38 nm^3 with periodic boundary conditions. 30 temperature cycles of NVT dynamics were run between 300 and 700 K, with a total annealing time of 30 ps.

3. Synthesis and Analytical Data

3.1 Intermediates

3.1.1 Biphenyl based building blocks

4-Bromo-2-hydroxybenzoic acid:[S3] 4-Amino-2-hydroxybenzoic acid (50 g, 0.33 mol) was added in small portions to 24% HBr (175 ml). The suspension was cooled to 0 °C and under vigorous stirring a 2.5M solution of $NaNO_2$ (22.5 g in 130 ml H_2O) was added dropwise. During addition the temperature was kept always below 5 °C. The reaction mixture was checked with iodine/starch paper for excess of nitrite. Nitrite solution was added until positive proof. The excess was removed by addition of urea. The resulting diazonium salt was added immediately to the cooled Cu(I)Br solution [$CuSO_4 * 5\ H_2O$ (108.7 g, 0.44 mol) was dissolved in H_2O (350 ml) and KBr (77.7 g, 0.66 mol) was added; while stirring, a solution of Na_2SO_3 (27.4 g, 0.22 mol) in H_2O (90 ml) was added; after cooling to r.t., the resulting precipitate was washed with H_2O (2x 100 ml); the precipitate then was dissolved in 48% HBr (175 ml) at 0 °C under vigorous stirring]. After the formation of N_2 ceased, the reaction mixture was heated and kept at 70 °C for 1 h. The mixture was cooled to r.t. and the precipitate was filtered off. The solid was dissolved in EtOAc (200 ml) and washed with H_2O (100 ml). After separation the organic phase was dried over Na_2SO_4. The solvent was evaporated and the crude product was crystallised from ethanol. Yield: 23.8 g (34 %); beige coloured solid; mp = 214 °C (subl.) [lit.[S4] 210-212 °C (petroleum ether)]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.80 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 7.17 (d, 1H, ^4J(H,H) = 2.0 Hz, 1H, Ar-H), 7.13 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H).

4-Bromo-3-hydroxybenzoic acid:[S3] Synthesized and purified in an analogues way from 4-amino-3-hydroxybenzoic acid (50 g, 0.33 mol). Yield: 62 g (88 %); red-brownish solid; mp = 221 °C [lit.[S5] 225-226 °C (water)]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.64 (s, 1H, Ar-H), 7.63 (d,^3J(H,H) = 6.4 Hz, 1H; Ar-H), 7.43 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H).

Methyl 4-bromo-2-hydroxybenzoate: 4-Bromo-2-hydroxybenzoic acid (23.8 g, 109.6 mmol) was dissolved in dry MeOH (200 ml) and conc. H_2SO_4 (5 ml) was added dropwise. The solution was then refluxed for 10 h. After the the solution was poured on ice (500 g) the resulting precipitate was filtered off. The solid was dissolved in Et_2O (100 ml) and washed with sat. aq. $NaHCO_3$ and brine (50 ml each). The organic phase was dried over Na_2SO_4, the solvent was evaporated and the crude product was purified by crystallisation from MeOH. Yield: 21.0 g (83 %); brownish solid; mp = 33-36 °C [lit.[S6] 41-42 °C]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 10.83 (s, 1H, OH), 7.76 (d, ^3J(H,H) = 8.6 Hz, 1H, Ar-H), 7.19 (d, ^4J(H,H) = 2.0 Hz, 1H, Ar-H), 7.13 (d, ^3J(H,H) = 8.5 Hz, 1H, Ar-H), 3.96 (s, 3H, CH_3).

Methyl 4-bromo-3-hydroxybenzoate:[S7] Synthesized and purified in an analogues way from 4-bromo-3-hydroxybenzoic acid (50 g, 230.4 mmol). Yield: 51.1 g (96 %); reddish solid; mp = 119 °C [lit.[S7] 121-123 °C (methanol)]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 9.25 (s, 1H, OH), 7.63 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.60 (d, ^4J(H,H) = 2.0 Hz, 1H, Ar-H), 7.40 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 3.85 (s, 3H, CH_3).

Methyl 2-benzyloxy-4-bromobenzoate: Methyl 4-bromo-2-hydroxybenzoat (8.75 g, 37.9 mmol) was dissolved in dry acetone (75 ml). After adding K_2CO_3 (10.5 g, 76.0 mmol) and benzylbromide (7.8 g, 45.6 mmol) the reaction mixture was refluxed for 10 h. After cooling to r.t. the mixture was poured on ice the aqueous phase was extracted with Et_2O (2x 50 ml). The combined organic phases were washed with H_2O, sat. aq. $NaHCO_3$ and brine (50 ml each). The organic phase was dried over Na_2SO_4, the solvent was evaporated and the resulting solid was crystallised from MeOH. Yield: 11.25 g (93 %); pale yellow solid; mp = 48-49.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.48-7.46 (m, 2H, 1H, Ar-H), 7.40-7.36 (m, 2H, 1H, Ar-H), 7.33-7.29 (m, 1H, 1H, Ar-H), 7.17 (d, ^4J(H,H) = 1.8 Hz, 1H, Ar-H), 7.13 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 5.14 (s, 2H, Ph-CH_2), 3.87 (s, 3H, CH_3).

Methyl 3-benzyloxy-4-bromobenzoate: Synthesized and purified in an analogues way from methyl 4-bromo-3-hydroxybenzoate (50 g, 216 mmol), K_2CO_3 (59.8 g, 433 mmol), BnBr (44.4 g, 260 mmol) in acetone (300 ml). Yield: 65.2 g (94 %); reddish solid; mp = 73-75 °C [lit.[S8] 81-83 °C (ethanol)]; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.63-7.60 (m, 2H, Ar-H), 7.52-7.47 (m, 3H, Ar-H), 7.41-7.37 (m, 2H, Ar-H), 7.34-7.30 (m, 1H, Ar-H), 5.19 (s, 2H, Ph-CH_2), 3.89 (s, 3H, CH_3).

2-Benzyloxy-4-bromobenzoic acid 1a:[S9] Methyl 2-benzyloxy-4-bromobenzoate (26.5 g, 82.5 mmol) was dissolved in EtOH (50 ml). After the addition of a solution of KOH (16.2 g, 289 mmol) in H_2O (20.5 ml) the mixture was refluxed for 12 h. The reaction was cooled to r.t. and conc. HCl was carefully added until pH < 5. The resulting pale yellow precipitate was filtered off and the aqueous phase was extracted with Et_2O (100 ml). The precipitate was dissolved in Et_2O (150 ml) and the combined organic phases were washed with H_2O (150 ml). After the Et_2O phase was dried over Na_2SO_4, the solvent was evaporated. The resulting product was used without further purification. Yield: 25.3 g (99 %); pale yellow solid; mp = 118 °C [lit.[S9] 112-116 °C (ethanol, water)]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 11.08 (s, 1H, OH), 7.79 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.46 (d, ^4J(H,H) = 1.8 Hz, 1H, Ar-H), 7.42-7.38 (m, 2H, Ar-H), 7.36-7.31 (m, 1H, Ar-H), 7.26 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 5.34 (s, 2H, Ph-CH_2).

3-Benzyloxy-4-bromobenzoic acid 1b:[S10] Synthesized and purified in an analogues way from methyl 3-benzyloxy-4-bromobenzoate (60.0 g, 187 mmol). Yield: 57.0 g (99.3 %); colourless solid; mp = 197-202 °C [lit.[S10] 196-198 °C (ethanol)]; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.72 (m, 2H), 7.56 (d, 3H, ^3J(H,H) = 8.2 Hz), 7.41 (m, 2H), 7.33 (m, 1H), 5.32 (s, 2H, Ph-CH_2).

Pentafluorophenyl 2-benzyloxy-4-bromobenzoate: To a solution of **1a** (13.7 g, 44.6 mmol) in dry THF (100 ml) DCC (10.1 g, 49.1 mmol) and pentafluorophenol (9.0 g, 49.1 mmol) were added at 0 °C. The reaction was allowed to come to r.t. and stirred for 24 h. The solvent was evaporated and the resulting solid was dissolved in $CHCl_3$. The insoluble parts were filtered off and the dissolved product was purified by column chromatography (eluent: $CHCl_3$, R_F = 0.66). Yield: 14.5 g (69 %); pale yellow solid; mp = 101 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, ^3J(H,H) = 8.5 Hz, 1H, Ar-H), 7.47-7.45 (m, 2H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.32-7.29 (m, 1H, Ar-H), 7.27 (d, ^4J(H,H) = 1.7 Hz, 1H, Ar-H), 7.22 (d, ^3J(H,H) =

8.4 Hz, 1H, Ar-H), 5.20 (s, 2H, Ph-CH_2); ^{19}F-NMR (200 MHz, $CDCl_3$): δ = -152.46 (2F), -158.30 (1F), -162.57 (2F).

Pentafluorophenyl 3-benzyloxy-4-bromobenzoate: Synthesized and purified in an analogues way from **1b** (55.0 g, 179 mmol), DCC (40.6 g, 197 mmol), pentafluorophenol (36.3 g, 197 mmol) in THF (350 ml), purified by column chromatography (eluent: $CHCl_3$, R_F = 0.70). Yield: 76.5 g (90 %); colourless solid; mp = 107 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.78-7.68 (m, 3H, Ar-H), 7.54-7.50 (m, 2H, Ar-H), 7.44-7.29 (m, 3H, Ar-H), 5.24 (s, 2H, Ph-CH_2); ^{19}F-NMR (200 MHz, $CDCl_3$): δ = -152.52 (2F), -157.68 (1F), -162.21 (2F).

2-Benzyloxy-4-bromo-*N*-(2,3-dihydroxypropyl)benzamide: To a solution of 1-amino-propane-2,3-diol (3.9 g, 42.9 mmol) in dry THF (200 ml) a solution of pentafluorophenyl 2-benzyloxy-4-bromobenzoat (20.3 g, 42.9 mmol) in dry THF (70 ml) was added dropwise. The reaction was stirred at r.t. for 48 h. The solvent was evaporated and the yielding yellow oil dissolved in EtOAc (150 ml). The organic phase was washed with Na_2CO_3 solution and H_2O (50 ml each). The organic phase was dried over Na_2SO_4 and the solvent evaporated. The yellowish crude material was purified by crystallisation from EtOAc (150 ml). Yield: 16.1 g (99 %); colourless solid; mp = 93-96 °C; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 8.24 (s, 1H, N-H), 7.96 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.44-7.40 (m, 3H, Ar-H), 7.38-7.34 (m, 1H, Ar-H), 7.25 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 5.39 (s, 2H, Ph-CH_2), 3.72-3.67 (m, 1H, CHO), 3.55-3.48 (m, 1H, CH_2O), 3.45-3.38 (m, 3H, CH_2O).

3-Benzyloxy-4-bromo-*N*-(2,3-dihydroxypropyl)benzamide: Synthesized in an analogues way from pentafluorophenyl 3-benzyloxy-4-bromobenzoate (76.4 g, 161.5 mmol), 1-amino-propane-2,3-diol (17.7 g, 194 mmol) in THF (450 ml). After evaporation of THF the product was crystallized from EtOAc (2x 200 ml). The resulting solid was filtered off and washed with Et_2O (200 ml). Yield: 55.3 g (90 %); colourless solid; mp = 113-115 °C; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.93 (s, 1H, N-H), 7.71 (d, ^4J(H,H) = 2.0 Hz, 1H, Ar-H), 7.66 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.55 (d, ^3J(H,H) = 7.4 Hz, 2H, Ar-H), 7.45-7.39 (m, 3H, Ar-H), 7.35-7.32 (m, 1H, Ar-H), 5.28 (s, 2H, Ph-CH_2), 3.80-3.76 (m, 1H, CHO), 3.57-3.43 (m, 4H, CH_2O).

2-Benzyloxy-4-bromo-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide 3a: 2-Benzyloxy-4-bromo-*N*-(2,3-dihydroxypropyl)benzamide (25.0 g, 65.7 mmol) was dissolved in 2,2-dimethoxypropane (200 ml). Pyridinium p-toluenesulfonate (200 mg) was added and the solution was stirred at r.t. for 48 h. The solvent was then evaporated and the residue was dissolved in Et_2O (200 ml). The organic phase was washed with sat. aq. $NaHCO_3$ and brine (75 ml each). After phase separation and drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by column chromatography (eluents: $CHCl_3$/MeOH = 10:0.2 (v/v), R_F = 0.50). Yield: 20.3 g (74 %); waxy, colourless solid; mp = 90-92 °C; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 8.07 (s, 1H, N-H), 7.96 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 7.59-7.57 (m, 2H, Ar-H), 7.47-7.42 (m, 3H, Ar-H), 7.41-7.37 (m, 1H, Ar-H), 7.25 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 5.38 (s, 2H, Ph-CH_2), 4.18-4.12 (m, 1H, CHO), 3.91 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 3.58 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 3.54-3.48 (m, 1H, CH_2O), 3.45-3.39 (m, 1H, CH_2O), 1.26 (s, 3H, CH_3), 1.22 (s, 3H, CH_3).

3-Benzyloxy-4-bromo-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide 3b:
Synthesized in an analogues way from 3-benzyloxy-4-bromo-*N*-(2,3-dihydroxypropyl)-benzamide (25.0 g, 65.7 mmol), R_F = 0.51. Yield: 26.0 g (94 %); waxy, colourless solid; mp = 88-92 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.48-7.46 (m, 3H, Ar-H), 7.40-7.36 (m, 2H, Ar-H), 7.33-7.29 (m, 1H, Ar-H), 7.13 (d, ^3J(H,H) = 8.2 Hz,

1H, Ar-H), 6.43 (s, 1H, N-H), 5.19 (s, 2H, Ph-CH_2), 4.35-4.29 (m, 1H, CHO), 4.07 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.74-3.67 (m, 2H, CH_2O), 3.51-3.44 (m, 1H, CH_2O), 1.43 (s, 3H, CH_3), 1.35 (s, 3H, CH_3).

3-Benzyloxy-4´-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]biphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (4aBn): A mixture of **3a** (8.9 g, 21.2 mmol), 4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)benzeneboronic acid **2**[S11] (5.9 g, 23.3 mmol), $Pd(PPh_3)_4$ (0.7 g, 0.61 mmol), glyme (100 ml), sat. aq. $NaHCO_3$ (100 ml) was refluxed for 10 h under an argon atmosphere. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in $CHCl_3$ (150 ml). The resulting solution was filtered through a plug of silica gel to remove the catalyst and then washed with H_2O and brine (100 ml each). After separation and drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by column chromatography (eluents: $CHCl_3$/MeOH = 10:0.2 (v/v), R_F = 0.47). Yield: 9.5 g (82 %); pale yellow solid; mp. = 103-105 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, ^3J(H,H) = 8.20 Hz, 1H, Ar-H), 8.18 (t, ^3J(H,H) = 5.7 Hz, 1H, N-H), 7.50-7.35 (m, 7H, Ar-H), 7.26 (d, ^4J(H,H) = 1.6 Hz, 1H, Ar-H), 7.17 (d, ^4J(H,H) = 1.6 Hz, 1H, Ar-H), 6.97 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 5.26 (s, 2H, Ph-CH_2), 4.51-4.46 (m, 1H, CHO), 4.21-4.15 (m, 2H, CHO, CH_2O), 4.09 (d, ^3J(H,H) = 9.6 Hz, 1H, CH_2O), 3.99-3.89 (m, 3H, CH_2O), 3.67-3.61 (m, 1H, CH_2O), 3.57 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 3.50-3.44 (m, 1H, CH_2O), 1.46 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.27 (s, 3H, CH_3).

2-Benzyloxy-4´-[(2,2-dimethyl-1,3-dioxolan-4-yl)methoxy]biphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (4bBn): Synthesized in an analogues way from **3b** (15.0 g, 35.7 mmol), **2** (9.9 g, 39.2 mmol), purified by column chromatography (eluents: $CHCl_3$/MeOH = 10:0.2 (v/v), R_F = 0.46. Yield: 14.4 g (73 %); colourless solid; mp = 74-76 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, ^4J(H,H) = 1.4 Hz, 1H, Ar-H), 7.50 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.37-7.31 (m, 6H, Ar-H), 7.29-7.25 (m, 1H, Ar-H), 6.94 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 6.47 (t, ^3J(H,H) = 5.6 Hz, 1H, N-H), 5.12 (s, 2H, Ph-CH_2), 4.52-4.46 (m, 1H, CHO), 4.37-4.31 (m, 1H, CHO), 4.17 (d, ^3J(H,H) = 8.6 Hz, 1H, CH_2O), 4.11-4.07 (m, 2H, CH_2O), 3.96 (d, ^3J(H,H) = 9.5 Hz, 1H, CH_2O), 3.90 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.77-3.69 (m, 2H, CH_2O), 3.56-3.50 (m, 1H, CH_2O), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.36 (s, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-hydroxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide 4a: **4aBn** (9.5 g, 17.3 mmol) was dissolved in EtOAc (120 ml) under an argon atmosphere. Pd/C (0.1 g, 10 % Pd) was added and after rinsing with H_2 (3x) the hydrogen pressure was set to 3.2 bar and the temperature was set to 45 °C. After 6 hours the solution was filtered and the filtrate was washed with hot EtOAc (200 ml). Finally the solvent was evaporated. Yield: 6.0 g (76 %); colourless solid; mp = 122 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 12.28 (s, 1H, OH), 7.52 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.38 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 7.15 (d, ^4J(H,H) = 1.8 Hz, 1H, Ar-H), 7.03 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 6.96 (d, ^3J(H,H) = 9.0 Hz, 2H, Ar-H), 6.63 (t, ^3J(H,H) = 5.5 Hz, 1H, N-H), 4.51-4.45 (m, 1H, CHO), 4.37-4.31 (m, 1H, CHO), 4.16 (d, ^3J(H,H) = 8.6 Hz, 1H, CH_2O), 4.11-4.07 (m, 2H, CH_2O), 3.97 (d, ^3J(H,H) = 9.5 Hz, 1H, CH_2O), 3.90 (d, ^3J(H,H) = 8.6 Hz, 1H, CH_2O), 3.77-3.69 (m, 2H, CH_2O), 3.53-3.46 (m, 1H, CH_2O), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.36 (s, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolane-4-yl)methoxy]-2-hydroxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide 4b: Synthesized in an analogues way from **4bBn** (14.2 g, 25.9 mmol); Yield: 8.34 g (70 %); colorless solid; mp. = 125-128 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 1H, Ar-H), 7.44 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.28-7.26

(m, 2H, Ar-H), 6.98 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 6.83 (s, 1H, OH), 6.59 (t, ^3J(H,H) = 5.6 Hz, 1H, N-H,), 4.51-4.46 (m, 1H, CHO), 4.35-4.29 (m, 1H, CHO), 4.16 (d, ^3J(H,H) = 8.6 Hz, 1H, CH_2O), 4.10-4.05 (m, 2H, CH_2O), 3.96 (d, ^3J(H,H) = 9.5 Hz, 1H, CH_2O), 3.89 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.77-3.69 (m, 2H, CH_2O), 3.53-3.46 (m, 1H, CH_2O), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.34 (s, 3H, CH_3).

4´-(2,3-Dihydroxypropoxy)-3-hydroxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide 5a: A mixture of **4a** (5.8 g, 12.7 mmol), pyridinium p-toluenesulfonate (100 mg), H_2O (10 ml) and MeOH (100 ml) was refluxed for 6h. After cooling to r.t. the solvent was evaporated. The crude product was purified by crystallisation from MeOH. Yield: 4.6 g (96 %); colourless solid; mp = 173-175 °C; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.82 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.57 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.14-7.10 (m, 2H, Ar-H), 7.03 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.12-4.08 (m, 1H, CHO), 4.03-3.97 (m, 2H, CHO, CH_2O), 3.85-3.81 (m, 1H, CH_2O), 3.71-3.54 (m, 5H, CH_2O), 3.45-3.40 (m, 1H, CH_2O).

4´-(2,3-Dihydroxypropoxy)-2-hydroxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide 5b: A mixture of **4b** (2.0 g, 4.4 mmol), 10% HCl (10 ml) and MeOH (50 ml) was refluxed for 6h. After cooling to r.t. the solvent was evaporated. The residue was extracted with MeOH (3x 75 ml). The combined organic phases were filtrated and the solvent was evaporated. The resulting product was used without further purification. Yield: 521 mg (32 %); colourless solid; mp = 35-40 °C; ^{1}H-NMR (400 MHz, CD_3OD): δ = 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.36-7.28 (m, 3H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.11-4.06 (m, 1H, CHO), 4.02-3.96 (m, 2H, CHO, CH_2O), 3.86-3.81 (m, 1H, CH_2O), 3.73-3.53 (m, 5H, CH_2O), 3.45-3.40 (m, 1H, CH_2O).

3.1.2 Silylated chains

1-Bromo-11-(1,1,1,3,3-pentamethyldisiloxy)undecane: To a solution of 1-bromoundec-11-ene (1.0 g, 4.3 mmol) and 1,1,1,3,3-pentamethyldisiloxane (290 mg, 3.3 mmol) in dry toluene (20 ml) 1 drop of Karstedt catalyst is added under an argon atmosphere. After stirring at r.t. for 7d, $CHCl_3$ (100 ml) was added and the solution was filtered through a plug of silica gel and finally the solvent was evaporated. Yield: 1.42 g (87 %); colourless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.38 (t, ^3J(H,H) = 6.9 Hz, 2H, $BrCH_2$), 1.87-1.80 (m, 2H, $BrCH_2\mathbf{CH_2}$), 1.42-1.37 (m, 2H, $BrCH_2CH_2\mathbf{CH_2}$), 1.28-1.25 (m, 14H, CH_2), 0.50-0.47 (m, 2H, $SiCH_2$), 0.04 (s, 9H, $SiCH_3$), 0.02 (s, 6H, $SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 7.62, -21.47.

1-Bromo-11-(1,1,1,3,3,5,5-heptamethyltrisiloxy)undecane: Synthesized and purified as described above from 1-bromoundec-11-ene (1.0 g, 4.3 mmol) and 1,1,1,3,3,5,5-heptamethyltrisiloxane (1.43 g, 6.4 mmol). Yield: 1.88 g (96 %); colourless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.38 (t, ^3J(H,H) = 6.8 Hz, 2H, $BrCH_2$), 1.87-1.80 (m, 2H, $BrCH_2\mathbf{CH_2}$), 1.43-1.37 (m, 2H, $BrCH_2CH_2\mathbf{CH_2}$), 1.28-1.25 (m, 14H, CH_2), 0.53-0.49 (m, 2H, $SiCH_2$), 0.07 (s, 9H, $SiCH_3$), 0.04 (s, 6H, $SiCH_3$), 0.01 (s, 6H, $SiCH_3$). ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 7.47, 7.02, -21.08.

1-Bromo-11-(1,1,1,3,5,5,5-heptamethyltrisiloxy)undecane: Synthesized and purified as described above from 1-bromoundec-11-ene (1.0 g, 4.3 mmol) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.43 g, 6.4 mmol). Yield: 1.80 g (92 %); colourless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.38 (t, ^3J(H,H) = 7.0 Hz, 2H, $BrCH_2$), 1.87-1.80 (m, 2H, $BrCH_2\mathbf{CH_2}$), 1.42-1.37 (m, 2H, $BrCH_2CH_2\mathbf{CH_2}$), 1.27-1.20 (m, 14H, CH_2), 0.45-0.41 (m, 2H, $SiCH_2$), 0.07 (s, 18H, $SiCH_3$), -0.02 (s, 3H, $SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 7.61, -21.19.

3.2 Synthesis of the alkyl substituted compounds H1-6

3.2.1 Acetonides

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-tetradecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H1-acetonide): A mixture of **4a** (250 mg, 0.55 mmol), 1-bromotetradecane (167 mg, 0.60 mmol), K_2CO_3 (415 mg, 3.0 mmol), Bu_4NI (50 mg) in dry DMF (50 ml) was heated to 80 °C for 8 h under an argon atmosphere. After cooling to r.t. H_2O (100 ml) was added and the mixture was extracted with EtOAc (3x 70 ml). The combined organic phases were washed with sat. aq. LiCl (2x 50 ml), H_2O and brine (50 ml each). After drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$). Yield: 350 mg (98 %); colourless solid; mp = 67-69 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.6 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.21 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.07 (d, ^4J(H,H) = 1.2 Hz, 1H, Ar-H), 6.97 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.50-4.46 (m, 1H, CHO), 4.31-4.27 (m, 1H, CHO), 4.19-4.15 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.97 (d, ^3J(H,H) = 9.5 Hz, 1H, CH_2O), 3.90 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.68 (d, ^3J(H,H) = 8.3 Hz, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 1.95-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.28-1.20 (m, 22H, CH_2), 0.86 (t, ^3J(H,H) = 6.7 Hz, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-hexadecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H2-acetonide): Synthesized from **4a** (300 mg, 0.66 mmol) and 1-bromohexadecane (220 mg, 0.72 mmol), K_2CO_3 (500 mg, 3.62 mmol), Bu_4NI (50 mg) in DMF (50 ml). Yield: 423 mg (95 %); colourless solid; mp = 77-80 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.6 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.21 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.07 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 6.97 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.52-4.46 (m, 1H, CHO), 4.33-4.27 (m, 1H, CHO), 4.19-4.15 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.97 (d, ^3J(H,H) = 9.5 Hz, 1H, CH_2O), 3.90 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.68 (d, ^3J(H,H) = 8.3 Hz, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 1.95-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.28-1.19 (m, 26H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-octadecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H3-acetonide): Synthesized from **4a** (300 mg, 0.66 mmol), 1-bromooctadecane (240 mg, 0.72 mmol), K_2CO_3 (500 mg, 3.62 mmol), Bu_4NI (50 mg) in DMF (50 ml). Yield: 460 mg (99 %); colourless solid; mp = 72-74 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.5 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.21 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.07 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 6.97 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.52-4.46 (m, 1H, CHO), 4.33-4.27 (m, 1H, CHO), 4.18-4.15 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.97 (d, ^3J(H,H) = 9.4 Hz, 1H, CH_2O), 3.90 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.68 (d, ^3J(H,H) = 8.3 Hz, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 1.95-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.28-1.20 (m, 30H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-2-tetradecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H4-acetonide): Synthesized from **4b** (250

mg, 0.55 mmol), 1-bromotetradecane (167 mg, 0.60 mmol), K_2CO_3 (415 mg, 3.0 mmol), Bu_4NI (50 mg) in DMF (50 ml). Yield: 317 mg (89 %); colourless solid; mp = 45-47 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50-7.47 (m, 3H, Ar-H), 7.35-7.33 (m, 1H, Ar-H), 7.30-7.28 (m, 1H, Ar-H), 6.95 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 6.48 (t, ^3J(H,H) = 5.7 Hz, 1H, N-H), 4.52-4.49 (m, 1H, CHO), 4.37-4.34 (m, 1H, CHO), 4.18 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 4.12-4.09 (m, 2H, CH_2O), 4.03-3.96 (m, 3H, CH_2O), 3.92 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 3.76-3.71 (m, 2H, CH_2O), 3.60-3.53 (m, 1H, CH_2O), 1.75-1.71 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.47 (s, 6H, CH_3), 1.41 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.28-1.20 (m, 22H, CH_2), 0.87 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-2-hexadecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H5-acetonide): Synthesized from **4b** (300 mg, 0.66 mmol), 1-bromohexadecane (220 mg, 0.72 mmol), K_2CO_3 (500 mg, 3.62 mmol), Bu_4NI (50 mg) in DMF (50 ml). Yield: 331 mg (70 %); colourless solid; mp = 48-50 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, ^3J(H;H) = 8.6 Hz, 2H, Ar-H), 7.45 (d, ^4J(H,H) = 1.4 Hz, 1H, Ar-H), 7.33-7.26 (m, 2H, Ar-H), 6.93 (d, ^3J(H,H) = 9.0 Hz, 1H, Ar-H), 6.49 (t, ^3J(H,H) = 5.8 Hz, 1H, N-H), 4.52-4.46 (m, 1H, CHO), 4.36-4.32 (m, 1H, CHO), 4.17 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 4.11-4.07 (m, 2H, CH_2O), 4.01-3.95 (m, 3H, CH_2O), 3.91 (d, ^3J(H,H) = 8.4 Hz, 1H, CH_2O), 3.76-3.69 (m, 2H, CH_2O), 3.58-3.51 (m, 1H, CH_2O), 1.75-1.68 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.28-1.20 (m, 26H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-2-octadecyloxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (H6-acetonide): Synthesized from **4b** (300 mg, 0.66 mmol), 1-bromooctadecane (240 mg, 0.72 mmol), K_2CO_3 (500 mg, 3.62 mmol), Bu_4NI (50 mg) in DMF (50 ml). Yield: 440 mg (95 %); colourless solid; mp = 56-58 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.45 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.32 (d, ^3J(H,H) = 7.7 Hz, 1H, Ar-H), 7.27 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.93 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 6.51 (t, ^3J(H,H) = 5.7 Hz, 1H, N-H), 4.50-4.46 (m, 1H, CHO), 4.36-4.31 (m, 1H, CHO), 4.17 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 4.09-4.05 (m, 2H, CH_2O), 4.01-3.95 (m, 3H, CH_2O), 3.91 (d, ^3J(H,H) = 8.5 Hz, 1H, CH_2O), 3.76-3.69 (m, 2H, CH_2O), 3.58-3.51 (m, 1H, CH_2O), 1.75-1.68 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.29-1.19 (m, 30H, CH_2), 0.86 (t, ^3J(H,H) = 6.9 Hz, 3H, CH_3).

3.2.2 Compounds H1-6

4´-(2,3-Dihydroxypropoxy)-3-tetradecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H1: A mixture of **H1-acetonide** (328 mg, 0.5 mmol) and 10% HCl (10 ml) in MeOH (50 ml) was refluxed for 6 h. After cooling to r.t. the solvent was evaporated and the residue was dissolved in EtOAc (100 ml). The organic phase was washed with sat. aq. $NaHCO_3$ (2x 50 ml), H_2O and brine (50 ml each). After drying over Na_2SO_4 the solvent was evaporated. The crude product was purified by preparative centrifugal thin layer chromatography (eluents: $CHCl_3$/MeOH = 10:0.2-10:1(v/v)); Yield: 202 mg (70 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 8.44 (t, ^3J(H,H) = 5.2 Hz, 1H, N-H), 8.12 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.66 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.35 (d, ^4J(H,H) = 1.7 Hz, 1H, Ar-H), 7.29 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.04 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.32 (t, ^3J(H,H) = 6.5 Hz, 2H, CH_2O), 4.16-3.93 (m, 5H, CHO, CH_2O), 4.05-3.98 (m, 2H, CH_2O), 3.93-3.75 (m, 2H, CH_2O), 3.72-3.60 (m, 3H, CH_2O), 3.55-3.46 (m, 3H, CH_2O), 1.99-1.92 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.59-1.51 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.39-1.27 (m, 22H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 166.56, 160.51,

158.75 (2C), 146.16 (2C), 133.33, 133.26 (2C), 129.24, 121.00, 119.73, 116.06, 111.79 (2C), 72.40, 71.67, 70.87, 70.43 (2C), 64.98, 64.43 (2C), 43.70, 32.94, 30.67, 30.56, 30.41, 30.37, 30.24, 30.17, 29.34, 27.29, 23.64 (CH_2), 14.66 (CH_3); anal. calcd. for $C_{33}H_{51}NO_7$: C 69.08, H 8.96, N 2.44; found: C 68.83, H 8.94, N 2.45.

4´-(2,3-Dihydroxypropoxy)-3-hexadecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H2: Synthesized in an analogues way as **H1** from **H2-acetonide** (403 mg, 0.59 mmol). Purification by crystallisation from EtOAc (2x). Yield: 229 mg (65 %); colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.44 (t, ^3J(H,H) = 5.8 Hz, 1H, N-H), 8.09 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.40 (d, ^3J(H,H) = 8.3 Hz, 2H, Ar-H), 7.07 (d, ^3J(H,H) = 7.7 Hz, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 6.89 (d, ^3J(H,H) = 8.3 Hz, 2H, Ar-H), 4.13-4.11 (m, 3H, CHO, CH_2O), 4.04-4.03 (m, 2H, CH_2O), 3.87-3.84 (m, 2H, CH_2O), 3.79-3.75 (m, 1H, CH_2O), 3.68-3.56 (m, 4H, CH_2O), 3.51 (s, 2H, OH), 3.22 (s, 1H, OH), 2.73 (s, 1H, OH), 1.88-1.83 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.45-1.41 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.19 (m, 24H, CH_2), 0.85 (t, ^3J(H,H) = 6.9 Hz, 3H, CH_3,); ^{13}C-NMR (100 MHz, CD_3OD): δ = 168.01, 160.60, 158.95 (2C), 147.01 (2C), 133.63, 132.78 (2C), 129.19, 120.43, 119.90, 116.0, 111.73 (2C), 71.87, 71.80, 70.58, 70.52 (2C), 65.20, 64.20 (2C), 43.71, 33.07, 30.78, 30.75, 30.72, 30.46, 30.27, 27.29, 23.74 (CH_2), 14.45 (CH_3); anal. calcd. for $C_{35}H_{55}NO_7$: C 69.85, H 9.21, N 2.33; found: C 69.79, H 9.19, N 2.15.

4´-(2,3-Dihydroxypropoxy)-3-octadecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H3: Synthesized in an analogues way as **H1** from **H3-acetonide** (426 mg, 0.6 mmol). Purification by crystallisation from EtOAc (2x). Yield: 274 mg (73 %); colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.43 (t, ^3J(H,H) = 6.1 Hz, 1H, N-H), 8.13 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.44 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.13 (d, ^3J(H,H) = 8.5 Hz, 1H, Ar-H), 7.05 (s, 1H, Ar-H), 6.93 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.15-4.13 (m, 3H, CHO, CH_2O), 4.09-4.05 (m, 2H, CH_2O), 3.87-3.85 (m, 2H, CH_2O), 3.78-3.68 (m, 1H, CH_2O), 3.66-3.55 (m, 4H, CH_2O), 3.35 (s, 2H, OH), 2.99 (s, 1H, OH), 2.46 (s, 1H, OH), 1.91-1.84 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.50-1.43 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.36-1.19 (m, 28H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, CD_3OD): δ = 168.01, 160.59, 158.95 (2C), 147.0 (2C), 133.62, 132.78 (2C), 129.18, 120.42, 119.89, 116.0, 111.73 (2C), 71.86, 71.79, 70.58, 70.52 (2C), 65.19, 64.20 (2C), 43.71, 33.07, 30.77, 30.71, 30.46, 30.27, 27.29, 23.74 (CH_2), 14.45 (CH_3); anal. calcd. for $C_{37}H_{59}NO_7$: C 70.55, H 9.44, N 2.22; found: C 70.55, H 9.26, N 2.04.

4´-(2,3-Dihydroxypropoxy)-2-tetradecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H4: Synthesized and purified in an analogues way as **H1** from **H4-acetonide** (301 mg, 0.46 mmol). Yield: 210 mg (80 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.95 (s, 1H, N-H), 7.60 (d, ^4J(H,H) = 1. 5 Hz, 1H, Ar-H), 7.54 (d, ^3J(H,H) = 8.0 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.18-3.92 (m, 6H, CHO, CH_2O), 3.81-3.75 (m, 2H, CH_2O), 3.73-3.63 (m, 2H, CH_2O), 3.60-3.46 (m, 4H, OH, CH_2O), 1.77-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.45-1.41 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.39-1.28 (m, 22H, CH_2), 0.86 (t, ^3J(H,H) = 6.7 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 168.56, 159.53, 156.97 (2C), 135.31, 134.33 (2C), 131.54, 131.22, 131.06, 120.47, 115.07, 112.65 (2C), 72.47, 71.65, 70.66, 69.46 (2C), 64.92, 64.43 (2C), 44.20, 32.89, 30.62, 30.58, 30.57, 30.52, 30.33, 30.21, 30.13, 27.10, 23.59 (CH_2), 14.62 (CH_3); anal. calcd. for $C_{33}H_{51}NO_7$*0.25 H_2O: C 68.54, H 8.98, N 2.42; found: C 68.71, H 8.95, N 2.39.

4´-(2,3-Dihydroxypropoxy)-2-hexadecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H5: Synthesized and purified in an analogues way as **H1** from **H5-acetonide** (283

mg, 0.42 mmol). Yield: 110 mg (44 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.94 (s, 1H, N-H), 7.60 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.55 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.18-3.91 (m, 6H, CHO, CH_2O), 3.79-3.73 (m, 2H, CH_2O), 3.70-3.64 (m, 2H, CH_2O), 3.59-3.46 (m, 4H, OH, CH_2O), 1.77-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.45-1.40 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.20 (m, 24H, CH_2), 0.86 (t, ^3J(H,H) = 6.8 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 168.57, 159.57, 157.0 (2C), 135.35, 134.36 (2C), 131.57, 131.25, 131.08, 120.49, 115.03, 112.67 (2C), 72.51, 71.67, 70.69, 69.49 (2C), 64.93, 64.45 (2C), 44.22, 32.92, 30.67, 30.65, 30.61, 30.59, 30.54, 30.35, 30.24, 30.16, 27.13, 23.62 (CH_2), 14.64 (CH_3); anal. calcd. for $C_{35}H_{55}NO_7$: C 69.85, H 9.21, N 2.33; found: C 69.64, H 9.18, N 2.29.

4´-(2,3-Dihydroxypropoxy)-2-octadecyloxybiphenyl-4-yl-*N*-(2,3-dihydroxypropyl)-benzamide H6: Synthesized and purified in an analogues way as **H1** from **H6-acetonide** (355 mg, 0.5 mmol). Yield: 155 mg (49 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.95 (s, 1H, N-H), 7.60 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.54 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.19-3.93 (m, 6H, CHO, CH_2O), 3.81-3.75 (m, 2H, CH_2O), 3.72-3.64 (m, 2H, CH_2O), 3.57-3.46 (m, 4H, OH, CH_2O), 1.77-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.45-1.40 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.28-1.22 (m, 28H, CH_2), 0.86 (t, ^3J(H,H) = 6.7 Hz, 3H, CH_3); ^{13}C-NMR (100 MHz, acetone-d_6): δ = 168.60, 159.64, 157.07 (2C), 135.45, 134.44 (2C), 131.62, 131.34, 131.14, 120.55, 115.11, 112.76 (2C), 72.58, 71.73, 70.77, 69.57 (2C), 65.0, 64.51 (2C), 44.29, 32.97, 30.74, 30.66, 30.64, 30.58, 30.39, 30.20, 29.37, 27.19, 23.67 (CH_2), 14.69 (CH_3); anal. calcd. for $C_{37}H_{59}NO_7$: C 70.55, H 9.44, N 2.22; found: C 70.34, H 9.26, N 2.10.

3.3 Synthesis of the carbosilanes C1-C3

3.3.1 Acetonides

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-undec-10-enoxybiphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (7a): Synthesized by etherification as described for **H1-acetonide** from **4a** (700 mg, 1.53 mmol), 1-bromo-undec-10-ene (390 mg, 1.68 mmol), K_2CO_3 (2.1 mg, 15.3 mmol), Bu_4NI (50 mg) in dry DMF (100 ml). The crude product was purified by preparative centrifugal thin layer chromatography (eluent: $CHCl_3$). Yield: 828 mg (89 %), colourless solid, R_f = 0.56 ($CHCl_3$/MeOH = 10:0.2(v/v)), mp.: 75-78 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.7 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.51 (dd, ^3J(H,H) = 11.8 Hz, ^4J(H,H) = 2.9 Hz, 2H, Ar-H), 7.22 (dd, ^3J(H,H)= 8.1 Hz, ^4J(H,H) = 1.66 Hz, 2H, Ar-H), 7.08 (d, ^3J(H,H) = 1.5 Hz, 1H, Ar-H), 6.98 (dd, ^3J(H,H) = 11.8 Hz, ^4J(H,H) = 3.1 Hz, 2H, Ar-H), 5.84-5.74 (m, 1H, $\mathbf{CH}$=CH_2), 5.00-4.89 (m, 2H, CH=$\mathbf{CH_2}$), 4.52-4.46 (m, 1H, CHO), 4.33-4.27 (m, 1H, CHO), 4.21-4.13 (m, 3H, CH_2O), 4.11-4.05 (m, 2H, CH_2O), 3.99-3.92 (m, 1H, CH_2O), 3.91-3.89 (m, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.71-3.67 (m, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 2.05-1.99 (m, 2H, $\mathbf{CH_2}$-CH=CH_2), 1.95-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.52-1.24 (m, 24H, CH_2, CH_3).

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(12,12-dimethyl-12-silatetradecyloxy)biphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (C1-acetonide): To a solution of **7a** (200 mg, 0.33 mmol) and ethyldimethylsilane (290 mg, 3.3 mmol) in dry toluene (20 ml) 1 drop of Karstedt catalyst (divinyltetramethyl-disiloxane-platinum(0)-complex in xylene, 2.2-2.4% Pt) is added under an argon atmosphere. After stirring at r.t. for 72 h the solvent was evaporated. The crude product was purified by

preparative centrifugal thin layer chromatography (eluents: petrol ether/$CHCl_3$ = 1/1-0/1 (v/v)).Yield: 212 mg (93 %), colourless solid, R_f = 0.65 ($CHCl_3$/MeOH = 10:0.2 (v/v)), mp = 60-62 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.7 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.51 (dd, ^3J(H,H) = 11.7 Hz, ^4J(H,H) = 3.0 Hz, 2H, Ar-H), 7.22 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.7 Hz, 2H, Ar-H), 7.08 (d, ^3J(H,H) = 1.7 Hz, 1H, Ar-H), 6.98 (dd, ^3J(H,H) = 11.7 Hz, ^4J(H,H) = 3.0 Hz, 2H, Ar-H), 4.52-4.46 (m, 1H, CHO), 4.33-4.27 (m, 1H, CHO), 4.19-4.15 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.99-3.92 (m, 1H, CH_2O), 3.91-3.89 (m, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.71-3.67 (m, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 1.95-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.52-1.26 (m, 28H, CH_2, CH_3), 0.89 (t, ^3J(H,H) = 7.9 Hz, 3H, CH_3), 0.47-0.41 (m, 4H, $SiCH_2$), -0.08 (s, 6H, $SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 3.58.

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(6,6,10,10,14,14-hexamethyl-6,10,14-trisilaundecyloxy)biphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (C2-acetonide): Synthesized from **7a** (250 mg, 0.41 mmol) and 1,1,5,5,9,9-hexamethyl-1,5,9-trisiladecane (124 mg, 0.45 mmol). Purified by preparative centrifugal thin layer chromatography (eluents: petrol ether/$CHCl_3$ = 1/1-0/1 (v/v)). Yield: 135 mg (37 %), colourless solid, R_f = 0.70 ($CHCl_3$/MeOH = 10:0.2 (v/v)), mp = 52-54 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.36 (t, ^3J(H,H) = 5.60 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.52 (dd, ^3J(H,H) = 11.6 Hz, ^4J(H,H) = 3.1 Hz, 2H, Ar-H), 7.22 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.3 Hz, 2H, Ar-H), 7.08 (d, ^3J(H,H) = 1.5 Hz, 1H, Ar-H), 6.98 (dd, ^3J(H,H) = 11.6 Hz, ^4J(H,H) = 2.9 Hz, 2H, Ar-H), 4.52-4.46 (m, 1H, CHO), 4.33-4.27 (m, 1H, CHO), 4.19-4.13 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.99-3.93 (m, 1H, CH_2O), 3.91-3.89 (m, 1H, CH_2O), 3.85-3.79 (m, 1H, CH_2O), 3.71-3.67 (m, 1H, CH_2O), 3.49-3.43 (m, 1H, CH_2O), 1.96-1.88 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.52-1.21 (m, 32H, CH_2, CH_3), 0.55-0.51 (m, 8H, $SiCH_2$), 0.47-0.45 (m, 2H, $SiCH_2$),-0.05 (s, 9H, $SiCH_3$),-0.08 (s, 12H, $SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 1.60, 0.99, 0.58.

4´-[(2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy]-3-(12,12,16,16,20,20,24,24-octamethyl-12,-16,20,24-tetrasilapentacosyloxy)biphenyl-4-yl-*N*-[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]benzamide (C3-acetonide): Synthesized from **7a** (220 mg, 0.36 mmol) and 1,1,5,5,9,9,13,13-octamethyl-1,5,9,13-tetrasilatetradecane (200 mg, 0.53 mmol). Purified by preparative centrifugal thin layer chromatography (eluents: petrol ether/$CHCl_3$ = 1/1-0/1 (v/v)). Yield: 181 mg (51 %), colourless solid, R_f = 0.72 ($CHCl_3$/MeOH = 10:0.2 (v/v)), mp = 48-50 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.37 (t, ^3J(H,H) = 5.5 Hz, 1H, N-H), 8.22 (d, ^3J(H,H) = 8.2 Hz, 1H, Ar-H), 7.52 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.22 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.4 Hz, 2H, Ar-H), 7.08 (d, ^3J(H,H) = 1.2 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.50-4.47 (m, 1H, CHO), 4.31-4.29 (m, 1H, CHO), 4.19-4.15 (m, 3H, CH_2O), 4.11-4.06 (m, 2H, CH_2O), 3.99-3.92 (m, 1H, CH_2O), 3.91-3.89 (m, 1H, CH_2O), 3.83-3.80 (m, 1H, CH_2O), 3.70-3.67 (m, 1H, CH_2O), 3.48-3.45 (m, 1H, CH_2O), 1.93-1.90 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.50-1.22 (m, 34H, CH_2, CH_3), 0.54-0.51 (m, 12H, $SiCH_2$), 0.46-0.44 (m, 2H, $SiCH_2$),-0.05 (s, 9H, $SiCH_3$),-0.08 (s, 18H, $SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 1.64, 1.02 (2Si), 0.62.

3.3.2 Compounds C1-C3

4´-(2,3-Dihydroxypropoxy)-3-(12,12-dimethyl-12-silatetradecyloxy)biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide C1: Synthesized in an analogues way as **H1** from **C1-acetonide** (210 mg, 0.30 mmol). Purified by crystallisation from EtOAc/petrol ether. Yield: 142 mg (76 %); colourless solid; ^{1}H-NMR (400 MHz, CD_3OD): δ = 8.02 (d, ^3J(H,H) = 8.51 Hz, 1H, Ar-H), 7.60 (dd, ^3J(H,H) = 11.7 Hz, ^4J(H,H) = 3.0 Hz, 2H, Ar-H), 7.26-7.24 (m, 2H,

Ar-H), 7.04 (dd, ^{3}J(H,H) = 11.7 Hz, ^{4}J(H,H) = 3.0 Hz, 2H, Ar-H), 4.24 (t, ^{3}J(H,H) = 6.5 Hz, 2H, CH_2O), 4.14-4.07 (m, 1H, CHO), 4.03-3.96 (m, 2H, CHO, CH_2O), 3.83-3.78 (m, 1H, CH_2O), 3.72-3.63 (m, 3H, CH_2O), 3.59-3.54 (m, 2H, CH_2O), 3.45-3.39 (m, 1H, CH_2O), 1.96-1.89 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.56-1.49 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.41-1.29 (m, 14H, CH_2), 0.92 (t, ^{3}J(H,H) = 7.9 Hz, 3H, $SiCH_2\mathbf{CH_3}$), 0.50-0.44 (m, 4H, $SiCH_2$), -0.07 (s, 6H, $SiCH_3$); ^{13}C-NMR (100 MHz, CD_3OD): δ = 168.03 (2C), 160.59, 158.93 (2C), 146.99 (2C), 133.64, 132.78 (2C), 129.18, 120.48 (2C), 119.91, 116.03, 111.76 (2C), 71.89, 71.80, 70.60, 70.56 (2C), 65.21, 64.23 (2C), 43.72, 34.76, 30.72, 30.67, 30.45, 30.43, 30.27, 27.28, 25.00 (CH_2), 15.81 (CH_3), 7.91, 7.69 ($SiCH_2$), -3.69 ($SiCH_3$); ^{29}Si-NMR (99 MHz, CD_3OD): δ = 3.36. anal. calcd. for $C_{34}H_{55}NO_7Si$*0.5 H_2O: C 65.14, H 9.00, N 2.23; found: C 65.32, H 8.97, N 2.13.

4´-(2,3-Dihydroxypropoxy)-3-(6,6,10,10,14,14-hexamethyl-6,10,14-trisilaundecyloxy)-biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide C2: Synthesized and purified in an analogues way as **H1** from **C2-acetonide** (133 mg, 0.15 mmol). Yield: 73 mg (60 %); colourless solid; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.43 (t, ^{3}J(H,H) = 6.1 Hz, 1H, N-H), 8.14 (d, ^{3}J(H,H) = 7.9 Hz, 1H, Ar-H), 7.46 (d, ^{3}J(H,H) = 8.9 Hz, 2H, Ar-H), 7.15 (dd, ^{3}J(H,H) = 8.2 Hz, ^{4}J(H,H) = 1.5 Hz, 1H, Ar-H), 7.06 (d, ^{3}J (H,H)= 1.5 Hz, 1H, Ar-H), 6.94 (dd, ^{3}J(H,H) = 11.8 Hz, ^{4}J(H,H) = 2.9 Hz, 2H, Ar-H), 4.17-4.11 (m, 3H, CHO, CH_2O), 4.08-4.05 (m, 2H, CH_2O), 3.87-3.84 (m, 2H, CH_2O), 3.78-3.74 (m, 1H, CH_2O), 3.65-3.57 (m, 4H, CH_2O), 3.30 (s, 2H, OH), 2.95 (s, 1H, OH), 2.42 (s, 1H, OH), 1.91-1.85 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.48-1.44 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.37-1.25 (m, 18H, CH_2), 0.54-0.50 (m, 8H, $SiCH_2$), 0.46-0.44 (m, 2H, $SiCH_2$), -0.05 (s, 9H, $SiCH_3$), -0.08 (s, 12H, $SiCH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.20, 158.66, 157.40 (2C), 145.60 (2C), 132.88, 132.65 (2C), 128.29, 119.48, 118.78, 114.93, 110.46 (2C), 71.64, 70.39, 69.36, 69.33 (2C), 63.70, 63.65 (2C), 42.58, 33.80, 29.74, 29.71, 29.50, 29.45, 29.30, 26.31, 24.03, 21.47, 20.23, 20.14, 20.12, 18.52 (CH_2), 15.53 (CH_3), -1.39, -3.03, -3.12 ($SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 1.59, 0.99, 0.58; anal. calcd. for $C_{43}H_{77}NO_7Si_3$: C 64.21, H 9.65, N 1.74; found: C 64.07, H 9.64, N 1.64.

4´-(2,3-Dihydroxypropoxy)-3-(12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasila-pentacosyloxy)-biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide C3: Synthesized and purified in an analogues way as **H1** from **C3-acetonide** (171 mg, 0.17 mmol). Yield: 137 mg (87 %), colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.42 (t, ^{3}J(H,H) = 6.0 Hz, 1H, N-H), 8.17 (d, ^{3}J(H,H) = 8.3 Hz, 1H, Ar-H), 7.49 (d, ^{3}J(H,H) = 8.9 Hz, 2H, Ar-H), 7.19 (dd, ^{3}J(H,H) = 8.2 Hz, ^{4}J(H,H) = 1.56 Hz, 1H, Ar-H), 7.07 (d, ^{3}J(H,H) = 1.5 Hz, 1H, Ar-H), 6.97 (d, ^{3}J(H,H) = 8.9 Hz, 2H, Ar-H), 4.19-4.11 (m, 3H, CHO, CH_2O), 4.08-4.06 (m, 2H, CH_2O), 3.88-3.83 (m, 2H, CH_2O), 3.78-3.74 (m, 1H, CH_2O), 3.64-3.60 (m, 4H, CH_2O), 2.40 (bs, 4H, OH), 1.91-1.85 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.50-1.44 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.37-1.26 (m, 20H, CH_2), 0.55-0.50 (m, 12H, $SiCH_2$), 0.47-0.45 (m, 2H, $SiCH_2$), -0.05 (s, 9H, $SiCH_3$), -0.08 (s, 18H, $SiCH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.26, 158.67, 157.43 (2C), 145.65 (2C), 132.94, 132.69 (2C), 128.33, 119.53, 118.79, 114.95, 110.49 (2C), 71.66, 70.39, 69.39, 69.34 (2C), 63.66 (2C), 42.59, 33.84, 29.77, 29.74, 29.53, 29.48, 29.34, 26.34, 24.06, 21.50, 20.26, 20.17, 20.15, 18.55 (CH_2), 15.56 (CH_3), -1.36, -3.01, -3.09 ($SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 1.57, 0.97 (2Si), 0.56; anal. calcd. for $C_{48}H_{89}NO_7Si_4$: C 63.73, H 9.92, N 1.55; found: C 63.82, H 10.08, N 1.31.

3.4 Synthesis of the carbosilanes C4-C7

3.4.1 Olefins 7b

3-Allyloxy-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl 7b/3:
A mixture of 4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl-3-ol **6**[S12] (300 mg, 0.70 mmol), allyl bromide (88 mg, 0.73 mmol), K_2CO_3 (482 mg, 3.48 mmol) and Bu_4NI (5 mg) in anhydrous DMF (50 ml) was stirred at 80 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into ice-water (50 ml) and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with water and brine. After drying over anhydrous Na_2SO_4, filtration and evaporation of the solvent, the crude product was purified by preparative thin layer chromatography (silica gel, petroleum ether/chloroform, 1:2, v/v); Yield: 220 mg (67 %); colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, ^3J(H,H) = 8.8, 2H, Ar-H), 7.06-7.04 (m, 2H, Ar-H), 6.95 (d, ^3J(H,H) = 8.8, 1H, Ar-H), 6.94 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 6.12-6.02 (m, 1H C**H**=CH_2) 5.44-5.39 (m, 1H, C**H**$_2$=CH), 5.29-5.25 (m, 1H, C**H**$_2$=CH), 4.48 (td, ^3J(H,H) = 5.3 Hz, ^4J(H,H) = 1.5 Hz, 2H, C**H**$_2$CH=CH_2), 4.48 (quint, ^3J(H,H) = 7.5 Hz, 2H, OCH), 4.18-4.06 (m, 4H, OCH_2), 4.01-3.88 (m, 4H, OCH_2), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-undec-10-en-1-yloxybiphenyl 7b/11:
Synthesized and purified in an analogues way as **7b/3** from **6**[S12] (300 mg, 0.70 mmol), 11-bromoundecen (172 mg, 0.73 mmol), K_2CO_3 (482 mg, 3.48 mmol) and Bu_4NI iodide (5 mg); Yield: 220 mg (54 %); colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.5 Hz, 3H, Ar-H), 5.85-5.74 (m, 1H C**H**=CH_2) 5.00-4.89 (m, 2H, C**H**$_2$=CH), 4.48 (quint, ^3J(H,H) = 5.9 Hz, 2H, OCH), 4.18-4.06 (m, 4H, OCH_2), 4.03-3.88 (m, 6H, OCH_2), 2.03 (q, ^3J(H,H) = 7.1 Hz, 2H, C**H**$_2$CH=CH_2), 1.81 (quint, ^3J(H,H) = 7.1 Hz, 2H, OCH_2C**H**$_2$), 1.48-1.44 (m, 8H, CH_3, CH_2), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.38-1.27 (m, 10H, CH_2).

3.4.2 Acetonides

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)biphenyl (C4-acetonide): To a solution of **7b/3** (350 mg, 0.74 mmol) and 1,1,5,5-tetramethyl-1,5-disilahexane (259 mg, 1.49 mmol) in dry toluene (20 ml) 1 drop of Karstedt catalyst is added under an argon atmosphere. After stirring at r.t. for 7 d, $CHCl_3$ (100 ml) was added and the solution was filtered through a plug of silica gel. The solvent was evaporated and the crude product was purified by preparative thin layer chromatography (silica gel, petroleum ether/$CHCl_3$, 1:2, v/v) Yield: 400 mg (84 %); colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.05-7.02 (m, 2H, Ar-H), 6.95 (d, ^3J(H,H) = 8.9 Hz, 3H, Ar-H), 4.51-4.55 (m, 2H, OCH), 4.17-4.06 (m, 4H, OCH_2), 4.00-3.88 (m, 6H, OCH_2), 1.85-1.78 (m, 2H, OCH_2C**H**$_2$), 1.46 (s, 6H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.37-1.31 (m, 2H, CH_2), 0.62-0.54 (m, 6H, $SiCH_2$), 0.00 (s, 6H, $SiCH_3$), -0.03 (s, 9H, $SiCH_3$); ^{29}Si NMR (100 MHz, $CDCl_3$,): δ = 2.29, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12-hexamethyl-4,8,12-trisilatridecyloxy)biphenyl (C5-acetonide): Synthesized and purified in an analogues way as **C4-acetonide** from **7b/3** (350 mg, 0.74 mmol) and 1,1,5,5,9,9-hexamethyl-1,5,9-trisiladecane (409 mg, 1.49 mmol); Yield: 420 mg (76 %); colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, ^3J(H,H) = 8.6 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.95 (d, ^3J(H,H) = 8.7 Hz, 3H, Ar-H), 4.52-4.55 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH_2), 4.01-3.89 (m, 6H, OCH_2),

1.85-1.77 (m, 2H, $OCH_2C\mathbf{H}_2$), 1.46 (s, 6H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.36-1.28 (m, 4H, CH_2), 0.62-0.52 (m, 10H, $SiCH_2$), -0.01 (s, 6H, $SiCH_3$), -0.04 (s, 9H, $SiCH_3$), -0.06 (s, 6H, $SiCH_3$); ^{29}Si NMR (100 MHz, $CDCl_3$,): δ = 2.29, 0.99, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12,16,16-octamethyl-4,8,12,16-tetrasilaheptadecyloxy)biphenyl (C6-acetonide): Synthesized and purified in an analogues way as **C4-acetonide** from **7b/3** (220 mg, 0.47 mmol) and 1,1,5,5,9,9,13,13-octamethyl-1,5,9,13-tetrasilatetradecane (351 mg, 0.94 mmol); Yield: 240 mg (60 %); colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.8 Hz, 3H, Ar-H), 4.48 (quint, ^3J(H,H) = 5.8 Hz, 2H, OCH), 4.18-4.06 (m, 4H, OCH_2), 4.00-3.88 (m, 6H, OCH_2), 1.85-1.77 (m, 2H, $OCH_2C\mathbf{H}_2$), 1.46 (s, 6H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.37-1.27 (m, 6H, CH_2), 0.62-0.51 (m, 14H, $SiCH_2$), 0.00-(-0.01) (m, 6H, $SiCH_3$), -0.04 (s, 9H, $SiCH_3$), -0.06-(-0.07) (m, 12H, $SiCH_3$); ^{29}Si NMR (100 MHz, $CDCl_3$): δ = 2.29, 0.98, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy)biphenyl (C7-acetonide): Synthesized and purified in an analogues way as **C4-acetonide** from **7b/11** (230 mg, 0.39 mmol) and 1,1,5,5,9,9,13,13-octamethyl-1,5,9,13-tetrasilatetra-decane (296 mg, 0.79 mmol); Yield: 230 mg (62 %); colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.9 Hz, 3H, Ar-H), 4.48 (quint, ^3J(H,H) = 6.0 Hz, 2H, OCH), 4.18-4.07 (m, 4H, OCH_2), 4.03-3.89 (m, 6H, OCH_2), 1.81 (quint, ^3J(H,H) = 7.1 Hz, 2H, $OCH_2C\mathbf{H}_2$), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35-1.26 (m, 16H, CH_2), 0.55-0.52 (m, 12H, $SiCH_2$), 0.47-0.44 (m, 2H, $SiCH_2$), -0.04 (s, 9H, $Si(CH_3)_3$), -0.07 (s, 18H, $Si(CH_3)_2$); ^{29}Si NMR (100 MHz, $CDCl_3$): δ = 2.29, 0.98, 0.57.

3.4.3 Compounds C4-7

4-[4'-(2,3-Dihydroxypropoxy)-3-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)biphenyl-4-yloxy]propane-1,2-diol C4: A mixture of **C4-acetonide** (400 mg, 0.62 mmol) and 10% HCl (5 mL) in MeOH (20 mL) was heated to reflux for 3 h. The progress of the reaction was monitored by TLC. The solvent was evaporated and the residue was dissolved in EtOAc, washed with sat. aq. $NaHCO_3$ (20 ml), water (20 ml) and brine (20 ml). After drying over anhydrous Na_2SO_4, filtration and evaporation of the solvent, the crude product was purified by repeated crystallization from EtOAc/petroleum ether (5:3, v/v). Yield: 250 mg (71 %); colourless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.8 Hz, 1H, Ar-H), 6.93 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.20-4.02 (m, 6H, OCH, OCH_2), 3.99 (t, ^3J(H,H) = 7.0 Hz, 2H, $OC\mathbf{H}_2CH_2$), 3.87-3.74 (m, 4H, OCH_2), 1.86-1.78 (m, 2H, $OCH_2C\mathbf{H}_2$), 1.37-1.29 (m, 2H, CH_2), 0.61-0.52 (m, 6H, $SiCH_2$), -0.01 (s, 6H, $Si(CH_3)_2$), -0.04 (s, 9H, $Si(CH_3)_3$); ^{29}Si NMR (100 MHz, $CDCl_3$): δ = 2.31, 0.59; ^{13}C NMR (125 MHz, $CDCl_3$,): δ = 157.7, 149.5, 147.3, 135.4, 134.1, 127.9 (2C), 119.2, 115.9, 114.8 (2C), 112.0, 73.2 (OCH_2), 71.8, 70.3 (2C), 69.9, 69.3, 63.9, 63.6 (2C), 23.8, 21.3, 19.7, 18.4, 11.3, (CH_2), -1.4 (3C, CH_3), -3.3 (2C, CH_3); anal. calcd. for $C_{29}H_{48}O_7Si_2$: C 61.66 %, H 8.57 %; found: C 61.40 %, H 8.80 %.

4-[4'-(2,3-Dihydroxypropoxy)-3-(4,4,8,8,12,12-hexamethyl-4,8,12-trisilatridecyloxy)-biphenyl-4-yloxy]propane-1,2-diol C5: Synthesized and purified in an analogues way as **C4** from **C5-acetonide** (420 mg, 0.56 mmol). Yield: 180 mg (48 %); colourless solid; ^{1}HNMR (200 MHz, $CDCl_3$): δ = 7.42 (d, ^3J(H,H) = 8.5 Hz, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.6 Hz, 3H, Ar-H), 4.20-4.03 (m, 6H, OCH, OCH_2), 3.98 (t, ^3J(H,H) = 6.9 Hz, 2H, $OC\mathbf{H}_2CH_2$), 3.87-3.73 (m, 4H, OCH_2), 2.42 (bs, 4H, OH), 1.86-1.78 (m, 2H, $OCH_2C\mathbf{H}_2$),

1.37-1.27 (m, 4H, CH_2), 0.60-0.51 (m, 10H, $SiCH_2$), -0.01 (s, 6H, $Si(CH_3)_2$), -0.05 (s, 9H, $Si(CH_3)_3$), -0.07-(-0.08) (s, 6H, $Si(CH_3)_2$); ^{29}Si NMR (100 MHz, $CDCl_3$): δ = 2.29, 0.98, 0.57; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 149.5, 147.3, 135.4, 134.1, 127.9 (2C), 119.2, 115.9, 114.8 (2C), 112.0, 73.1 (OCH_2), 71.8, 70.3 (2C), 69.9, 69.3, 63.9, 63.6 (2C), 23.8, 21.4, 20.1, 20.0, 19.9, 18.4, 18.4, 11.3, (CH_2), -1.4 (3C, CH_3), -3.1 (2C, CH_3), -3.3 (2C, CH_3); anal. calcd. for $C_{34}H_{60}O_7Si_3$: C 61.40 %, H 9.09 %; found: C 61.13 %, H 9.43 %.

4-[4'-(2,3-Dihydroxypropoxy)-3-(4,4,8,8,12,12,16,16-octamethyl-4,8,12,16-tetrasilaheptadecyloxy)biphenyl-4-yloxy]propane-1,2-diol C6: Synthesized and purified in an analogues way as **C4** from **C6-acetonide** (240 mg, 0.28 mmol). Yield: 180 mg (83 %); colourless solid; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.4 Hz, 1H, Ar-H), 6.93 (d, ^3J(H,H) = 8.8 Hz, 2H, Ar-H), 4.20-4.03 (m, 6H, OCH, OCH_2), 3.98 (t, ^3J(H,H) = 7.0 Hz, 2H, $OC\mathbf{H}_2CH_2$), 3.86-3.74 (m, 4H, OCH_2), 3.26 (bs, 1H, OH), 2.66 (bs, 1H, OH), 2.47-2.44 (m, 1H, OH), 2.09 (bs, 1H, OH), 1.85-1.78 (m, 2H, $OCH_2C\mathbf{H}_2$), 1.35-1.27 (m, 6H, CH_2), 0.60-0.56 (m, 4H, $SiCH_2$), 0.55-0.50 (m, 10H, $SiCH_2$), -0.01 (s, 6H, $Si(CH_3)_2$), -0.05 (s, 9H, $Si(CH_3)_3$), -0.07-(-0.08) (m, 12H, $Si(CH_3)_2$); ^{29}Si NMR (100 MHz, $CDCl_3$): δ = 2.29, 0.98 (2Si), 0.57; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 149.5, 147.3, 135.4, 134.1, 127.9 (2C), 119.2, 115.8, 114.8 (2C), 111.9, 73.1 (OCH_2), 71.7, 70.3 (2C), 69.8, 69.3, 63.8, 63.6 (2C), 30.9, 23.7, 21.3, 20.1, 20.1, 20.1, 20.0, 19.8, 18.4, 18.4, 18.3, 11.2, (CH_2), -1.5 (3C, CH_3), -3.1 (2C, CH_3), -3.2 (2C, CH_3), -3.3 (2C, CH_3); anal. calcd. for $C_{39}H_{72}O_7Si_4$: C 61.20 %, H 9.48 %; found: C 61.46 %, H 9.77 %.

4-[4'-(2,3-Dihydroxypropoxy)-3-(12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy)biphenyl-4-yloxy]propane-1,2-diol C7: Synthesized and purified in an analogues way as **C4** from **C7-acetonide** (230 mg, 0.24 mmol). Yield: 165 mg (78 %); colourless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ^3J(H,H) = 8.7 Hz, 3H, Ar-H), 4.21-4.01 (m, 8H, OCH, OCH_2), 3.87-3.73 (m, 4H, OCH_2), 3.24 (d, ^3J(H,H) = 5.6 Hz, 1H, OH), 2.62 (d, ^3J(H,H) = 4.6 Hz, 1H, OH), 2.49 (t, ^3J(H,H) = 6.4 Hz, 1H, OH), 2.04 (t, ^3J(H,H) = 6.5 Hz, 1H, OH), 1.83 (quint, ^3J(H,H) = 7.2 Hz, 2H, $OCH_2C\mathbf{H}_2$), 1.48-1.42 (m, 2H, CH_2), 1.36-1.25 (m, 20H, CH_2), 0.54-0.51 (m, 12H, $SiCH_2$), 0.46-0.43 (m, 2H, $SiCH_2$), -0.05 (s, 9H, $Si(CH_3)_3$), -0.08 (s, 18H, $Si(CH_3)_2$); ^{29}Si NMR (100 MHz, $CDCl_3$) δ = 1.59, 0.98 (2Si), 0.57; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.7, 149.5, 147.3, 135.4, 134.1, 127.9 (2C), 119.1, 115.9, 114.8 (2C), 111.8, 73.3, 70.3 (2C), 69.8, 69.3, 69.0 (OCH_2), 63.9, 63.6 (2C), 33.7, 30.9, 29.6, 29.6, 29.6, 29,4, 29.4, 29.2, 26.0, 23.9, 21.3, 20.1, 20.0, 20.0, 18.4, 15.4 (CH_2) -1.5 (3C, CH_3), -3.1 (2C, CH_3), -3.2 (2C, CH_3), -3.3 (2C, CH_3); anal. calcd. for $C_{47}H_{88}O_7Si_4$: C 64.33 %, H 10.11 %; found: C 64.61 %, H 9.88 %.

3.5 Synthesis of the siloxanes Si1-6

4´-(2,3-Dihydroxypropoxy)-3-[11-(1,1,1,3,3-pentamethyldisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si1: Synthesized as described for **H1-acetonide** by etherification of **5a** (200 mg, 0.53 mmol) with 1-bromo-11-(1,1,1,3,3-pentamethyldisiloxy)undecane (202 mg, 0.53 mmol), K_2CO_3 (400 mg, 2.89 mmol) in DMF (50 ml); 10 h at 50-60 °C. Purified by preparative centrifugal thin layer chromatography (eluents: $CHCl_3$/MeOH = 10:0.2 -10:1 (v/v)); Yield: 167 mg (47 %); colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.47 (t, ^3J(H,H) = 5.6 Hz, 1H, N-H), 7.98 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.28 (d, ^3J(H,H) = 8.3 Hz, 2H, Ar-H), 6.97 (s, 1H, Ar-H), 6.92 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 6.81 (d, ^3J(H,H) = 8.5 Hz, 2H, Ar-H), 4.12-4.03 (m, 3H, CHO, CH_2O), 3.97-3.45 (m, 13H, OH, CH_2O), 1.83-1.80 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.43-1.39 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.33-1.25 (m, 14H, CH_2), 0.49-0.46 (m, 2H, $SiCH_2$), 0.03 (s, 9H, $SiCH_3$), 0.01 (s, 6H, $SiCH_3$);

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.11, 158.73, 157.43 (2C), 145.53 (2C), 132.72, 132.62 (2C), 128.23, 119.41, 118.84, 114.97, 110.43 (2C), 71.50, 70.47, 69.36, 63.85, 63.69 (2C), 42.66, 33.47, 29.72, 29.69, 29.67, 29.47, 29.44, 29.30, 26.29, 23.37, 18.51 (CH_2), 2.09, 1.13, 0.48 ($SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 7.62, -21.93; anal. calcd. for $C_{35}H_{59}NO_8Si_2$: C 62.00, H 8.77, N 2.07; found: C 62.29, H 8.95, N 1.98.

4´-(2,3-Dihydroxypropoxy)-3-[11-(1,1,1,3,3,5,5-heptamethyltrisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si2: Synthesized as described for **H1-acetonide** by etherification of **5a** (150 mg, 0.40 mmol) with 1-bromo-11-(1,1,1,3,3,5,5-heptamethyltrisiloxy)undecane (217 mg, 0.48 mmol), K_2CO_3 (302 mg, 2.19 mmol) in DMF (50 ml). Yield: 162 mg (54 %); colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.45 (t, ^3J(H,H) = 6.0 Hz, 1H, N-H), 8.09 (d, ^3J(H,H) = 8.1 Hz, 1H, Ar-H), 7.40 (d, ^3J(H,H) = 8.5 Hz, 2H, Ar-H), 7.07 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.03 (s, 1H, Ar-H), 6.89 (d, ^3J(H,H) = 8.5 Hz, 2H, Ar-H), 4.14-4.11 (m, 3H, CHO, CH_2O), 4.04-4.00 (m, 2H, CH_2O), 3.87-3.83 (m, 2H, CH_2O), 3.78-3.74 (m, 1H, CH_2O), 3.68-3.54 (m, 6H, OH, CH_2O), 3.27 (s, 1H, OH), 2.80 (s, 1H, OH), 1.90-1.83 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.47-1.42 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.26 (m, 14H, CH_2), 0.52-0.49 (m, 2H, $SiCH_2$), 0.06 (m, 9H, $SiCH_3$), 0.04 (m, 6H, $SiCH_3$), 0.00 (m, 6H, $SiCH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.01, 158.74, 157.43 (2C), 145.41 (2C), 132.55, 132.47 (2C), 128.13, 119.28, 118.75, 114.92, 110.27 (2C), 71.50, 70.50, 69.31, 69.26, 63.93, 63.69 (2C), 42.68, 33.51, 29.73, 29.70, 29.69, 29.49, 29.44, 29.26, 26.27, 23.32, 18.40 (CH_2), 1.92, 1.38, 0.33 ($SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 7.46, 7.03, -21.05; anal. calcd. for $C_{37}H_{65}NO_9Si_3$: C 59.08, H 8.71, N 1.86; found: C 58.80, H 8.68, N 1.84.

4´-(2,3-Dihydroxypropoxy)-3-[11-(1,1,1,3,5,5,5-heptamethyltrisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si3: Synthesized as described for **H1-acetonide** by etherification of **5a** (150 mg, 0.40 mmol) with 1-bromo-11-(1,1,1,3,5,5,5-heptamethyltrisiloxy)undecane (190 mg, 0.42 mmol), K_2CO_3 (302 mg, 2.19 mmol) in DMF (50 ml). Yield: 112 mg (37 %); colourless solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.44 (t, ^3J(H,H) = 6.1 Hz, 1H, N-H), 8.12 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.44 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.13 (d, ^3J(H,H) = 8.3 Hz, 1H, Ar-H), 7.05 (d, ^4J(H,H) = 1.0 Hz, 1H, Ar-H), 6.93 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 4.15-4.10 (m, 3H, CHO, CH_2O), 4.06-4.02 (m, 2H, CH_2O), 3.87-3.83 (m, 2H, CH_2O), 3.78-3.74 (m, 1H, CH_2O), 3.67-3.55 (m, 4H, CH_2O), 3.37 (s, 2H, OH), 3.04 (s, 1H, OH), 2.52 (s, 1H, OH), 1.91-1.84 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.48-1.43 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.36-1.26 (m, 14H, CH_2), 0.45-0.41 (m, 2H, $SiCH_2$), 0.06 (s, 18H, $SiCH_3$), -0.03 (s, 3H, $SiCH_3$); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.20, 158.70, 157.43 (2C), 145.62 (2C), 132.94, 132.68 (2C), 128.30, 119.52, 118.89, 114.98, 110.52 (2C), 71.68, 70.42, 69.42, 69.37, 63.76, 63.68 (2C), 42.63, 33.30, 29.71, 29.67, 29.47, 29.33, 26.31, 23.18, 17.76 (CH_2), 1.98, -0.13 ($SiCH_3$); ^{29}Si-NMR (99 MHz, $CDCl_3$): δ = 6.84, -21.18; anal. calcd. for $C_{37}H_{65}NO_9Si_3$: C 59.08, H 8.71, N 1.86; found: C 59.15, H 8.89, N 1.75.

4´-(2,3-Dihydroxypropoxy)-2-[11-(1,1,1,3,3-pentamethyldisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si4: Synthesized as described for **H1-acetonide** by etherification of **5b** (150 mg, 0.40 mmol) with 1-bromo-11-(1,1,1,3,3-pentamethyldisiloxy)undecane (182 mg, 0.48 mmol), K_2CO_3 (302 mg, 2.19 mmol) in DMF (50 ml). Yield: 54 mg (20 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.94 (t, ^3J(H,H) = 5.39 Hz, 1H, N-H), 7.60 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.55 (d, ^4J(H,H) = 1.7 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.18-3.93 (m, 6H, CHO, CH_2O), 3.79-3.73 (m, 2H, CH_2O), 3.70-3.63 (m, 2H, CH_2O), 3.59-3.45 (m, 4H, OH, CH_2O), 1.76-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.44-1.40 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.33-1.29 (m, 14H, CH_2), 0.55-0.51 (m, 2H, $SiCH_2$), 0.06 (s, 9H, $SiCH_3$), 0.04 (s, 6H, $SiCH_3$); ^{13}C-NMR (125 MHz, acetone-d_6): δ =

170.76, 161.74, 159.15, 137.44, 136.44, 133.72, 133.35, 133.23, 122.62, 117.11, 114.67, 74.53, 73.68, 72.67, 71.45, 66.89, 66.43, 46.16, 36.41, 32.62, 32.59, 32.50, 32.34, 29.10, 26.28, 21.23 (CH_2), 4.35, 2.78 ($SiCH_3$); ^{29}Si-NMR (99 MHz, acetone-d_6): δ = 7.53, 6.93; anal. calcd. for $C_{35}H_{59}NO_8Si_2$: C 62.00, H 8.77, N 2.07; found: C 62.08, H 8.94, N 2.00.

4´-(2,3-Dihydroxypropoxy)-2-[11-(1,1,1,3,3,5,5-heptamethyltrisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si5: Synthesized as described for **H1-acetonide** by etherification of **5b** (150 mg, 0.40 mmol) with 1-bromo-11-(1,1,1,3,3,5,5-heptamethyltrisiloxy)undecane (217 mg, 0.48 mmol), K_2CO_3 (302 mg, 2.19 mmol) in DMF (50 ml). Yield: 58 mg (19 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.95 (s, 1H, N-H), 7.60 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.54 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.13-3.93 (m, 6H, CHO, CH_2O), 3.79-3.74 (m, 2H, CH_2O), 3.71-3.64 (m, 2H, CH_2O), 3.59-3.46 (m, 4H, OH, CH_2O), 1.75-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.45-1.42 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.35-1.29 (m, 14H, CH_2), 0.59-0.55 (m, 2H, $SiCH_2$), 0.09 (s, 9H, $SiCH_3$), 0.07 (s, 6H, $SiCH_3$), 0.03 (s, 6H, $SiCH_3$); ^{13}C-NMR (125 MHz, acetone-d_6): δ = 168.40, 159.37, 156.78, 135.07, 134.07, 131.35, 130.98, 130.86, 120.25, 114.74, 112.21, 72.16, 71.31, 70.29, 69.08, 64.52, 64.07, 43.79, 34.09, 30.27, 30.23, 30.13, 29.97, 29.83, 26.73, 23.87, 18.80 (CH_2), 1.85, 1.37, 0.31 ($SiCH_3$); ^{29}Si-NMR (99 MHz, acetone-d_6): δ = 7.42, 6.98, -21.18; anal. calcd. for $C_{37}H_{65}NO_9Si_3$: C 59.08, H 8.71, N 1.86; found: C 59.05, H 8.84, N 1.81.

4´-(2,3-Dihydroxypropoxy)-2-[11-(1,1,1,3,5,5,5-heptamethyltrisiloxy)]biphenyl-4-yl-*N*-(2,3-dihydroxypropyl)benzamide Si6: Synthesized as described for **H1-acetonide** by etherification of **5b** (150 mg, 0.40 mmol) with 1-bromo-11-(1,1,1,3,5,5,5-heptamethyltrisiloxy)undecane (217 mg, 0.48 mmol), K_2CO_3 (302 mg, 2.19 mmol) in DMF (50 ml). Yield: 44 mg (15 %); colourless solid; ^{1}H-NMR (400 MHz, acetone-d_6): δ = 7.95 (s, 1H, N-H), 7.60 (d, ^4J(H,H) = 1.5 Hz, 1H, Ar-H), 7.54 (d, ^3J(H,H) = 8.0 Hz, 1H, Ar-H), 7.51 (d, ^3J(H,H) = 8.7 Hz, 2H, Ar-H), 7.36 (d, ^3J(H,H) = 7.9 Hz, 1H, Ar-H), 6.98 (d, ^3J(H,H) = 8.9 Hz, 2H, Ar-H), 4.14-3.94 (m, 6H, CHO, CH_2O), 3.78-3.72 (m, 2H, CH_2O), 3.69-3.64 (m, 2H, CH_2O), 3.59-3.45 (m, 4H, OH, CH_2O), 1.76-1.70 (m, 2H, $OCH_2\mathbf{CH_2}$), 1.43-1.40 (m, 2H, $OCH_2CH_2\mathbf{CH_2}$), 1.33-1.30 (m, 14H, CH_2), 0.49-0.47 (m, 2H, $SiCH_2$), 0.09 (s, 18H, $SiCH_3$), 0.01 (s, 3H, $SiCH_3$); ^{13}C-NMR (125 MHz, acetone-d_6): δ = 131.36, 130.99, 130.87, 123.68, 120.26, 114.75, 112.32, 71.31, 70.30, 69.09, 33.84, 30.27, 30.13, 29.98, 26.74, 23.75, 18.18 (CH_2), 1.90, -0.08 ($SiCH_3$); ^{29}Si-NMR (99 MHz, acetone-d_6): δ = 6.82, -21.27; anal. calcd. for $C_{37}H_{65}NO_9Si_3$: C 59.08, H 8.71, N 1.86; found: C 59.10, H 8.98, N 1.68.

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