Electronic Supplementary Information

Amplifying (Im)perfection: The Impact of Crystallinity in Discrete and Disperse Block Co-oligomers

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1. Materials and Methods

All chemicals were purchased from commercial sources and used without further purification. Disperse siloxane hydride **1** was purchased from Gelest and has an average DP of 15 (estimated with ^{1}H NMR) and a dispersity of 1.13 (measured by SEC ($CHCl_3$, RI)). Siloxane-7 hydride (**12**), discrete Me-Si_{15}-LLA_1-COOH (**6a**) and disperse Bu-$Si_{\sim 15}$-LLA_1-COOH (**6b**) were synthesized according to literature procedures.[1,2] Dry solvents were obtained with an MBRAUN Solvent Purification System (MB-SPS). Toluene was dried over 4Å molecular sieves before use. Oven-dried glassware (120 °C) was used for all reactions carried out under argon atmosphere. Reactions were followed by thin-layer chromatography (TLC) using 60-F254 silica gel plates from Merck and visualized by UV light at 254 nm and/or cerium molybdate (CeMo) staining. Automated column chromatography was conducted on a Grace Reveleris X2 Flash Chromatography System using Reveleris Silica Flash Cartridges.

NMR spectra were recorded on Bruker 400 MHz Ultrashield spectrometers (400 MHz for ^{1}H NMR). Deuterated solvents used are indicated in each case. Chemical shifts (δ) are expressed in ppm and are referred to the residual peak of the solvent. Peak multiplicity is abbreviated as s: singlet; d: doublet; t: triplet; dt: doublet of triplets; ddt: doublet of doublets of triplets; td: triplet of doublets; tt: triplet of triplets; q: quartet; qd: quartet of doublets; m: multiplet.

Matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer using α-cyano-4-hydroxycinnamic acid (CHCA) or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as matrix.

Gas chromatography-mass spectrometry (GC-MS) measurements were conducted on a Shimadzu GC-17A gas chromatograph with a Shimadzu AOC-20i auto injector, Shimadzu GCMS-QP5000 gas chromatograph mass spectrometer and Phenomenex Zebron ZB-35 column (l = 30 meters, ID = 0.25 mm, film thickness = 0.25 μm).

Size exclusion chromatography (SEC) measurements were conducted on a Shimadzu Prominence-i LC-2030C 3D with a Shimadzu RID-20A Refractive index detector, using an eluent flow of 1 mL min^{-1} (THF or $CHCl_3$). The molecular weight is determined based on narrow dispersity polystyrene standards purchased from Polymer Source Inc.

Differential scanning calorimetry (DSC) data were collected on a DSC Q2000 from TA instruments, calibrated with an indium standard. The samples (4–8 mg) were weighed directly into aluminum pans and hermetically sealed. The samples were initially heated to 180 °C and then

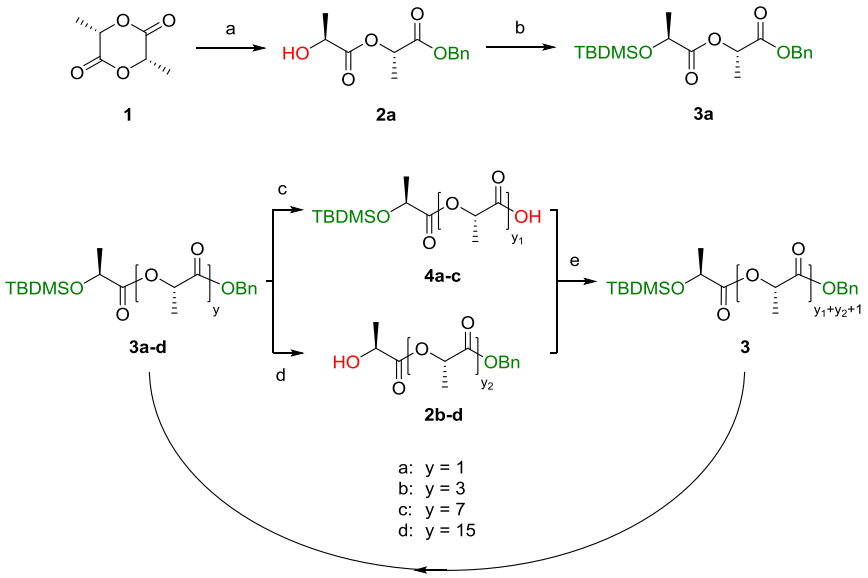
subjected to two cooling/heating cycles from -50 °C to 180 °C with a rate of 10 °C min^{-1}. The data that is presented, represents the second heating/cooling cycle.

Polarized optical microscopy (POM) images were obtained with a Jenaval polarization microscope equipped with a Linkam THMS 600 temperature controller. Images were captured with crossed polarizers. The samples were positioned between two coverslips and mounted directly on the Linkam heating stage. Micrographs were taken during cooling runs at a rate of 0.1–1 °C min^{-1}, starting from the molten (isotropic) state.

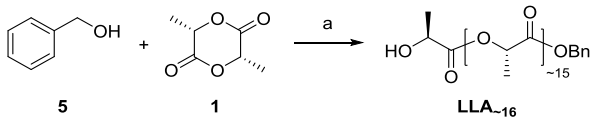
Bulk **small angle X-ray scattering** (SAXS) was performed on an instrument from Ganesha Lab. The flight tube and sample holder are all under vacuum in a single housing, with a GeniX-Cu ultra-low divergence X-ray generator. The source produces X-rays with a wavelength (λ) of 0.154 nm and a flux of 1×10^8 ph s^{-1}. Samples were put inside 1 mm diameter glass capillaries, and annealed by heating above the (expected) melting point and slow (0.5 °C min^{-1}) cooling to room temperature. Disperse samples [$\mathbf{Si_{15}\text{-}LLA_{\sim 17}}$] and [$\mathbf{Si_{\sim 15}\text{-}LLA_{\sim 17}}$] were annealed in a vial and then smeared onto Kapton tape. For room temperature measurements, the samples were positioned directly in the beamline. Variable temperature measurements (VT-SAXS) were performed using a Linkam heating stage. Samples were equilibrated at each temperature for 5 minutes prior to measuring and a heating/cooling rate of 5 °C min^{-1} was used in between the measurements. Scattered X-rays were captured on a 2-dimensional Pilatus 300K detector with 487 × 619 pixel resolution. Samples were measured in MAXS mode for 1200 seconds and WAXS mode for 300 seconds. The sample-to-detector distance was 0.084 m (WAXS mode) or 0.431 m (MAXS mode). The instrument was calibrated with diffraction patterns from silver behenate. The raw data files were calibrated and reduced to 1-D data with the SAXSGui software provided by JJ X-Ray Systems ApS. MAXS and WAXS regions were merged into a single data file using the SAXSutilities software package provided by Michael Sztucki.

2. Synthetic procedures

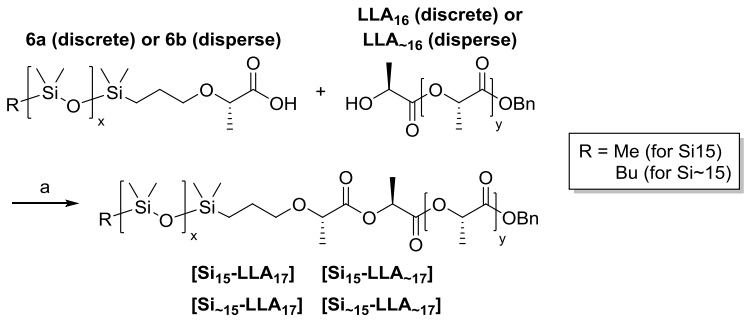
Synthetic schemes



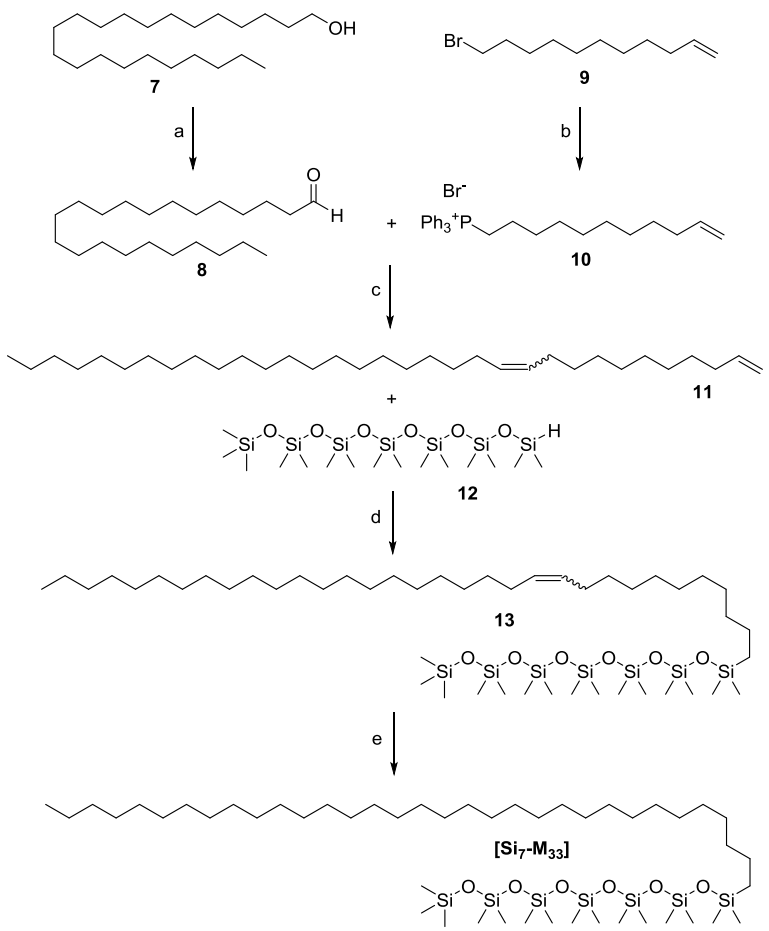
Scheme S1. The synthesis of discrete, monoprotected L-lactic acid oligomer **LLA$_{16}$ (2d)**. Reagents and conditions: (a) BnOH, CSA, toluene, 80 °C, 2 h (64%); (b) TBDMSCl, imidazole, DMF, room temperature, O/N (60%); (c) H_2, Pd/C, EtOAc, room temperature, 2 h (quant.); (d) $BF_3{\cdot}Et_2O$, DCM, room temperature, O/N (79–92%); (e) EDC·HCl, DPTS, DCM, room temperature, O/N (72–90%). TBDMS = *tert*-butyldimethylsilyl, Bn = benzyl, EDC·HCl = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride, DPTS = *N*,*N*-dimethylaminopyridinium *p*-toluene sulfonate.



Scheme S2. Synthesis of disperse *o*LLA **LLA$_{\sim 16}$** by ring opening polymerization. Reagents and conditions: (a) DBU, DCM, room temperature, 1 h (92%). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

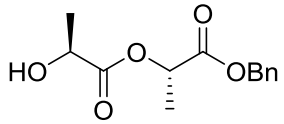


Scheme S3. Formation of *o*DMS-*o*LLA BCOs. Reagents and conditions: (a) EDC·HCl, DPTS, DCM, room temperature, O/N (64–90%). EDC·HCl = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride, DPTS = *N*,*N*-dimethylaminopyridinium *p*-toluene sulfonate.



Scheme S4. Formation of BCO [**Si$_7$-M$_{33}$**]. Reagents and conditions: (a) TEMPO, tetrabutylammonium chloride, *N*-chlorosuccinimide, $NaHCO_3$, K_2CO_3, DCM, water, room temperature, 20 h (86%); (b) PPh_3, acetonitrile, reflux, 24 h (92%); (c) KO*t*Bu, THF, 0–20 °C, 2 h (41%); (d) Karstedt catalyst, DCM, room temperature, 1 h (59%); (e) H_2, Pd/C, EtOAc, room temperature, 3 h (quant.). TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

HO-LLA$_2$-Bn (**2a**)

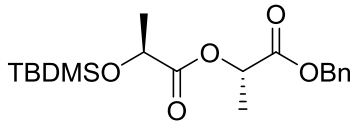


Optically pure L-lactide **1** (25.43g, 0.176 mol, 1 eq), dry benzyl alcohol (20 mL, 0.176 mol, 1 eq) and D-camphorsulfonic acid (2.05 g, 8.8 mmol, 0.05 eq) were dissolved in toluene (90 mL) in a 250 mL round-bottom flask under an argon atmosphere. The mixture was stirred for 2 hours at 80 °C and cooled down afterwards. Subsequently, extra toluene (100 mL) was added and the solution washed with 0.2 M aq. $NaHCO_3$ soln. (2x 100 mL). The combined aqueous layers were extracted with EtOAc (100 mL) and the combined organic layers were washed with brine (60 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo* giving the crude product as a colorless oil (49.12 g). The crude material was purified by automated column chromatography in five separate portions of 10 grams each using heptane/EtOAc (gradient 75/25 to 50/50) as eluent. The product **2a** (with traces of lactide and monomeric by-product) was obtained as a colorless oil (28.4 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.28 (m, 5H, Ar-H), 5.31–5.08 (m, 3H, O-CH(CH$_3$)-CO and O-CH$_2$-Ar), 4.42–4.23 (m, 1H, HO-CH(CH$_3$)-CO), 2.67–2.65 (d, ^3J = 6.1 Hz, 1H, HO-CH(CH$_3$)), 1.53 (d, ^3J = 7.1 Hz, 3H, O-CH(CH$_3$)-CO), 1.43 ppm (d, ^3J = 6.9 Hz, 3H, HO-CH(CH$_3$)-CO); ^{13}C

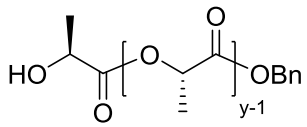
NMR (100 MHz, $CDCl_3$): δ = 175.07, 169.99, 135.05, 128.61, 128.52, 128.22, 69.35, 67.23, 66.69, 20.41, 16.82 ppm.

TBDMS-LLA$_2$-Bn (**3a)**



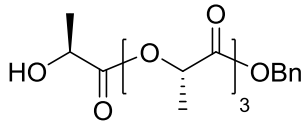
Alcohol **2a** (15.30 g, 60.7 mmol) was dissolved in dry DMF (90 mL) in 250 mL round-bottom flask under an argon atmosphere. Imidazole (10.28 g, 152 mmol, 2.5 eq) and *tert*-butyldimethylsilyl chloride (TBDMS-Cl, 10.97 g, 72.8 mmol, 1.2 eq) were added as solids and the resulting yellow solution was stirred overnight at room temperature. Full conversion of the alcohol was confirmed by TLC analysis (hept/EtOAc 50/50; CeMo stain; $R_{f,prod}$ = 0.85). The mixture was poured into sat. aq. $NaHCO_3$ soln. (200 mL) and extracted with pentane (4x 100 mL). The combined organic layers were dried with $MgSO_4$ and the solvent was removed in *vacuo*, giving in the crude product as a colorless oil (23.02 g). The crude material was purified by automated column chromatography in two separate portions of 11–12 grams each using heptane/EtOAc (gradient 100/0 to 85/15) as eluent. Pure **3a** (without any residual lactide or monomeric by-product) was obtained as a colorless oil (13.35 g, 60%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 5H, Ar-H), 5.24–5.08 (m, 3H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.38 (q, ^3J = 6.8 Hz, 1H, Si-O-CH(CH_3)-CO), 1.51 (d, ^3J = 7 Hz, 3H, O-CH(CH_3)-CO), 1.41 (d, ^3J = 6.8 Hz, 3H, Si-O-CH(CH_3)-CO), 0.90 (s, 9H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.07 ppm (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.44, 170.32, 135.23, 128.56, 128.39, 128.19, 68.97, 68.05, 67.01, 25.68, 21.17, 18.27, 16.87, 5.32, 4.94 ppm.

*General procedure **A** for removal of the TBDMS protective group, giving HO-LLA$_y$-Bn* (**2b-d**)



The TBDMS protected oligomer **3** (*e.g.*, 6 mmol) was dissolved in dry DCM (40 mL, 0.15 M) in a 100 mL round-bottom flask under an argon atmosphere. The solution was cooled down to 0 °C in icewater. Next, BF_3-etherate (18 mmol, 3 eq) was added slowly and the mixture was allowed to warm to room temperature. Stirring was continued at room temperature until full conversion of the starting material was reached (TLC analysis (hept/EtOAc 50/50; CeMo stain); maximum reaction time: 18 hours). Subsequently, the solution was poured into a mixture of sat. aq. $NaHCO_3$ soln. (50 mL) and brine (15 mL). The resulting colorless organic layer was separated, washed with another portion of brine (10 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo*, giving the crude product. Purification by automated column chromatography gave the pure material **2**.

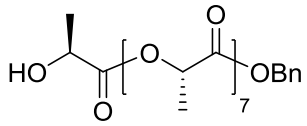
HO-LLA$_4$-Bn (**2b**)



Starting from TBDMS protected tetramer **3b** (3.37 g, 6.6 mmol) and BF_3-etherate (2.88 g, 2.5 mL, 3 eq), crude deprotected tetramer **2b** was obtained (2.74 g) using general method **A** for the removal of the TBDMS protective group. The material was purified by automated column chromatography using heptane/EtOAc (gradient 70/30 to 50/50) as eluent, giving the pure material as a colorless oil (2.07 g, 79%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.27 (m, 5H, Ar-H), 5.26–5.08 (m, 5H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.34 (m, 1H, HO-CH(CH_3)-CO), 2.84 (s, 1H, HO-CH(CH_3)-CO), 1.59 (d, ^3J = 7.1 Hz, 3H, HO-CH(CH_3)-CO), 1.55–1.45 ppm (m, 9H, O-CH(CH_3)-CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.27, 170.13, 169.95, 169.77, 135.30, 128.88, 128.86, 128.84, 128.77, 128.74, 128.73, 128.47, 69.53, 69.33, 69.27, 69.23, 67.44, 66.93, 20.69, 16.97, 16.95, 16.81 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{19}H_{24}O_9$+Na^+: 419.13 $[M+Na]^+$; found 419.17 Da; *m/z* calcd for $C_{19}H_{24}O_9$+K^+: 435.11 $[M+K]^+$; found 435.13 Da.

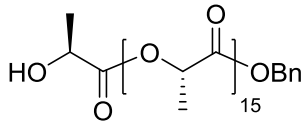
HO-LLA$_8$-Bn (**2c**)



Starting from TBDMS protected octamer **3c** (3.13 g, 9.92 mmol) and BF_3-etherate (1.67 g, 1.5 mL, 3 eq), crude deprotected octamer **2c** was obtained (2.90 g) using general method **A** for the removal of the TBDMS protective group. The reaction was complete in 3 hours, and the material was purified by automated column chromatography using heptane/EtOAc (gradient 60/40 to 35/65) as eluent, giving the pure material as a colorless oil (2.30 g, 89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.30 (m, 5H, Ar-H), 5.27–5.06 (m, 9H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.34 (m, 1H, HO-CH(CH_3)-CO), 2.75 (s, 1H, HO-CH(CH_3)-CO), 1.58 (m, 15H, O-CH(CH_3)-CO), 1.51 (m, 6H, O-CH(CH_3)-CO), 1.48 ppm (d, ^3J = 6.9 Hz, 3H, HO-CH(CH_3)-CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.41, 170.20, 169.97, 169.89, 169.88, 169.83, 135.38, 128.92, 128.83, 128.55, 69.59, 69.37, 69.35, 69.33, 67.52, 67.01, 20.82, 17.05, 16.98, 16.95, 16.88 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{31}H_{40}O_{17}$+Na^+: 707.22 $[M+Na]^+$; found 707.25; *m/z* calcd for $C_{31}H_{40}O_{17}$+K^+: 723.19 $[M+K^+]$; found 723.21.

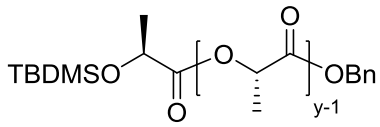
HO-LLA$_{16}$-Bn (**2d**)



Starting from TBDMS protected 16-mer **3d** (0.78 g, 0.564 mmol) and BF_3-etherate (0.28 g, 0.25 mL, 4 eq), crude deprotected 16-mer **2d** was obtained (0.71 g) using general method **A** for the removal of the TBDMS protective group. The material was purified by automated column chromatography using heptane/EtOAc (gradient 50/50 to 20/80) as eluent, giving the pure material as a white solid (0.66 g, 92%).

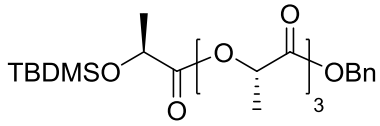
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5H, Ar-H), 5.28–5.09 (m, 17H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.34 (qd, ^3J = 6.8 Hz, ^3J = 6.0 Hz, 1H, HO-CH(CH_3)-CO), 2.66 (d, ^3J = 6.0 Hz, 1H, HO-CH(CH_3)-CO), 1.58 (m, 39H, O-CH(CH_3)-CO), 0.52 (m, 6H, O-CH(CH_3)-CO), 1.49 ppm (d, ^3J = 7 Hz, 3H, HO-CH(CH_3)-CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.48, 170.23, 169.98, 169.93, 169.86, 135.40, 128.96, 128.87, 128.58, 69.62, 69.45, 69.39, 69.35, 67.56, 67.05, 20.87, 17.09, 17.02, 16.99, 16.92 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{55}H_{72}O_{33}$+Na^+: 1283.39 $[M+Na]^+$; found 1283.39; *m/z* calcd for $C_{55}H_{72}O_{33}$+K^+: 1299.36 $[M+K^+]$; found 1299.37.

*General procedure **B** for the oLLA coupling reactions giving TBDMS-LLA$_y$-Bn* (**3b-d**)



TBDMS protected oligomer **4** (*e.g.*, 3 mmol, 1.06 eq) was dissolved in dry DCM (5 mL, 0.6 M) in a 3-necked round-bottom flask under an argon atmosphere. The solution was cooled to 0 °C in icewater and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 0.57 mmol, 0.2 eq) and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl, 3.9 mmol, 1.3 eq) were added. The mixture was stirred for 10 min at 0 °C, followed by the addition of benzyl protected oligomer **2** (2.83 mmol, 1.0 eq). The resulting solution was stirred overnight at room temperature until full conversion of the starting material **2** was reached (TLC analysis (hept/EtOAc 50/50; CeMo stain); maximum reaction time: 18 hours). The reaction mixture was diluted with DCM (20 mL) and washed with brine (20 mL). The organic layer was dried with $MgSO_4$ and concentrated in *vacuo*, giving the crude product **3**. Purification by automated column chromatography gave the pure product.

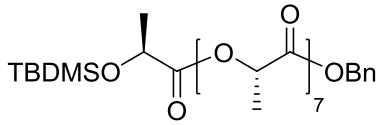
TBDMS-LLA$_4$-Bn (**3b**)



Starting with TBDMS protected dimer **4a** (4.66 g, 16.85 mmol, 1.06 eq), benzyl protected dimer **2a** (4.01 g, 15.9 mmol, 1 eq), DPTS (0.94 g, 3.18 mmol, 0.2 eq) and EDC·HCl (3.96 g, 20.66 mmol, 1.3 eq), crude double protected tetramer **3b** was obtained as a light yellow oil (8.78 g) using general method **B** for the coupling reactions. The material was purified by automated column chromatography using hept/EtOAc (gradient 100/0 to 75/25) as eluent, giving the pure material as a white solid (6.74 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.28 (m, 5H, Ar-H), 5.26–5.05 (m, 5H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.40 (q, ^3J = 6.7 Hz, 1H, Si-O-CH(CH_3)-CO), 1.57 (d, ^3J = 7.1 Hz, 3H, O-CH(CH_3)-CO), 1.52 (m, 6H, O-CH(CH_3)-CO), 1.45 (d, ^3J = 6.7 Hz, 3H, Si-O-CH(CH_3)-CO), 0.90 (s, 9H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.11 (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.09 ppm (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.85, 170.30, 170.27, 169.98, 135.42, 128.94, 128.83, 128.57, 128.56, 69.57, 69.16, 68.87, 68.33, 67.52, 26.03, 21.55, 18.61, 17.09, 17.07, 16.93, -4.57, -4.96 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{25}H_{38}O_9Si$+Na^+: 533.22 $[M+Na]^+$; found 533.25; *m/z* calcd for $C_{25}H_{38}O_9Si$+K^+: 549.19 $[M+K]^+$; found 549.20.

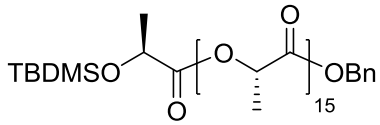
TBDMS-LLA$_8$-Bn (**3c**)



Starting with TBDMS protected tetramer **4b** (2.33 g, 5.54 mmol, 1.06 eq), benzyl protected tetramer **2b** (2.07g, 5.22 mmol, 1 eq), DPTS (0.31 g, 1.04 mmol, 0.2 eq) and EDC·HCl (1.30 g, 6.79 mmol, 1.3 eq), crude double protected octamer **3c** was obtained as a light yellow oil (9.5 g) using general method **B** for the coupling reactions. The material was purified by automated column chromatography using hept/EtOAc (gradient 90/10 to 50/50) as eluent, giving the pure material as a colorless oil (3.74 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.3 (m, 5H, Ar-H), 5.32–5.04 (m, 9H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.39 (q, ^3J = 6.7 Hz, 1H, Si-O-CH(CH_3)-CO), 1.57 (m, 15H, O-CH(CH_3)-CO), 1.51 (m, 6H, O-CH(CH_3)-CO), 1.44 (d, ^3J = 6.8 Hz, 3H, Si-O-CH(CH_3)-CO), 0.90 (s, 9H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.07 ppm (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.80, 171.37, 170.27, 170.17, 170.00, 169.92, 169.89, 169.87, 169.81, 135.37, 128.91, 128.82, 128.54, 69.57, 69.31, 69.28, 69.25, 69.11, 68.83, 68.29, 67.50, 26.00, 21.52, 21.33, 18.57, 17.05, 16.97, 16.94, 16.87, -4.61, -5.00 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{37}H_{54}O_{17}Si+Na^+$: 821.30 $[M+Na]^+$; found 821.30.

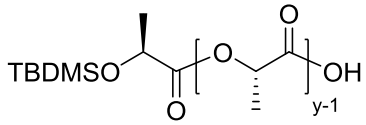
TBDMS-LLA$_{16}$-Bn (**3d**)



Starting with TBDMS protected octamer **4c** (2.05 g, 2.89 mmol, 1.06 eq), benzyl protected octamer **2c** (1.87 g, 2.73 mmol, 1 eq), DPTS (0.16 g, 0.546 mmol, 0.2 eq) and EDC·HCl (0.68 g, 3.55 mmol, 1.3 eq), crude double protected 16-mer **3d** was obtained as a light yellow solid (3.98 g) using general method **B** for the coupling reactions. The material was purified by automated column chromatography using hept/EtOAc (gradient 75/25 to 40/60) as eluent, giving the pure material as a white solid (2.70 g, 72%).

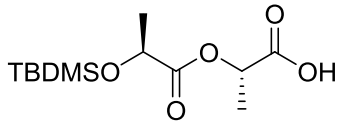
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.27 (m, 5H, Ar-H), 5.27–5.06 (m, 17H, O-CH(CH_3)-CO and O-CH_2-Ar), 4.39 (q, ^3J = 6.8 Hz, 1H, Si-O-CH(CH_3)-CO), 1.57–1.55 (m, 39H, O-CH(CH_3)-CO), 1.51 (m, 6H, O-CH(CH_3)-CO), 1.44 (d, ^3J = 6.8 Hz, 3H, Si-O-CH(CH_3)-CO), 0.89 (s, 9H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$), 0.07 ppm (s, 3H, (CH_3)$_3$C-Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.82, 170.29, 170.19, 170.02, 169.94, 169.89, 169.88, 169.82, 135.38, 128.93, 128.84, 128.55, 69.59, 69.31, 69.27, 69.12, 68.84, 68.31, 67.52, 26.01, 21.53, 18.59, 17.06, 16.99, 16.96, 16.88, -4.59, -4.99 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{61}H_{86}O_{33}Si+Na^+$: 1397.47 $[M+Na]^+$; found 1397.48; *m/z* calcd for $C_{61}H_{86}O_{33}Si+K^+$: 1413.45 $[M+K^+]$; found 1413.45.

*General procedure **C** for removal of the benzyl protective group giving TBDMS-LLA$_y$-COOH* (**4a-c**)



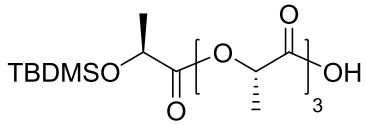
The benzyl protected oligomer **3** (*e.g.*, 19 mmol) was dissolved in EtOAc (65 mL, 0.3 M). The solution was purged with argon, and palladium (10% on carbon, 0.03 eq Pd) was added. The mixture was stirred overnight under hydrogen atmosphere at room temperature until full conversion of the starting material was reached (TLC analysis (hept/EtOAc 50/50; CeMo stain; $R_{f,prod}$ = 0.01–0.2 (tailing)); maximum reaction time: 18 hours. The black suspension was filtered through a 4 cm thick layer of Celite and the filter cake was washed with EtOAc (100 mL in small portions). The filtrate was concentrated in *vacuo*, giving the title compound **4** in high purity.

TBDMS-LLA$_2$-COOH (**4a**)



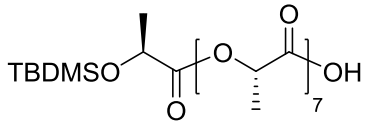
Starting from benzyl protected dimer **3a** (7.14 g, 19.5 mmol), pure deprotected dimer **4a** was obtained as a colorless oil (5.41 g, quant.) using general procedure **C** for the removal of the benzyl group.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.12 (q, ^3J = 7.1 Hz, 1H, O-C<u>H</u>(CH_3)-COOH), 4.40 (q, ^3J = 6.8 Hz, 1H, Si-O-C<u>H</u>(CH_3)-CO), 1.55 (d, ^3J = 7.1 Hz, 3H, O-CH(C<u>H</u>$_3$)-COOH), 1.44 (d, ^3J = 6.7 Hz, 3H, O-CH(C<u>H</u>$_3$)-CO), 0.90 (s, 9H, (C<u>H</u>$_3$)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(C<u>H</u>$_3$)$_2$), 0.08 ppm (s, 3H, (CH_3)$_3$C-Si(C<u>H</u>$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.81, 173.84, 68.70, 68.42, 26.02, 21.50, 18.63, 17.09, -4.97, -4.61 ppm.

TBDMS-LLA$_4$-COOH (**4b**)



Starting from benzyl protected tetramer **3b** (3.21 g, 6.29 mmol), pure deprotected dimer **4b** was obtained as a colorless oil (2.68 g, quant.) using general procedure **C** for the removal of the benzyl group.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26–5.05 (m, 3H, O-C<u>H</u>(CH_3)-CO), 4.39 (q, ^3J = 6.7 Hz, 1H, Si-O-C<u>H</u>(CH_3)-CO), 1.26–1.50 (m, 9H, O-CH(C<u>H</u>$_3$)-COOH), 1.44 (d, ^3J = 6.8 Hz, 3H, Si-O-CH(C<u>H</u>$_3$)-CO), 0.89 (s, 9H, (C<u>H</u>$_3$)$_3$C-Si(CH_3)$_2$), 0.10 (s, 3H, (CH_3)$_3$C-Si(C<u>H</u>$_3$)$_2$), 0.08 ppm (s, 3H, (CH_3)$_3$C-Si(C<u>H</u>$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.07, 173.95, 170.35, 169.98, 69.13, 69.07, 68.91, 68.34, 60.88, 26.02, 21.53, 21.37, 18.60, 17.05, 16.97, 16.93, 14.50, -4.59, -4.98 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{18}H_{32}O_9Si+Na^+$: 443.17 $[M+Na]^+$; found 443.20; *m/z* calcd for $C_{18}H_{32}O_9Si+K^+$: 459.14 $[M+K]^+$; found 459.17.

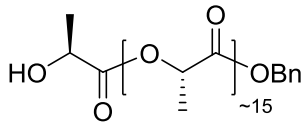
TBDMS-LLA$_8$-COOH (**4c**)



Starting from benzyl protected octamer **3c** (2.57 g, 3.21 mmol), pure deprotected dimer **4c** was obtained as a colorless oil (2.25 g, 99%) using general procedure **C** for the removal of the benzyl group. The reaction was completed in 5 hours.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.23–5.06 (m, 7H, O-C<u>H</u>(CH_3)-COOH and O-C<u>H$_2$</u>-Ar), 4.39 (q, ^3J = 6.8 Hz, 1H, Si-O-C<u>H</u>(CH_3)-CO), 1.67–1.49 (m, 21H, O-CH(C<u>H$_3$</u>)-COOH), 1.43 (d, ^3J = 6.7 Hz, 3H, Si-O-CH(C<u>H$_3$</u>)-CO), 0.89 (s, 9H, ($C\underline{H}_3$)$_3$C-Si(CH_3)$_2$), 0.11 (s, 3H, (CH_3)$_3$C-Si($C\underline{H}_3$)$_2$), 0.08 ppm (s, 3H, (CH_3)$_3$C-Si($C\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.60, 173.91, 170.32, 170.06, 169.98, 169.96, 169.86, 69.34, 69.32, 69.30, 69.16, 69.09, 68.89, 68.33, 26.02, 21.53, 18.60, 17.07, 16.99, 16.97, 16.90, -4.59, -4.97 ppm; HRMS (MALDI-TOF): *m*/*z* calcd for $C_{30}H_{48}O_{17}Si+Na^+$: 731.26 $[M+Na]^+$; found 731.29 Da; *m*/*z* calcd for $C_{30}H_{48}O_{17}Si+K^+$: 747.23 $[M+K^+]$; found 747.26.

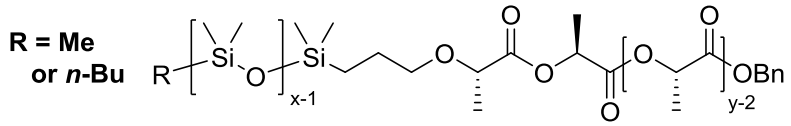
Synthesis of disperse HO-LLA$_{\sim 16}$-Bn (ring opening polymerization) (**LLA$_{\sim 16}$**).



L–lactide **1** was dried for 6 hours at 45 °C under vacuum. The lactide (202.0 mg, 1.40 mmol, 8 eq) was dissolved in dry DCM (3 mL) in a dry 10 mL Schlenk tube under an argon atmosphere. Dry benzyl alcohol **5** (19.0 mg, 0.175 mmol, 1 eq) was added. Next, a 10 w% solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dry DCM was prepared. Then, 21 mg of the DBU solution (2.1 mg, 0.014 mmol, 0.08 eq DBU) was added to the stirred reaction mixture. The reaction progress was checked with TLC (hept/EtOAc 50/50; CeMo stain). After completion (~1 h), benzoic acid (0.24 eq) was added to quench the reaction, and the solution was concentrated in *vacuo* to give crude disperse oligolactic acid as a yellowish wax. The material was purified by automated column chromatography using hept/EtOAc (gradient 88/12 to 15/85) as eluent. The pure product **LLA$_{\sim 16}$** was obtained as a white, waxy solid (203 mg, 92%).

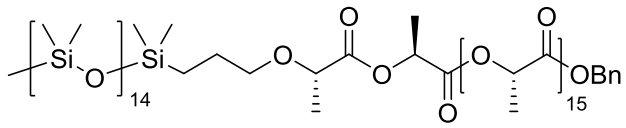
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 5H, Ar-<u>H</u>), 5.23–5.08 (m, 17H, O-C<u>H</u>(CH_3)-CO and Ar-C<u>H$_2$</u>-O), 4.33 (q, ^3J = 6.2 Hz, 1H, HO-C<u>H</u>(CH_3)-CO), 1.62–1.35 ppm (m, 54H, O-CH(C<u>H$_3$</u>)-CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.96, 169.85–169.04, 134.99, 128.56–128.41, 128.13, 69.37, 68.91, 67.08, 66.59, 20.39, 16.72–16.32 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{55}H_{72}O_{33}+Na^+$ (HO-LLA$_{16}$-Bn): 1283.38 $[M+Na]^+$; found 1283.40; (multiple, equally spaced (144.04 *m/z*) peaks were found between 500–3000 Da, each corresponding to the desired product with a different DP); SEC (THF): M_n = 1905; $Đ$ = 1.49.

*General procedure **D** for the oDMS-oLLA coupling reactions giving Me/Bu-Si$_x$-LLA$_y$-Bn* (**[Si$_x$-LLA$_y$]**).



*o*DMS acid **6a** or **6b** (*e.g.*, 0.16 mmol, 1.0 eq) was dissolved in dry DCM (1 mL, ~0.15 M) in a 10 mL Schlenk tube under an argon atmosphere. The solution was cooled to 0 °C in icewater and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 0.08 mmol, 0.5 eq) and *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl, 0.322 mmol, 2.0 eq) were added. The mixture was stirred for 10 minutes at 0 °C, followed by the addition of benzyl protected *o*LLA **LLA$_{16}$** or **LLA$_{\sim 16}$** (0.16 mmol, 1.0 eq). The mixture was then stirred overnight at room temperature, during which the formation of a suspension/emulsion of co-oligomer in DCM was observed. The reaction mixture was diluted with DCM (15 mL) to bring all material in solution and the material was washed with a 50/50 mixture of water and brine (10 mL in total). The organic layer was dried with $MgSO_4$ and concentrated in *vacuo*, giving the crude product **[Si$_x$-LLA$_y$]**. The material was purified by automated column chromatography.

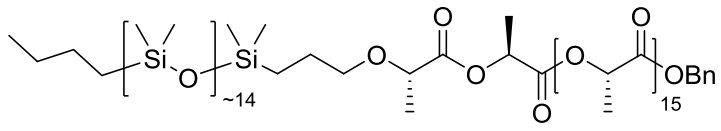
Me-Si$_{15}$-LLA$_{17}$-Bn (**[Si$_{15}$-LLA$_{17}$]**)



Starting from *o*DMS acid **6a** (160 mg, 0.13 mmol, 1 eq), **LLA$_{16}$** (163 mg, 0.13 mmol, 1 eq), DPTS (19 mg, 0.07 mmol, 0.5 eq) and EDC·HCl (50 mg, 0.26 mmol, 2 eq), crude oligomer **[Si$_{15}$-LLA$_{17}$]** was obtained as a white solid (252 mg) using general method **D**. The material was purified by automated column chromatography using hept/EtOAc (gradient 80/20 to 60/40) as eluent, giving the product in pure form as a white solid (216 mg, 80%).

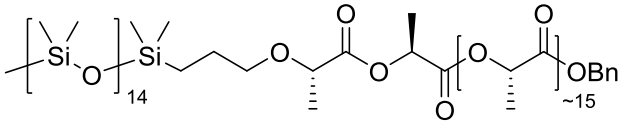
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 5H, Ar-H), 5.25–5.07 (m, 18H, CO-O-CH(CH$_3$)-CO and O-CH$_2$-Ar), 4.02 (q, ^3J = 6.9 Hz, 1H, CH$_2$-O-CH(CH$_3$)-CO), 3.58 (dt, ^2J = 8.8 Hz, ^3J = 7.0 Hz, 1H, CH$_2$-CH$_2$-O), 3.32 (dt, ^2J = 8.8 Hz, ^3J = 7.0 Hz, 1H, CH$_2$-CH$_2$-O), 1.65–1.6 (m, 2H, Si(CH$_3$)$_2$-CH$_2$-CH$_2$-CH$_2$-O), 1.58 (m, 42H, CO-O-CH(CH$_3$)-CO), 1.51 (m, 6H, CO-O-CH(CH$_3$)-CO), 1.45 (d, ^3J = 6.9 Hz, 3H, CH$_2$-O-CH(CH$_3$)-CO), 0.59–0.49 (m, 2H, Si(CH$_3$)$_2$-CH$_2$-CH$_2$-CH$_2$-O), 0.11–0.01 ppm (m, 93H, Si(CH$_3$)$_2$-CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.39, 170.28, 170.23, 170.04, 169.98, 169.95, 169.94, 169.92, 169.87, 135.38, 128.96, 128.87, 128.58, 74.86, 73.46, 69.61, 69.34, 69.30, 69.20, 68.73, 67.56, 23.85, 19.02, 17.09, 17.02, 16.98, 16.91, 14.41, 2.13, 1.76, 1.50, 1.49, 1.39, 1.02, 0.43, 0.40, 0.34 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{92}H_{174}O_{49}Si_{15}+Na^+$: 2505.76 $[M+Na]^+$; found 2505.75; *m/z* calcd for $C_{92}H_{174}O_{49}Si_{15}+K^+$: 2521.73 $[M+K]^+$; found 2521.70.

Bu-Si$_{\sim 15}$-LLA$_{17}$-Bn ([**Si$_{\sim 15}$-LLA$_{17}$**]).



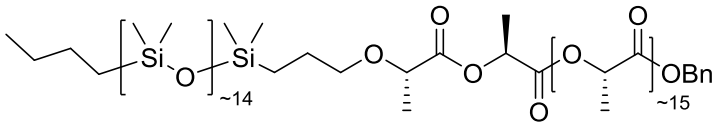
Starting from *o*DMS acid **6b** (61.4 mg, 0.048 mmol, 1 eq), *o*LLA **LLA$_{16}$** (58 mg, 0.046 mmol, 1 eq), DPTS (7 mg, 0.023 mmol, 0.5 eq) and EDC·HCl (18 mg, 0.093 mmol, 2 eq), crude oligomer [**Si$_{\sim15}$-LLA$_{17}$**] was obtained as a white solid using general method **D**. The material was purified by automated column chromatography using hept/EtOAc (gradient 80/20 to 60/40) as eluent, giving the product in pure form as a white solid (102 mg, 88%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.28 (m, 5H, Ar-H), 5.22–5.11 (m, 18H, CO-O-CH(CH_3)-CO and O-CH_2-Ar), 4.02 (q, ^3J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.58 (dt, ^2J = 8.8 Hz, ^3J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.32 (dt, ^2J = 8.8 Hz, ^3J = 7.1 Hz, 1H, CH_2-O-CH(CH_3)-CO), 1.68–1.42 (m, 53H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O and O-CH(CH_3)-CO), 1.36–1.23 (m, 4H, CH_3-CH_2-CH_2), 0.87 (t, ^3J = 6.8 Hz, 3H, CH_3-CH_2-CH_2), 0.56–0.49 (m, 4H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O and CH_2-CH_2-Si(CH_3)$_2$), 0.10–0.01 ppm (m, 90H, Si(CH_3)$_2$-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.16, 170.05, 170.00, 169.82, 169.76, 169.71, 169.64, 135.19, 128.74, 128.65, 128.37, 74.66, 73.23, 69.41, 69.13, 68.99, 68.53, 67.34, 26.48, 25.57, 23.65, 18.79, 18.07, 16.87, 16.83–16.73, 16.69, 14.21, 13.92, 1.29, 1.17, 0.30, 0.22, 0.19 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{95}H_{180}O_{49}Si_{15}$+$Na^+$: 2547.80 $[M+Na]^+$; found 2547.82 (multiple, equally spaced (74.02 *m/z*) peaks were found between 1700–4000 Da, each corresponding to the desired product with a different DP); SEC (THF): M_n = 4444; $Đ$ = 1.04.

Synthesis of Me-Si$_{15}$-LLA$_{\sim17}$-Bn ([**Si$_{15}$-LLA$_{\sim17}$**]).



Starting from *o*DMS acid **6a** (93 mg, 0.075 mmol, 1.2 eq), *o*LLA **LLA$_{\sim16}$** (79 mg, 0.062 mmol, 1 eq), DPTS (11 mg, 0.037 mmol, 0.6 eq) and EDC·HCl (29 mg, 0.15 mmol, 2.4 eq), crude oligomer [**Si$_{15}$-LLA$_{\sim17}$**] was obtained as a white wax using general method **D**. The material was purified by automated column chromatography using hept/EtOAc (gradient 80/20 to 60/40) as eluent, giving the product in pure form as a white, waxy solid (140 mg, 90%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 5H, Ar-H), 5.22–5.10 (m, 18H, CO-O-CH(CH_3)-CO and O-CH_2-Ar), 4.02 (q, ^3J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.58 (dt, ^2J = 8.7 Hz, ^3J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.32 (dt, ^2J = 8.7 Hz, ^3J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 1.69–1.42 (m, 53H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O and O-CH(CH_3)-CO), 0.58–0.48 (m, 2H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O), 0.10–0.03 ppm (m, 93H, Si(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.14, 170.04, 169.99, 169.80, 169.73, 169.69, 169.62, 135.20, 128.73, 128.64, 128.35, 74.66, 73.21, 69.40, 69.13, 68.98, 68.52, 67.32, 23.64, 18.77, 16.86, 16.75, 16.68, 14.21, 1.89, 1.27, 1.25, 1.16, 0.21, 0.19 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{92}H_{174}O_{49}Si_{15}$+$Na^+$: 2505.76 $[M+Na]^+$; found 2505.82 (multiple, equally spaced (144.04 *m/z*) peaks were found between 1500–4000 Da, each corresponding to the desired product with a different DP); SEC (THF): M_n = 4482; $Đ$ = 1.13.

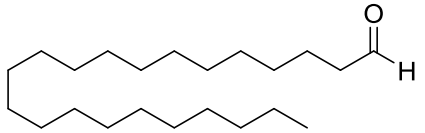
Synthesis of Bu-Si$_{\sim15}$-LLA$_{\sim17}$-Bn ([**Si$_{\sim15}$-LLA$_{\sim17}$**]).



Starting from *o*DMS acid **6b** (59.5 mg, 0.046 mmol, 1 eq), *o*LLA **LLA$_{\sim16}$** (58.4 mg, 0.046 mmol, 1 eq), DPTS (6.8 mg, 0.023 mmol, 0.5 eq) and EDC·HCl (18 mg, 0.093 mmol, 2 eq), crude oligomer [**Si$_{\sim15}$-LLA$_{\sim17}$**] was obtained as a waxy solid using general method **D**. The material was purified by

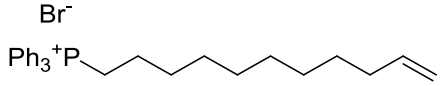
automated column chromatography using hept/EtOAc (gradient 80/20 to 60/40) as eluent, giving the product in pure form as a white wax (74.5 mg, 64%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.29 (m, 5H, Ar-H), 5.23–5.09 (m, 18H, CO-O-CH(CH_3)-CO and O-CH_2-Ar), 4.02 (q, ^{3}J = 6.9 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.58 (dt, ^{2}J = 8.8 Hz, ^{3}J = 7 Hz, 1H, CH_2-O-CH(CH_3)-CO), 3.32 (dt, ^{2}J = 8.8 Hz, ^{3}J = 7 Hz, 1H, CH_2-O-CH(CH_3)-CO), 1.68–1.43 (m, 53H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O and O-CH(CH_3)-CO), 1.37–1.24 (m, 4H, CH_3-CH_2-CH_2), 0.88 (t, ^{3}J = 6.8 Hz, 3H, CH_3-CH_2-CH_2), 0.57–0.50 (m, 4H, Si(CH_3)$_2$-CH_2-CH_2-CH_2-O and CH_2-CH_2-Si(CH_3)$_2$), 0.10–0.02 ppm (m, 90H, Si(CH_3)$_2$-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.18, 170.07, 170.02, 169.83, 169.77, 169.72, 169.66, 135.21, 128.75, 128.66, 128.38, 74.67, 73.25, 69.42, 69.15–69.11, 69.00, 68.54, 67.35, 26.49, 25.58, 23.66, 18.80, 18.08, 16.89, 16.81–16.78, 16.70, 14.22, 13.93, 1.30, 1.18, 0.31, 0.23, 0.20 ppm; HRMS (MALDI-TOF): *m/z* calcd for $C_{95}H_{180}O_{49}Si_{15}$+$Na^+$: 2547.80 $[M+Na]^+$; found 2547.94 (a range of masses was found between 1500–4000 Da, each corresponding to the desired product with a different DP); SEC (THF): M_n = 4063; $Đ$ = 1.13.

Synthesis of docosanal (**8**)



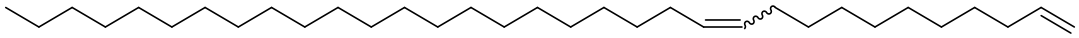
Alcohol **7** (20.5 g, 62.9 mmol, 1 eq), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 0.98 g, 6.29 mmol, 0.1 eq), tetrabutylammonium chloride (TBAC, 1.75 g, 6.29 mmol, 0.1 eq) were transferred to a 2 L round-bottom flask. DCM (300 mL) was added and the resulting orange/pink suspension stirred at room temperature (under argon atmosphere to prevent possible over-oxidation). A solution of $NaHCO_3$ (26.4 g, 314 mmol, 5 eq) and K_2CO_3 (4.35 g, 31.4 mmol, 0.5 eq) in water (350 mL, conc. ~1 M and ~0.1 M resp.) was added and the biphasic mixture stirred at high speed (~1000 rpm). *N*-Chlorosuccinimide (10.1 g, 75.5 mmol, 1.2 eq) was added as a solid and stirring of the suspension/emulsion was continued for 20 h at room temperature (most of the solids dissolved over time). Next, the mixture was transferred to a separation funnel, the organic layer was removed and the aq. layer extracted with DCM (2x 200 mL). The combined organic layers were washed with water (200 mL) and brine (100 mL), dried with $MgSO_4$ and concentrated in *vacuo*, resulting in a light yellow oil. The crude product was purified by automated column chromatography using heptane/DCM (isocratic 60/40) as eluent. Pure aldehyde **8** was obtained as a white solid (17.6 g, 86%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, ^{3}J = 1.9 Hz, 1H, CHO), 2.41 (td, ^{3}J = 7.4 Hz, ^{3}J = 1.9 Hz, 2H, CHO-CH_2-CH_2), 1.63 (tt, ^{3}J = 6.6 Hz, ^{3}J = 6.6 Hz, 2H, CHO-CH_2-CH_2-CH_2), 1.36–1.20 (m, 36H, CH_2), 0.88 ppm (t, ^{3}J = 6.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.09, 44.08, 32.08, 29.86, 29.82, 29.80, 29.74, 29.59, 29.52, 29.33, 22.85, 22.25, 14.27 ppm; GC-MS (EI, oven 80-330 °C): *t* = 7.81 min.

Synthesis of triphenyl(undec-10-en-1-yl)phosphonium bromide (**10**)



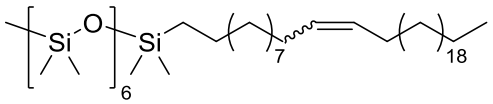
Alkene bromide **9** (1.04 g, 4.45 mmol, 1 eq) and triphenylphosphine (1.40 g, 5.34 mmol, 1.2 eq) were suspended in acetonitrile (4 ml) in a 25 mL RB flask with condenser. The mixture was heated to reflux, resulting in a light brown, clear solution. After 24 h, the mixture was cooled to room temperature and transferred to a separation funnel. More acetonitrile (8 mL) was added and the solution washed with heptane (6x 20 mL). The acetonitrile layer was then concentrated in *vacuo* giving the title compound as a light brown, very thick oil (2.02 g, 92%). The material is hygroscopic, and drying in high vacuum at 40 °C prior to further use is advised.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.68 (m, 9H, Ar-H), 7.66–7.58 (m, 6H, Ar-H), 5.67 (ddt, ^{3}J = 17 Hz, ^{3}J = 10.1 Hz, ^{2}J = 6.7 Hz, 1H, CH_2=CH-CH_2), 4.85 (ddt, ^{3}J = 17 Hz, ^{2}J = 2 Hz, ^{4}J = 1.6 Hz, 1H, CH_2=CH-CH_2 (*cis*)), 4.79 (ddt, ^{3}J = 10.1 Hz, ^{2}J = 2 Hz, ^{4}J = 1.2 Hz, 1H, CH_2=CH-CH_2 (*trans*)), 3.64–3.54 (m, 2H, CH_2-P), 1.93–1.85 (m, 2H, CH_2=CH-CH_2), 1.58–1.46 (m, 4H, CH_2), 1.26–1.05 ppm (m, 10H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.00, 134.98, 134.95, 133.53, 133.43, 130.49, 130.36, 118.54, 117.69, 113.98, 33.59, 30.37, 30.21, 29.16, 29.01, 28.97, 28.85, 28.68, 22.92, 22.49, 22.45, 22.43 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.20 ppm.

Synthesis of tritriaconta-1,11-diene (**11**)



Phosphonium salt **10** (510 mg, 1.03 mmol, 1.1 eq) was dissolved in dry THF (5 mL) in a 25 mL two-necked flask under argon and cooled in icewater. KO*t*Bu (1 M in THF, 1.08 mmol, 1.15 eq) was added dropwise, resulting in a color change from light yellow to dark orange/red. After stirring for 15 minutes, a solution of aldehyde **8** (304 mg, 0.936 mmol, 1 eq) in THF (5 mL) was added. Within 5 minutes, a white precipitate formed and the color changed to light brown. Stirring was continued for 10 minutes at 0 °C and then for 2 hours at room temperature. Afterwards, the reaction mixture was concentrated in vacuo, the remaining thick brown oil suspended in heptane (15 mL) and filtered through Celite. The residue was washed with heptane (3x 10 mL) and the combined filtrates concentrated in *vacuo*, resulting in the crude product as a light brown oil. The material was further purified by automated column chromatography using heptane (100%, isocratic) as eluent, giving the pure product as a colorless oil (194 mg, 41%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (ddt, ^{3}J = 17.0 Hz, ^{3}J = 10.2 Hz, ^{3}J = 6.7 Hz, 1H, CH_2=CH-CH_2), 5.44–5.31 (m, 2H, CH_2-CH=CH-CH_2), 5.00 (ddt, ^{3}J = 17.0 Hz, ^{2}J = 2.0 Hz, ^{4}J = 1.6 Hz, 1H, CH_2=CH-CH_2 (*cis*)), 4.94 (ddt, ^{3}J = 10.2 Hz, ^{2}J = 2.0 Hz, ^{4}J = 1.2 Hz, 1H, CH_2=CH-CH_2 (*trans*)), 2.09–1.94 (m, 6H, CH_2-CH=CH-CH_2, CH_2=CH-CH_2), 1.44–1.22 (m, 50H, CH_2), 0.89 ppm (t, ^{3}J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.34, 130.54, 130.48, 130.07, 130.01, 114.25, 34.01, 32.80, 32.13, 29.97, 29.96, 29.91, 29.87, 29.78, 29.70, 29.69, 29.57, 29.52, 29.49, 29.38, 29.35, 29.14, 27.39, 22.89, 14.29 ppm; GC-MS (EI, oven 80-300 °C): *t* = 6.88 min.

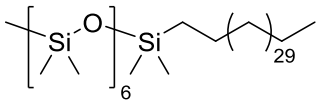
Synthesis of [**Si_7-M_{11}=M_{22}**] (**13**)



Alkene **11** (85 mg, 0.184 mmol, 1 eq) and Si_7 hydride **12** (96 mg, 0.184 mmol, 1 eq) were dissolved in dry DCM (1 mL) in a 10 mL Schlenk tube under argon atmosphere. Karstedt catalyst (1% Pt solution in xylenes, 1 drop) was added, and the mixture stirred for 60 min at room temperature. Then, the reaction mixture was concentrated in *vacuo* and purified by automated column

chromatography using heptane/chloroform (gradient 100/0 to 95/5 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (107 mg, 59%).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.31 (m, 2H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.07–1.94 (m, 4H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.38–1.20 (m, 54H, C<u>H</u>$_2$), 0.89 (t, ^{3}J = 6.8 Hz, 3H, C<u>H</u>$_3$-CH_2), 0.57–0.51 (m, 2H, C<u>H</u>$_2$-Si), 0.10 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.09 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.08 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.08 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.07 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.06 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.06 ppm (s, 6H, Si(C<u>H</u>$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.52, 130.06, 33.68, 32.82, 32.13, 30.00, 29.98, 29.91, 29.87, 29.84, 29.79, 29.77, 29.74, 29.62, 29.57, 29.55, 29.52, 29.40, 29.38, 27.42, 27.41, 23.43, 22.89, 18.47, 14.30, 1.96, 1.35, 1.32, 1.24, 0.37 ppm; HRMS (MALDI-TOF): m/z calcd for $C_{48}H_{110}O_6Si_7$+Na^+: 1001.66 $[M+Na]^+$; found: 1001.65.

Synthesis of **[Si$_7$-M$_{33}$]**



Unsaturated BCO **13** (87 mg, 0.089 mmol, 1 eq) was dissolved in EtOAc (4 mL) in a 50 mL round-bottom flask. Pd/C (10w% Pd, 11 mg, 8.9 µmol Pd, 0.1 eq) was added and the flask purged with hydrogen and stirred at room temperature. After 3 hours, the mixture was filtered through Celite, and the residue rinsed with EtOAc (3x 5 mL). The combined filtrates were concentrated in *vacuo*, giving the product as a semi-transparent, white wax (88 mg, quant.).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36–1.20 (m, 62H, C<u>H</u>$_2$), 0.89 (t, ^{3}J = 6.8 Hz, 3H, C<u>H</u>$_3$-CH_2), 0.57–0.50 (m, 2H, C<u>H</u>$_2$-Si), 0.10 (s, 9H, Si(C<u>H</u>$_3$)$_3$), 0.09 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.08 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.08 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.07 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.06 (s, 6H, Si(C<u>H</u>$_3$)$_2$), 0.05 ppm (s, 6H, Si(C<u>H</u>$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.67, 32.13, 29.90, 29.84, 29.62, 29.57, 23.42, 22.89, 18.46, 14.30, 2.26, 1.96, 1.35, 1.32, 1.24, 0.37 ppm; HRMS (MALDI-TOF): m/z calcd for $C_{48}H_{112}O_6Si_7$+Na^+: 1003.67 $[M+Na]^+$; found: 1003.68.

3. NMR spectra of the final BCOs

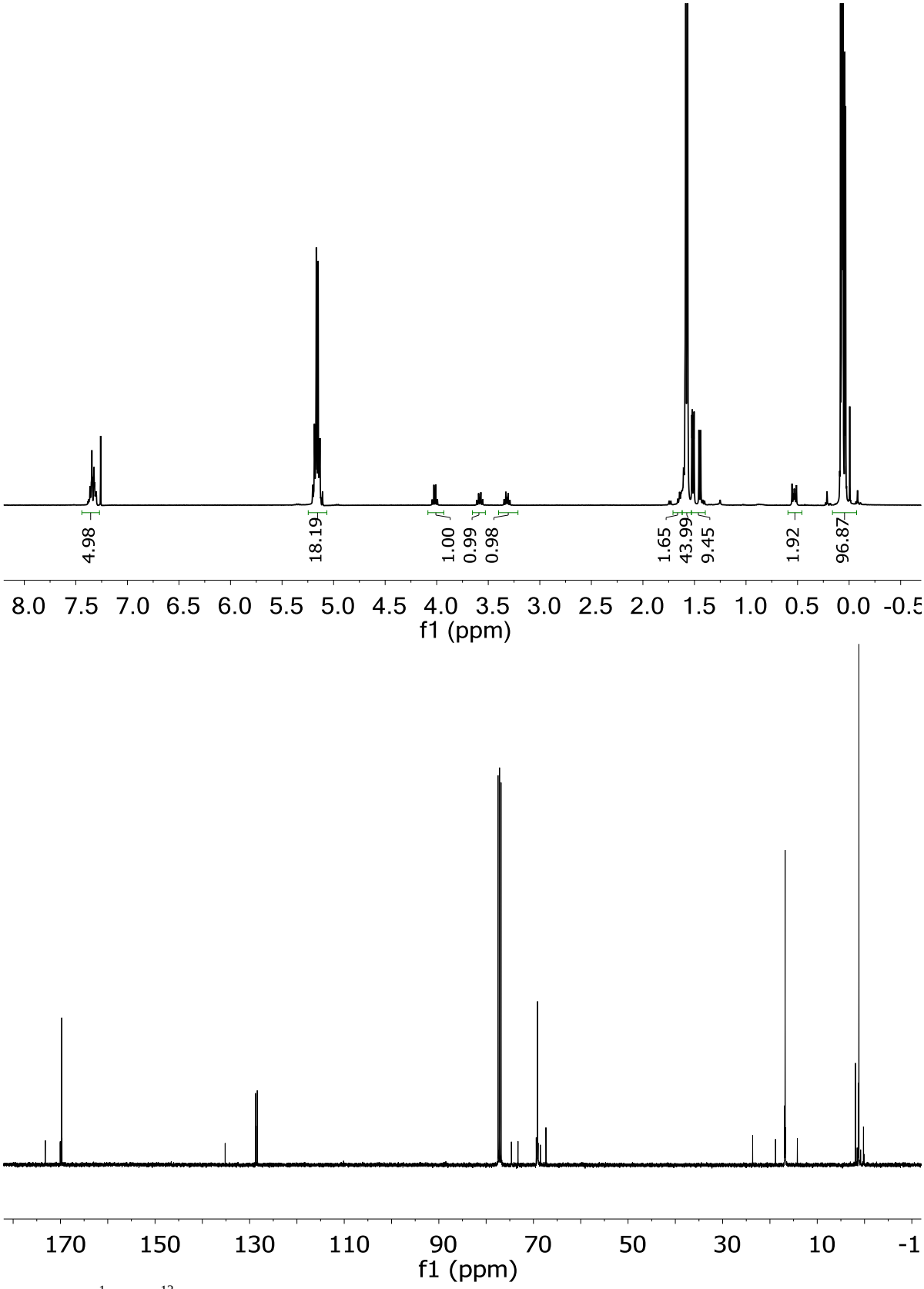


Figure S1. ^{1}H and ^{13}C NMR spectra of [**Si$_{15}$-LLA$_{17}$**].

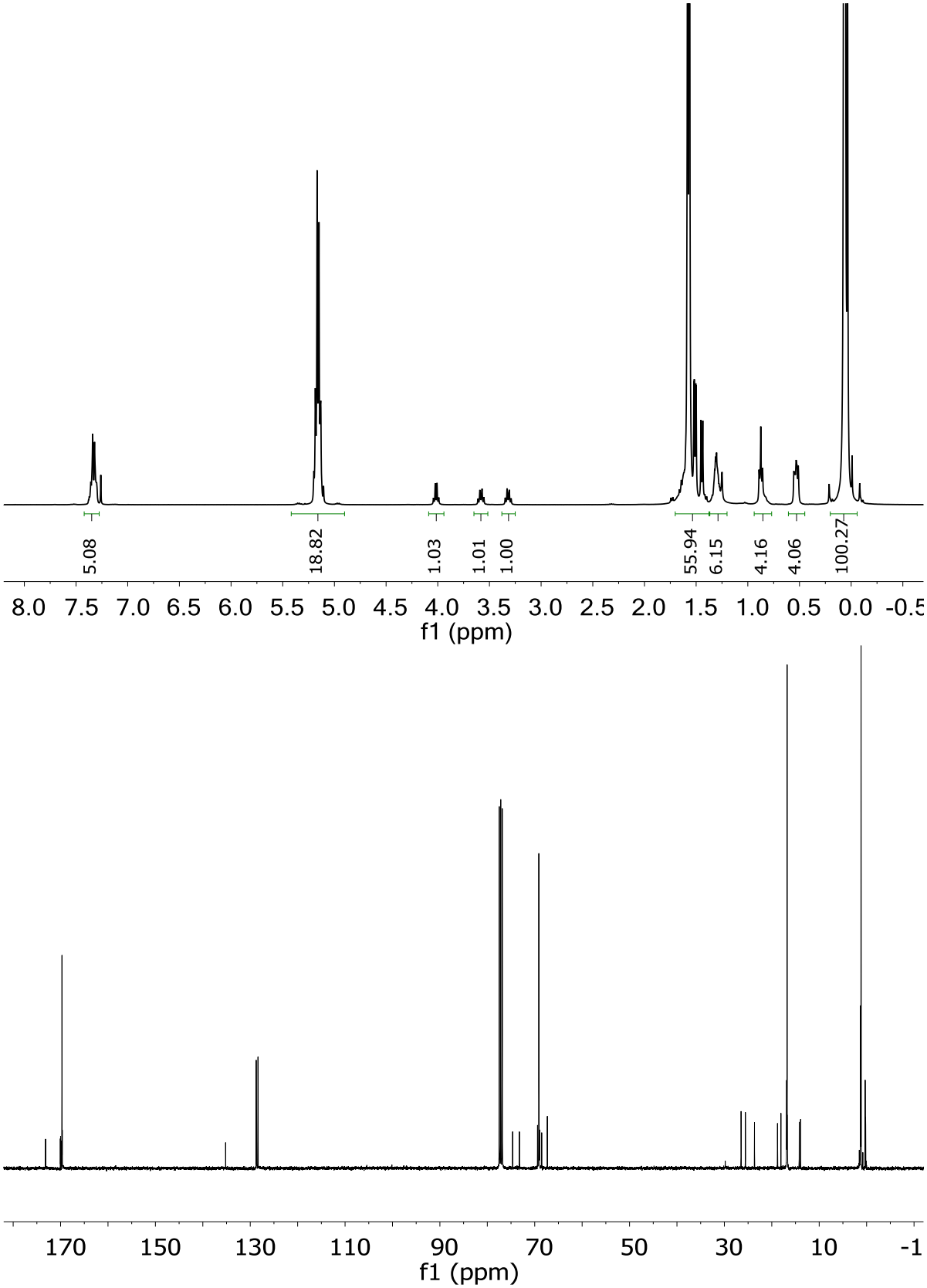


Figure S2. ^{1}H and ^{13}C NMR spectra of [**Si$_{\sim 15}$-LLA$_{17}$**]. Peaks at 0.87 and 1.26 ppm are partially resulting from residual heptane.

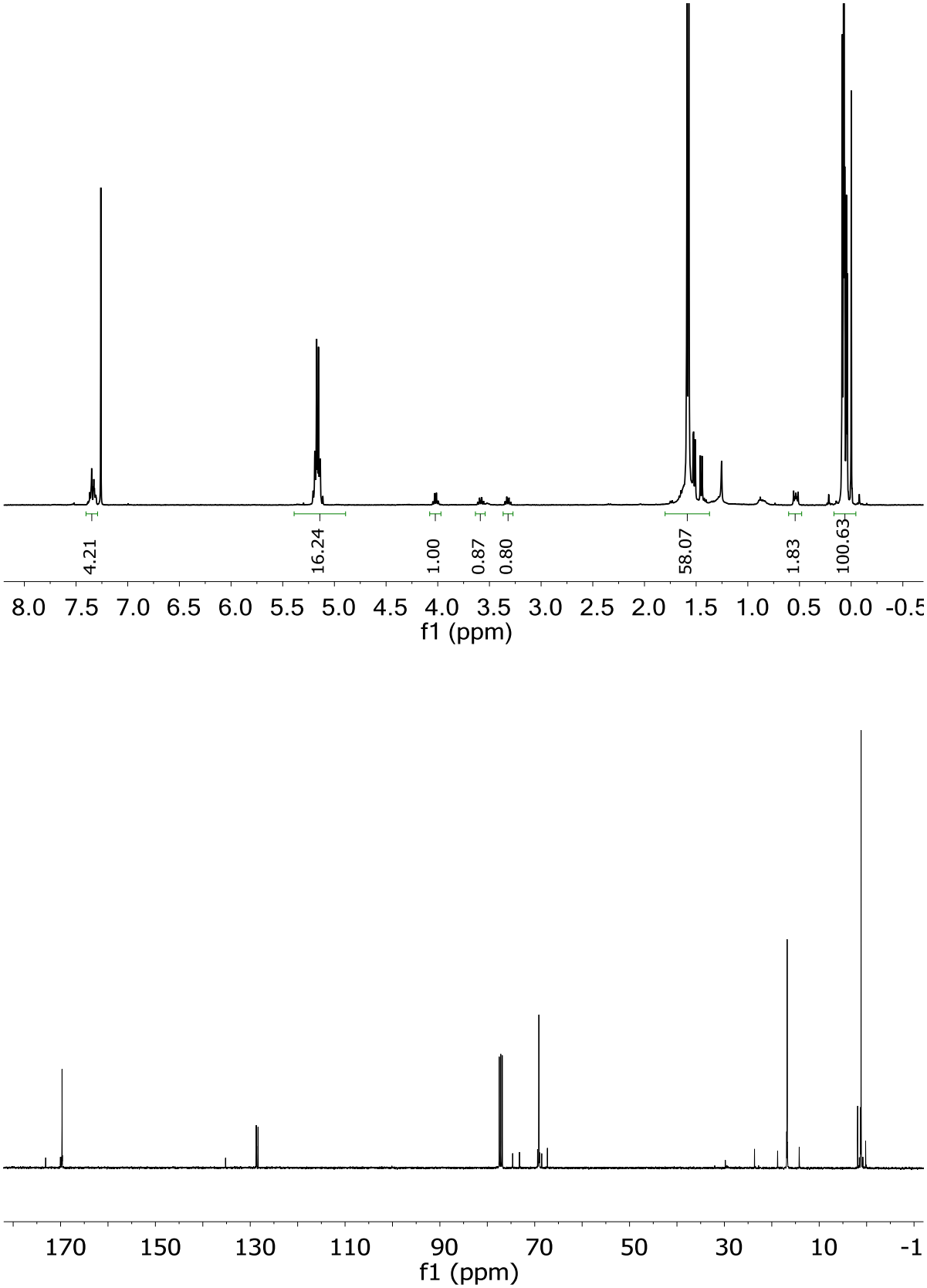


Figure S3. ^{1}H and ^{13}C NMR spectra of [**Si$_{15}$-LLA$_{\sim 17}$**]. Peaks at 0.87 and 1.26 ppm are coming from residual heptane.

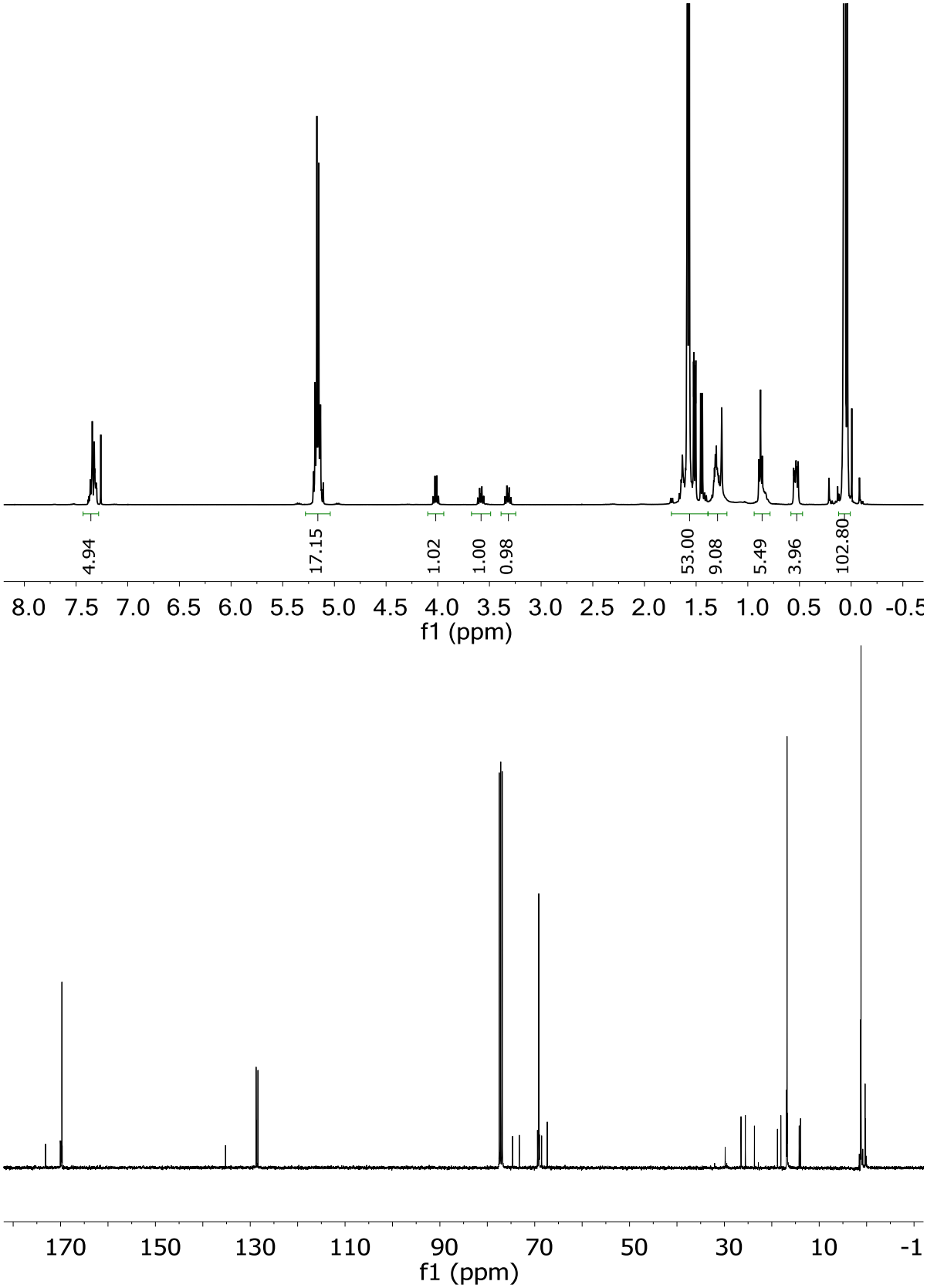


Figure S4. ^{1}H and ^{13}C NMR spectra of [**Si**$_{\sim 15}$-**LLA**$_{\sim 17}$]. Peaks at 0.87 and 1.26 ppm are partially resulting from residual heptane.

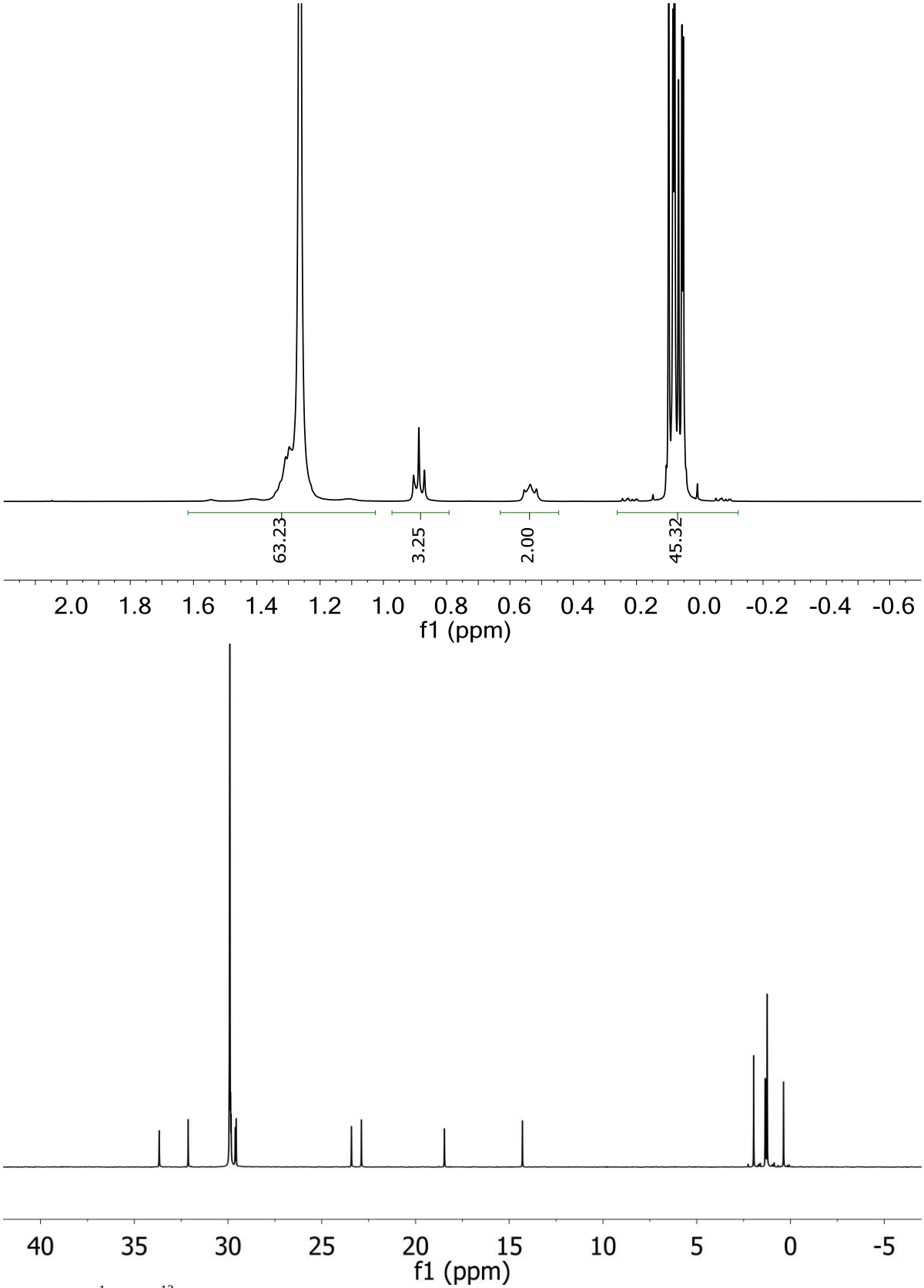


Figure S5. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_7}$-$\mathbf{M_{33}}$].

4. POM micrographs of [Si_{15}-LLA_{17}] and [Si_7-M_{33}]

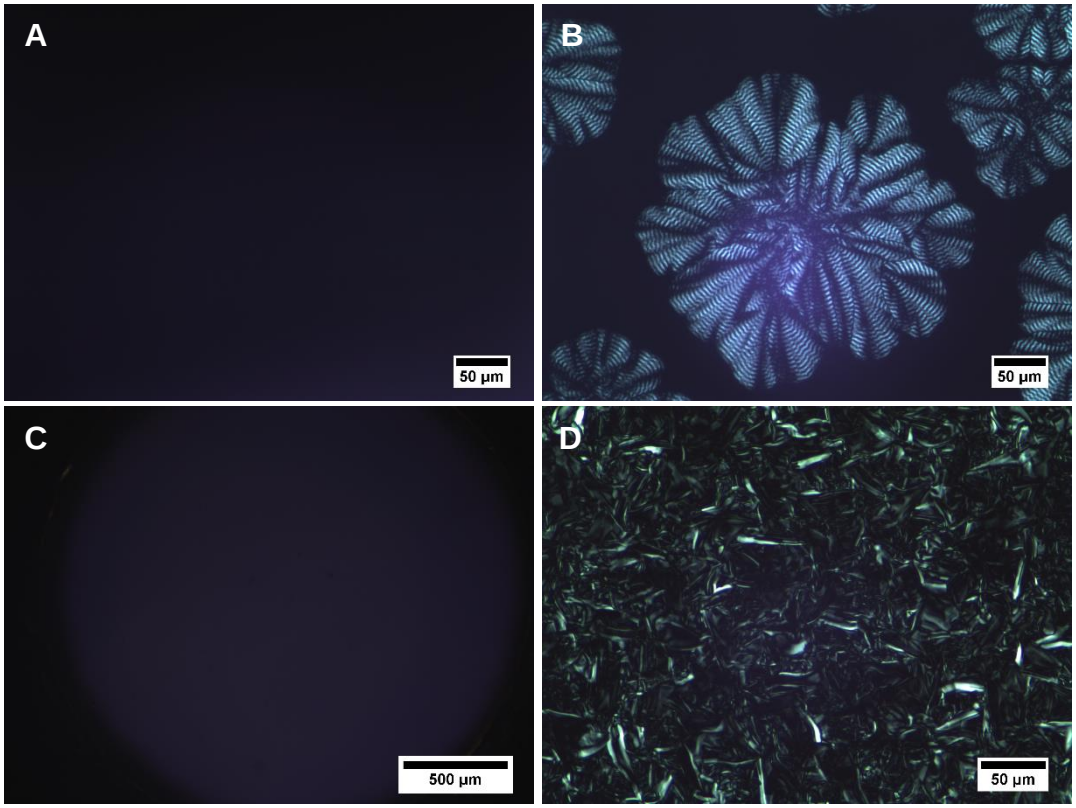


Figure S6. (**A**-**B**) POM micrographs (crossed polarizers) of [**Si_{15}-LLA_{17}**] directly above (**A**) and below (**B**) the melting point (85.1 °C). (**C**-**D**) POM micrographs (crossed polarizers) of [**Si_7-M_{33}**] directly above (**C**) and below (**D**) the melting point (43.8 °C).

5. Additional SAXS measurements

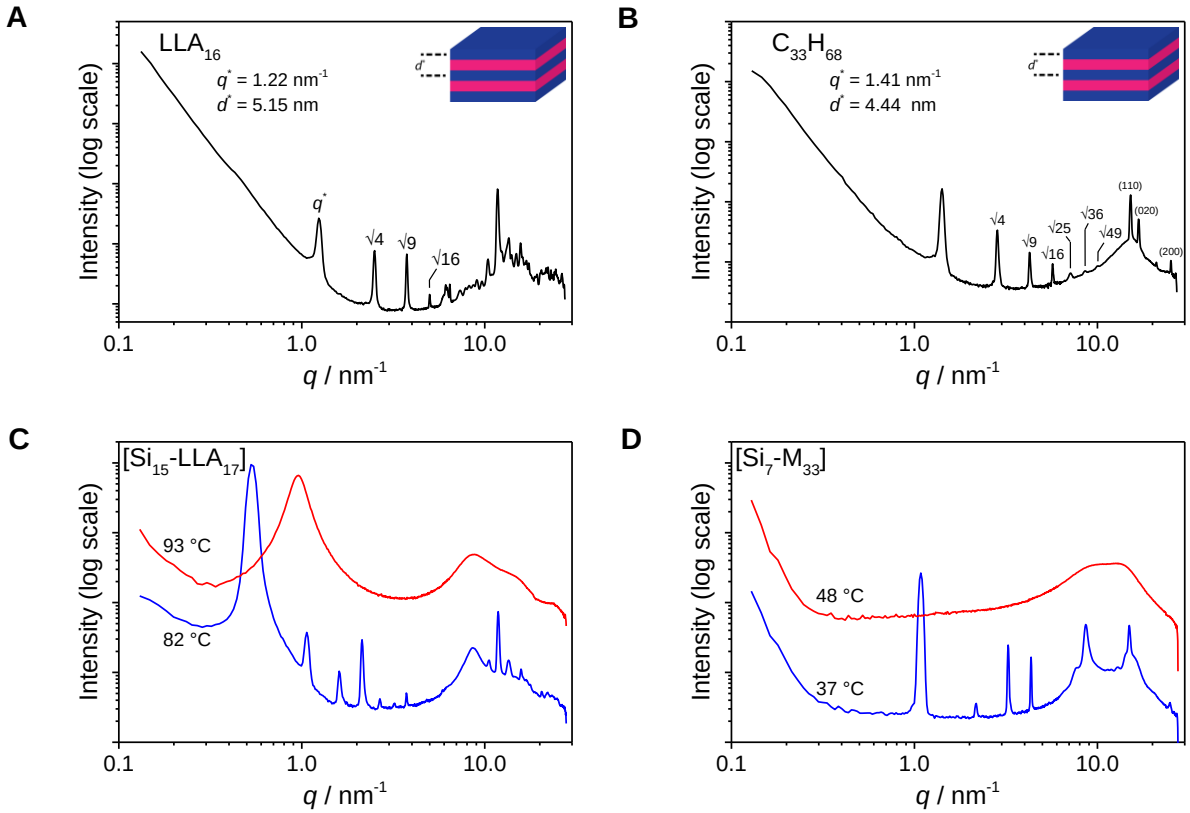


Figure S7. (**A**–**B**) Room temperature SAXS data for discrete **LLA$_{16}$** (**A**) and tritriacontane **C$_{33}$H$_{68}$** (**B**). A selection of higher order reflections is indicated. (**C**–**D**) Variable temperature SAXS data for discrete [**Si$_{15}$-LLA$_{17}$**] (**C**) and [**Si$_7$-M$_{33}$**] (**D**) at temperatures below (in blue) and above (in red) the temperatures attributed to the melting of the crystalline block (as observed in the DCS data, see Main Text, Figure 1C). The data is shifted vertically for clarity. The broad reflection at $q \approx 1$ nm^{-1} for [**Si$_{15}$-LLA$_{17}$**] at 93 °C results from correlation hole scattering in the disordered state.[3]

6. Proposed BCO packing models

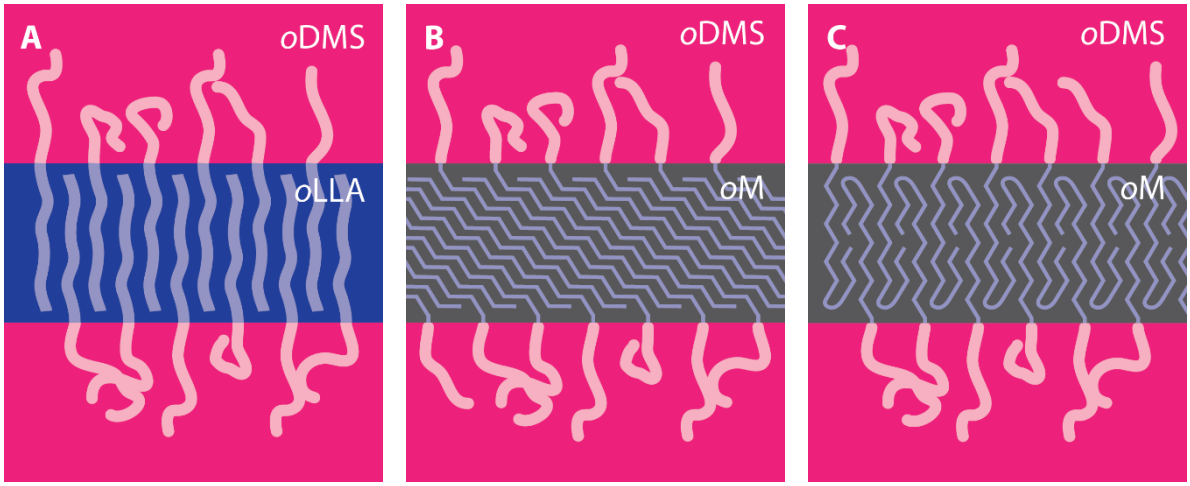


Figure S8. Proposed packing models for *o*DMS-*o*LLA and *o*DMS-*o*M BCOs. Only 3 lamellar domains (2x *o*DMS, 1x *o*LLA or *o*M) are drawn. A) Interdigitated and stretched *o*LLA chains, oriented parallel to the domain boundary normal. B) Interdigitated and stretched *o*M chains, tilted away from the domain boundary normal. C) Interdigitated and folded *o*M chains, oriented (nearly) parallel to the domain boundary normal. Although the models pictured here are the most trivial ones, alternative packing modes might apply.

7. MALDI-TOF analyses of *o*DMS-*o*LLA BCOs

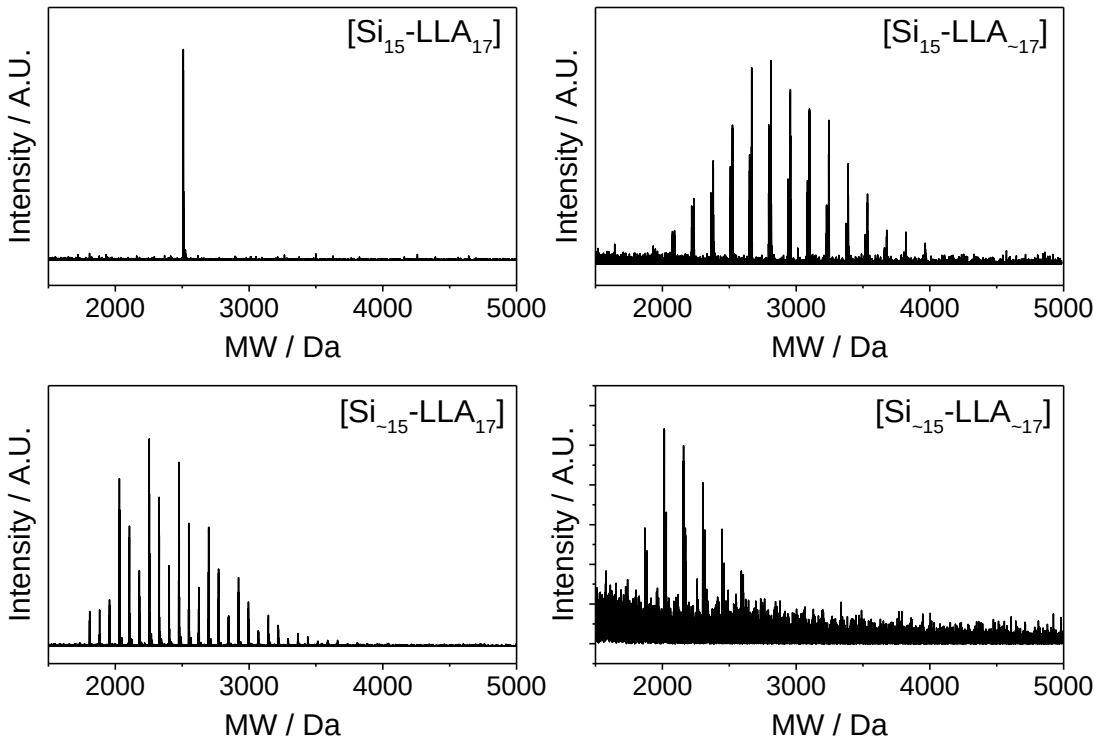


Figure S9. MALDI-TOF spectra of all *o*DMS-*o*LLA BCOs (DCTB matrix).

8. Additional DSC measurements

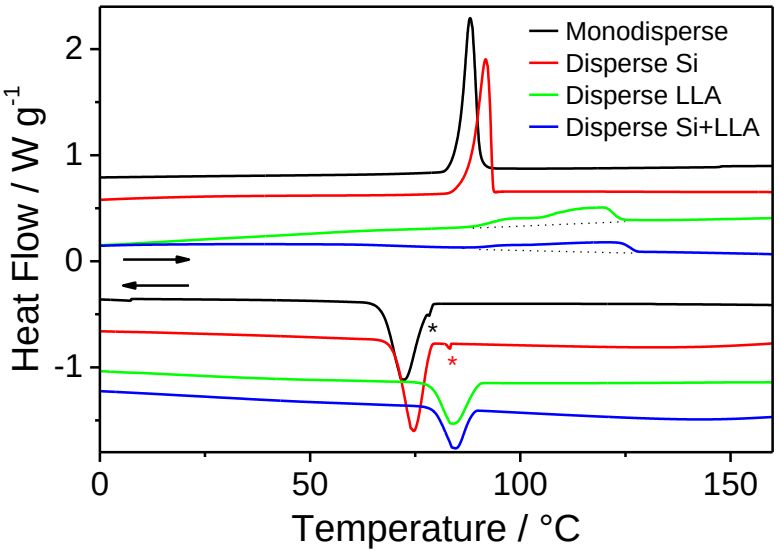


Figure S10. DSC traces (second cycle) of all *o*DMS-*o*LLA BCOs. The data is shifted vertically for clarity. A heating/cooling rate of 10 °C min^{-1} was used. Order-disorder transitions unrelated to the crystallization process are indicated with an asterisk.

9. References

(1) van Genabeek, B.; de Waal, B. F. M.; Gosens, M. M. J.; Pitet, L. M.; Palmans, A. R. A.; Meijer, E. W. *J. Am. Chem. Soc.* **2016**, *138*, 4210.

(2) van Genabeek, B.; de Waal, B. F. M.; Ligt, B.; Palmans, A. R. A.; Meijer, E. W. *ACS Macro Lett.* **2017**, *6*, 674.

(3) Bates, F. S. *Macromolecules* **1985**, *18*, 525.