Electronic Supplementary Information

Discrete oligodimethylsiloxane–oligomethylene di- and triblock co-oligomers: synthesis, self-assembly and molecular organisation

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1. Experimental

1.1. Materials and methods

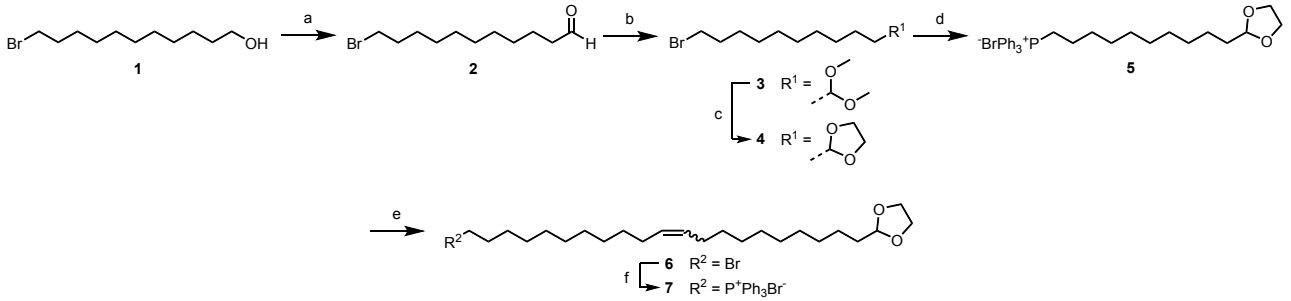
All chemicals were purchased from commercial sources and used without further purification. Discrete siloxane hydrides Me-Si_7-H (**36a**), Me-Si_{11}-H (**36b**), Me-Si_{15}-H (**36c**), Me-Si_{23}-H (**36d**), H-Si_{16}-H (**40**), siloxane disilanol HO-Si_8-OH (**42**), and building block Cl-Si_4-H (**43**) were synthesised according to literature procedures.[1,2] The syntheses of docosanal (**9**), triphenyl(undec-10-en-1-yl)phosphonium bromide (**30**), tritriaconta-1,11-diene (**32**), unsaturated BCO [$\mathbf{Si_7}$-$\mathbf{M_{11}}$=$\mathbf{M_{22}}$] (**37a**), and BCO [$\mathbf{Si_7}$-$\mathbf{M_{33}}$] are also described elsewhere.[3] 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 visualised 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. Elution gradients are specified in column volumes (CVs).

NMR spectra were recorded on Varian Mercury Vx 400 MHz, Varian 400MR 400 MHz, Bruker 400 MHz Ultrashield (400 MHz for ^{1}H NMR), and/or Varian Inova 500 MHz (500 MHz for ^{1}H NMR) spectrometers. 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; ABq: AB quartet; dq: doublet of quartets; qd: quartet of doublets; sept: septet; m: multiplet; bs: broad singlet. **Matrix assisted laser desorption/ionisation 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, typically from −50 °C to 180 °C with a rate of 10 °C min^{-1}. The data that are presented, represent the second heating/cooling cycle unless stated otherwise. 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 stuck to Kapton tape, or 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. 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.

1.2. Synthesis of aliphatic aldehydes

Bifunctional M_{22} building block **7** was prepared according to Scheme S1. This building block consisted of a triphenylphosphonium salt and an aldehyde protected as the ethylene acetal. Both functionalities were linked though a linear, monounsaturated aliphatic spacer of 21 carbons with a double bond (a mixture of *cis* and *trans*) between carbon 11 and 12. As such, this block can be used to chain-extend existing aldehydes with 22 methylene units. An added bonus

of this strategy is the incorporation of one double bond after every 9 methylene residues, which greatly enhances the solubility of the materials with longer chain lengths.



Scheme S1. Synthesis of bifunctional M_{22} building block **7**. Reagents and conditions: (a) TEMPO, tetrabutylammonium chloride, *N*-chlorosuccinimide, $NaHCO_3$, K_2CO_3, DCM, water, room temperature, 24 h (85%); (b) methanol, trimethyl orthoformate, TsOH, room temperature, 6 h (85%); (c) ethylene glycol, TsOH, toluene, 95 °C, 3.5 h (99%); (d and f) triphenylphosphine, 2,2-dimethyl-1,3-dioxolane, acetonitrile, reflux, 24 h (79–80%); (e) **2**, KO*t*Bu, THF, 0–20 °C, 24 h (58%). TsOH = *p*-toluene sulfonic acid.

To obtain the building block, 11-bromoundecanol **1** was first oxidised to bromoaldehyde **2** under mild oxidation conditions (TEMPO/*N*-chlorosuccinimide) in a biphasic (DCM/water) reaction mixture.[4] The material was obtained as a white solid in 85% yield. Next, part of the material was converted to the corresponding ethylene acetal **4** in a two-step procedure. First, the dimethyl acetal **3** was prepared in 85% yield by stirring the aldehyde in an excess of methanol with *p*-toluene sulfonic acid (TsOH) as a catalyst and trimethyl orthoformate as a water scavenger. Subsequently, ethylene acetal **4** was obtained by the acid-catalysed reaction of the dimethyl acetal with ethylene glycol at elevated temperatures under the continuous removal of methanol by evaporation. The material was then reacted with triphenylphosphine in refluxing acetonitrile, followed by trituration of the solids formed with ethyl acetate. This gave pure phosphonium salt **5** in good yield (79%). Initially, we observed the formation of minor amounts of aldehyde byproduct, resulting from degradation of the ethylene acetal. Therefore, 2,2-dimethyl-1,3-dioxolane was added during the preparation of the phosphonium salt to compensate for this side-reaction. The Wittig reaction between the phosphonium salt and 11-bromoundecanal **2** in THF using KO*t*Bu as a base gave the M_{22} bromo acetal **6** in decent yield (58%). Finally, the material was converted to phosphonium salt **7** under the same conditions as described above. In this case, the material was purified by precipitation in hexane from a solution in ethyl acetate. The compound was obtained as a white solid in good yield (80%) and stored under argon to prevent uptake of moisture.

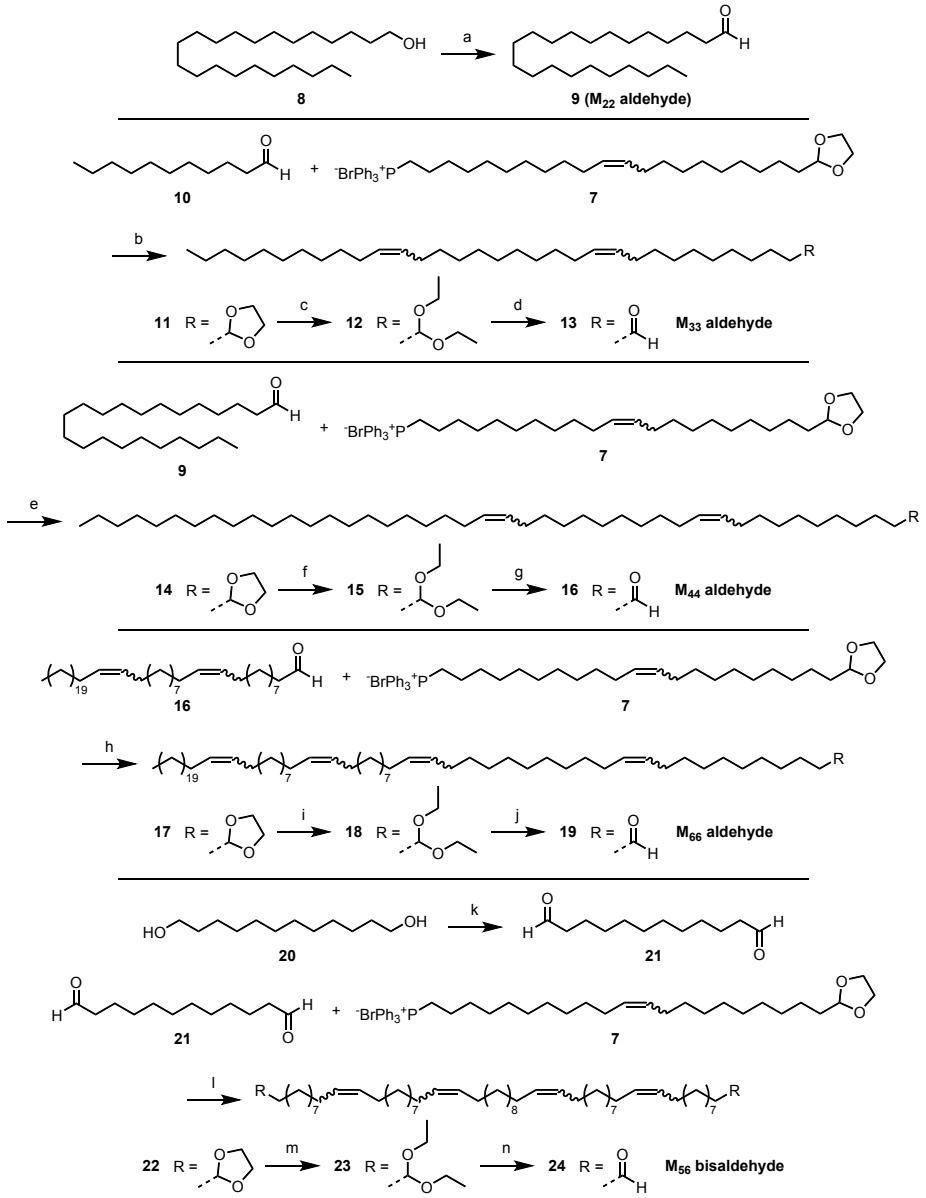
The synthesis of aliphatic aldehydes is depicted in Scheme S2. The lowest MW aldehyde, docosanal **9**, was obtained in one step from commercially available compounds. For this, docosanol **8** was converted to the aldehyde under similar conditions as those for the oxidation of 11-bromoundecanol. Large amounts of M_{22} aldehyde **9** (20–30 g) could be obtained in good yield (78%).

The Wittig reaction between building block **7** and undecanal **10** in THF with using KO*t*Bu as a base gave unsaturated M_{33} aldehyde **11** in good yield (73%). Notable is the presence of both *cis*- and *trans* configurations in the two double bonds (approximately 80% *cis*, determined with ^{1}H NMR), resulting in four different isomers. As expected from the Wittig reaction, formation of the *cis*-isomer is preferred under these conditions.[5]

For the deprotection of ethylene acetal **11** we developed a two-step procedure, since other methods proved to be too unsuccessful or unpractical.[6] First, ethylene acetal **11** was converted to diethyl acetal **12** by stirring a solution of the protected aldehyde in a large excess of refluxing ethanol in the presence of TsOH as a catalyst. After completion of the reaction, the mixture was basified with powdered KOH. Extraction with heptane and removal of the solvent afforded the M_{33} diethyl acetal in an excellent yield (97%). Without further purification, the acetal was then reacted with an excess of acetone, again in the presence of catalytic amounts of TsOH. Basic work-up gave the deprotected M_{33} acetal (M_{33} aldehyde) **13** in 95% yield.

A similar strategy was used to obtain M_{44} aldehyde **16**. Starting from docosanal **9**, ethylene acetal **14** was produced in 78% yield. Deprotection in two steps gave the M_{44} diethyl acetal **15** and M_{44} aldehyde **16** in 88% and 74% yield, respectively. Part of the aldehyde was subsequently converted to M_{66} ethylene acetal **17**, diethyl acetal **18** and aldehyde **19** in a good overall yield of 62%. For the deprotection of the longer acetals, chloroform was added as a co-solvent.

For the synthesis of homotelechelic M_{56} bisaldehyde, dodecanediol **20** was oxidised to bisaldehyde **21** under similar conditions as those for the oxidation of docosanol. The material was obtained as a white solid in 45% yield. Reaction with two equivalents of M_{22} building block **7** using the procedures described above, followed by removal of the acetal protective groups finally gave M_{56} bisaldehyde **24** in 71% yield over 3 steps.



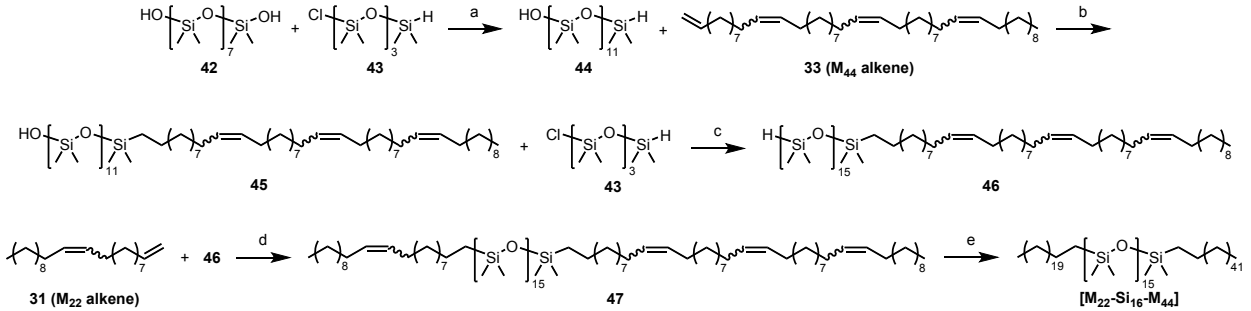
Scheme S2. Synthesis of unsaturated, long-chain aldehydes. Reagents and conditions: (a and k) TEMPO, tetrabutylammonium chloride, *N*-chlorosuccinimide, $NaHCO_3$, K_2CO_3, DCM, water, room temperature, 20 h (45–86%); (b, e, h and l) KO*t*Bu, THF, 0–20 °C, 1–21 h (60–77%); (c, f, i and m) EtOH, TsOH, reflux, 1–2 h (88–100%); (d, g, j and n) acetone, TsOH, room temperature, 1–3 h (95–99%). TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

1.3. Synthesis of BCO [M_{22}-Si_{16}-M_{44}]

According to Scheme S3, disilanol HO-Si_8-OH **42** was reacted with 1 equivalent of chlorosilane building block **43** in toluene, using pyridine as a base. The resulting mixture of product HO-Si_{12}-H **44**, remaining starting material HO-Si_8-OH, and disubstituted byproduct H-Si_{16}-H could be separated in a straightforward manner by automated column chromatography because of the large differences in affinity of the different components for the column material. Thus, monohydride **44** was obtained in a very good yield of 44%.

Next, monohydride **44** was coupled to M_{44} alkene **33** with the Karstedt catalyst, resulting in diblock-like molecule **45**. During the reaction and purification, the silanol remained fully intact, as was evidenced by ^{1}H NMR and MALDI-TOF MS. Subsequent reaction with one additional equivalent of chlorosilane building block **43** gave compound **46**, with the required length of 16 siloxane repeat units, in good yield (80%). The new hydride functionality in this molecule was used to attach the shorter M_{22} alkene **31**, giving unsaturated BCO **47** in pure form after column chromatography. Care was taken to select only the purest fractions for the last hydrogenation step, hence the low yield of 27%. Finally, the molecule was hydrogenated at 60 °C with the standard procedure, giving the pure tri-BCO [**M_{22}-Si_{16}-M_{44}**] in good yield (88%).

The high purity of all BCOs and absence of oligomers with a different number of repeat units was confirmed with NMR and mass spectrometry.



Scheme S3. Formation of asymmetric BCO [$\mathbf{M_{22}}$-$\mathbf{Si_{16}}$-$\mathbf{M_{44}}$]. Reagents and conditions: (b and d) Karstedt catalyst, DCM, room temperature, 1 h (27–75%); (a and c) pyridine, toluene, room temperature, 2.5–3h (44–80%); (e) H_2, Pd/C, EtOAc, 60 °C, 3 h (88%).

1.4. Synthetic procedures

*General method **A** for Wittig reaction between aldehyde and phosphonium salt*.

Phosphonium salt (*e.g.*, compound **30**, 1.03 mmol, 1.1 eq) was dissolved in dry THF (5 mL) in a 25 mL two-necked round-bottom flask under argon, and the mixture was cooled in ice water. 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 bright yellow, dark orange, red, or brown. After stirring for 15 minutes, a solution of aldehyde (*e.g.*, **9**, 0.936 mmol, 1 eq) in THF (5 mL) was added. Within 5 minutes, a white precipitate formed and the color changed to light orange or light brown. Stirring was continued for 10 minutes at 0 °C and then for 2–24 hours at room temperature. A typical work-up procedure involved concentrating the reaction mixture in *vacuo*, followed by suspending the remaining dark colored oil in heptane (15 mL). The suspension was then filtered through Celite, the residue was washed with heptane (3 × 10 mL), and the combined filtrates were concentrated in *vacuo*. This gave the crude product as a light brown oil.

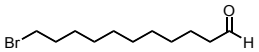
*General method **B** for the Karstedt reaction between siloxane hydrides and terminal alkenes.*

Terminal alkene (*e.g.*, alkene **32**, 0.184 mmol, 1 eq) and Si_x hydride (*e.g.*, **36a**, 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 30–60 min at room temperature. TLC (CeMo staining) and ^{1}H NMR were used to check for completion of the reaction. Then, the reaction mixture was concentrated in *vacuo*, giving the crude product.

*General method **C** for the synthesis of saturated BCOs* [$\mathbf{Si_x}$-$\mathbf{M_z}$].

Unsaturated BCO (*e.g.*, BCO **37a**, 0.089 mmol, 1 eq) was dissolved in EtOAc (4 mL) in a 50 mL round-bottom flask. Pd/C (10 w% Pd, 8.9 µmol Pd, 0.1 eq) was added and the flask was purged with hydrogen and stirred at room temperature or elevated temperatures (reactions at elevated temperatures were conducted with a reflux set-up). After 3 hours, the mixture was filtered through Celite, and the residue rinsed with EtOAc (3 × 5 mL). The combined filtrates were concentrated in *vacuo*, giving the pure product.

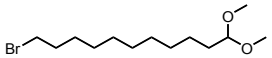
Synthesis of 11-bromo-1-undecanal (**2**).



A solution of 11-bromoundecanol **1** (8.00 g, 31.8 mmol, 1 eq), TEMPO (530 mg, 3.39 mmol, 0.11 eq), and tetrabutylammonium chloride (TBAC, 750 mg, 2.70 mmol, 0.08 eq) in DCM (200 mL) was stirred in a 1 L round-bottom flask under argon. A solution of $NaHCO_3$ (13.37 g, 0.159 mol, 5 eq) and K_2CO_3 (2.23 g, 16.1 mmol, 0.5 eq) in water (300 mL) was added, and the biphasic mixture was vigorously stirred at room temperature. *N*-Chlorosuccinimide (6.0 g, 44.9 mmol, 1.4 eq) was added to the emulsion as a solid, and the mixture was stirred 24 hours at room temperature. Afterward, the mixture was transferred to a separatory funnel and washed with water (2 × 200 mL) and brine (200 mL). The orange colored organic layer was dried with $MgSO_4$, and the solvent was removed in *vacuo*. The remaining crude product (dark orange liquid; 8.15 g) was purified by automated column chromatography using heptane/chloroform (gradient 100/0 to 40/60) as eluent. The pure material was obtained as a white solid (6.75 g, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, ^3J = 1.9 Hz, 1H, CH_2-C<u>H</u>O), 3.41 (t, ^3J = 6.8 Hz, 2H, Br-C<u>H</u>$_2$-CH_2), 2.42 (td, ^3J = 7.4 Hz, ^3J = 1.9 Hz, 2H, CH_2-C<u>H</u>$_2$-CHO), 1.85 (tt, ^3J = 7.4 Hz, ^3J = 6.9 Hz, 2H, CH_2-C<u>H</u>$_2$-CH_2-Br), 1.67–1.58 (m, 2H, CH_2-C<u>H</u>$_2$-CH_2-CHO), 1.46–1.38 (m,

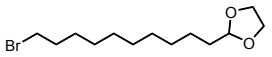
2H, C$\underline{H}_2$), 1.36–1.25 ppm (m, 10H, C$\underline{H}_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.99, 44.04, 34.14, 32.95, 29.47, 29.42, 29.27, 28.85, 28.28, 22.20 ppm.

Synthesis of 11-bromo-1,1-dimethoxyundecane (**3**).



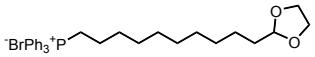
To a well stirred solution of bromoaldehyde **2** (15.91 g, 63.8 mmol, 1 eq) in methanol (100 mL). *p*-Toluene sulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 80 mg, 0.42 mmol, 0.007 eq) and trimethyl orthoformate (4.85 g, 5.0 ml, 45.7 mmol, 0.72 eq) were added. The mixture was stirred for 6 hours at room temperature, followed by the addition of NaOH solution (1 M, 100 mL) (the mixture heated up slightly). After stirring for an additional 30 minutes at room temperature, the contents were transferred to a separatory funnel and extracted with toluene (2 × 200 mL). The combined toluene fractions were concentrated in *vacuo*. Remaining water was removed by co-evaporation with toluene (100 mL), giving the pure product as a white solid (16.0 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.36 (t, ^3J = 5.8 Hz, 1H, CH_2-C$\underline{H}$(OCH_3)$_2$), 3.40 (t, ^3J = 6.9 Hz, 2H, Br-C$\underline{H}_2$-CH_2), 3.31 (s, 6H, CH_2-CH(OC$\underline{H}_3$)$_2$), 1.85 (tt, ^3J = 7.1 Hz, ^3J = 7.1 Hz, 2H, CH_2-C$\underline{H}_2$-CH_2-Br), 1.59 (td, ^3J = 7.6 Hz, ^3J = 5.8 Hz, 2H, CH_2-C$\underline{H}_2$-CH(OCH_3)$_2$), 1.46–1.37 (m, 2H, C$\underline{H}_2$), 1.37–1.23 ppm (m, 12H, C$\underline{H}_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.70, 52.73, 34.18, 32.98, 32.64, 29.64, 29.59, 29.56, 29.54, 28.89, 28.31, 24.73 ppm.

Synthesis of 2-(10-bromodecyl)-1,3-dioxolane (**4**).



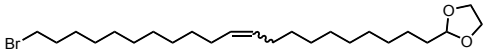
A mixture of bromo dimethyl acetal **3** (15.9 g, 53.9 mmol, 1 eq), ethylene glycol (6.68 g, 6.0 ml, 108 mmol, 2 eq), *p*-toluene sulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 160 mg, 0.84 mmol, 0.016 eq), and toluene (50 mL) was heated to 95 °C in a 250 mL round-bottom flask. The flask was continuously purged with nitrogen gas to remove the methanol that was liberated during the reaction. After 3.5 hours, total conversion to the ethylene acetal was confirmed by ^{1}H NMR of a basified sample. The mixture was cooled down to room temperature, transferred to a beaker with K_2CO_3 solution (10 w%, 100 mL) and stirred for 15 minutes. The contents of the beaker were then transferred to a separatory funnel and extracted with toluene (100 mL). The organic layer was washed with water (100 mL) and brine (200 mL). Removal of the solvent gave the title compound as a white solid (13.95 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.84 (t, ^3J = 4.8 Hz, 1H, CH_2-C$\underline{H}$(-O-CH_2-CH_2-O-)), 4.01–3.91 (m, 2H, CH_2-CH(-O-C$\underline{H}_2$-C$\underline{H}_2$-O-)), 3.89–3.80 (m, 2H, CH_2-CH(-O-C$\underline{H}_2$-C$\underline{H}_2$-O-)), 3.40 (t, ^3J = 6.9 Hz, 2H, CH_2-C$\underline{H}_2$-Br), 1.91–1.80 (m, 2H, CH_2-C$\underline{H}_2$-CH_2-Br), 1.69–1.61 (m, 2H, CH_2-C$\underline{H}_2$-CH(-O-CH_2-CH_2-O-)), 1.48–1.24 ppm (m, 14H, C$\underline{H}_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 104.84, 64.98, 34.19, 34.06, 32.99, 29.66, 29.62, 29.53, 28.89, 28.32, 24.22 ppm.

Synthesis of (10-(1,3-dioxolan-2-yl)decyl)triphenylphosphonium bromide (**5**).



Bromo ethylene acetal **4** (13.85 g, 47.2 mmol, 1 eq) was co-evaporated with dry toluene (100 mL) to remove any residual water. Next, dry acetonitrile (20 mL), 2,2-dimethyl-1,3-dioxolane (2.78 g, 3.0 mL, 27.2 mmol, 0.58 eq) and triphenylphosphine (18.1 g, 69 mmol, 1.5 eq) were added. The mixture was stirred under reflux for 24 hours under argon. Next, the mixture was concentrated in *vacuo*. Ethyl acetate (300 mL) was added to the remaining viscous oil, and the mixture was stirred for 30 minutes. The solvent was then decanted, fresh ethyl acetate (200 mL was added), and the residue was again stirred for 30 minutes. Finally, the mixture was filtered over a Büchner filter and the residue washed with ethyl acetate (2 × 50 mL). The product was dried in vacuum at 40 °C, resulting in a white solid (20.84 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.70 (m, 9H, Ar-$\underline{H}$), 7.68–7.60 (m, 6H, Ar-$\underline{H}$), 4.74 (t, ^3J = 4.8 Hz, 1H, CH_2-C$\underline{H}$(-O-CH_2-CH_2-O-)), 3.93–3.71 (m, 4H, CH_2-CH(-O-C$\underline{H}_2$-C$\underline{H}_2$-O-)), 3.69–3.57 (m, 2H, CH_2-C$\underline{H}_2$-P), 1.60–1.48 (m, 2H, CH_2-C$\underline{H}_2$-CH(-O-CH_2-CH_2-O-)), 1.34–1.05 ppm (m, 16H, C$\underline{H}_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.10, 135.07, 133.86, 133.76, 130.65, 130.52, 118.98, 118.13, 104.77, 64.92, 33.98, 30.58, 30.42, 29.80, 29.56, 29.51, 29.45, 29.30, 29.22, 24.15, 23.15, 22.79, 22.74, 22.66 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.17 ppm; MS (MALDI-TOF): m/z calcd for $C_{31}H_{40}BrPO_2{-}Br^-$: 475.28 $[M{-}Br]^+$; found: 475.30.

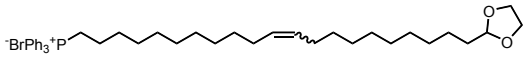
Synthesis of 2-(21-bromohenicos-10-en-1-yl)-1,3-dioxolane (**6**).



Phosphonium salt **5** (2.58 g, 4.6 mmol, 1.03 eq) and 11-bromoundecanal **2** (1.12 g, 4.5 mmol, 1 eq) were coupled using general method **A**. The crude product was obtained as a dark yellow oil and further purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 90/10) as eluent. The pure product was obtained as a colorless

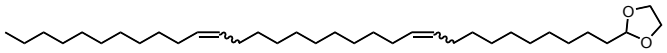
oil (1.18 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.29 (m, 2H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.84 (t, ^3J = 4.9 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_2-O-)), 4.02–3.91 (m, 2H, CH_2-CH(-O-C<u>H_2</u>-C<u>H_2</u>-O-)), 3.91–3.79 (m, 2H, CH_2-CH(-O-C<u>H_2</u>-C<u>H_2</u>-O-)), 3.40 (t, ^3J = 6.9 Hz, 2H, CH_2-C<u>H_2</u>-Br), 2.06–1.93 (m, 4H, C<u>H_2</u>-CH=CH-C<u>H_2</u>), 1.85 (tt, ^3J = 7.0 Hz, ^3J = 7.0 Hz, 2H, CH_2-C<u>H_2</u>-CH_2-Br), 1.70–1.61 (m, 2H, CH_2-C<u>H_2</u>-CH(-O-CH_2-CH_2-O-)), 1.47–1.21 ppm (m, 28H, C<u>H_2</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.52, 130.46, 130.06, 130.00, 104.86, 64.98, 34.19, 34.08, 33.00, 32.75, 29.92, 29.91, 29.71, 29.70, 29.68, 29.66, 29.65, 29.58, 29.45, 29.43, 29.30, 28.93, 28.34, 27.37, 27.35, 24.25 ppm.

Synthesis of (21-(1,3-dioxolan-2-yl)henicos-11-en-1-yl)triphenylphosphonium bromide (**7**).



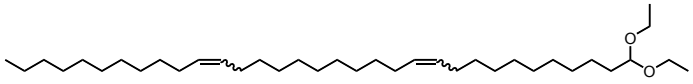
A mixture of bromoacetal **6** (7.0 g, 15.7 mmol, 1 eq), 2,2-dimethyl-1,3-dioxolane (1.39 g, 1.5 ml, 13.6 mmol, 0.87 eq), and triphenylphosphine (11 g, 41.9 mmol, 2.7 eq), and acetonitrile (12 mL) was stirred under reflux for 24 hours in a 100 mL round-bottom flask. Full conversion to the phosphonium salt was confirmed by ^{1}H NMR. The mixture was concentrated in *vacuo*, and the remaining crude product was dissolved in ethyl acetate (70 mL). The solution was added dropwise to well-stirred hexane (700 mL), resulting in precipitation of the product. The supernatant was decanted, and the remaining product was stirred with fresh hexane (250 mL) for 30 minutes. The mixture was filtered, and the residue was washed with hexane (3 × 50 mL). The remaining pure product (white solid) was dried in *vacuo* at 40 °C (8.85 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.65 (m, 15H, Ar-<u>H</u>), 5.39–5.27 (m, 2H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.83 (t, ^3J = 4.8 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_2-O-)), 3.99–3.79 (m, 6H, CH_2-CH(-O-C<u>H_2</u>-C<u>H_2</u>-O-) and CH_2-C<u>H_2</u>-P), 2.03–1.91 (m, 4H, C<u>H_2</u>-CH=CH-C<u>H_2</u>), 1.67–1.55 (m, 2H, CH_2-C<u>H_2</u>-CH(-O-CH_2-CH_2-O-)), 1.45–1.14 ppm (m, 30H, C<u>H_2</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.07, 135.04, 133.90, 133.80, 130.63, 130.51, 130.00, 129.97, 119.05, 118.20, 104.82, 64.95, 34.04, 30.62, 30.46, 29.89, 29.77, 29.68, 29.66, 29.64, 29.61, 29.41, 29.39, 29.31, 29.28, 27.34, 24.22, 23.16, 22.82, 22.78, 22.67 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.56 ppm; MS (MALDI-TOF): m/z calcd for $C_{42}H_{60}BrO_2P-Br^-$: 627.43 $[M-Br]^+$; found: 627.49.

Synthesis of 2-(dotriaconta-10,21-dien-1-yl)-1,3-dioxolane (M_{33} ethylene acetal) (**11**).



Phosphonium salt **7** (1.979 g, 2.796 mmol, 1.1 eq) was dissolved in dry THF (6 mL) in a 25 mL 2-necked round-bottom flask under argon, and the light yellow solution was cooled in ice water. The mixture was stirred, and KO*t*Bu (1M in THF, 3.050 mmol, 1.20 eq) was added dropwise, resulting in a dark orange-red solution. After 15 minutes, a solution of undecanal **10** (0.433 g, 2.542 mmol, 1 eq) in THF (0.5 mL) was added dropwise. The mixture changed color from red to light orange and a white precipitate was formed. The mixture was stirred for an additional hour at room temperature. ^{1}H NMR showed full consumption of the aldehyde. The reaction mixture was poured out in heptane (60 mL) and stirred for 1 hour. The white precipitate (PPh_3O) was filtered off over a Büchner funnel, and the residue was washed with additional heptane (30 mL). The slightly turbid, combined filtrates were washed with acetonitrile (50 mL), and the heptane layer was concentrated in *vacuo*. The crude product was purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 90/10) as eluent. Pure aldehyde acetal **11** was obtained as a colorless oil (1.065 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40–5.29 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.84 (t, ^3J = 4.8 Hz, 1H, C<u>H</u>(-OCH_2CH_2O-)), 4.01–3.79 (m, 4H, CH(-OC<u>H_2</u>C<u>H_2</u>O-)), 2.10–1.91 (m, 8H, C<u>H_2</u>-CH=CH-C<u>H_2</u>), 1.71–1.60 (m, 2H, C<u>H_2</u>-CH(-OCH_2CH_2O-)), 1.49–1.17 (m, 44H, C<u>H_2</u>), 0.88 ppm (t, ^3J = 6.8 Hz, 3H, C<u>H_3</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.49, 130.03, 104.86, 64.97, 34.09, 32.77, 32.08, 32.04, 29.93, 29.82, 29.80, 29.78, 29.72, 29.71, 29.69, 29.67, 29.52, 29.48, 29.46, 29.33, 27.37, 24.26, 22.85, 14.27 ppm.

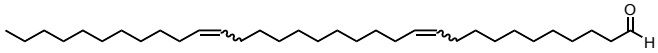
Synthesis of 1,1-diethoxytritriaconta-11,22-diene (M_{33} diethyl acetal) (**12**).



M_{33} ethylene acetal **11** (557 mg, 1.07 mmol, 1 eq) was suspended in ethanol (150 mL) in a 500 mL round-bottom flask. *p*-Toluene sulfonic acid monohydrate ($TsOH·H_2O$, 13 mg, 0.075 mmol, 0.07 eq) was added as solid, and the mixture was heated to reflux (all material was dissolved at elevated temperatures). After 1 hour, nearly all ethylene acetal was converted (checked with TLC (hept/EtOAc 90/10; CeMo staining). The reaction mixture was cooled down to room temperature, resulting in partial precipitation of the product. Powdered KOH (~10 mg, 0.14 eq) was added to quench the TsOH, and the mixture was concentrated in *vacuo*. The crude material was dissolved in heptane (40 mL), and resulting slightly turbid solution was washed with water (2 × 25 mL). The clear organic layer was dried with $MgSO_4$ and

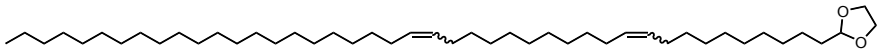
concentrated in *vacuo*. The crude product was obtained as a colorless oil (576 mg, 97%) and was pure enough for further deprotection. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39–5.29 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.47 (t, ^3J = 5.7 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_3)$_2$), 3.64 (dq, ^2J = 9.4 Hz, ^3J = 7.2 Hz, 4H, CH(-OC<u>H</u>$_2$$CH_3$)$_2$), 3.49 (dq, ^2J = 9.4 Hz, ^3J = 7.2 Hz, 4H, CH(-OC<u>H</u>$_2$$CH_3$)$_2$), 2.07–1.93 (m, 8H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.61 (dt, ^3J = 8.7 Hz, ^3J = 6.2 Hz, 2H, C<u>H</u>$_2$-CH(-OCH$_2$CH$_3$)$_2$), 1.38–1.23 (m, 44H, C<u>H</u>$_2$), 1.20 (t, ^3J = 6.9 Hz, 6H, O-CH_2-C<u>H</u>$_3$), 0.88 ppm (t, ^3J = 7.2 Hz, 3H, CH_2-C<u>H</u>$_3$); ^{13}C NMR (100 MHz, CDCl3): δ = 130.03, 103.13, 60.96, 33.77, 32.08, 39.94–29.48, 27.37, 24.93, 22.85, 15.51, 14.23 ppm.

Synthesis of tritriaconta-11,22-dienal (M_{33} aldehyde) (**13**).



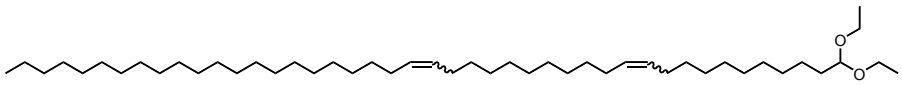
M_{33} diethyl acetal **12** (518 mg, 0.998 mmol, 1 eq) was dissolved in acetone (150 mL) in a 500 mL round-bottom flask. The solution was purged with argon to remove oxygen. *p*-Toluene sulfonic acid monohydrate ($TsOH \cdot H_2O$, 9 mg, 0.050 mmol, 0.05 eq) was added as a solid, and the mixture was stirred at room temperature under argon. After 3 hours, formation of the product was observed with TLC (hept/EtOAc; CeMo staining). The reaction was quenched with 10% Na_2CO_3 soln. (20 mL), and the resulting solution extracted with heptane (3 × 30 mL). The organic layer was washed with water (30 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo*, giving deprotected product as a colorless oil (450 mg, 95%). ^{1}H NMR confirmed the complete absence of starting material. The product was stored under N_2 in the fridge. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.77 (t, ^3J = 1.9 Hz, 1H, CH_2-C<u>H</u>O), 5.40–5.30 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.42 (dt, ^3J = 5.5 Hz, ^3J = 1.9 Hz, 2H, C<u>H</u>$_2$-CHO), 2.07–1.93 (m, 8H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.63 (tt, ^3J = 7.2 Hz, ^3J = 7.2 Hz, 2H, CH_2-C<u>H</u>$_2$-CH_2-CHO), 1.93–1.19 (m, 42H, C<u>H</u>$_2$), 0.88 ppm (t, ^3J = 6.7 Hz, 3H, CH_2-C<u>H</u>$_3$); ^{13}C NMR (100 MHz, CDCl3): δ = 203.06, 130.09, 130.07, 130.03, 129.98, 44.08, 32.08, 30.94–29.33, 27.37, 27.36, 24.85, 22.24, 14.35 ppm.

Synthesis of 2-(tritetraconta-10,21-dien-1-yl)-1,3-dioxolane (M_{44} ethylene acetal) (**14**).



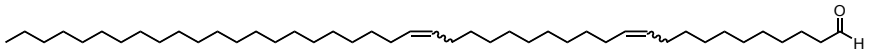
Phosphonium salt **7** (7.0 g, 9.89 mmol, 1.03 eq) and docosanal **9** (3.0 g, 9.62 mmol, 1 eq) were coupled using general method **A**. The crude product was obtained as a dark yellow oil and further purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 98/2) as eluent. The pure product was obtained as a white solid (3.97 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.44–5.26 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.84 (t, ^3J = 4.8 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_2-O-)), 4.02–3.79 (m, 4H, CH_2-CH(-O-C<u>H</u>$_2$-C<u>H</u>$_2$-O-)), 2.06–1.93 (m, 8H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.69–1.61 (m, 2H, CH_2-C<u>H</u>$_2$-CH(-O-CH_2-CH_2-O-)), 1.45–1.20 (m, 66H, C<u>H</u>$_2$), 0.88 ppm (t, ^3J = 6.9 Hz, 3H, C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.50, 130.05, 130.04, 104.87, 64.98, 34.09, 32.77, 32.09, 29.94, 29.86, 29.82, 29.79, 29.73, 29.71, 29.69, 29.67, 29.53, 29.49, 29.46, 29.34, 27.38, 24.26, 22.86, 14.28 ppm.

Synthesis of 1,1-diethoxytetratetraconta-11,22-diene (M_{44} diethyl acetal) (**15**).



M_{44} ethylene acetal **14** (3.71 g, 5.51 mmol, 1 eq) was suspended in ethanol (500 mL) in a 1 L round-bottom flask. *p*-Toluene sulfonic acid monohydrate ($TsOH \cdot H_2O$, 55 mg, 0.32 mmol, 0.06 eq) was added as solid, and the mixture was heated to reflux (all material was dissolved at elevated temperatures). After 1.5 hour, all ethylene acetal was converted (checked with TLC (hept/EtOAc 90/10; CeMo staining). The reaction mixture was cooled down to room temperature, resulting in partial precipitation of the product. Powdered KOH (~145 mg, 0.47 eq) was added to quench the TsOH, and the mixture was concentrated in *vacuo*. The crude material was dissolved in heptane (200 mL), and resulting slightly turbid solution was washed with water (2 × 200 mL). The clear organic layer was dried with $MgSO_4$ and concentrated in *vacuo*. The crude product was obtained as a white solid (3.40 g, 88%) and pure enough for further deprotection. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.28 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.47 (t, ^3J = 5.8 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_3)$_2$), 3.64 (dq, ^2J = 9.5 Hz, ^3J = 7.1 Hz, 2H, CH(-O-C<u>H</u>$_2$-CH_3)$_2$), 3.49 (dq, ^2J = 9.5 Hz, ^3J = 7.1 Hz, 2H, CH(-O-C<u>H</u>$_2$-CH_3)$_2$), 2.06–1.93 (m, 8H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.63–1.57 (m, 2H, CH_2-C<u>H</u>$_2$-CH(-O-CH_2-CH_3)$_2$), 1.41–1.23 (m, 66H, C<u>H</u>$_2$), 1.20 (t, ^3J = 7.1 Hz, 6H, CH(-O-CH_2-C<u>H</u>$_3$)$_2$), 0.88 ppm (t, ^3J = 6.9 Hz, 3H, C<u>H</u>$_3$);

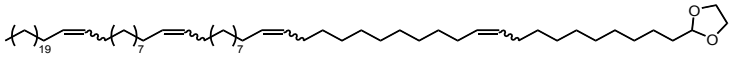
Synthesis of tetratetraconta-11,22-dienal (M_{44} aldehyde) (**16**).



M_{44} diethyl acetal **15** (1.85 g, 2.63 mmol, 1 eq) was dissolved in a mixture of acetone (100 mL) and chloroform (100 mL) in a 500 mL round-bottom flask. The solution was purged with argon to remove oxygen. *p*-Toluene sulfonic acid

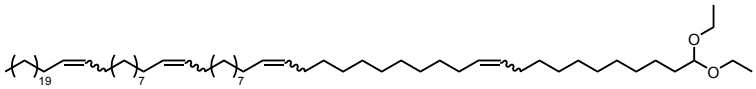
monohydrate ($TsOH{\cdot}H_2O$, 48 mg, 0.28 mmol, 0.11 eq) was added as a solid, and the mixture was stirred at room temperature under argon. After 3 hours, formation of the product was observed with TLC (hept/EtOAc; CeMo staining). The reaction was quenched with 10% Na_2CO_3 soln. (90 mL), and the resulting solution extracted with heptane (3 × 70 mL). The organic layer was washed with water (60 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo*, giving deprotected product as a white solid (1.65 g, quant.). ^{1}H NMR confirmed the complete absence of starting material. The product was stored under N_2 in the fridge. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, ^3J = 1.9 Hz, 1H, CH_2-C<u>H</u>O), 5.41–5.29 (m, 4H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.42 (td, ^3J = 7.4 Hz, ^3J = 1.9 Hz, 2H, CH_2-C<u>H$_2$</u>-CHO), 2.09–1.92 (m, 8H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u>), 1.63 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H, CH_2-C<u>H$_2$</u>-CH_2-CHO), 1.40–1.17 (m, 64H, C<u>H$_2$</u>), 0.88 ppm (t, ^3J = 6.9 Hz, 3H, C<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.04, 130.09, 130.06, 130.02, 129.97, 44.08, 32.77, 32.09, 29.94, 29.91, 29.87, 29.83, 29.79, 29.73, 29.63, 29.56, 29.53, 29.49, 29.43, 29.33, 27.38, 27.36, 22.86, 22.25, 14.28 ppm.

Synthesis of 2-(pentahexaconta-10,21,32,43-tetraen-1-yl)-1,3-dioxolane (M_{66} ethylene acetal) (**17**).



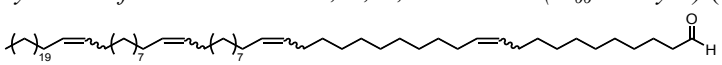
Phosphonium salt **7** (1.10 g, 1.55 mmol, 1.14 eq) and M_{44} aldehyde **16** (0.86 g, 1.36 mmol, 1 eq) were coupled using general method **A**. The crude product was obtained as a dark yellow oil and further purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 98/2) as eluent. The pure product was obtained as a white solid (870 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40–5.28 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.84 (t, ^3J = 4.9 Hz, 1H, CH_2-C<u>H</u>(-O-CH_2-CH_2-O-)), 4.01–3.80 (m, 4H, CH_2-CH(-O-C<u>H$_2$</u>-C<u>H$_2$</u>-O-)), 2.08–1.92 (m, 16H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u>), 1.70–1.60 (m, 2H, CH_2-C<u>H$_2$</u>-CH(-O-CH_2-CH_2-O-)), 1.47–1.20 (m, 94H, C<u>H$_2$</u>), 0.88 ppm (t, ^3J = 6.7 Hz, 3H, C<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.50, 130.04, 104.87, 64.98, 34.09, 32.78, 32.09, 29.94, 29.87, 29.83, 29.79, 29.73, 29.69, 29.67, 29.53, 29.49, 29.47, 29.35, 27.38, 24.26, 22.86, 14.28 ppm.

Synthesis of 1,1-diethoxyhexahexaconta-11,22,33,44-tetraene (M_{66} diethyl acetal) (**18**).



M_{66} ethylene acetal **17** was (310 mg, 0.317 mmol, 1 eq) was suspended in a mixture of ethanol (35 mL, ~2000 eq) and chloroform (10 mL) in a 100 mL round-bottom flask. *p*-Toluene sulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 3 mg, 0.016 mmol, 0.05 eq) was added as a solid, and the mixture was heated to reflux (all material was dissolved at elevated temperatures). After 2 hours, nearly all ethylene acetal was converted (checked with TLC (hept/EtOAc 90/10; CeMo staining). The reaction mixture was cooled down to room temperature, resulting in partial precipitation of the product. Powdered KOH (~4 mg, 0.20 eq) was added to quench the TsOH, and the mixture was concentrated in *vacuo*. The crude material was dissolved in heptane (30 mL), and resulting slightly turbid solution was washed with water (2 × 20 mL). The clear organic layer was dried with $MgSO_4$ and concentrated in *vacuo*. The crude product was obtained as a colorless oil (332 mg, quant.) and was pure enough for further deprotection. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40–5.30 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.48 (t, ^3J = 5.8 Hz, 1H, C<u>H</u>(-OCH_2CH_3)$_2$), 3.64 (dq, ^2J = 9.4 Hz, ^3J = 7.1 Hz, 2H, CH(-OC<u>H$_2$</u>CH_3)$_2$), 3.49 (dq, ^2J = 9.4 Hz, ^3J = 7.1 Hz, 2H, CH(-OC<u>H$_2$</u>CH_3)$_2$), 2.05–1.93 (m, 16H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u>), 1.64–1.56 (m, 2H, C<u>H$_2$</u>-CH(-OCH_2CH_3)$_2$), 1.38–1.23 (m, 94H, C<u>H$_2$</u>), 1.20 (t, ^3J = 7.1 Hz, 6H, C<u>H$_3$</u>-CH_2-O), 0.88 ppm (t, ^3J = 6.8 Hz, 3H, C<u>H$_3$</u>-CH_2-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.49, 130.03, 103.13, 60.94, 33.77, 32.78, 32.09, 29.95, 29.87, 29.83, 29.79, 29.74, 29.70, 29.67, 29.53, 29.49, 29.35, 27.38, 24.94, 22.86, 15.52, 14.27 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{70}H_{134}O_2$+Na^+: 1030.03 $[M+Na]^+$; found: 1030.17.

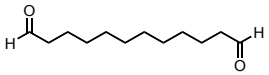
Synthesis of hexahexaconta-11,22,33,44-tetraenal (M_{66} aldehyde) (**19**).



M_{66} diethyl acetal **18** (320 mg, 0.318 mmol, 1 eq) was dissolved in a mixture of chloroform (5 mL) and acetone (5 mL) in a 25 mL round-bottom flask. The solution was purged with argon to remove oxygen. *p*-Toluene sulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 3 mg, 0.016 mmol, 0.05 eq) was added as solid, and the mixture was stirred at room temperature under argon. After 2 hours, formation of the product was observed with TLC (hept/EtOAc; CeMo staining). The reaction was quenched with 10% Na_2CO_3 soln. (20 mL), and the resulting solution extracted with heptane (20 mL). The organic layer was washed with water (10 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo*, giving partially deprotected product (320 mg). ^{1}H NMR revealed the presence of ~5 % starting material. The above procedure was repeated, giving the title compound (286 mg, 96%) as a colorless oil (the material solidified upon cooling to 0 °C). ^{1}H NMR confirmed the complete absence of starting material. The product was stored under N_2 in the fridge. ^{1}H NMR

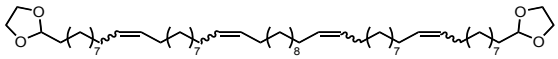
(400 MHz, $CDCl_3$): δ = 9.76 (t, ^3J = 1.8 Hz, 1H, CH_2-C<u>H</u>O), 5.41–5.29 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.41 (td, ^3J = 7.4 Hz, ^3J = 1.9 Hz, 2H, CH_2-C<u>H</u>$_2$-CHO), 2.02 (td, ^3J = 6.7 Hz, ^3J = 6.5 Hz, 16H, CH_2-C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$-CH_2), 1.63 (tt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H, CH_2-C<u>H</u>$_2$-CH_2-CHO), 1.41–1.18 (m, 92H, C<u>H</u>$_2$), 0.89 ppm (t, ^3J = 6.9 Hz, 3H, C<u>H</u>$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.56, 130.46, 130.03, 130.00, 129.98, 129.91, 44.07, 32.80, 32.13, 32.07, 29.96, 29.91, 29.87, 29.83, 29.77, 29.66, 29.59, 29.57, 29.55, 29.51, 29.45, 29.38, 29.36, 29.22, 27.39, 27.37, 22.87, 22.26, 14.25 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{66}H_{124}O^+$: 932.97 M^+; found: 932.99.

Synthesis of dodecanedial (**21**).



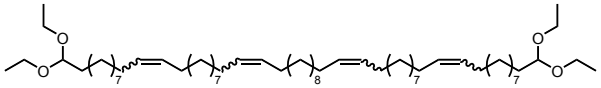
Dodecanediol (5.18 g, 25.6 mmol, 1 eq), tetrabutylammonium chloride (758 mg, 6.92 mmol, 0.27 eq), and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 610 mg, 3.90 mmol, 0.15 eq) were added to DCM (200 mL) in a 1L round-bottom flask. A solution of $NaHCO_3$ (21.6 g, 257 mmol), K_2CO_3 (3.61 g, 26.1 mmol) in water (320 mL) was added, and the mixture vigorously stirred to get two intimately mixed layers (under argon atmosphere to prevent possible over-oxidation). *N*-Chlorosuccinimide (9.45 g, 70.8, 2.8 eq) was added as a solid and stirring of the suspension/emulsion was continued for 20 h at room temperature. After 20 hours, a ^{1}H NMR sample taken from the DCM layer confirmed complete conversion of the alcohol functionality. The DCM layer was washed with water (2 × 200 mL) and brine (300 mL). The organic layer was dried with MgSO4 and concentrated in *vacuo*, giving the crude product as a red oil (6.04 g). The materials was stirred in hot heptane (30 mL), cooled down to −20 °C in a freezer, and the supernatant was removed from the formed crystals with a Pasteur pipette. This procedure was repeated three times. The residue was subjected to automated column chromatography using heptane/chloroform (gradient 80/20 to 0/100) as eluent. Pure dodecanedial was obtained as a white solid (2.30 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, ^3J = 1.9 Hz, 2H, CH_2-C<u>H</u>O), 2.41 (td, ^3J = 7.3 Hz, ^3J = 1.9 Hz, 4H, CH_2-C<u>H</u>$_2$-CHO), 1.67–1.57 (m, 4H, CH_2-C<u>H</u>$_2$-CH_2-CHO), 1.36–1.22 ppm (m, 12H, C<u>H</u>$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.04, 44.03, 29.43, 29.25, 22.18 ppm.

Synthesis of 2,2'-(tetrapentaconta-10,21,33,44-tetraene-1,54-diyl)bis(1,3-dioxolane) (M_{56} bis(ethylene acetal) (**22**).



Phosphonium salt **7** (2.33 g, 3.29 mmol, 2.2 eq) and dodecanedial **21** (296 mg, 1.50 mmol, 1 eq) were coupled using general method **A**. After filtration, the heptane layer 100 mL) was washed with acetonitrile (6 × 50 mL). The heptane was removed in *vacuo*, giving the product as a white solid (1.032 g, 77%). No further purification was necessary. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.29 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4,48 (t, ^3J = 4,8 Hz, 2H, CH_2-C<u>H</u>(-O-CH_2-CH_2-O-)), 4.02–3.79 (m, 8H, CH_2-CH(-O-C<u>H</u>$_2$-C<u>H</u>$_2$-O-)), 2.07–1.93 (m, 16H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.70–1.61 (m, 4H, CH_2-C<u>H</u>$_2$-CH(-O-CH_2-CH_2-O-)), 1.46–1.21 ppm (m, 72H, C<u>H</u>$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.50, 130.04, 104.87, 64.98, 34.09, 32.78, 29.94, 29.82, 29.79, 29.73, 29.72, 29.69, 29.67, 29.49, 29.46, 29.35, 27.38, 24.26 ppm.

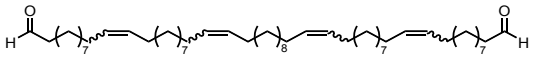
Synthesis of 1,1,56,56-tetraethoxyhexapentaconta-11,22,34,45-tetraene (M_{56} bis(diethyl acetal)) (**23**).



M_{56} bis(ethylene acetal) **22** (550 mg, 0.614 mmol, 1 eq) was suspended in a mixture of ethanol (80 mL, ~2000 eq) and chloroform (10 mL) in a 250 mL round-bottom flask. *p*-Toluene sulfonic acid monohydrate ($TsOH·H_2O$, 12 mg, 0.061 mmol, 0.1 eq) was added as a solid, and the mixture was heated to reflux (all material was dissolved at elevated temperatures). After 2 hours, nearly all ethylene acetal was converted (checked with TLC (hept/EtOAc 90/10; CeMo staining). The reaction mixture was cooled down to room temperature, resulting in partial precipitation of the product. Powdered KOH (~4 mg, 0.20 eq) was added to quench the TsOH, and the mixture was concentrated in *vacuo*. The crude material was dissolved in DCM (20 mL), and resulting solution was washed with water (2 × 15 mL). The organic layer was dried with $MgSO_4$ and concentrated in *vacuo*. The crude product was obtained as a colorless oil (548 mg, 93%) and pure enough for further deprotection. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.28 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.47 (t, ^3J = 5.8 Hz, 2H, C<u>H</u>(O-CH_2-CH_3)$_2$), 3.63 (dq, ^2J = 9.4, ^3J = 7.0 Hz, 4H, CH(O-C<u>H</u>$_2$-CH_3)$_2$), 3.49 (dq, ^2J = 9.4, ^3J = 7.1 Hz, 4H, CH(O-C<u>H</u>$_2$-CH_3)$_2$), 2.07–1.93 (m, 16H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.63–1.57 (m, 4H, C<u>H</u>$_2$-CH(-OCH_2CH_3)$_2$), 1.38–1.23 (m, 76H, C<u>H</u>$_2$), 1.20 ppm (t, ^3J = 7.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.50, 130.04, 103.13, 60.95, 33.77,

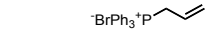
32.78, 29.94, 29.82, 29.79, 29.73, 29.72, 29.70, 29.66, 29.49, 29.47, 27.38, 24.93, 15.52 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{64}H_{122}O_4$+Na^+: 977.92 $[M+Na]^+$; found: 977.93.

Synthesis of hexapentaconta-11,22,34,45-tetraenedial (M_{56} bisaldehyde) (**24**).



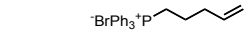
M_{56} bis(diethyl acetal) **23** (538 mg, 0.563 mmol, 1 eq) was dissolved in a mixture of DCM (8 mL) and acetone (8 mL) in a 50 mL round-bottom flask. The solution was purged with argon to remove oxygen. *p*-Toluene sulfonic acid monohydrate ($TsOH{\cdot}H_2O$, 5 mg, 0.03 mmol, 0.05 eq) was added as a solid, and the mixture was stirred at room temperature under argon. After 1 hour, formation of the product was observed with TLC (hept/EtOAc; CeMo staining). The reaction was quenched with 10% Na_2CO_3 soln. (15 mL), and the resulting solution extracted with heptane (20 mL). The organic layer was washed with water (10 mL) and dried with $MgSO_4$. The solvent was removed in *vacuo*, giving partially deprotected product (457 mg). ^{1}H NMR revealed the presence of ~15 % starting material. The above procedure was repeated, giving the title compound (451 mg, 99%) as a colorless oil. ^{1}H NMR confirmed the complete absence of starting material. The product was stored under N_2 in the fridge. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (t, ^3J = 1.9 Hz, 2H, CH_2-C<u>H</u>O), 5.39–5.27 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.39 (td, ^3J = 7.4 Hz, ^3J = 1.9 Hz, 4H, C<u>H_2</u>-CHO), 2.08–1.91 and 1.65–1.55 (m, 16H, C<u>H_2</u>-CH=CH-C<u>H_2</u>), 1.38–1.18 ppm (m, 72H, C<u>H_2</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.71, 130.46, 130.42, 130.40, 130.35, 129.98, 129.95, 129.93, 129.88, 44.00, 32.72, 32.70, 29.89, 29.85, 29.77, 29.74, 29.68, 29.58, 29.54, 29.51, 29.47, 29.43, 29.37, 29.29, 29.28, 27.32, 27.30, 22.19 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{56}H_{102}O_2$+Na^+: 829.78 $[M+Na]^+$; found: 829.79.

Synthesis of allyltriphenylphosphonium bromide (**28**).



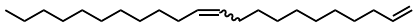
Triphenylphosphine (1.094 g, 4.171 mmol, 1 eq) was dissolved in acetonitrile (10 mL) in a 50 mL round-bottom flask. Allyl bromide (0.505 g, 4.171 mmol, 1 eq) was added, and the resulting clear solution was stirred under reflux. After 45 min, a white crystalline precipitate had formed. The reaction mixture was cooled down to room temperature and diethyl ether (20 mL) was added. The mixture was stirred for 5 min at, resulting in further precipitation of the product. Afterward, the precipitate was allowed to settle, and the top layer of liquid was decanted. Additional diethyl ether (10 mL) was added, and the above described decantation procedure was repeated 2 more times. The remaining solid was dried in *vacuo*, resulting in the pure as white, fine crystals (1.339 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.74 (m, 9H, Ar-<u>H</u>), 7.70–7.64 (m, 6H, Ar-<u>H</u>), 5.69 (ddtd, ^3J = 16.5 Hz, ^3J = 9.6 Hz, ^3J = 6.9 Hz, $^3J_{P,H}$ = 5.0 Hz, 1H, CH_2=C<u>H</u>-CH_2-P), 5.57 (ddt, ^3J = 16.9 Hz, ^3J = 5.2 Hz, ^3J = 1.2 Hz, 1H, C<u>H_2</u>=CH-CH_2 (cis)), 5.36 (ddt, ^3J = 9.6 Hz, ^3J = 5.2 Hz, ^3J = 1.1 Hz, 1H, C<u>H_2</u>=CH-CH_2 (trans)), 4.78 ppm (dd, $^3J_{P,H}$ = 15.4 Hz, ^3J = 6.9 Hz, 2H, CH-C<u>H_2</u>-P); ^{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 = 24.11 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{21}H_{20}BrP{-}Br^-$: 303.13 $[M{-}Br]^-$; found: 303.21.

Synthesis of pent-4-en-1-yltriphenylphosphonium bromide (**29**).



Triphenylphosphine (1.848 g, 7.046 mmol, 1.05 eq) and 5-bromopent-1-ene **26** (1.000 g, 6.710 mmol, 1 eq) were dissolved in acetonitrile (10 mL). The solution heated to reflux and stirred for 2 hours, resulting in the precipitation of the product. The mixture was then allowed to cool down to room temperature, most of the acetonitrile was removed in *vacuo*, and diethyl ether (40 mL) was added. The resulting suspension was stirred for 5 min at room temperature. Afterward, the precipitate was allowed to settle, and the top layer of liquid was decanted. Additional diethyl ether (15 mL) was added, and the above described decantation procedure was repeated 2 more times. The remaining solid was dried in *vacuo*, giving the pure product as white, fine crystals (2.327 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.75 (m, 9H, Ar-<u>H</u>), 7.72–7.66 (m, 6H, Ar-H), 5.70 (ddt, ^3J = 17.0 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, CH_2=C<u>H</u>-CH_2), 5.07–4.96 (m, 2H, C<u>H_2</u>=CH-CH_2), 3.92–3.83 (m, 2H, C<u>H_2</u>-P), 2.47–2.40 (m, 2H, CH_2=CH_2-CH_2-C<u>H_2</u>), 1.79–1.67 ppm (m, 2H, CH_2=CH_2-C<u>H_2</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.56, 135.12, 135.09, 133.91, 133.81, 130.67, 130.54, 118.96, 118.11, 117.00, 33.98, 33.81, 22.41, 22.08, 22.04, 21.91 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.66 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{23}H_{24}BrP{-}Br^-$: 331.16 $[M{-}Br]^+$; found: 331.20.

Synthesis of docosa-1,11-diene (M_{22} alkene) (**31**).

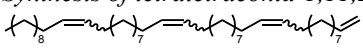


Phosphonium salt **30** (610 mg, 1.23 mmol, 1.1 eq) and undecanal **10** (191 mg, 1.12 mmol, 1 eq) were coupled using general method **A**. The crude product was obtained as a dark yellow oil and further purified by automated column chromatography using heptane (100%, isocratic) as eluent. The pure product was obtained as a colorless oil (120 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (ddt, ^3J = 16.9 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H, CH_2-C<u>H</u>=CH_2), 5.40–5.31 (m, 2H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.99 (ddt, ^3J = 16.9 Hz, ^2J = 1.9 Hz, ^4J = 1.8 Hz, 1H, CH_2-CH=C<u>H$_2$</u>), 4.93 (ddt, ^3J = 10.2 Hz, ^2J = 1.9 Hz, ^4J = 0.9 Hz, 1H, CH_2-CH=C<u>H$_2$</u>), 2.08–1.93 (m, 6H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u> and C<u>H$_2$</u>-CH=CH_2), 1.43–1.19 (m, 28H, C<u>H$_2$</u>), 0.88 ppm (t, ^3J = 6.7 Hz, 3H, CH_2-C<u>H$_3$</u>); ^{13}C NMR (100 MHz, CDCl3): δ = 139.40, 130.06, 114.24, 33.98, 32.09, 29.94, 29.93, 29.87, 29.83, 29.73, 29.66, 29.64, 29.53, 29.49, 29.46, 29.31, 29.11, 27.37, 22.86, 14.28 ppm; GC-MS (EI, oven 80–300 °C): t = 3.63 min.

Synthesis of tritriacontane ($C_{33}H_{68}$).

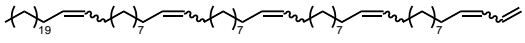
M_{33} alkene **32** (58 mg, 0.125 mmol, 1 eq) was dissolved in EtOAc (4 mL) in a 25 mL round-bottom flask. Pd/C (10 w% Pd, 15 mg, 12.5 µmol Pd, 0.1 eq) was added and the flask was purged with hydrogen and stirred at room temperature. After 3 hours, the mixture was filtered through Celite, and the residue rinsed with EtOAc (3 × 5 mL). The combined filtrates were concentrated in *vacuo*, giving the pure product as a white solid (56 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32–1.21 (m, 62H, C<u>H$_2$</u>), 0.88 ppm (t, ^3J = 6.7 Hz, 6H, C<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.02, 29.79, 29.45, 22.78, 14.18 ppm.

Synthesis of tetratetraconta-1,11,22,33-tetraene (M_{44} alkene) (**33**).



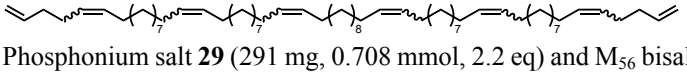
Phosphonium salt **30** (446 mg, 0.93 mmol, 1.1 eq) and M_{33} aldehyde **13** (401 mg, 0.85 mmol, 1 eq) were coupled using general method **A**. The crude product was obtained as a light brown oil and further purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 95/5) as eluent. The pure product was obtained as a colorless oil (146 mg, 28%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.81 (ddt, ^3J = 16.9 Hz, ^3J = 10.1 Hz, ^3J = 6.6 Hz, 1H, CH_2=C<u>H</u>-CH_2), 5.40–5.29 (m, 6H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 5.03–4.90 (m, 2H, C<u>H$_2$</u>=CH-CH_2), 2.08–1.93 (m, 14H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u> and CH_2=CH-C<u>H$_2$</u>), 1.41–1.20 (m, 56H, C<u>H$_2$</u>), 0.88 ppm (t, ^3J = 6.7 Hz, 3H, CH_2-C<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.38, 130.05, 130.03, 114.24, 33.98, 32.77, 32.09, 29.94, 29.92, 29.83, 29.81, 29.79, 29.73, 29.66, 29.64, 29.52, 29.49, 29.46, 29.31, 29.11, 27.58, 27.38, 22.86, 14.28 ppm.

Synthesis of nonahexaconta-1,3,14,25,36,47-hexaene (M_{69} alkene) (**34**).



Phosphonium salt **28** (111 mg, 0.289 mmol, 1.05 eq) and M_{44} aldehyde **16** (257 mg, 0.275 mmol, 1 eq) were coupled using general method **A**. The waxy, orange residue was purified by automated column chromatography, using heptane as eluent, giving the pure product as a colorless oil (120 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.65 (ddd, ^3J = 16.9 Hz, ^3J = 11.2 Hz, ^3J = 10.1 Hz, ~0.5H, CH_2=C<u>H</u>-CH=CH-CH_2 (*cis*)), 6.31 (ddd, ^3J = 16.9 Hz, ^3J = 10.2 Hz, ~0.5H, CH_2=C<u>H</u>-CH=CH-CH_2 (*trans*)), 6.10–5.96 (m, 1H, CH_2=CH-C<u>H</u>=CH-CH_2), 5.71 (dt, ^3J = 14.6 Hz, ^3J = 7.0 Hz, ~0.5H, CH_2=CH-CH=C<u>H</u>-CH_2 (*trans*)), 5.46 (dt, ^3J = 11.1 Hz, ^3J = 7.8 Hz, ~0.5H, CH_2=CH-CH=C<u>H</u>-CH_2 (*cis*)), 5.41–5.30 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 5.18 (dd, ^3J = 16.9 Hz, ^3J = 2.0 Hz, 1H, C<u>H$_2$</u>=CH-CH=CH-CH_2 (*cis*,*cis*)), 5,09 (dd, ^3J = 11,2 Hz, ^3J = 2.0 Hz, 1H, C<u>H$_2$</u>=CH-CH=CH-CH_2 (*cis*,*trans*)), 5,08 (dd, ^3J = 16,9 Hz, ^3J = 1.7 Hz, 1H, C<u>H$_2$</u>=CH-CH=CH-CH_2 (*trans*,*cis*)), 4,95 (dd, ^3J = 11,2 Hz, ^3J = 1,7 Hz, 1H, C<u>H$_2$</u>=CH-CH=CH-CH_2 (*trans*,*trans*)), 2.23–2.04 (m, 2H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u>), 2.06–1.95 (m, 108H, C<u>H$_2$</u>), 0,89 ppm (t , ^3J = 6,9 Hz, 3H, C<u>H$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.51, 135.70, 133.16, 132.49, 131.02, 130.49, 130.04, 130.02, 129.28, 116.77, 114.67, 32.79, 32.74, 32.11, 29.96, 29.89, 29.85, 29.81, 29.80, 29.76, 29.72, 29.68, 29.55, 29.51, 29.48, 29.42, 29.40, 29.38, 29.37, 27.91, 27.39, 22.87, 14.28 ppm.

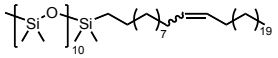
Synthesis of hexahexaconta-1,5,16,27,38,49,60,65-octaene (M_{66} bisalkene) (**35**).



Phosphonium salt **29** (291 mg, 0.708 mmol, 2.2 eq) and M_{56} bisaldehyde **24** (260 mg, 0.322 mmol, 1 eq) were coupled using general method **A** (0.740 mmol, 2.3 eq of KO*t*Bu were used). The waxy, orange residue was purified by automated column chromatography, using heptane as eluent, giving the pure product as a colorless oil (212 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddt, ^3J = 16.7 Hz, ^3J = 10.3 Hz, ^3J = 6.3 Hz, 2H, CH_2=C<u>H</u>-CH_2), 5.44–5.30 (m, 12H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 5.06–4.93 (m, 4H, C<u>H$_2$</u>=CH-CH_2), 2.18–1.92 (m, 28H, C<u>H$_2$</u>-CH=CH-C<u>H$_2$</u> and CH_2=CH-C<u>H$_2$</u>), 2.37–1.22

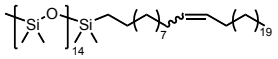
ppm (m, 72H, C$\underline{H}_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.68, 130.63, 130.51, 130.04, 128.97, 114.67, 77.48, 77.16, 76.84, 34.04, 32.77, 32.04, 29.94, 29.87, 29.82, 29.78, 29.73, 29.72, 29.49, 29.47, 29.18, 27.42, 27.38, 26.83 ppm;

Synthesis of [**Si$_{11}$-M$_{11}$=M$_{22}$**] (**37b**).



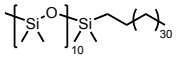
Alkene **32** (72 mg, 0.156 mmol, 1 eq) and Si_{11} hydride **36b** (127 mg, 0.156 mmol, 1 eq) were coupled using general method **B**. The crude material was purified by automated column chromatography using heptane/chloroform (100/0 for 3 CV, then gradient 100/0 to 95/5 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (122 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.33 (m, 2H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.08–1.93 (m, 4H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.39–1.20 (m, 54H, C$\underline{H}_2$), 0.89 (t, ^3J = 6.7 Hz, 3H, C$\underline{H}_3$-CH_2), 0.57–0.51 (m, 2H, C$\underline{H}_2$-Si), 0.10 (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.09 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.08 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.08 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.07 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.06 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.06 ppm (s, 6H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.53, 130.06, 33.69, 32.83, 32.14, 32.10, 30.00, 29.99, 29.92, 29.87, 29.85, 29.80, 29.78, 29.63, 29.58, 29.55, 29.53, 29.41, 29.39, 27.43, 27.41, 23.44, 22.90, 18.47, 14.30, 1.96, 1.35, 1.32, 1.24, 0.37 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{56}H_{134}O_{10}Si_{11}$+$Na^+$: 1297.734 $[M+Na]^+$; found: 1297.75.

Synthesis of [**Si$_{15}$-M$_{11}$=M$_{22}$**] (**37c**).



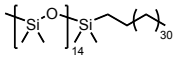
Alkene **32** (97 mg, 0.210 mmol, 1 eq) and Si_{15} hydride **36c** (234 mg, 0.210 mmol, 1 eq) were coupled using general method **B**. The crude material was purified by automated column chromatography using heptane/chloroform (100/0 for 5 CV, then gradient 100/0 to 96/4 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (269 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.40–5.32 (m, 2H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.06–1.93 (m, 4H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.37–1.21 (m, 54H, C$\underline{H}_2$), 0.88 (t, ^3J = 6.8 Hz, 3H, C$\underline{H}_3$), 0.56–0.50 (m, 2H, C$\underline{H}_2$-Si), 0.12–0.02 ppm (m, 93H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.51, 130.05, 33.65, 32.79, 32.10, 32.05, 29.97, 29.95, 29.87, 29.83, 29.81, 29.76, 29.74, 29.60, 29.53, 29.52, 29.49, 29.35, 29.19, 27.39, 27.38, 23.40, 22.86, 18.44, 14.28, 1.94, 1.58, 1.33, 1.30, 1.21, 0.84, 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{64}H_{158}O_{14}Si_{15}$+$Na^+$: 1593.81 $[M+Na]^+$; found: 1593.83.

Synthesis of [**Si$_{11}$-M$_{33}$**].



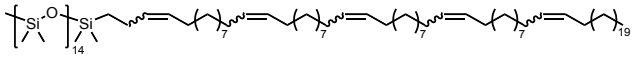
Unsaturated BCO **37b** (99 mg, 0.078 mmol, 1 eq) was hydrogenated at room temperature according to general method **C**. The product was obtained as a semi-transparent, white wax (93 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36–1.19 (m, 62H, C$\underline{H}_2$), 0.89 (t, ^3J = 6,8 Hz, 3H, C$\underline{H}_3$-CH_2), 0.56–0.51 (m, 2H, C$\underline{H}_2$-Si), 0.10 (s, 9H, Si(C$\underline{H}_3$)$_3$), 0.08 (s, 30H, Si(C$\underline{H}_3$)$_2$), 0.08 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.08 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.07 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.06 (s, 6H, Si(C$\underline{H}_3$)$_2$), 0.05 ppm (s, 6H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.67, 32.13, 29.94–29.90, 29.86, 29.84, 29.62, 29.56, 23.42, 22.89, 18.46, 14.30, 1.96, 1.35, 1.32, 1.23, 0.37.ppm; MS (MALDI-TOF): *m/z* calcd for $C_{56}H_{136}O_{10}Si_{11}$+$Na^+$: 1299.75 $[M+Na]^+$; found: 1299.75.

Synthesis of [**Si$_{15}$-M$_{33}$**].



Unsaturated BCO **37c** (130 mg, 0.082 mmol, 1 eq) was hydrogenated at room temperature according to general method **C**. The product was obtained as a semi-transparent, white wax (119 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.21 (m, 62H, C$\underline{H}_2$), 0.89 (t, ^3J = 6.7 Hz, 3H, C$\underline{H}_3$-CH_2), 0.57–0.51 (m, 2H, C$\underline{H}_2$-Si), 0.12–0.02 ppm (m, 93H, Si(C$\underline{H}_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.67, 32.13, 29.95–29.85, 29.62, 29.56, 23.42, 22.89, 18.46, 14.30, 1.96, 1.59 (^{29}Si satellite), 1.35, 1.31, 1.22, 0.85 (^{29}Si satellite) ppm; MS (MALDI-TOF): *m/z* calcd for $C_{64}H_{160}O_{14}Si_{15}$+$Na^+$: 1595.83 $[M+Na]^+$; found: 1595.83.

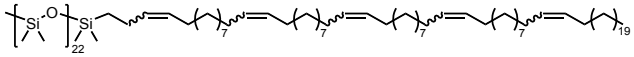
Synthesis of [**Si$_{15}$-M$_3$=M$_{11}$=M$_{11}$=M$_{11}$=M$_{11}$=M$_{22}$**] (**38c**).



Alkene **34** (40 mg, 0.042 mmol, 1.05 eq) and Si_{15} hydride **36c** (44 mg, 0.040 mmol, 1 eq) were coupled using general method **B**. The crude material was purified by automated column chromatography using heptane/chloroform (gradient 100/0 to 94/6 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (47 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46–5.15 (m, 10H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.09–1.92 (m, 20H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.45–1.11 (m, 94H,

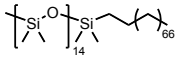
C$\underline{H}_2$), 0.89 (t, ^3J = 6.9 Hz, 3H, CH_3), 0.65–0.57 (m, 2H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.13 to −0.02 ppm (m, 93H, Si(C$\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.51, 130.06, 130.04, 33.17, 32.79, 32.11, 32.06, 29.96, 29.88, 29.84, 29.81, 29.77, 29.75, 29.72, 29.54, 29.53, 29.50, 29.37, 29.20, 27.40, 22.87, 18.37, 14.28, 1.95, 1.58, 1.34, 1.30, 1.21, 0.84, 0.41 ppm; MS (MALDI-TOF): m/z calcd for $C_{110}H_{222}O_{14}Si_{15}$+$Na^+$: 2090.31 [M+Na]$^+$; found: 2090.34.

Synthesis of [**Si_{23}-M_3=M_{11}=M_{11}=M_{11}=M_{11}=M_{22}**] (**38d**).



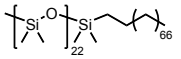
Alkene **34** (21 mg, 0.022 mmol, 1.05 eq) and Si_{23} hydride **36d** (36 mg, 0.21 mmol, 1 eq) were coupled using general method **B**. The crude material was purified by automated column chromatography using heptane/chloroform (gradient 100/0 to 94/6 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (39 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.45–5.15 (m, 10H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.10–1.92 (m, 20H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.48–1.10 (m, 94H, C$\underline{H}_2$), 0.88 (t, ^3J = 6.9 Hz, 3H, C$\underline{H}_3$), 0.65–0.57 (m, 2H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.14 to −0.02 ppm (m, 141H, Si(C$\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.51, 130.07, 130.04, 33.17, 32.79, 32.10, 32.06, 29.96, 29.88, 29.84, 29.80, 29.77, 29.75, 29.71, 29.54, 29.50, 29.36, 27.39, 22.86, 14.28, 1.94, 1.57, 1.33, 1.30, 1.20, 0.83, 0.45 ppm; MS (MALDI-TOF): m/z calcd for $C_{116}H_{270}O_{22}Si_{23}$+$Na^+$: 2682.46 [M+Na]$^+$; found: 2682.51.

Synthesis of [**Si_{15}-M_{69}**].



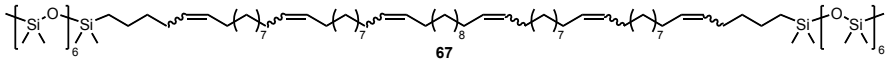
Unsaturated BCO **38c** (47 mg, 0.047 mmol, 1 eq) was hydrogenated at 60 °C according to general method **C**. After completion of the reaction (3 h), the solvent was removed in *vacuo* and the residue dissolved in chloroform, and the resulting black suspension was filtered hot (~45 °C) through Celite. The Celite was rinsed with warm chloroform (3 × 5 mL). The combined filtrates were concentrated in *vacuo*, giving the pure product as a white, waxy solid (47 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.13 (m, 134H, C$\underline{H}_2$), 0.88 (m, ^3J = 6.9 Hz, 3H, C$\underline{H}_3$), 0.64–0.57 (m, 2H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.11–0.01 ppm (m, 93H, Si(C$\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.09, 29.87, 29.53, 22.86, 14.28, 1.94, 1.57, 1.33, 1.30, 1.21, 0.84, 0.47 ppm; MS (MALDI-TOF): m/z calcd for $C_{11}H_{232}O_{14}Si_{15}$+$Na^+$: 2100.39 [M+Na]$^+$; found: 2100.39.

Synthesis of [**Si_{23}-M_{69}**].



Unsaturated BCO **38d** (39 mg, 0.015 mmol, 1 eq) was hydrogenated at 60 °C according to general method **C**. After completion of the reaction (3 h), the solvent was removed in *vacuo* and the residue dissolved in chloroform, and the resulting black suspension was filtered through Celite. The Celite was rinsed with chloroform (3 × 5 mL). The combined filtrates were concentrated in *vacuo*, giving the pure product as a white, waxy solid (21 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37–1.12 (m, 134H, C$\underline{H}_2$), 0.88 (m, ^3J = 6.9 Hz, 3H, C$\underline{H}_3$), 0.65–0.57 (m, 2H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.12 to −0.01 ppm (m, 141H, Si(C$\underline{H}_3)_2$); MS (MALDI-TOF): m/z calcd for $C_{116}H_{280}O_{22}Si_{23}$+$Na^+$: 2692.54 [M+Na]$^+$; found: 2692.52.

Synthesis of [**Si_7-M_5=M_{11}=M_{11}=M_{12}=M_{11}=M_{11}=M_5-Si_7**] (**39**).



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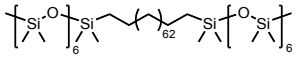
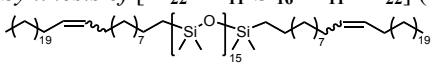
Alkene **35** (97 mg, 0.106 mmol, 1 eq) and Si_7 hydride **36a** (116 mg, 0.223 mmol, 2.1 eq) were coupled using general method **B**. The crude material was first purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 95/5 in 10 CV) as eluent. The purest fractions were combined and further purified by automated column chromatography using heptane/chloroform (gradient 95/5 to 85/15 in 10 CV) as eluent The pure title compound was obtained as a colorless oil (120 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.32 (m, 12H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.05–1.92 (m, 24H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.39–1.23 (m, 80H, C$\underline{H}_2$), 0.57–0.50 (m, 4H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.11–0.02 ppm (m, 90H, Si(C$\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.50, 130.04, 33.67, 32.78, 29.95, 29.84, 29.73, 29.50, 29.36, 27.38, 27.16, 23.10, 18.34, 1.95, 1.34, 1.31, 1.23, 0.36 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{96}H_{210}O_{12}Si_{14}$+$Na^+$: 1970.25 [M+Na]$^+$; found: 1970.38.

Synthesis of [**Si$_7$-M$_{66}$-Si$_7$**].



Unsaturated BCO **39** (87 mg, 0.045 mmol, 1 eq) was hydrogenated at 70 °C according to general method **C**. The product was obtained as a flaky, white solid (67 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.21 (m, 128H, C$\underline{H}_2$), 0.57–0.50 (m, 4H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.11–0.03 ppm (m, 90H, Si(C$\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.64, 29.87, 29.59, 23.39, 18.43, 1.95, 1.34, 1.31, 1.23, 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{96}H_{222}O_{12}Si_{14}$+Na$^+$: 1982.34 [M+Na]$^+$; found: 1982.44.

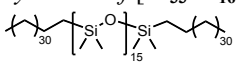
Synthesis of [**M$_{22}$=M$_{11}$-Si$_{16}$-M$_{11}$=M$_{22}$**] (**41**).



Alkene **32** (220 mg, 0.48 mmol, 2.2 eq) and H-Si$_{16}$-H **40** (272 mg, 1.23 mmol, 1 eq) were coupled using general method **B**. The crude material was 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 (345 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (dt, ^3J = 14.4 Hz, ^3J = 4.8 Hz, 4H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.05–1.93 (m, 8H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.38–1.20 (m, 104H, C$\underline{H}_2$), 0.88 (t, ^3J = 6.4 Hz, 6H, C$\underline{H}_3$),

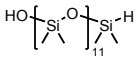
0.57–0.50 (m, 4H, CH_2-C$\underline{H}_2$-Si$(CH_3)_2$), 0.12–0.02 ppm (m, 96H, Si$(CH_3)_2$); ^{13}C NMR (100 MHz, CDCl3): δ = 130.04, 32.09, 29.86, 29.82, 29.52, 22.85, 18.43, 14.28, 1.33, 1.20, 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{98}H_{226}O_{15}Si_{16}$+Na$^+$: 2114.31 [M+Na]$^+$; found: 2114.40.

Synthesis of [**M$_{33}$-Si$_{16}$-M$_{33}$**].



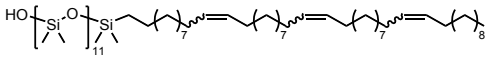
Unsaturated BCO **41** (204 mg, 0.097 mmol, 1 eq) was hydrogenated at room temperature according to general method **C**. After full conversion of the double bonds, the crude reaction mixture was not filtered, but the solvent was removed in a stream of nitrogen. The black-gray residue was suspended in heptane and directly purified by automated column chromatography using heptane/EtOAc (gradient 99/1 to 95/5 in 10 CV) as eluent. The product was obtained as a colorless oil (202 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34–1.20 (m, 124H, C$\underline{H}_2$), 0.88 (t, ^3J = 6.7 Hz, 6H, CH_2-C$\underline{H}_3$), 0.57–0.51 (m, 4H, CH_2-CH_2-Si$(CH_3)_2$), 0.11–0.03 ppm (m, 96H, Si$(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.66, 32.09, 29.86, 29.82, 29.52, 23.39, 22.85, 18.43, 14.28, 1.33, 1.20, 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{98}H_{230}O_{15}Si_{16}$+Na$^+$: 2118.34 [M+Na]$^+$; found: 2118.39.

Synthesis of HO-Si$_{12}$-H (**44**).



Silanol HO-Si$_8$-OH **42** (1.071 g, 1.752 mmol, 1 eq) was dissolved in dry toluene (10 mL) in a 100 mL round-bottom flask under argon. Dry pyridine (~0.20 mL, ~ 2.5 mmol, 1.4 eq) was added, and the solution was cooled in an icebath. Chlorosilane **43** (0.556 g, 1.752 mmol, 1 eq) was dissolved in dry toluene (3 mL) and added dropwise (over a period of 10 min) to the cooled silanol solution. During the addition, a white suspension was formed. After the addition, the mixture was stirred for 3 h at room temperature. Afterward, the reaction mixture was diluted with toluene (50 mL) and washed with water (3 × 20 mL) to remove the white precipitate of pyridinium chloride. The organic layers was dried with $MgSO_4$, and the solvent was removed in *vacuo*. The remaining crude product was purified by automated column chromatography using heptane/DCM (gradient 100/0 to 20/80 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (692 mg, 44%). SEC ($CHCl_3$, RI) confirmed the absence of byproduct H-Si$_{16}$-H. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.7 (h, ^3J = 2.7 Hz, 1H, Si$(CH_3)_2$-H), 2.24 (s, 1H, Si$(CH_3)_2$-OH), 0.20–0.17 (m, 6H, Si$(CH_3)_2$-H), 0.15–0.13 (m, 6H, Si$(CH_3)_2$-OH), 0.11–0.05 (m, 60H, Si$(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.21, 1.18, 1.15, 1.01, 0.84, 0.47 ppm;

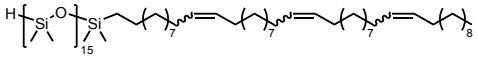
Synthesis of HO-Si$_{12}$-M$_{11}$-M$_{11}$=M$_{11}$=M$_{11}$ (**45**).



Alkene **33** (110 mg, 0.180 mmol, 1.1 eq) and HO-Si$_{12}$-H **44** (146 mg, 0.164 mmol, 1 eq) were coupled using general method **B**. The crude material (a dark brown oil) was purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 90/10 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (203 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.41–5.30 (m, 6H, CH_2-C$\underline{H}$=C$\underline{H}$-CH_2), 2.26 (s, 1H, Si$(CH_3)_2$-O$\underline{H}$), 2.08–1.93 (m, 12H, C$\underline{H}_2$-CH=CH-C$\underline{H}_2$), 1.40–1.20 (m, 60H, C$\underline{H}_2$), 0.88 (t, ^3J = 6.6 Hz, 3H, C$\underline{H}_3$), 0.57–0.50 (m, 2H, CH_2-C$\underline{H}_2$-

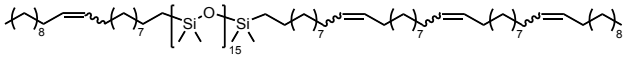
$Si(CH_3)_2$), 0.14 (s, 6H, $Si(C\underline{H}_3)_2$-OH), 0.12–0.04 ppm (m, 66H, $Si(C\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.51, 130.06, 130.04, 33.66, 32.79, 32.10, 29.98, 29.95, 29.88, 29.84, 29.82, 29.80, 29.78, 29.74, 29.60, 29.54, 29.50, 29.35, 27.40, 27.39, 23.41, 22.87, 18.44, 14.29, 1.59 (^{29}Si satellite), 1.34, 1.22, 1.15, 0.84 (^{29}Si satellite) , 0.48, 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{68}H_{156}O_{12}Si_{12}+Na^+$: 1523.873 $[M+Na]^+$; found: 1523.92.

Synthesis of H-Si_{16}-M_{11}=M_{11}=M_{11}=M_{11} (**46**).



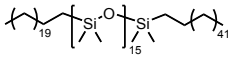
Chlorosilane **43** (47 mg, 0.150 mmol, 1.5 eq) and dry pyridine (13 mg, 0.170 mmol, 1.7 eq) were dissolved in dry toluene (0.5 mL) in a 10 mL Schlenk tube under argon. The mixture was cooled in ice water, and a solution of silanol **45** (150 mg, 0.100 mmol, 1 eq) in dry toluene (0.5 mL) was added dropwise, resulting in the formation of a white precipitate. Stirring was continued at room temperature. After 2.5 h, the reaction mixture was diluted with toluene (5 mL) and washed with water (3 × 3 mL). The slightly turbid toluene layer was dried with $MgSO_4$, and the solvent was removed in *vacuo*. The remaining light yellow oil was dissolved in heptane (4 mL) in a 50 mL round-bottom flask and washed with acetonitrile (4 × 2 mL) to remove low-MW siloxanes (the acetonitrile was carefully removed with a glass pipette). The heptane layer was concentrated in *vacuo*. The remaining crude product was purified by automated column chromatography using heptane/DCM (gradient 100/0 to 20/80 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (142 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.45–5.30 (m, 6H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 4.72 (h, ^3J = 2.8 Hz, 1H, $Si(CH_3)_2$-<u>H</u>), 2.11–1.91 (m, 12H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.46–1.19 (m, 60H, C<u>H</u>$_2$), 0.89 (t, ^3J = 6.7 Hz, 3H, C<u>H</u>$_3$), 0.58–0.51 (m, 2H, CH_2-C<u>H</u>$_2$-$Si(CH_3)_2$), 0.21–0.18 (m, 6H, $Si(C\underline{H}_3)_2$-H), 0.12–0.04 ppm (m, 90H, $Si(C\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.53, 130.07, 130.05, 33.68, 32.81, 32.13, 32.09, 30.00, 29.98, 29.91, 29.89, 29.87, 29.84, 29.80, 29.77, 29.74, 29.70, 29.63, 29.57, 29.55, 29.52, 29.42, 29.38, 27.43, 27.41, 23.43, 22.89, 18.47, 14.30, 1.59 (^{29}Si satellite), 1.35, 1.22, 1.19, 1.02, 0.86, 0.37 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{76}H_{180}O_{15}Si_{16}+Na^+$: 1803.953 $[M+Na]^+$; found: 1803.95.

Synthesis of M_{11}=M_{11}-Si_{16}-M_{11}=M_{11}=M_{11}=M_{11} (**47**).



Alkene **31** (22 mg, 0.072 mmol, 1.2 eq) and silyl hydride H-Si_{16}-M_{11}=M_{11}=M_{11}=M_{11} **46** (107 mg, 0.060 mmol, 1 eq) were coupled using general method **B**. The crude material (a dark brown oil) was purified by automated column chromatography using heptane/DCM (gradient 100/0 to 80/20 in 10 CV) as eluent. The pure title compound was obtained as a colorless oil (34 mg, 27%). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.44–5.28 (m, 8H, CH_2-C<u>H</u>=C<u>H</u>-CH_2), 2.06–1.92 (m, 16H, C<u>H</u>$_2$-CH=CH-C<u>H</u>$_2$), 1.38–1.21 (m, 92H, C<u>H</u>$_2$), 0.88 (t, ^3J = 6.6 Hz, 6H, C<u>H</u>$_3$), 0.57–0.49 (m, 4H, CH_2-C<u>H</u>$_2$-$Si(CH_3)_2$), 0.11–0.02 ppm (m, 96H, $Si(C\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 130.51, 130.05, 33.65, 32.78, 32.09, 29.96, 29.95, 29.87, 29.83, 29.81, 29.76, 29.73, 29.70, 29.67, 29.59, 29.53, 29.49, 29.39, 29.35, 27.38, 23.40, 22.86, 18.44, 14.28, 1.58 (^{29}Si satellite), 1.33, 1.21, 0.84 (^{29}Si satellite), 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{98}H_{222}O_{15}Si_{16}+Na^+$: 2110.2817 $[M+Na]^+$; found: 2110.3.

Synthesis of [**M_{22}-Si_{16}-M_{44}**].



Unsaturated BCO **47** (34 mg, 0.0163 mmol, 1 eq) was hydrogenated at 60 °C according to general method **C**. After full conversion of the double bonds, the crude reaction mixture was not filtered, but the solvent was removed in a stream of nitrogen. The black-gray residue was suspended in heptane and directly purified by automated column chromatography using heptane/EtOAc (gradient 100/0 to 90/10 in 10 CV) as eluent. The product was obtained as a white solid (30 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34–1.21 (m, 124H, C<u>H</u>$_2$), 0.88 (t, ^3J = 6.7 Hz, 6H, C<u>H</u>$_3$), 0.56–0.50 (m, 4H, CH_2-C<u>H</u>$_2$-$Si(CH_3)_2$), 0.11–0.02 ppm (m, 96H, $Si(C\underline{H}_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.64, 32.09, 29.87, 29.59, 29.53, 23.39, 22.86, 18.43, 14.28, 1.58 (^{29}Si satellite), 1.33, 1.21, 0.83 (^{29}Si satellite), 0.35 ppm; MS (MALDI-TOF): *m/z* calcd for $C_{98}H_{230}O_{15}Si_{16}+Na^+$: 2118.3443 $[M+Na]^+$; found: 2118.35;

2. NMR spectra of the final BCOs

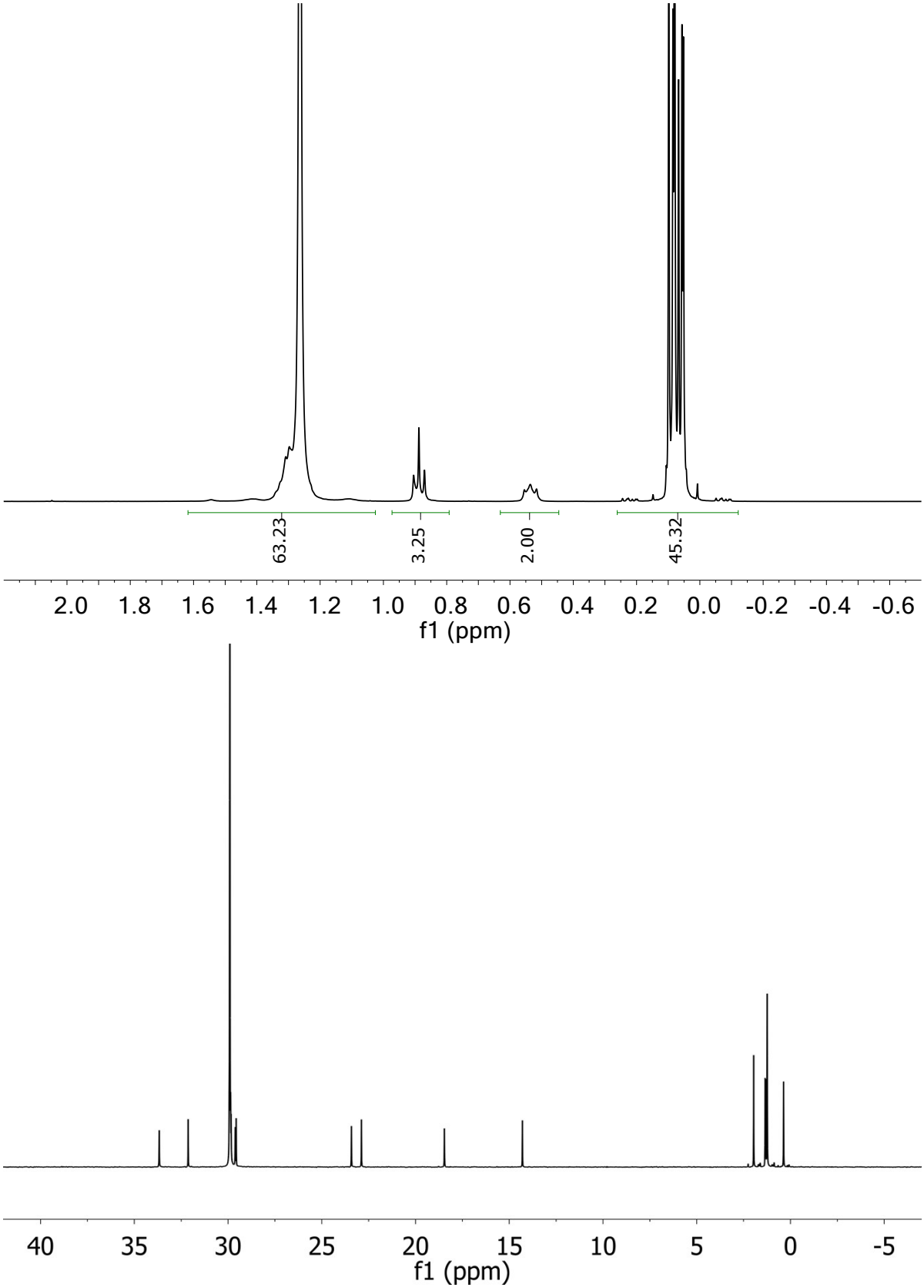


Figure S1. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_7\text{-}M_{33}}$].

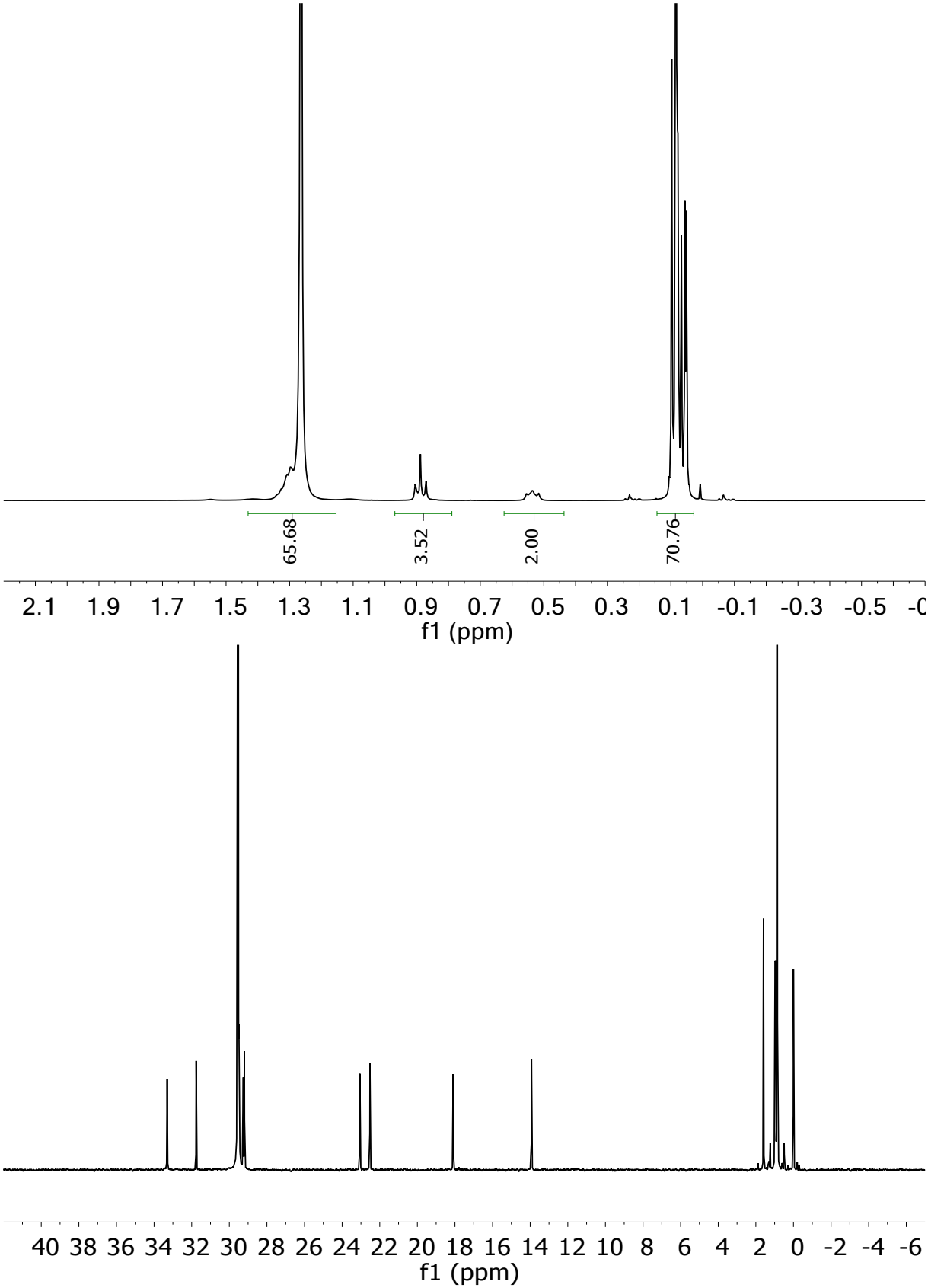


Figure S2. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_{11}}$-$\mathbf{M_{33}}$].

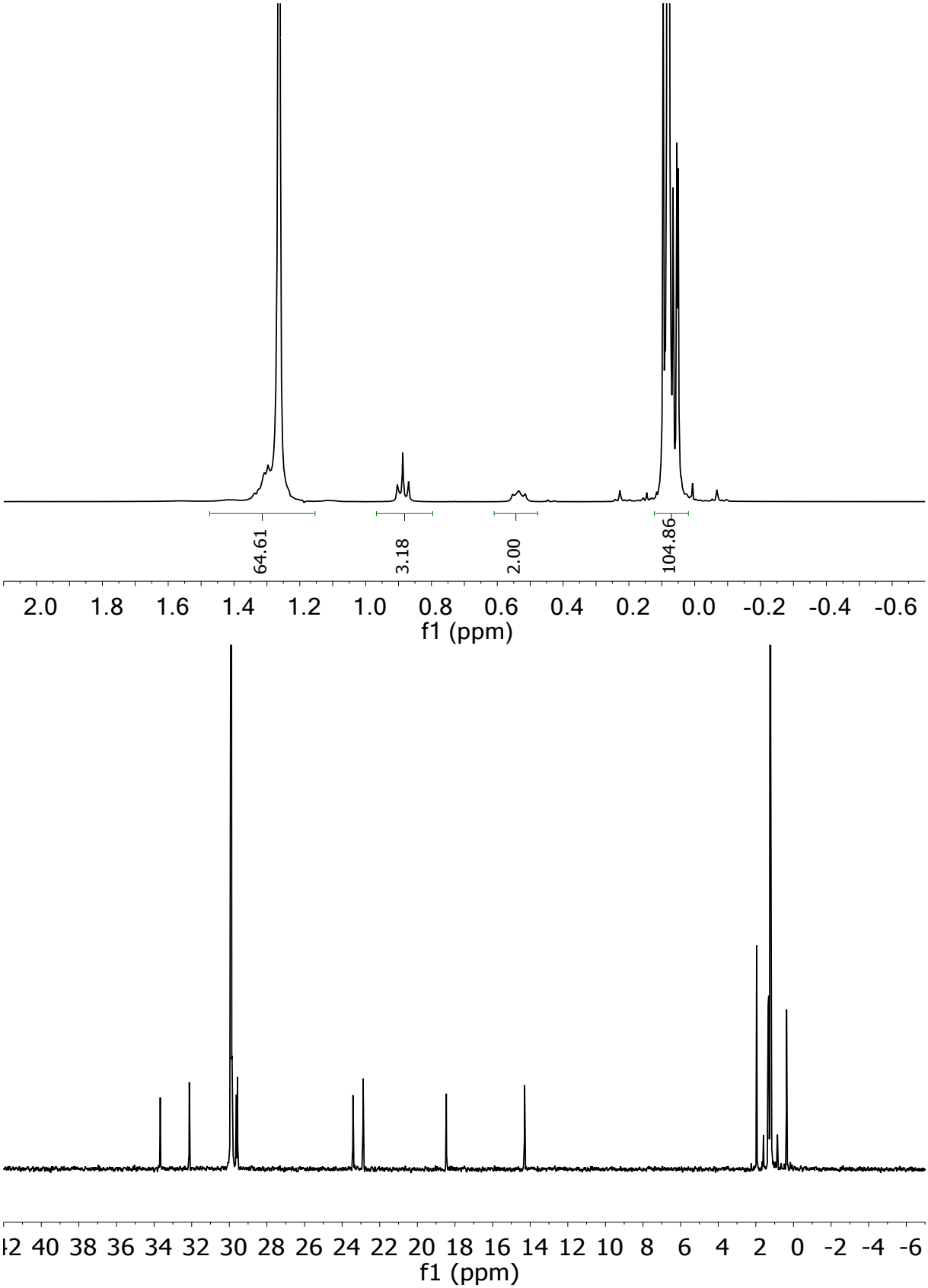


Figure S3. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_{15}}$-$\mathbf{M_{33}}$].

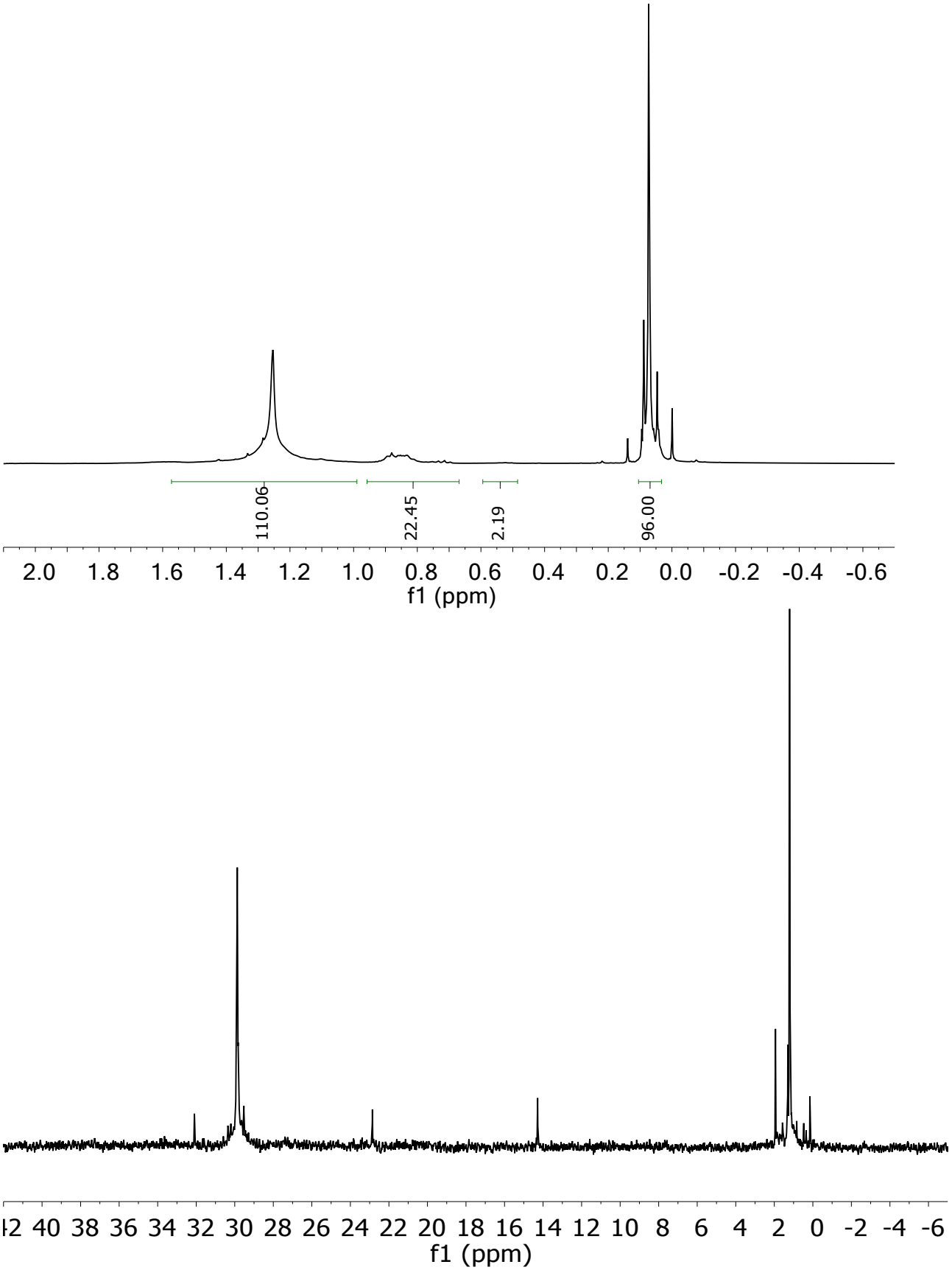
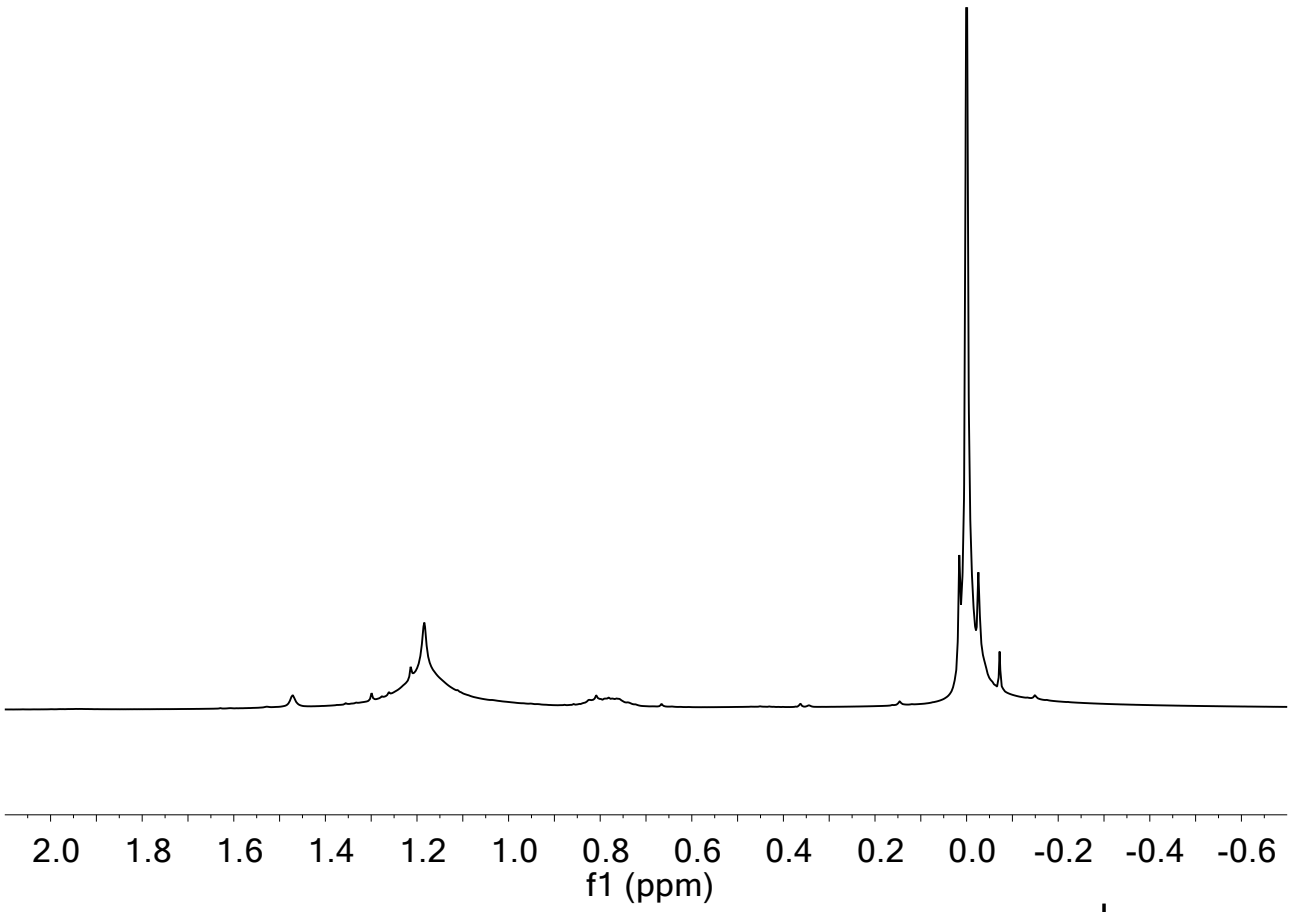


Figure S4. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_{15}\text{-}M_{69}}$]. The alkane peaks are broadened as a result of the relatively solubility of the material at room temperature.



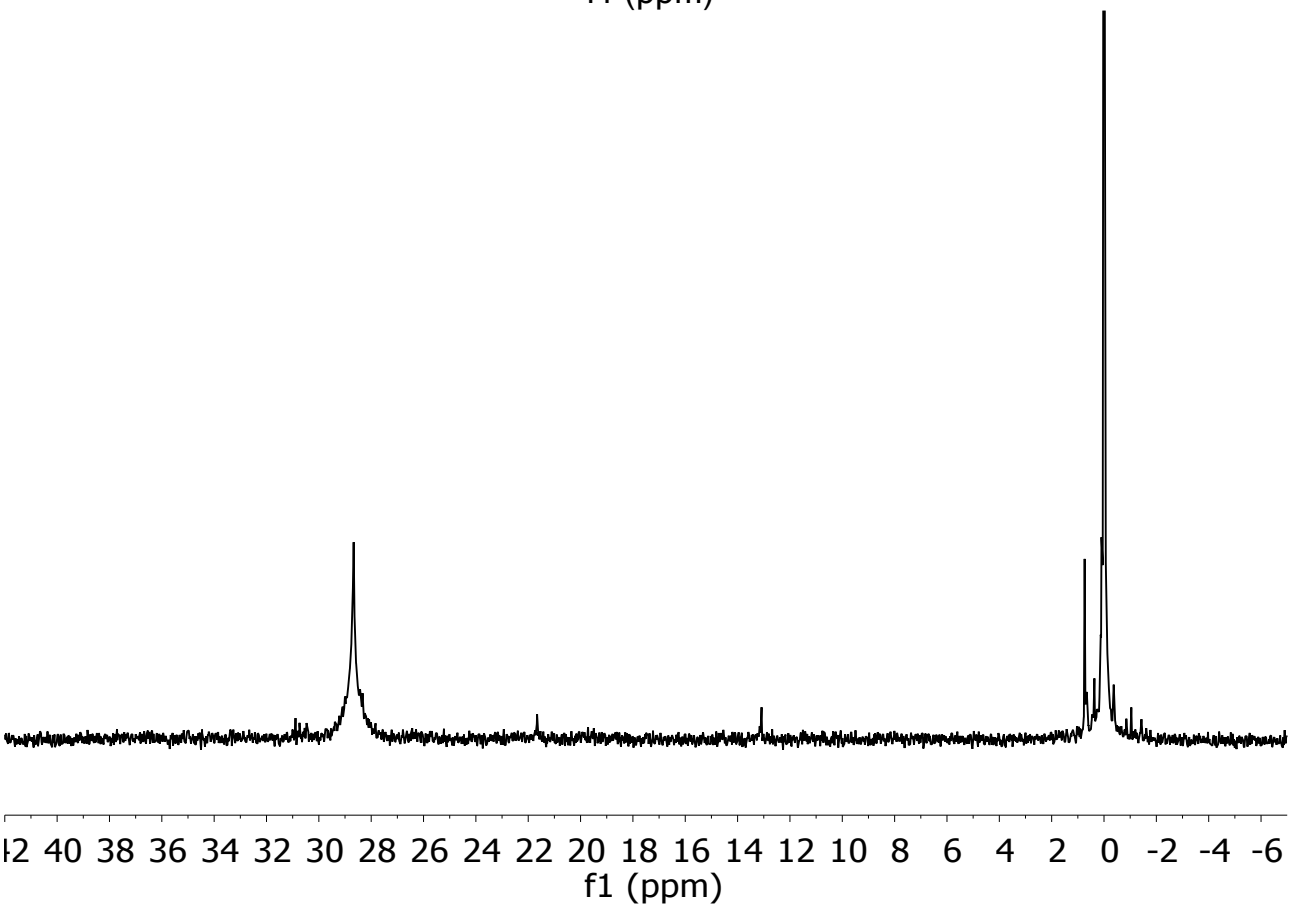


Figure S5. ^{1}H and ^{13}C NMR spectra of [$\mathbf{Si_{23}}$-$\mathbf{M_{69}}$]. The alkane peaks are broadened as a result of the relatively solubility of the material at room temperature.

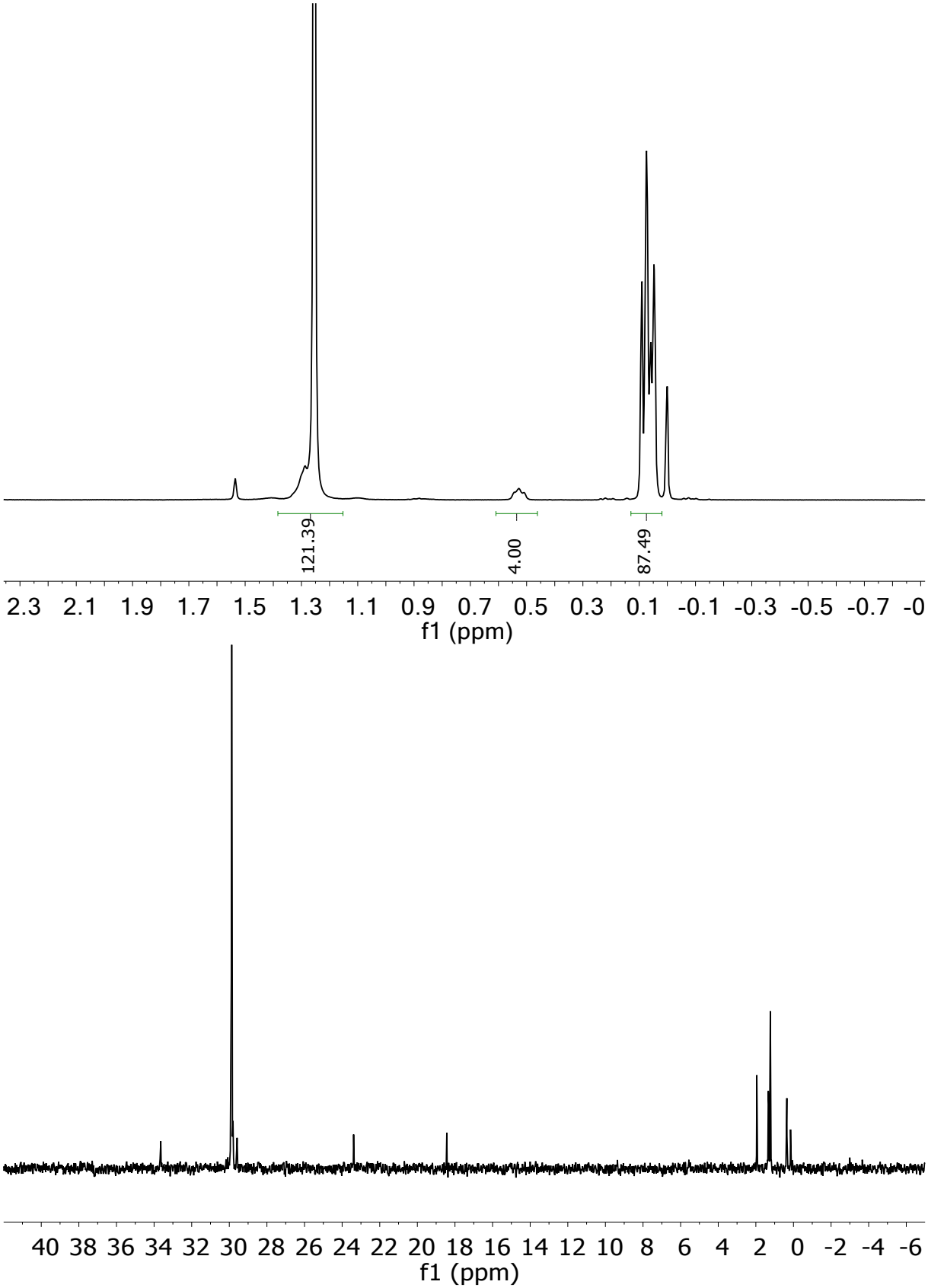


Figure S6. ^{1}H and ^{13}C NMR spectra of [**Si$_7$-M$_{66}$-Si$_7$**]. The peak at 1.56 ppm originates from a trace of water in the NMR solvent.

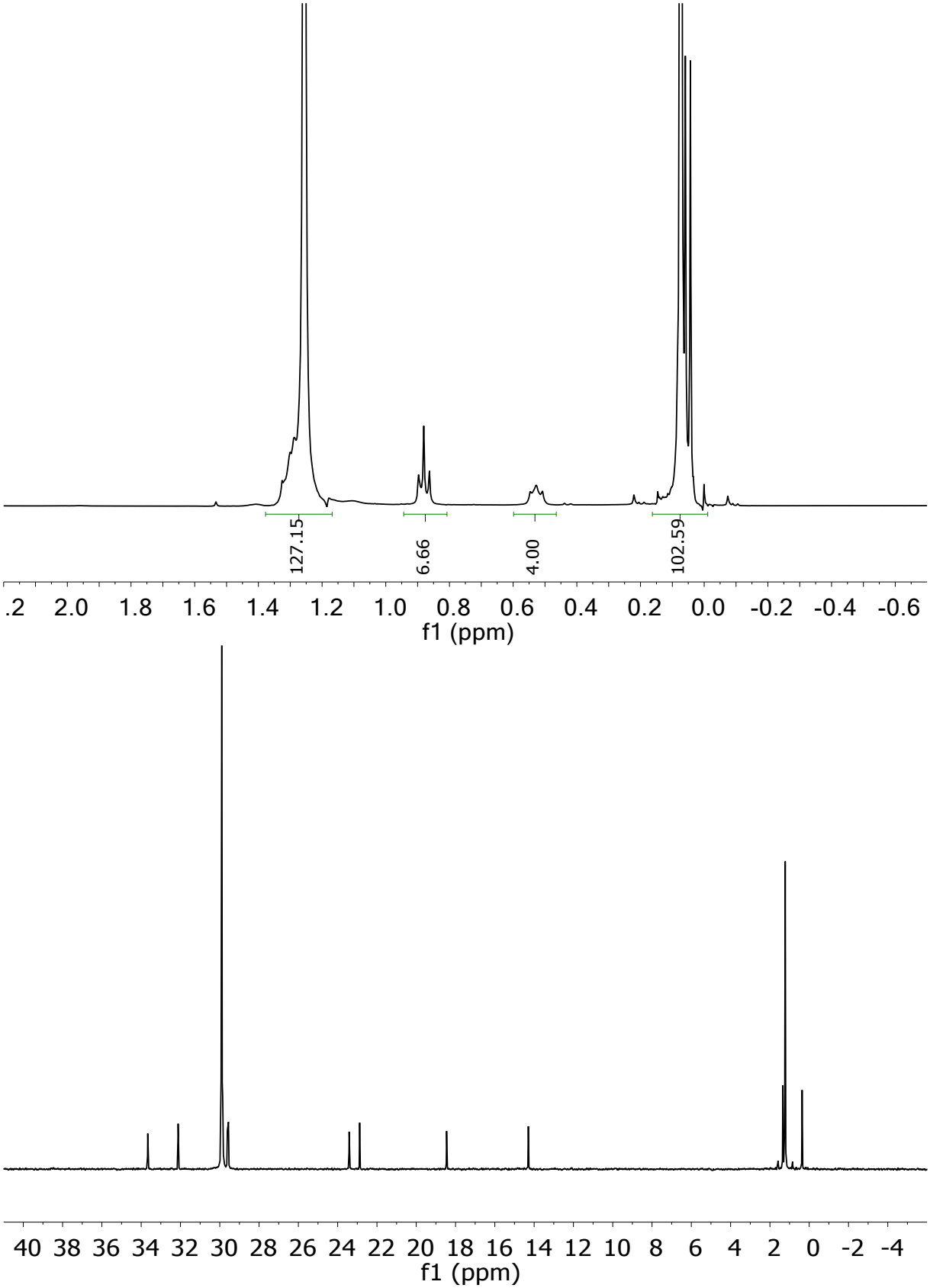


Figure S7. ^{1}H and ^{13}C NMR spectra of [$\mathbf{M_{33}\text{-}Si_{16}\text{-}M_{33}}$].

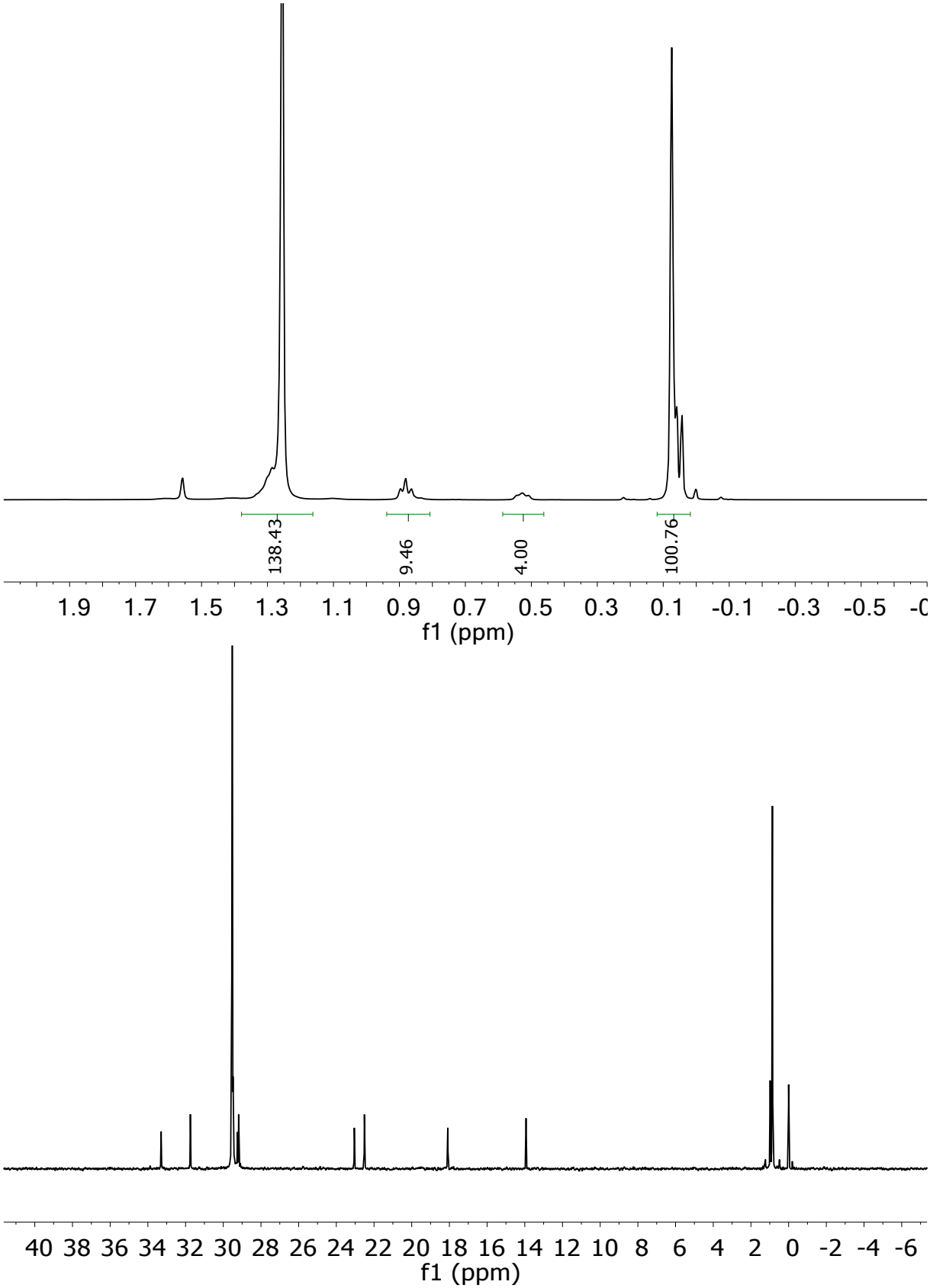


Figure S8. ^{1}H and ^{13}C NMR spectra of [$\mathbf{M_{22}\text{-}Si_{16}\text{-}M_{44}}$]. The peak at 1.56 ppm originates from a trace of water in the NMR solvent.

3. DSC tri-BCOs

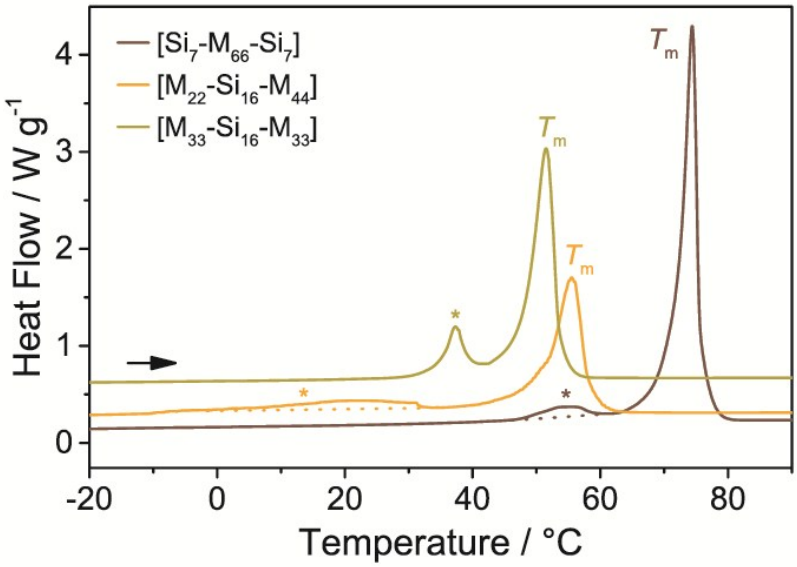


Figure S9. DSC traces (second cycle) for tri-BCOs. Endothermic heat flows have a positive value. The data are shifted vertically for clarity. Order–order transitions preceding the melting transition are indicated with an asterisk. As a guide to the eye, continuation of the baseline is provided as a dotted line under the OOTs of [**Si$_7$-M$_{66}$-Si$_7$**] and [**M$_{22}$-Si$_{16}$-M$_{44}$**]. A temperature ramp of 10 °C min^{-1} was used.

4. Additional VT-SAXS BCO [Si$_7$-M$_{33}$]

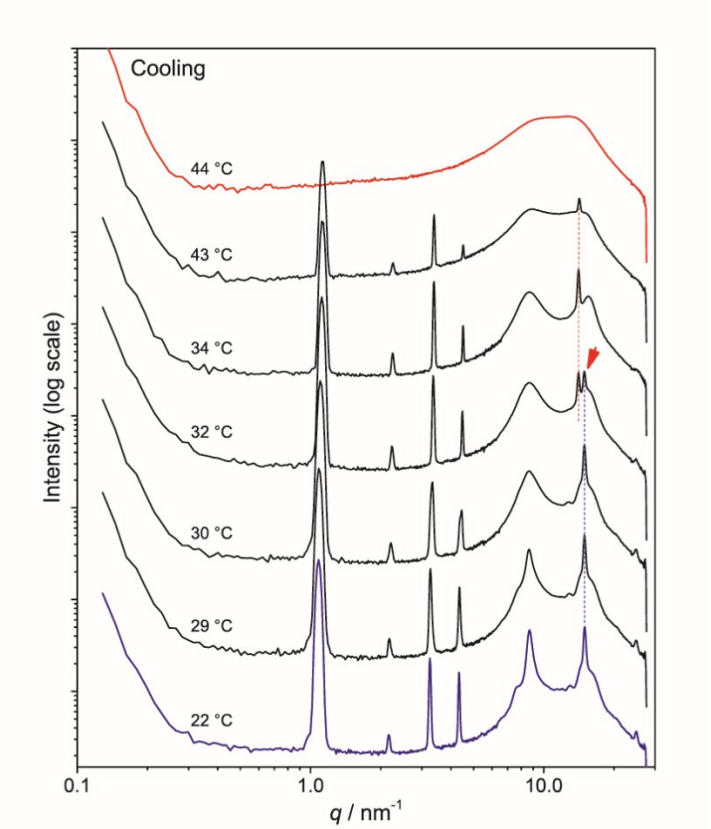


Figure S10. Reduced variable temperature transmission-SAXS data for [**Si$_7$-M$_{33}$**] upon cooling down from the isotropic state. The data are shifted vertically for clarity. Lowest and highest temperature data are plotted in blue and red, respectively. The blue and red, vertical, dashed lines follow the most intense alkane reflection in the WAXS region.

5. References

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