

Supplementary Information

Reading the mixture of uniform sequence defined macromolecules to increase data storage capacity

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1 Supplementary Methods

1.1 Materials

The following chemicals were used as received from the following suppliers unless otherwise noted: propionaldehyde **14l** (97% Merck), isobutyraldehyde **14c** (98%, Sigma-Aldrich), 3-methylbutyraldehyde **14g** ($\geq 98\%$, VWR), cyclohexanecarboxaldehyde **14j** (98%), heptanal **14b** ($\geq 95\%$, Sigma-Aldrich), octanal **14i** (99%, Sigma-Aldrich), dodecanal **14h** ($\geq 95\%$, VWR), 2-phenylpropanal **14e** (98%, Fisher Scientific), 4-chlorobutyric acid **TAG3** (99% Sigma-Aldrich), succinic anhydride **11** ($>99.0\%$, Sigma-Aldrich), 4-(dimethylamino)-pyridin **12** (DMAP) (99% Alfa Aesar), sodium sulfate **9** (Merck), 2,2,3,3,4,4-heptafluoro-1-butanol (98%, Alfa Aesar) **13**, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (97%, Alfa Aesar) **10**, acetaldehyde (99.5%, Fluka) **14f**, 2-ethylbutanal (98%, TCI) **14a**, nonanal (97%, Alfa Aesar), **14k**, tridecanal (96%, Alfa Aesar) **14d**, 11-aminoundecanoic acid **1** (97%, Sigma-Aldrich), benzyl alcohol **2** (99%, Sigma-Aldrich), thionyl chloride **3** (99%, Sigma-Aldrich), trimethyl orthoformate **5** (99%, Sigma-Aldrich), phosphoryl trichloride **8** (99%, Sigma-Aldrich), diisopropylamine **7** ($> 99.5\%$, Sigma-Aldrich), palladium on activated charcoal **16** (10% palladium basis, Sigma-Aldrich), hydrogen (99,999%, Air Liquide), TLC silica gel F₂₅₄ (Sigma-Aldrich), silica gel 60 (0.040 - 0.063, Sigma-Aldrich and Rocc), cerium(IV)-sulfate (99%, Sigma-Aldrich), phosphomolybdic acid hydrate (99%, Sigma-Aldrich), sodium carbonate (98%, Sigma-Aldrich), sodium hydrogen carbonate ($> 95\%$, Sigma-Aldrich), sodium sulfate ($> 99\%$, anhydrous, Sigma-Aldrich), magnesium sulfate ($\geq 99\%$, Carl Roth), DMSO-d₆ ($\geq 99.8\%$, Euriso-top), MeOH-d₄ ($\geq 99.8\%$, Euriso-top), CDCl₃ ($\geq 99.8\%$, Euriso-top), dichloromethane (DCM, HPLC grade $\geq 99.9\%$, Sigma-Aldrich), methanol (HPLC grade 99.8%, Acros Organics), tetrahydrofuran (THF, 99.5%, extra dry over molecular sieves, Acros Organics), ethanol (analytical reagent grade, Fisher Scientific), diethyl ether (analytical reagent grade, Fisher Scientific), cyclohexane (technical grade), ethyl acetate (technical grade). All solvents were used without further purification, unless otherwise noted. Water, when used in the synthesis, was de-ionised.

1.2 Instrumentation

NMR

^1H , ^{19}F and ^{13}C spectra were recorded at the Karlsruhe Institute of Technology (KIT, Germany) on a Bruker Avance 400 NMR instrument at 400 MHz for ^1H NMR, at 376 MHz for ^{19}F and 101 MHz for ^{13}C NMR. ^1H spectra were recorded on a Bruker Avance 300 NMR instrument at 300 MHz for ^1H NMR or on a Bruker AVANCE DRX at 500 MHz for ^1H NMR and 126 MHz for ^{13}C NMR. CDCl_3 or CD_3OD were used as solvents. Chemical shifts are presented in parts per million (δ) relative to the resonance signal at 7.26 ppm (^1H , CDCl_3) and 77.16 ppm (^{13}C , CDCl_3) or 3.31 ppm (^1H , CD_3OD) and 49.00 ppm (^{13}C , CD_3OD), respectively. The spin multiplicity and corresponding signal patterns were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, sext. = sextet, m = multiplet and br = broad signal. Coupling constants (J) are reported in Hertz (Hz). All measurements were recorded in a standard fashion at 25 °C unless otherwise stated. Full assignment of structures was aided by 2D NMR analysis (COSY, HSQC and HMBC). If isomers of a substance were observed, all species which could be assigned clearly were labelled with additional appendices (a, b, c. etc.). Hereby, the main isomer was labelled with the appendix “a”, the second isomer with appendix “b” and so on.

Size Exclusion Chromatography (SEC) measurements were performed on a SHIMADZU Size Exclusion Chromatography (SEC) system equipped with a SHIMADZU isocratic pump (LCYCLO20AD), a SHIMADZU refractive index detector (24°C) (RID-20A), a SHIMADZU autosampler (SIL-20A) and a VARIAN column oven (510, 50°C). For separation, a three-column setup was used with one SDV 3 μm , 8×50 mm precolumn and two SDV 3 μm , 1000 Å, 3×300 mm columns supplied by PSS, Germany. Tetrahydrofuran (THF) stabilized with 250 ppm butylated hydroxytoluene (BHT, $\geq 99.9\%$) supplied by SIGMA-ALDRICH was used at a flow rate of 1.0 mL min⁻¹. Calibration was carried out by injection of eight narrow polymethylmethacrylate (PMMA) standards ranging from 102 to 58300 kDa.

Orbitrap Electrospray-Ionisation Mass Spectrometry (ESI-MS) mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionisation source operating in the nebuliser assisted electrospray mode. The instrument was calibrated in the m/z -range 150-2000 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621, all from SIGMA-ALDRICH). A constant spray voltage of 3.5 kV, a dimensionless sheath gas of 6, and a sweep gas flow rate of 2 were applied. The capillary voltage and the S-lens RF level were set to 68.0 V and 320 °C, respectively. For the interpretation of the spectra, molecular peaks $[\text{M}]^+$, peaks of pseudo molecules $[\text{M}+\text{H}]^+$ and $[\text{M}+\text{Na}]^+$ characteristic fragment peaks are indicated with their mass to charge ratio (m/z) and their intensity in percent, relative to the most intense peak (100%).

Electron ionisation (EI) mass spectra were recorded on a Finnigan instrument, model MAT 90 (70 eV). 3-nitrobenzyl alcohol (3-NBA) was used as matrix. For the interpretation of the spectra, molecular peaks $[M]^+$, peaks of pseudo molecules $[M+H]^+$ and characteristic fragment peaks are indicated with their mass to charge ratio (m/z) and their intensity in percent, relative to the most intense peak (100%).

Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 instrument. The protonated molecule ion is expressed by the term: $[M+H]^+$ and $[M+Na]^+$

Infrared spectra (IR) were recorded on a Bruker Alpha-p instrument in a frequency range from 3998 to 374 cm^{-1} applying KBr and Attenuated Total Reflection (ATR) technology. IR (Type of measurement) ν / cm^{-1} = wave number (signal intensity, molecular oscillation assignment). The signal shape and intensity is reported relative to the signal of highest intensity and was abbreviated in the following pattern: br = brought, vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

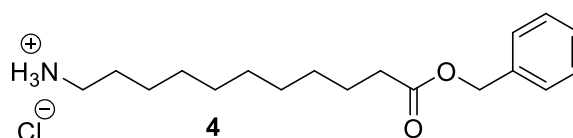
All **thin layer chromatography** experiments were performed on silica gel coated aluminium foil (silica gel 60 F₂₅₄, SIGMA-ALDRICH). Compounds were visualized by staining with Seebach-solution (mixture of phosphomolybdic acid hydrate, cerium(IV)-sulfate, sulfuric acid and water).

1.3 Experimental procedures

1.3.1 Synthesis of the monomer M1

1.3.1.1 Esterification

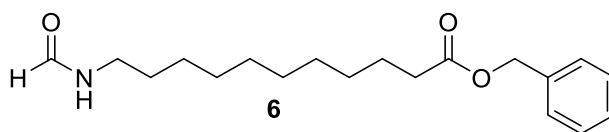
Monomer **M1** was synthesised according to the reported procedure from Meier *et al.*¹



In a 500 mL three necked flask 15.0 g 11-aminoundecanoic acid **1** (74.5 mmol, 1.00 eq.) were suspended in 75 mL THF and 96.7 g (895 mmol, 12.0 eq.) benzyl alcohol **2** were added. The suspension was cooled in an ice bath and subsequently 16.5 mL thionyl chloride **3** (27.1 g, 231 mmol, 3.10 eq.) were added dropwise at 0 °C. After addition of the thionyl chloride **3**, the solution was warmed to room temperature and stirred overnight. The yellow solution was then poured into 500 mL diethylether and stored in the freezer for one hour. The product was filtered off and dried under high vacuum. The 11-(benzyloxy)-11-oxoundecan-1-aminium chloride **4** was obtained as a white solid in a yield of 72.4% (17.6 g, 53.9 mmol).

¹H-NMR (300 MHz, CDO₃D): δ / ppm = 7.53 – 6.77 (m, 5 H, CH_{Ar}), 5.08 (s, 2 H, CH₂), 3.03 – 2.71 (m, 2 H, CH₂), 2.39 – 2.08 (m, 2 H, CH₂), 1.76 – 1.45 (m, 4 H, CH₂), 1.42 – 1.02 (m, 12 H, CH₂). ¹H-NMR was in accordance to the literature.¹

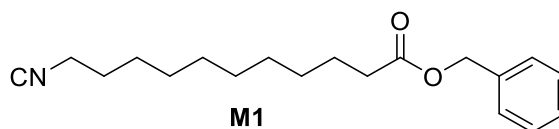
1.3.1.2 N-Formylation



In a 250 mL round bottom flask 17.6 g 11-(benzyloxy)-11-oxoundecan-1-aminium chloride **4** (53.9 mmol, 1.00 eq.) were dissolved in 58.9 mL trimethyl orthoformate **5** (57.2 g, 539 mmol, 10.0 eq.) and heated to 100 °C for 12 hours. Trimethyl orthoformate **5** was removed under reduced pressure and the product was used without further purification. The product **6** was obtained in quantitative yield (17.2 g, 53.9 mmol).

¹H-NMR (300 MHz, CDCl₃): δ / ppm = 8.01 (s, 1 H, CH), 7.38 – 7.08 (m, 5 H, CH_{Ar}), 5.03 (s, 2 H, CH₂), 4.52 (s, 1 H, NH), 3.31 – 3.18 (m, 2 H, CH₂), 2.26 (t, J = 7.6 Hz, 2 H, CH₂), 1.67 – 1.30 (m, 4 H, CH₂), 1.18 (s, 12 H, CH₂). ¹H-NMR was in accordance to the literature.¹

1.3.1.3 Dehydration

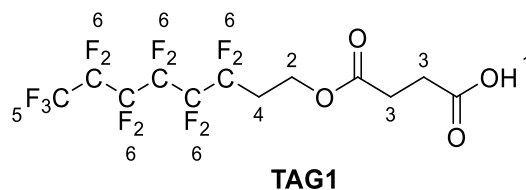


In a 500 mL three necked flask, 17.2 g of benzyl 11-formamidoundecanoate **6** (53.8 mmol, 1.00 eq.) were dissolved in 200 mL DCM, 24.7 mL diisopropylamine **7** (17.7 g, 167 mmol, 3.10 eq.) were added and the reaction mixture was cooled to 0 °C. Subsequently, 6.54 mL phosphorus oxychloride **8** (10.7 g, 69.9 mmol, 1.30 eq.) were added dropwise and the reaction mixture was then stirred at room temperature for two hours. The reaction was quenched by addition of sodium carbonate solution (20 %, 75 mL) at 0 °C. After stirring this mixture for 30 min, 50 mL water and 50 mL DCM were added. The aqueous phase was separated, and the organic layer was washed with water (3 × 80 mL) and brine (80 mL). The combined organic layers were dried over sodium sulfate **9** and the solvent was evaporated under reduced pressure. The crude product was then purified by column chromatography (hexane / ethyl acetate 19:1 → 8:1). The product monomer **M1** was obtained as slightly yellow oil in a yield of 57.1% (9.30 g, 30.8 mmol).

¹H-NMR (300 MHz, CDCl₃): δ / ppm = 7.47 – 7.03 (m, 5 H, CH_{Ar}), 5.00 (s, 2 H, CH₂), 3.24 (s, 2 H, CH₂), 2.33 – 2.13 (m, 2 H, CH₂), 1.62 – 1.47 (m, 4 H, CH₂), 1.36 – 1.31 (m, 12 H, CH₂). ¹H-NMR was in accordance to the literature.¹

1.3.2 TAG synthesis

1.3.2.1 TAG1 synthesis



In a 500 mL round bottom flask, 606 μ L 1*H*,1*H*,2*H*,2*H*-Perfluoro-1-octanol **10** (1.00 g, 2.75 mmol), 316 mg succinic anhydride **11** (3.16 mmol, 1.15 eq.) and 26.8 mg DMAP **12** (219 μ mol, 0.08 eq.) were dissolved in 6.00 mL DCM. After 2 days stirring at room temperature, the solution was washed with 10 % NaHSO₄ (ca. 15 mL) and 10 mL DCM. The aqueous phase was separated and washed with DCM (2 $\times$ 60 mL). The organic layer was washed with water (3 $\times$ 80 mL). The combined organic layers were dried over sodium sulfate **9** and the solvent was evaporated under reduced pressure. The product **TAG1** was obtained as a colourless solid in a yield of 83.7% (1.06 g, 2.30 mmol).

R_f = 0.48 in cyclohexane / ethyl acetate (2:1).

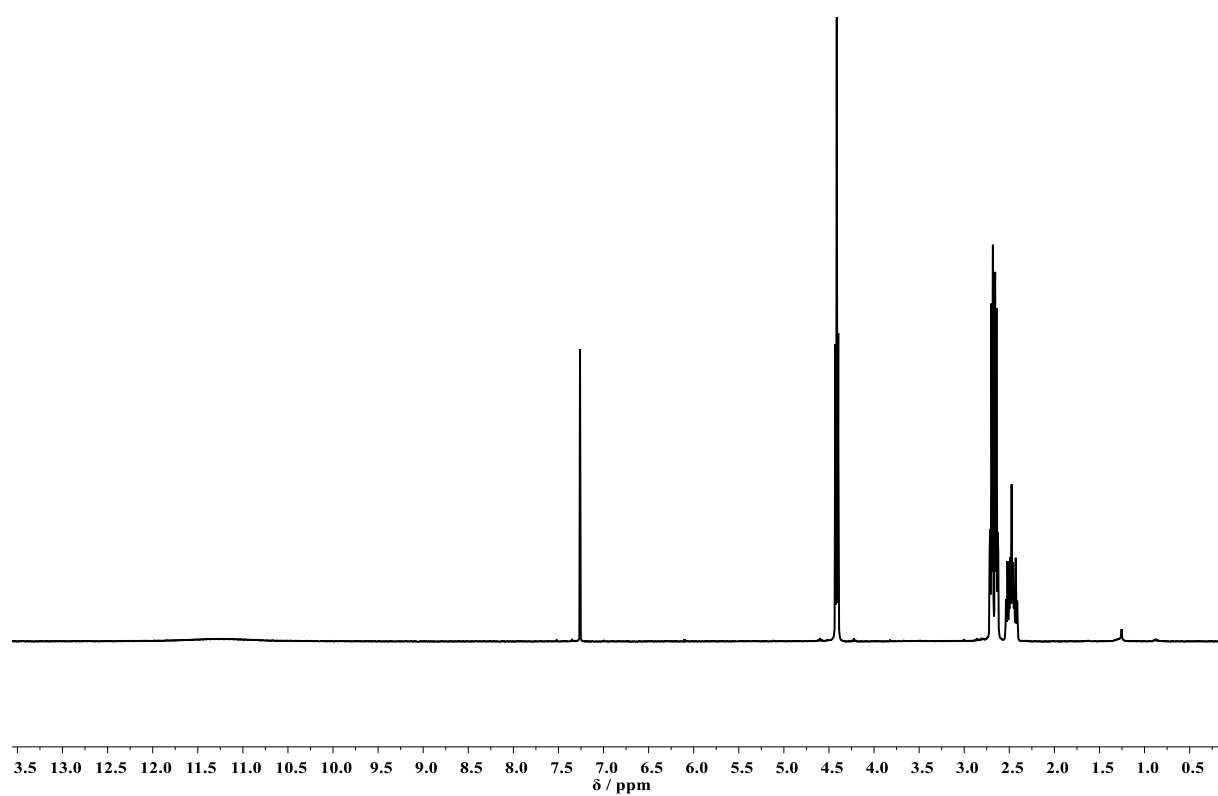
IR (ATR): ν / cm⁻¹ = 2971.4 (w), 1731.5 (vs), 1697.1 (vs), 1435.2 (w), 1405.6 (m), 1364.0 (s), 1173.0 (vs), 1137.5 (vs), 1080.8 (vs), 1022.1 (s), 947.0 (s), 871.5 (w), 834.0 (s), 781.1 (s), 734.2 (vs), 706.2 (vs), 646.5 (vs), 563.7 (s), 532.2 (s), 506.3 (m), 463.1 (m).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 11.25 (s, 1 H, OH¹), 4.41 (t, J = 6.5 Hz, 2 H, CH₂²), 2.76 – 2.59 (m, 4 H, CH₂³), 2.56 – 2.38 (m, 2 H, CH₂⁴).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 178.06, 171.82, 56.81, 30.60, 28.83, 28.79.

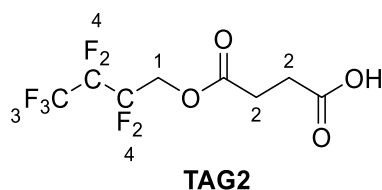
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -84.82 – -85.49 (m, 3 F, CF₃⁵), -117.80 – -118.24 (m, 2 F, CF₂⁶), 125.96 – -126.62 (m, 2 F, CF₂⁶), -126.68 – -127.49 (m, 2 F, CF₂⁶), -127.68 – -128.41 (m, 2 F, CF₂⁶), -130.13 – -130.91 (m, 2 F, CF₂⁶). Total integral of CF₂ region normalized with respect to the CF₃⁵ group = 10.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₁₂¹H₉¹⁶O₄¹⁹F₁₃, 465.0366; found, 465.0354, Δ = 1.2 mmu.



Supplementary Figure 1: ^1H -NMR of compound TAG1 measured in CDCl_3 .

1.3.2.2 TAG2 synthesis



In a 500 mL round bottom flask, 625 mL 2,2,3,3,4,4,4-heptafluoro-1-butanol **13** (1.00 g, 4.99 mmol, 1.00 eq.), 575 mg succinic anhydride **11** (5.75 mmol, 1.15 eq.) and 48.9 mg DMAP **12** (400 μ mol, 0.08 eq.) were dissolved in 6.00 mL DCM. After 2 days stirring at room temperature the solution was washed with 10 % NaHSO₄ (ca. 15 mL) and 10 mL DCM. The aqueous phase was separated and washed with DCM (2 $\times$ 60 mL). The organic layer was washed with water (3 $\times$ 80 mL). The combined organic layers were dried over sodium sulfate **9** and the solvent was evaporated under reduced pressure. The product **TAG2** was obtained as a colourless solid in a yield of 85.0% (1.28 g, 424 mmol).

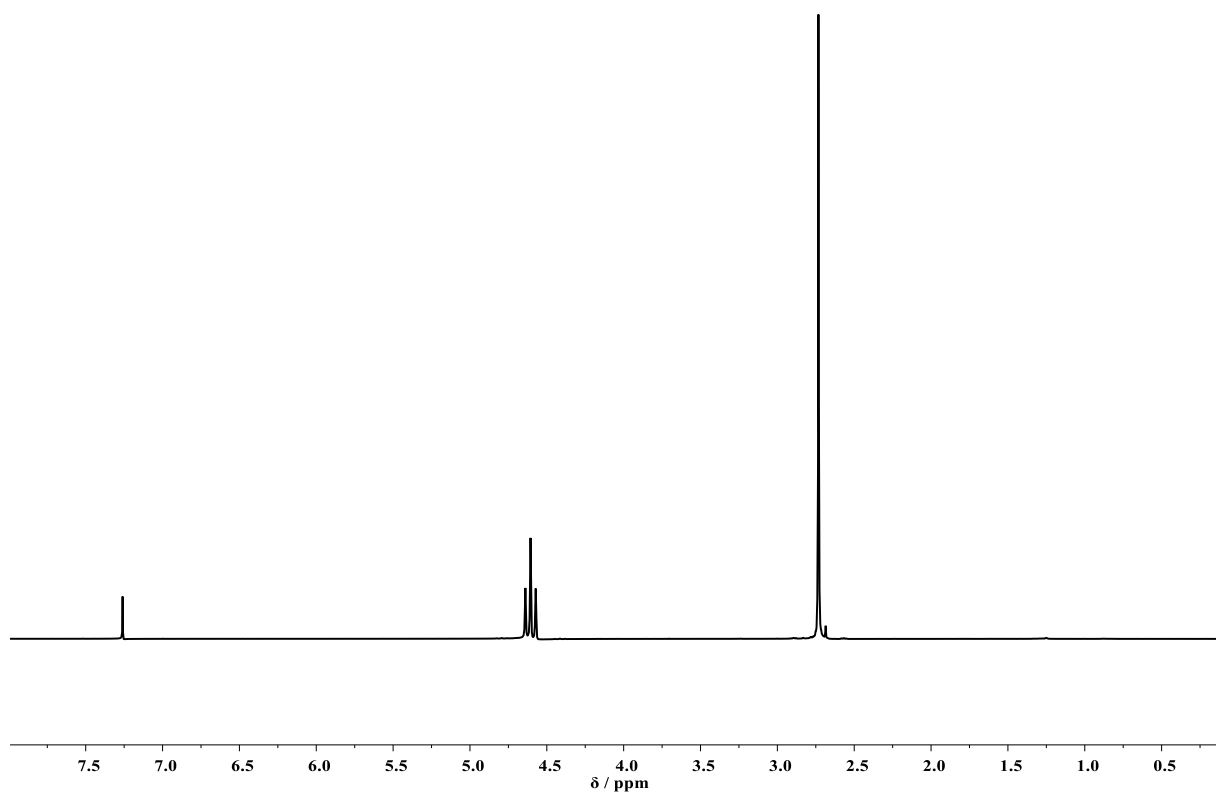
IR (ATR): ν/cm^{-1} = 2934.2 (w), 1749.3 (s), 1690.9 (s), 1454.2 (w), 1420.8 (m), 1400.3 (m), 1367.9 (m), 1350.8 (m), 1302.6 (m), 1280.5 (m), 1255.6 (s), 1223.6 (vs), 1175.1 (vs), 1143.5 (vs), 1120.4 (vs), 1030.1 (m), 1018.2 (m), 991.7 (s), 974.6 (m), 950.2 (s), 913.0 (vs), 846.3 (m), 780.6 (w), 733.2 (vs), 689.4 (m), 654.5 (w), 631.6 (w), 588.6 (w), 539.9 (s), 437.3 (w).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 4.76 – 4.39 (m, 2 H, CH₂¹), 2.73 (s, 4 H, CH₂²).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 177.97, 170.71, 59.67, 28.73, 28.47.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.27 (t, J = 9.7 Hz, 3 F, CF₃³), -123.85 – -126.58 (m, 2 F, CF₂⁴), -131.47 – -134.72 (m, 2 F, CF₂⁴). Total integral of CF₂ region normalized with respect to the CF₃³ group = 4.

ESI-MS [m/z]: [M + Na]⁺ calculated for ¹²C₈¹H₇¹⁶O₄¹⁹F₇, 323.0125; found, 323.0117, Δ = 0.8 mmu.

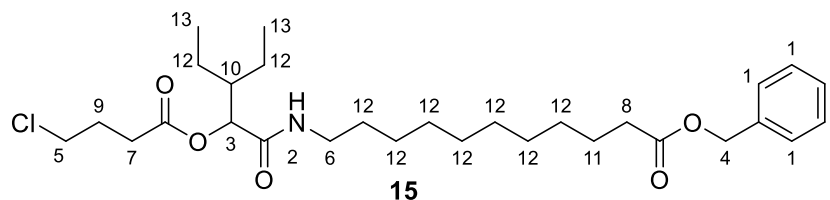


Supplementary Figure 2: ^1H -NMR of compound TAG2 measured in CDCl_3 .

1.3.3 Oligomer synthesis with TAG3

1.3.3.1 Synthesis of tetramer T1

Passerini reaction



In a 50 mL round bottom flask, 205 μ L 4-chlorobutyric acid **TAG3** (254 mg, 2.07 mmol, 1.00 eq.) was stirred in 2.00 mL DCM, subsequently 328 μ L 2-ethylbutanal **14a** (311 mg, 3.11 mmol, 1.50 eq.) and 936 mg of the monomer **M1** (3.11 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradient solvent mixture of ethyl acetate and cyclohexane (8:1 $\rightarrow$ 6:1) to yield product **15** as a yellow, highly viscous oil. (992 mg, 1.88 mmol, 90.8%).

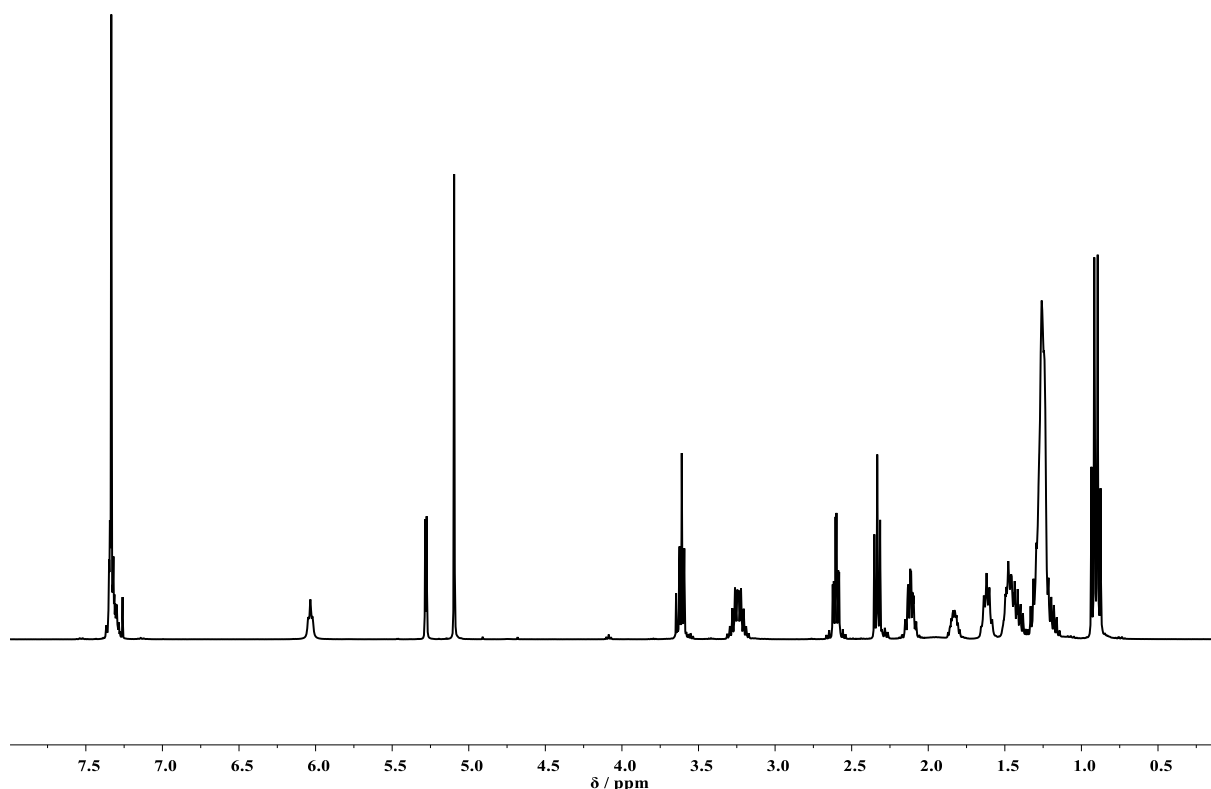
R_f: 0.52 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν / cm^{-1} = 3326.0 (vw), 2926.4 (m), 2854.3 (w), 1735.5 (vs), 1654.2 (s), 1531.1 (m), 1456.1 (m), 1379.6 (w), 1142.9 (s), 1004.2 (m), 785.6 (vw), 735.0 (m), 697.1 (m), 650.8 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.40 – 7.28 (m, 5 H, CH_{Ar}^1), 6.03 (t, J = 5.9 Hz, 1 H, NH^2), 5.28 (d, J = 3.8 Hz, 1 H, CH^3), 5.10 (s, 2 H, CH_2^4), 3.68 – 3.50 (m, 2 H, CH_2^5), 3.36 – 3.15 (m, 2 H, CH_2^6), 2.60 (td, J = 7.1, 2.5 Hz, 2 H, CH_2^7), 2.33 (t, J = 7.5 Hz, 2 H, CH_2^8), 2.18 – 2.07 (m, 2 H, CH_2^9), 1.88 – 1.77 (m, 1 H, CH^{10}), 1.69 – 1.33 (m, 2 H, CH_2^{11}), 1.53 – 1.13 (m, 18 H, CH_2^{12}), 0.95 – 0.86 (m, 6 H, CH_3^{13}).

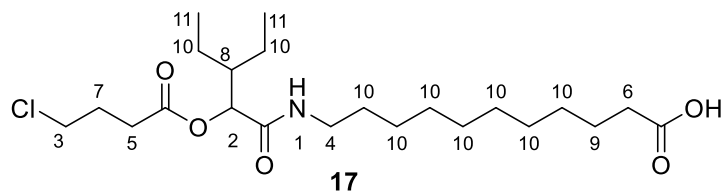
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.74, 171.58, 169.57, 136.21, 128.60, 128.22, 75.47, 66.12, 63.43, 44.02, 43.60, 39.32, 34.38, 31.17, 29.57, 29.49, 29.39, 29.26, 29.15, 26.91, 25.00, 22.33, 21.97, 11.67, 11.65.

ESI-MS [m/z]: [$\text{M}+\text{H}$] $^+$ calculated for $^{12}\text{C}_{29}^{1}\text{H}_{46}^{16}\text{O}_5^{14}\text{N}^{35}\text{Cl}$: 524.3137; found: 524.3126; Δ = 1.1 mmu.



Supplementary Figure 3: ^1H -NMR of compound **15** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 444 mg of the passerini product **15** (850 μmol , 1.00 eq.) were dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Afterwards, 99.0 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **17** was obtained as a pale highly viscous oil in a yield of 99.2% (365 mg, 843 μmol).

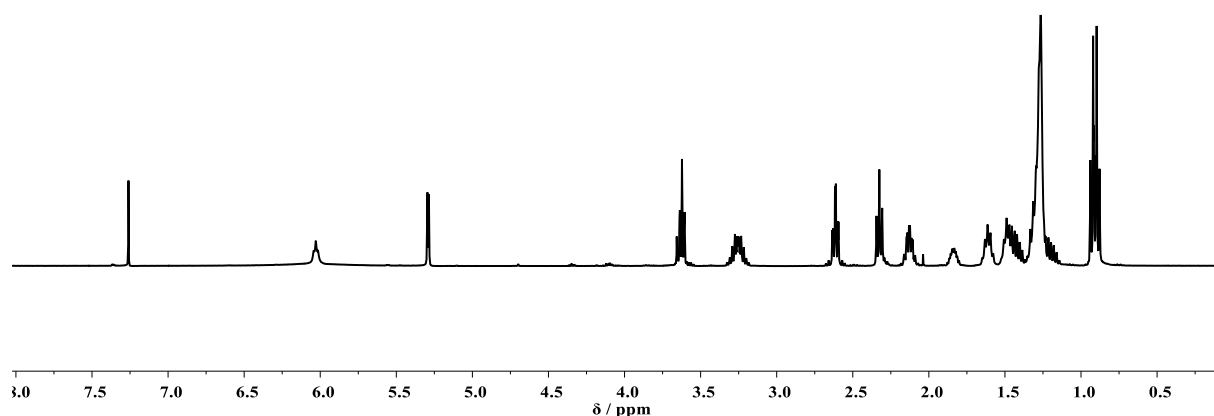
IR (ATR): ν/cm^{-1} = 3307.3 (w), 2926.2 (m), 2854.6 (w), 1736.9 (m), 1648.5 (m), 1535.7 (w), 1459.4 (w), 1379.7 (vw), 1175.9 (w), 1140.4 (w), 1047.1 (vw), 1006.5 (vw), 784.9 (vw), 722.2 (vw), 649.7 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 5.97 (t, J = 5.9 Hz, 1 H, NH^1), 5.23 (d, J = 3.8 Hz, 1 H, CH^2), 3.62 – 3.52 (m, 2 H, CH_2^3), 3.30 – 3.11 (m, 2 H, CH_2^4), 2.56 (td, J = 7.1, 2.3 Hz, 2 H, CH_2^5), 2.27 (t,

$J = 7.5$ Hz, 2 H, CH₂⁶), 2.13 – 2.01 (m, 2 H, CH₂⁷), 1.83 – 1.72 (m, 1 H, CH⁸), 1.60 – 1.51 (m, 2 H, CH₂⁹), 1.47 – 1.09 (m, 18 H, CH₂¹⁰), 0.91 – 0.79 (m, 6 H, CH₂¹¹).

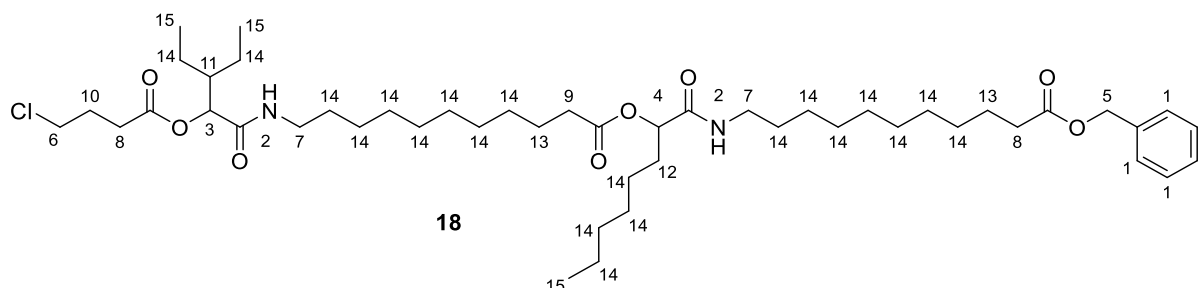
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 179.16, 171.69, 169.77, 75.53, 44.09, 43.62, 39.41, 34.18, 31.22, 29.57, 29.46, 29.36, 29.23, 29.10, 27.46, 26.92, 24.83, 22.35, 22.00, 11.71, 11.68.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₂₂¹H₄₀¹⁶O₅¹⁴N³⁵Cl, 434.2668; found, 434.2659, $\Delta = 0.9$ mmu.



Supplementary Figure 4: ¹H-NMR of compound 17 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 313 mg **17** (722 μ mol, 1.00 eq.) was stirred in 2.00 mL DCM, subsequently 151 μ L heptanal **14b** (124 mg, 1.08 mmol, 1.50 eq.) and 326 mg of the monomer **M1** (1.08 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto

celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 → 2:1) to yield the passerini product **18** as a yellow highly viscous oil. (533 mg, 630 μmol, 87.3%).

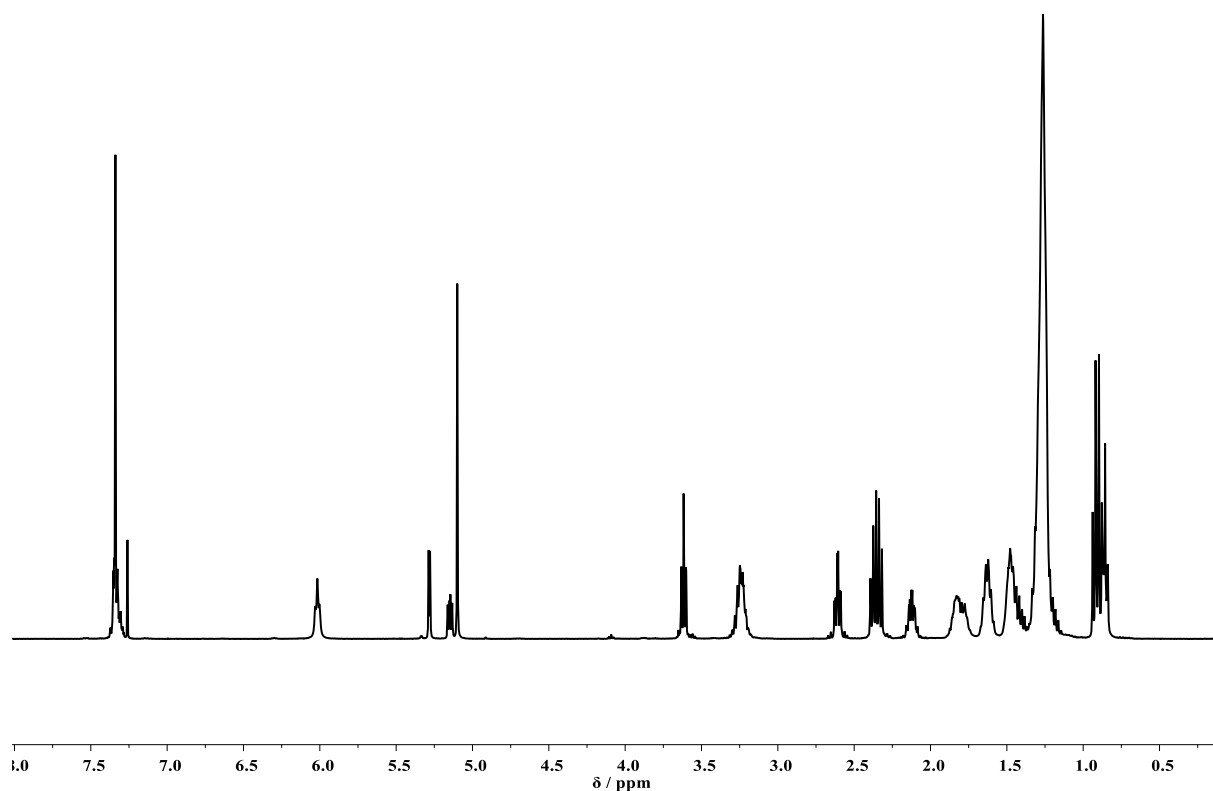
R_f: 0.20 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm⁻¹ = 3305.8 (vw), 2924.9 (s), 2854.1 (m), 1737.2 (vs), 1653.5 (s), 1533.8 (m), 1456.8 (m), 1377.3 (w), 1163.3 (s), 1005.5 (w), 732.4 (w), 696.8 (m), 651.4 (w).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.40 – 7.28 (m, 5 H, CH_{Ar}¹), 6.04 – 5.95 (m, 2 H, NH²), 5.28 (d, J = 3.8 Hz, 1 H, CH³), 5.18 – 5.12 (m, 1 H, CH⁴), 5.10 (s, 2 H, CH₂⁵), 3.62 (t, J = 6.2 Hz, 2 H, CH₂⁶), 3.33 – 3.17 (m, 4 H, CH₂⁷), 2.61 (td, J = 7.1, 2.7 Hz, 2 H, CH₂⁸), 2.41 – 2.30 (m, 4 H, CH₂⁹), 2.18 – 2.07 (m, 2 H, CH₂¹⁰), 1.90 – 1.74 (m, 3 H, CH¹¹, CH₂¹²), 1.68 – 1.57 (m, 4 H, CH₂¹³), 1.54 – 1.15 (m, 40H, CH₂¹⁴), 0.96 – 0.82 (m, 9 H, CH₃¹⁵).

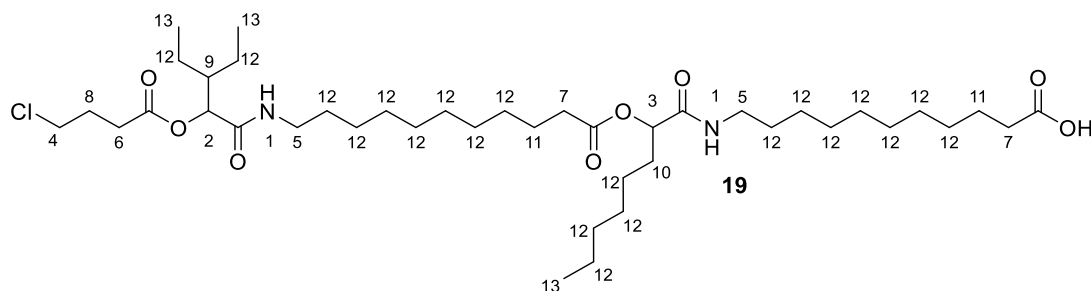
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.79, 172.57, 171.62, 169.96, 169.62, 136.23, 128.64, 128.27, 128.26, 75.52, 74.04, 66.17, 44.06, 43.64, 39.35, 39.30, 34.43, 32.02, 31.73, 31.20, 29.65, 29.62, 29.55, 29.45, 29.32, 29.28, 29.20, 27.46, 26.95, 26.94, 25.07, 25.04, 24.81, 22.63, 22.37, 22.01, 14.15, 11.70, 11.69.

ESI-MS [m/z]: [M+H]⁺ calculated for ¹²C₄₈¹H₈₁¹⁶O₈¹⁴N₂³⁵Cl: 849.5754; found: 849.5734; Δ = 2.0 mmu.



Supplementary Figure 5: ¹H-NMR of compound **18** measured in CDCl₃.

Deprotection



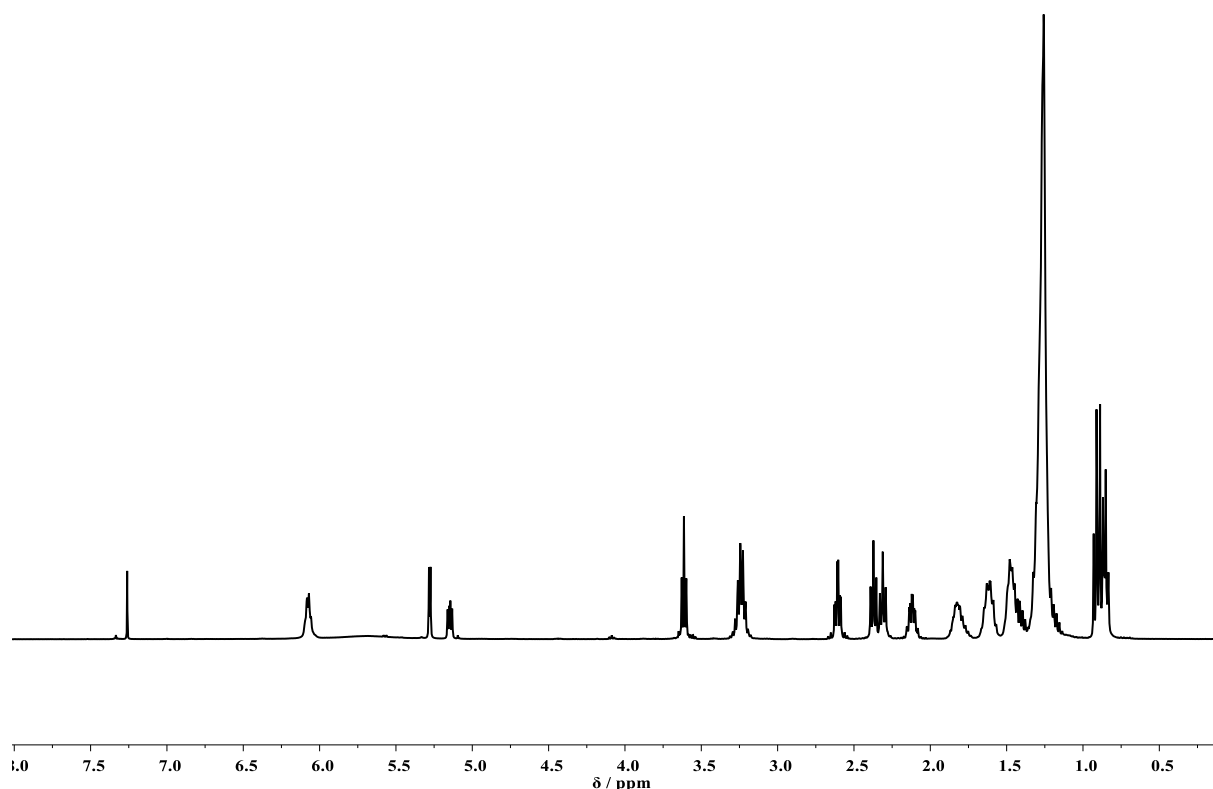
In a 50 mL round bottom flask, 474 mg of passerini product **18** (560 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 95.0 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **19** was obtained as a pale highly viscous oil in a yield of 96.2% (407 mg, 537 μmol).

IR (ATR): ν/cm^{-1} = 3307.0 (vw), 2924.9 (s), 2854.2 (m), 1738.8 (m), 1650.5 (m), 1536.4 (w), 1459.5 (w), 1376.3 (w), 1142.4 (m), 722.2 (vw), 643.9 (vw), 384.8 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.15 – 6.02 (m, 2 H, NH^1), 5.28 (d, J = 3.9 Hz, 1 H, CH^2), 5.21 – 5.10 (m, 1 H, CH^3), 3.61 (t, J = 6.1 Hz, 2 H, CH_2^4), 3.33 – 3.15 (m, 4 H, CH_2^5), 2.61 (td, J = 7.1, 2.8 Hz, 2 H, CH_2^6), 2.37 (t, J = 7.5 Hz, 2 H, CH_2^7), 2.31 (t, J = 7.5 Hz, 2 H, CH_2^7), 2.18 – 2.05 (m, 2 H, CH_2^8), 1.88 – 1.74 (m, 3 H, CH^9 , CH_2^{10}), 1.69 – 1.54 (m, 4 H, CH_2^{11}), 1.52 – 1.14 (m, 40 H, CH_2^{12}), 0.95 – 0.81 (m, 9 H, CH_3^{13}).

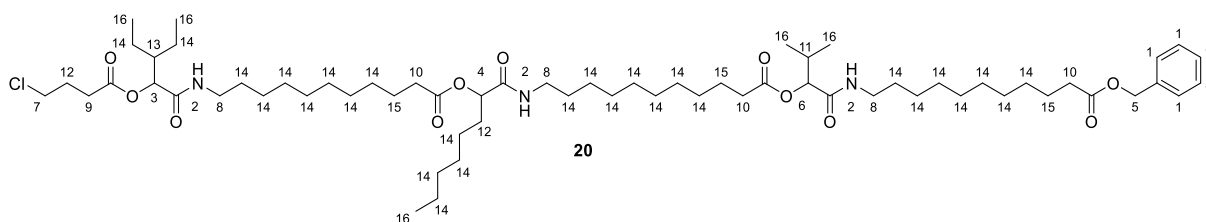
^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 178.33, 172.62, 171.70, 170.11, 169.81, 75.50, 74.03, 44.07, 43.59, 39.41, 39.31, 34.43, 34.16, 31.99, 31.72, 31.20, 29.58, 29.56, 29.47, 29.37, 29.33, 29.28, 29.25, 29.21, 29.12, 29.01, 27.45, 26.95, 26.89, 25.08, 24.88, 24.81, 22.63, 22.33, 21.97, 14.15, 11.67, 11.65.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{41}^{1}\text{H}_{75}^{16}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}$, 759.5285; found, 759.5267, Δ = 1.8 mmu.



Supplementary Figure 6: ^1H -NMR of compound **19** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 325 mg **19** (460 μmol , 1.00 eq.) was stirred in 4.00 mL DCM. Subsequently, 63.0 μL isobutyraldehyde **14c** (50.0 mg, 690 μmol , 1.50 eq.) and 210 mg of the monomer **M1** (690 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 2:1) to yield the passerini product **20** as a yellow highly viscous oil. (460 mg, 410 μmol , 89.1%).

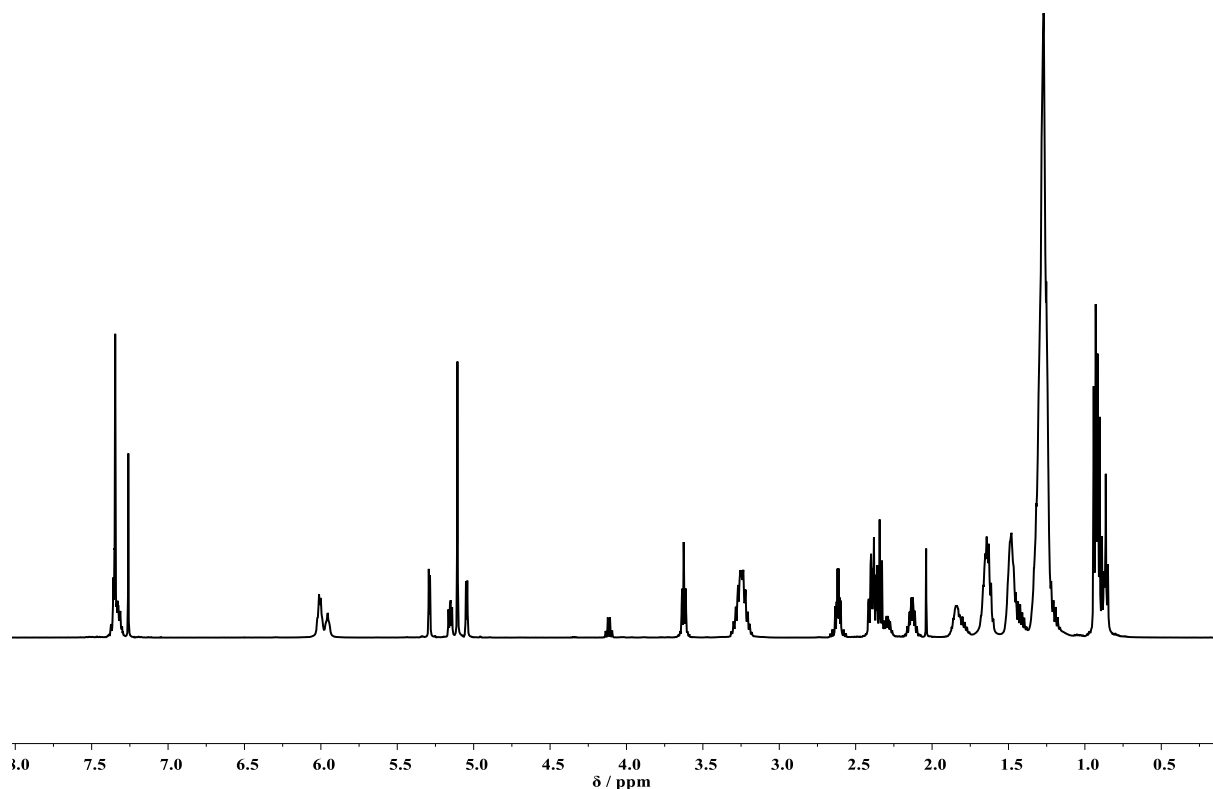
R_f: 0.13 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν / cm^{-1} = 3306.7 (vw), 2924.8 (s), 2853.8 (m), 1737.6 (vs), 1652.7 (vs), 1533.9 (m), 1458.0 (w), 1373.7 (w), 1162.4 (s), 1905.3 (w), 724.8 (w), 697.0 (w), 650.1 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.35 – 7.23 (m, 5 H, CH_{Ar}^1), 6.05 – 5.82 (m, 3 H, NH^2), 5.23 (d, J = 3.8 Hz, 1 H, CH^3), 5.12 – 5.05 (m, 1 H, CH^4), 5.04 (s, 2 H, CH_2^5), 4.98 (d, J = 4.4 Hz, 1 H, CH_2^6), 3.56 (t, J = 6.2 Hz, 2 H, CH_2^7), 3.27 – 3.09 (m, 6 H, CH_2^8), 2.55 (td, J = 7.1, 3.9 Hz, 2 H, CH_2^9), 2.39 – 2.18 (m, 7 H, CH^{10} , CH_2^{11}), 2.12 – 2.02 (m, 2 H, CH_2^{12}), 1.87 – 1.67 (m, 5 H, CH^{13} , CH_2^{14}), 1.66 – 1.51 (m, 6 H, CH_2^{15}), 1.48 – 1.08 (m, 54 H, CH_2^{14}), 0.91 – 0.77 (m, 15 H, CH_3^{16}).

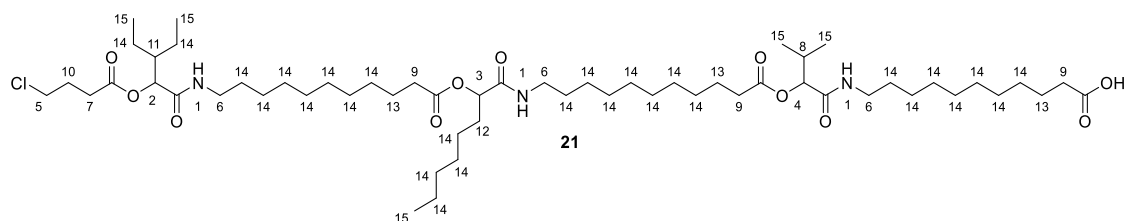
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.69, 172.60, 171.64, 170.00, 169.64, 169.39, 136.22, 128.66, 128.27, 78.03, 75.50, 74.03, 66.19, 60.52, 44.09, 43.63, 39.36, 39.29, 39.28, 34.43, 34.40, 32.02, 31.74, 31.20, 30.63, 29.69, 29.68, 29.63, 29.57, 29.55, 29.47, 29.47, 29.33, 29.32, 29.24, 29.21, 29.03, 27.46, 26.95, 26.93, 25.12, 25.08, 25.05, 24.82, 22.65, 22.35, 22.00, 21.18, 18.90, 17.07, 14.32, 14.17, 11.71, 11.70.

ESI-MS [m/z]: [$\text{M}+\text{Na}$] $^+$ calculated for $^{12}\text{C}_{64}^{1}\text{H}_{110}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}$: 1154.7721 found: 1154.7698; Δ = 2.3 mmu.



Supplementary Figure 7: ^1H -NMR of compound 20 measured in CDCl_3 .

Deprotection



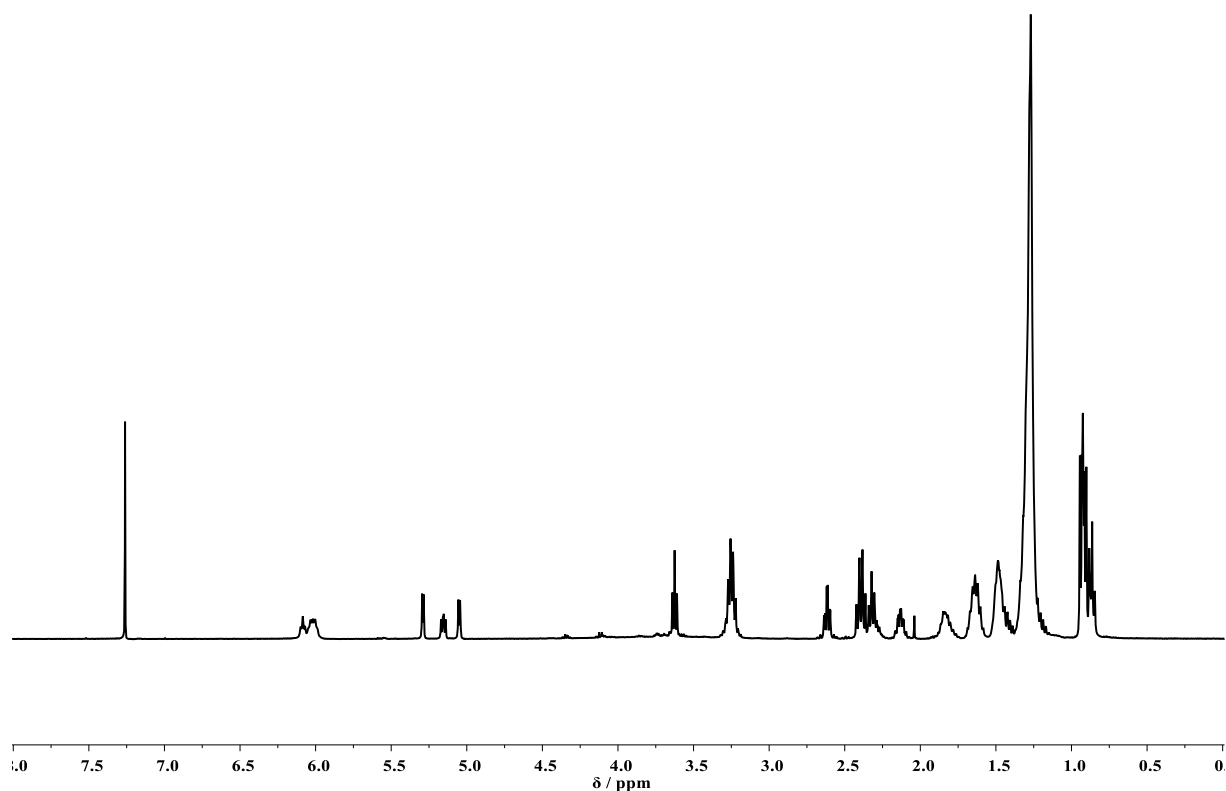
In a 50 mL round bottom flask, 400 mg of the passerini product **20** (353 μmol , 1.00 eq.) were dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Afterwards, 80.0 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **21** was obtained as a pale highly viscous oil in a yield of 98.6% (363 mg, 348 μmol).

IR (ATR): ν / cm^{-1} = 3305.7 (vw), 2924.5 (s), 2853.6 (m), 1738.3 (s), 1650.5 (s), 1536.1 (s), 1460.6 (m), 1371.4 (w), 1165.6 (s), 1008.1 (w), 722.1 (w), 650.1 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.08 (t, J = 5.9 Hz, 1 H, NH^1), 6.06 – 5.98 (m, 2 H, NH^1), 5.29 (d, J = 3.8 Hz, 1 H, CH^2), 5.18 – 5.13 (m, 1 H, CH^3), 5.05 (d, J = 4.5 Hz, 1 H, CH^4), 3.62 (t, J = 6.2 Hz, 2 H, CH_2^5), 3.34 – 3.18 (m, 6 H, CH_2^6), 2.62 (td, J = 7.1, 2.6 Hz, 2 H, CH_2^7), 2.44 – 2.25 (m, 7 H, $\text{CH}^8, \text{CH}_2^9$), 2.18 – 2.08 (m, 2, CH_2^{10}), 1.94 – 1.74 (m, 3 H, $\text{CH}^{11}, \text{CH}_2^{12}$), 1.71 – 1.57 (m, 6 H, CH_2^{13}), 1.37 – 1.14 (m, 54 H, CH_2^{14}), 0.98 – 0.82 (m, 15 H, CH_3^{15}).

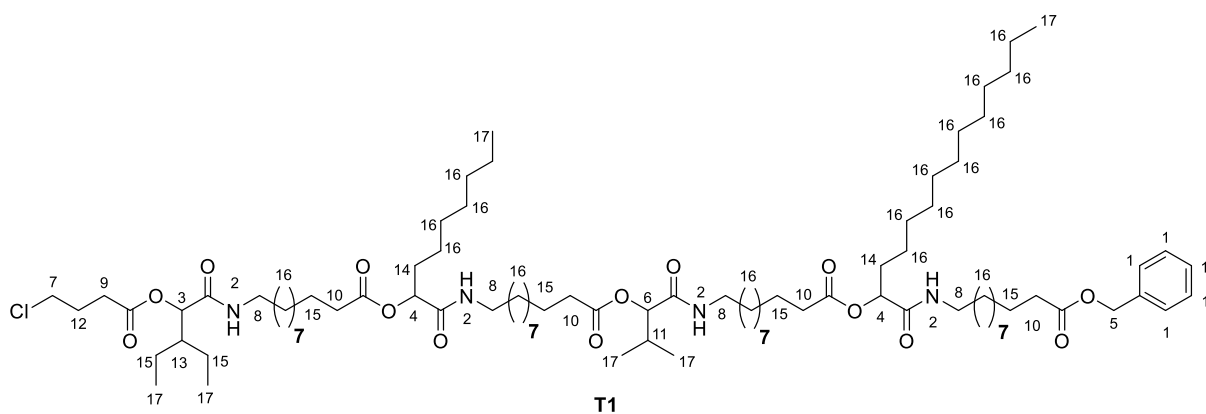
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 172.71, 172.70, 171.67, 170.17, 169.74, 169.49, 78.09, 75.55, 74.07, 44.10, 43.65, 39.41, 39.39, 39.27, 34.46, 34.44, 32.02, 31.76, 31.23, 30.62, 29.67, 29.62, 29.51, 29.48, 29.42, 29.37, 29.28, 29.23, 29.21, 29.10, 29.04, 27.49, 26.97, 26.90, 25.17, 25.10, 24.92, 24.85, 22.67, 22.39, 22.03, 18.92, 17.10, 14.18, 11.73.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{57}^{1}\text{H}_{104}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}$, 1042.7432; found, 1042.7412, Δ = 2.0 mmu.



Supplementary Figure 8: ^1H -NMR of compound **21** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 688 mg **21** (659 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 235 μL tridecanal (196 mg, 989 μmol , 1.50 eq.) and 298 mg of the monomer **M1** (989 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 1:1) to yield the passerini product **T1** as a yellow highly viscous oil. (981 mg, 635 μmol , 96.4%).

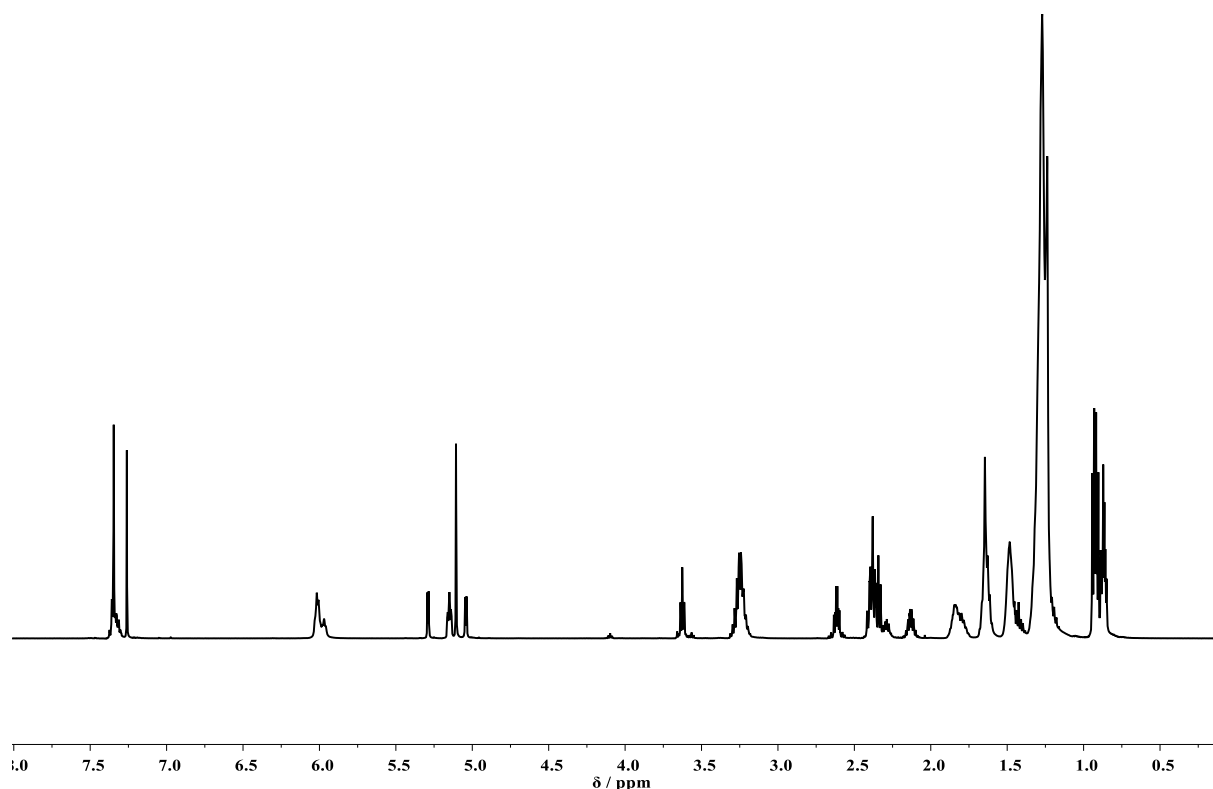
R_f: 0.75 in cyclohexane / ethyl acetate (1:1).

IR (ATR): ν / cm^{-1} = 3304.4 (vw), 2923.0 (s), 2852.8 (m), 1738.5 (s), 1653.1 (s), 1534.7 (m), 1458.5 (m), 1372.7 (w), 1163.1 (s), 1006.7 (w), 723.1 (w), 696.9 (w).

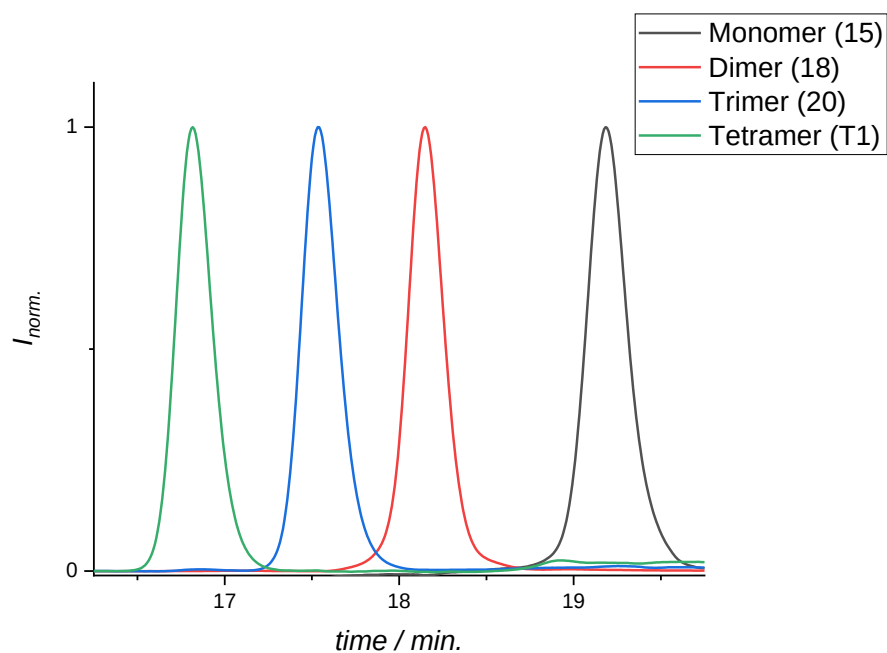
^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.43 – 7.29 (m, 5 H, CH_{Ar}^1), 6.08 – 5.93 (m, 4 H, NH^2), 5.29 (d, J = 3.8 Hz, 1 H, CH^3), 5.17 – 5.12 (m, 2 H, CH^4), 5.11 (s, 2 H, CH_2^5), 5.04 (d, J = 4.5 Hz, 1 H, CH^6), 3.63 (t, J = 6.2 Hz, 2 H, CH_2^7), 3.33 – 3.17 (m, 8 H, CH_2^8), 2.68 – 2.56 (m, 2 H, CH_2^9), 2.43 – 2.26 (m, 9 H, CH^{10} , CH_2^{11}), 2.18 – 2.08 (m, 2 H, CH_2^{12}), 1.91 – 1.74 (m, 5 H, CH^{13} , CH_2^{14}), 1.69 – 1.58 (m, 12 H, CH_2^{15}), 1.54 – 1.16 (m, 84 H, CH_2^{16}), 0.96 – 0.82 (m, 18 H, CH_3^{17}).

^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.82, 172.70, 172.61, 171.65, 169.99, 169.98, 169.64, 169.40, 136.25, 128.67, 128.30, 128.29, 78.05, 75.53, 74.07, 74.05, 66.20, 44.10, 43.65, 39.37, 39.31, 39.28, 34.45, 34.42, 32.05, 31.76, 31.22, 30.65, 29.80, 29.78, 29.76, 29.73, 29.69, 29.68, 29.65, 29.58, 29.50, 29.49, 29.39, 29.35, 29.33, 29.32, 29.31, 29.26, 29.24, 29.04, 27.47, 26.97, 26.96, 25.13, 25.09, 25.07, 24.89, 24.84, 22.82, 22.66, 22.38, 22.02, 18.92, 17.09, 14.26, 14.18, 11.73, 11.71.

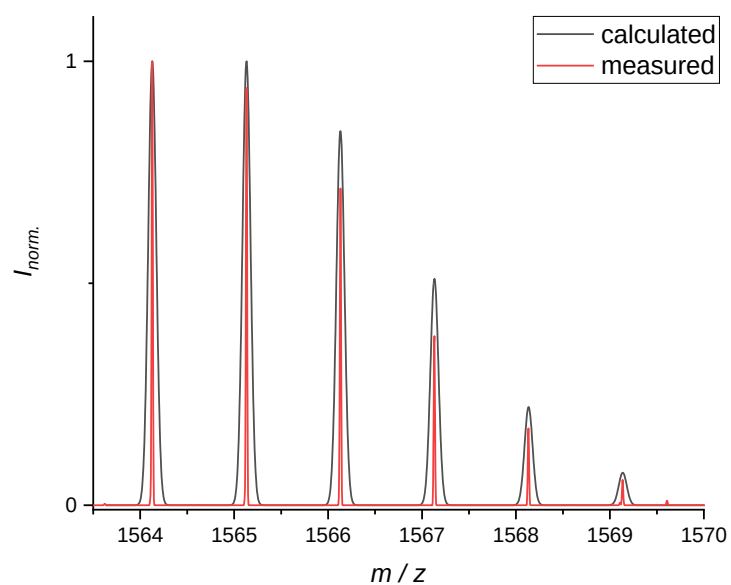
ESI-MS [m/z]: [$\text{M}+\text{Na}$] $^+$ calculated for $^{12}\text{C}_{89}^{1}\text{H}_{157}^{16}\text{O}_{14}^{14}\text{N}_4^{35}\text{Cl}$: 1564.1277; found: 1564.1282; Δ = 0.5 mmu.



Supplementary Figure 9: ^1H -NMR of compound T1 measured in CDCl_3 .



Supplementary Figure 10: SEC traces of the intermediates after each P3CR in the synthesis of product T1.



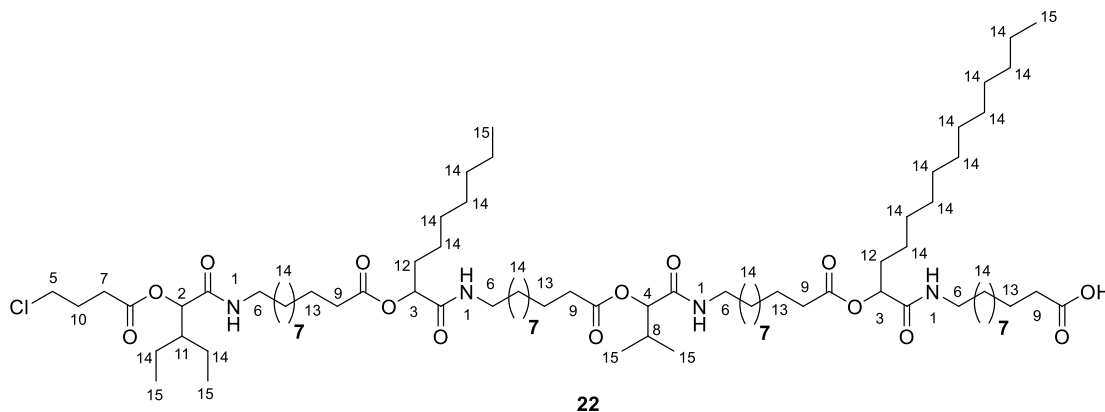
Supplementary Figure 11: High resolution ESI-MS measurement of T1. The observed isotopic pattern is compared with the calculated isotopic pattern from mMass (black).

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.csv, maximum is 1.000000 found for mass 1564.124010
matching mass 1564.12401
cutoff 0.50000: 0 solutions (12 peaks)
cutoff 0.25000: 0 solutions (35 peaks)
cutoff 0.12500: 0 solutions (74 peaks)
cutoff 0.06250: 0 solutions (144 peaks)
cutoff 0.03125: 0 solutions (229 peaks)
cutoff 0.01562: 0 solutions (326 peaks)
cutoff 0.00781: 1 solutions (467 peaks)
1564.12401  $\approx$  121.005630 + 311.246050 + 325.261700 + 283.214750 + 409.355600 + 91.054780 (sides 2-Ethylbutanal, Heptanal,
Isobutyraldehyde, Tridecanal; error -22.98550)
Press ENTER to quit ...
```

Supplementary Figure 12: Screenshot of the automated read-out of T1, sodium trifluoroacetate was used as additive during the measurement.

1.3.3.2 Synthesis of hexamer H1

Deprotection



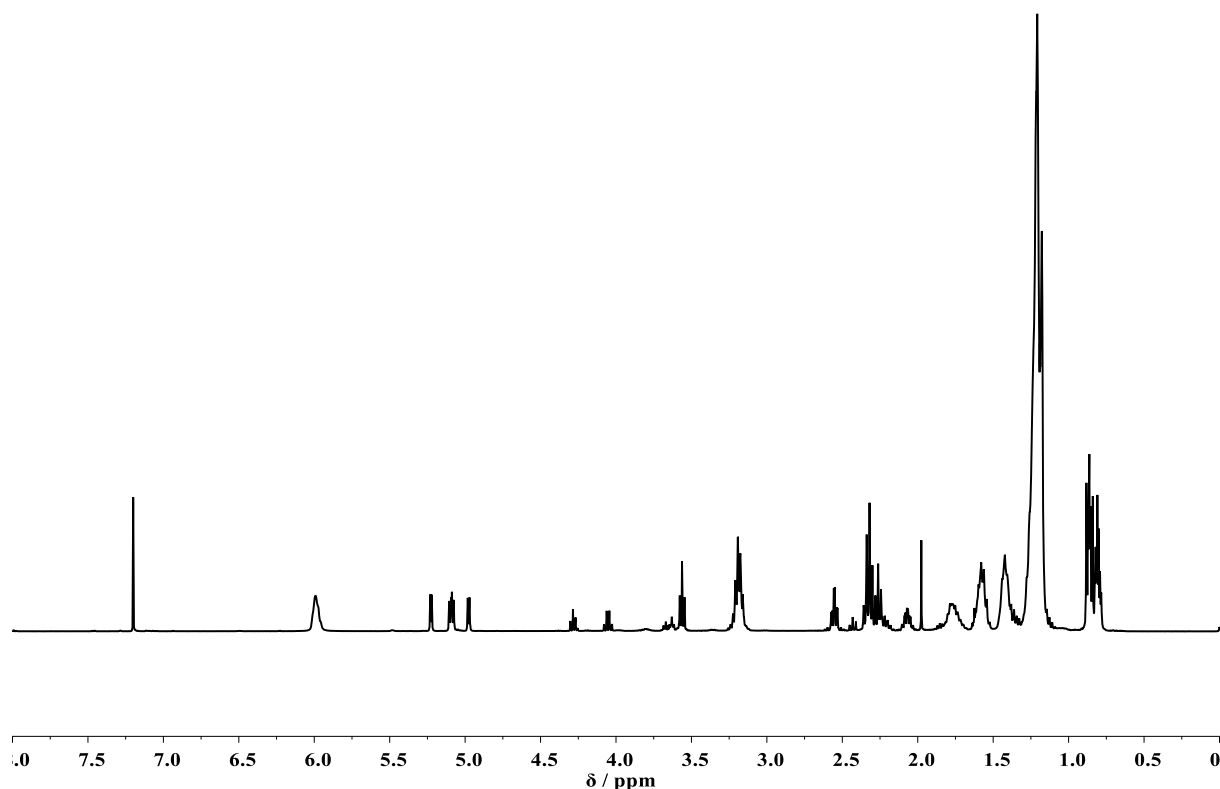
In a 25 mL round bottom flask, 874 mg of the passerini product **T1** (566 μmol , 1.00 eq.) was dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Subsequently, 174 mg (20 wt.-%) palladium on activated charcoal **16** were added to the solution. The resulting mixture was purged with hydrogen gas and stirred for one day at room temperature under hydrogen atmosphere (balloon). The crude reaction mixture was filtered over celite® and flushed with 50 mL dichloromethane. After evaporation of the solvents and drying under reduced pressure the corresponding acid **22** was obtained as a colorless solid. (806 mg, 555 μmol , 98.1%).

IR (ATR): ν/cm^{-1} = 3305.8 (vw), 2922.9 (vs), 2852.8 (s), 1739.6 (s), 1651.6 (s), 1536.8 (m), 1461.1 (m), 1371.7 (w), 1163.7 (s), 722.0 (w), 652.9 (w).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.14 – 5.98 (m, 4 H, NH^1), 5.29 (d, J = 3.8 Hz, 1 H, CH^2), 5.19 – 5.11 (m, 2 H, CH^3), 5.04 (d, J = 4.5 Hz, 1 H, CH^4), 3.62 (t, J = 6.2 Hz, 2 H, CH_2^5), 3.33 – 3.16 (m, 8 H, CH_2^6), 2.68 – 2.57 (m, 2 H, CH_2^7), 2.50 – 2.23 (m, 9 H, CH^8 , CH_2^9), 2.21 – 2.06 (m, 2 H, CH_2^{10}), 1.94 – 1.73 (m, 5 H, CH^{10} , CH_2^{12}), 1.73 – 1.56 (m, 8 H, CH_2^{13}), 1.57 – 1.17 (m, 88 H, CH_2^{14}), 0.98 – 0.82 (m, 18 H, CH_3^{15}).

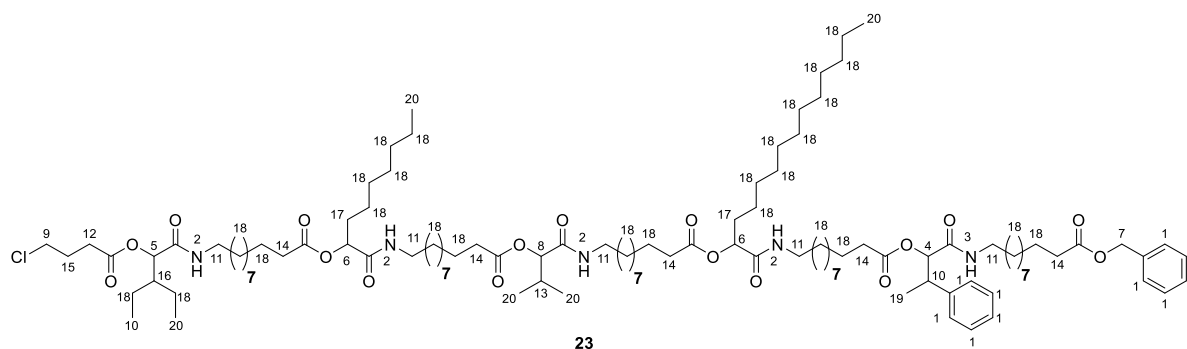
^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 177.00, 172.80, 172.63, 171.67, 170.11, 170.08, 169.72, 169.58, 78.08, 75.53, 74.09, 74.04, 44.09, 43.64, 39.39, 39.34, 39.30, 34.45, 34.41, 33.95, 32.04, 32.03, 32.01, 31.75, 31.22, 30.62, 29.79, 29.77, 29.75, 29.69, 29.67, 29.63, 29.60, 29.57, 29.50, 29.48, 29.44, 29.38, 29.35, 29.32, 29.25, 29.23, 29.10, 29.03, 27.48, 26.97, 26.94, 26.89, 25.12, 25.09, 24.91, 24.90, 24.84, 22.82, 22.66, 22.37, 22.01, 18.89, 17.11, 14.25, 14.17, 11.71, 11.70.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{82}\text{H}_{151}^{16}\text{O}_{14}^{14}\text{N}_4^{35}\text{Cl}$, 1452.0988; found, 1452.0990, Δ = 0.2 mmu.



Supplementary Figure 13: ^1H -NMR of compound **22** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask 752 mg **22** (518 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 104 μL 2-phenylpropionaldehyde **14e** (104 mg, 776 μmol , 1.50 eq.) and 234 mg of the monomer **M1** (776 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 1:1) to yield the passerini product **23** as a yellow highly viscous oil (911 mg, 482 μmol , 93.2%).

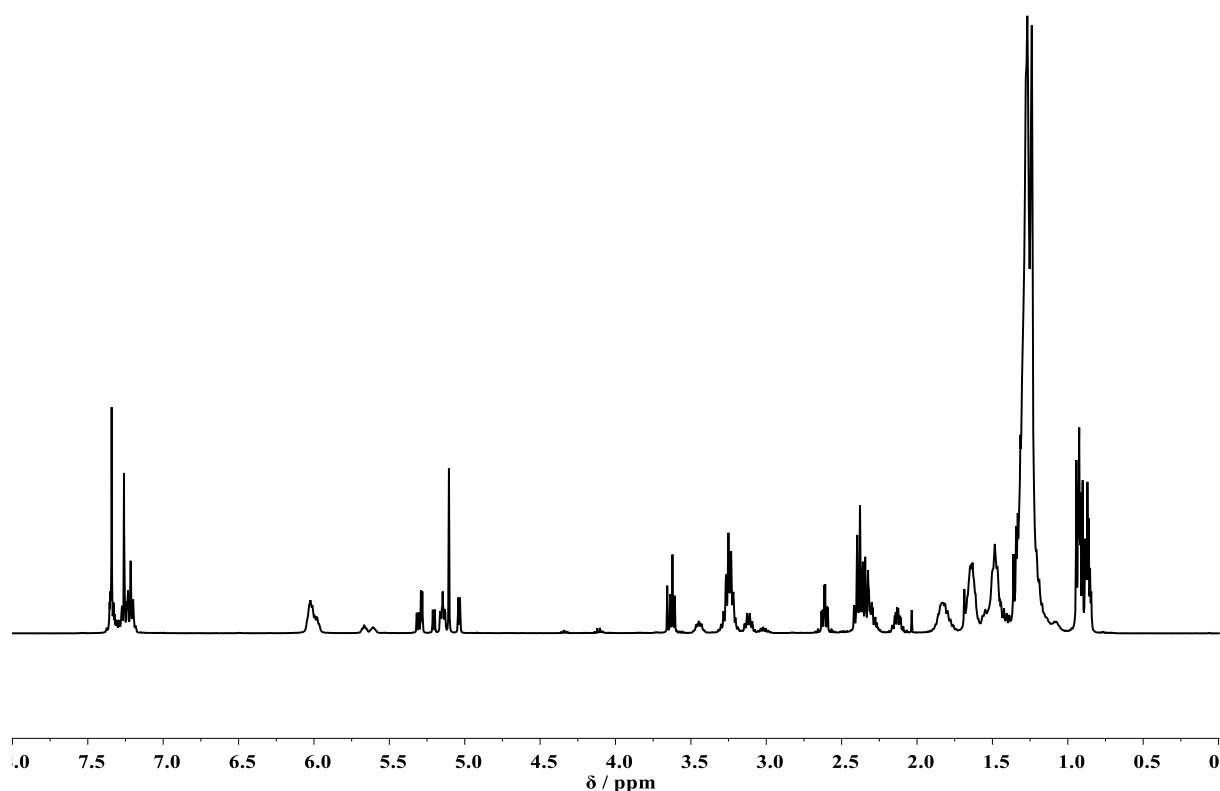
R_f: 0.41 in cyclohexane / ethyl acetate (3:2).

IR (ATR): $\nu / \text{cm}^{-1} = 3306.0$ (vw), 3087.6 (vw), 2923.2 (vs), 2853.0 (s), 2314.0 (vw), 2078.9 (vw), 1948.6 (vw), 1738.7 (vw), 1652.5 (vs), 1534.6 (s), 1456.2 (m), 1373.7 (w), 1231.6 (m), 1161.3 (s), 1107.7 (m), 1005.2 (w), 722.3 (w), 698.6 (m), 653.3 (w), 537.7 (vw), 429.7 (vw), 400.4 (vw).

^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 7.44 - 7.16$ (m, 10 H, CH_{Ar}^1), 6.12 – 5.93 (m, 4 H, NH^2), 5.67 (t, $J = 5.9$ Hz, 0.5 H, NH^{3a}), 5.64 – 5.58 (m, 0.5 H, NH^{3b}), 5.31 (d, $J = 5.4$ Hz, 0.5 H, CH^{4a}), 5.29 (d, $J = 3.8$ Hz, 1 H, CH^5), 5.21 (d, $J = 5.4$ Hz, 0.5 H, CH^{4b}), 5.17 – 5.12 (m, 2 H, CH^6), 5.10 (s, 2 H, CH_2^7), 5.04 (d, $J = 4.4$ Hz, 1 H, CH^8), 3.75 – 3.53 (m, 1 H, CH^9), 3.50 – 3.39 (m, 10 H, CH_2^{10}), 3.34 – 2.95 (m, 2 H, CH_2^{11}), 2.69 – 2.55 (m, 2 H, CH_2^{12}), 2.52 – 2.22 (m, 11 H, CH^{13} , CH_2^{14}), 2.20 – 2.06 (m, 2 H, CH_2^{15}), 1.96 – 1.72 (m, 5 H, CH^{16} , CH_2^{17}), 1.72 – 1.04 (m, 115 H, CH_2^{18} , CH_3^{19}), 0.97 – 0.82 (m, 18 H, CH_3^{20}).

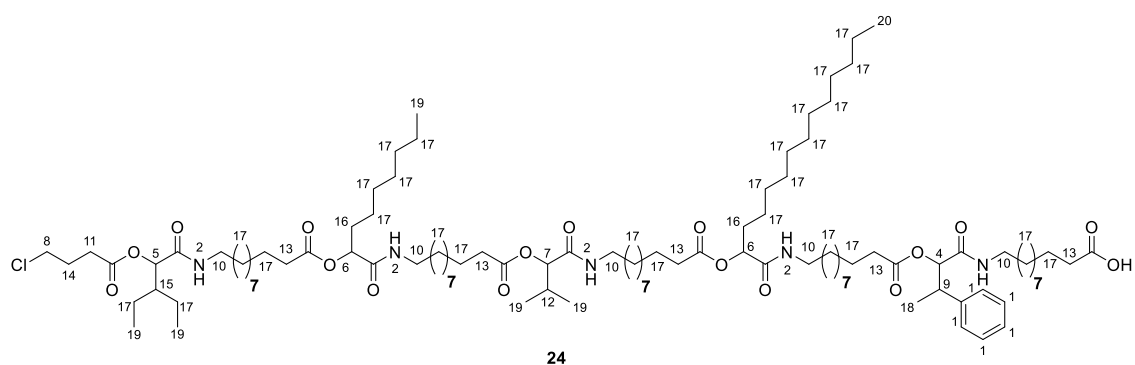
^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 173.79, 172.69, 172.60, 172.43, 171.63, 169.98, 169.61, 169.38, 168.82, 168.61, 141.73, 141.20, 136.26, 128.66, 128.52, 128.31, 128.30, 128.29, 127.97, 127.12, 127.05, 78.06, 77.86, 75.54, 74.06, 66.19, 44.08, 43.66, 41.58, 41.30, 39.36, 39.30, 39.28, 39.21, 34.45, 34.41, 34.35, 34.30, 32.04, 31.75, 31.22, 30.64, 29.79, 29.77, 29.74, 29.70, 29.67, 29.65, 29.58, 29.52, 29.51, 29.47, 29.38, 29.34, 29.33, 29.32, 29.24, 29.18, 29.16, 29.03, 27.48, 26.96, 29.65, 26.87, 26.80, 25.13, 25.09, 25.07, 24.98, 24.91, 24.84, 22.81, 22.65, 22.39, 22.03, 18.91, 17.63, 17.10, 15.34, 14.25, 14.17, 11.72, 11.71.$

ESI-MS [m/z]: [$\text{M}+\text{H}$] $^+$ calculated for $^{12}\text{C}_{110}^{1}\text{H}_{188}^{16}\text{O}_{17}^{14}\text{N}_5^{35}\text{Cl}$: 1887.3762; found 1887.3793; $\Delta = 3.1$ mmu.



Supplementary Figure 14: ^1H -NMR of compound **23** measured in CDCl_3 .

Deprotection



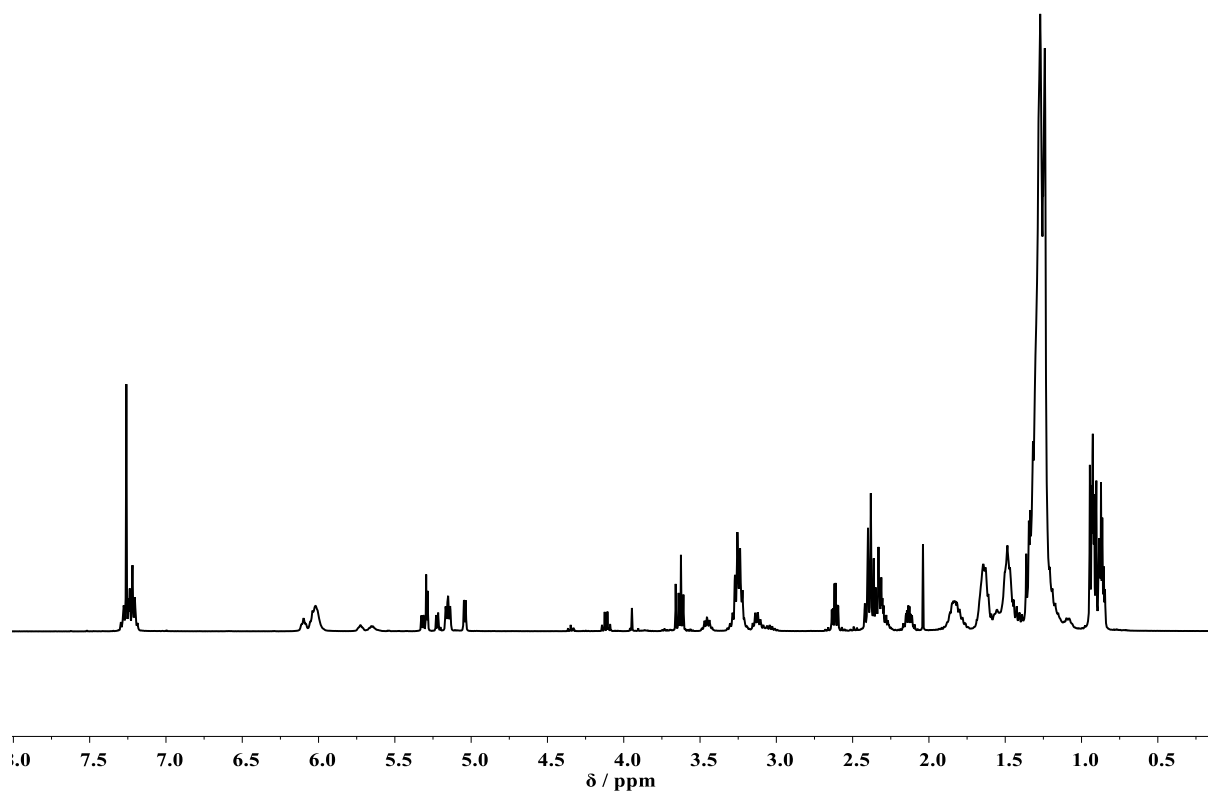
In a 50 mL round bottom flask, 718 mg of **24** (414 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 156 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **24** was obtained as a high viscous oil in a yield of 99.3% (739 mg, 411 μmol).

IR (ATR): ν / cm^{-1} = 3305.9 (vw), 3085.2 (vw), 2923.4 (vs), 2853.1 (s), 2075.0 (vw), 1739.2 (s), 1460.2 (m), 1373.3 (w), 1237.3 (m), 1162.2 (s), 1106.6 (m), 1021.1 (w), 923.9 (vw), 761.0 (vw), 721.2 (w), 699.8 (m), 653.9 (w), 538.2 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.34 – 7.15 (m, 5 H, CH_{Ar}^1), 6.15 – 5.94 (m, 4 H, NH^2), 5.76 – 5.59 (m, 1 H, NH^3), 5.34 – 5.27 (m, 0.5 H, 1 H, CH^{4a} , CH^5), 5.22 (d, J = 5.5 Hz, 0.5 H, CH^{4b}), 5.18 – 5.12 (m, 2 H, CH^6), 5.04 (d, J = 4.5 Hz, 1 H, CH^7), 3.67 – 3.59 (m, 2 H, CH_2^8), 3.52 – 3.40 (m, 1 H, CH^9), 3.35 – 2.97 (m, 10 H, CH_2^{10}), 2.68 – 2.56 (m, 2 H, CH_2^{11}), 2.44 – 2.23 (m, 11 H, CH^{12} , CH_2^{13}), 2.18 – 2.08 (m, 2 H, CH_2^{14}), 1.93 – 1.73 (m, 5 H, CH^{15} , CH_2^{16}), 1.71 – 1.04 (m, 115 H, CH_2^{17} , CH_3^{18}), 0.99 – 0.82 (m, 18 H, CH_3^{19}).

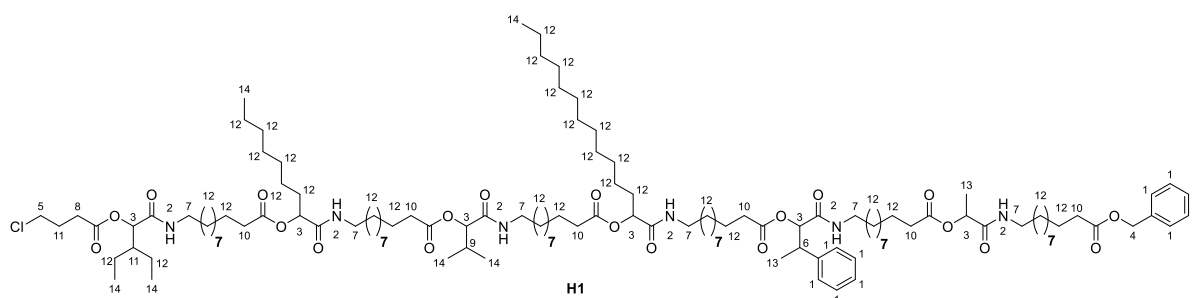
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 176.41, 172.74, 172.71, 172.63, 171.66, 170.07, 169.69, 169.51, 168.71, 141.19, 128.53, 128.33, 127.98, 127.14, 127.07, 78.07, 77.87, 75.55, 74.08, 74.06, 44.09, 43.66, 41.56, 41.26, 39.39, 39.34, 39.33, 39.26, 39.17, 34.46, 34.42, 34.41, 34.36, 34.24, 33.87, 32.05, 31.76, 31.23, 30.65, 29.80, 29.78, 29.76, 29.72, 29.68, 29.65, 29.59, 29.49, 29.39, 29.36, 29.33, 29.27, 29.24, 29.20, 29.14, 29.08, 29.04, 27.49, 26.97, 26.78, 26.71, 25.14, 25.10, 24.92, 24.91, 24.85, 22.82, 22.67, 22.40, 22.03, 18.92, 17.65, 17.12, 15.31, 14.26, 14.18, 11.73, 11.71.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{103}^{1}\text{H}_{182}^{16}\text{O}_{17}^{14}\text{N}_5^{35}\text{Cl}$, 1797.3292; found, 1797.3300, Δ = 1.8 mmu.



Supplementary Figure 15: ^1H -NMR of compound 24 measured in CDCl_3 .

Passerini reaction



In a 25 mL round bottom flask, 641 mg **24** (356 μmol , 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 59.8 μL acetaldehyde **14f** (47.1 mg, 1.07 mmol, 3.00 eq.) and 161 mg of the monomer **M1** (535 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 1:2) to yield the passerini product **H1** as a pale highly viscous oil. (433.1 mg, 626 μmol , 56.7%).

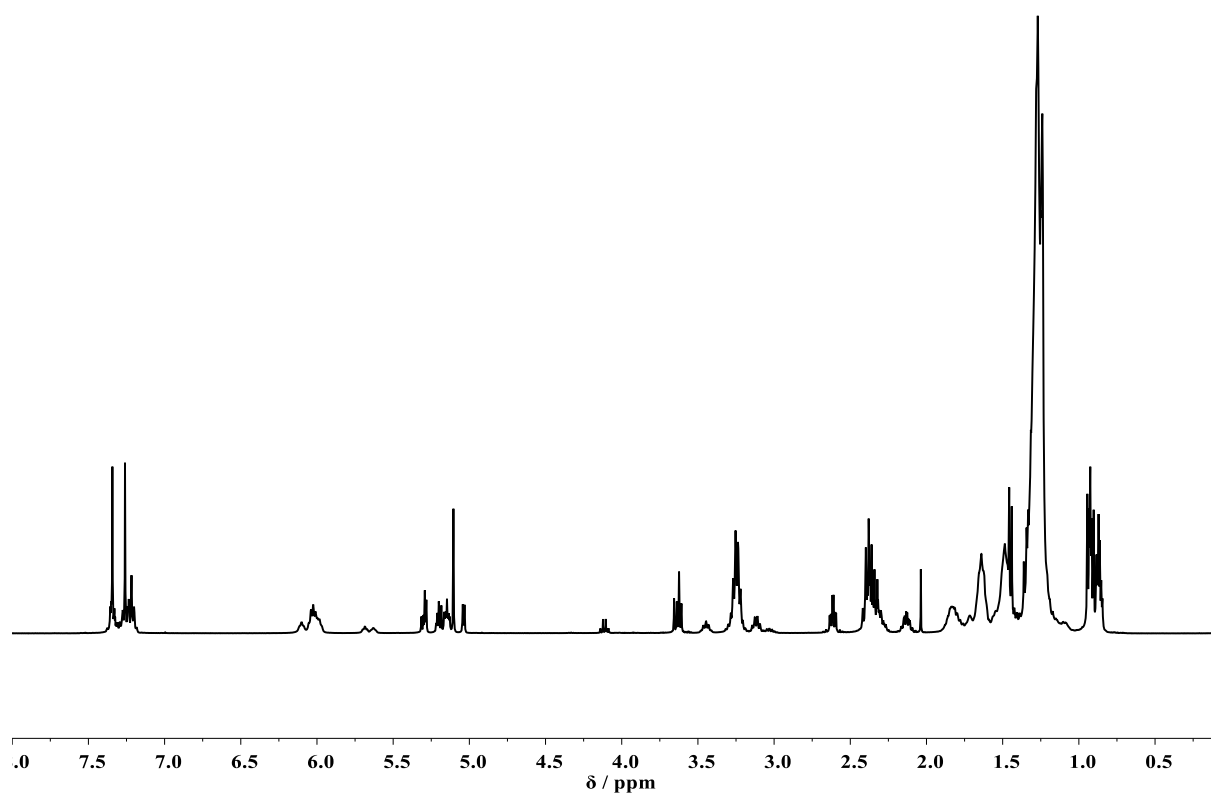
$R_f = 0.39$ in cyclohexane / ethyl acetate (1:1).

IR (ATR): $\nu / \text{cm}^{-1} = 3304.9$ (vw), 2323.4 (vs), 2852.9 (s), 1738.7 (vs), 1652.6 (vs), 1535.3 (s), 1456.1 (m), 1372.2 (w), 1232.5 (m), 1161.6 (s), 1105.5 (m), 722.1 (w), 698.9 (m).

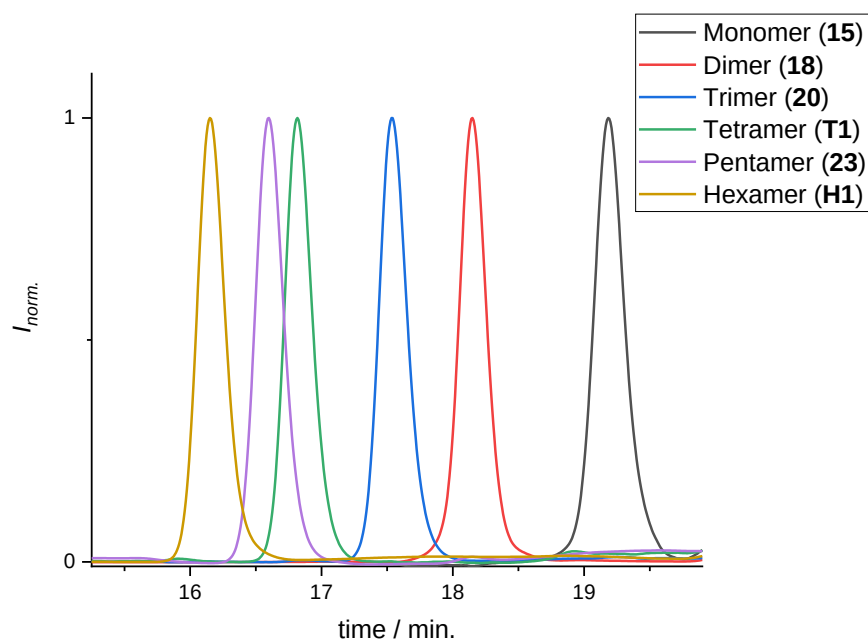
^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 7.46 - 7.13$ (m, 10 H, CH_{Ar}^1), 6.20 – 5.92 (m, 5 H, NH^2), 5.75 – 5.59 (m, 1 H, NH^2), 5.34 – 5.08 (m, 7 H, CH^3 , CH_2^4), 5.04 (d, $J = 4.5$ Hz, 1 H, CH^3), 3.69 – 3.58 (m, 2 H, CH_2^5), 3.49 – 3.39 (m, 1 H, CH^6), 3.34 – 2.97 (m, 12 H, CH_2^7), 2.66 – 2.57 (m, 2 H, CH_2^8), 2.45 – 2.23 (m, 13 H, CH^9 , CH_2^{10}), 2.19 – 2.07 (m, 2 H, CH_2^{11}), 1.92 – 1.05 (m, 138 H, CH^{12} , CH_2^{12} , CH_3^{13}), 0.99 – 0.82 (m, 18 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 173.80, 172.71, 172.61, 172.46, 172.38, 171.64, 170.43, 170.00, 169.63, 169.40, 168.85, 168.65, 141.74, 141.23, 136.26, 128.67, 128.53, 128.31, 128.28, 127.97, 127.13, 127.05, 78.07, 77.87, 75.55, 74.07, 70.59, 66.19, 44.09, 43.66, 41.59, 41.30, 39.37, 39.32, 39.31, 39.22, 34.45, 34.42, 34.36, 34.30, 32.05, 31.75, 31.23, 30.65, 29.80, 29.75, 29.70, 29.69, 29.58, 29.53, 29.48, 29.35, 29.28, 29.26, 29.23, 29.21, 29.16, 29.04, 27.49, 26.97, 26.87, 26.81, 25.14, 25.10, 25.07, 25.01, 24.92, 24.85, 22.82, 22.66, 22.39, 22.03, 18.91, 18.10, 17.64, 17.11, 15.35, 14.25, 14.17, 11.73, 11.71.$

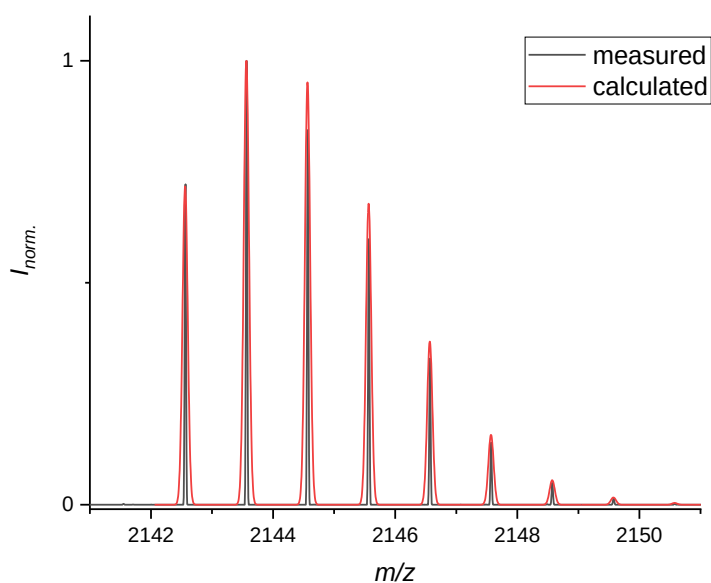
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{124}^{1}\text{H}_{213}^{16}\text{O}_{20}^{14}\text{N}_6^{35}\text{Cl}$, 2142.5596; found, 2142.5607, $\Delta = 1.1$ mmu.



Supplementary Figure 16: ^1H -NMR of compound H1 measured in CDCl_3 .



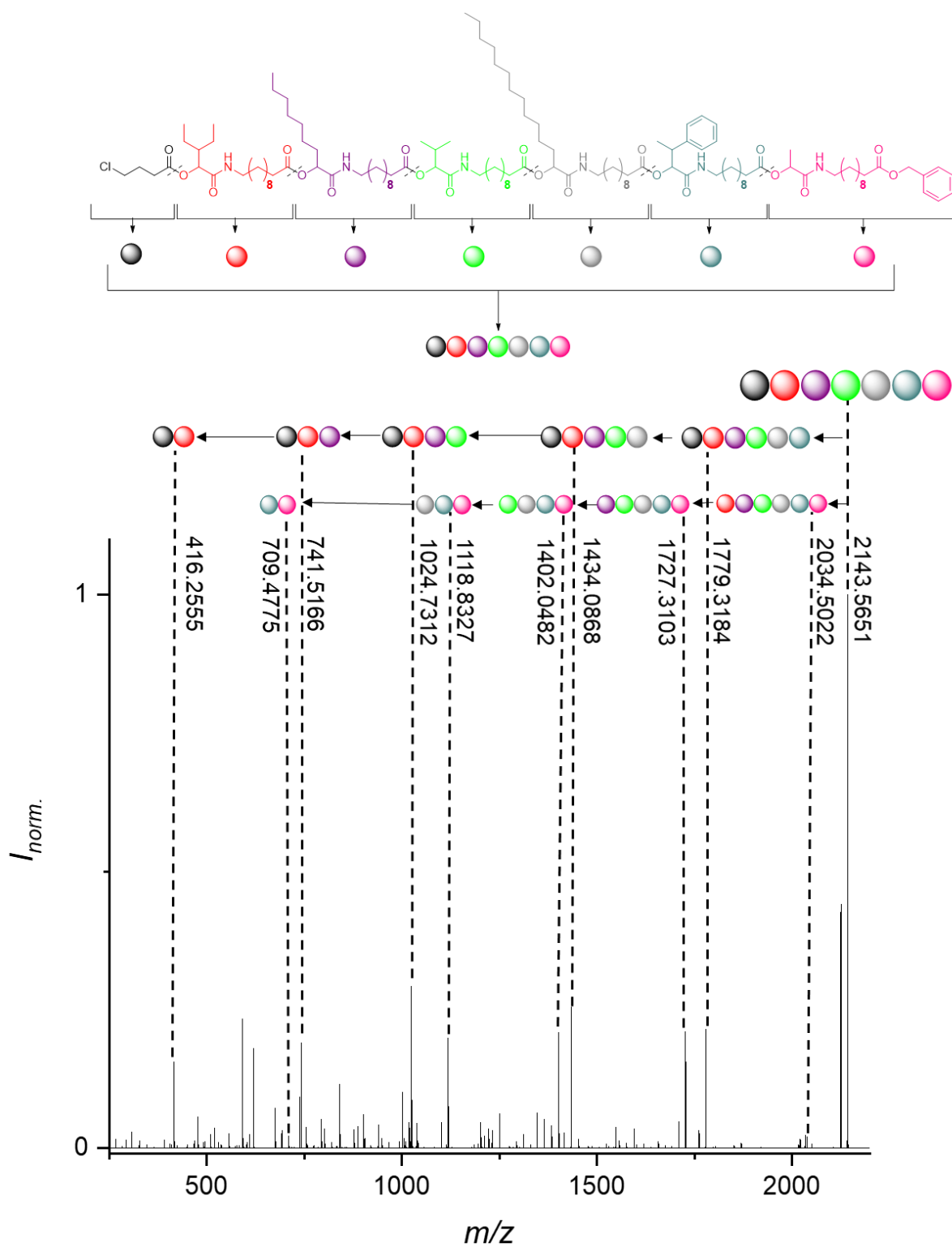
Supplementary Figure 17: SEC traces of the intermediates obtained after each P3CR in the synthesis of product H1.



Supplementary Figure 18: High resolution ESI-MS measurement of H1. The isotopic observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (red).

```
found 24339 values in C:\Users\Maxi\Desktop\MF 222 with 5 nce 19.CSV, maximum is 1.000000 found for mass 2142.562410
matching mass 2142.56241
cutoff 0.50000: 0 solutions (18 peaks)
cutoff 0.25000: 0 solutions (62 peaks)
cutoff 0.12500: 0 solutions (128 peaks)
cutoff 0.06250: 0 solutions (268 peaks)
cutoff 0.03125: 0 solutions (469 peaks)
cutoff 0.01562: 1 solutions (787 peaks)
2142.56241 = 105.017020 + 311.246050 + 325.261700 + 283.214750 + 409.355600 + 345.230400 + 255.183450 + 107.049690 (sides
2-Ethylbutanal, Heptanal, Isobutyraldehyde, Tridecanal, 2-Phenylpropionaldehyde, Acetaldehyde; error -1.00375)
Press ENTER to quit ...
```

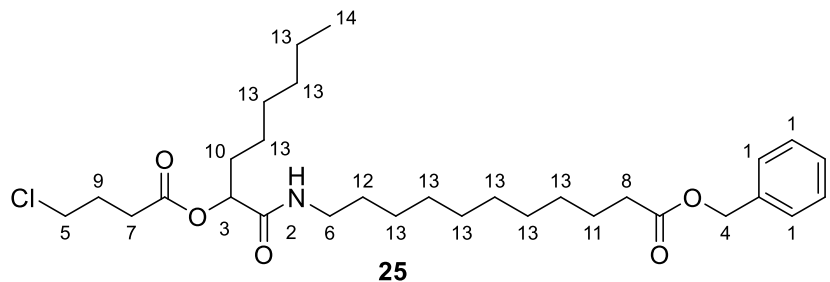
Supplementary Figure 19: Screenshot of the automated read-out of H1.



Supplementary Figure 20: Read-out of the sequence-defined hexamer H1. Read-out of the hexamer **H1** via tandem ESI-MS/MS with an NCE of 18. In the spectrum, the read-out from both ends of the oligomer using the fragmentation next to the carbonyl are shown.

1.3.3.3 Synthesis of tetramer T2

Passerini reaction



In a 50 mL round bottom flask, 74.5 mg 4-chlorobutyric acid **TAG3** (608 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 130 μL heptanal **14b** (104 mg, 912 μmol , 1.50 eq.) and 275 mg of monomer **M1** (912 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 8:1 $\rightarrow$ 6:1) to afford product **25** as a high viscous oil in a yield of 78.9% (258 mg, 480 μmol).

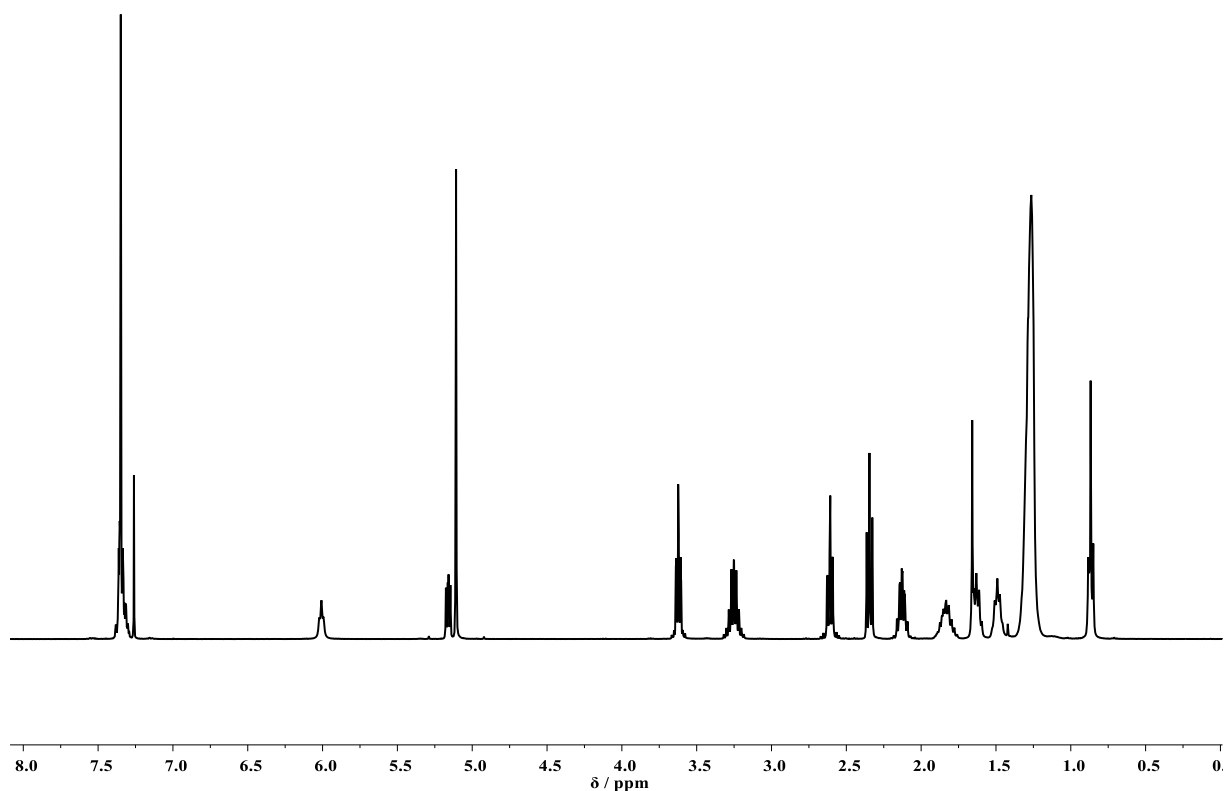
R_f = 0.32 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm^{-1} = 3306.6 (vw), 2924.7 (s), 2854.1 (m), 1735.9 (vs), 1655.6 (s), 535.1 (m), 1455.4 (w), 1377.2 (w), 1143.9 (s), 734.2 (w), 696.9 (m), 648.9 (w), 401.0 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.42 – 7.29 (m, 5 H, CH_{Ar}^1), 6.01 (t, J = 5.9 Hz, 1 H, NH^2), 5.18 – 5.14 (m, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 3.62 (td, J = 6.3, 1.4 Hz, 2 H, CH_2^5), 3.36 – 3.17 (m, 2 H, CH_2^6), 2.61 (td, J = 7.1, 1.5 Hz, 2 H, CH_2^7), 2.35 (t, J = 7.5 Hz, 2 H, CH_2^8), 2.18 – 2.06 (m, 2 H, CH_2^9), 1.93 – 1.74 (m, 2 H, CH_2^{10}), 1.69 – 1.59 (m, 2 H, CH_2^{11}), 1.54 – 1.44 (m, 2 H, CH_2^{12}), 1.40 – 1.13 (m, 20 H, CH_2^{13}), 0.91 – 0.83 (m, 3 H, CH_3^{14}).

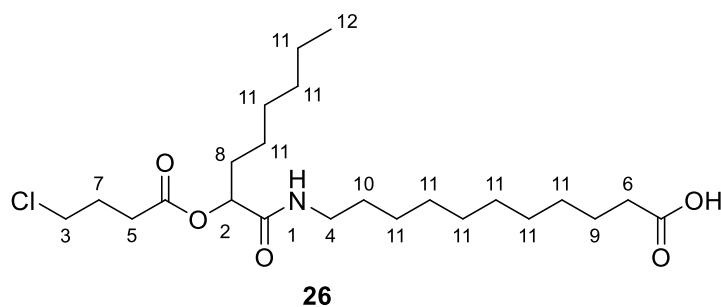
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 171.58, 169.74, 136.25, 128.66, 128.28, 74.47; 66.20, 44.07, 39.37, 34.45, 32.05, 31.73, 31.25, 29.65, 29.56, 29.47, 29.33, 29.23, 29.03, 27.50, 26.95, 25.07, 24.86, 22.66, 14.17.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{30}^{1}\text{H}_{48}^{16}\text{O}_5^{14}\text{N}^{35}\text{Cl}$, 538.3294; found, 538.3282, Δ = 1.2 mmu.



Supplementary Figure 21: ^1H -NMR of compound **25** measured in CDCl_3 .

Deprotection



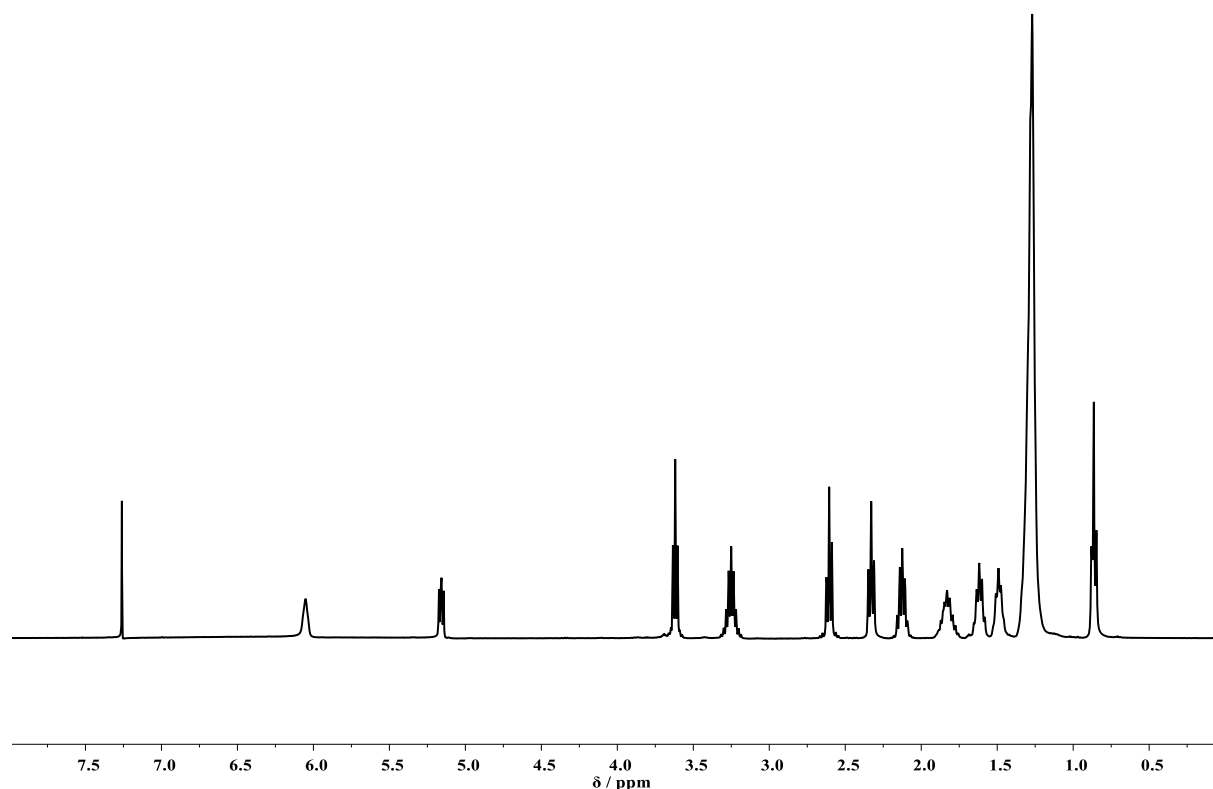
In a 50 mL round bottom flask, 209 mg of **25** (389 μmol , 1.00 eq.) were dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Afterwards, 41.8 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **26** was obtained as a pale highly viscous oil in a yield of 99.0% (172 mg, 385 μmol).

IR (ATR): ν/cm^{-1} = 3296.9 (w), 2918.7 (vs), 2850.5 (s), 1731.7 (vs), 1694.2 (vs), 1651.8 (vs), 1557.9 (s), 1468.6 (m), 1430.0 (m), 1378.9 (m), 1330.2 (m), 1277.1 (s), 1219.4 (vs), 1173.2 (vs), 1082.2 (m), 925.5 (m), 794.1 (w), 722.8 (m), 683.4 (m), 650.5 (m), 473.8 (vw), 437.5 (w), 388.7 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.11 – 6.01 (m, 1 H, NH^1), 5.20 – 5.11 (m, 1 H, CH^2), 3.62 (t, J = 6.1 Hz, 2 H, CH_2^3), 3.35 – 3.17 (m, 2 H, CH_2^4), 2.60 (t, J = 6.6 Hz, 2 H, CH_2^5), 2.36 – 2.28 (m, 2 H, CH_2^6), 2.19 – 2.06 (m, 2 H, CH_2^7), 1.92 – 1.75 (m, 2 H, CH_2^8), 1.67 – 1.56 (m, 2 H, CH_2^9), 1.56 – 1.43 (m, 2 H, CH_2^{10}), 1.38 – 1.12 (m, 20 H, CH_2^{11}), 0.92 – 0.81 (m, 3 H, CH_3^{12}).

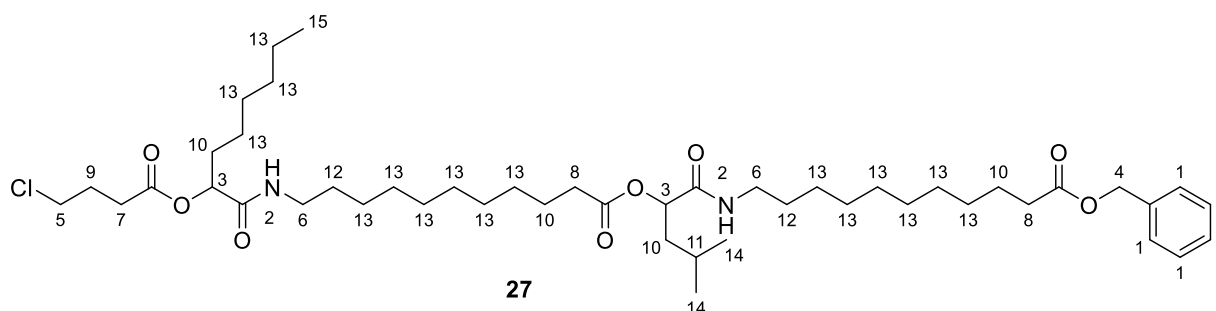
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 179.09, 171.64, 169.91, 74.47, 44.05, 39.41, 34.13, 32.03, 31.72, 31.26, 29.59, 29.48, 29.37, 29.25, 29.11, 29.02, 27.51, 26.91, 24.85, 24.83, 22.65, 14.15.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{23}^{1}\text{H}_{42}^{16}\text{O}_5^{14}\text{N}^{35}\text{Cl}$, 470.2644; found, 470.2639, Δ = 0.5 mmu.



Supplementary Figure 22: ^1H -NMR of compound **26** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 172 mg **26** (384 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 62.1 μL 3-methylbutanal **14g** (49.7 mg, 577 μmol , 1.50 eq.) and 174 mg of monomer **M1** (577 μmol ,

1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 2:1) to afford product **27** as a high viscous oil in a yield of 70.6% (227 mg, 271 μ mol).

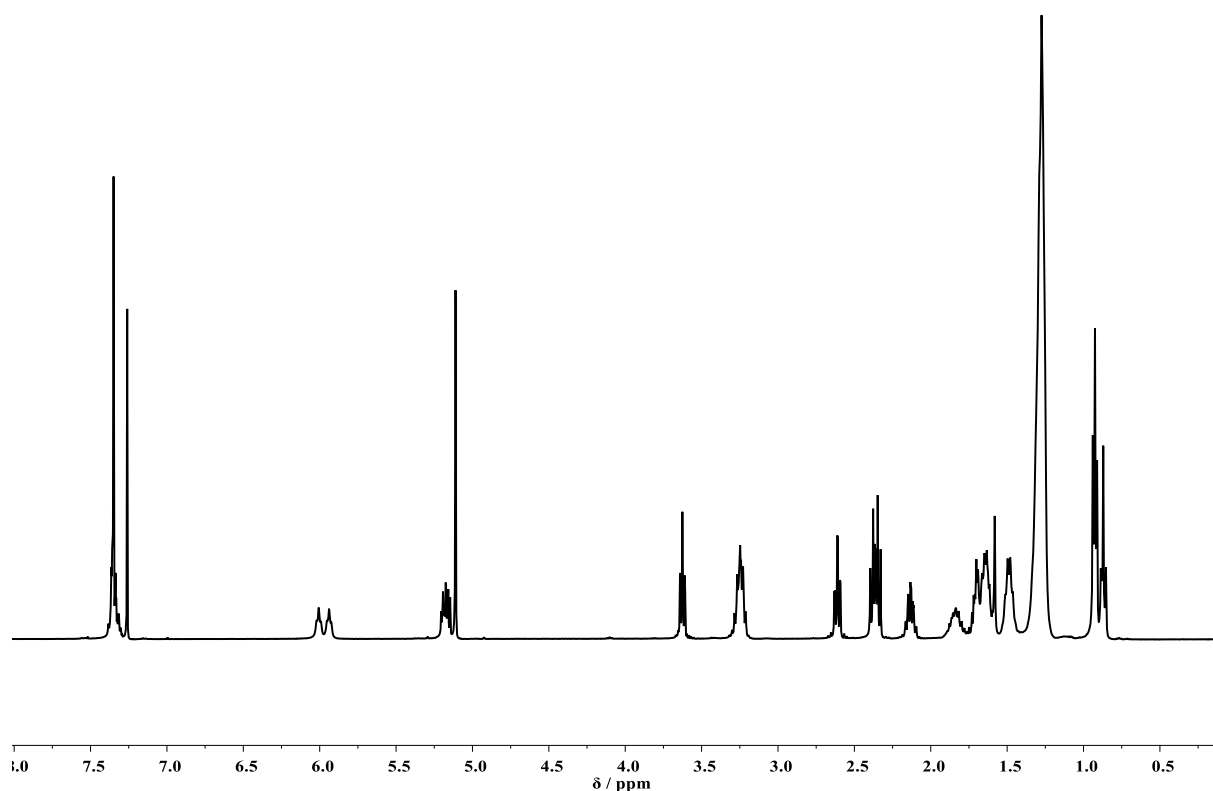
R_f = 0.39 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν / cm^{-1} = 304.3 (vw), 2924.8 (s), 2854.1 (m), 1737.4 (vs), 1654.9 (vs), 1536.0 (m), 1456.3 (m), 1371.1 (w), 1164.8 (s), 1061.8 (w), 732.8 (w), 697.0 (m).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.37 – 7.21 (m, 5 H, CH_{Ar}^1), 5.98 – 5.91 (m, 1 H, NH^2), 5.90 – 5.81 (m, 1 H, NH^2), 5.16 – 5.06 (m, 2 H, CH^3), 5.04 (s, 2 H, CH_2^4), 3.56 (t, J = 5.7 Hz, 2 H, CH_2^5), 3.26 – 3.11 (m, 4 H, CH_2^6), 2.58 – 2.49 (m, 2 H, CH_2^7), 2.35 – 2.24 (m, 4 H, CH_2^8), 2.11 – 2.00 (m, 2 H, CH_2^9), 1.85 – 1.52 (m, 9 H, CH^{10} , CH_2^{11}), 1.47 – 1.36 (m, 4 H, CH_2^{12}), 1.31 – 1.12 (m, 32 H, CH_2^{13}), 0.86 (t, J = 5.6 Hz, 6 H, CH_3^{14}), 0.83 – 0.78 (m, 3 H, CH_3^{15}).

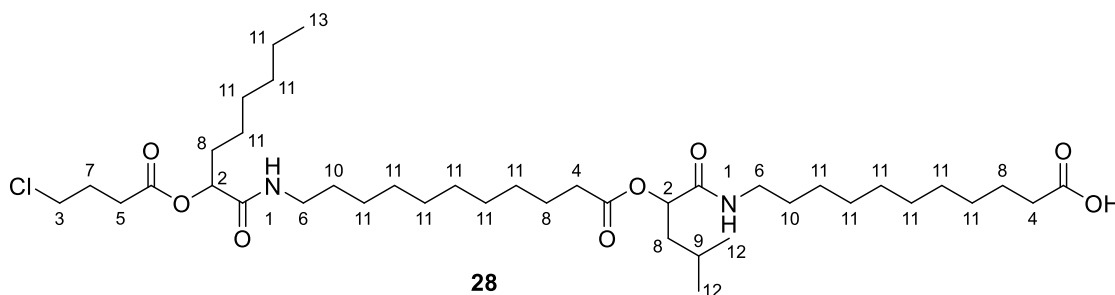
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.84, 172.78, 171.61, 170.34, 169.78, 128.69, 128.31, 74.49, 72.80, 66.22, 44.09, 40.99, 39.38, 34.47, 34.45, 32.07, 31.74, 31.26, 29.67, 29.58, 29.49, 29.35, 29.25, 29.24, 29.04, 27.51, 26.96, 26.95, 25.08, 24.88, 24.70, 23.28, 22.67, 21.95, 14.18.

ESI-MS [m/z]: [$M + H$] $^+$ calculated for $^{12}\text{C}_{47}^{1}\text{H}_{79}^{6}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}$, 835.5598; found, 835.5588, Δ = 1.0 mmu.



Supplementary Figure 23: ^1H -NMR of compound **27** measured in CDCl_3 .

Deprotection



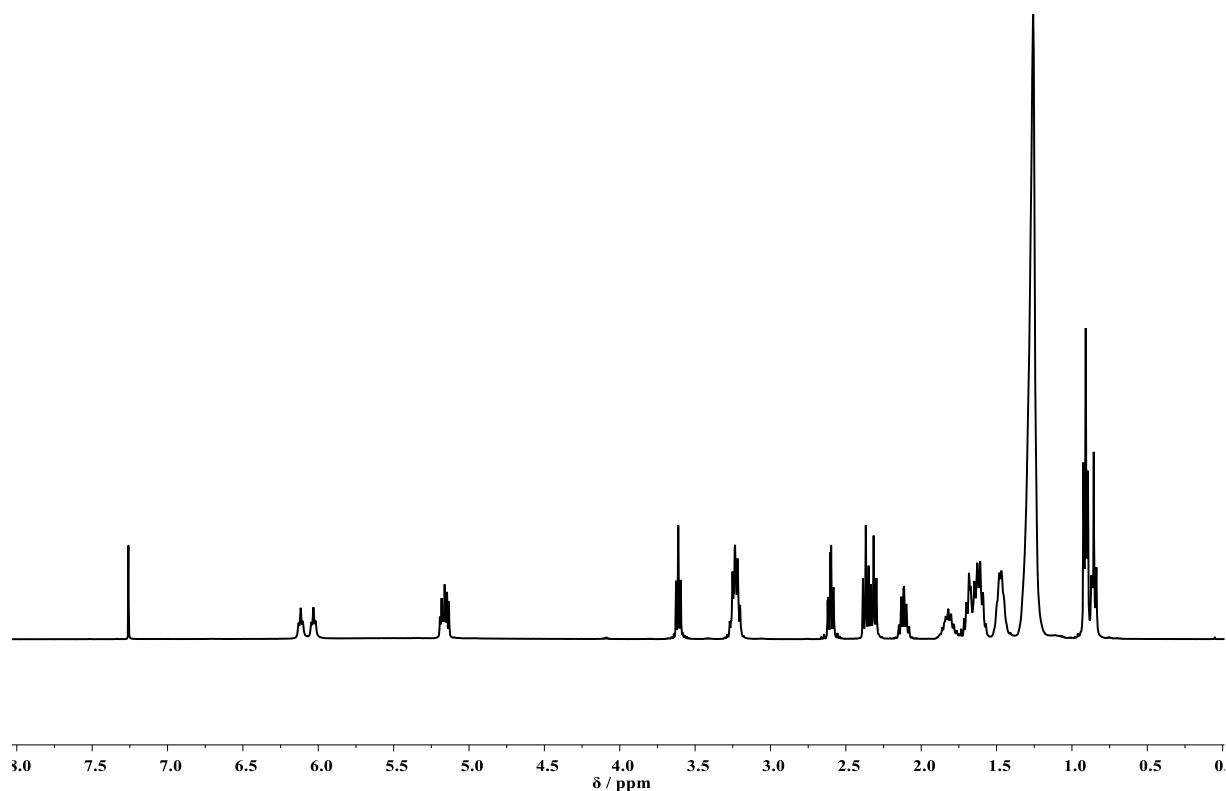
In a 50 mL round bottom flask, 176 mg of **27** (211 μmol , 1.00 eq.) were dissolved in 2.00 mL of ethyl acetate and 2.00 mL THF. Afterwards, 35.2 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **28** was obtained as a pale highly viscous oil in a yield of 97.6% (153 mg, 206 μmol).

IR (ATR): ν / cm^{-1} = 3306.8 (vw), 2924.2 (s), 2853.7 (m), 1738.2 (s), 1651.7 (s), 1540.2 (m), 1463.1 (w), 1370.1 (w), 1143.5 (s), 1061.2 (w), 722.6 (w), 650.3 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.12 – 6.03 (m, 1 H, NH^1), 5.98 (t, J = 5.8 Hz, 1 H, NH^1), 5.16 – 5.07 (m, 2 H, CH^2), 3.62 – 3.52 (m, 2 H, CH_2^3), 3.24 – 3.13 (m, 4 H, CH_2^4), 2.59 – 2.50 (m, 2 H, CH_2^5), 2.36 – 2.22 (m, 4 H, CH_2^6), 2.11 – 2.01 (m, 2 H, CH_2^7), 1.85 – 1.69 (m, 2 H, CH_2^8), 1.68 – 1.50 (m, 7 H, CH^9 , CH_2^8), 1.50 – 1.34 (m, 4 H, CH_2^{10}), 1.31 – 1.13 (m, 32 H, CH_2^{11}), 0.86 (t, J = 5.8 Hz, 6 H, CH_3^{12}), 0.83 – 0.77 (m, 3 H, CH_3^{13}).

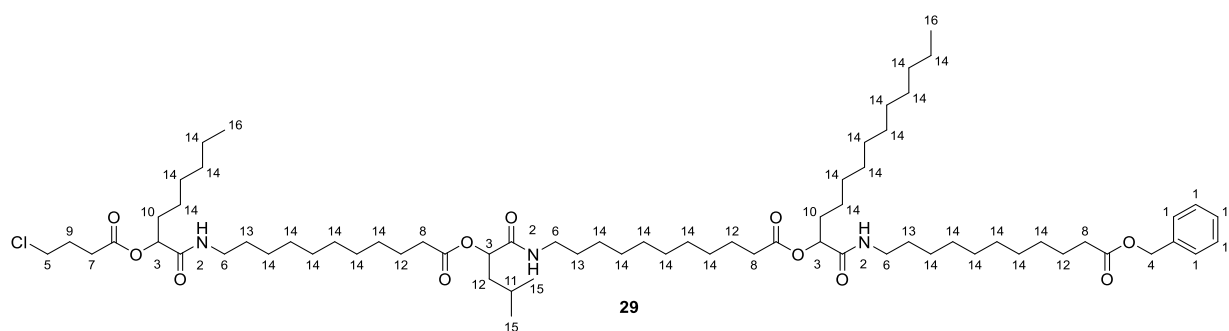
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 178.33, 172.81, 171.67, 170.47, 169.97, 74.42, 72.75, 44.05, 40.92, 39.40, 39.35, 34.40, 34.11, 32.01, 31.70, 31.22, 29.60, 29.56, 29.53, 29.46, 29.45, 29.36, 29.31, 29.30, 29.23, 29.21, 29.10, 29.00, 27.47, 26.93, 26.86, 25.04, 24.86, 24.84, 24.65, 23.23, 22.63, 21.89, 14.15.

ESI-MS [m/z]: $[\text{M} + \text{H}]^+$ calculated for $^{12}\text{C}_{40}^{1}\text{H}_{73}^{6}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}^{23}$, 745.5128; found, 745.5113, Δ = 1.5 mmu.



Supplementary Figure 24: ^1H -NMR of compound **28** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 91.2 mg **28** (122 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 40.8 μL dodecanal **14h** (33.8 mg, 184 μmol , 1.50 eq.) and 55.3 mg of monomer **M1** (184 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 8:1 $\rightarrow$ 6:1) to afford product **29** as a high viscous oil in a yield of 82.8% (124 mg, 101 μmol).

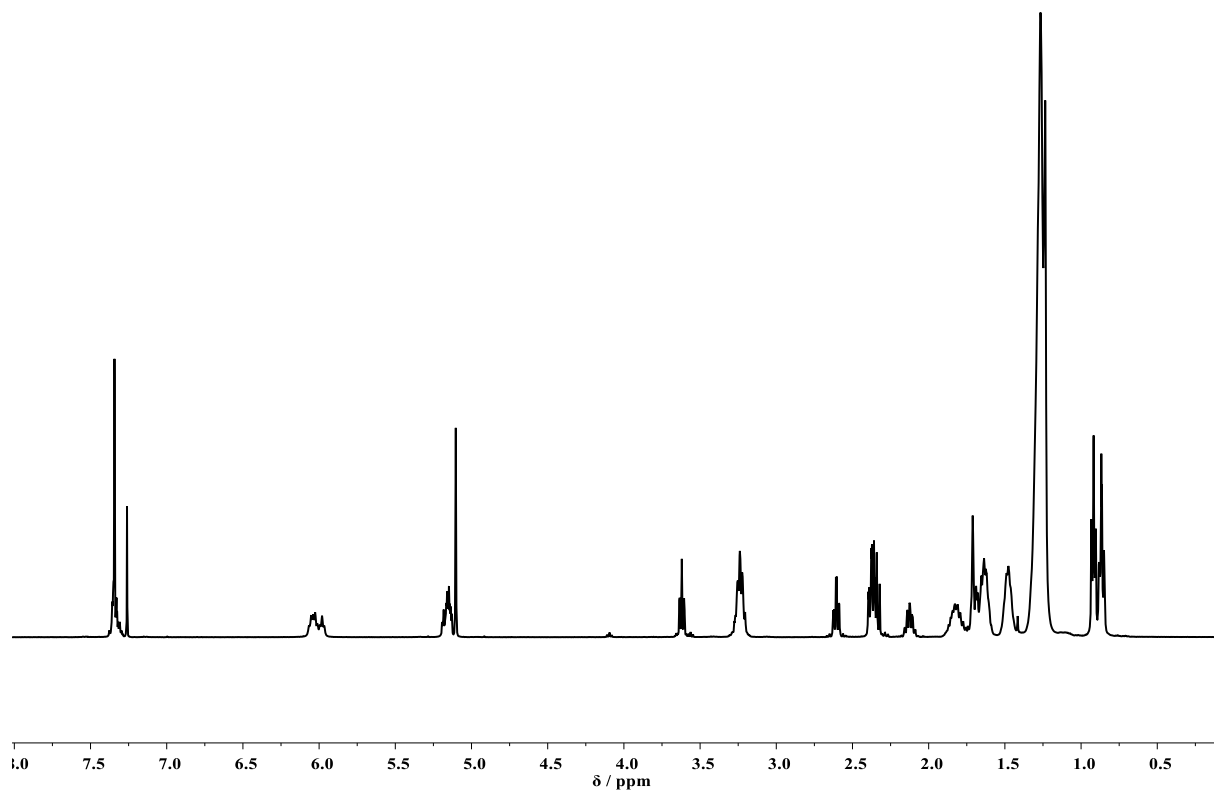
R_f = 0.77 in cyclohexane / ethyl acetate (1:1).

IR (ATR): ν / cm^{-1} = 3294.1 (w), 2923.0 (s), 2852.9 (m), 1738.2 (s), 1654.5 (s), 1535.6 (m), 1457.0 (w), 1371.2 (w), 1163.3 (s), 723.5 (w), 697.0 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.36 – 7.23 (m, 5 H, CH_{Ar}^1), 6.04 – 5.88 (m, 3 H, NH^2), 5.16 – 5.05 (m, 3 H, CH^3), 5.04 (s, 2 H, CH_2^4), 3.62 – 3.53 (m, 2 H, CH_2^5), 3.27 – 3.12 (m, 6 H, CH_2^6), 2.59 – 2.50 (m, 2 H, CH_2^7), 2.34 – 2.24 (m, 6 H, CH_2^8), 2.12 – 2.01 (m, 2 H, CH_2^9), 1.84 – 1.67 (m, 4 H, CH_2^{10}), 1.64 – 1.51 (m, 9 H, CH^{11} , CH_2^{12}), 1.47 – 1.37 (m, 6 H, CH_2^{13}), 1.30 – 1.14 (m, 62 H, CH_2^{14}), 0.86 (t, J = 5.8 Hz, 6 H, CH_3^{15}), 0.83 – 0.77 (m, 6 H, CH_3^{16}).

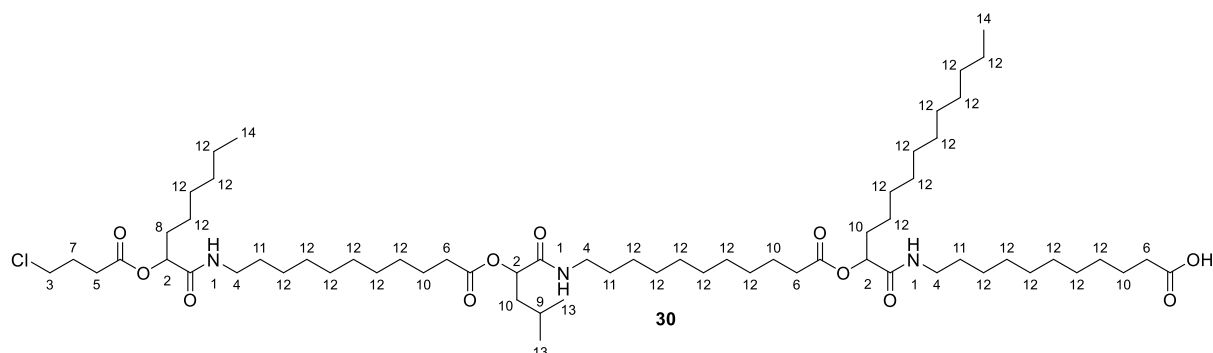
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.78, 172.61, 171.61, 170.36, 169.99, 169.78, 136.23, 128.66, 128.29, 128.28, 74.44, 74.06, 72.75, 66.19, 44.07, 40.97, 39.33, 39.32, 34.44, 32.03, 31.72, 31.22, 29.74, 29.66, 29.65, 29.57, 29.55, 29.47, 29.38, 29.34, 29.32, 29.23, 29.21, 29.02, 27.48, 26.95, 26.92, 25.08, 25.05, 25.04, 24.88, 24.86, 24.66, 23.26, 22.81, 22.65, 21.91, 14.25, 14.16.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{71}^{1}\text{H}_{124}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}$, 1230.8997; found, 1230.8976, Δ = 2.1 mmu.



Supplementary Figure 25: ^1H -NMR of compound 29 measured in CDCl_3 .

Deprotection



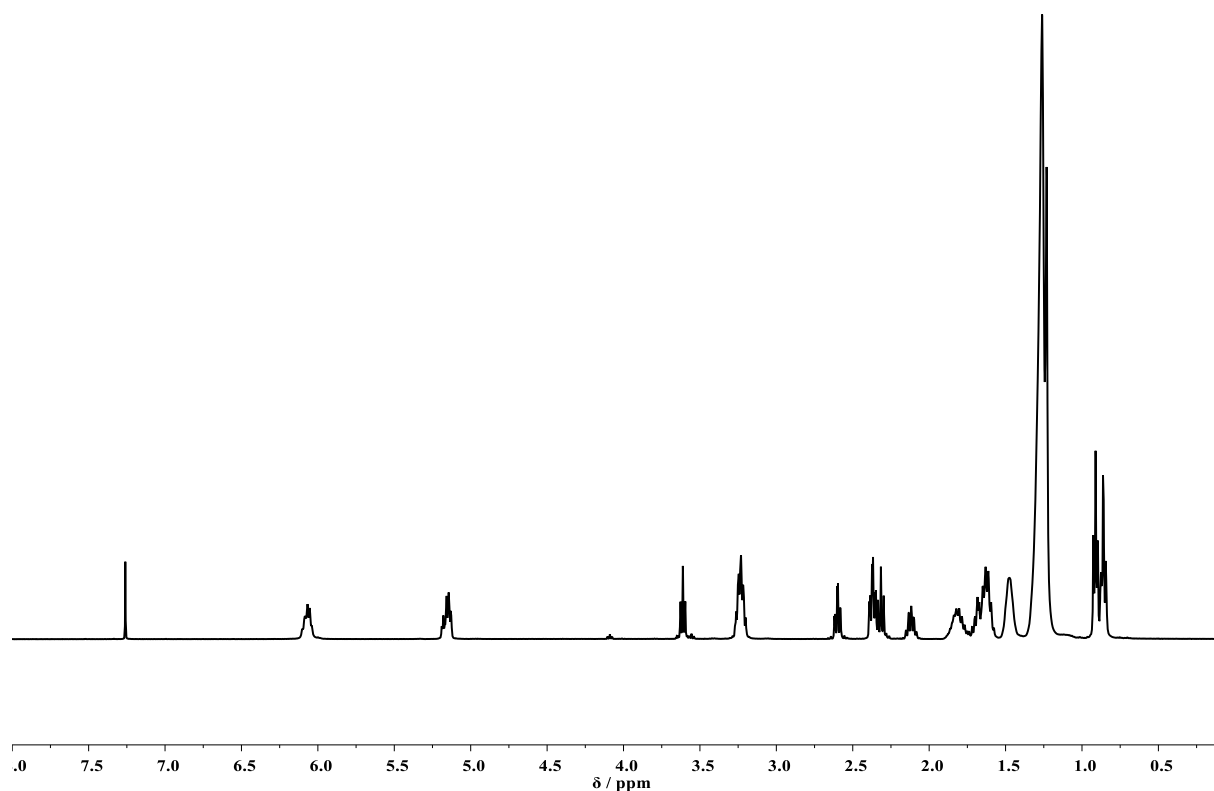
In a 50 mL round bottom flask, 75.3 mg of **29** (61.0 μmol , 1.00 eq.) were dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Afterwards, 15.6 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **30** was obtained as a pale highly viscous oil in a yield of 89.2% (62.3 mg, 54.4 μmol).

IR (ATR): ν / cm^{-1} = 3292.6 (vw), 2822.8 (vs), 2852.9 (s), 1739.4 (s), 1652.5 (s), 1539.6 (m), 1463.5 (w), 1370.3 (w), 1165.3 (m), 722.0 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.10 – 5.95 (m, 3 H, NH^1), 5.18 – 5.01 (m, 3 H, CH^2), 3.61 – 3.49 (m, 2 H, CH_2^3), 3.25 – 3.12 (m, 6 H, CH_2^4), 2.60 – 2.50 (m, 2 H, CH^5), 2.36 – 2.20 (m, 6 H, CH_2^6), 2.13 – 2.00 (m, 2 H, CH_2^7), 1.85 – 1.67 (m, 4 H, CH_2^8), 1.67 – 1.50 (m, 9 H, CH^9 , CH_2^{10}), 1.48 – 1.37 (m, 6 H, CH_2^{11}), 1.30 – 1.13 (m, 22 H, CH_2^{12}), 0.86 (t, J = 5.9 Hz, 6 H, CH_3^{13}), 0.84 – 0.77 (m, 6 H, CH_3^{14}).

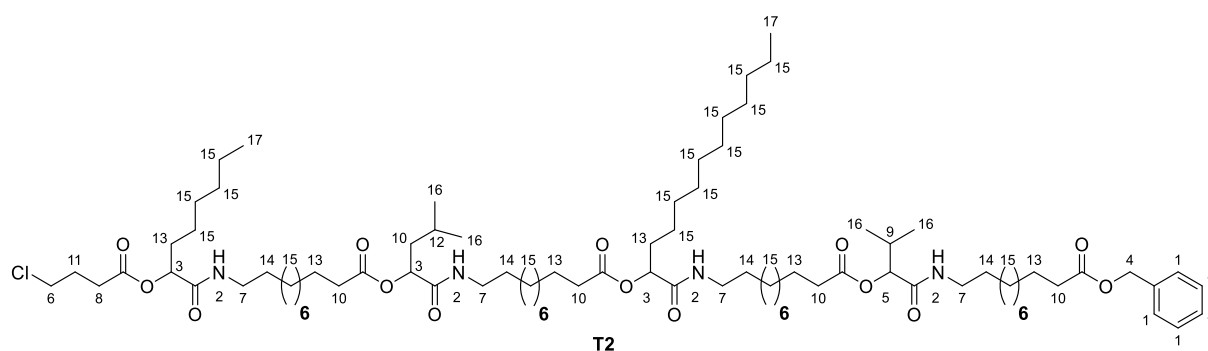
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 177.57, 172.86, 172.62, 171.63, 170.50, 170.09, 169.90, 74.44, 74.08, 72.77, 44.04, 40.93, 39.40, 39.39, 39.31, 34.44, 34.40, 34.01, 32.02, 31.99, 31.71, 31.24, 29.73, 29.65, 29.61, 29.57, 29.55, 29.49, 29.45, 29.36, 29.30, 29.24, 29.20, 29.11, 29.00, 27.50, 26.92, 26.91, 26.89, 25.10, 25.02, 24.89, 24.87, 24.85, 24.66, 23.23, 22.79, 22.63, 21.91, 14.22, 14.14.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{64}^{1}\text{H}_{118}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}^{23}$, 1140.8528; found, 1140.8505, Δ = 2.3 mmu.



Supplementary Figure 26: ^1H -NMR of compound **30** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 62.0 mg **30** (54.0 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 8.00 μL isobutyraldehyde **14c** (5.90 mg, 81.0 μmol , 1.50 eq.) and 29.2 mg of monomer **M1** (81.0 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 24 hours. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane / ethyl acetate 4:1 $\rightarrow$ 2:1) to afford product **T2** as a high viscous oil in a yield of 70.7% (58.2 mg, 38.2 μmol).

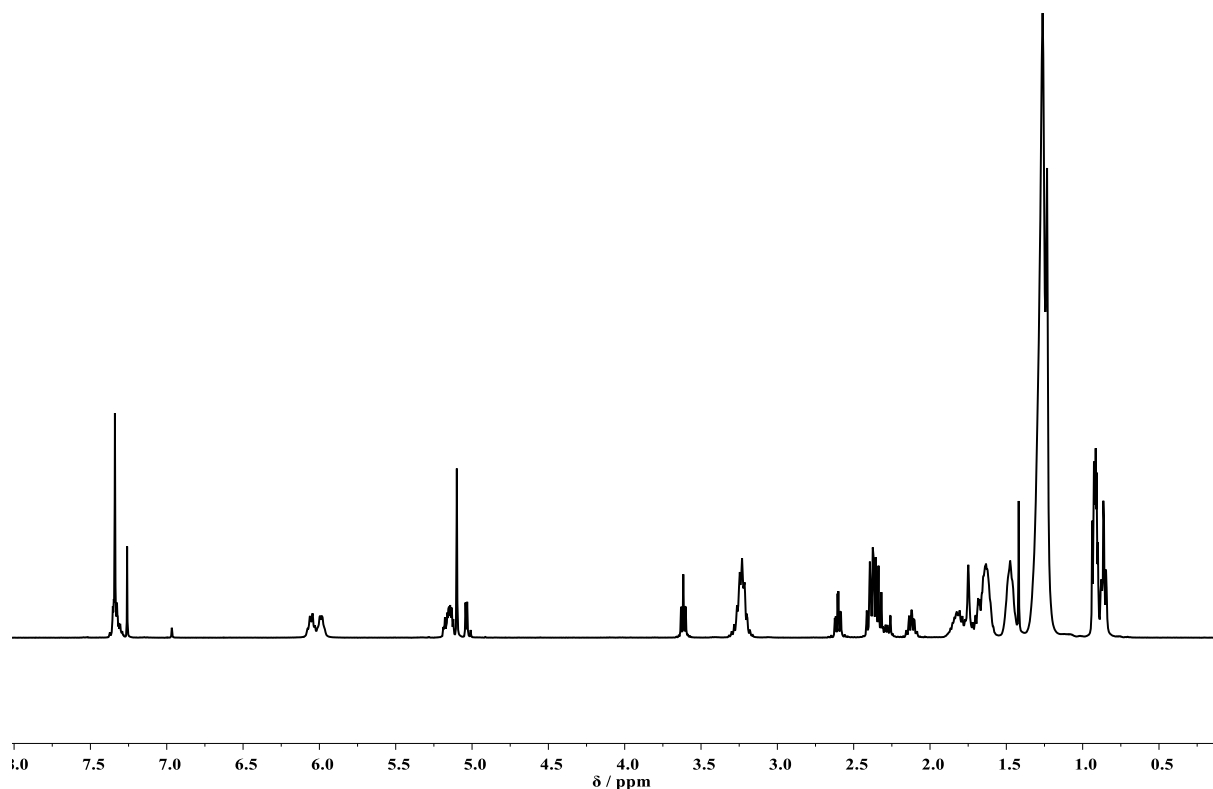
R_f = 0.53 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν/cm^{-1} = 3293.2541 (vw), 2919.9 (m), 2851.4 (w), 1736.3 (m), 1654.9 (s), 1556.3 (w), 1466.3 (w), 1374.3 (w), 1243.1 (w), 1207.6(w), 1176.0 (m), 1059.7 (w), 1000.8 (w), 879.3 (vw), 841.2 (vw), 721.1395 (w), 689.2593 (w), 430.7457 (vw).

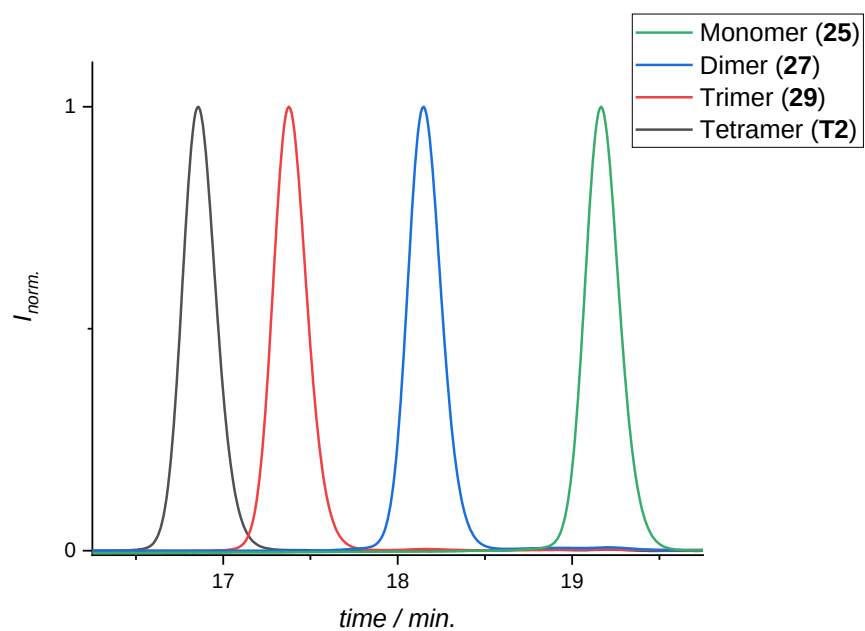
^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.35 – 7.23 (m, 5 H, CH_{Ar}^1), 6.07 – 5.89 (m, 4 H, NH^2), 5.16 – 5.07 (m, 3 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.98 (d, J = 4.4 Hz, 1 H, CH^5), 3.56 (t, J = 6.1 Hz, 2 H, CH_2^6), 3.27 – 3.09 (m, 8 H, CH_2^7), 2.60 – 2.50 (m, 2 H, CH_2^8), 2.38 – 2.18 (m, 9 H, CH^9 , CH_2^{10}), 2.11 – 2.02 (m, 2 H, CH_2^{11}), 1.85 – 1.51 (m, 15 H, CH^{12} , CH_2^{13}), 1.48 – 1.37 (m, 8 H, CH_2^{14}), 1.32 – 1.10 (m, 74 H, CH_2^{15}), 0.90 – 0.83 (m, 12 H, CH_2^{16}), 0.83 – 0.78 (m, 6 H, CH_2^{17}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.78, 172.69, 172.62, 171.61, 170.36, 170.00, 169.78, 169.39, 136.24, 128.65, 128.28, 128.27, 125.63, 78.05, 74.44, 74.06, 72.75, 66.18, 44.06, 40.97, 39.34, 39.28, 34.43, 34.40, 32.03, 31.72, 31.23, 30.64, 30.44, 29.74, 29.69, 29.68, 29.65, 29.57, 29.55, 29.48, 29.46, 29.38, 29.37, 29.35, 29.34, 29.33, 29.31, 29.25, 29.23, 29.22, 29.01, 27.49, 26.96, 26.92, 25.12, 25.07, 25.05, 25.04, 24.90, 24.86, 24.66, 23.25, 22.80, 22.64, 21.91, 18.90, 17.09, 14.24, 14.15.

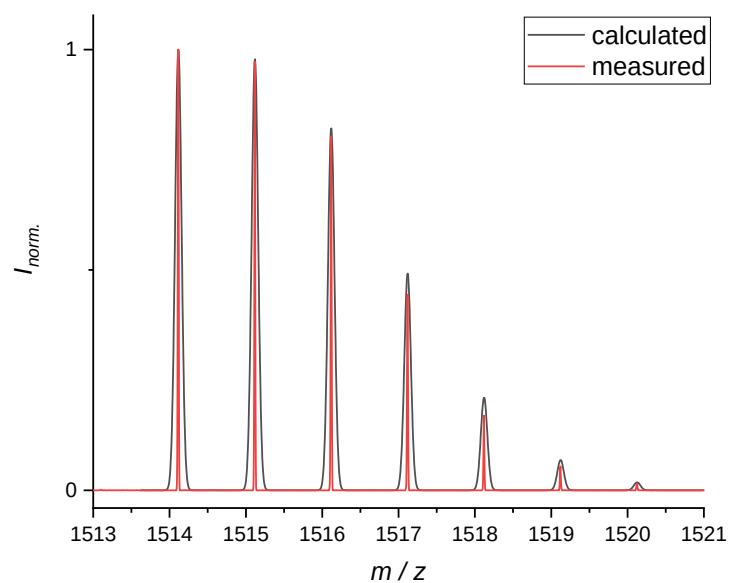
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{87}^{1}\text{H}_{153}^{16}\text{O}_{14}^{14}\text{N}_4^{35}\text{Cl}$, 1514.1145; found, 1514.1137, Δ = 0.8 mmu.



Supplementary Figure 27: ^1H -NMR of compound T2 measured in CDCl_3 .



Supplementary Figure 28: SEC traces of the intermediates after each P3CR in the synthesis of product T2.



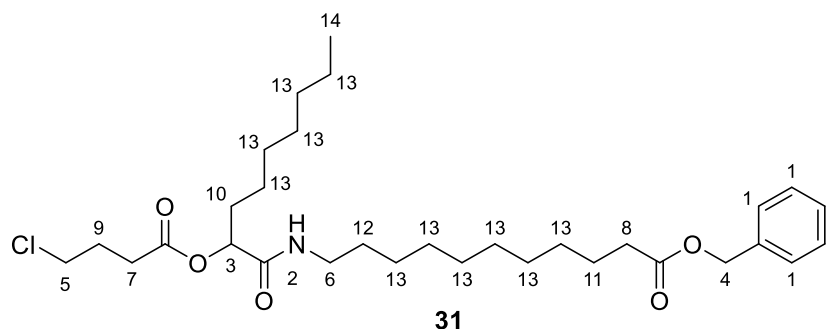
Supplementary Figure 29: High resolution ESI-MS measurement of T2. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

```
er.CSV, maximum is 100.000000 found for mass 1536.089620
matching mass 1536.08962
cutoff 0.50000: 0 solutions (22 peaks)
cutoff 0.25000: 0 solutions (75 peaks)
cutoff 0.12500: 0 solutions (140 peaks)
cutoff 0.06250: 1 solutions (239 peaks)
1536.08962  $\approx$  121.005630 + 325.261700 + 297.230400 + 395.339950 + 283.214750 + 91.054780 (sides Heptanal, 3-Methylbutanal, Dodecanal, Isobutyraldehyde; error -22.98241)
Press ENTER to quit ...
```

Supplementary Figure 30: Screenshot of the automated read-out of T2, sodium trifluoroacetate was used as additive during the measurement.

1.3.3.4 Synthesis of tetramer T3

Passerini reaction



In a 50 mL round bottom flask, 161 mg 4-chlorobutyric acid **TAG3** (1.31 mmol, 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 308 μ L octanal **14i** (252 mg, 1.97 mmol, 1.50 eq.) and 594 mg of the monomer **M1** (1.97 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (8:1 $\rightarrow$ 6:1) to yield the passerini product **31** as a yellow highly viscous oil. (675 mg, 1.22 mmol, 86.2%).

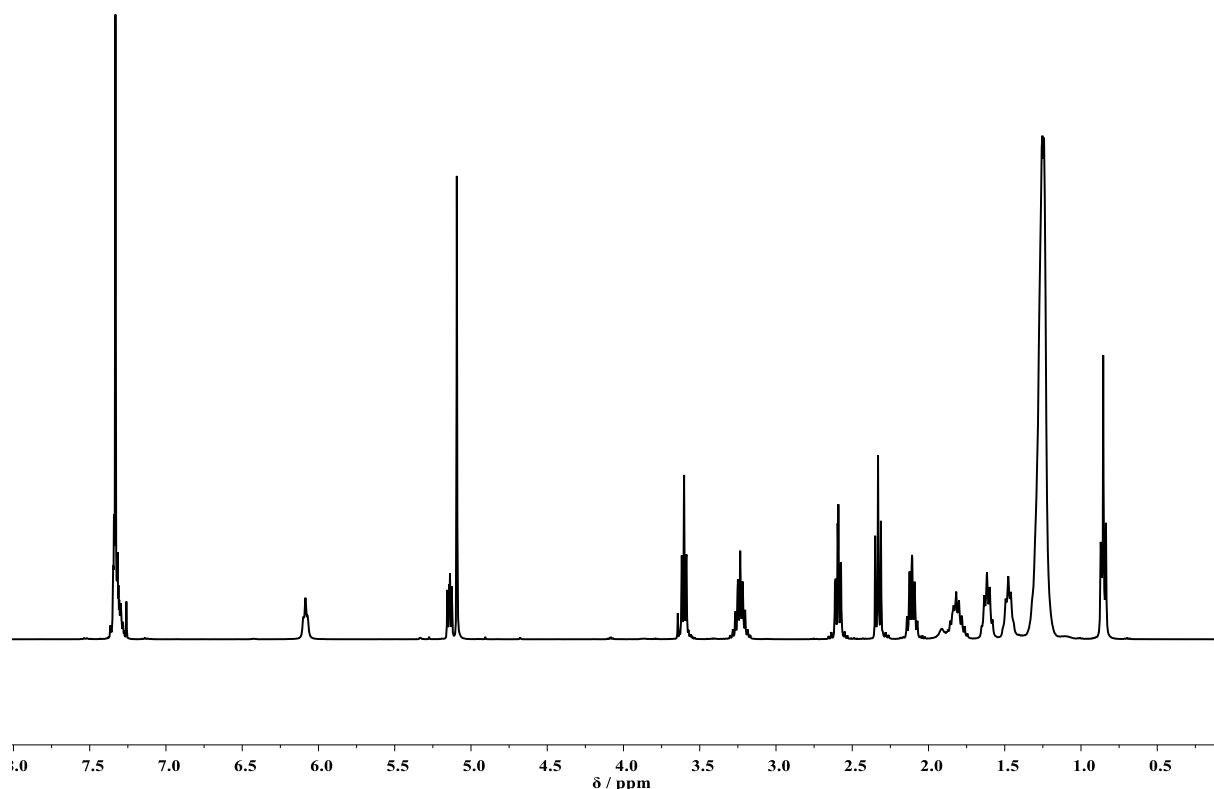
R_f = 0.34 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm^{-1} = 3306.6 (vw), 2924.1 (s), 2853.7 (m), 1736.1 (vs), 1655.7 (s), 1535.9 (m), 1455.5 (w), 1377.0 (w), 1144.0 (s), 733.8 (m), 697.0 (m), 650.8 (w). 1455.5 (w), 1377.0 (w), 1144.0 (s), 733.8 (m), 697.0 (m), 650.8 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.27 (m, 5 H, CH_{Ar}^1), 6.09 (t, J = 5.9 Hz, 1 H, NH^2), 5.18 – 5.12 (m, 1 H, CH^3), 5.09 (s, 2 H, CH_2^4), 3.60 (td, J = 6.3, 1.2 Hz, 2 H, CH_2^5), 3.32 – 3.16 (m, 2 H, CH_2^6), 2.59 (td, J = 7.1, 1.7 Hz, 2 H, CH_2^7), 2.33 (t, J = 7.5 Hz, 2 H, CH^8), 2.16 – 2.06 (m, 2 H, CH_2^9), 1.95 – 1.73 (m, 2 H, CH_2^{10}), 1.66 – 1.56 (m, 2 H, CH_2^{11}), 1.52 – 1.45 (m, 2 H, CH_2^{12}), 1.37 – 1.14 (m, 22 H, CH_2^{13}), 0.92 – 0.81 (m, 3 H, CH_3^{14}).

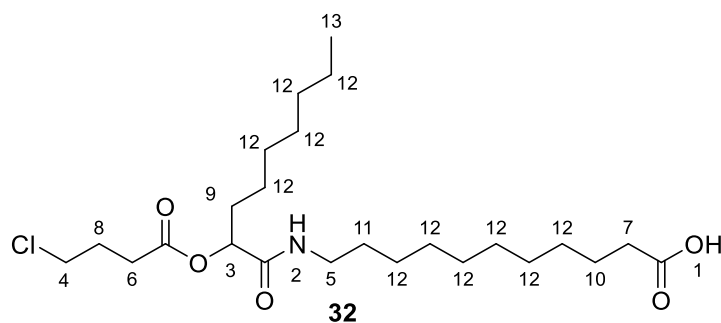
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.74, 171.54, 169.72, 136.19, 128.59, 128.20, 74.37, 66.11, 44.00, 39.30, 34.37, 31.99, 31.78, 31.16, 29.57, 29.49, 29.39, 29.26, 29.15, 29.14, 27.44, 26.88, 24.99, 24.85, 22.66, 14.13.

ESI-MS [m/z]: [$\text{M}+\text{H}$]⁺ calculated for $^{12}\text{C}_{31}\text{H}_{50}^{16}\text{O}_5\text{N}^{35}\text{Cl}$, 552.3450; found: 552.3438; Δ = 1.2 mmu.



Supplementary Figure 31: ^1H -NMR of compound **31** measured in CDCl_3 .

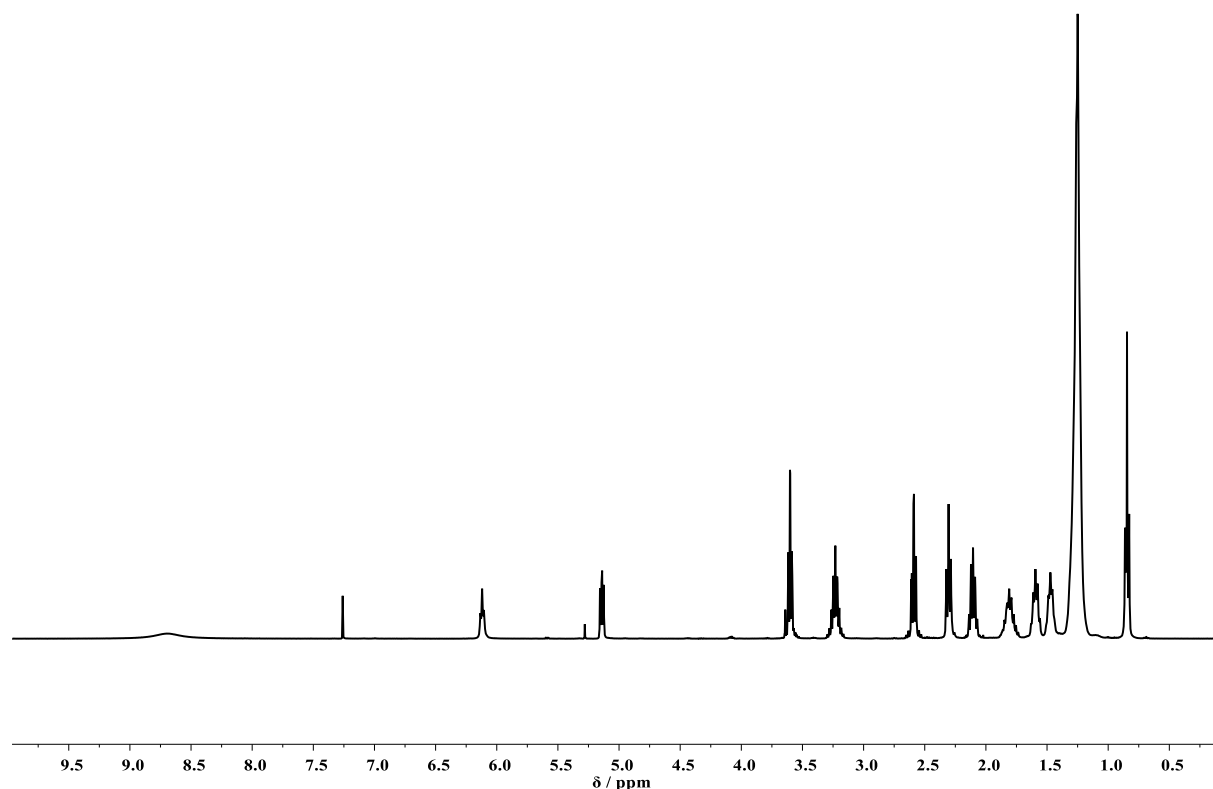
Deprotection



In a 50 mL round bottom flask, 606 mg of **31** (1.10 mmol, 1.00 eq.) were dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Afterwards, 121 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **32** was obtained as a pale highly viscous oil in a yield of 98.2% (502 mg, 1.08 mmol).

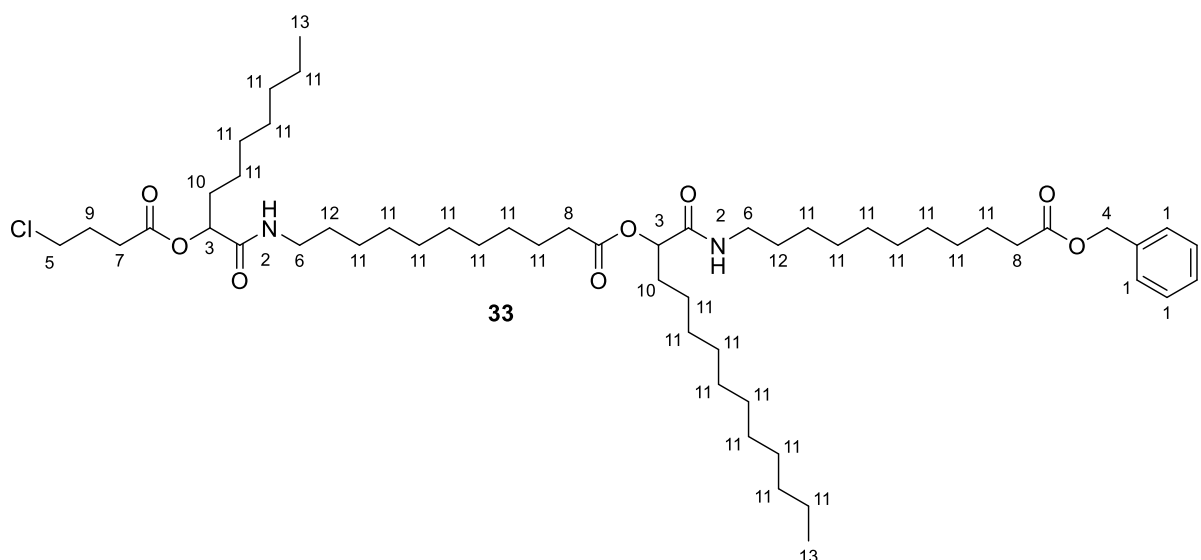
IR (ATR): ν/cm^{-1} = 3294.8 (vw), 2923.7 (s), 2853.7 (m), 1737.3 (s), 1649.0 (s), 1541.6 (m), 1457.9 (w), 1376.1 (w), 1296.9 (w), 1173.7 (s), 1141.8 (s), 787.3 (w), 722.9 (w), 652.1 (w), 427.9 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 8.65 (s (broad), 1 H, OH^1), 6.08 (t, J = 5.9 Hz, 1 H, NH^2), 5.13 – 5.02 (m, 1 H, CH^3), 3.61 – 3.51 (m, 2 H, CH_2^4), 3.28 – 3.11 (m, 2 H, CH_2^5), 2.62 – 2.49 (m, 2 H, CH_2^6), 2.26 (t, J = 7.5 Hz, 2 H, CH_2^7), 2.13 – 2.01 (m, 2 H, CH_2^8), 1.86 – 1.69 (m, 2 H, CH_2^9), 1.61 – 1.50 (m, 2 H, CH_2^{10}), 1.47 – 1.38 (m, 2 H, CH_2^{11}), 1.32 – 1.13 (m, 22 H, CH_2^{12}), 0.84 – 0.76 (m, 3 H, CH_3^{13}).
 ^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 179.33, 171.62, 169.96, 74.37, 44.02, 39.37, 34.23, 31.98, 31.80, 31.18, 29.53, 29.47, 29.37, 29.27, 29.24, 29.16, 29.10, 27.44, 26.87, 24.85, 24.82, 22.68, 14.15.
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{24}\text{H}_{44}\text{O}_5\text{N}^{35}\text{Cl}$, 462.2981; found, 462.2971, Δ = 1.0 mmu.



Supplementary Figure 32: ^1H -NMR of compound 32 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 882 mg **32** (815 μmol , 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 564 mg dodecanal **14h** (1.22 mmol, 1.50 eq.) and 922 mg of the monomer **M1** (1.22 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (7:1 $\rightarrow$ 4:1) to yield the passerini product **33** as a yellow highly viscous oil. (1.65 g, 755 μmol , 92.6%).

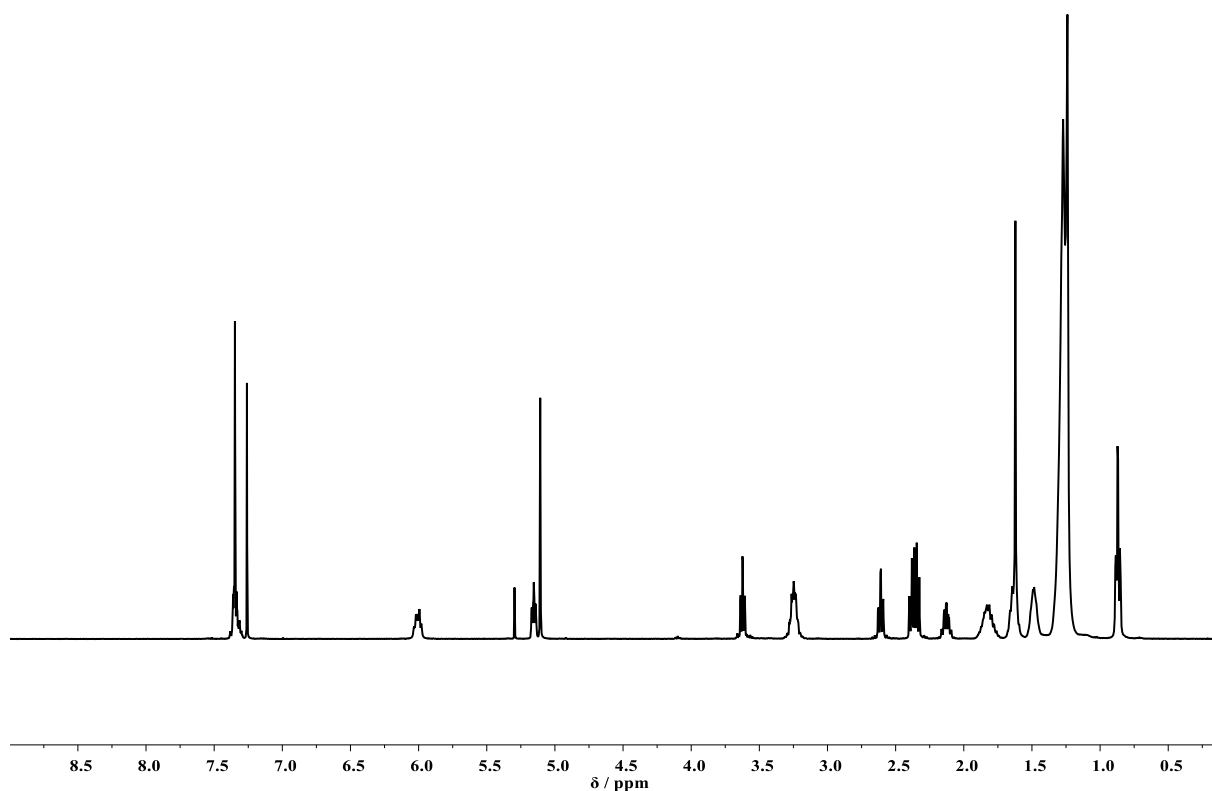
R_f: 0.21 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm^{-1} = 3304.4 (w), 2922.2 (s), 2852.3 (m), 1737.3 (s), 1654.0 (s), 1536.8 (m), 1456.1 (w), 1376.6 (w), 1166.4 (m), 723.0 (w), 696.9 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.29 (m, 5 H, CH_{Ar}^1), 6.08 – 5.92 (m, 2 H, NH^2), 5.21 – 5.14 (m, 2 H, CH^3), 5.11 (s, 2 H, CH^4), 3.66 – 3.59 (m, 2 H, CH_2^5), 3.32 – 3.19 (m, 4 H, CH_2^6), 2.61 (td, J = 7.1, 1.7 Hz, 2 H, CH_2^7), 2.41 – 2.31 (m, 4 H, CH_2^8), 2.19 – 2.07 (m, 2 H, CH_2^9), 1.92 – 1.73 (m, 4 H, CH_2^{10}), 1.69 – 1.57 (m, 8 H, CH_2^{11}), 1.54 – 1.42 (m, 4 H, CH_2^{12}), 1.36 – 1.19 (m, 48 H, CH_2^{11}), 0.91 – 0.83 (m, 6 H, CH_3^{13}).

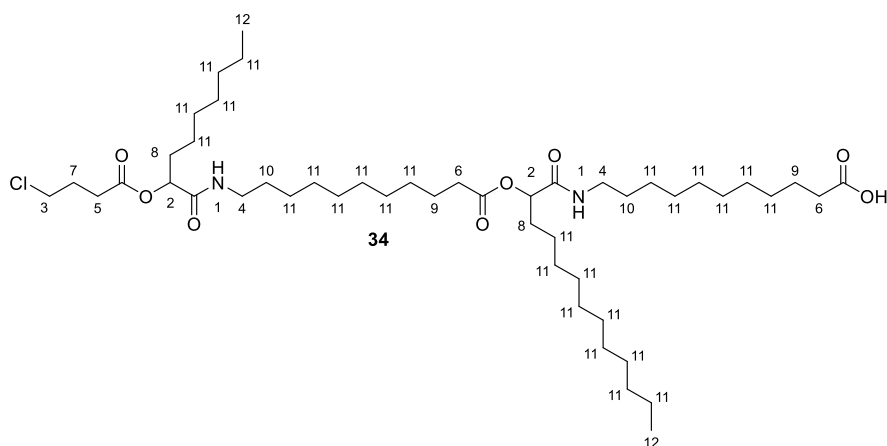
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 172.68, 171.45, 170.46, 168.84, 168.62, 135.11, 127.52, 127.15, 73.32, 72.93, 65.05, 42.92, 38.21, 38.18, 33.30, 30.89, 30.70, 30.09, 28.60, 28.53, 28.52, 28.43, 28.42, 28.34, 28.33, 28.24, 28.19, 28.18, 28.09, 28.06, 26.35, 25.81, 23.94, 23.92, 23.77, 23.74, 21.67, 21.59, 13.10, 13.05.

ESI-MS [m/z]: [$\text{M}+\text{H}$]⁺ calculated for $^{12}\text{C}_{55}^{1}\text{H}_{95}^{16}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}$, 947.6850; found: 947.6823; Δ = 1.8 mmu.



Supplementary Figure 33: ^1H -NMR of compound **33** measured in CDCl_3 .

Deprotection



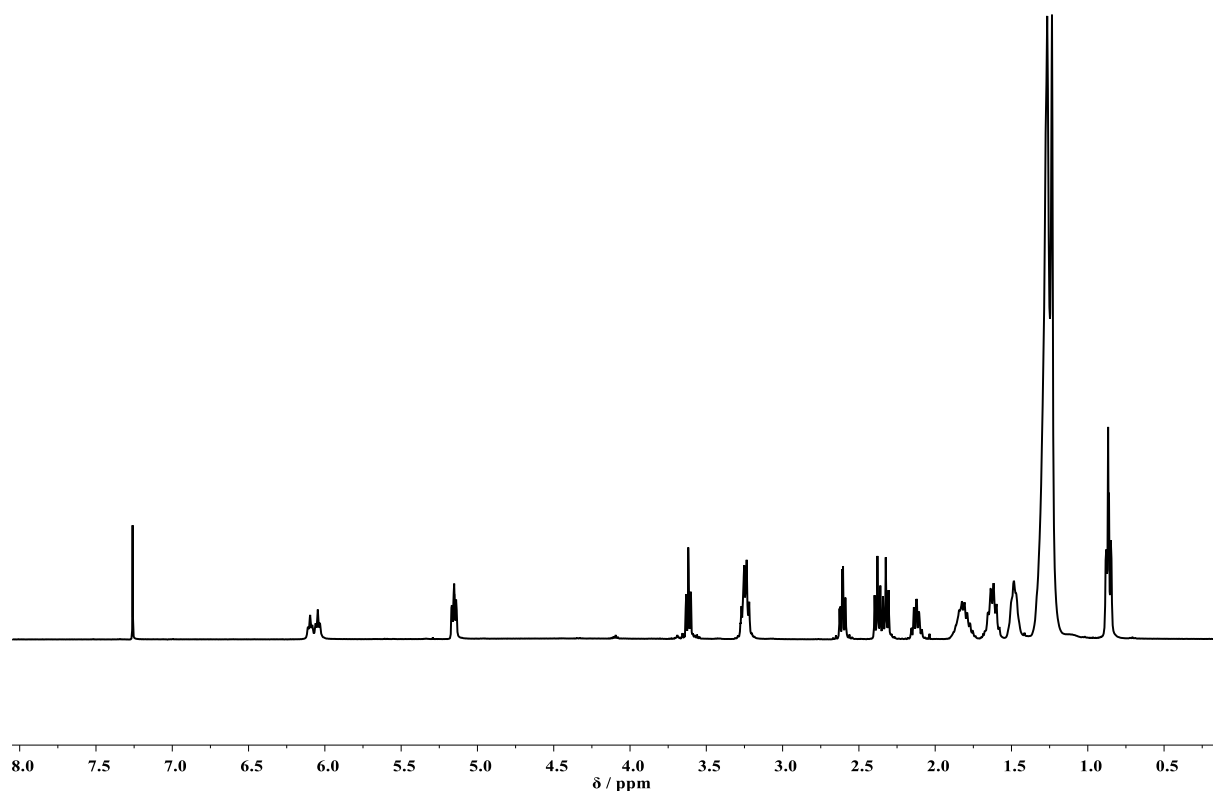
In a 50 mL round bottom flask, 525 mg of **33** (610 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 117 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **34** was obtained as a pale highly viscous oil in a yield of 96.7% (502 mg, 590 μmol).

IR (ATR): ν/cm^{-1} = 3291.2 (w), 2919.5 (vs), 2850.7 (s), 1736.6 (s), 1698.2 (m), 1655.5 (vs), 1560.4 (m), 1466.9 (m), 1377.2 (w), 1302.3 (w), 1170.6 (s), 938.1 (vw), 721.1 (w), 445.9 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.04 (t, J = 5.9 Hz, 1 H, NH^1), 5.99 (t, J = 5.8 Hz, 1 H, NH^1), 5.14 – 5.06 (m, 2 H, CH^2), 3.67 – 3.48 (m, 2 H, CH_2^3), 3.25 – 3.10 (m, 4 H, CH_2^4), 2.55 (td, J = 7.1, 1.9 Hz, 2 H, CH_2^5), 2.32 (t, J = 7.5 Hz, 2 H, CH_2^6), 2.27 (t, J = 7.5 Hz, 2 H, CH_2^6), 2.11 – 2.00 (m, 2 H, CH_2^7), 1.87 – 1.65 (m, 4 H, CH_2^8), 1.65 – 1.49 (m, 4 H, CH_2^9), 1.50 – 1.31 (m, 4 H, CH_2^{10}), 1.32 – 0.98 (m, 52 H, CH_2^{11}), 0.84 – 0.74 (m, 6 H, CH_3^{12}).

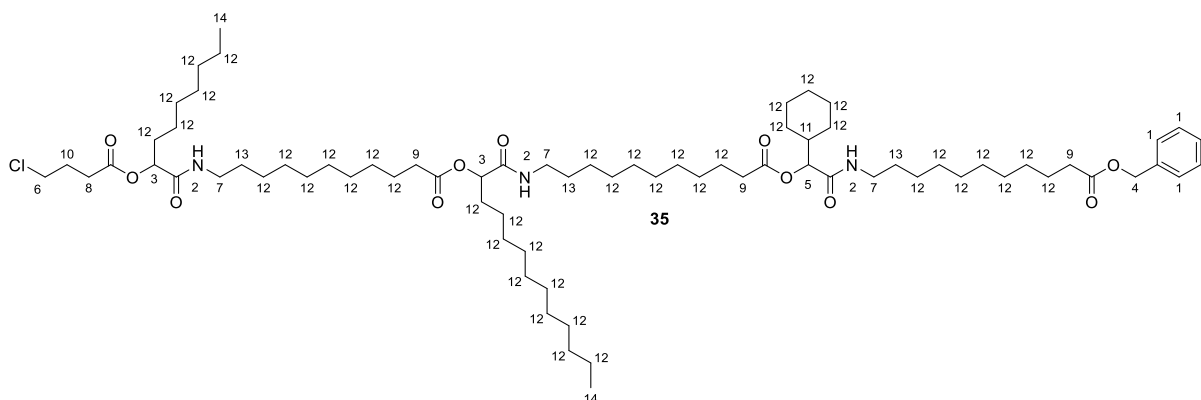
^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 178.05, 172.63, 171.68, 170.11, 169.97, 74.45, 74.08, 44.06, 39.42, 39.32, 34.45, 34.05, 32.04, 31.84, 31.24, 29.75, 29.66, 29.63, 29.58, 29.57, 29.50, 29.47, 29.37, 29.32, 29.24, 29.20, 29.11, 27.49, 26.95, 26.89, 25.10, 24.90, 24.89, 24.87, 22.81, 22.73, 14.25, 14.20.

ESI-MS [m/z]: $[\text{M} + \text{H}]^+$ calculated for $^{12}\text{C}_{48}^{1}\text{H}_{89}^{16}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}$, 857.6380 found, 857.6366, Δ = 1.4 mmu.



Supplementary Figure 34: ^1H -NMR of compound 34 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 1.35 g **34** (1.58 mmol, 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 286 μ L cyclohexanecarboxaldehyde **14j** (265 mg, 2.37 mmol, 1.50 eq.) and 714 mg of the monomer **M1** (2.37 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **35** as a yellow highly viscous oil. (1.88 g, 1.48 mmol, 93.7%).

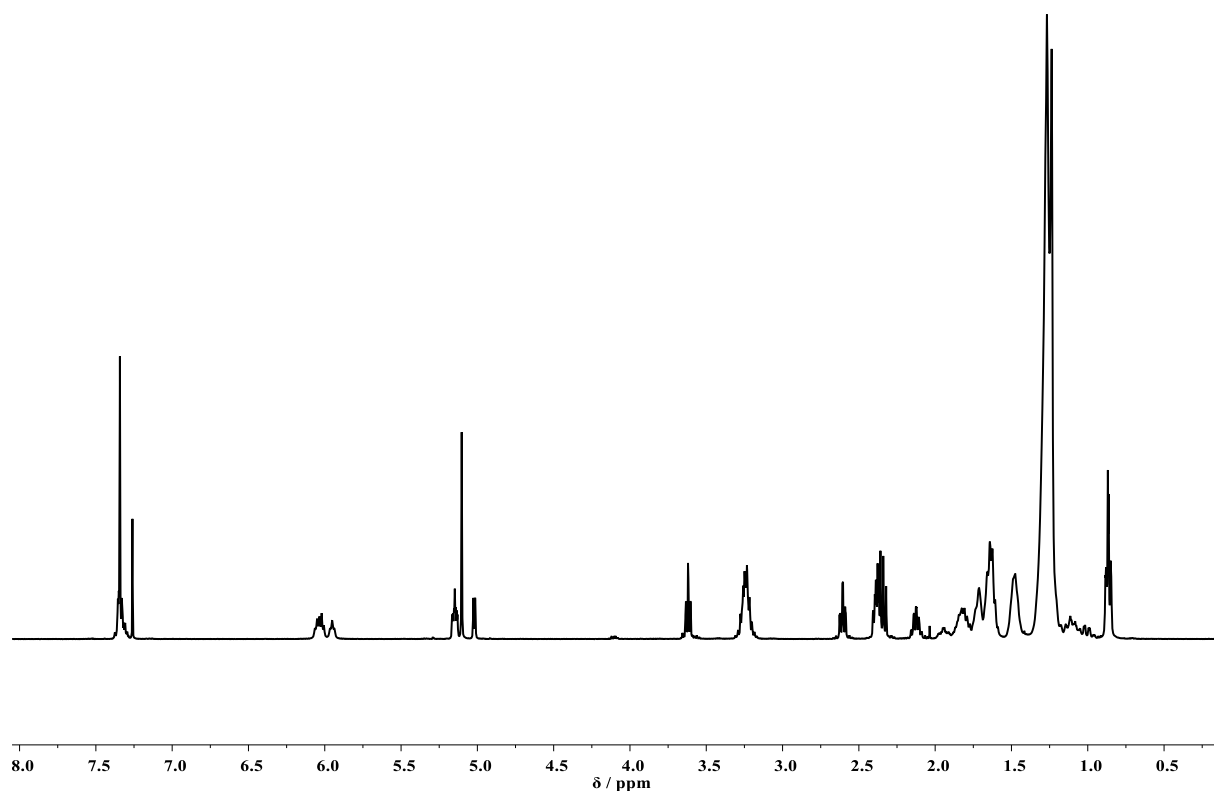
R_f: 0.20 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm^{-1} = 3293.1 (w), 2918.0 (vs), 2850.4 (s), 1733.1 (vs), 1655.0 (vs), 1558.1 (m), 1466.2 (m), 1378.1 (m), 1238.1 (m), 1207.0 (s), 1172.8 (vs), 980.7 (w), 721.9 (m), 695.9 (m), 453.1 (vw).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.41 – 7.29 (m, 5 H, CH_{Ar}¹), 6.09 – 6.00 (m, 2 H, NH²), 5.95 (t, J = 6.0 Hz, 1 H, NH²), 5.18 – 5.12 (m, 2 H, CH³), 5.10 (s, 2 H, CH₂⁴), 5.02 (d, J = 4.6 Hz, 1 H, CH⁵), 3.67 – 3.58 (m, 2 H, CH₂⁶), 3.32 – 3.16 (m, 6 H, CH₂⁷), 2.61 (td, J = 7.1, 1.9 Hz, 2 H, CH₂⁸), 2.44 – 2.29 (m, 6 H, CH₂⁹), 2.19 – 2.07 (m, 2 H, CH₂¹⁰), 2.00 – 1.58 (m, 17 H, CH¹¹, CH₂¹²), 1.54 – 1.42 (m, 6 H, CH₂¹³), 1.39 – 1.05 (m, 68 H, CH₂¹²), 0.91 – 0.82 (m, 6 H, CH₃¹⁴).

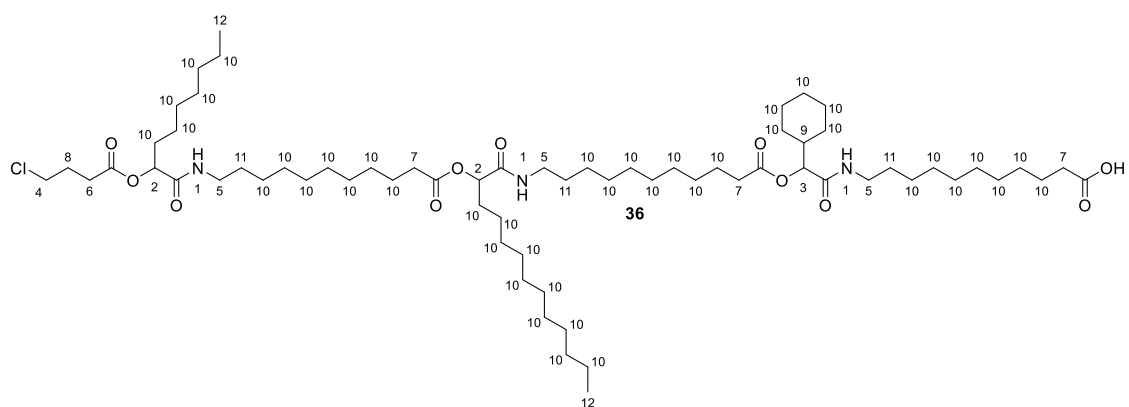
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.81, 172.67, 172.60, 171.61, 170.00, 169.77, 169.33, 136.23, 128.66, 128.29, 128.28, 77.74, 74.44, 74.05, 66.19, 44.07, 40.09, 39.35, 39.30, 39.27, 34.44, 34.41, 32.04, 32.03, 31.84, 31.22, 29.74, 29.68, 29.66, 29.58, 29.57, 29.49, 29.46, 29.38, 29.35, 29.32, 29.25, 29.22, 29.20, 27.49, 27.41, 26.96, 26.95, 26.19, 26.11, 26.00, 25.11, 25.08, 25.06, 24.90, 24.89, 22.81, 22.73, 14.25, 14.20.

ESI-MS [m/z]: [M+Na]⁺ calculated for ¹²C₇₄¹H₁₂₈¹⁶O₁₁¹⁴N₃³⁵Cl, 1292.9130; found: 1292.9134; Δ = 0.4 mmu.



Supplementary Figure 35: ^1H -NMR of compound **35** measured in CDCl_3 .

Deprotection



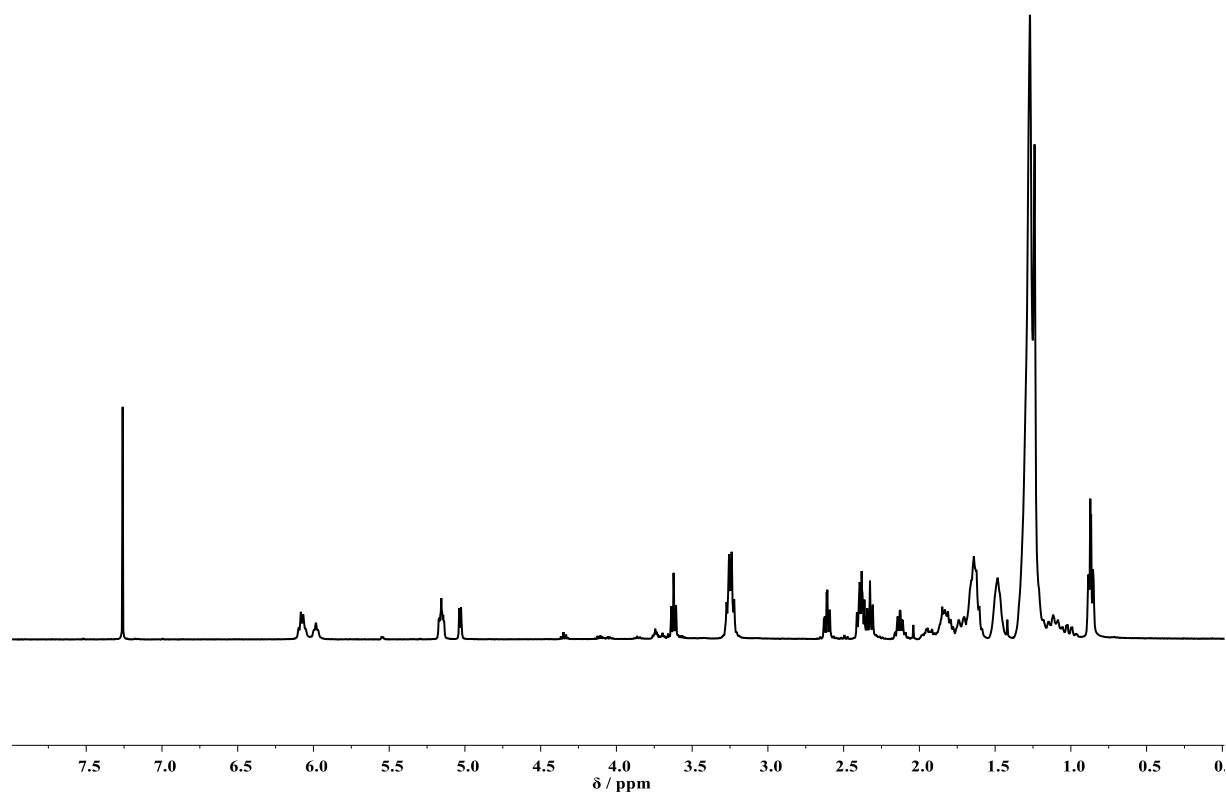
In a 50 mL round bottom flask, 1.49 g of **35** (1.17 mmol, 1.00 eq.) were dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Afterwards, 149 mg (10 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **36** was obtained as a pale highly viscous oil in a yield of 99.1% (1.37 g, 1.16 mmol).

IR (ATR): ν/cm^{-1} = 3292.4 (w), 2918.6 (vs), 2850.6 (vs), 1735.6 (s), 1654.9 (vs), 1556.3 (m), 1466.0 (m), 1377.5 (m), 1244.8 (m), 1207.9 (s), 1177.3 (vs), 941.3 (vw), 721.6 (w), 454.0 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.06 – 5.97 (m, 2 H, NH^1), 5.92 (t, J = 6.0 Hz, 1 H, NH^1), 5.13 – 5.06 (m, 2 H, CH^2), 4.97 (d, J = 4.6 Hz, 1 H, CH^3), 3.62 – 3.51 (m, 2 H, CH_2^4), 3.24 – 3.09 (m, 6 H, CH_2^5), 2.55 (td, J = 7.1, 1.8 Hz, 2 H, CH_2^6), 2.36 – 2.22 (m, 6 H, CH_2^7), 2.12 – 2.01 (m, 2 H, CH_2^8), 1.93 – 1.51 (m, 15 H, CH^9 , CH_2^{10}), 1.50 – 1.38 (m, 6 H, CH_2^{11}), 1.32 – 0.93 (m, 70 H, CH_2^{10}), 0.85 – 0.74 (m, 6 H, CH_3^{12}).

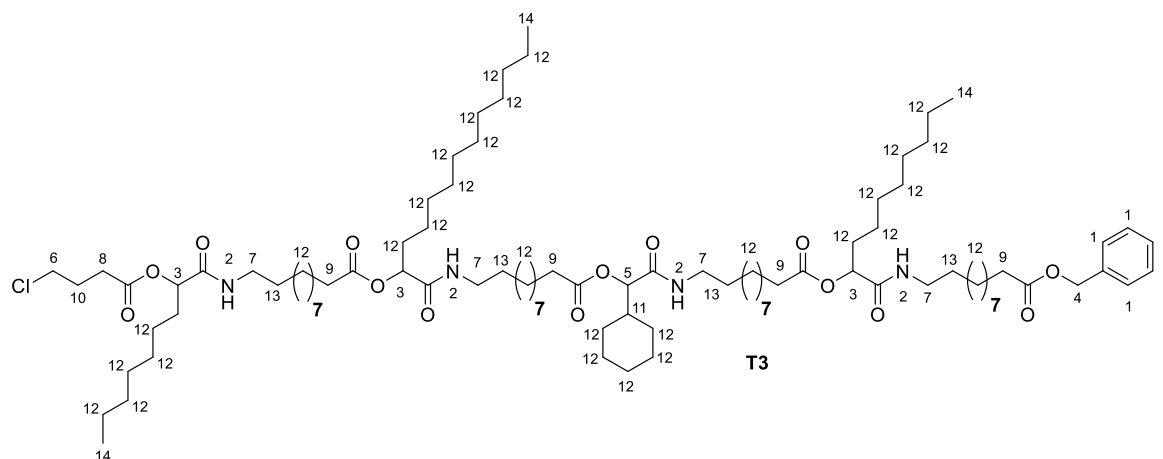
^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 172.71, 171.65, 170.19, 169.90, 169.44, 77.78, 74.46, 74.08, 44.08, 40.06, 39.40, 39.24, 34.45, 33.96, 32.05, 32.01, 31.86, 31.25, 29.76, 29.68, 29.65, 29.61, 29.58, 29.53, 29.50, 29.49, 29.41, 29.38, 29.35, 29.34, 29.29, 29.24, 29.21, 29.20, 29.08, 27.50, 27.42, 26.96, 26.89, 26.20, 26.12, 26.01, 25.16, 25.09, 24.92, 24.91, 22.82, 22.74, 14.26, 14.21.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{67}^{1}\text{H}_{122}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}$, 1180.8841 found, 1180.8837, Δ = 0.4 mmu.



Supplementary Figure 36: ^1H -NMR of compound 36 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 415 mg **36** (351 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 91.6 μL nonanal **14k** (74.9 mg, 527 μmol , 1.50 eq.) and 159 mg of the monomer **M1** (517 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 2:1) to yield the passerini product **T3** as a yellow highly viscous oil. (527 mg, 323 μmol , 92.0%).

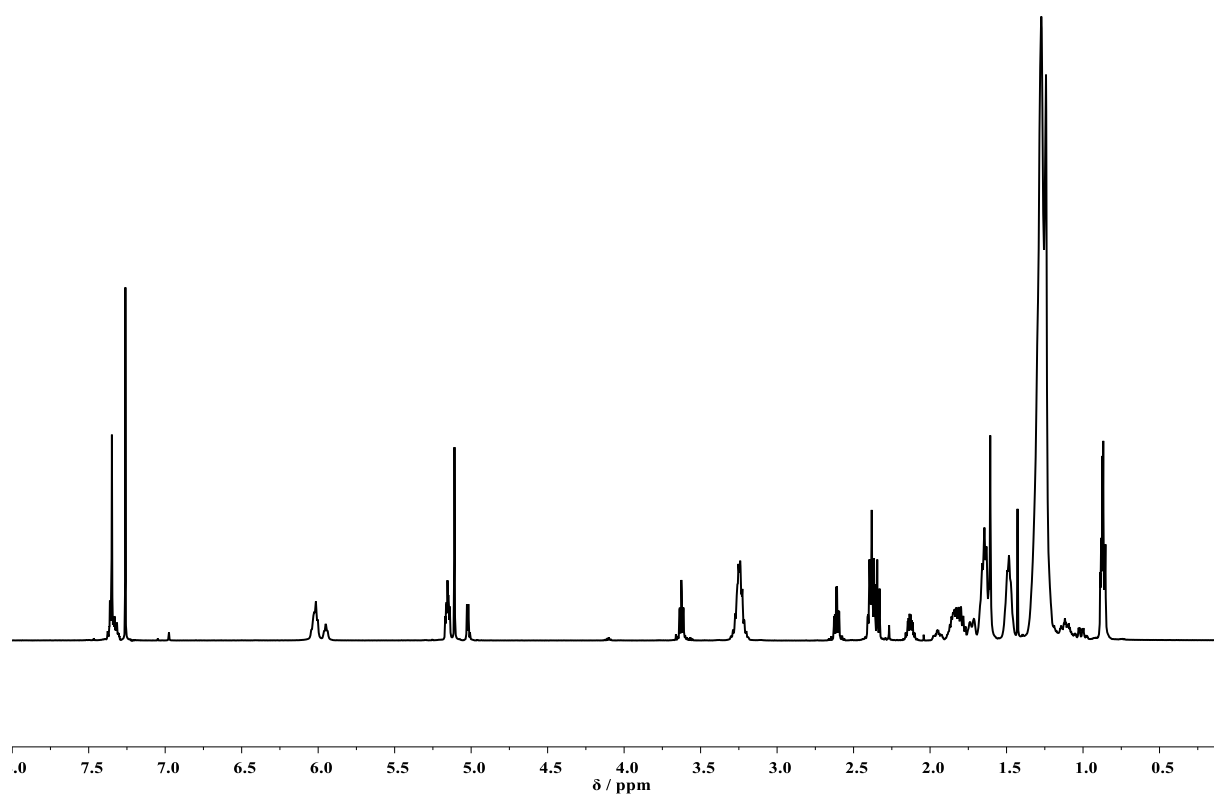
R_f: 0.17 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν / cm^{-1} = 3291.6 (w), 2920.0 (vs), 2851.1 (s), 1736.4 (vs), 1654.9 (vs), 1557.0 (m), 1465.8 (m), 1377.3 (w), 1243.8 (m), 1207.8 (m), 1173.6 (vs), 1112.7 (m), 721.9 (w), 696.4 (m), 453.3 (vw), 384.2 (vw).

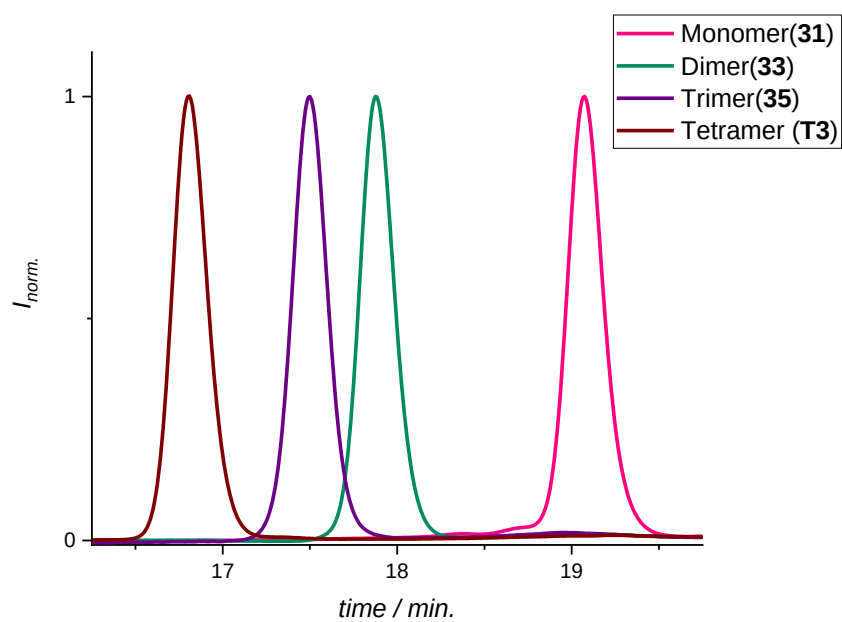
¹H NMR (500 MHz, CDCl₃): δ / ppm = 7.44 – 7.31 (m, 5 H, CH_{Ar}¹), 6.10 – 5.99 (m, 3 H, NH²), 5.97 – 5.87 (m, 1 H, NH²), 5.18 – 5.13 (m, 3 H, CH³), 5.11 (s, 2 H, CH₂⁴), 5.02 (d, J = 4.6 Hz, 1 H, CH⁵), 3.67 – 3.56 (m, 2 H, CH₂⁶), 3.33 – 3.16 (m, 8 H, CH₂⁷), 2.67 – 2.56 (m, 2 H, CH₂⁸), 2.44 – 2.29 (m, 8 H, CH₂⁹), 2.19 – 2.10 (m, 2 H, CH₂¹⁰), 2.01 – 1.58 (m, 23 H, CH¹¹, CH₂¹²), 1.54 – 1.44 (m, 8 H, CH₂¹³), 1.38 – 0.97 (m, 88 H, CH₂¹²), 0.94 – 0.80 (m, 9 H, CH₃¹⁴).

¹³C NMR (126 MHz, CDCl₃): δ / ppm = 173.83, 172.70, 172.61, 171.62, 170.01, 169.98, 169.78, 169.35, 136.26, 128.68, 128.30, 77.76, 74.47, 74.07, 66.21, 44.09, 40.11, 34.46, 34.43, 32.07, 32.06, 31.96, 31.86, 31.24, 30.46, 29.76, 29.73, 29.71, 29.70, 29.68, 29.60, 29.58, 29.53, 29.51, 29.49, 29.40, 29.36, 29.35, 29.33, 29.28, 29.25, 29.22, 27.50, 27.43, 26.99, 26.97, 26.21, 26.13, 26.02, 25.13, 25.10, 25.08, 24.92, 24.89, 22.83, 22.78, 22.75, 14.27, 14.25, 14.22.

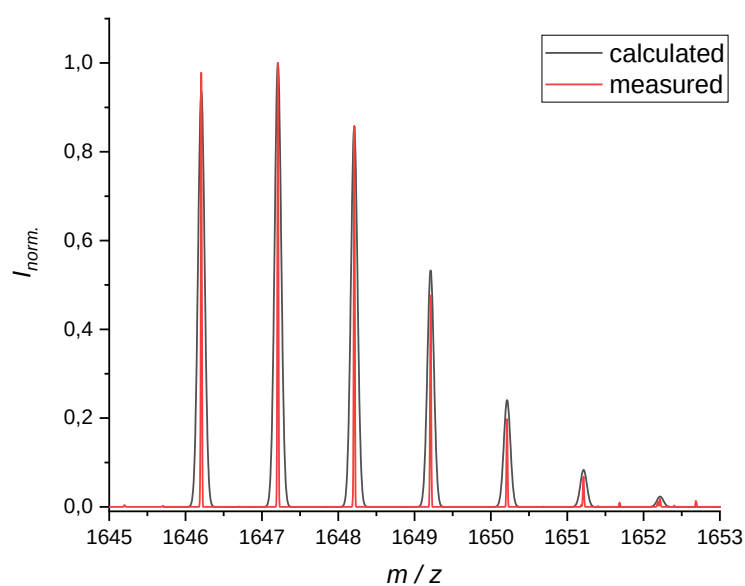
ESI-MS [m/z]: [M+Na]⁺ calculated for ¹²C₉₅¹H₁₆₇¹⁶O₁₄¹⁴N₄³⁵Cl, 1646.2060; found: 1646.2066; Δ = 0.6 mmu.



Supplementary Figure 37: ^1H -NMR of compound T3 measured in CDCl_3 .



Supplementary Figure 38: SEC traces of the intermediates after each P3CR in the synthesis of product T3.



Supplementary Figure 39: High resolution ESI-MS measurement of T3. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

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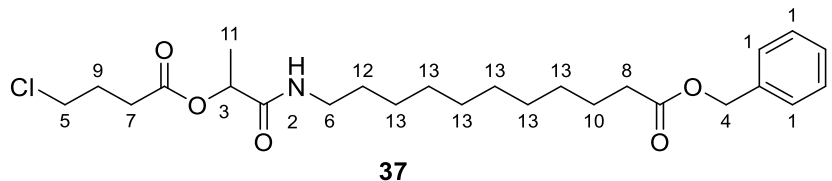
tramer.CSV, maximum is 1.000000 found for mass 1647.207720
matching mass 1647.20772
cutoff 0.50000: 0 solutions (10 peaks)
cutoff 0.25000: 0 solutions (24 peaks)
cutoff 0.12500: 0 solutions (62 peaks)
cutoff 0.06250: 0 solutions (121 peaks)
cutoff 0.03125: 0 solutions (193 peaks)
cutoff 0.01562: 0 solutions (305 peaks)
cutoff 0.00781: 1 solutions (436 peaks)
1647.20772 ≈ 121.005630 + 339.277350 + 395.339950 + 323.246050 + 353.293000 + 91.054780 (sides Octanal, Dodecanal,
Cyclohexancarboxaldehyde, Nonanal; error -23.99096)
Press ENTER to quit ...

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Supplementary Figure 40: Screenshot of the automated read-out of T3, sodium trifluoroacetate was used as additive during the measurement.

1.3.3.5 Synthesis of tetramer T4

Passerini reaction



In a 50 mL round bottom flask, 125 mg 4-chlorobutyric acid **TAG3** (1.02 mmol, 1.00 eq.) was dissolved in 2.00 mL dichloromethane and 171 μ L acetaldehyde **14f** (461 mg, 3.06 mmol, 3.00 eq.) and 461 mg of monomer **M1** (1.53 mol, 3.00 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 $\rightarrow$ 2:1) to yield the passerini product **37** as a pale highly viscous oil with 92.3% (441 mg, 941 μ mol).

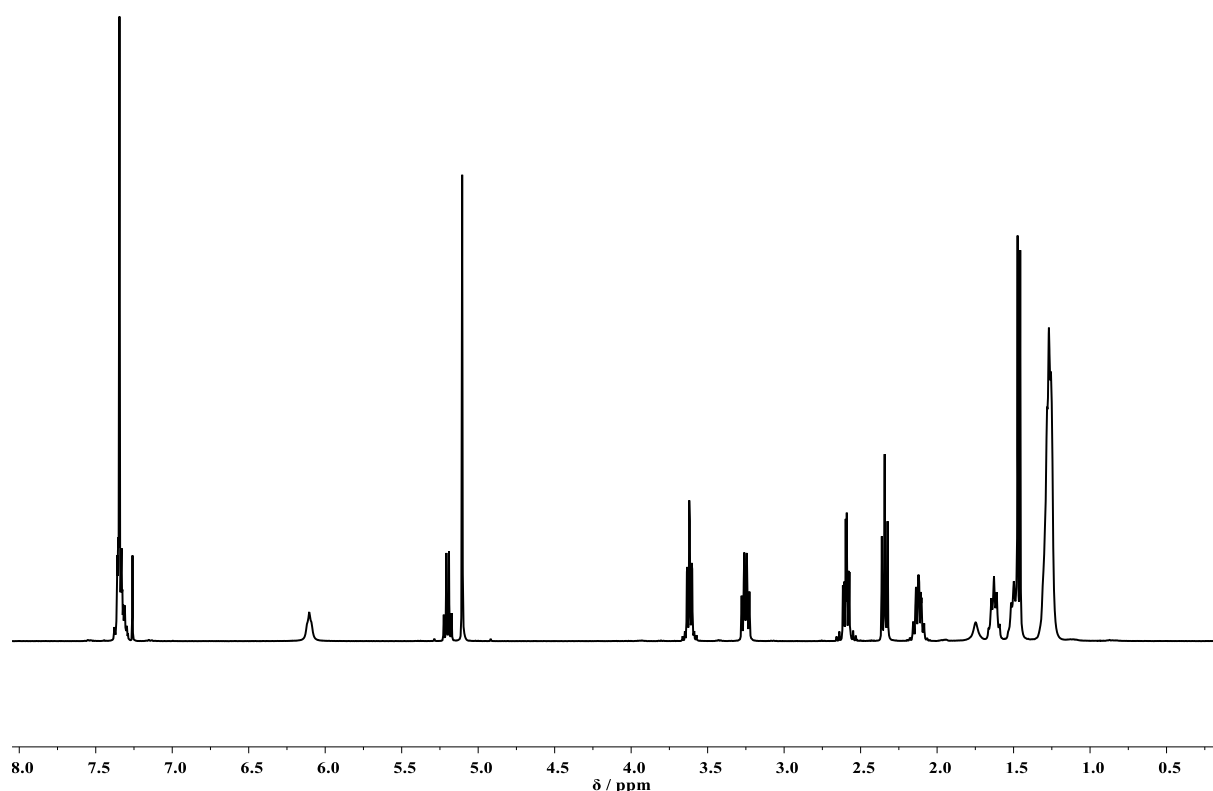
R_f = 0.16 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm^{-1} = 3317.5 (vw), 2926.7 (w), 2854.4 (w), 1734.8 (s), 1660.0 (m), 1538.4 (w), 1498.1 (vw), 1454.9 (w), 1373.5 (w), 1298.4 (w), 1166.8 (m), 1144.5 (s), 1097.3 (w), 1031.5 (vw), 878.2 (vw), 787.6 (vw), 735.8 (w), 697.2 (m), 648.5 (vw), 432.2 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.40 – 7.28 (m, 5 H, CH^1), 6.10 (t, J = 5.9 Hz, 1H, NH^2), 5.20 (q, J = 6.8 Hz, 1 H, CH^3), 5.10 (s, 2 H, CH_2^4), 3.71 – 3.55 (m, 2 H, CH_2^5), 3.32 – 3.19 (m, 2 H, CH_2^6), 2.59 (td, J = 7.1, 2.7 Hz, 2 H, CH_2^7), 2.34 (t, J = 7.5 Hz, 2 H, CH_2^8), 2.21 – 2.04 (m, 2 H, CH_2^9), 1.69 – 1.56 (m, 2 H, CH_2^{10}), 1.55 – 1.43 (m, 5 H, CH^{11} , CH_2^{12}), 1.34 – 1.21 (m, 12 H, CH_2^{13}).

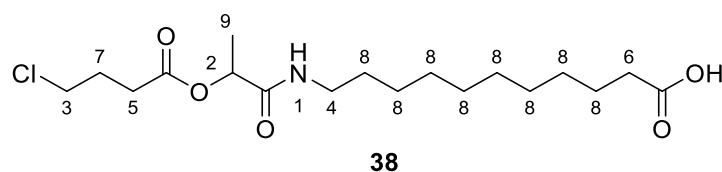
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 171.36, 170.21, 136.23, 128.65, 128.27, 70.93, 66.18, 44.06, 39.39, 34.43, 31.29, 29.60, 29.52, 29.43, 29.31, 29.30, 29.20, 27.46, 26.92, 25.04, 18.09.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{25}^{1}\text{H}_{38}^{16}\text{O}_5^{14}\text{N}^{35}\text{Cl}$, 468.2511; found, 468.2511, Δ = 0.0 mmu.



Supplementary Figure 41: ^1H -NMR of compound **37** measured in CDCl_3 .

Deprotection



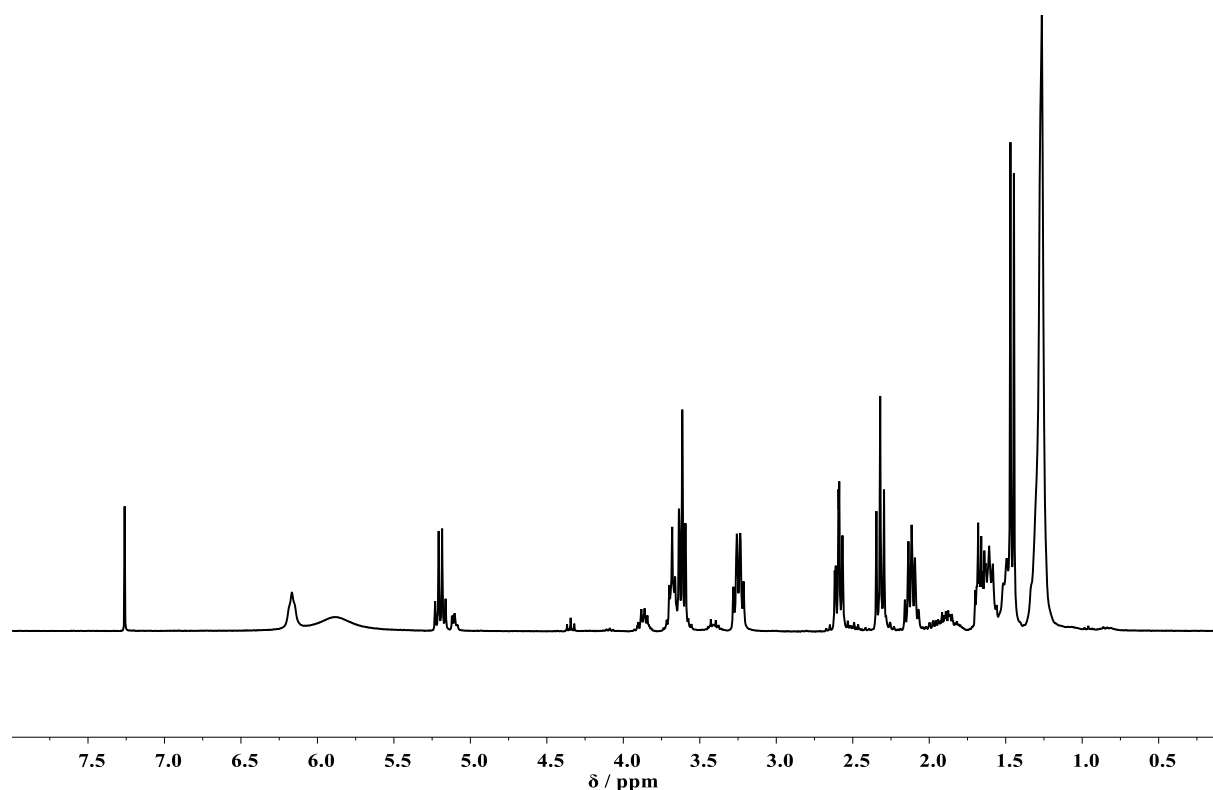
In a 25 mL round bottom flask equipped with a magnetic stir bar, 394 mg of passerini product **37** (841 μmol , 1.00 eq.) was dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Subsequently, 99.4 mg (20 wt.-%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 2 d at room temperature under hydrogen atmosphere (3 balloons). The heterogeneous catalyst was filtered over celite[®] and the solvent was evaporated under reduced pressure. The product **38** was obtained as a pale highly viscous oil in a yield of 97.5% (310 mg, 820 μmol).

IR (ATR): ν/cm^{-1} = 3295.2790 (w), 2919.4 (m), 2850.1 (w), 1729.4 (w), 1690.9 (w), 1653.4 (m), 1550.8 (m), 1453.5 (w), 1435.5 (w), 1407.6 (w), 1372.9 (w), 1330.3 (w), 1278.1 (w), 1256.2 (w), 1235.8 (w), 1187.4 (w), 1145.0(w), 1092.2 (w), 1057.9 (w), 1037.6 (w), 999.7 (w), 880.21 (vw), 840.8 (vw), 721.4 (w), 686.6 (w), 542.3(vw), 431.0 (vw).

^1H NMR (300 MHz, CDCl_3): δ / ppm = 6.26 – 5.72 (m, 1 H, NH^1), 5.27 – 5.06 (m, 1 H, CH^2), 3.92 – 3.53 (m, 2 H, CH_2^3), 3.49 – 3.17 (m, 2 H, CH_2^4), 2.69 – 2.45 (m, 2 H, CH_2^5), 2.32 (t, J = 7.5 Hz, 2 H, CH_2^6), 2.19 – 1.86 (m, 2 H, CH_2^7), 2.03 – 0.77 (m, 19 H, CH_2^8 , CH_3^9).

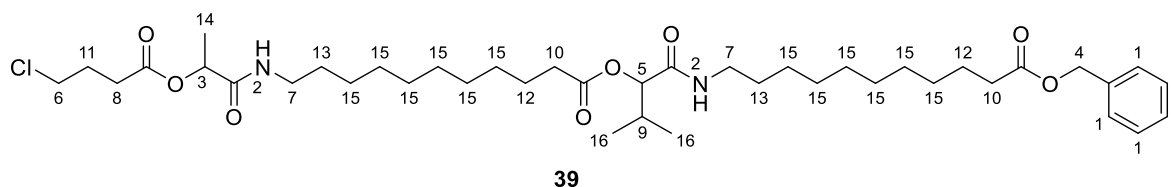
^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 178.74, 171.41, 170.44, 70.89, 67.31, 67.12, 64.18, 62.76, 62.38, 44.05, 39.43, 34.08, 31.27, 29.92, 29.51, 29.43, 29.34, 29.22, 29.08, 27.44, 26.86, 24.80, 18.06.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{18}^{1}\text{H}_{33}^{16}\text{O}_5^{14}\text{N}^{35}\text{Cl}$, 378.2042; found, 378.2030, Δ = 1.2 mmu.



Supplementary Figure 42: ^1H -NMR of compound **38** measured in CDCl_3 .

Passerini reaction



In a 25 mL round bottom flask, 263 mg of **38** (695 μmol , 1.00 eq.) was dissolved in 3.00 mL dichloromethane (DCM) and 37.6 μL isobutyraldehyde **14c** (30.1 mg, 417 μmol , 0.60 eq.) and 126 mg of monomer **M1** (417 μmol , 0.60 eq.) were added. The mixture was stirred at room temperature for 24 hours and subsequently the solvent was removed under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture

of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **39** with 73.9% (232 mg, 514 μ mol).

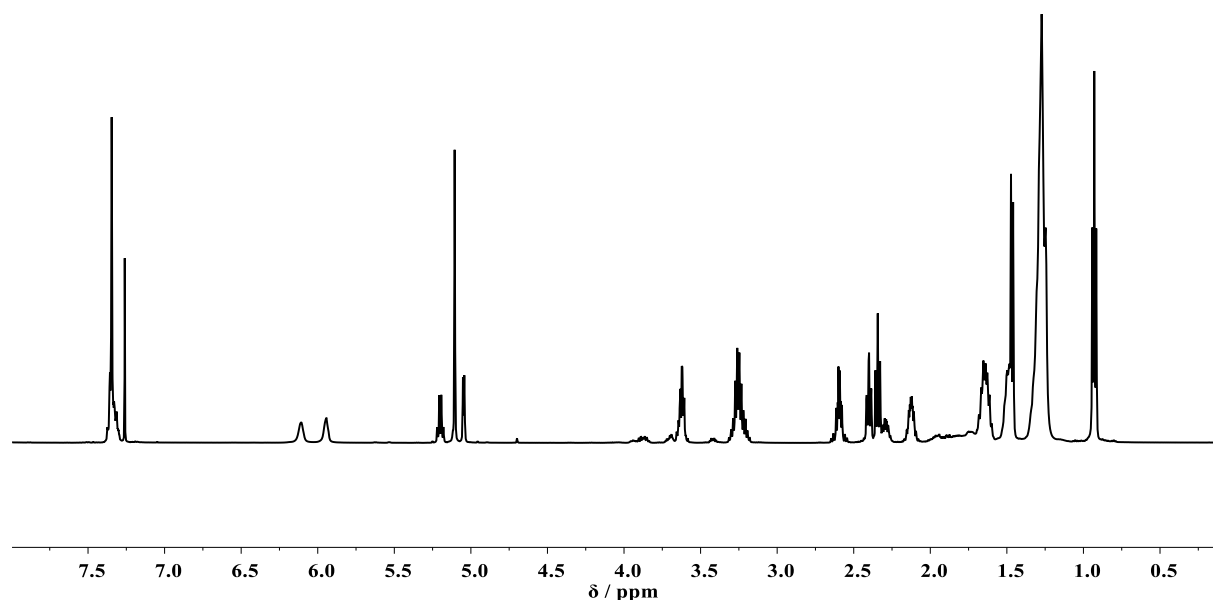
R_f = 0.64 in cyclohexane / ethyl acetate (1:1).

IR (ATR): ν / cm^{-1} = 3304.8 (vw), 2926.0 (m), 2854.2 (m), 1737.0 (vs), 1656.0 (s), 1537.2 (m), 1455.2 (w), 1371.1 (w), 1166.4 (s), 1098.9 (m), 1034.3 (w), 734.6 (w), 697.3 (m), 646.2 (vw).

^1H -NMR (500 MHz, CDCl_3): δ / ppm = 7.35 – 7.22 (m, 5 H, CH_{Ar}^1), 6.13 – 6.00 (m, 1 H, NH^2), 5.96 – 5.79 (m, 1 H, NH^2), 5.14 (q, J = 6.8 Hz, 1 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.98 (d, J = 4.4 Hz, 1 H, CH^5), 3.69 – 3.46 (m, 2 H, CH_2^6), 3.28 – 3.07 (m, 4 H, CH_2^7), 2.58 – 2.43 (m, 2 H, CH_2^8), 2.41 – 2.16 (m, 5 H, CH^9 , CH_2^{10}), 2.11 – 1.97 (m, 2 H, CH_2^{11}), 1.65 – 1.46 (m, 4 H, CH_2^{12}), 1.49 – 1.37 (m, 7 H, CH_2^{13} , CH_3^{14}), 1.32 – 1.08 (m, 4 H, CH_2^{15}), 0.87 (t, J = 6.5 Hz, 6 H, CH_3^{16}).

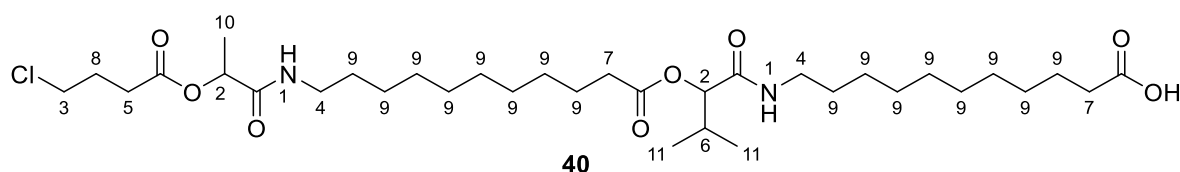
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.83, 172.68, 171.39, 170.24, 169.40, 136.27, 128.68, 128.29, 78.06, 70.97, 66.20, 44.08, 39.40, 39.30, 34.46, 34.43, 31.32, 30.81, 30.65, 29.98, 29.71, 29.64, 29.56, 29.47, 29.33, 29.24, 27.49, 26.97, 26.94, 25.89, 25.14, 25.07, 24.09, 23.98, 18.92, 18.10, 17.09.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{41}^{1}\text{H}_{67}^{16}\text{O}_8^{14}\text{N}_2^{35}\text{Cl}$, 751.4659; found, 751.4636, Δ = 2.3 mmu.



Supplementary Figure 43: ^1H -NMR of compound **39** measured in CDCl_3 .

Deprotection



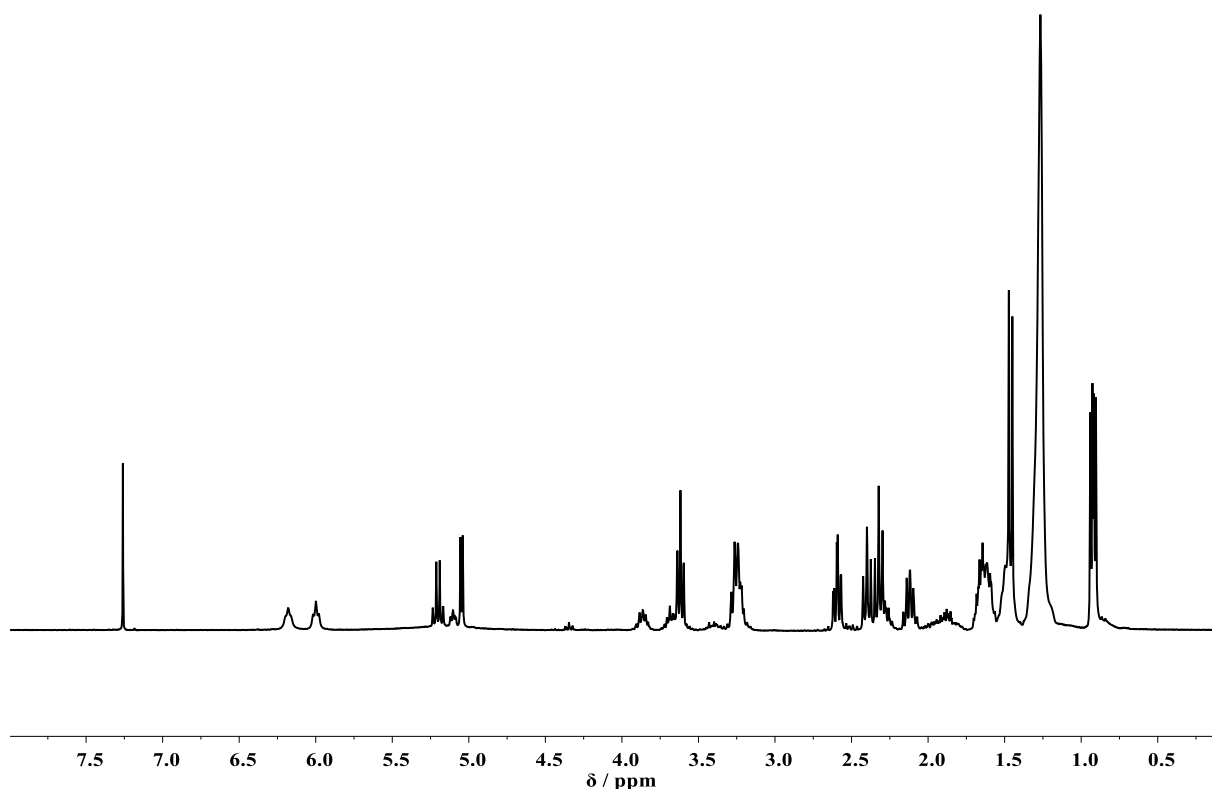
In a 25 mL round bottom flask, 186 mg of **39** (247 μmol , 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 37.2 mg (20 wt.-%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 2 days at room temperature under hydrogen atmosphere (balloon). The crude reaction mixture was filtered over celite[®]. After evaporation of the solvents and drying under reduced pressure, the corresponding acid **40** was obtained in a yield of 94.8% (155 mg, 234 μmol).

IR (ATR): ν/cm^{-1} = 3311.0 (vw), 2925.9 (w), 2854.2 (vw), 2123.5 (vw), 2050.5 (vw), 2031.8 (vw), 2012.5 (vw), 1984.6 (vw), 1738.9 (w), 1652.2 (w), 1541.2 (vw), 1462.4 (vw), 1371.6 (vw), 1171.43 (vw), 1145.1 (vw), 1099.1 (vw), 921.6 (vw), 723.7 (vw), 649.7 (vw), 451.9 (vw), 405.9 (vw).

¹H-NMR (300 MHz, CDCl₃): δ / ppm = 6.19 – 6.08 (m, 1 H, NH¹), 6.01 – 5.85 (m, 1 H, NH¹), 5.21 – 4.96 (m, 2 H, CH²), 3.70 – 3.51 (m, 2 H, CH₂³), 3.42 – 3.08 (m, 4 H, CH₂⁴), 2.65 – 2.43 (m, 2 H, CH₂⁵), 2.40 – 2.16 (m, 5 H, CH⁶, CH₂⁷), 2.14 – 2.00 (m, 2 H, CH₂⁸), 1.93 – 1.31 (m, 13 H, CH₂⁹, CH₃¹⁰), 1.32 – 1.08 (m, 22 H, CH₂⁹), 0.87 (dd, J = 6.8, 4.1 Hz, 6 H, CH₃¹¹).

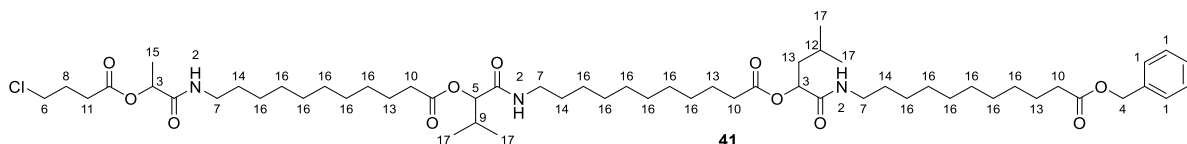
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 177.46, 172.72, 171.45, 170.44, 169.51, 78.06, 70.94, 44.09, 39.46, 39.27, 34.43, 31.30, 30.61, 29.61, 29.59, 29.57, 29.40, 29.35, 29.31, 29.26, 29.19, 27.46, 26.93, 26.88, 25.15, 24.85, 18.92, 18.09, 17.08.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₃₄¹H₆₁¹⁶O₈¹⁴N₂³⁵Cl; 661.4189 found, 661.4197, Δ = 0.8 mmu.



Supplementary Figure 44: ^1H -NMR of compound **40** measured in CDCl_3 .

Passerini reaction



In a 25 mL round bottom flask, 117 mg of **40** (177 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 28.5 μL 3-methylbutanal **14g** (22.8 mg, 265 μmol , 1.50 eq.) and 79.9 mg of monomer **M1** (265 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 1 day and subsequently the solvent was removed under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 1:1) to yield the passerini product **41** with 64.1% (119 mg, 113 μmol).

R_f = 0.64 in cyclohexane / ethyl acetate (1:1).

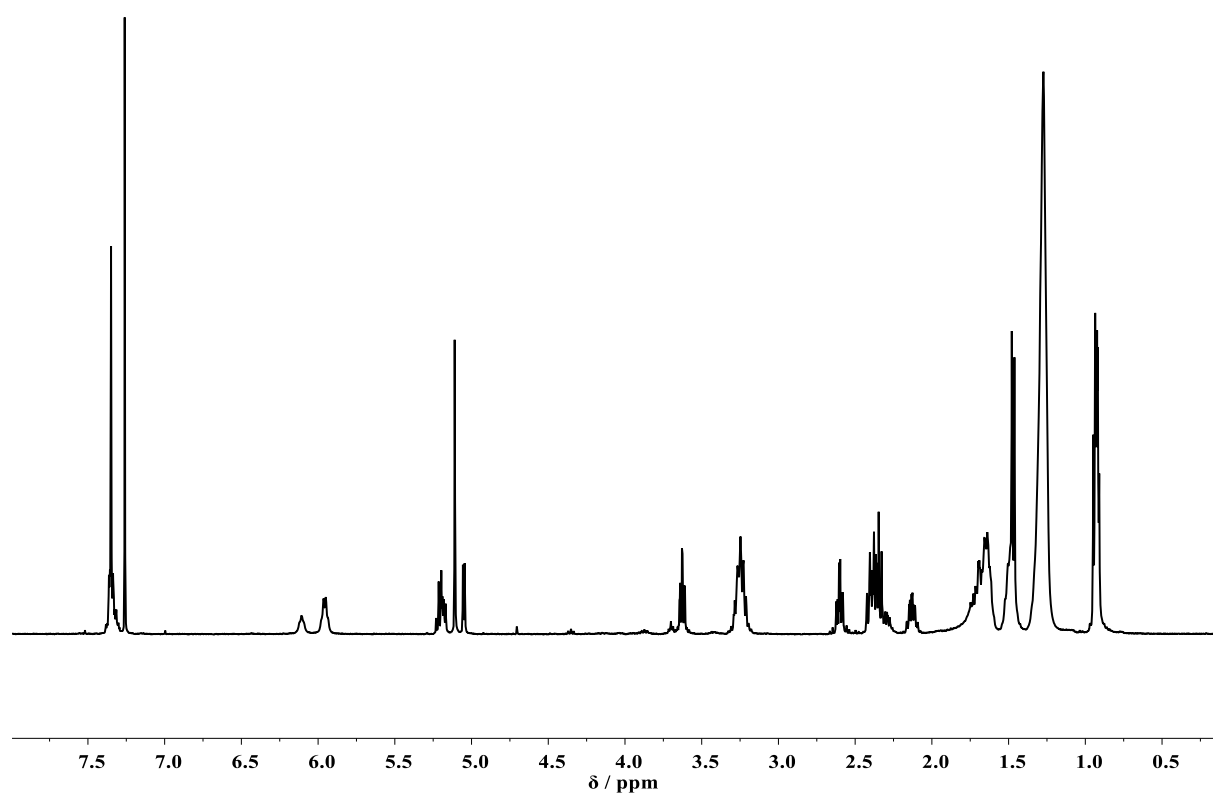
IR (ATR): ν / cm^{-1} = 3292.6 (vw), 2925.4 (w), 2853.9 (vw), 1737.8 (w), 1655.1 (w), 1536.4 (w), 1456.2 (vw), 1370.4 (vw), 1164.8 (w), 1100.7 (vw), 733.0 (vw), 697.6 (vw), 650.2 (vw), 463.2 (vw).

^1H -NMR (400 MHz, CDCl_3): δ / ppm = 7.42 – 7.29 (m, 5 H, CH_{Ar}^1), 6.11 (s, 1 H, NH^2), 5.96 (d, J = 6.3 Hz, 2 H, NH^2), 5.26 – 5.16 (m, 2 H, CH^3), 5.11 (s, 2 H, CH_2^4), 5.05 (d, J = 4.4 Hz, 1 H, CH^5), 3.63 (td, J = 6.2, 1.6 Hz, 2 H, CH_2^6), 3.32 – 3.15 (m, 6 H, CH_2^7), 2.60 (td, J = 7.1, 3.0 Hz, 2 H, CH_2^8), 2.47 – 2.23

(m, 7 H, CH⁹, CH₂¹⁰), 2.21 – 2.08 (m, 2 H, CH₂¹¹), 1.86 – 1.59 (m, 9 H, CH¹², CH₂¹³), 1.55 – 1.42 (m, 9 H, CH₂¹⁴, CH₃¹⁵), 1.36 – 1.15 (m, 36 H, CH₂¹⁶), 1.07 – 0.57 (m, 12 H, CH₃¹⁷).

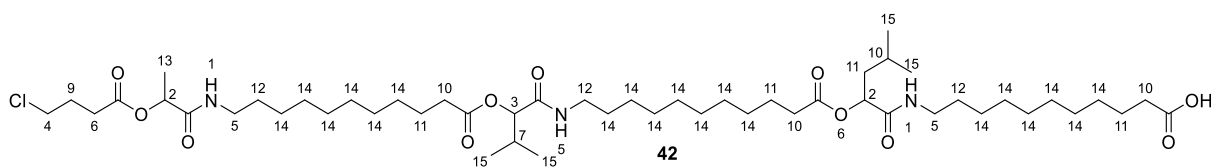
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.83, 172.78, 172.70, 171.40, 170.34, 170.24, 169.42, 136.26, 128.69, 128.30, 78.06, 72.78, 70.97, 66.21, 44.09, 41.00, 39.41, 39.37, 39.29, 34.46, 34.44, 31.32, 30.66, 29.73, 29.66, 29.58, 29.49, 29.35, 29.34, 29.25, 27.49, 26.97, 26.95, 25.15, 25.08, 24.69, 23.28, 21.94, 18.93, 18.12, 17.10.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₅₈¹H₉₈¹⁶O₁₁¹⁴N₃³⁵Cl, 1048.6963; found, 1048.6944, Δ = 1.9 mmu.



Supplementary Figure 45: ¹H-NMR of compound 41 measured in CDCl₃.

Deprotection



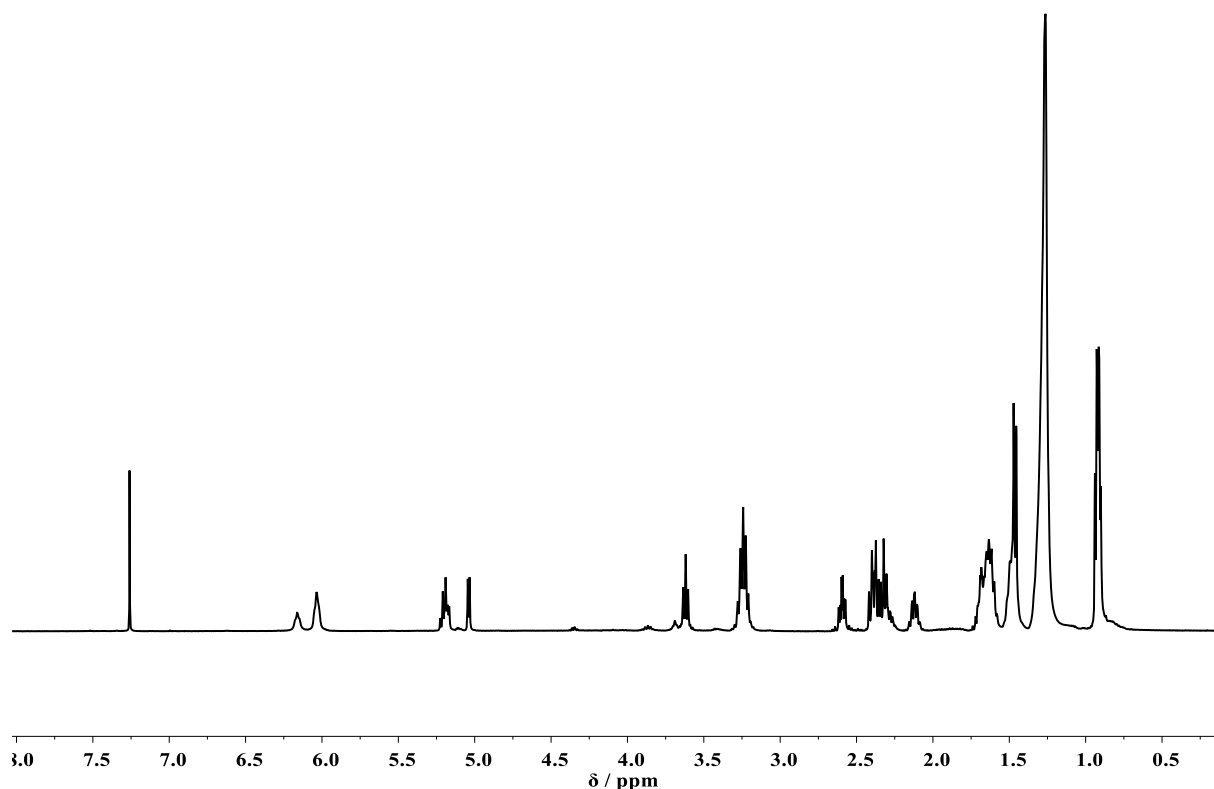
In a 25 mL round bottom flask, 88.9 mg of **41** (85.0 μmol , 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 17.8 mg (20 wt.-%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 2 days at room temperature under hydrogen atmosphere (balloon). The crude reaction mixture was filtered over celite[®]. After evaporation of the solvents and drying under reduced pressure the product **42** was obtained in a yield of 98.2% (79.8 mg, 83.0 μmol).

IR (ATR): ν / cm^{-1} = 3306.7 (vw), 2925.3 (m), 2854.0 (w), 1739.2 (m), 1653.2 (m), 1539.6 (w), 1463.9 (w), 1370.3 (w), 1168.9 (m), 722.3 (vw), 650.7 (vw), 426.7 (vw).

¹H-NMR (400 MHz, CDCl₃): δ / ppm = 6.25 – 6.11 (m, 1 H, NH¹), 6.09 – 5.98 (m, 2 H, NH¹), 5.26 – 5.14 (m, 2 H, CH²), 5.04 (d, J = 4.5 Hz, 1 H, CH³), 3.62 (td, J = 6.4, 1.6 Hz, 2 H, CH⁴), 3.32 – 3.17 (m, J = 6.1 Hz, 6 H, CH₂⁵), 2.59 (td, J = 7.1, 3.2 Hz, 2 H, CH₂⁶), 2.44 – 2.23 (m, 7 H, CH⁷, CH₂⁸), 2.19 – 2.06 (m, 2 H, CH₂⁹), 1.74 – 1.56 (m, 9 H, CH¹⁰, CH₂¹¹), 1.54 – 1.40 (m, 9 H, CH₂¹², CH₃¹³), 1.39 – 1.12 (m, 36 H, CH₂¹⁴), 1.01 – 0.85 (m, 12 H, CH₃¹⁵).

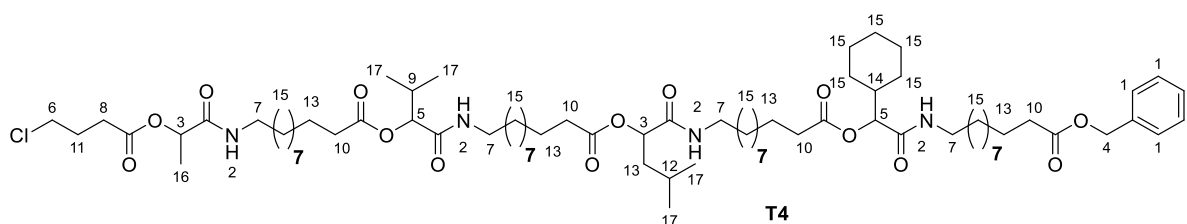
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 177.43, 172.82, 171.42, 170.45, 170.38, 169.59, 78.07, 72.79, 70.93, 44.08, 40.94, 39.43, 39.34, 34.42, 33.98, 31.30, 30.62, 29.68, 29.61, 29.57, 29.53, 29.48, 29.45, 29.34, 29.31, 29.22, 29.09, 27.48, 26.96, 26.92, 26.86, 25.11, 25.07, 24.87, 24.68, 23.25, 21.92, 18.89, 18.09, 17.11.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₅₁¹H₉₂¹⁶O₁₁¹⁴N₃³⁵Cl, 958.6493; found, 958.6476, Δ = 1.7 mmu.



Supplementary Figure 46: ^1H -NMR of compound **42** measured in CDCl_3 .

Passerini reaction



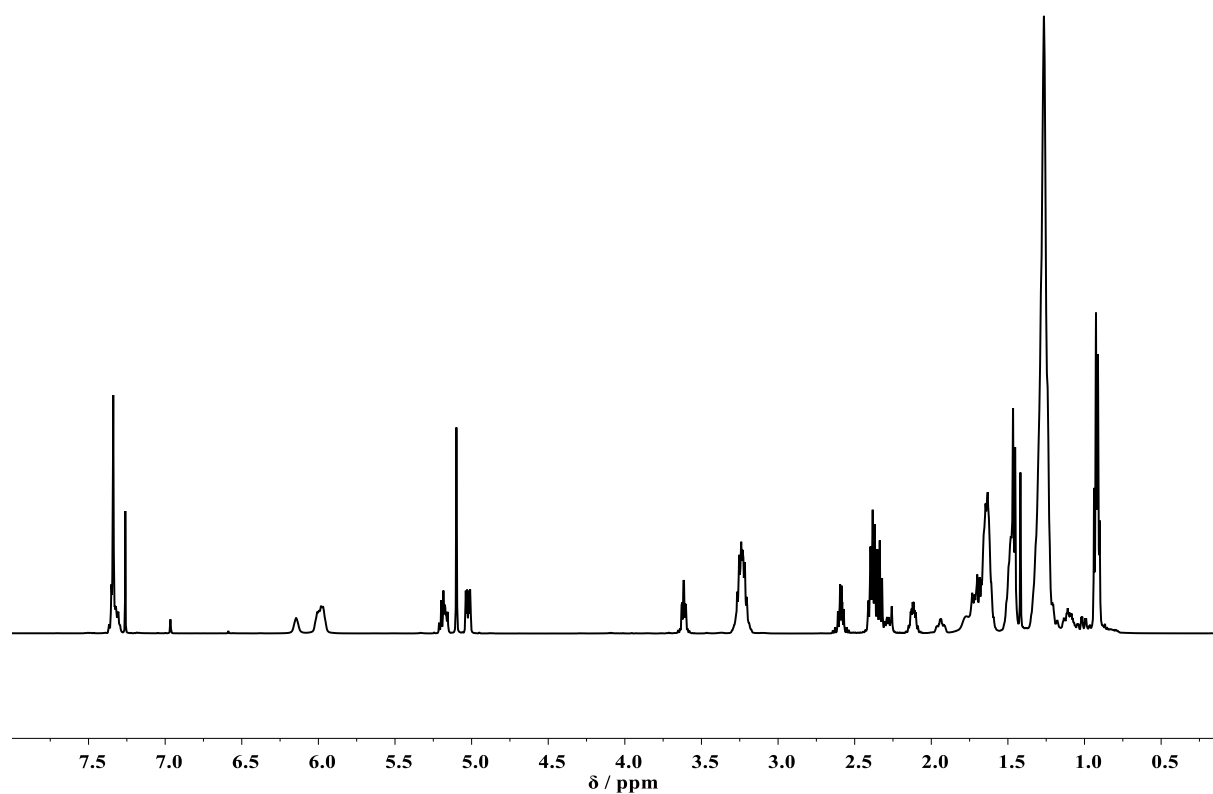
In a 25 mL round bottom flask, 51.6 mg of **42** (54.0 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 9.10 mg cyclohexanecarboxaldehyde **14j** (81.0 μmol , 1.50 eq.) and 24.3 mg of monomer **M1** (81.0 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 1 day and subsequently the solvent was removed under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (2:1 $\rightarrow$ 0:1) to yield the passerini product **T4** with 88.5% (65.4 mg, 48 μmol). R_f = 0.76 in cyclohexane / ethyl acetate (1:2).

IR (ATR): ν/cm^{-1} = 3299.7 (vw), 2924.9 (w), 2853.4 (w), 1738.5 (w), 1654.9 (w), 1536.8 (w), 1453.9 (vw), 1370.5 (vw), 1165.7 (w), 1101.3 (vw), 722.8 (vw), 697.9 (vw), 488.6 (vw), 461.0 (vw), 417.6 (vw).

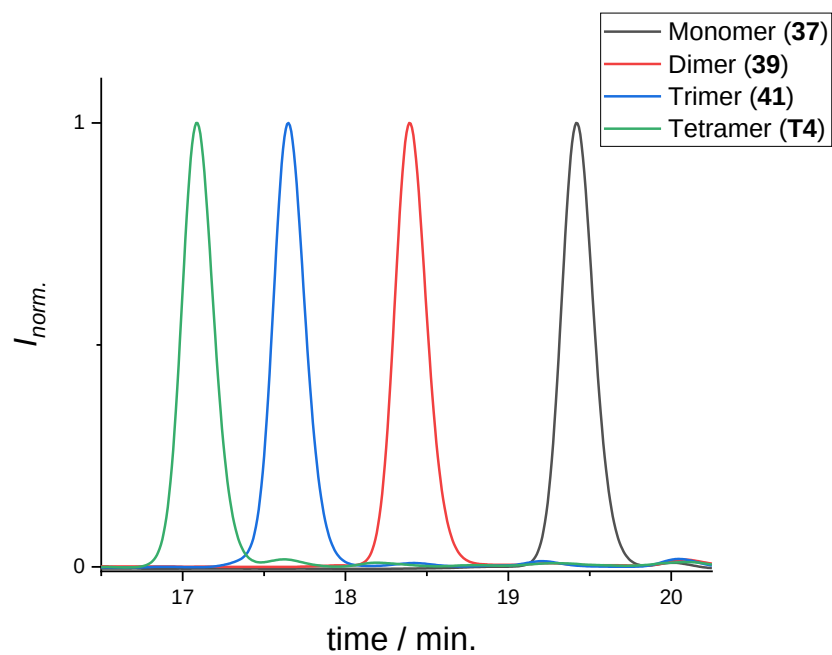
^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.40 – 7.28 (m, 5 H, CH_{Ar}^1), 6.15 (t, J = 6.0 Hz, 1 H, NH^2), 6.06 – 5.90 (m, 3 H, NH^2), 5.25 – 5.13 (m, 2 H, CH^3), 5.10 (s, 2 H, CH_2^4), 5.05 – 4.98 (m, 2 H, CH^5), 3.67 – 3.57 (m, 2 H, CH_2^6), 3.35 – 3.14 (m, 8 H, CH_2^7), 2.66 – 2.53 (m, 2 H, CH_2^8), 2.44 – 2.25 (m, 9 H, CH^9 , CH_2^{10}), 2.16 – 2.06 (m, 2 H, CH_2^{11}), 2.01 – 1.90 (m, 1 H, CH^{12}), 1.84 – 1.58 (m, 18 H, CH_2^{13}), 1.56 – 1.38 (m, 12 H, CH^{14} , CH_2^{15} , CH_3^{16}), 1.35 – 1.05 (m, 50 H, CH_2^{15}), 0.98 – 0.88 (m, 12 H, CH_3^{17}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.73, 172.72, 172.64, 171.35, 170.31, 170.21, 169.35, 169.28, 136.16, 135.86, 128.58, 128.20, 77.96, 77.66, 72.66, 70.82, 66.11, 44.01, 40.91, 40.03, 39.31, 39.27, 39.20, 34.36, 34.32, 31.22, 30.56, 30.37, 29.61, 29.49, 29.39, 29.24, 29.15, 27.42, 27.35, 26.87, 26.12, 26.05, 25.93, 25.66, 25.04, 24.98, 24.59, 23.19, 21.84, 18.84, 18.02, 17.03.

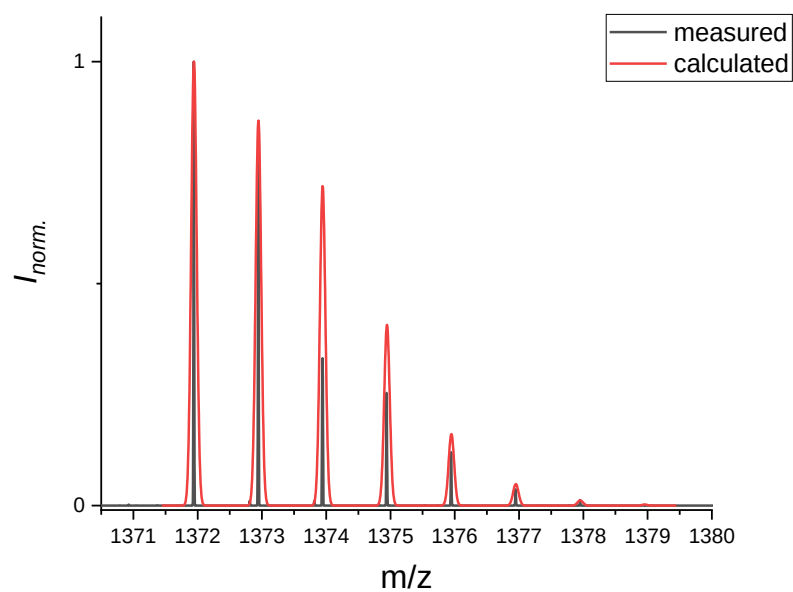
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{77}^{1}\text{H}_{131}^{16}\text{O}_{14}^{14}\text{N}_4^{35}\text{Cl}$, 1371.9423; found, 1371.9403, Δ = 2.0 mmu.



Supplementary Figure 47: ^1H -NMR of compound T4 measured in CDCl_3 .



Supplementary Figure 48: SEC traces of the intermediates after each P3CR in the synthesis of product T4.



Supplementary Figure 49: High resolution ESI-MS measurement of T4. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (red).

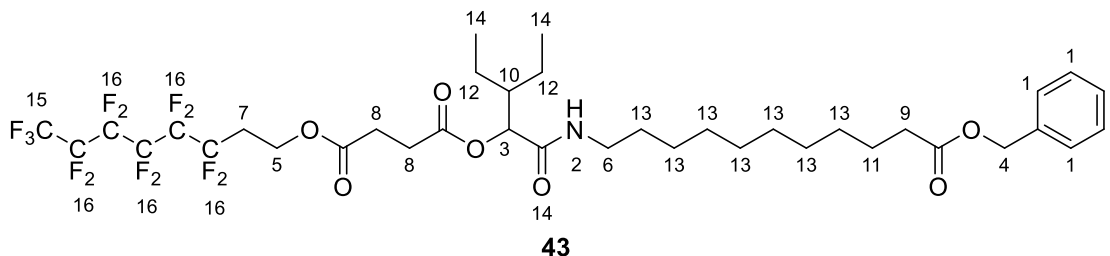
```
ximum is 1.000000 found for mass 1371.940480
matching mass 1371.94048
cutoff 0.50000: 0 solutions (7 peaks)
cutoff 0.25000: 0 solutions (27 peaks)
cutoff 0.12500: 0 solutions (60 peaks)
cutoff 0.06250: 0 solutions (105 peaks)
cutoff 0.03125: 0 solutions (175 peaks)
cutoff 0.01562: 0 solutions (281 peaks)
cutoff 0.00781: 1 solutions (454 peaks)
1371.94048  $\approx$  105.017020 + 255.183450 + 283.214750 + 297.230400 + 323.246050 + 107.049690 (sides
Acetaldehyde, Isobutyraldehyde, 3-Methylbutanal, Cyclohexancarboxaldehyde; error -0.99912)
Press ENTER to quit ...
```

Supplementary Figure 50: Screenshot of the automated read-out of T4.

1.3.4 Oligomer synthesis with TAG1

1.3.4.1 Synthesis of tetramer T5

Passerini reaction



In a 10 mL round bottom flask, 1.20 g **TAG1** (2.59 mmol, 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 477 μ L 2-ethylbutyraldehyde **14a** (388 mg, 3.88 mmol, 1.50 eq.) and 1.17 g of the monomer **M1** (3.88 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 6 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (7:1 $\rightarrow$ 5:1) to yield the Passerini product **43** as a pale highly viscous oil. (2.16 g, 2.49 mmol, 96.3%).

R_f = 0.46 in cyclohexane / ethyl acetate (3:1).

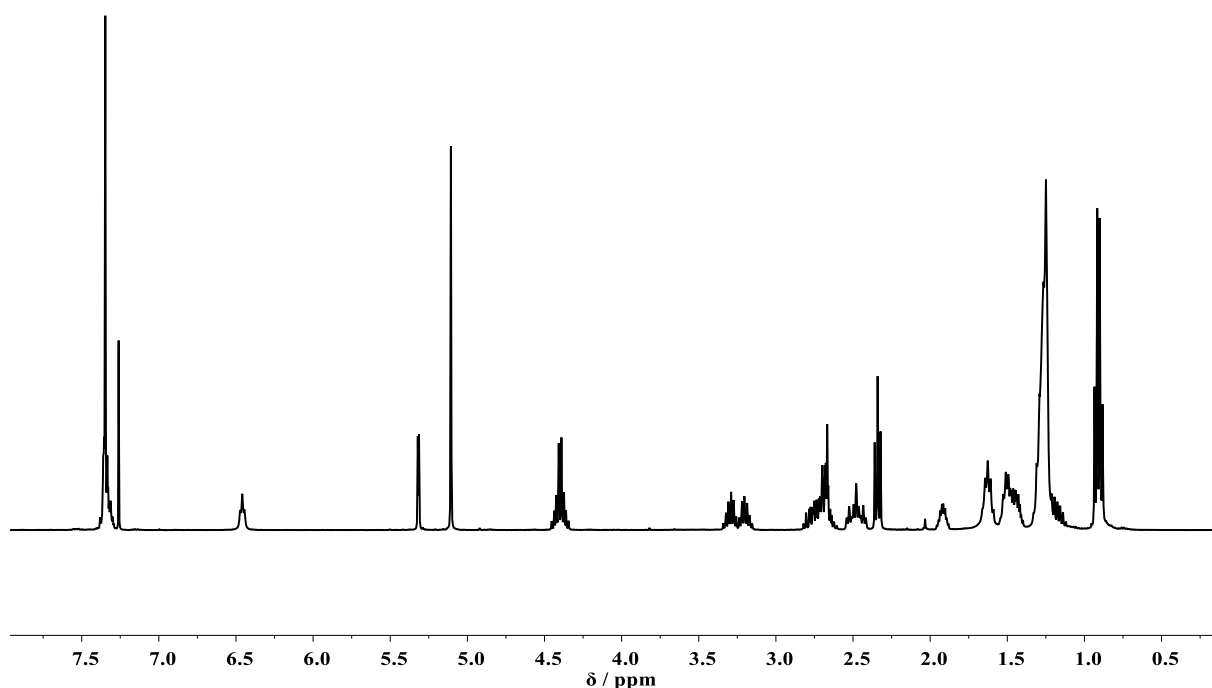
IR (ATR): ν / cm^{-1} = 2929.0 (w), 2856.2 (w), 1737.2 (s), 1656.7 (m), 1533.7 (w), 1458.1 (w), 1358.2 (w), 1234.5 (vs), 1191.7 (vs), 1144.2 (vs), 1005.0 (m), 841.9 (w), 808.7 (w), 732.9 (m), 697.4 (s), 651.0 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.20 (m, 5 H, CH_{Ar}^1), 6.39 (t, J = 5.8 Hz, 1 H, NH^2), 5.25 (d, J = 3.1 Hz, 1 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.47 – 4.18 (m, 2 H, CH_2^5), 3.34 – 3.05 (m, 2 H, CH_2^6), 2.81 – 2.54 (m, 2 H, CH_2^7), 2.50 – 2.33 (m, 4 H, CH_2^8), 2.27 (t, J = 7.5 Hz, 2 H, CH_2^9), 1.85 (td, J = 5.0, 3.0 Hz, 1 H, CH^{10}), 1.61 – 1.52 (m, 2 H, CH_2^{11}), 1.50 – 1.35 (m, 4 H, CH_2^{12}), 1.29 – 1.04 (m, 14 H, CH_2^{13}), 0.85 (t, J = 7.3, 3 H, CH_3^{14}), 0.83 (t, J = 7.3, 3 H, CH_3^{14}).

^{13}C NMR (101MHz, CDCl_3): δ / ppm = 174.57, 173.59, 171.98, 170.36, 137.03, 129.42, 129.04, 76.56, 66.95, 57.75, 44.12, 40.25, 35.21, 31.56, 31.34, 31.12, 30.60, 30.36, 30.26, 30.25, 30.12, 30.11, 30.00, 29.96, 29.91, 27.75, 25.83, 23.32, 22.93, 12.62, 12.50.

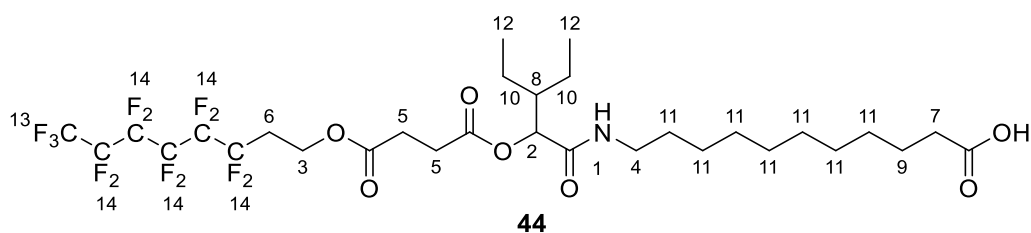
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.73 – -85.64 (m, 3 F, CF_3^{15}), -117.60 – -119.25 (m, 2 F, CF_2^{16}), -126.03 – -126.50 (m, 2 F, CF_2^{16}), -126.75 – -127.62 (m, 2 F, CF_2^{16}), -127.46 – -128.50 (m, 2 F, CF_2^{16}), -130.04 – -131.52 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$]⁺ calculated for $^{12}\text{C}_{37}^{1}\text{H}_{48}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 888.3115; found, 888.3144, Δ = 2.9 mmu.



Supplementary Figure 51: ^1H -NMR of compound **43** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 2.02 g of **43** (2.33 mmol, 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 403 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloon) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **44** was obtained as a pale highly viscous oil in a quantitative yield.

IR (ATR): ν / cm^{-1} = 2928.2 (m), 2856.4 (w), 1738.7 (s), 1649.6 (m), 1540.7 (w), 1461.4 (w), 1360.9 (w), 1234.0 (vs), 1192.5 (vs), 1144.2 (vs), 1082.8 (m), 1006.9 (m), 841.9 (w), 808.8 (w), 732.4 (w), 697.7 (w), 651.4 (w), 530.7 (w).

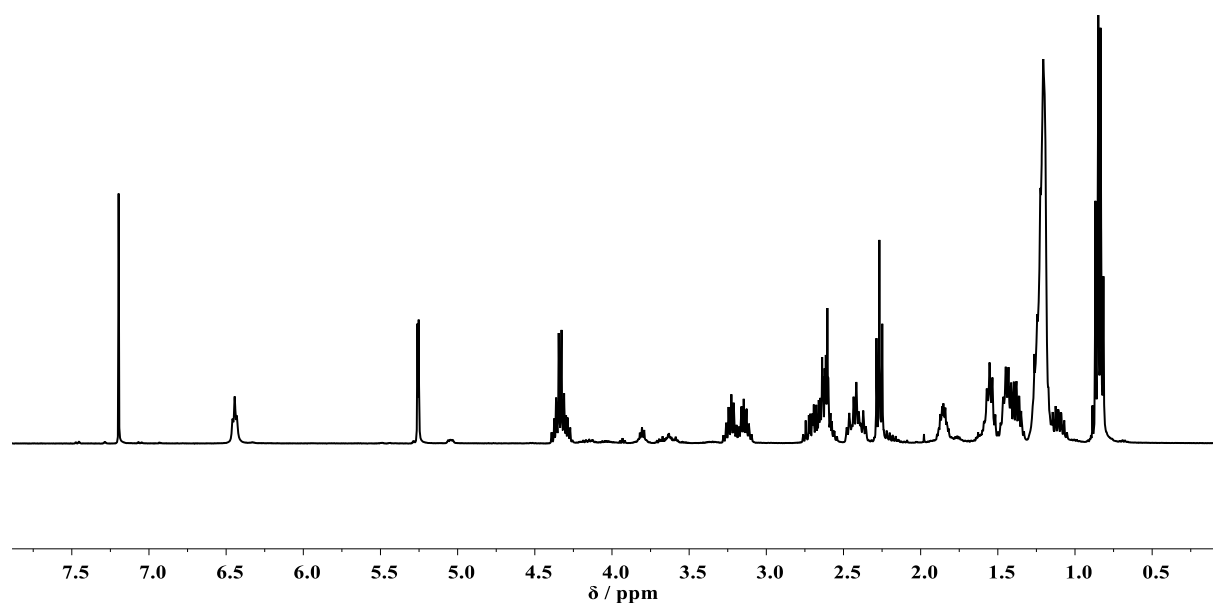
^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.51 (t, J = 5.8 Hz, 1 H, NH^1), 5.32 (d, J = 3.1 Hz, 1 H, CH^2), 4.48 – 4.28 (m, 2 H, CH_2^3), 3.39 – 3.11 (m, 2 H, CH_2^4), 2.87 – 2.60 (m, 4 H, CH_2^5), 2.59 – 2.40 (m, 2

H, CH₂⁶), 2.33 (t, $J = 7.5$ Hz, 2 H, CH₂⁷), 1.97 – 1.86 (m, 1 H, CH⁸), 1.72 – 1.56 (m, 2 H, CH₂⁹), 1.58 – 1.38 (m, 4 H, CH₂¹⁰), 1.39 – 1.14 (m, 14 H, CH₂¹¹), 0.99 – 0.79 (m, 6 H, CH₃¹²).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 178.81, 172.91, 171.29, 169.78, 75.76, 57.01, 43.32, 39.51, 34.01, 30.56 (t, $J = 21.8$ Hz), 29.46, 29.40, 29.34, 29.23, 29.20, 29.15, 29.06, 26.92, 24.93, 24.78, 22.15, 11.85, 11.73.

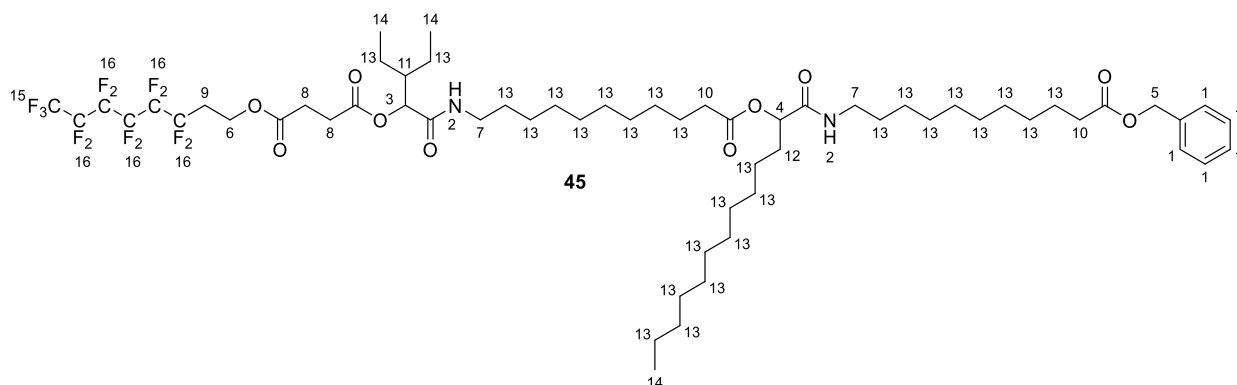
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.11 (t, $J = 10.2$ Hz, 3 F, CF₃¹³), -117.83 – -118.35 (m, 3 F, CF₃¹⁴), -126.02 – -126.56 (m, 2 F, CF₂¹⁴), -126.73 – -127.51 (m, 2 F, CF₂¹⁴), -127.64 – -128.11 (m, 2 F, CF₂¹⁴), -130.37 – -130.95 (m, 2 F, CF₂¹⁴). Total integral of CF₂ region normalized with respect to the CF₃¹³ group = 10.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₃₀¹H₄₂¹⁶O₇¹⁴N¹⁹F₁₃, 776.2826; found, 776.2811, $\Delta = 1.5$ mmu.



Supplementary Figure 52: ¹H-NMR of compound 44 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 1.20 g of **44** (1.55 mmol, 1.00 eq.) was dissolved in 3.00 mL DCM and 395 mg octanal **14i** (2.32 mmol, 1.50 eq.) and 699 mg of monomer **M1** (2.32 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 6:1 → 4:1) to afford product **45** as a pale highly viscous oil in a yield of 96.4% (1.88 g, 1.49 mmol).

R_f = 0.29 in cyclohexane / ethyl acetate (3:1).

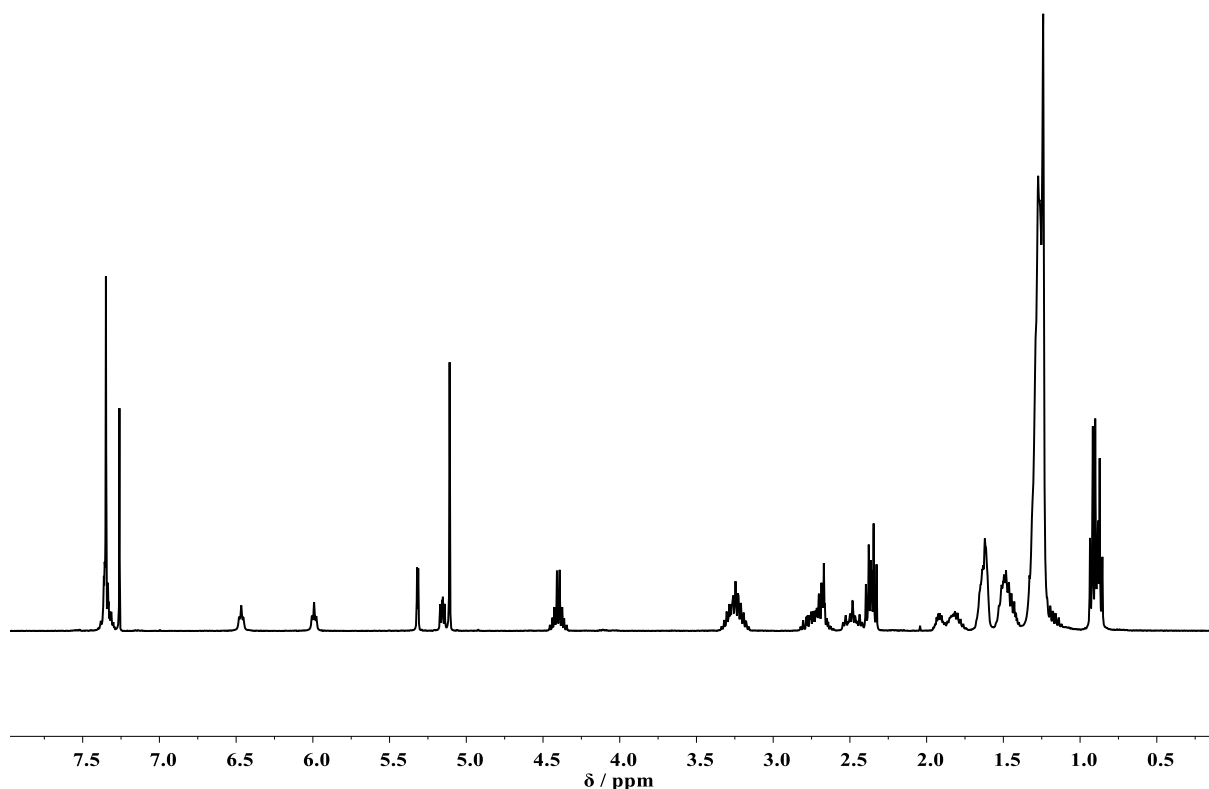
IR (ATR): ν / cm^{-1} = 3296.1 (w), 2916.7 (s), 2849.1 (m), 1741.0 (vs), 1655.0 (vs), 1560.8 (w), 1468.4 (w), 1359.5 (w), 1235.4 (vs), 1204.7 (vs), 1143.0 (vs), 1083.7 (s), 1010.3 (m), 949.2 (w), 841.9 (vw), 803.4 (vw), 746.5 (w), 696.8 (vs), 652.0 (m), 566.1 (w), 528.3 (w), 439.6 (vw), 389.8 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.48 – 7.27 (m, 5 H, CH_{Ar}^1), 6.47 (t, J = 5.8 Hz, 1 H, NH^2), 6.00 (t, J = 5.8 Hz, 1 H, NH^2), 5.31 (d, J = 3.1 Hz, 1 H, CH^3), 5.17 – 5.13 (m, 1 H, CH^4), 5.11 (s, 2 H, CH_2^5), 4.47 – 4.33 (m, 2 H, CH_2^6), 3.34 – 3.15 (m, 4 H, CH_2^7), 2.85 – 2.61 (m, 4 H, CH_2^8), 2.58 – 2.40 (m, 2 H, CH_2^9), 2.41 – 2.30 (m, 4 H, CH_2^{10}), 1.97 – 1.73 (m, 3 H, CH^{11} , CH_2^{12}), 1.70 – 1.58 (m, 6 H, CH_2^{13}), 1.57 – 1.38 (m, 6 H, CH_2^{13}), 1.36 – 1.10 (m, 42 H, CH_2^{13}), 0.96 – 0.80 (m, 9 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.80, 172.83, 172.57, 171.22, 169.98, 169.61, 136.27, 128.67, 128.28, 75.79, 74.07, 66.20, 56.99, 43.37, 39.47, 39.33, 34.45, 32.05, 30.59 (t, J = 21.9 Hz), 29.75, 29.69, 29.67, 29.62, 29.58, 29.57, 29.51, 29.49, 29.48, 29.39, 29.37, 29.35, 29.25, 29.20, 29.15, 26.99, 26.97, 25.08, 24.89, 22.82, 22.56, 22.18.

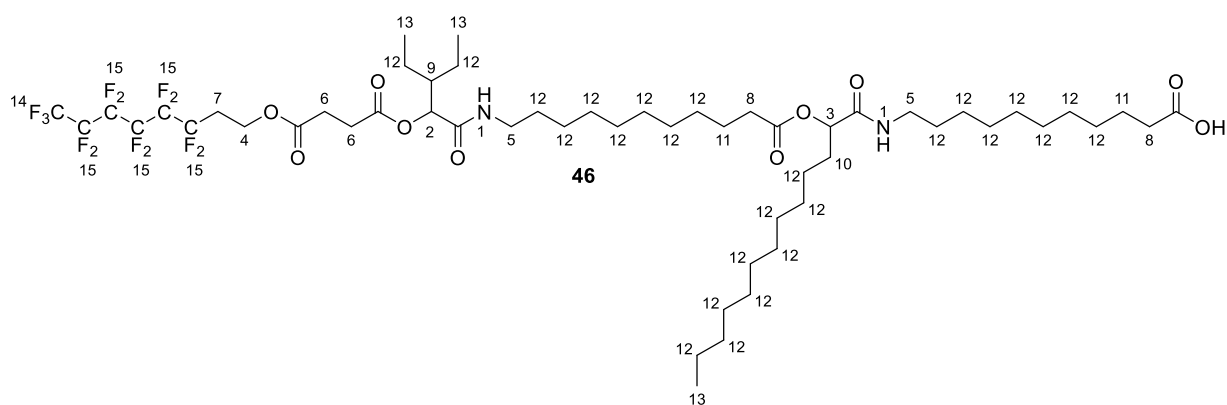
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.73 – -85.52 (m, 3 F, CF_3^{15}), -117.70 – -118.32 (m 2 F, CF_2^{16}), -125.97 – -126.42 (m 2 F, CF_2^{16}), -126.99 – -127.39 (m 2 F, CF_2^{16}), -127.77 – -128.04 (m 2 F, CF_2^{16}), -130.30 – -130.60 (m 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{61}^{1}\text{H}_{93}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1261.6695 found, 1261.6692, Δ = 0.3 mmu.



ijSupplementary Figure 53: ^1H -NMR of compound **45** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.80 g of **45** (1.43 mmol, 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 360 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **46** was obtained as a high viscos oil in a yield of 98.6% (1.65 g, 1.41 mmol).

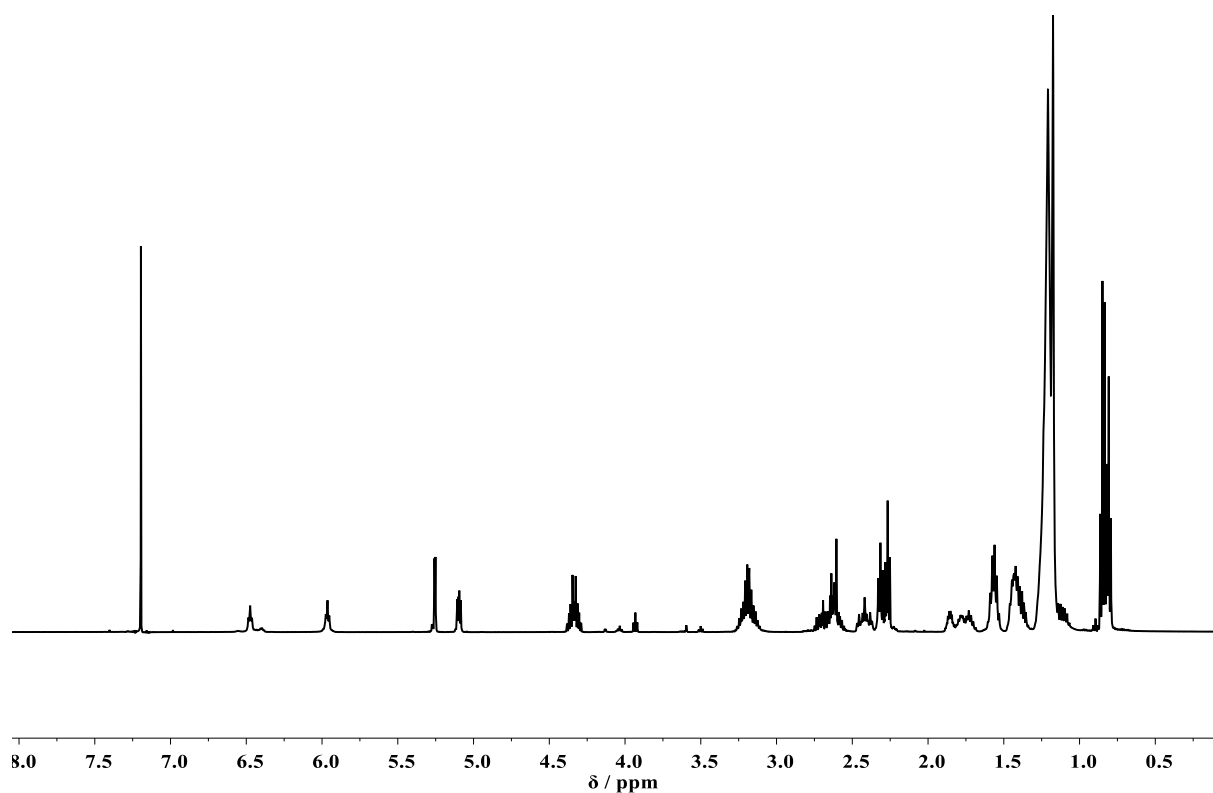
IR (ATR): ν/cm^{-1}] = 2924.6 (s), 2854.3 (m), 1740.3 (s), 1654.0 (m), 1539.1 (w), 1462.3 (w), 1361.4 (w), 1235.6 (vs), 1197.6 (vs), 1144.7 (vs), 1007.1 (w), 841.9 (vw), 808.5 (w), 697.6 (w), 651.5 (w).

^1H NMR (500 MHz, CDCl_3): δ/ppm = 6.54 (t, J = 5.8 Hz, 1 H, NH^1), 6.03 (t, J = 5.8 Hz, 1 H, NH^1), 5.32 (d, J = 3.2 Hz, 1 H, CH^2), 5.22 – 5.12 (m, 1 H, CH^3), 4.48 – 4.32 (m, 2 H, CH_2^4), 3.36 – 3.14 (m, 4 H, CH_2^5), 2.81 – 2.62 (m, 4 H, CH_2^6), 2.55 – 2.44 (m, 2 H, CH_2^7), 2.43 – 2.19 (m, 4 H, CH_2^8), 1.97 – 1.75 (m, 3 H, CH^9 , CH_2^{10}), 1.71 – 1.58 (m, 4 H, CH_2^{11}), 1.56 – 1.40 (m, 6 H, CH_2^{12}), 1.37 – 1.15 (m, 44 H, CH_2^{12}), 0.96 – 0.82 (m, 9 H, CH_3^{13}).

^{13}C NMR (126 MHz, CDCl_3): δ/ppm = 177.43, 172.92, 172.61, 171.29, 170.10, 169.87, 75.76, 74.09, 57.02, 43.31, 39.56, 39.30, 34.47, 33.94, 32.05, 32.01, 30.57 (t, J = 21.8 Hz), 29.76, 29.68, 29.65, 29.57, 29.56, 29.54, 29.49, 29.44, 29.40, 29.36, 29.34, 29.28, 29.21, 29.21, 29.15, 29.08, 27.00, 26.88, 25.13, 24.90, 24.87, 22.83, 22.54, 22.16, 14.25, 11.85, 11.73.

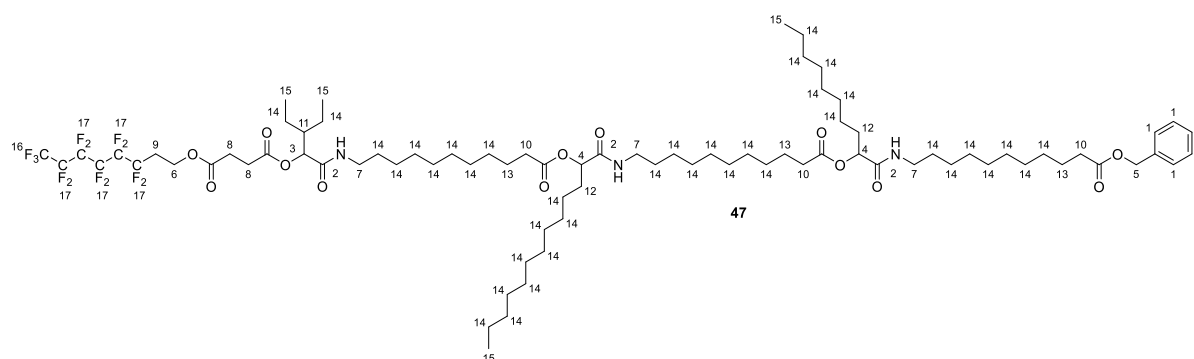
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -85.09 (t, J = 9.7 Hz, 3 F, CF_3^{14}), -117.79 – -118.40 (m, 2 F, CF_2^{15}), -125.89 – -126.53 (m, 2 F, CF_2^{15}), -126.69 – -127.45 (m, 2 F, CF_2^{15}), -127.74 – -128.14 (m, 2 F, CF_2^{15}), -130.00 – -130.81 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{54}^{1}\text{H}_{87}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1171.6226; found, 1171.6216, Δ = 1.0mmu.



Supplementary Figure 54: ^1H -NMR of compound 46 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 1.58 g of passerini **46** (1.35 mmol, 1.00 eq.) was dissolved in 5.00 mL DCM and 347 μ L nonanal **14k** (287 mg, 2.02 mmol, 1.50 eq.) and 608 mg of monomer **M1** (2.02 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 2 d and subsequently the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 2:1) to afford product **47** as a white solid in a yield of 91.9% (1.99 g, 1.24 mmol).

$R_f = 0.26$ in cyclohexane / ethyl acetate (3:1).

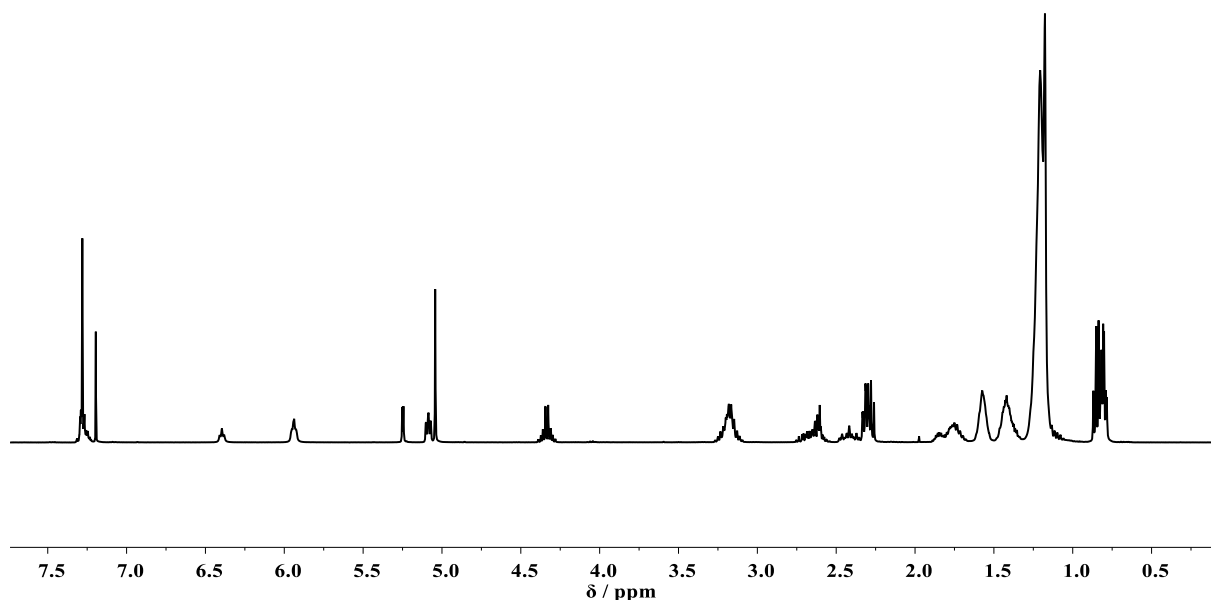
IR (ATR): ν/cm^{-1}] = 3300.8 (vw), 2919.0 (s), 2851.1 (m), 1737.1 (vs), 1655.0 (vs), 1541.3 (w), 1465.7 (w), 1362.8 (w), 1236.9 (s), 1204.7 (s), 1145.0 (vs), 1005.9 (w), 842.1 (vw), 809.1 (vw), 697.4 (m), 652.7 (w).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.39 – 7.29 (m, 5 H, CH_{Ar}¹), 6.47 (t, J = 5.7 Hz, 1 H, NH²), 6.07 – 5.98 (m, 2 H, NH²), 5.31 (d, J = 3.1 Hz, 1 H, CH³), 5.17 – 5.13 (m, 2 H, CH⁴), 5.11 (s, 2 H, CH₂⁵), 4.46 – 4.34 (m, 2 H, CH₂⁶), 3.35 – 3.14 (m, 6 H, CH₂⁷), 2.85 – 2.62 (m, 4 H, CH₂⁸), 2.57 – 2.42 (m, 2 H, CH₂⁹), 2.42 – 2.30 (m, 6 H, CH₂¹⁰), 1.95 – 1.75 (m, 5 H, CH₂¹¹, CH¹²), 1.70 – 1.58 (m, 6 H, CH₂¹³), 1.54 – 1.40 (m, 8 H, CH₂¹⁴), 1.38 – 1.15 (m, 68 H, CH₂¹⁴), 0.98 – 0.79 (m, 12 H, CH₃¹⁵).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.80, 172.83, 172.59, 171.22, 170.00, 169.98, 169.62, 136.27, 128.67, 128.28, 75.79, 74.08, 66.20, 56.99, 43.38, 39.47, 39.33, 34.46, 32.05, 31.96, 30.82, 30.60, 30.38, 29.75, 29.72, 29.70, 29.67, 29.63, 29.62, 29.59, 29.57, 29.52, 29.50, 29.48, 29.39, 29.38, 29.35, 29.32, 29.26, 29.25, 29.20, 29.15, 26.99, 26.97, 25.10, 25.09, 25.08, 24.91, 24.90, 22.82, 22.78, 22.57, 22.10, 14.23, 11.87, 11.75.

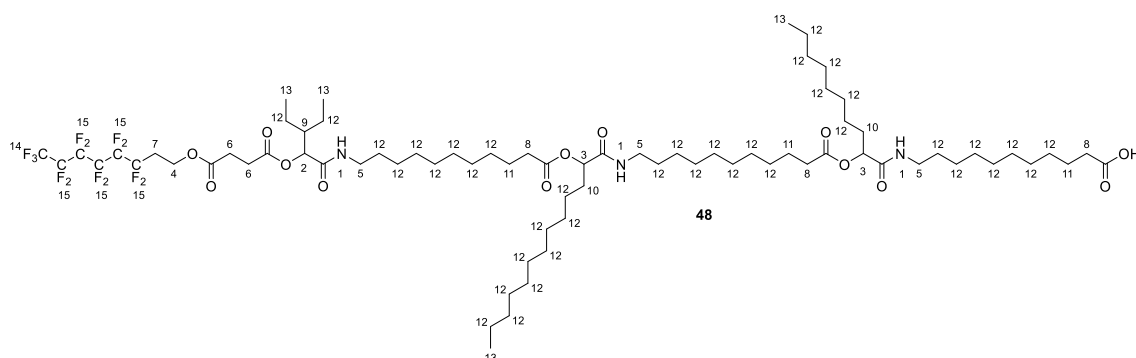
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -84.62 – -85.83 (m, 3 F, CF₃¹⁶), -117.63 – -118.90 (m, 2 F, CF₂¹⁷), -126.02 – -126.52 (m, 2 F, CF₂¹⁷), -126.81 – -127.48 (m, 2 F, CF₂¹⁷), -127.63 – -128.33 (m, 2 F, CF₂¹⁷), -130.01 – -131.02 (m, 2 F, CF₂¹⁷). Total integral of CF₂ region normalized with respect to the CF₃¹⁷ group = 10.

ESI-MS $[m/z]$: $[M + Na]^+$ calculated for $^{12}C_{82}^{1}H_{132}^{16}O_{13}^{14}N_3^{19}F_{13}$, 1636.9445; found, 1636.9430, $\Delta = 1.5$ mmu.



Supplementary Figure 55: ^1H -NMR of compound **47** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.94 g of **47** (1.20 mmol, 1.00 eq.) were dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Afterwards, 388 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **48** was obtained as a high viscous oil in a yield of 97.5% (1.79 g, 1.17 mmol).

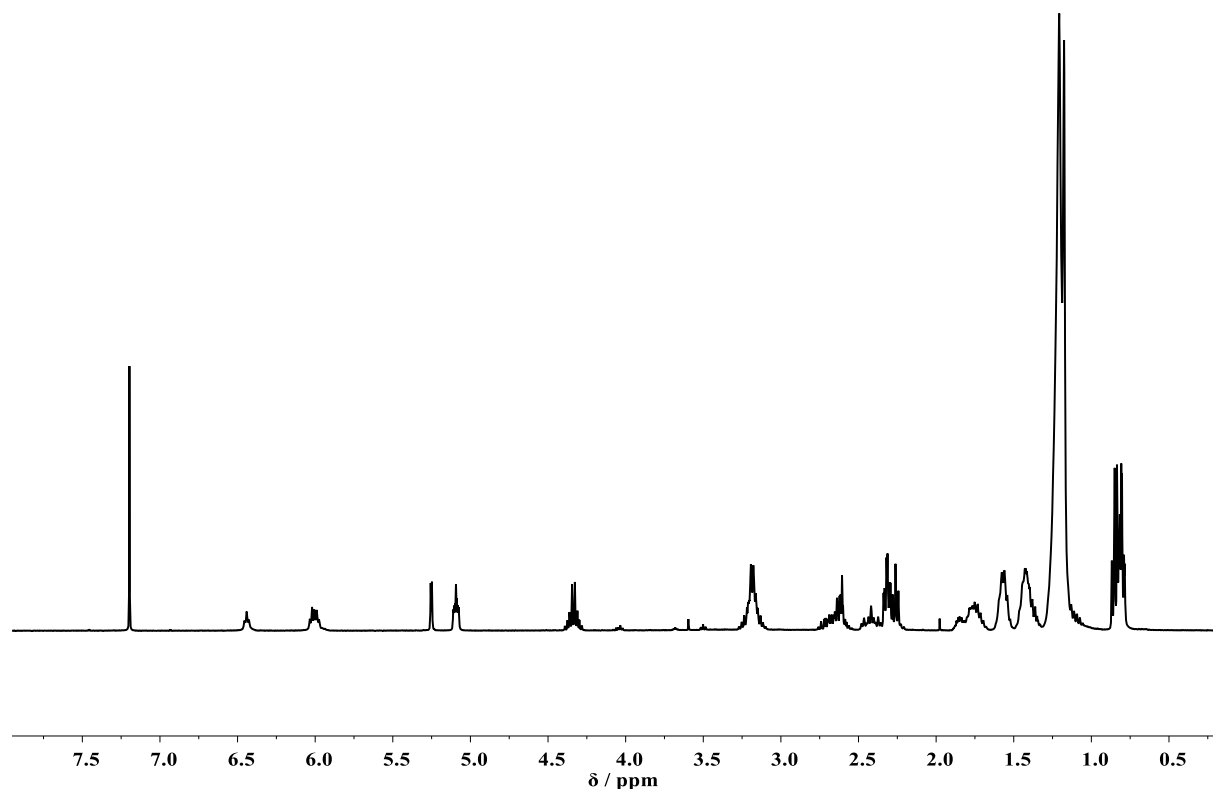
IR (ATR): ν/cm^{-1} = 3297.8 (vw), 2919.6 (s), 2851.4 (m), 1738.1 (s), 1655.5 (vs), 1555.1 (w), 1465.1 (w), 1364.1 (w), 1236.6 (vs), 1144.6 (vs), 1007.4 (w), 842.2 (vw), 809.3 (vw), 697.4 (w), 651.8 (w), 566.0 (vw), 530.6 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.49 – 6.39 (m, 1 H, NH^1), 6.06 – 5.94 (m, 2 H, NH^1), 5.25 (d, J = 3.2 Hz, 1 H, CH^2), 5.12 – 5.04 (m, 2 H, CH^3), 4.43 – 4.26 (m, 2 H, CH_2^4), 3.28 – 3.09 (m, 6 H, CH_2^5), 2.79 – 2.55 (m, 4 H, CH_2^6), 2.51 – 2.37 (m, 2 H, CH_2^7), 2.36 – 2.20 (m, 6 H, CH_2^8), 1.92 – 1.67 (m, 5 H, CH^9 , CH_2^{10}), 1.64 – 1.50 (m, 6 H, CH_2^{11}), 1.51 – 1.30 (m, 8 H, CH_2^{12}), 1.31 – 1.02 (m, 68H, CH_2^{12}), 0.89 – 0.76 (m, 12 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 176.95, 172.88, 172.70, 172.62, 171.25, 170.19, 170.08, 169.75, 75.77, 74.10, 74.07, 57.01, 43.35, 39.51, 39.40, 39.30, 34.48, 34.45, 33.96, 32.05, 32.02, 31.97, 29.76, 29.68, 29.63, 29.57, 29.56, 29.53, 29.51, 29.49, 29.43, 29.39, 29.37, 29.34, 29.28, 29.25, 29.22, 29.16, 29.09, 26.98, 26.89, 25.14, 25.08, 24.91, 22.83, 22.79, 22.56, 22.17, 14.25, 14.24, 11.87, 11.74.

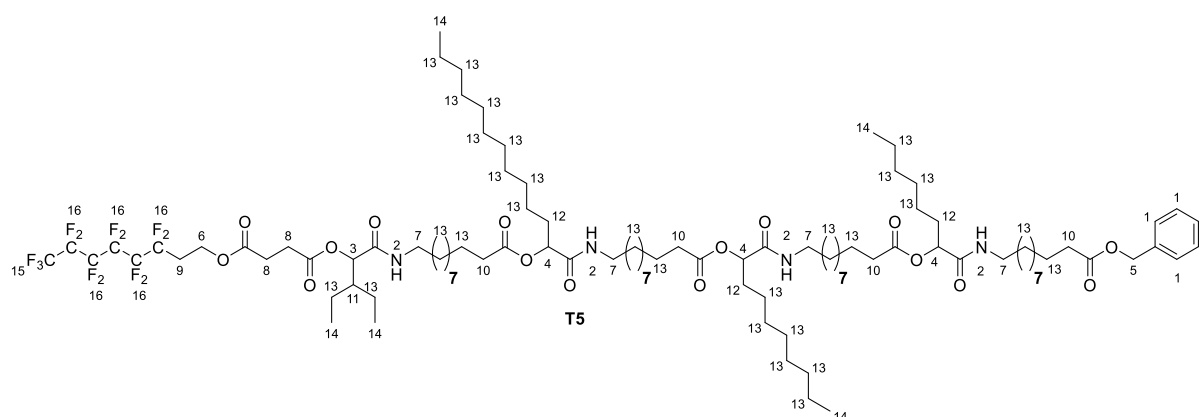
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -84.04 – -86.23 (m, 3 F, CF_3^{14}), -117.79 – -118.50 (m, 2 F, CF_2^{15}), -125.95 – -126.50 (m, 2 F, CF_2^{15}), -127.05 – -127.38 (m, 2 F, CF_2^{15}), -127.70 – -128.23 (m, 2 F, CF_2^{15}), -130.34 – -130.71 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{75}^{1}\text{H}_{126}^{16}\text{O}_{13}^{19}\text{F}_{13}^{14}\text{N}_3$, 1546.8975; found, 1546.8952, Δ = 2.3 mmu.



Supplementary Figure S6: ^1H -NMR of compound 48 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 1.71 g of **48** (1.12 mmol, 1.00 eq.) was dissolved in 5.00 mL DCM and 235 μ L heptanal **14b** (192 mg, 1.69 mmol, 1.50 eq.) and 508 mg of monomer **M1** (1.69 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 2 d and subsequently the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 1:1) to afford product **T5** as a white solid in a yield of 94.6% (2.06 g, 1.06 mmol).

R_f = 0.21 in cyclohexane / ethyl acetate (2:1).

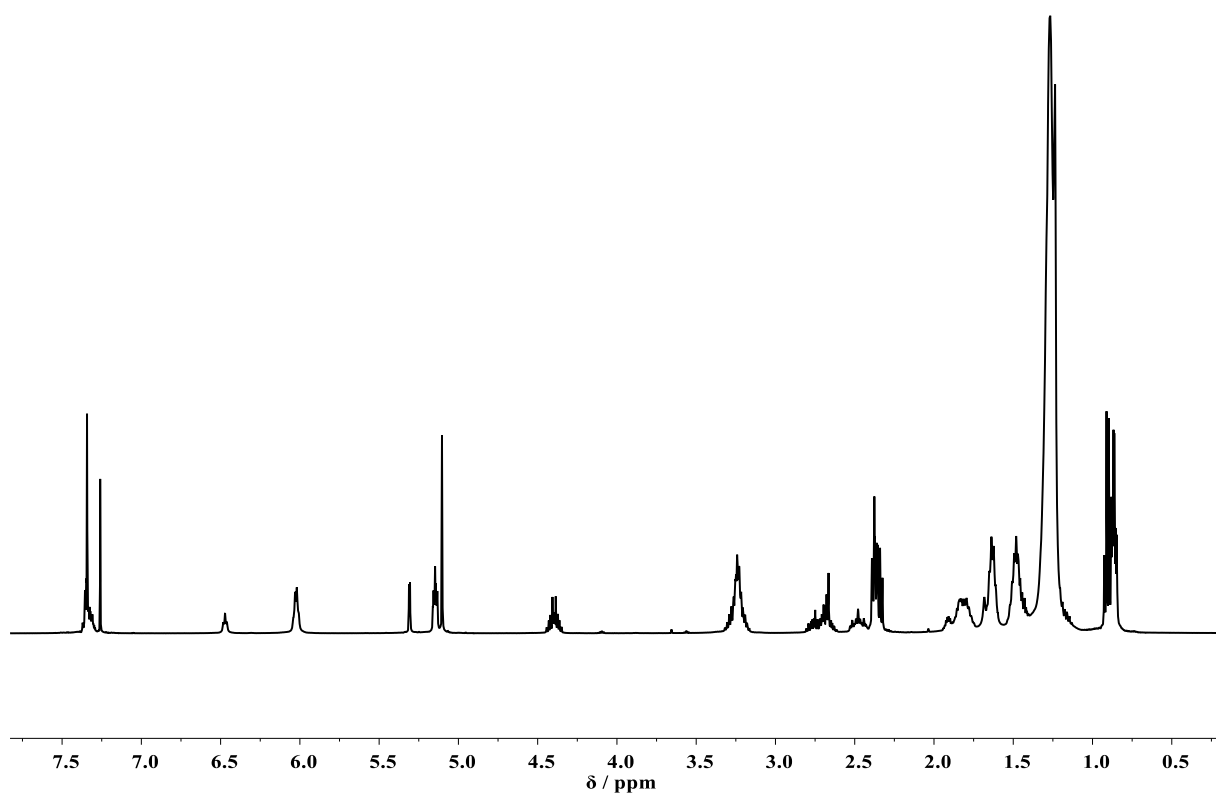
IR (ATR): ν / cm^{-1} = 3304.4 (vw), 2923.3 (s), 2853.1 (m), 1738.7 (s), 1655.1 (s), 1535.6 (m), 1464.1 (w), 1362.8 (w), 1236.8 (s), 1145.3 (vs), 697.1 (w), 651.1 (w), 396.3 (vw).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.45 – 7.28 (m, 5 H, CH_{Ar}^1), 6.47 (t, J = 5.8 Hz, 1 H, NH^2), 6.06 – 5.96 (m, 3 H, NH^2), 5.31 (d, J = 3.2 Hz, 1 H, CH^3), 5.17 – 5.13 (m, 3 H, CH^4), 5.10 (s, 2 H, CH_2^5), 4.47 – 4.33 (m, 2 H, CH_2^6), 3.33 – 3.14 (m, 8 H, CH_2^7), 2.82 – 2.60 (m, 4 H, CH_2^8), 2.56 – 2.41 (m, 2 H, CH_2^9), 2.42 – 2.30 (m, 8 H, CH_2^{10}), 1.96 – 1.74 (m, 7 H, CH^{11} , CH_2^{12}), 1.71 – 1.59 (m, 12 H, CH_2^{13}), 1.55 – 1.40 (m, 14 H, CH_2^{13}), 1.38 – 1.11 (m, 80 H, CH_2^{13}), 0.96 – 0.82 (m, 15 H, CH_3^{14}).

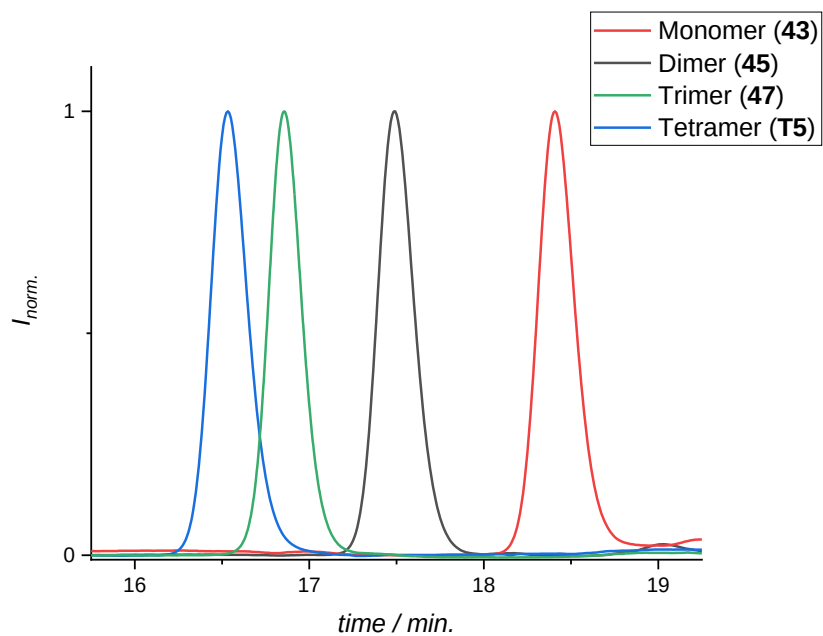
^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.70, 172.74, 172.48, 171.11, 169.88, 169.85, 169.51, 136.13, 128.55, 128.17, 75.64, 73.93, 66.08, 56.86, 43.23, 39.33, 39.19, 34.32, 31.92, 31.83, 31.63, 30.44 (t, J = 21.8 Hz), 29.62, 29.58, 29.56, 29.54, 29.49, 29.46, 29.44, 29.39, 29.39, 29.35, 29.26, 29.22, 29.20, 29.13, 29.06, 29.01, 28.92, 26.84, 24.97, 24.96, 24.77, 24.71, 22.69, 22.65, 22.54, 22.42, 22.04, 14.12, 14.11, 14.05, 11.74, 11.62.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.74 (t, J = 10.0 Hz, 3 F, CF_3^{15}), -113.42 – -113.95 (m, 2 F, CF_2^{16}), -121.56 – -122.14 (m, 2 F, CF_2^{16}), -122.38 – -123.21 (m, 2 F, CF_2^{16}), -123.25 – -123.72 (m, 2 F, CF_2^{16}), -125.70 – -126.66 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

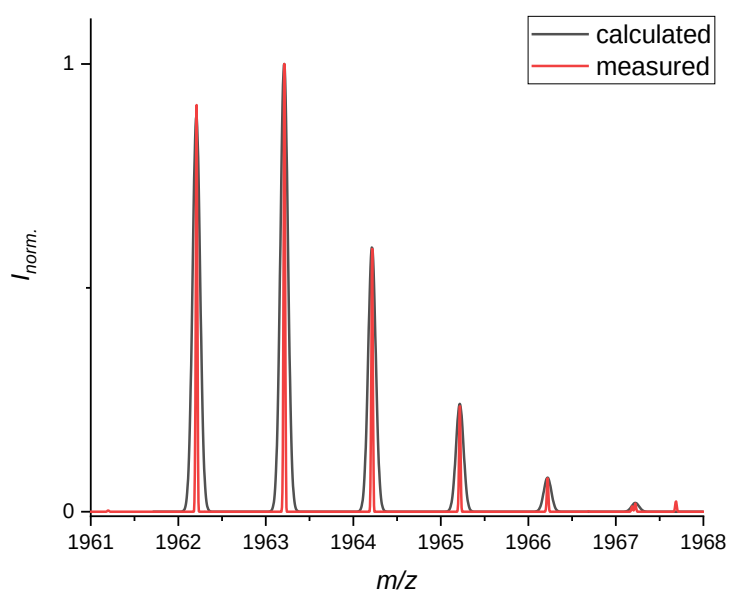
ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{101}^{1}\text{H}_{167}^{19}\text{F}_{13}^{14}\text{N}_4^{16}\text{O}_{16}$, 1962.2062; found, 1962.2090, Δ = 2.8 mmu.



Supplementary Figure 57: ^1H -NMR of compound T5 measured in CDCl_3 .



Supplementary Figure 58: SEC traces of the intermediates after each P3CR in the synthesis of product T5.



Supplementary Figure 59: High resolution ESI-MS measurement of T5. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

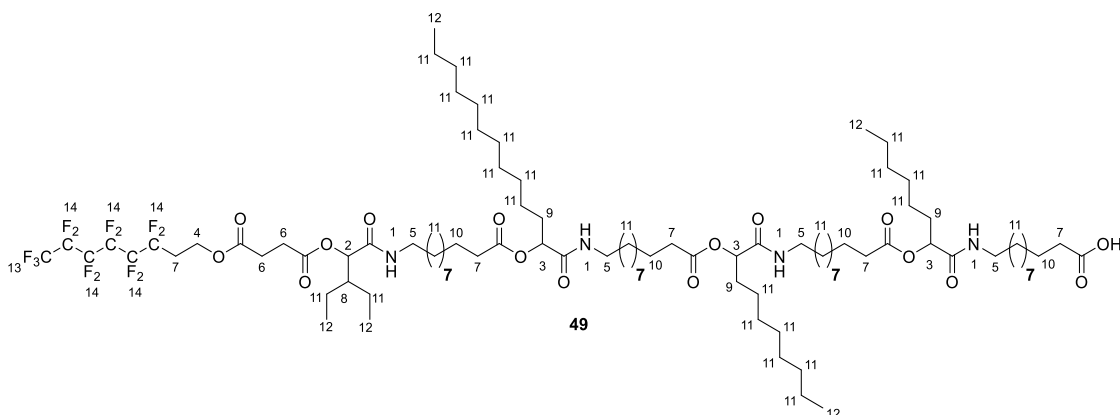
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maximum is 1.000000 found for mass 1963.205820
matching mass 1963.20582
cutoff 0.50000: 0 solutions (12 peaks)
cutoff 0.25000: 0 solutions (51 peaks)
cutoff 0.12500: 0 solutions (109 peaks)
cutoff 0.06250: 0 solutions (179 peaks)
cutoff 0.03125: 0 solutions (262 peaks)
cutoff 0.01562: 1 solutions (354 peaks)
1963.20582 ≈ 463.021500 + 311.246050 + 395.339950 + 353.293000 + 325.261700 + 91.054780 (sides 2-Ethylbutanal, Dodecanal,
Nonanal, Heptanal; error -23.98884)
Press ENTER to quit ...

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Supplementary Figure 60: Screenshot of the automated read-out of T5, sodium trifluoroacetate was used as additive during the measurement.

1.3.4.2 Synthesis of hexamer H2



In a 50 mL round bottom flask, 1.45 g of **T5** (748 μmol , 1.00 eq.) were dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Afterwards, 290 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **49** was obtained as a pale highly viscous oil in a yield of 99.5% (1.38 g, 745 μmol).

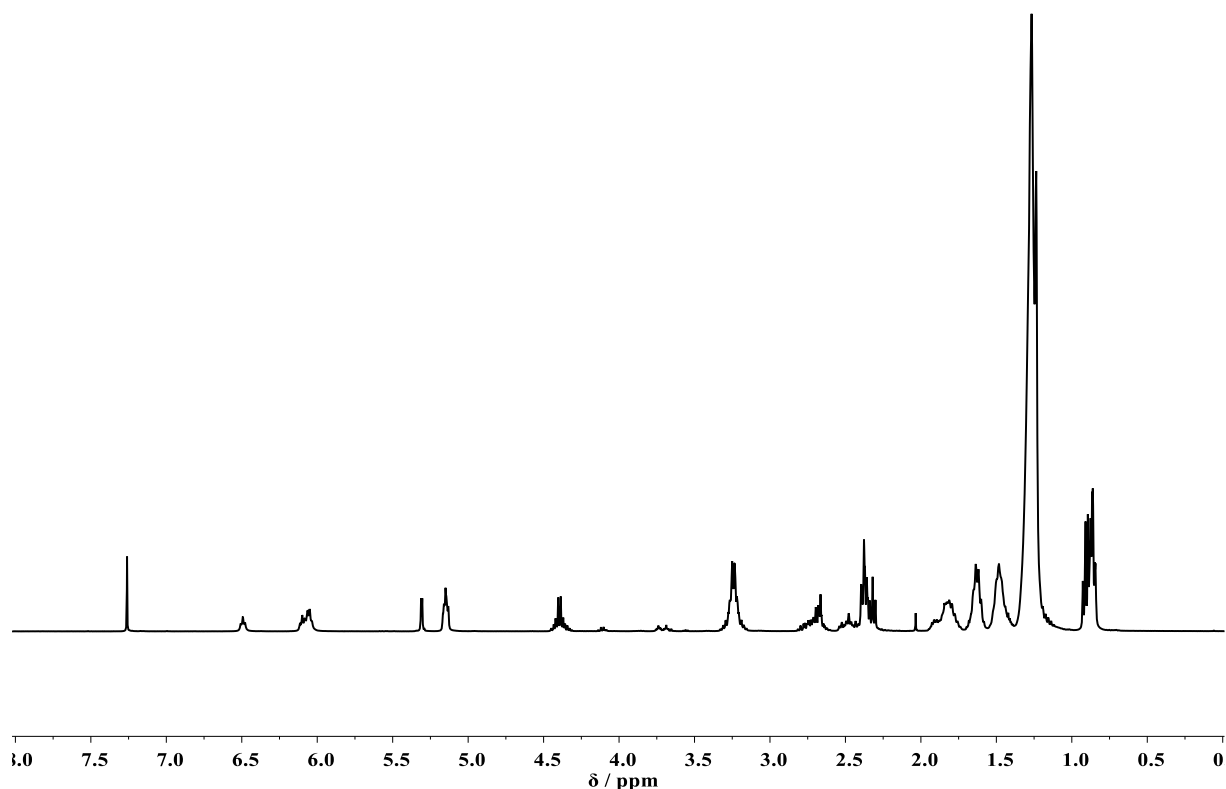
IR (ATR): ν / cm^{-1} = 3293.4 (vw), 2922.3 (vs), 2852.7 (s), 1738.6 (s), 1655.5 (vs), 1540.7 (m), 1465.3 (w), 1364.0 (w), 1236.5 (vs), 1145.1 (vs), 842.2 (vw), 697.5 (w), 651.7 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.43 (t, J = 5.8 Hz, 1 H, NH^1), 6.09 – 5.94 (m, 3 H, NH^1), 5.25 (d, J = 3.2 Hz, 1 H, CH^2), 5.14 – 5.05 (m, 3 H, CH^3), 4.43 – 4.24 (m, 2 H, CH_2^4), 3.30 – 3.05 (m, 8 H, CH_2^5), 2.78 – 2.54 (m, 4 H, CH_2^6), 2.51 – 2.16 (m, 10 H, CH_2^7), 1.91 – 1.66 (m, 7 H, CH^8 , CH_2^9), 1.65 – 1.51 (m, 8 H, CH_2^{10}), 1.49 – 0.98 (m, 101 H, CH_2^{11}), 0.92 – 0.74 (m, 15 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 177.11, 172.86, 172.68, 172.62, 171.24, 170.17, 170.11, 170.07, 169.72, 75.75, 74.07, 74.05, 56.98, 43.34, 34.43, 33.97, 32.03, 31.95, 31.75, 30.57, 29.74, 29.67, 29.61, 29.56, 29.51, 29.48, 29.46, 29.36, 29.35, 29.24, 29.18, 29.13, 29.10, 29.03, 26.96, 26.89, 25.11, 25.08, 24.89, 24.84, 22.80, 22.77, 22.65, 22.54, 22.15, 14.23, 14.16, 11.85, 11.72.

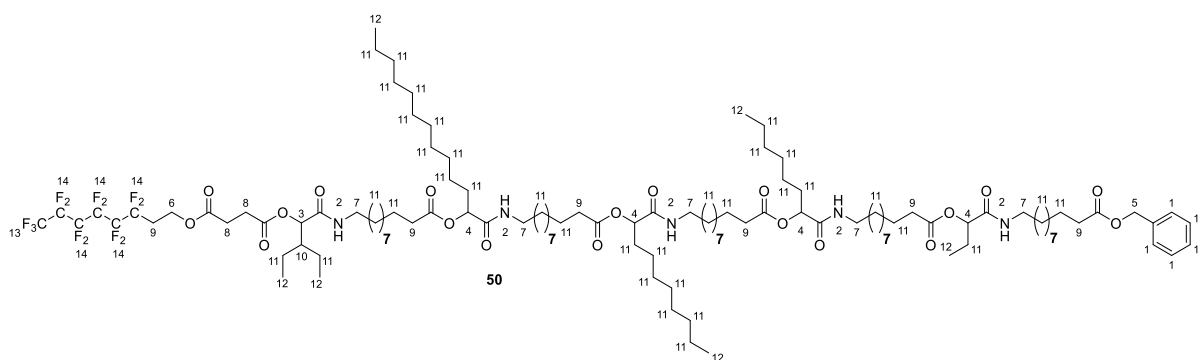
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.74 (t, J = 9.9 Hz, 3 F, CF_3^{13}), -113.52 – -113.84 (m, 2 F, CF_2^{14}), -121.68 – -121.98 (m, 2 F, CF_2^{14}), -122.48 – -122.99 (m, 2 F, CF_2^{14}), -123.39 – -123.65 (m, 2 F, CF_2^{14}), -125.48 – -126.44 (m, 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{94}^{1}\text{H}_{161}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_{13}$, 1850.1773; found, 1850.1772, Δ = 0.1 mmu.



Supplementary Figure 61: ^1H -NMR of compound **49** measured in CDCl_3 .

Passerini reaction



In a 10 mL round bottom flask, 1.28 g of **50** (690 μmol , 1.00 eq.) was stirred in 2.10 mL DCM. Subsequently, 148 μL propionaldehyde **14l** (120 mg, 2.07, 3.00 eq.) and 312 mg of the monomer **M1** (1.04 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 1:1) to yield the passerini product **50** as a pale highly viscous oil. (1.39 g, 626 μmol , 90.7%).

R_f = 0.61 in cyclohexane / ethyl acetate (3:2).

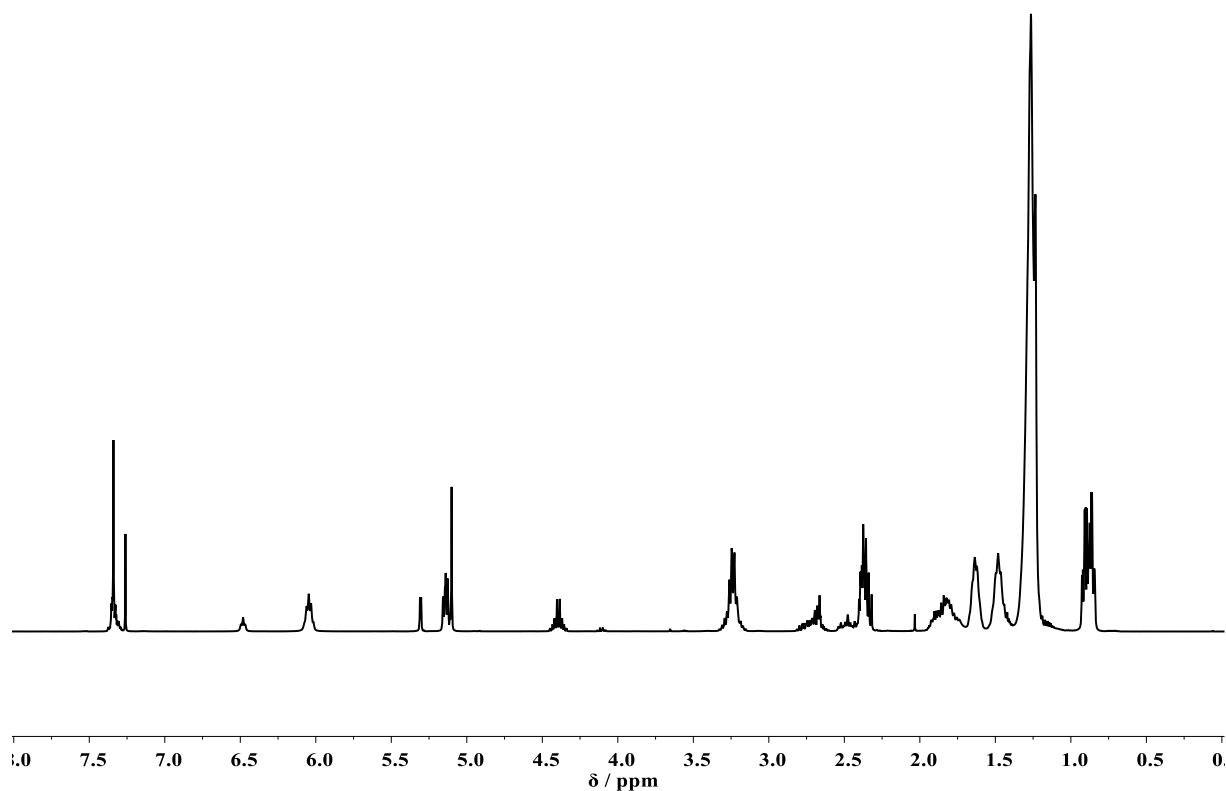
IR (ATR): ν/cm^{-1} = 3304.8 (vw), 2923.9 (s), 2853.8 (m), 1739.6 (s), 1654.1 (s), 1535.4 (m), 1459.0 (w), 1374.5 (w), 1236.5 (s), 1145.2 (vs), 697.1 (w), 651.2 (w).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 7.39 – 7.23 (m, 5 H, CH_{Ar}^1), 6.42 (t, J = 5.8 Hz, 1 H, NH^2), 6.12 – 5.89 (m, 4 H, NH^2), 5.25 (d, J = 3.1 Hz, 1 H, CH^3), 5.16 – 4.98 (m, 6 H, CH^4 , CH_2^5), 4.45 – 4.26 (m, 2 H, CH_2^6), 3.33 – 3.08 (m, 10 H, CH_2^7), 2.79 – 2.53 (m, 4 H, CH_2^8), 2.50 – 2.24 (m, 12 H, CH_2^9), 1.90 – 1.51 (m, 21 H, CH^{10} , CH_2^{11}), 1.50 – 1.02 (m, 112 H, CH_2^{11}), 0.90 – 0.70 (m, 18 H, CH_3^{12}).

^{13}C NMR (101MHz, CDCl_3): δ/ppm = 173.80, 172.84, 172.60, 172.55, 171.22, 170.00, 169.74, 169.62, 136.24, 128.66, 128.27, 75.75, 74.92, 74.04, 66.18, 56.97, 43.34, 39.45, 39.30, 34.43, 32.03, 31.94, 31.74, 29.73, 29.69, 29.65, 29.60, 29.57, 29.55, 29.50, 29.46, 29.37, 29.33, 29.24, 29.22, 29.18, 29.12, 29.03, 26.97, 26.95, 25.21, 25.08, 24.88, 24.83, 22.80, 22.76, 22.65, 22.53, 22.15, 14.22, 14.22, 14.16, 11.85, 11.73, 9.13.

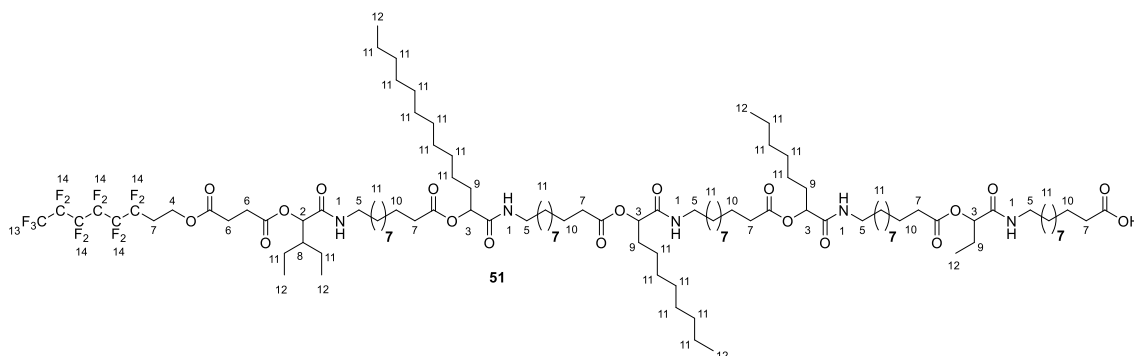
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -80.64 – -81.03 (m, 3 F, CF_3^{13}), -113.54 – -113.82 (m, 2 F, CF_2^{14}), -121.66 – -122.01 (m 2 F, CF_2^{14}), -122.72 – -122.99 (m 2 F, CF_2^{14}), -123.41 – -123.70 (m 2 F, CF_2^{14}), -125.95 – -126.19 (m 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{116}^{1}\text{H}_{194}^{16}\text{O}_{19}^{14}\text{N}^{19}\text{F}_{13}$, 2209.4233; found, 2209.4261, Δ = 2.8 mmu.



Supplementary Figure 62: ^1H -NMR of compound 50 measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.04 g of **50** (469 μmol , 1.00 eq.) were dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Afterwards, 207 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **51** was obtained as a pale highly viscous oil in a yield of 98.7% (981 mg, 462 μmol).

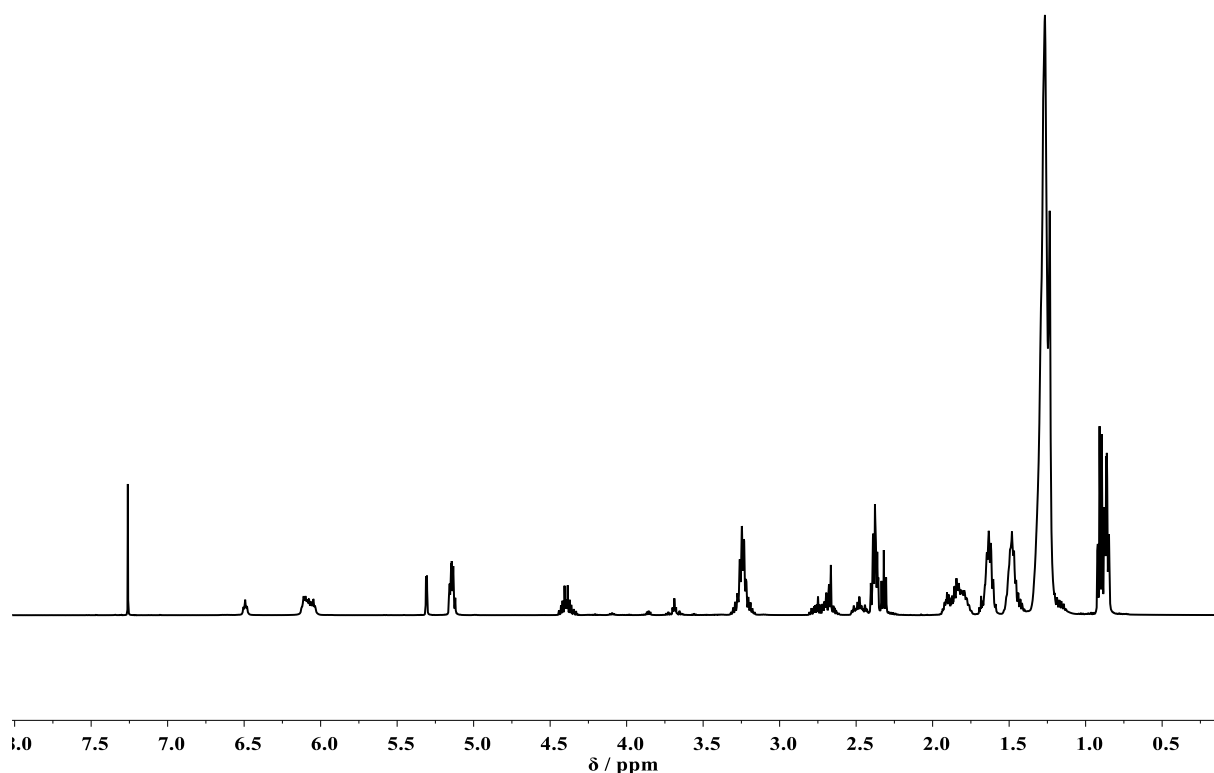
IR (ATR): ν/cm^{-1} = 3305.4 (vw), 2924.0 (s), 2854.0 (m), 1740.7 (s), 1654.4 (s), 1539.7 (m), 1463.5 (w), 1374.8 (w), 1236.9 (vs), 1145.3 (vs), 1008.3 (w), 841.8 (vw), 808.9 (vw), 720.6 (w), 651.0 (w), 400.3 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.49 (t, J = 5.8 Hz, 1 H, NH^1), 6.17 – 5.99 (m, 4 H, NH^1), 5.31 (d, J = 3.2 Hz, 1 H, CH^2), 5.16 – 5.08 (m, 4 H, CH^3), 4.49 – 4.30 (m, 2 H, CH_2^4), 3.35 – 3.14 (m, 10 H, CH_2^5), 2.84 – 2.58 (m, 4 H, CH_2^6), 2.55 – 2.25 (m, 12 H, CH_2^7), 1.98 – 1.72 (m, 9 H, CH^8 , CH_2^9), 1.70 – 1.56 (m, 10 H, CH_2^{10}), 1.53 – 1.12 (m, 127 H, CH_2^{11}), 0.96 – 0.82 (m, 18 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = ^{13}C NMR (126 MHz, Chloroform- d) δ 176.86, 172.87, 172.70, 172.64, 172.63, 172.59, 171.25, 170.18, 170.11, 170.09, 169.86, 169.70, 75.74, 74.94, 74.04, 62.92, 56.98, 43.34, 39.48, 39.37, 39.34, 39.29, 34.43, 33.96, 32.02, 32.01, 31.95, 31.75, 30.73, 30.56, 30.39, 30.00, 29.74, 29.69, 29.66, 29.61, 29.59, 29.56, 29.52, 29.50, 29.47, 29.42, 29.37, 29.37, 29.33, 29.24, 29.21, 29.18, 29.13, 29.09, 29.03, 26.98, 26.95, 26.87, 25.19, 25.11, 25.08, 24.91, 24.90, 24.84, 22.66, 22.53, 22.15, 14.24, 14.23, 14.17, 11.85, 11.73, 9.15.

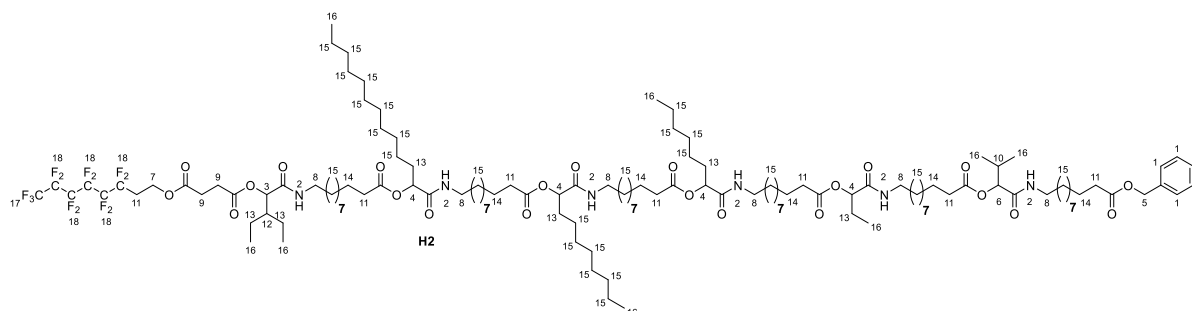
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.56 – -80.94 (m, 3 F, CF_3), -113.44 – -113.80 (m, 2 F, CF_2), -121.63 – -122.01 (m), -122.60 – -123.02 (m), -123.25 – -123.84 (m), -125.82 – -126.33 (m). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{109}^{1}\text{H}_{188}^{16}\text{O}_{19}^{14}\text{N}_5^{19}\text{F}_{13}$, 2119.3764; found, 2119.3829, Δ = 6.5 mmu.



Supplementary Figure 63: ^1H -NMR of compound **51** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 877 mg of **51** (414 μmol , 1.00 eq.) was dissolved in 2.50 mL DCM and 57.0 μL isobutyraldehyde **14c** (44.8 mg, 621 μmol , 1.50 eq.) and 187 mg of monomer **M1** (621 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 2 days and subsequently the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 $\rightarrow$ 1:2) to afford product **H2** as a white solid in a yield of 83.8% (863 mg, 347 μmol).

R_f = 0.71 in cyclohexane / ethyl acetate (1:1).

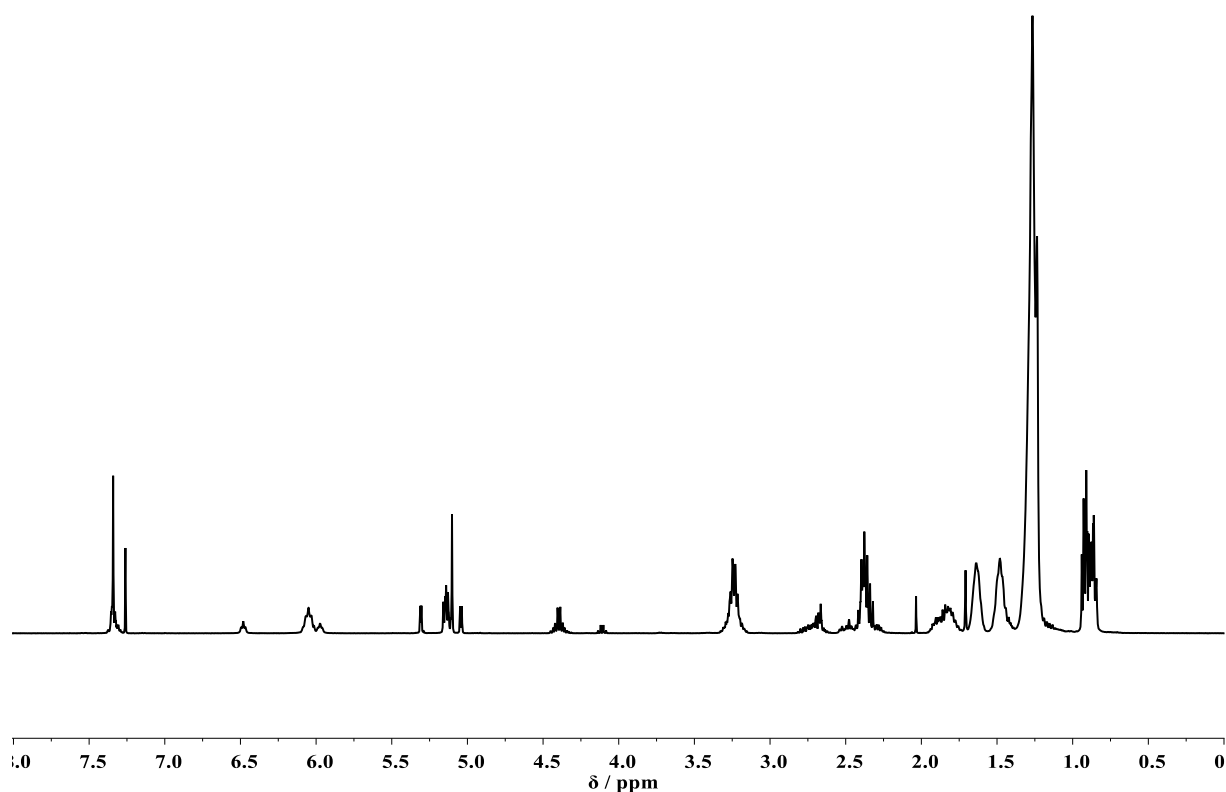
IR (ATR): ν / cm^{-1} = 3306.1 (vw), 2924.1 (s), 2853.9 (m), 1740.5 (s), 1654.5 (s), 1535.9 (m), 1462.7 (w), 1370.2 (w), 1237.3 (s), 1145.6 (s), 697.4 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.31 (m, 5 H, CH_{Ar}^1), 6.50 (t, J = 5.8 Hz, 1 H, NH^2), 6.13 – 5.96 (m, 5 H, NH^2), 5.33 (d, J = 3.1 Hz, 1 H, CH^3), 5.20 – 5.14 (m, 4 H, CH^4), 5.12 (s, 2 H, CH_2^5), 5.07 (d, J = 4.5 Hz, 1 H, CH^6), 4.50 – 4.33 (m, 2 H, CH_2^7), 3.38 – 3.16 (m, 12 H, CH_2^8), 2.84 – 2.61 (m, 4 H, CH_2^9), 2.58 – 2.25 (m, 15 H, CH^{10} , CH_2^{11}), 1.99 – 1.75 (m, 9 H, CH^{12} , CH_2^{13}), 1.71 – 1.60 (m, 12 H, CH_2^{14}), 1.57 – 1.11 (m, 126 H, CH_2^{15}), 0.98 – 0.83 (m, 24 H, CH_3^{16}).

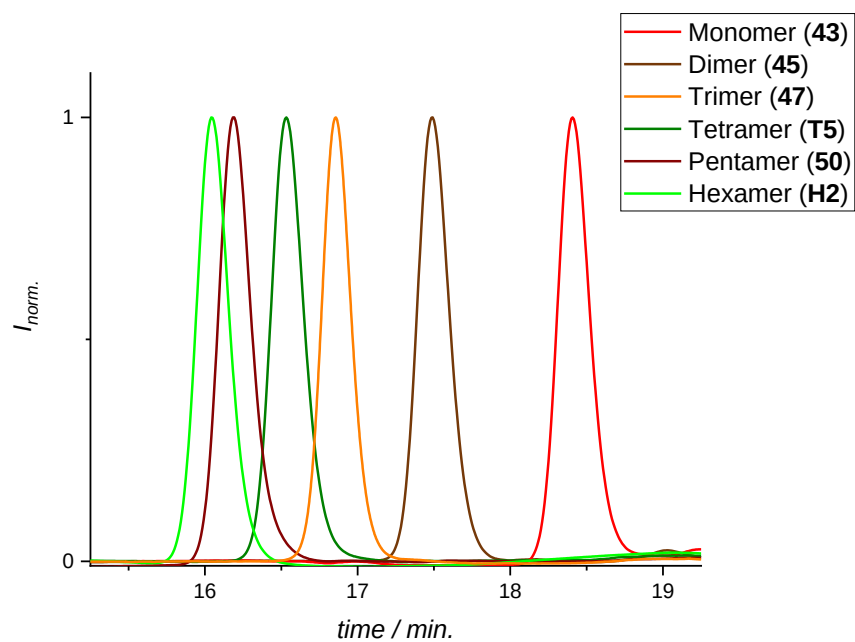
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.85, 172.68, 172.60, 172.57, 171.23, 169.99, 169.75, 169.61, 169.38, 136.24, 128.66, 128.28, 78.03, 75.74, 74.92, 74.04, 66.19, 56.97, 43.34, 39.45, 39.30, 39.28, 34.44, 34.41, 32.04, 31.95, 31.75, 30.64, 29.74, 29.70, 29.66, 29.61, 29.58, 29.56, 29.51, 29.47, 29.37, 29.33, 29.31, 29.24, 29.22, 29.18, 29.13, 29.03, 26.96, 25.21, 25.12, 25.08, 25.06, 24.89, 24.84, 22.80, 22.76, 22.65, 22.53, 22.15, 18.91, 17.08, 14.23, 14.21, 14.17, 11.86, 11.73, 9.15.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.08 (t, J = 9.9 Hz, 3 F, CF_3^{17}), -117.53 – -118.42 (m, 2 F, CF_2^{18}), -125.96 – -126.57 (m, 2 F, CF_2^{18}), -126.82 – -127.46 (m, 2 F, CF_2^{18}), -127.67 – -128.17 (m, 2 F, CF_2^{18}), -129.91 – -130.82 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{18} group = 10.

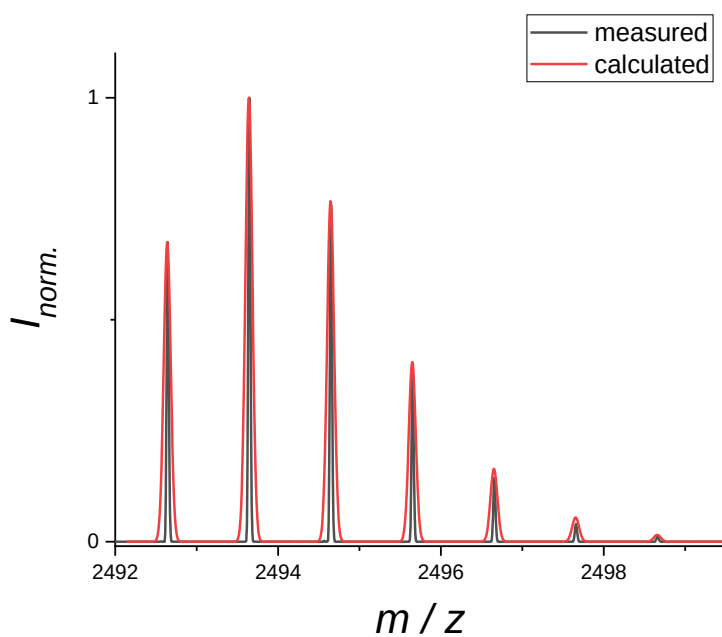
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{132}^{1}\text{H}_{223}^{19}\text{F}_{13}^{14}\text{N}_6^{16}\text{O}_{22}$, 2492.6381; found, 2492.6446, Δ = 6.5 mmu.



Supplementary Figure 64: ^1H -NMR of compound H2 measured in CDCl_3 .



Supplementary Figure 65: SEC traces of the intermediates after each P3CR in the synthesis of product H2



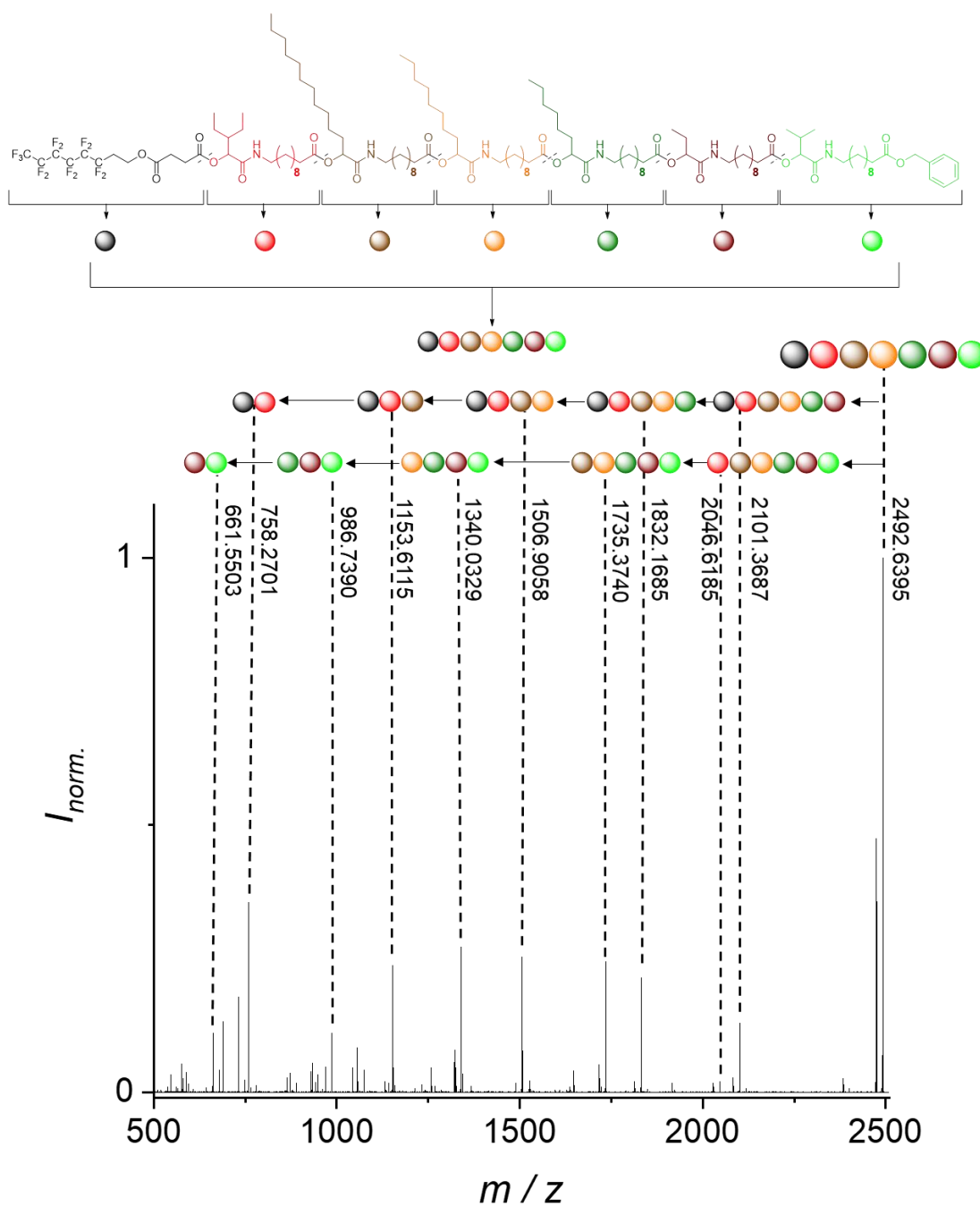
Supplementary Figure 66: High resolution ESI-MS measurement of H2. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

```

found 22260 values in C:\Users\Maxi\Documents\Mixture 2492 NCE 18 with 3.CSV, maximum is 1.000000 found for mass 2492.647
480
matching mass 2492.64748
cutoff 0.50000: 0 solutions (4 peaks)
cutoff 0.25000: 0 solutions (11 peaks)
cutoff 0.12500: 0 solutions (37 peaks)
cutoff 0.06250: 0 solutions (69 peaks)
cutoff 0.03125: 0 solutions (119 peaks)
cutoff 0.01562: 0 solutions (230 peaks)
cutoff 0.00781: 0 solutions (375 peaks)
cutoff 0.00391: 0 solutions (623 peaks)
cutoff 0.00195: 0 solutions (975 peaks)
cutoff 0.00098: 1 solutions (1465 peaks)
2492.64748 ≈ 447.026590 + 311.246050 + 395.339950 + 353.293000 + 325.261700 + 269.199100 + 283.214750 + 107.049690 (sides
2-Ethylbutanal, Dodecanal, Nonanal, Heptanal, Propionaldehyde, Isobutyraldehyde; error -1.01665)
Press ENTER to quit ...

```

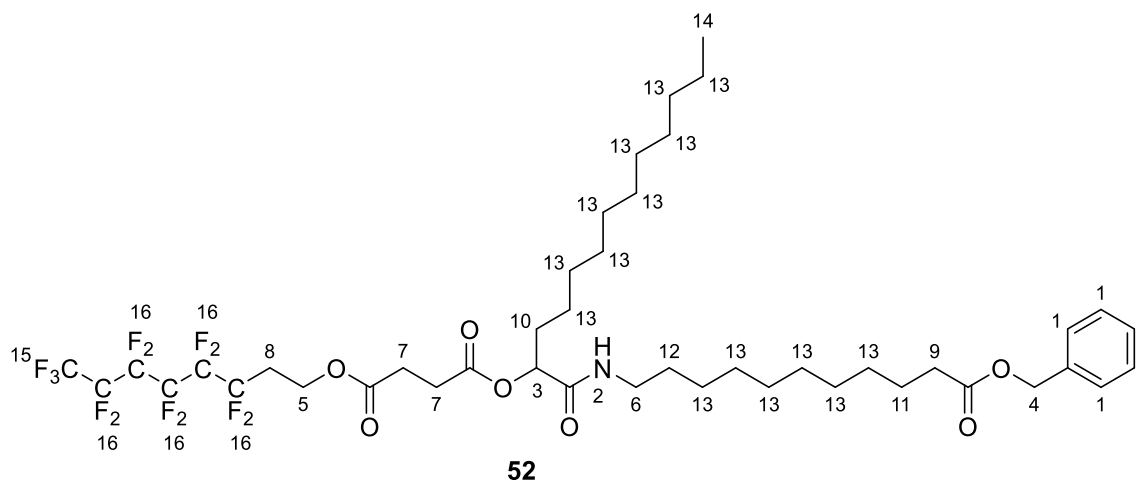
Supplementary Figure 67: Screenshot of the automated read-out of H2.



Supplementary Figure 68: Read-out of the sequence-defined hexamer H2. Read-out of the hexamer H2 via tandem ESI-MS/MS with an NCE of 18. In the spectrum, the read-out from both ends of the oligomer using the fragmentation next to the carbonyl are shown.

1.3.4.3 Synthesis of tetramer T6

Passerini reaction



In 50.0 mL round bottom flasks, 1.00 g **TAG1** (2.15 mmol, 1.00 eq.) were dissolved in 6.00 mL DCM and 550 mg dodecanal **14h** (3.23 mmol, 1.50 eq.) and 974 mg of monomer **M1** (3.23 mol, 1.50 eq.) were added. The mixture was stirred at room temperature for 2 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane / ethyl acetate 6:1 → 4:1) to afford product **52** as a yellow oil in a yield of 94.0% (1.93 g, 2.02 mmol).

R_f = 0.60 in cyclohexane / ethyl acetate (3:1).

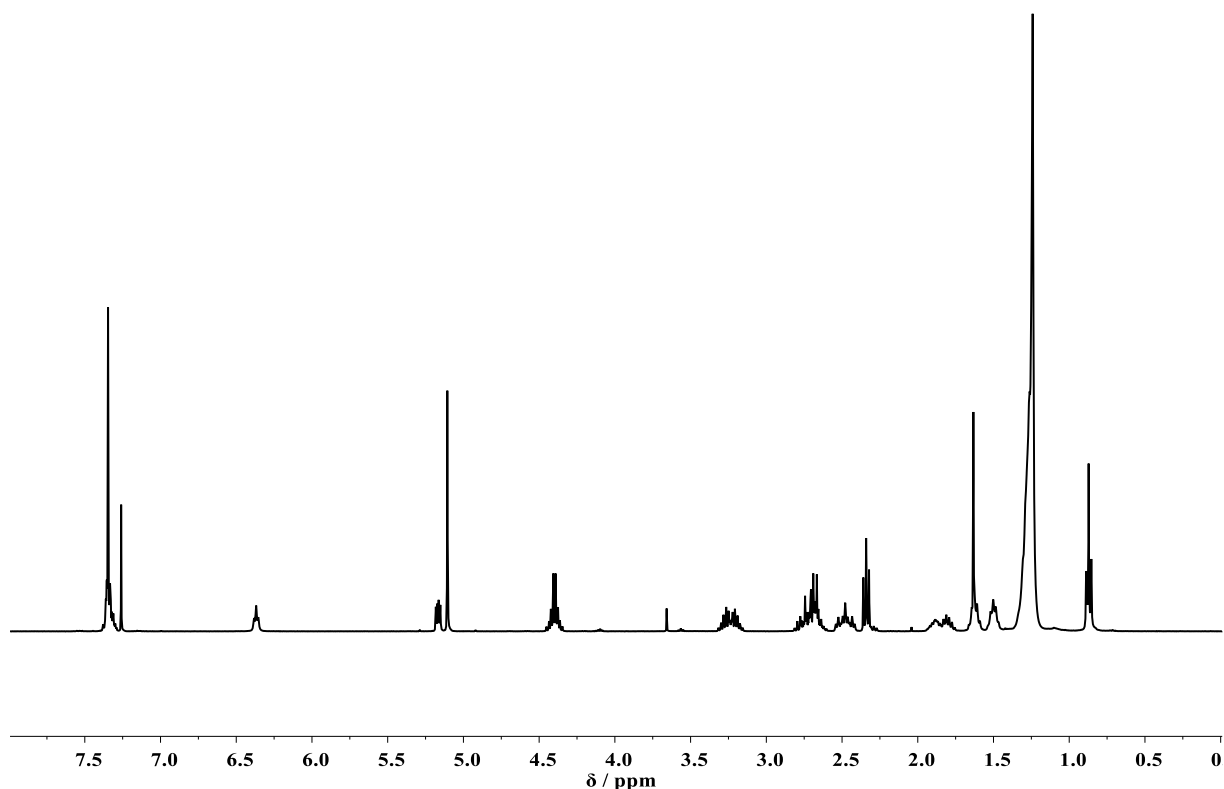
IR (ATR): ν / cm^{-1}] = 2925.0 (m), 2854.4 (w), 1738.1 (s), 1658.1 (w), 1535.5 (w), 1457.7 (w), 1359.5 (w), 1235.3 (vs), 12028m.1 (vs), 1144.6 (vs), 1081.9 (m), 1005.2 (w), 842.0 (vw), 808.9 (vw), 732.4 (w), 697.2 (m), 651.2 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.28 (m, 5 H, CH_{Ar}^1), 6.37 (t, J = 5.8 Hz, 1 H, NH^2), 5.19 – 5.15 (m, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 4.48 – 4.32 (m, 2 H, CH_2^5), 3.34 – 3.15 (m, 2 H, CH_2^6), 2.82 – 2.60 (m, 4 H, CH_2^7), 2.48 (s, 2 H, CH_2^8), 2.34 (t, J = 7.5 Hz, 2 H, CH_2^9), 1.96 – 1.74 (m, 2 H, CH_2^{10}), 1.68 – 1.58 (m, 2 H, CH_2^{11}), 1.56 – 1.44 (m, 2 H, CH_2^{12}), 1.36 – 1.19 (m, 30 H, CH_2^{13}), 0.87 (t, J = 6.8 Hz, 3 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.63, 171.24, 169.71, 136.26, 128.66, 128.28, 74.75, 66.19, 56.95, 39.46, 34.44, 32.04, 31.94, 30.57, 29.75, 29.69, 29.60, 29.58, 29.53, 29.49, 29.48, 29.38, 29.35, 29.24, 29.22, 29.13, 26.97, 25.06, 25.03, 22.82, 14.24.

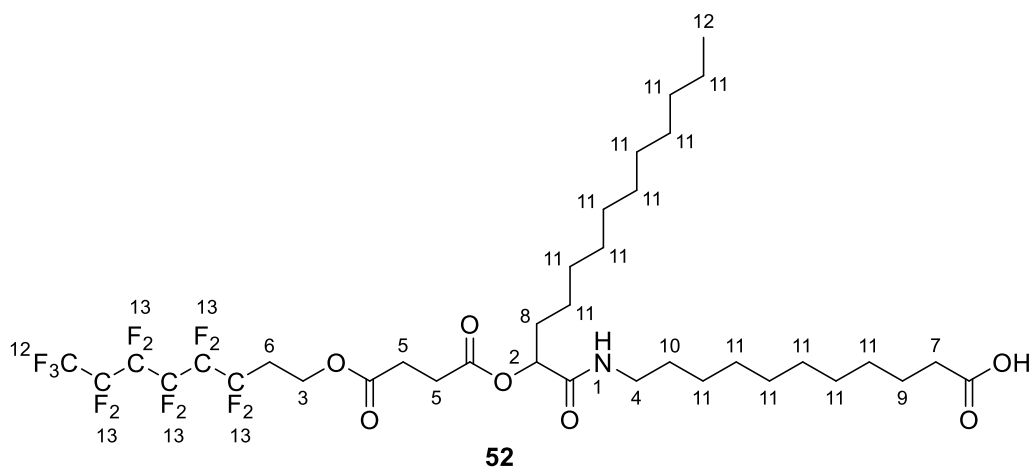
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -83.76 – -86.21 (m, 3 F, CF_3^{15}), -117.01 – -118.71 (m, 2 F, CF_2^{16}), -126.05 – -126.35 (m, 2 F, CF_2^{16}), -127.05 – -127.34 (m, 2 F, CF_2^{16}), -127.79 – -128.06 (m, 2 F, CF_2^{16}), -130.36 – -130.58 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{43}^{1}\text{H}_{60}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 950.4235; found, 950.4210, Δ = 2.5 mmu.



Supplementary Figure 69: ^1H -NMR of compound **51** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.82 g of **51** (1.91 mmol, 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 363 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **52** was obtained as a high viscous oil in a yield of 96.3% (1.58 g, 1.84 mmol).

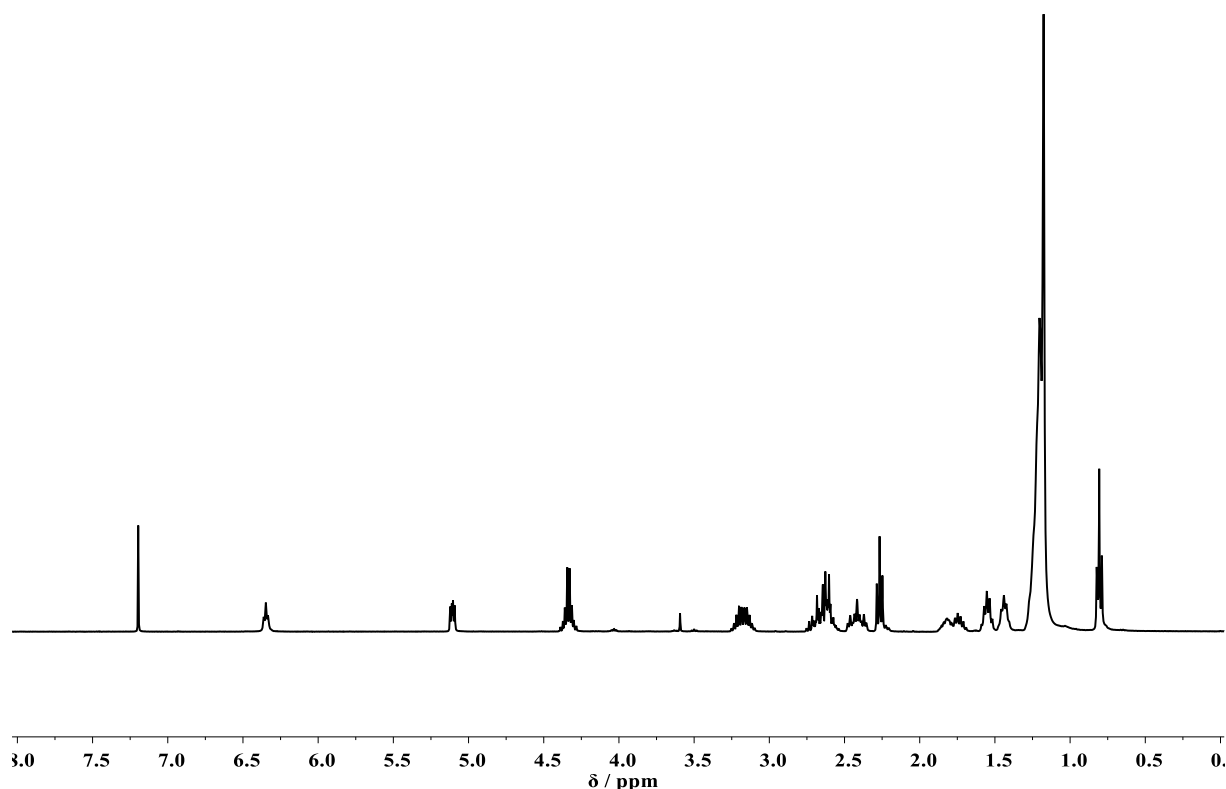
IR (ATR): ν/cm^{-1} = 3291.4 (w), 2913.2 (vs), 2847.8 (s), 1740.8 (vs), 1695.6 (s), 1659.5 (vs), 1556.4 (m), 1469.3 (m), 1414.0 (w), 1360.7 (m), 1188.8 (vs), 1162.5 (vs), 1141.8 (vs), 1080.1 (s), 905.0 (w), 839.7 (w), 808.4 (w), 732.6 (m), 698.7 (s), 651.0 (m), 565.9 (w), 529.5 (w), 460.5 (w).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.41 (t, J = 5.8 Hz, 1 H, NH^1), 5.21 – 5.13 (m, 1 H, CH^2), 4.50 – 4.31 (m, 2 H, CH_2^3), 3.33 – 3.14 (m, 2 H, CH_2^4), 2.84 – 2.60 (m, 4 H, CH_2^5), 2.56 – 2.40 (m, 2 H, CH_2^6), 2.33 (t, J = 7.5 Hz, 2 H, CH_2^7), 1.96 – 1.74 (m, 2 H, CH_2^8), 1.67 – 1.56 (m, 2 H, CH_2^9), 1.54 – 1.45 (m, 2 H, CH_2^{10}), 1.39 – 1.17 (m, 30 H, CH_2^{11}), 0.87 (t, J = 6.7 Hz, 3 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 178.65, 172.69, 171.28, 74.76, 56.98, 39.49, 33.99, 32.05, 31.93, 30.60, 29.76, 29.70, 29.59, 29.49, 29.46, 29.38, 29.35, 29.25, 29.23, 29.21, 29.15, 29.08, 26.91, 25.04, 24.79, 22.82, 14.24.

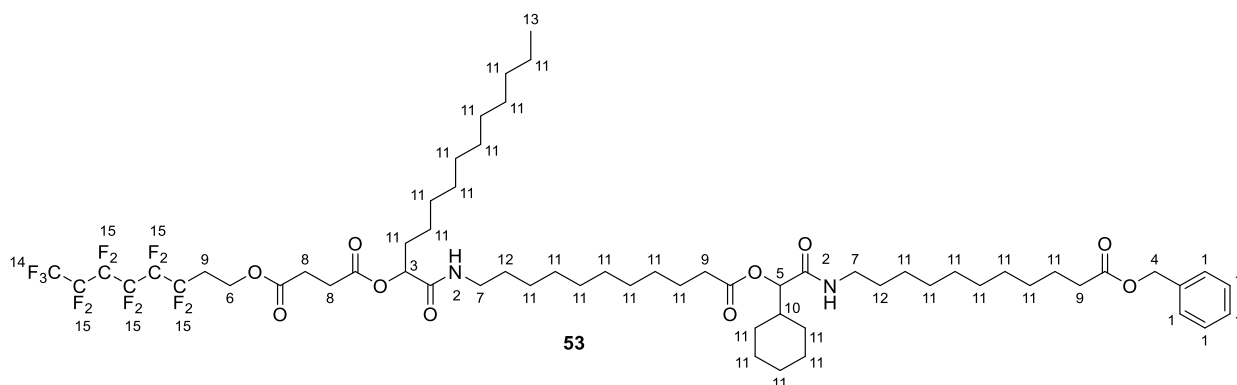
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -84.77 – -85.47 (m, 3 F, CF_3^{12}), -117.91 – -118.15 (m, 2 F, CF_2^{13}), -126.04 – -126.37 (m, 2 F, CF_2^{13}), -127.07 – -127.35 (m, 2 F, CF_2^{13}), -127.78 – -128.08 (m, 2 F, CF_2^{13}), -130.31 – -130.62 (m, 2 F, CF_2^{13}). Total integral of CF_2 region normalized with respect to the CF_3^{13} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{36}^{1}\text{H}_{54}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 882.3585; found, 882.3559, Δ = 2.6 mmu.



Supplementary Figure 70: ^1H -NMR of compound 52 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 1.53 g of **52** (1.78 mmol, 1.00 eq.) was dissolved in 4.00 mL DCM and 323 μ L cyclohexanecarboxaldehyde **14j** (319 mg, 2.67 mmol, 1.50 eq.) and 857 mg of monomer **M1** (2.67 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 2:1) to afford product **53** as a pale highly viscous oil in a yield of 91.1% (2.06 g, 1.62 mmol).

R_f = 0.50 in cyclohexane / ethyl acetate (3:1).

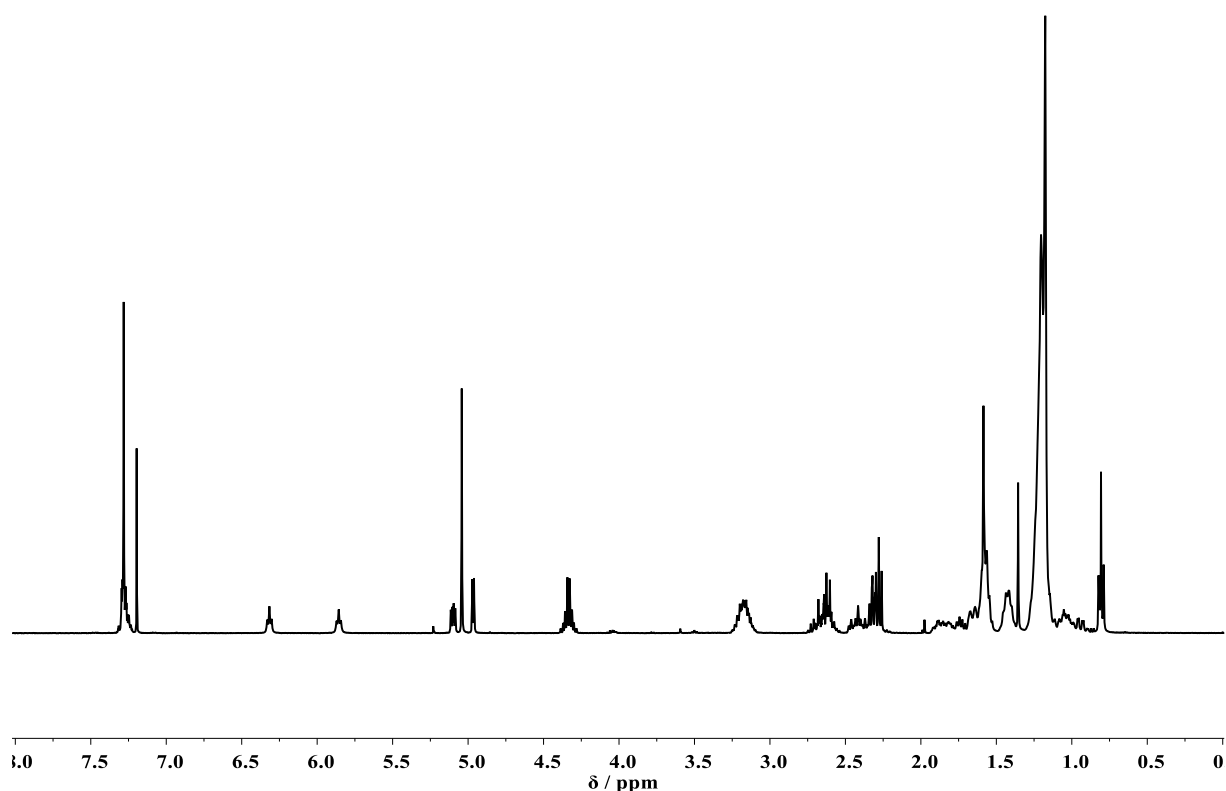
IR (ATR): ν / cm^{-1} = 3285.3 (vw), 2919.4 (s), 2850.8 (m), 1737.6 (vs), 1652.4 (s), 1552.7 (w), 1466.8 (w), 1362.9 (w), 1235.9 (vs), 1143.8 (vs), 1082.8 (m), 1005.2 (w), 842.4 (vw), 809.6 (vw), 697.3 (s), 652.3 (w), 567.2 (vw), 455.5 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.36 – 7.22 (m, 5 H, CH_{Ar}^1), 6.32 (t, J = 5.8 Hz, 1 H, NH^2), 5.86 (t, J = 5.9 Hz, 1 H, NH^2), 5.12 – 5.07 (m, 1 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.97 (d, J = 4.6 Hz, 1 H, CH^5), 4.43 – 4.25 (m, 2 H, CH_2^6), 3.25 – 3.06 (m, 4 H, CH_2^7), 2.78 – 2.55 (m, 4 H, CH_2^8), 2.51 – 2.21 (m, 6 H, CH_2^9), 1.95 – 1.51 (m, 13 H, CH^{10} , CH_2^{11}), 1.47 – 1.37 (m, 4 H, CH_2^{12}), 1.30 – 0.93 (m, 46 H, CH_2^{11}), 0.84 – 0.76 (m, 3 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.83, 172.65, 171.25, 169.74, 169.34, 136.26, 128.67, 128.29, 77.74, 74.75, 66.20, 56.94, 40.12, 39.44, 39.27, 34.45, 34.42, 32.04, 31.94, 30.57 (t, J = 21.6 Hz), 29.75, 29.70, 29.68, 29.61, 29.57, 29.54, 29.52, 29.47, 29.36, 29.32, 29.27, 29.24, 29.22, 29.13, 27.39, 27.05, 26.97, 26.19, 26.12, 26.01, 25.12, 25.07, 25.04, 22.81, 14.24.

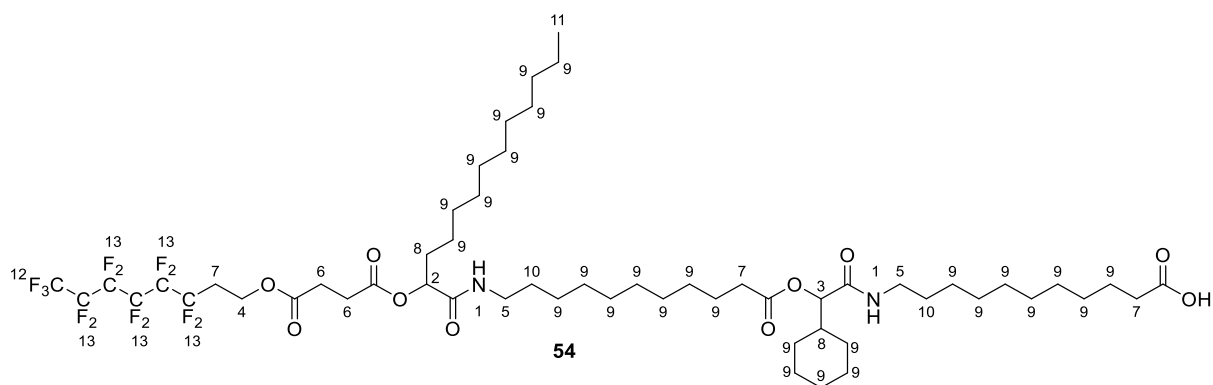
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.31 – -85.80 (m, 3 F, CF_3^{14}), -117.77 – -118.47 (m, 2 F, CF_2^{15}), -125.71 – -126.57 (m, 2 F, CF_2^{15}), -126.86 – -127.43 (m, 2 F, CF_2^{15}), -127.48 – -128.34 (m, 2 F, CF_2^{15}), -129.95 – -130.75 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{62}^{1}\text{H}_{93}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1295.6515; found, 1261.6500, Δ = 1.5 mmu.



Supplementary Figure 71: ^1H -NMR of compound **53** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.98 g of **54** (1.56 mmol, 1.00 eq.) were dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Afterwards, 396 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **54** was obtained as a high viscous oil in a yield of 98.7% (1.82 g, 1.54 mmol).

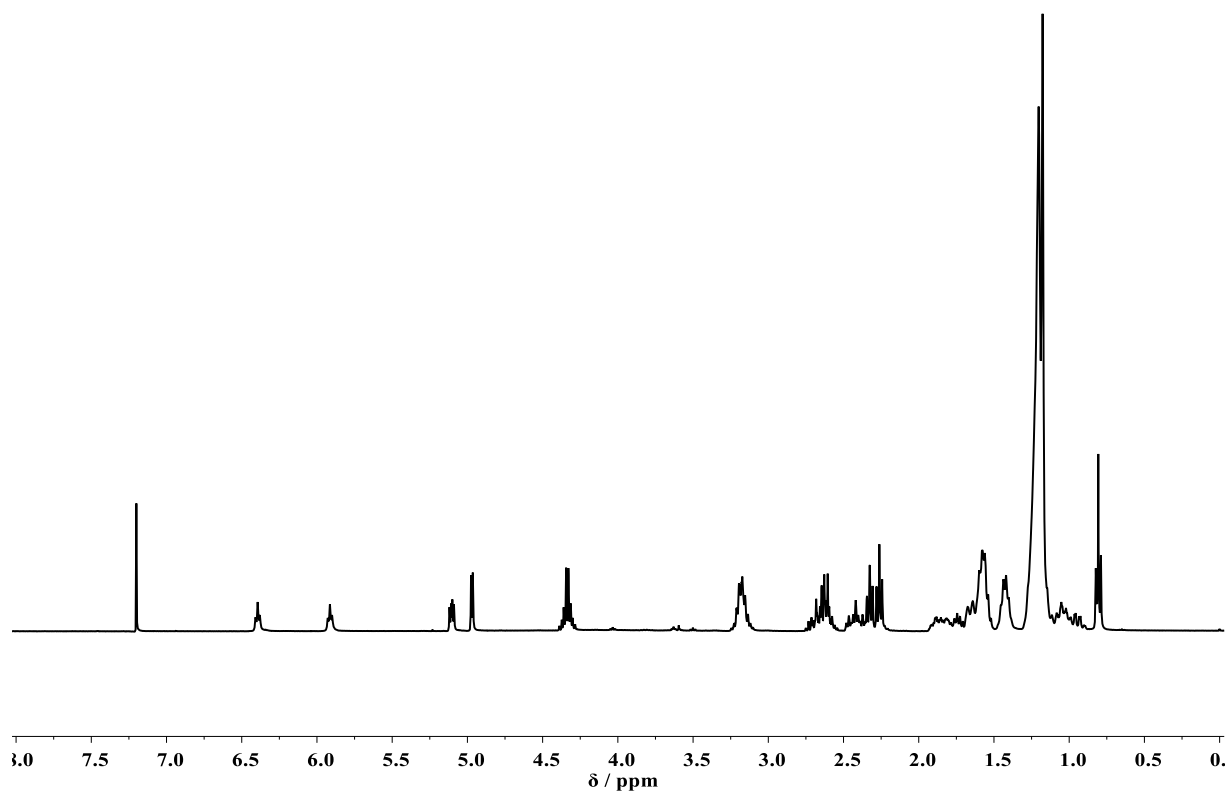
IR (ATR): ν/cm^{-1} = 3297.6 (w), 2919.4 (s), 2851.0 (m), 1736.5 (vs), 1655.2 (vs), 1555.0 (m), 1466.3 (w), 1364.5 (m), 1235.5 (vs), 1164.6 (vs), 1143.4 (vs), 1082.3 (m), 1006.9 (w), 842.1 (vw), 810.2 (vw), 697.9 (m), 652.2 (w), 567.0 (vw), 530.7 (vw), 453.2 (vw), 394.1 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.45 (t, J = 5.8 Hz, 1 H, NH^1), 5.97 (t, J = 5.8 Hz, 1 H, NH^1), 5.19 – 5.13 (m, 1 H, CH^2), 5.03 (d, J = 4.6 Hz, 1 H, CH^3), 4.46 – 4.33 (m, 2 H, CH_2^4), 3.31 – 3.15 (m, 4 H, CH_2^5), 2.81 – 2.58 (m, 4 H, CH_2^6), 2.56 – 2.28 (m, 6 H, CH_2^7), 2.00 – 1.56 (m, 13 H, CH^8 , CH_2^9), 1.55 – 1.42 (m, 4 H, CH_2^{10}), 1.37 – 0.97 (m, 46 H, CH_2^9), 0.93 – 0.82 (m, 3 H, CH_3^{11}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 178.65, 173.46, 172.07, 170.72, 170.23, 78.52, 75.49, 57.73, 40.84, 40.28, 40.02, 35.19, 34.81, 32.80, 32.67, 31.34 (t, J = 21.8 Hz), 30.51, 30.44, 30.38, 30.35, 30.33, 30.28, 30.27, 30.23, 30.21, 30.12, 30.04, 29.99, 29.97, 29.89, 29.86, 28.17, 27.73, 27.66, 26.95, 26.87, 26.76, 25.90, 25.79, 25.64, 23.57, 14.98.

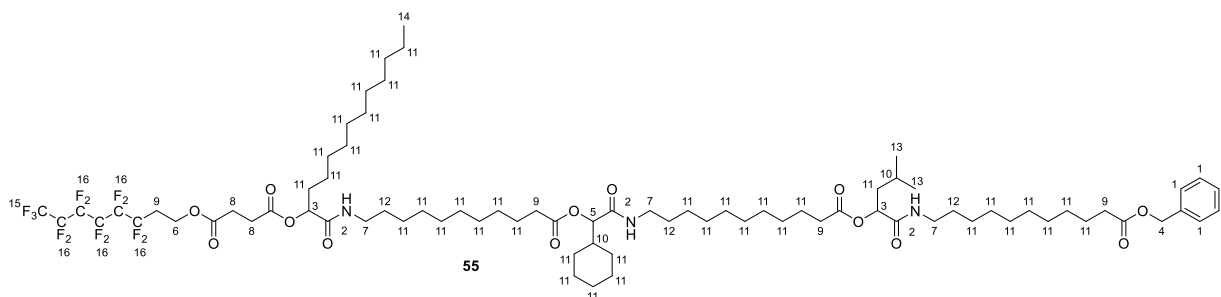
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -85.10 (t, J = 9.8 Hz, 3 F, CF_3^{12}), -117.60 – -118.27 (m, 2 F, CF_2^{13}), -125.80 – -126.54 (m, 2 F, CF_2^{13}), -126.84 – -127.47 (m, 2 F, CF_2^{13}), -127.62 – -128.11 (m, 2 F, CF_2^{13}), -130.25 – -130.87 (m, 2 F, CF_2^{13}). Total integral of CF_2 region normalized with respect to the CF_3^{12} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{55}^{1}\text{H}_{87}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1205.6045; found, 1205.6026, Δ = 1.9 mmu.



Supplementary Figure 72: ^1H -NMR of compound 54 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 1.05 g **54** (886 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 143 μL 3-methylbutyraldehyde **14g** (114 mg, 1.33 mmol, 1.50 eq.) and 401 mg of monomer **M1** (1.33 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 2:1) to afford product **55** as a pale highly viscous oil in a yield of 86.2% (1.20 g, 764 μmol).

R_f = 0.34 in cyclohexane / ethyl acetate (3:1).

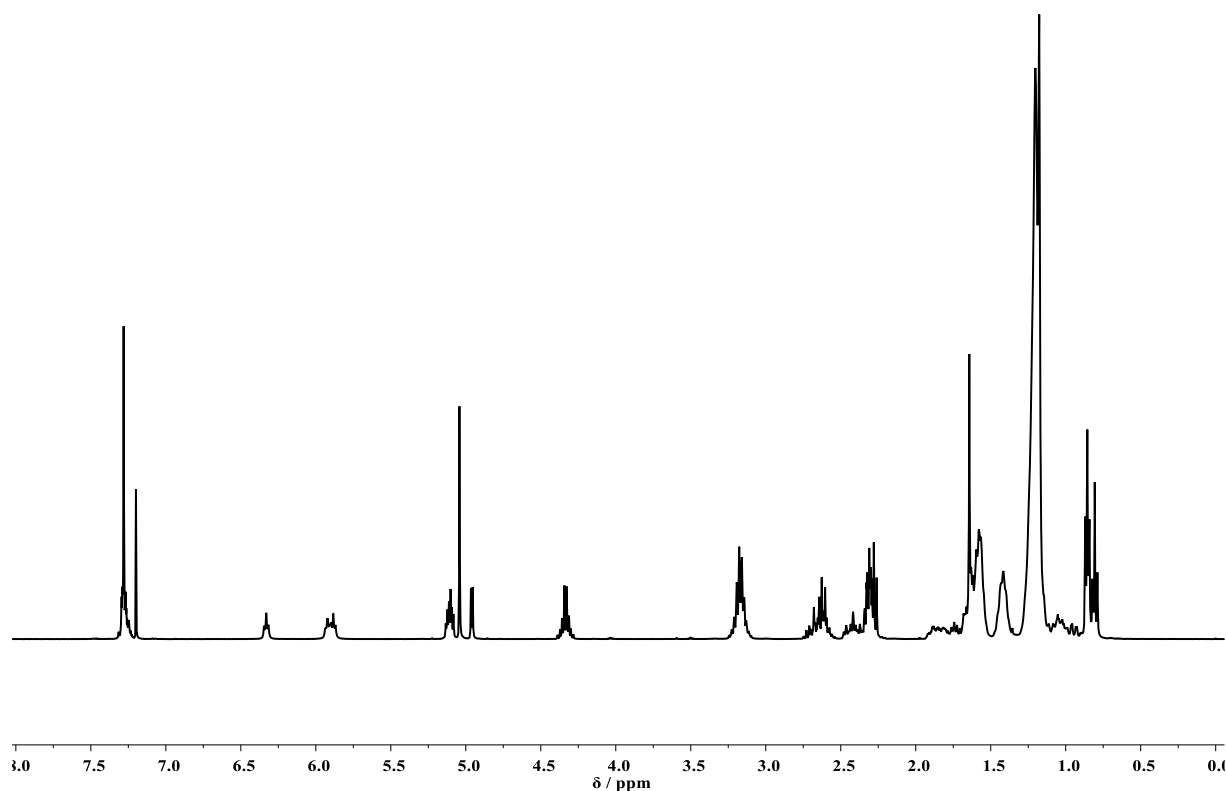
IR (ATR): ν / cm^{-1} = 3299.8 (vw), 2920.7 (s), 2851.3 (m), 1736.8 (s), 1655.3 (vs), 1553.2 (w), 1465.8 (w), 1365.0 (w), 1236.2 (s), 1206.9 (s), 1143.7 (vs), 1005.2 (w), 697.1 (m), 652.1 (w), 567.5 (vw), 450.7 (vw), 394.2 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.35 – 7.22 (m, 5 H, CH_{Ar}^1), 6.33 (t, J = 5.8 Hz, 1 H, NH^2), 5.97 – 5.82 (m, 2 H, NH^2), 5.15 – 5.06 (m, 2 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.96 (d, J = 4.6 Hz, 1 H, CH^5), 4.42 – 4.25 (m, 2 H, CH_2^6), 3.25 – 3.07 (m, 6 H, CH^7), 2.76 – 2.53 (m, 4 H, CH_2^8), 2.50 – 2.23 (m, 8 H, CH_2^9), 1.95 – 1.51 (m, 16 H, CH^{10} , CH_2^{11}), 1.48 – 1.35 (m, 6 H, CH_2^{12}), 1.32 – 0.96 (m, 60 H, CH_2^{11}), 0.86 (t, J = 5.7 Hz, 6 H, CH_3^{13}), 0.81 (t, J = 6.8 Hz, 3 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.77, 172.67, 172.65, 171.25, 170.34, 169.74, 169.36, 136.25, 128.66, 128.28, 77.74, 74.73, 72.76, 66.19, 56.94, 40.98, 40.10, 39.44, 39.35, 39.26, 34.44, 34.41, 32.03, 31.93, 30.57 (t, J = 21.7 Hz), 29.74, 29.70, 29.67, 29.64, 29.60, 29.56, 29.53, 29.51, 29.47, 29.35, 29.33, 29.29, 29.26, 29.22, 29.12, 27.40, 26.96, 26.92, 26.19, 26.11, 26.00, 25.11, 25.06, 25.05, 25.03, 24.67, 23.25, 22.80, 21.91, 14.23.

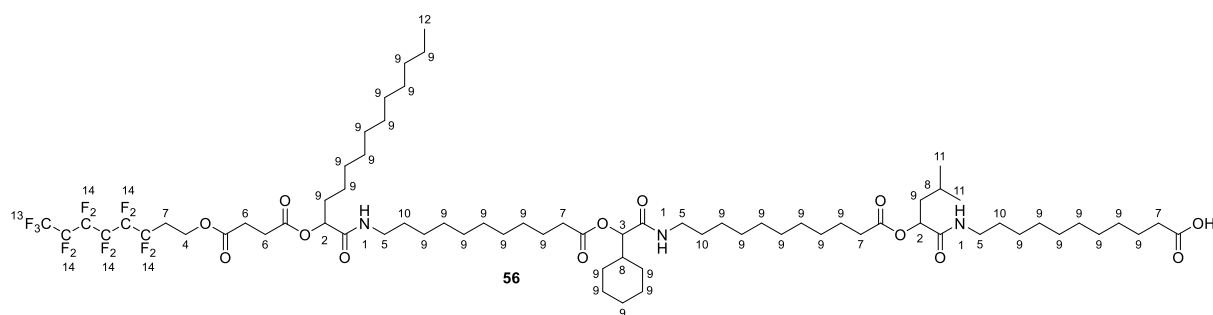
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.09 (t, J = 9.9 Hz, 3 F, CF_3^{15}), -117.70 – -118.56 (m, 2 F, CF_2^{16}), -126.00 – -126.49 (m, 2 F, CF_2^{16}), -126.86 – -127.42 (m, 2 F, CF_2^{16}), -127.72 – -127.97 (m, 2 F, CF_2^{16}), -130.25 – -130.99 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{79}^{1}\text{H}_{124}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_{13}$, 1570.8999; found, 1570.8988, Δ = 1.1 mmu.



Supplementary Figure 73: ^1H -NMR of compound 55 measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.51 g of **55** (964 μmol , 1.00 eq.) were dissolved in 7.00 mL ethyl acetate and 7.00 mL THF. Afterwards, 303 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **56** was obtained as a high viscous oil in a yield of 99.5% (1.42 g, 959 μmol).

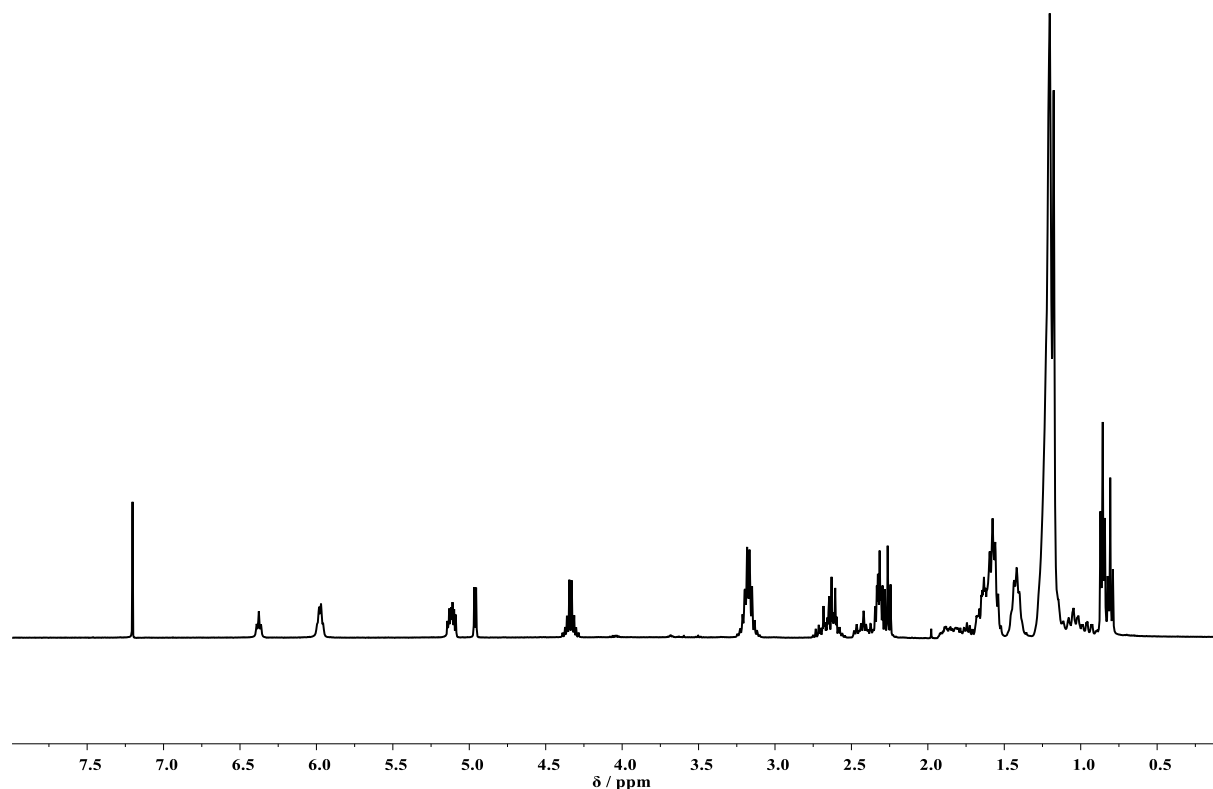
IR (ATR): ν/cm^{-1} = 3307.3 (vw), 2924.4 (s), 2853.4 (m), 1739.3 (s), 1655.0 (s), 1540.6 (m), 1465.2 (w), 1366.2 (w), 1235.8 (vs), 1144.5 (vs), 842.9 (vw), 808.8 (vw), 697.6 (w), 651.3 (w), 396.6 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.43 (t, J = 5.8 Hz, 1 H, NH^1), 6.09 – 5.99 (m, 2 H, NH^1), 5.23 – 5.13 (m, 2 H, CH^2), 5.02 (d, J = 4.7 Hz, 1 H, CH^3), 4.46 – 4.33 (m, 2 H, CH_2^4), 3.35 – 3.16 (m, 6 H, CH_2^5), 2.82 – 2.59 (m, 4 H, CH_2^6), 2.55 – 2.28 (m, 8 H, CH_2^7), 2.00 – 1.56 (m, 16 H, CH^8 , CH_2^9), 1.54 – 1.41 (m, 6 H, CH_2^{10}), 1.38 – 1.01 (m, 60 H, CH_2^9), 0.91 (t, J = 5.8 Hz, 6 H, CH_3^{11}), 0.89 – 0.83 (m, 3 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 177.49, 172.81, 172.78, 172.68, 171.27, 170.45, 169.88, 169.52, 77.75, 74.71, 72.78, 56.95, 40.93, 40.06, 39.47, 39.34, 39.32, 34.42, 34.40, 34.01, 32.03, 31.92, 30.57 (t, J = 21.7 Hz), 29.74, 29.67, 29.59, 29.56, 29.53, 29.50, 29.46, 29.43, 29.34, 29.29, 29.24, 29.23, 29.12, 29.10, 27.42, 26.95, 26.86, 26.18, 26.09, 25.98, 25.10, 25.07, 25.02, 24.88, 24.67, 23.24, 22.80, 21.90, 14.22.

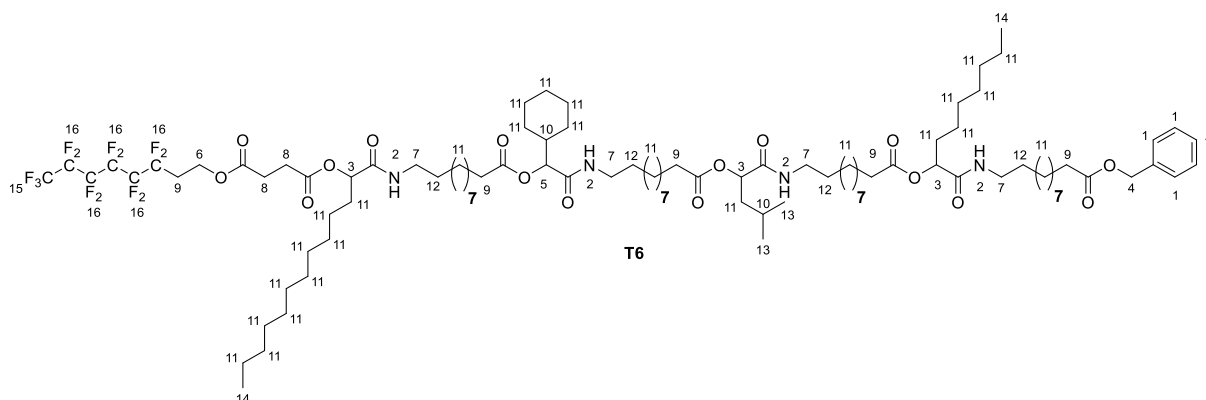
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.10 (t, J = 9.8 Hz, 3 F, CF_3^{13}), -117.52 – -118.47 (m, 2 F, CF_2^{14}), -125.86 – -126.49 (m, 2 F, CF_2^{14}), -126.92 – -127.34 (m, 2 F, CF_2^{14}), -127.44 – -128.06 (m, 2 F, CF_2^{14}), -130.27 – -130.61 (m, 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{13} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{72}^{1}\text{H}_{118}^{16}\text{O}_{13}^{14}\text{N}_2^{19}\text{F}_{13}$, 1480.8530; found, 1480.8527, Δ = 0.3 mmu.



Supplementary Figure 74: ^1H -NMR of compound 56 measured in CDCl_3 .

Passerini reaction



In a 25 mL round bottom flask equipped with a magnetic stir bar, 1.34 g of **56** (853 μmol , 1.00 eq.) was dissolved in 5.00 mL DCM. Afterwards, 200 μL octanal **14i** (164 mg, 1.28 mol, 1.50 eq.) and 386 mg of monomer **M1** (1.28 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days and subsequently the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 $\rightarrow$ 1:1) to afford product **T6** as a white solid in a yield of 89.4% (1.46 g, 763 μmol).

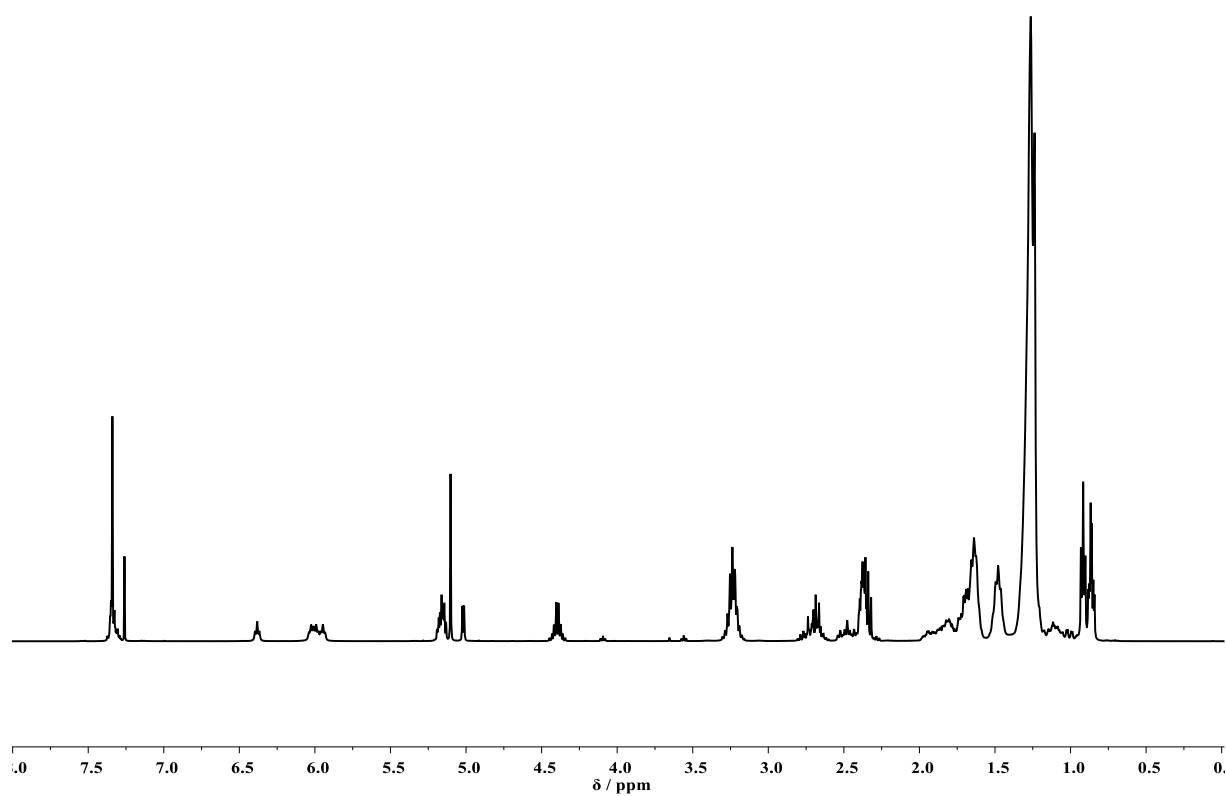
IR (ATR): ν / cm^{-1} = 3302.5 v(w), 2922.1 (s), 2851.9 (m), 2364.7 (vw), 2354.7 (vw), 2324.5 (vw), 1738.1 (s), 1655.8 (vs), 1555.9 (w), 1465.9 (w), 1365.9 (w), 1237.3 (s), 1207.8 (s), 1164.7 (vs), 1144.9 (vs), 1006.8 (vw), 697.6 (w), 653.2 (w), 568.5 (vw), 457.0 (vw), 389.9 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.28 (m, 5 H, CH_{Ar}^1), 6.38 (t, J = 5.7 Hz, 1 H, NH^2), 6.09 – 5.88 (m, 3 H, NH^2), 5.22 – 5.12 (m, 3 H, CH^3), 5.10 (s, 2 H, CH_2^4), 5.02 (d, J = 4.6 Hz, 1 H, CH^5), 4.47 – 4.32 (m, 2 H, CH_2^6), 3.32 – 3.14 (m, 8 H, CH^7), 2.85 – 2.59 (m, 4 H, CH_2^8), 2.58 – 2.27 (m, 10 H, CH_2^9), 1.99 – 1.57 (m, 22 H, CH^{10} , CH_2^{11}), 1.55 – 1.40 (m, 8 H, CH_2^{12}), 1.36 – 1.03 (m, 80 H, CH_2^{11}), 0.92 (t, J = 5.8 Hz, 6 H, CH_3^{13}), 0.89 – 0.80 (m, 6 H, CH_3^{14}).

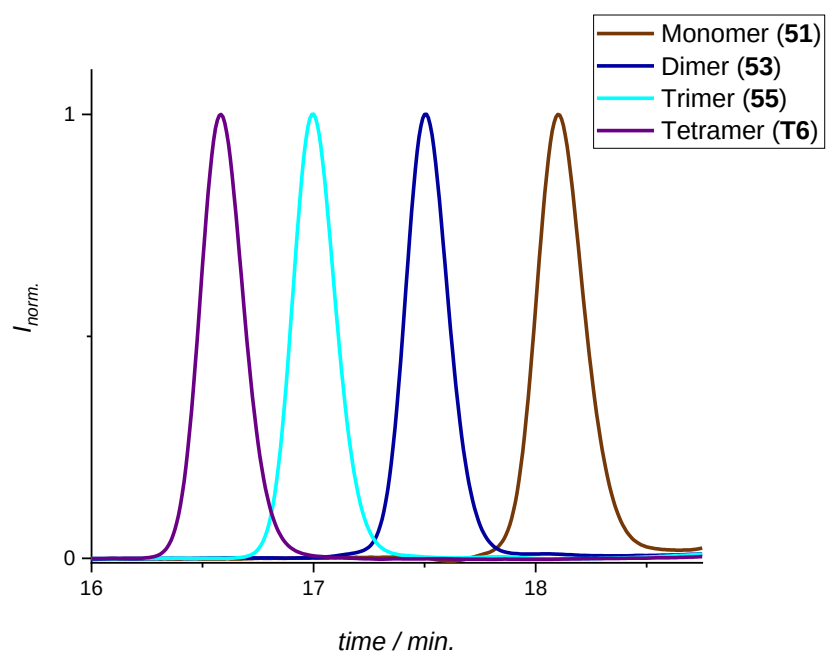
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.77, 172.65, 172.64, 172.59, 171.24, 170.35, 169.98, 169.74, 169.35, 136.24, 128.66, 128.28, 77.73, 74.73, 74.06, 72.76, 66.19, 56.94, 40.98, 40.10, 39.44, 39.34, 39.32, 39.26, 34.44, 34.41, 32.03, 31.94, 31.86, 29.74, 29.71, 29.68, 29.61, 29.59, 29.52, 29.49, 29.48, 29.35, 29.23, 29.13, 27.41, 26.96, 26.19, 26.12, 26.00, 25.11, 25.09, 25.08, 25.06, 24.89, 24.67, 23.26, 22.81, 22.74, 21.91, 14.23, 14.21.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.86 – -85.51 (m, 3 F, CF_3^{15}), -117.86 – -118.51 (m, 2 F, CF_2^{16}), -125.81 – -126.56 (m, 2 F, CF_2^{16}), -126.89 – -127.43 (m, 2 F, CF_2^{16}), -127.81 – -128.18 (m, 2 F, CF_2^{16}), -130.22 – -130.82 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

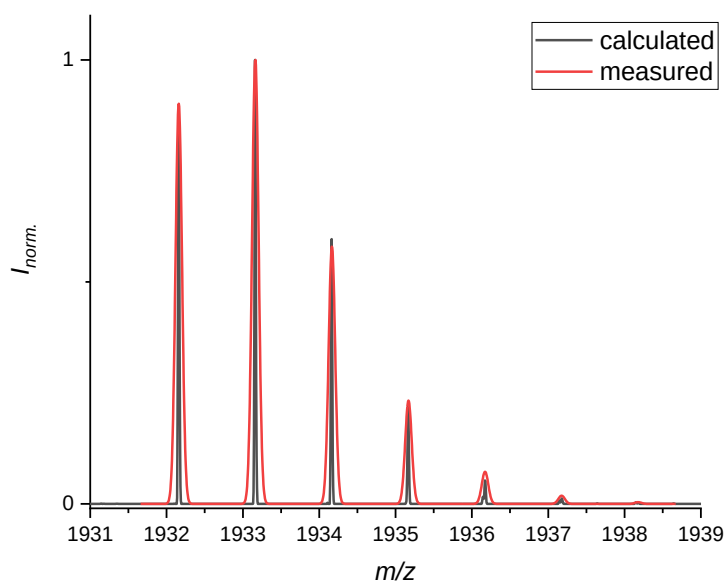
ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{99}^{1}\text{H}_{161}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_{13}$, 1932.1592; found, 1932.1591 Δ = 0.1 mmu.



Supplementary Figure 75: ^1H -NMR of compound T6 measured in CDCl_3 .



Supplementary Figure 76: SEC traces of the intermediated in the synthesis after each P3CR of product T6



Supplementary Figure 77: High resolution ESI-MS measurement of T6. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

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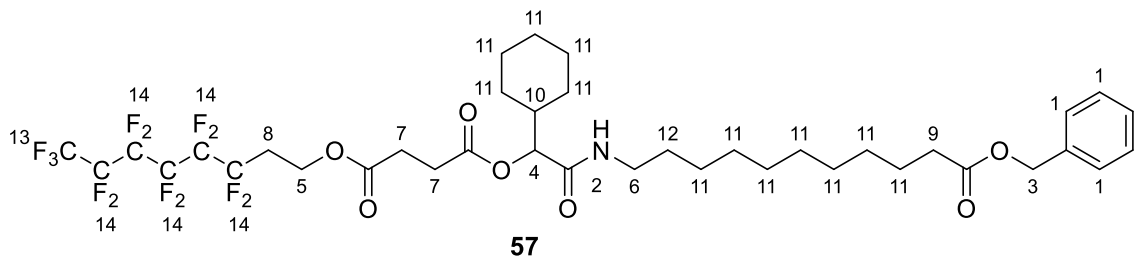
matching mass 1933.15486
cutoff 0.50000: 0 solutions (14 peaks)
cutoff 0.25000: 0 solutions (53 peaks)
cutoff 0.12500: 0 solutions (114 peaks)
cutoff 0.06250: 0 solutions (191 peaks)
cutoff 0.03125: 1 solutions (298 peaks)
1933.15486 ≈ 463.021500 + 395.339950 + 323.246050 + 297.230400 + 339.277350 + 91.054780 (sides Dodecanal,
Cyclohexancarboxaldehyde, 3-Methylbutanal, Octanal; error -23.98483)
Press ENTER to quit ...

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Supplementary Figure 78: Screenshot of the automated read-out of T6, sodium trifluoroacetate was used as additive during the measurement.

1.3.4.4 Synthesis of tetramer T7

Passerini reaction



In a 50 mL round bottom flask, 300 mg **TAG1** (646 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 117 μL cyclohexanecarboxaldehyde **14j** (109 mg, 969 μmol , 1.50 eq.) and 292 mg of the monomer **M1** (969 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 6 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 $\rightarrow$ 5:1) to yield the passerini product **57** as a pale highly viscous oil. (489 mg, 557 μmol , 86.2%).

R_f = 0.77 in cyclohexane / ethyl acetate (2:1).

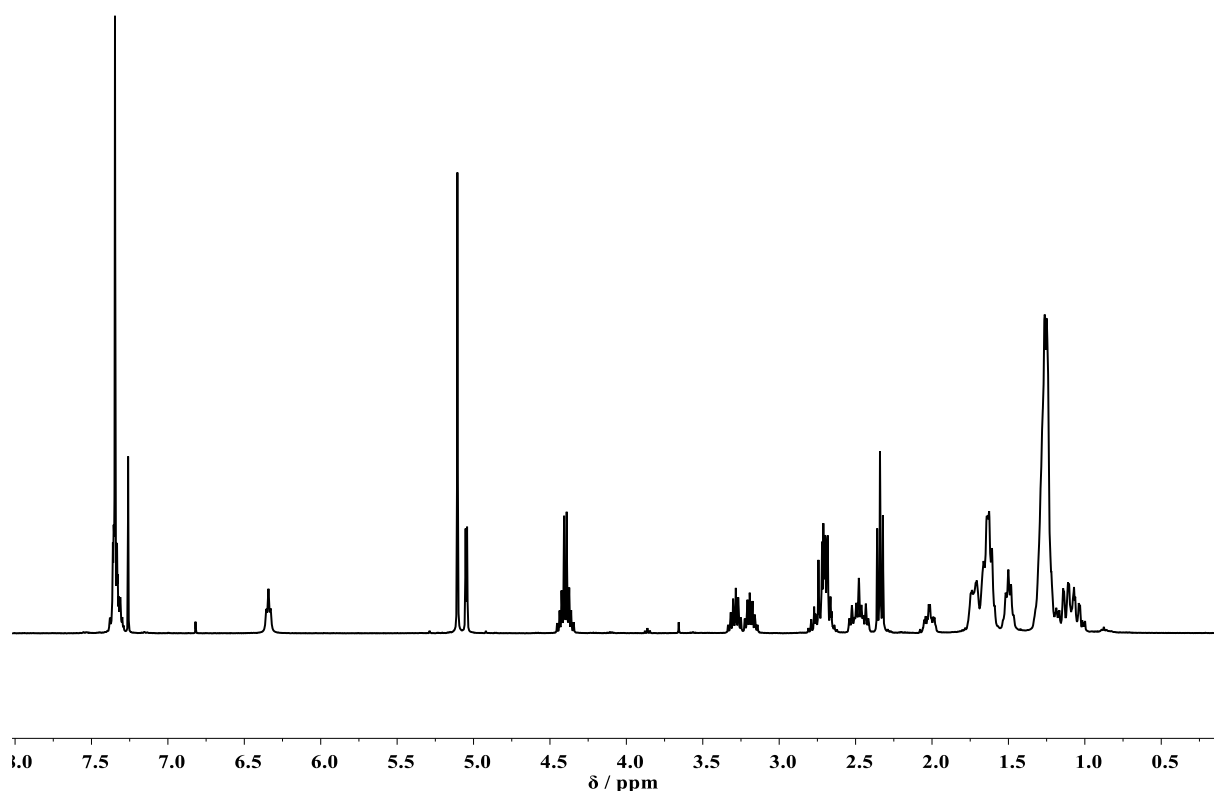
IR (ATR): ν / cm^{-1} = 2927.3 (m), 2854.9 (w), 1737.0 (vs), 1656.6 (m), 1534.7 (w), 1453.1 (w), 1359.5 (w), 1234.2 (vs), 1144.0 (vs), 1082.6 (s), 1002.9 (m), 842.2 (w), 808.9 (w), 733.0 (m), 697.3 (s), 651.4 (m), 566.0 (m).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.30 (m, 5 H, CH_{Ar}^1), 6.34 (t, J = 5.7 Hz, 1 H, NH^2), 5.11 (s, 2 H, CH_2^3), 5.05 (d, J = 3.9 Hz, 1 H, CH^4), 4.47 – 4.33 (m, 2 H, CH_2^5), 3.35 – 3.13 (m, 2 H, CH_2^6), 2.83 – 2.62 (m, 4 H, CH_2^7), 2.56 – 2.40 (m, 2 H, CH_2^8), 2.34 (t, J = 7.6 Hz, 2 H, CH_2^9), 2.08 – 1.96 (m, 1 H, CH^{10}), 1.79 – 1.58 (m, 8 H, CH_2^{11}), 1.55 – 1.47 (m, 2 H, CH_2^{12}), 1.35 – 0.96 (m, 16 H, CH_2^{11}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.69, 171.24, 169.03, 136.26, 128.66, 128.28, 78.44, 66.19, 56.96, 39.88, 39.41, 34.45, 30.57, 29.59, 29.55, 29.48, 29.35, 29.24, 29.17, 29.14, 27.04, 26.98, 26.18, 26.16, 26.04, 25.07.

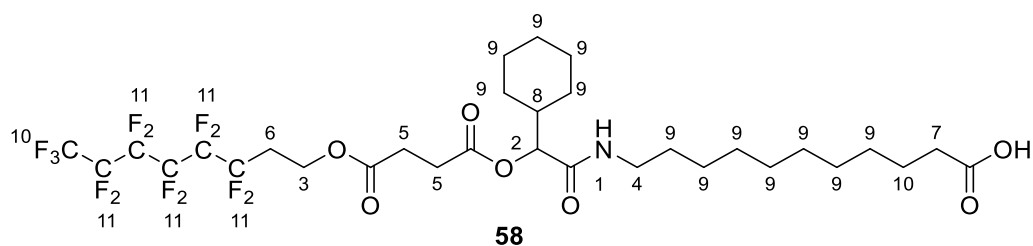
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.01 – -86.07 (m, 3 F, CF_3^{13}), -117.1 – -118.64 (m, 2 F, CF_2^{14}), -126.05 – -126.37 (m, 2 F, CF_2^{14}), -127.08 – -127.35 (m, 2 F, CF_2^{14}), -127.75 – -128.08 (m, 2 F, CF_2^{14}), -130.35 – -130.63 (m, 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{13} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$]⁺ calculated for $^{12}\text{C}_{38}^{1}\text{H}_{48}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 878.3296; found, 878.3271, Δ = 2.5 mmu.



Supplementary Figure 79: ^1H -NMR of compound **57** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 419 mg of **57** (478 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 83.8 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **58** was obtained as a pale highly viscous oil in a yield of 98.7% (372 mg, 472 μmol).

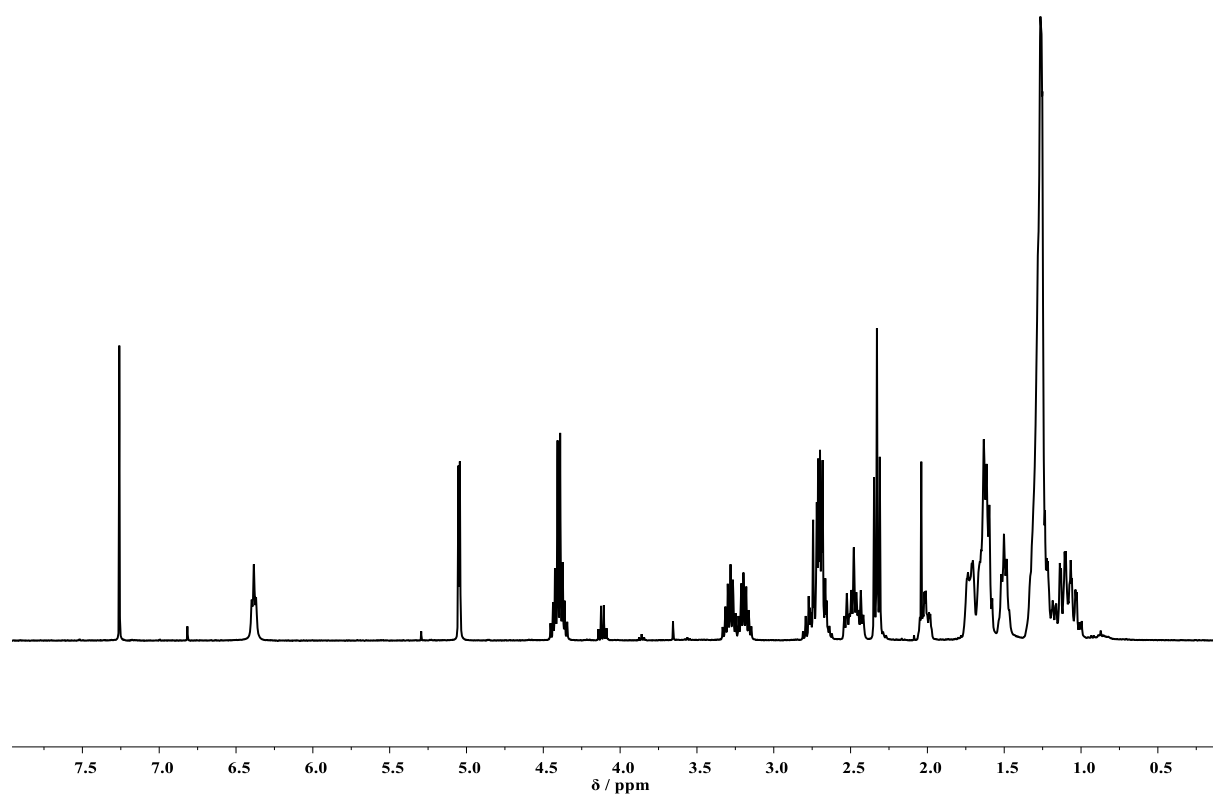
IR (ATR): ν/cm^{-1} = 2927.4 (m), 2855.3 (w), 1737.9 (s), 1650.1 (m), 1541.7 (w), 1451.4 (w), 1362.1 (w), 1233.6 (vs), 1192.2 (vs), 1143.8 (vs), 1082.9 (m), 1003.7 (w), 842.5 (w), 808.9 (w), 732.4 (w), 697.6 (m), 651.3 (w), 566.3 (w), 531.4 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.38 (t, J = 5.8 Hz, 1 H, NH^1), 5.05 (d, J = 3.9 Hz, 1 H, CH^2), 4.49 – 4.32 (m, 2 H, CH_2^3), 3.38 – 3.12 (m, 2 H, CH_2^4), 2.84 – 2.62 (m, 4 H, CH_2^5), 2.57 – 2.40 (m, 2 H, CH_2^6), 2.33 (t, J = 7.5 Hz, 2 H, CH_2^7), 2.11 – 1.94 (m, 1 H, CH^8), 1.78 – 1.68 (m, 2 H, CH_2^9), 1.68 – 1.54 (m, 4 H, $\text{CH}_2^{9,10}$), 1.56 – 1.43 (m, 2 H, CH_2^9), 1.37 – 0.96 (m, 18 H, CH_2^9).

^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 179.59, 173.49, 172.03, 169.93, 79.19, 57.73, 40.61, 40.18, 34.78, 31.34, 30.22, 30.09, 29.98, 29.96, 29.94, 29.90, 29.83, 27.80, 27.67, 26.93, 26.91, 26.78, 25.54.

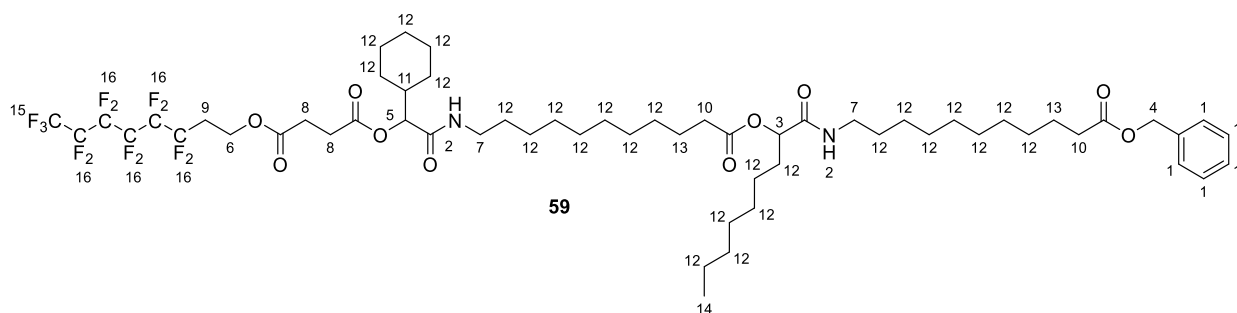
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.12 (t, J = 9.9 Hz, 3 F, CF_3^{10}), -117.58 – -118.68 (m, 2 F, CF_2^{11}), -125.95 – -126.43 (m, 2 F, CF_2^{11}), -127.08 – -127.31 (m, 2 F, CF_2^{11}), -127.70 – -128.07 (m, 2 F, CF_2^{11}), -130.32 – -131.42 (m, 2 F, CF_2^{11}). Total integral of CF_2 region normalized with respect to the CF_3^{10} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{31}\text{H}_{42}\text{O}_7\text{N}^{19}\text{F}_{13}$, 788.2826; found, 788.2803, Δ = 2.3 mmu.



Supplementary Figure 80: ^1H -NMR of compound 58 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 338 mg of **58** (429 μ mol, 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 101 μ L octanal **14i** (109 mg, 644 μ mol, 1.50 eq.) and 194 mg of the monomer **M1** (644 μ mol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 6 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 $\rightarrow$ 5:1) to yield the passerini product **59** as a pale highly viscous oil. (420 mg, 344 μ mol, 80.2%).

R_f = 0.50 in cyclohexane / ethyl acetate (2:1).

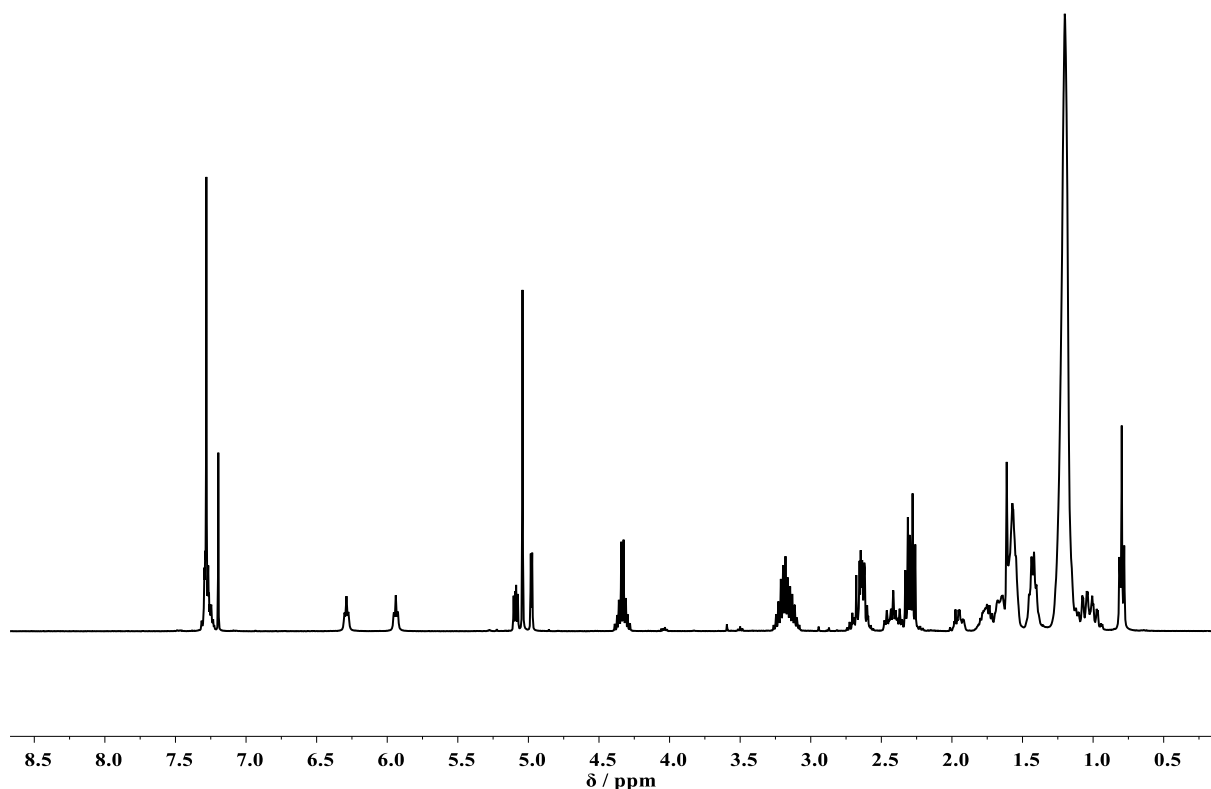
IR (ATR): ν / cm^{-1} = 3293.3 (vw), 2918.1 (s), 2851.0 (m), 1736.5 (vs), 1678.6 (m), 1651.2 (s), 1532.6 (m), 1466.9 (w), 1362.3 (w), 1235.6 (vs), 1143.9 (vs), 1082.2 (s), 1005.7 (m), 843.0 (w), 808.4 (w), 733.5 (m), 697.4 (s), 651.3 (w), 567.1 (vw), 531.6 (vw), 445.8 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.28 (m, 5 H, CH_{Ar}^1), 6.35 (t, J = 5.8 Hz, 1 H, NH^2), 6.00 (t, J = 5.9 Hz, 1 H, NH^2), 5.18 – 5.13 (m, 1 H, CH^3), 5.10 (s, 2 H, CH_2^4), 5.04 (d, J = 3.9 Hz, 1 H, CH^5), 4.48 – 4.33 (m, 2 H, CH_2^6), 3.33 – 3.15 (m, 4 H, CH_2^7), 2.79 – 2.64 (m, 4 H, CH_2^8), 2.54 – 2.41 (m, 2 H, CH_2^9), 2.41 – 2.31 (m, 4 H, CH_2^{10}), 2.08 – 1.96 (m, 1 H, CH^{11}), 1.90 – 1.57 (m, 12 H, CH_2^{12}), 1.55 – 1.43 (m, 4 H, CH_2^{13}), 1.36 – 0.99 (m, 38 H, CH_2^{12}), 0.91 – 0.82 (m, 3 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.69, 172.57, 171.23, 169.97, 169.04, 136.25, 128.66, 128.28, 78.43, 74.05, 66.20, 56.95, 39.87, 39.38, 39.32, 34.45, 32.04, 31.86, 30.57, 29.69, 29.61, 29.58, 29.55, 29.49, 29.48, 29.35, 29.34, 29.24, 29.23, 29.17, 29.13, 27.04, 26.97, 26.96, 26.17, 26.15, 26.03, 25.09, 25.07, 24.88, 22.74, 14.19.

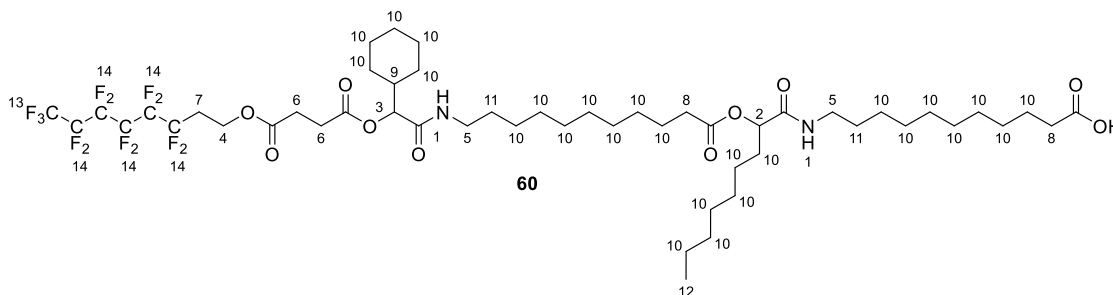
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.01 – -85.18 (m, 3 F, CF_3^{15}), -117.85 – -118.19 (m, 2 F, CF_2^{16}), -126.01 – -126.38 (m, 2 F, CF_2^{16}), -127.05 – -127.36 (m, 2 F, CF_2^{16}), -127.74 – -128.06 (m, 2 F, CF_2^{16}), -130.32 – -130.63 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{58}^{1}\text{H}_{85}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1217.6069; found, 1217.6050, Δ = 1.9 mmu.



Supplementary Figure 81: ^1H -NMR of compound **59** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 333 mg of **59** (273 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 66.6 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **60** was obtained as a pale highly viscous oil in a yield of 74.4% (230 mg, 203 μmol).

IR (ATR): ν/cm^{-1} = 2917.1 (s), 2849.7 (m), 1738.4 (vs), 1655.0 (m), 1552.6 (m), 1467.3 (w), 1364.4 (w), 1234.4 (vs), 1190.7 (vs), 1143.9 (vs), 1091.8 (s), 1007.4 (w), 843.1 (vw), 809.9 (vw), 732.7 (w), 697.9 (w), 651.6 (w), 619.5 (w), 531.3 (vw), 445.6 (vw), 388.9 (vw).

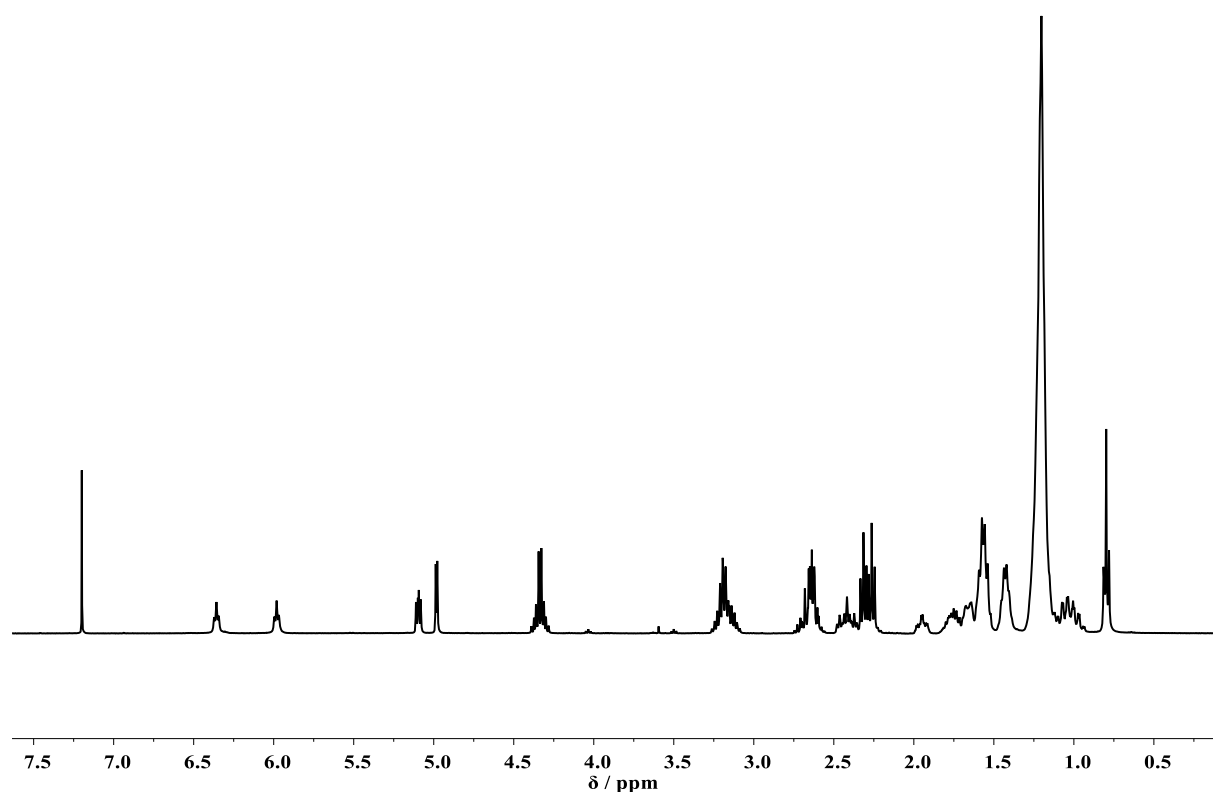
^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.42 (t, J = 5.8 Hz, 1 H, NH^1), 6.04 (t, J = 5.8 Hz, 1 H, NH^1), 5.19 – 5.12 (m, 1 H, CH^2), 5.04 (d, J = 3.9 Hz, 1 H, CH^3), 4.49 – 4.33 (m, 2 H, CH_2^4), 3.34 – 3.13 (m, 4

H, CH₂⁵), 2.83 – 2.62 (m, 4 H, CH₂⁶), 2.55 – 2.27 (m, 6 H, CH₂^{8,7}), 2.06 – 1.96 (m, 1 H, CH⁹), 1.91 – 1.55 (m, 12 H, CH₂¹⁰), 1.54 – 1.42 (m, 4 H, CH₂¹¹), 1.38 – 0.98 (m, 38 H, CH₂¹⁰), 0.89 – 0.83 (m, 3 H, CH₃¹²).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 178.71, 173.51, 173.37, 172.06, 170.86, 170.01, 79.18, 74.84, 57.73, 40.61, 40.22, 40.07, 35.22, 34.79, 32.77, 32.62, 31.57, 31.35, 31.13, 30.38, 30.34, 30.29, 30.27, 30.23, 30.13, 30.09, 30.01, 29.98, 29.93, 29.90, 29.87, 27.82, 27.74, 27.66, 26.93, 26.91, 26.78, 25.87, 25.64, 23.49.

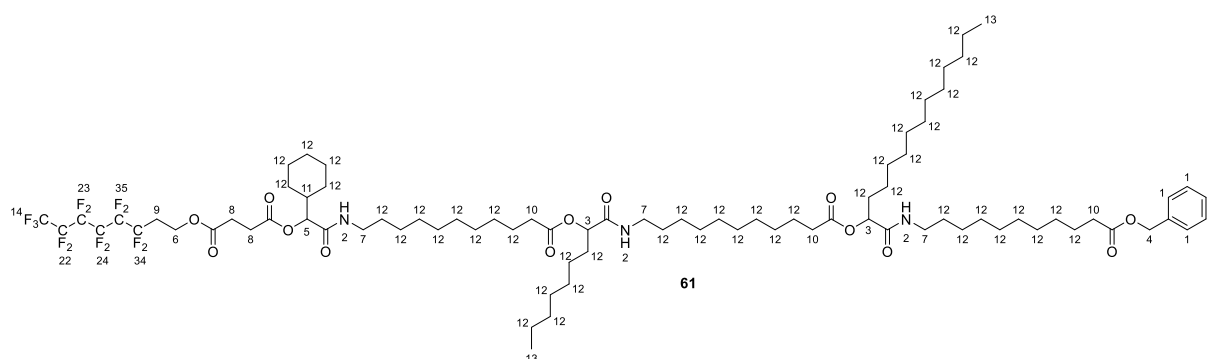
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.11 (t, J = 10.0 Hz, 3 F, CF₃¹³), -117.41 – -118.41 (m, 2 F, CF₂¹⁴), -125.94 – -126.53 (m, 2 F, CF₂¹⁴), -126.87 – -127.33 (m, 2 F, CF₂¹⁴), -127.67 – -128.39 (m, 2 F, CF₂¹⁴), -130.26 – -130.98 (m, 2 F, CF₂¹⁴). Total integral of CF₂ region normalized with respect to the CF₃¹³ group = 10.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₅₁¹H₇₉¹⁶O₁₀¹⁴N₂¹⁹F₁₃, 1127.5600; found, 1127.5581, Δ = 1.9 mmu.



Supplementary Figure 82: ¹H-NMR of compound 60 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 252 mg of **60** (224 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 79.7 μL tridecanal **14d** (66.5 mg, 335 μmol , 1.50 eq.) and 101 mg of the monomer **M1** (335 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **61** as a pale highly viscous oil. (255 mg, 157 μmol , 70.1%).

R_f = 0.15 in cyclohexane / ethyl acetate (2:1).

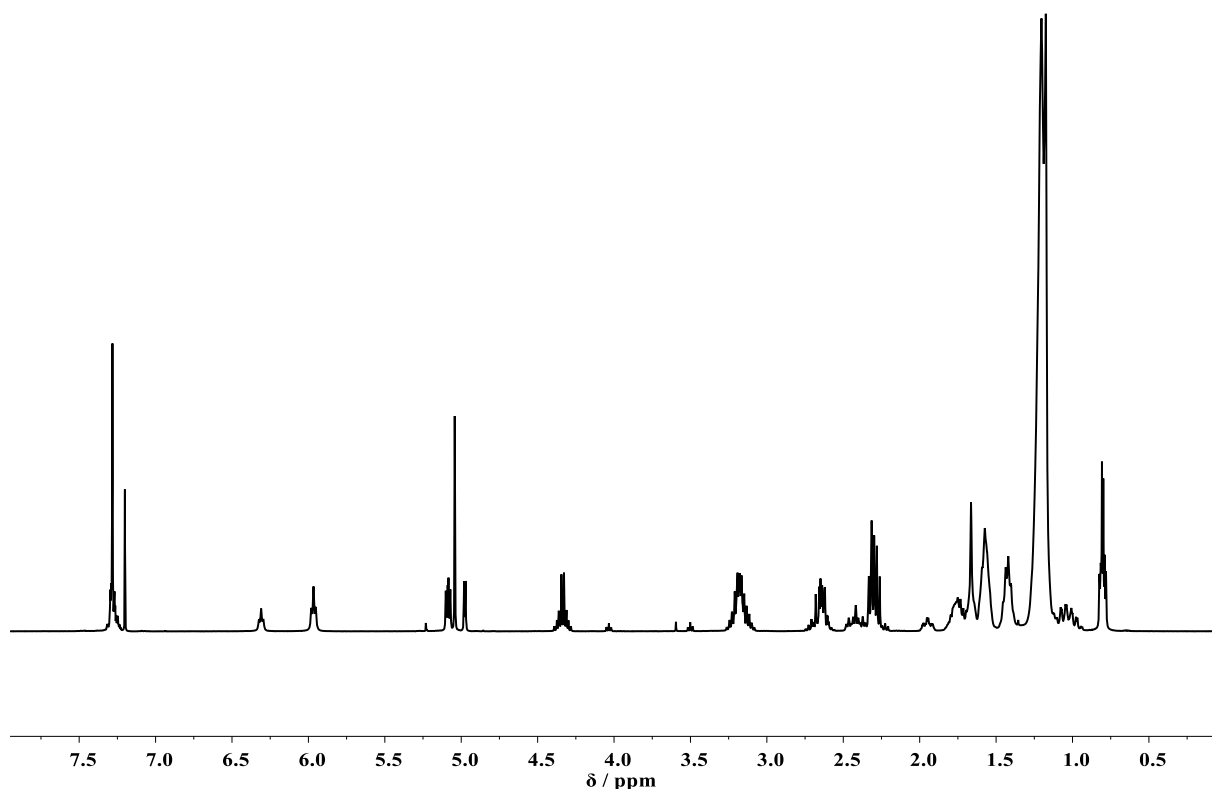
IR (ATR): ν / cm^{-1} = 3292.0 (w), 2917.4 (vs), 2850.3 (s), 1737.0 (vs), 1654.5 (vs), 1556.9 (m), 1466.7 (w), 1362.8 (w), 1236.8 (vs), 1205.0 (vs), 1144.7 (vs), 1082.6 (m), 1007.7 (w), 809.0 (vw), 696.6 (m), 652.3 (w), 566.2 (vw), 529.3 (vw), 440.8 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.36 – 7.23 (m, 5 H, CH_{Ar}^1), 6.31 (t, J = 5.8 Hz, 1 H, NH^2), 5.97 (t, J = 5.9 Hz, 2 H, NH^2), 5.17 – 5.12 (m, 2 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.98 (d, J = 3.9 Hz, 1 H, CH^5), 4.42 – 4.25 (m, 2 H, CH_2^6), 3.28 – 3.07 (m, 6 H, CH_2^7), 2.77 – 2.55 (m, 4 H, CH_2^8), 2.49 – 2.21 (m, 8 H, $\text{CH}_2^{9,10}$), 2.08 – 1.91 (m, 1 H, CH^{11}), 1.90 – 0.94 (m, 92 H, CH_2^{12}), 0.84 – 0.74 (m, 6 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 174.59, 173.47, 173.37, 172.02, 170.78, 170.76, 169.83, 137.02, 129.43, 129.05, 79.20, 74.84, 74.82, 66.96, 57.72, 40.64, 40.15, 40.09, 35.21, 32.81, 32.62, 31.55, 31.34, 31.12, 30.56, 30.54, 30.52, 30.47, 30.45, 30.37, 30.34, 30.32, 30.28, 30.25, 30.16, 30.11, 30.01, 29.99, 29.93, 29.90, 27.82, 27.74, 27.73, 26.94, 26.91, 26.80, 25.85, 25.85, 25.66, 23.58, 23.50, 15.01, 14.95.

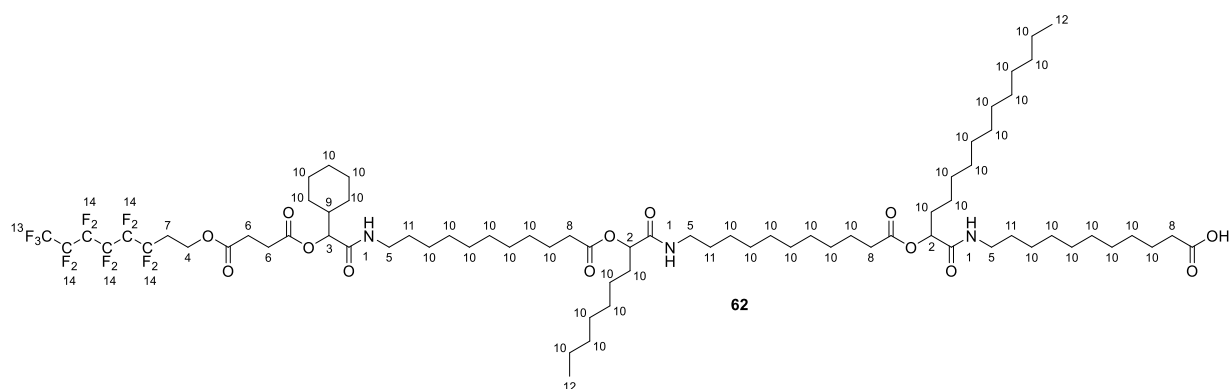
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.10 (t, J = 10.0 Hz, 3 F, CF_3^{14}), -117.98 – -118.64 (m, 2 F, CF_2^{15}), -126.01 – -126.41 (m, 2 F, CF_2^{15}), -126.96 – -127.26 (m, 2 F, CF_2^{15}), -127.76 – -128.52 (m, 2 F, CF_2^{15}), -130.27 – -130.87 (m, 2 F, CF_2^{15}) Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{83}^{1}\text{H}_{132}^{16}\text{O}_{13}^{14}\text{N}_3^9\text{F}_{13}$, 1648.9445; found, 1648.9487, Δ = 4.2 mmu.



Supplementary Figure 83: ^1H -NMR of compound **61** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask equipped with a magnetic stir bar, 175 mg of **61** (108 μmol , 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 35.2 mg (20 wt%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 1 day at room temperature under hydrogen atmosphere (3 balloons). The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **62** was obtained as a yellow highly viscous oil in a yield of 97.2% (160 mg, 105 μmol).

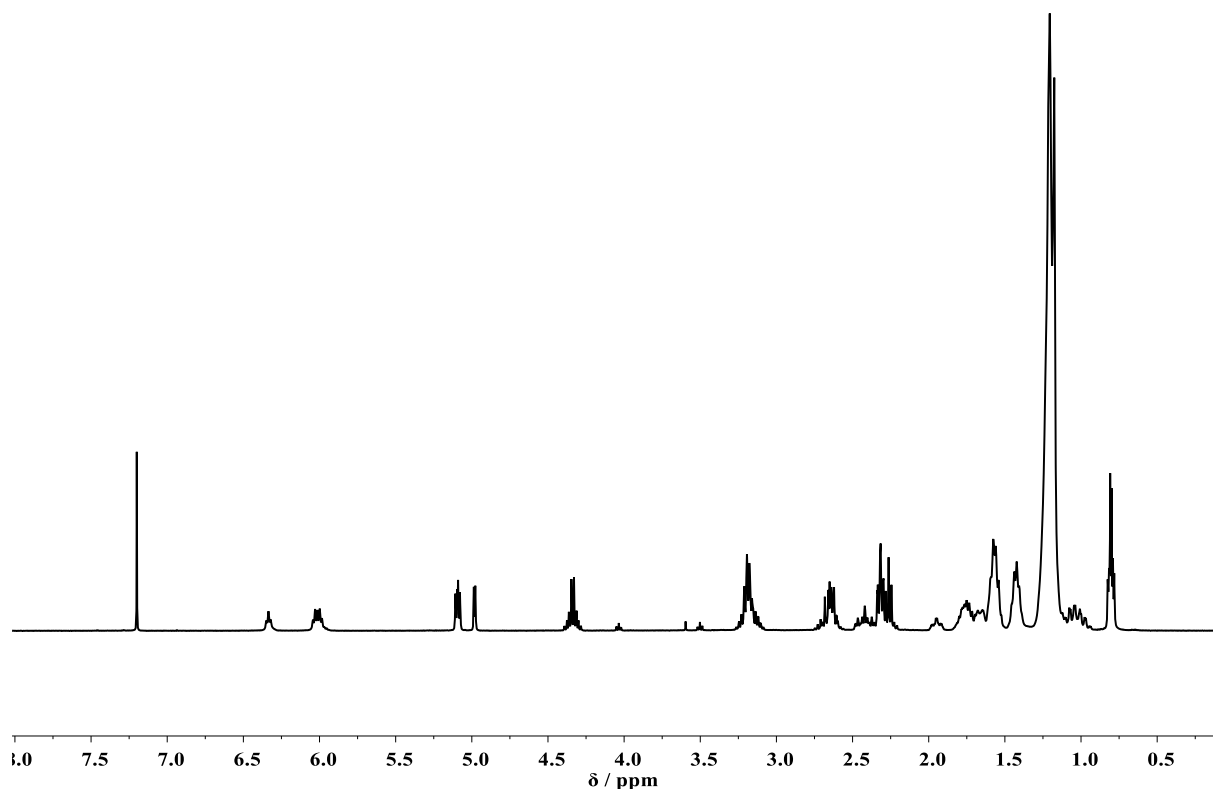
IR (ATR): ν/cm^{-1} = 3270.4 (vw), 2917.7 (m), 2850.0 (w), 2355.9 (vw), 2329.9 (vw), 1741.8 (m), 1651.7 (w), 1547.9 (w), 1466.9 (vw), 1365.0 (vw), 1238.2 (m), 1204.7 (m), 1146.3 (m), 1120.5 (w), 809.9 (vw), 721.8 (vw), 653.6 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.39 (t, J = 5.8 Hz, 1 H, NH^1), 6.15 – 6.00 (m, 2 H, NH^1), 5.21 – 5.10 (m, 2 H, CH^2), 5.04 (d, J = 3.8 Hz, 1 H, CH^3), 4.49 – 4.31 (m, 2 H, CH_2^4), 3.33 – 3.12 (m, 6 H, CH_2^5), 2.82 – 2.65 (m, 4 H, CH_2^6), 2.57 – 2.26 (m, 8 H, $\text{CH}_2^{7,8}$), 2.06 – 1.96 (m, 1 H, CH^9), 1.90 – 1.56 (m, 14 H, CH_2^{10}), 1.54 – 1.43 (m, 6 H, CH_2^{11}), 1.43 – 1.03 (m, 72 H, CH_2^{10}), 0.95 – 0.80 (m, 6 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 177.15, 172.73, 172.70, 172.63, 171.27, 170.19, 170.10, 169.18, 78.42, 74.10, 74.06, 56.97, 39.87, 39.42, 39.39, 39.30, 34.46, 34.45, 33.95, 32.05, 32.01, 31.86, 30.80, 30.58, 30.37, 29.79, 29.78, 29.68, 29.62, 29.57, 29.54, 29.49, 29.44, 29.39, 29.34, 29.27, 29.22, 29.17, 29.14, 29.10, 27.05, 26.97, 26.89, 26.17, 26.15, 26.03, 25.12, 25.08, 24.89, 22.82, 22.74, 14.24, 14.19.

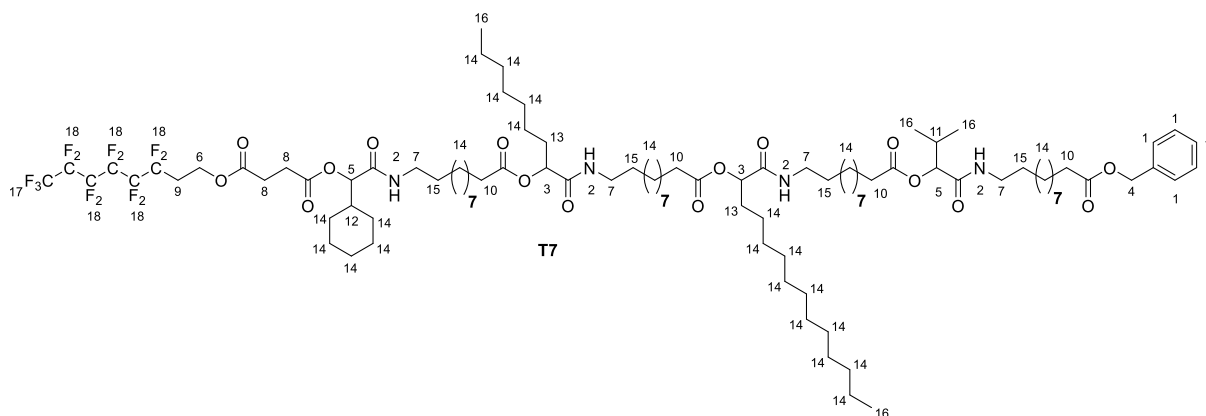
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -83.45 – -86.27 (m, 3 F, CF_3^{13}), -117.14 – -118.77 (m, 2 F, CF_2^{14}), -125.77 – -126.36 (m, 2 F, CF_2^{14}), -126.88 – -127.40 (m, 2 F, CF_2^{14}), -127.40 – -128.01 (m, 2 F, CF_2^{14}), -130.23 – -131.00 (m, 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{13} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{76}^{1}\text{H}_{126}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_{13}$, 1536.9156; found, 1536.9133, Δ = 2.3 mmu.



Supplementary Figure 84: ^1H -NMR of compound 62 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 118 mg of **62** (77.0 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 10.5 μL isobutyraldehyde **14c** (8.30 mg, 115 μmol , 1.50 eq.) and 34.7 mg of the monomer **M1** (115 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 3 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 1:1) to yield the passerini product **T7** as a pale highly viscous oil. (45.5 mg, 23.9 μmol , 31.0%).

R_f = 0.55 in cyclohexane / ethyl acetate (3:2).

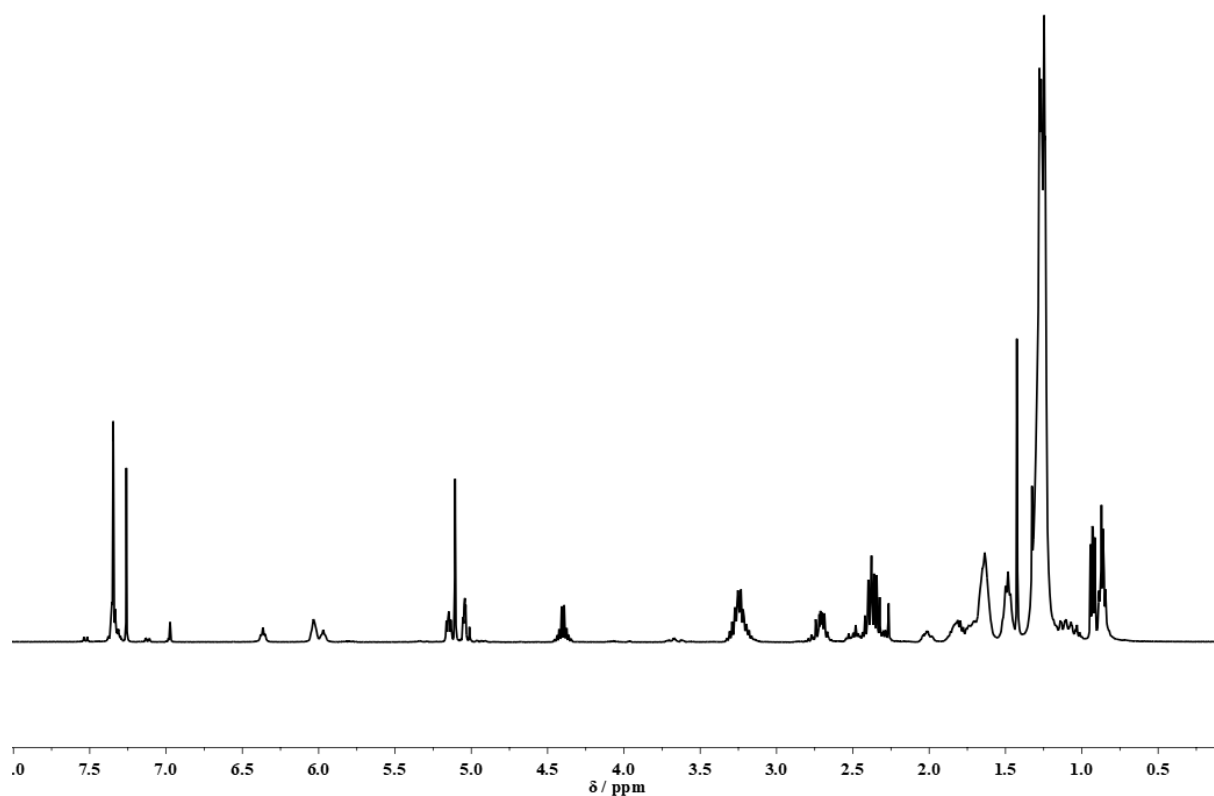
IR (ATR): ν / cm^{-1} = 3292.9 (vw), 2920.8 (m), 2851.5 (m), 1737.1 (m), 1655.5 (m), 1555.5 (w), 1465.7 (w), 1364.5 (vw), 1237.2 (m), 1206.0 (m), 1145.5 (m), 1008.4 (vw), 808.7 (vw), 697.2 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.42 – 7.29 (m, 5 H, CH_{Ar}^1), 6.44 – 6.30 (m, 1 H, NH^2), 6.11 – 5.92 (m, 3 H, NH^2), 5.19 – 5.09 (m, 2 H, CH^3), 5.11 (s, 2 H, CH_2^4), 5.08 – 5.02 (m, 2 H, CH^5), 4.49 – 4.34 (m, 2 H, CH_2^6), 3.37 – 3.15 (m, 8 H, CH_2^7), 2.82 – 2.63 (m, 4 H, CH_2^8), 2.57 – 2.44 (m, 2 H, CH_2^9), 2.44 – 2.24 (m, 9 H, CH^{10} , CH_2^{11}), 2.10 – 1.96 (m, 1 H, CH^{12}), 1.90 – 1.57 (m, 20 H, CH_2^{13} , CH_2^{14}), 1.55 – 1.44 (m, 8 H, CH_2^{15}), 1.37 – 1.02 (m, 80, CH_2^{14}), 0.97 – 0.82 (m, 12 H, CH_3^{16}).

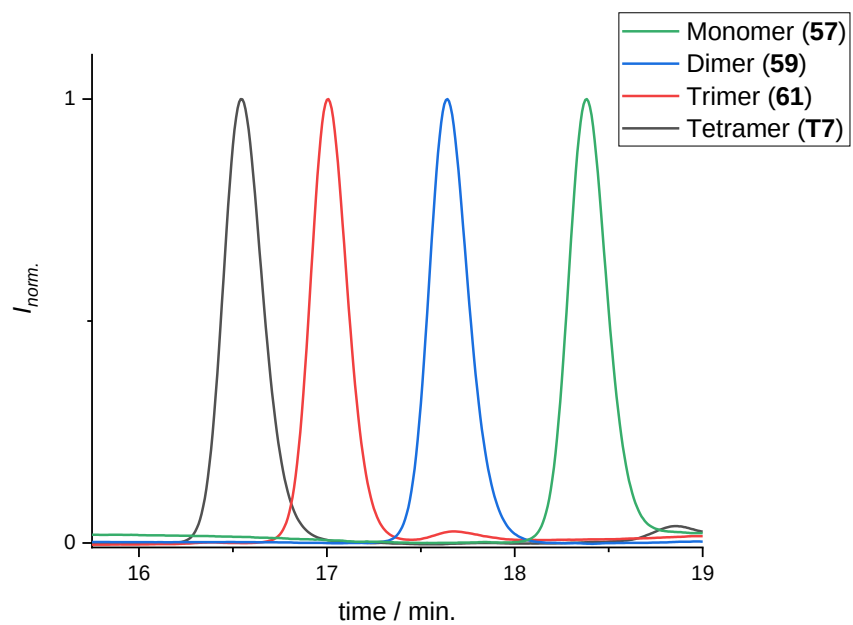
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.83, 172.71, 172.71, 172.61, 171.25, 170.01, 169.40, 169.06, 136.24, 128.67, 128.29, 125.65, 78.42, 78.04, 74.05, 74.03, 66.20, 56.95, 39.87, 39.38, 39.31, 39.31, 34.44, 34.42, 32.05, 31.86, 31.57, 30.65, 30.44, 30.31, 29.83, 29.80, 29.78, 29.76, 29.71, 29.68, 29.61, 29.59, 29.57, 29.52, 29.50, 29.49, 29.38, 29.35, 29.33, 29.24, 29.17, 29.13, 27.03, 26.97, 26.17, 26.14, 26.03, 25.14, 25.09, 25.07, 24.91, 24.90, 22.82, 22.74, 18.92, 17.08, 14.26, 14.20.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -83.70 – -85.90 (m, 3 F, CF_3^{17}), -117.79 – -118.30 (m, 2 F, CF_2^{18}), -125.87 – -126.56 (m, 2 F, CF_2^{18}), -127.01 – -127.46 (m, 2 F, CF_2^{18}), -127.81 – -128.10 (m, 2 F, CF_2^{18}), -130.33 – -130.97 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 10.

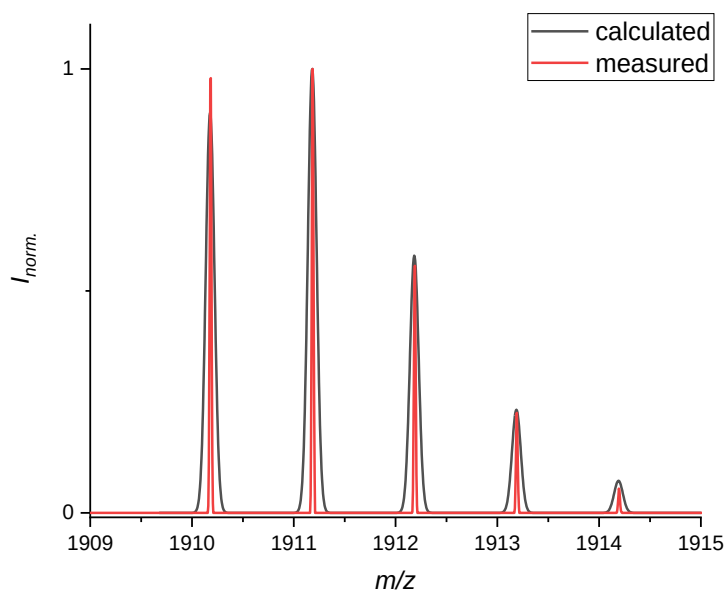
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{99}^{1}\text{H}_{161}^{16}\text{O}_{16}^{14}\text{N}_4^9\text{F}_{13}$, 1910.1773; found, 1910.1826, Δ = 5.3 mmu.



Supplementary Figure 85: ^1H -NMR of compound T7 measured in CDCl_3 .



Supplementary Figure 86: SEC traces of the intermediates after each P3CR in the synthesis of product T7



Supplementary Figure 87: High resolution ESI-MS measurement of T7. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

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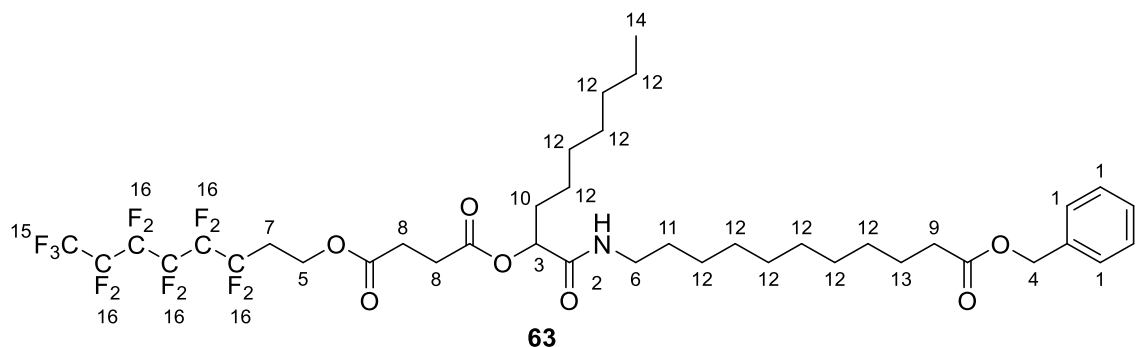
matching mass 1910.18541
cutoff 0.50000: 0 solutions (8 peaks)
cutoff 0.25000: 0 solutions (19 peaks)
cutoff 0.12500: 0 solutions (41 peaks)
cutoff 0.06250: 0 solutions (76 peaks)
cutoff 0.03125: 0 solutions (138 peaks)
cutoff 0.01562: 0 solutions (238 peaks)
cutoff 0.00781: 1 solutions (368 peaks)
1910.18541 = 447.026590 + 323.246050 + 339.277350 + 409.355600 + 283.214750 + 107.049690 (sides Cyclohexancarboxaldehyde,
Octanal, Tridecanal, Isobutyraldehyde; error -1.01538)
Press ENTER to quit ...

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Supplementary Figure 88: Screenshot of the automated read-out of T7, sodium trifluoroacetate was used as additive during the measurement.

1.3.4.5 Synthesis of tetramer T8

Passerini reaction



In a 50.0 mL round bottom flasks, 300 mg **TAG1** (646 μmol , 1.00 eq.) were dissolved in 2.00 mL DCM and 151 μL octanal **14i** (109 mg, 969 μmol , 1.50 eq.) and 292 mg of monomer **M1** (969 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (hexane / ethyl acetate 6:1 $\rightarrow$ 5:1) to afford product **63** as a yellow oil in a yield of 97.1% (560 mg, 627 μmol).

R_f = 0.40 in cyclohexane / ethyl acetate (3:1).

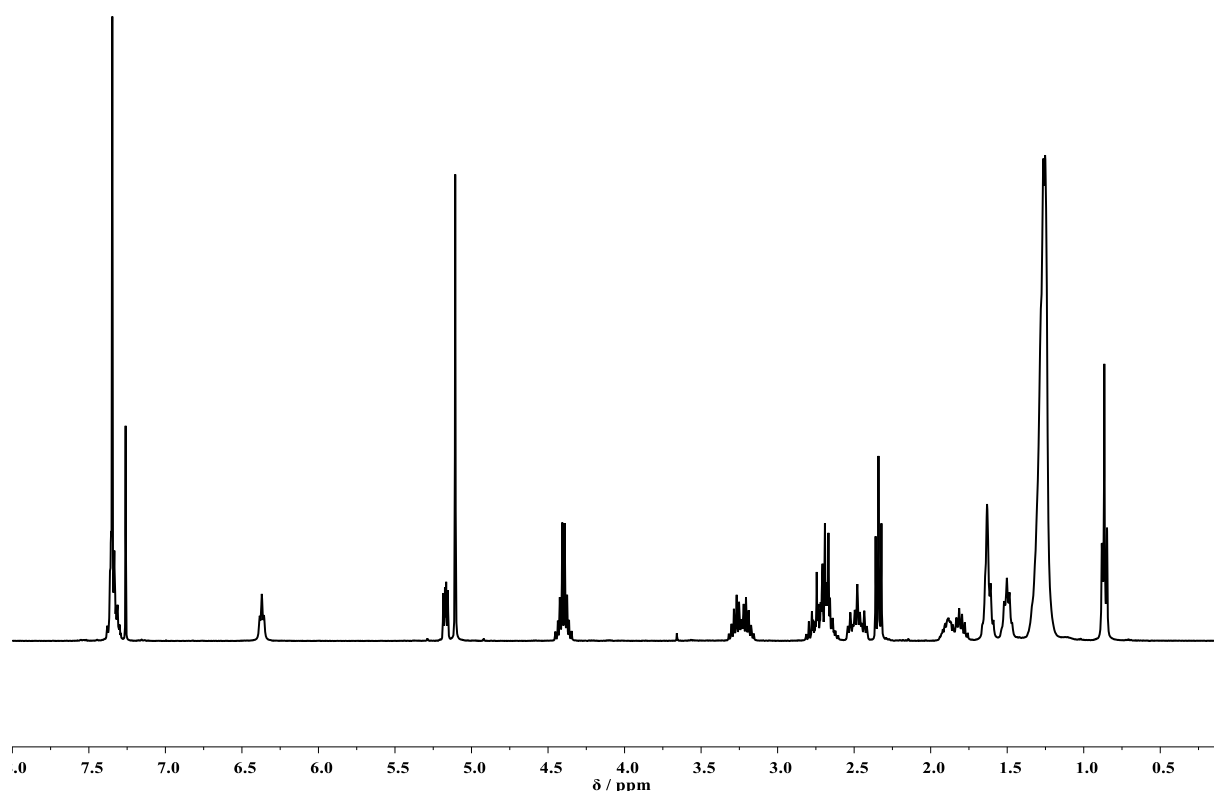
IR (ATR): ν / cm^{-1} = 2927.0 (m), 2855.8 (w), 1737.6 (s), 1659.3 (w), 1536.1 (w), 1456.7 (vw), 1359.7 (w), 1234.7 (vs), 1190.6 (vs), 1144.1 (vs), 1081.2 (m), 1003.3 (w), 841.5 (vw), 808.5 (vw), 732.4 (w), 696.9 (m), 650.7 (w), 565.4 (vw), 530.2 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.28 (m, 5 H, CH_{Ar}^1), 6.37 (t, J = 5.8 Hz, 1 H, NH^2), 5.17 (q, J = 7.6, 4.3 Hz, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 4.47 – 4.33 (m, 2 H, CH_2^5), 3.34 – 3.14 (m, 2 H, CH_2^6), 2.85 – 2.60 (m, 2 H, CH_2^7), 2.55 – 2.40 (m, 4 H, CH_2^8), 2.34 (t, J = 7.6 Hz, 2 H, CH_2^9), 1.95 – 1.74 (m, 2 H, CH_2^{10}), 1.69 – 1.58 (m, 4 H, $\text{CH}_2^{11,12}$), 1.55 – 1.43 (m, 2 H, CH_2^{13}), 1.38 – 1.21 (m, 20 H, CH_2^{12}), 0.86 (t, J = 7.0 Hz, 3 H, CH_3^{14})

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.64, 171.24, 169.71, 136.27, 128.67, 128.29, 76.84, 66.20, 56.96, 39.47, 34.45, 31.94, 31.88, 30.80, 30.59, 30.37, 29.60, 29.54, 29.50, 29.39, 29.35, 29.33, 29.25, 29.23, 29.15, 26.98, 25.07, 25.02, 22.74.

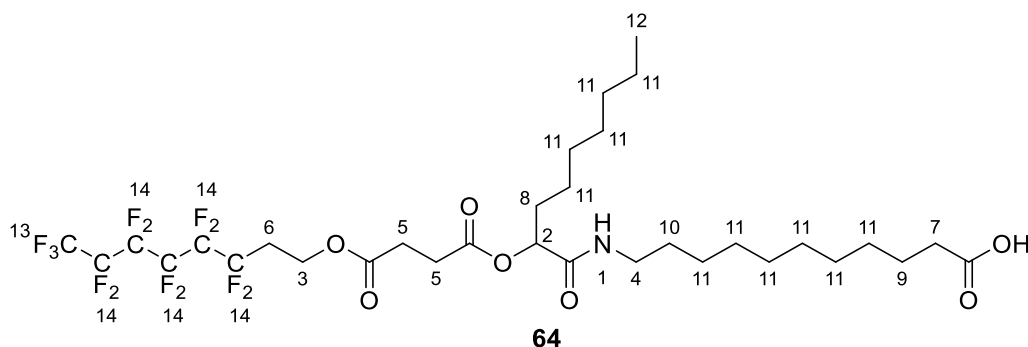
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -83.86 – -86.34 (m, 3 F, CF_3^{15}), -117.65 – -118.28 (m, 2 F, CF_2^{16}), -125.99 – -126.38 (m, 2 F, CF_2^{16}), -127.05 – -127.38 (m, 2 F, CF_2^{16}), -127.71 – -128.09 (m, 2 F, CF_2^{16}), -130.31 – -130.71 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{39}^{1}\text{H}_{52}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 894.3609; found, 894.3597, Δ = 1.2 mmu.



Supplementary Figure 89: ^1H -NMR of compound **63** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask equipped with a magnetic stir bar, 457 mg of the **63** (511 μmol , 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 91.4 mg (20 wt%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 5 days at room temperature under hydrogen atmosphere (3 balloons). The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **64** was obtained as a yellow highly viscous oil in a yield of 94.3%. (388 mg, 482 μmol).

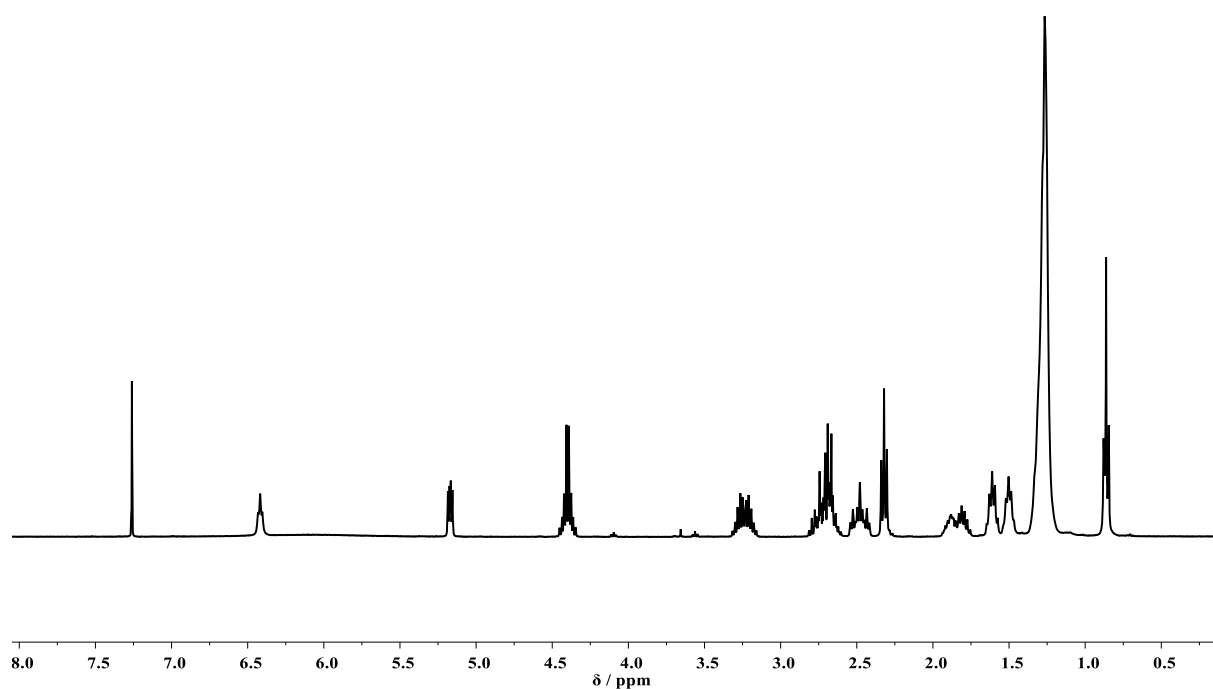
IR (ATR): ν / cm^{-1} = 3296.2 (w), 2923.7 (s), 2851.9 (m), 1742.9 (vs), 1696.1 (s), 1653.5 (s), 1560.3 (w), 1468.4 (w), 1411.5 (w), 1358.8 (m), 1233.0 (vs), 1189.4 (vs), 1141.7 (vs), 1082.3 (vs), 1009.6 (w), 938.0 (w), 841.3 (w), 698.3 (vs), 651.3 (s), 567.5 (w), 528.7 (w), 437.6 (w), 389.0 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.35 (t, J = 5.9 Hz, 1 H, NH^1), 5.19 – 5.01 (m, 1 H, CH^2), 4.41 – 4.23 (m, 2 H, CH_2^3), 3.34 – 3.02 (m, 2 H, CH_2^4), 2.77 – 2.54 (m, 4 H, CH_2^5), 2.49 – 2.35 (m, 2 H, CH_2^6), 2.30 – 2.23 (m, 2 H, CH_2^7), 1.90 – 1.67 (m, 2 H, CH_2^8), 1.61 – 1.49 (m, 2 H, CH_2^9), 1.49 – 1.39 (m, 2 H, CH_2^{10}), 1.34 – 1.14 (m, 22 H, CH_2^{11}), 0.80 (t, J = 6.7 Hz, 3 H, CH_3^{12}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.43, 172.02, 170.60, 116.31, 75.50, 57.72, 40.23, 34.77, 32.67, 32.63, 31.56, 31.34, 31.13, 30.20, 30.10, 30.08, 29.98, 29.90, 29.83, 27.66, 25.77, 25.55, 23.49, 14.93.

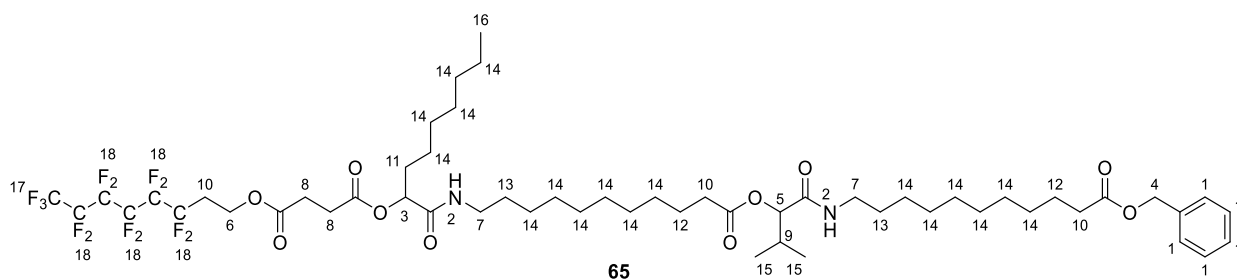
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.01 – -85.29 (m, 3 F, CF_3^{13}), -117.90 – -118.20 (m, 2 F, CF_2^{14}), -125.96 – -126.43 (m, 2 F, CF_2^{14}), -126.99 – -127.42 (m, 2 F, CF_2^{14}), -127.82 – -128.11 (m, 2 F, CF_2^{14}), -130.29 – -130.76 (m, 2 F, CF_2^{14}). Total integral of CF_2 region normalized with respect to the CF_3^{13} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{32}\text{H}_{46}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_{13}$, 804.3139; found, 804.3115, Δ = 2.4 mmu.



Supplementary Figure 90: ^1H -NMR of compound 64 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 413 mg of **64** (514 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 70.4 μL isobutyraldehyde **14c** (55.6 mg, 772 μmol , 1.50 eq.) and 233 mg of monomer **M1** (772 mmol, 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 5:1 $\rightarrow$ 1:1) to afford product **65** as a pale highly viscous oil in a yield of 96.5% (555 mg, 496 μmol).

R_f = 0.20 in cyclohexane / ethyl acetate (3:1).

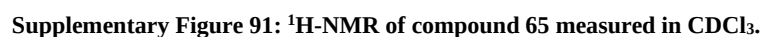
IR (ATR): ν / cm^{-1} = 3315.8 (vw), 2923.9 (m), 2852.2 (w), 1736.6 (vs), 1656.1 (vs), 1548.7 (w), 1466.1 (w), 1363.6 (w), 1236.4 (vs), 1144.2 (vs), 1009.0 (m), 841.8 (w), 809.6 (vw), 732.3 (w), 697.3 (m), 652.0 (w), 567.3 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.28 (m, 5 H, CH_{Ar}^1), 6.39 (t, J = 5.8 Hz, 1 H, NH^2), 5.94 (t, J = 5.9 Hz, 1 H, NH^2), 5.20 – 5.14 (m, 1 H, CH^3), 5.11 (s, 2 H, CH^4), 5.05 (d, J = 4.4 Hz, 1 H, CH^5), 4.46 – 4.34 (m, 2 H, CH^6), 3.36 – 3.15 (m, 4 H, CH^7), 2.83 – 2.60 (m, 4 H, CH_2^8), 2.56 – 2.24 (m, 7 H, CH^9 , CH_2^{10}), 1.97 – 1.74 (m, 2 H, CH_2^{11}), 1.72 – 1.61 (m, 4 H, CH_2^{12}), 1.55 – 1.45 (m, 4 H, CH_2^{13}), 1.38 – 1.20 (m, 34 H, CH_2^{14}), 0.95 – 0.90 (m, 6 H, CH_3^{15}), 0.89 – 0.84 (m, 3 H, CH_3^{16}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.66, 172.64, 171.24, 169.72, 169.39, 136.25, 128.66, 128.28, 78.03, 74.74, 66.20, 56.94, 39.44, 39.29, 34.45, 34.42, 31.93, 31.87, 30.65, 29.72, 29.60, 29.56, 29.54, 29.50, 29.47, 29.35, 29.33, 29.26, 29.23, 29.14, 26.97, 25.14, 25.07, 25.02, 22.74, 18.90, 17.05, 14.19.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.77 – -85.55 (m, 3 F, CF_3^{17}), -117.72 – -118.51 (m, 2 F, CF_2^{18}), -126.00 – -126.49 (m, 2 F, CF_2^{18}), -126.94 – -127.43 (m, 2 F, CF_2^{18}), -127.58 – -128.18 (m, 2 F, CF_2^{18}), -129.96 – -130.99 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{55}^{1}\text{H}_{81}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_{13}$, 1199.5576; found, 1199.5555, Δ = 2.1 mmu.



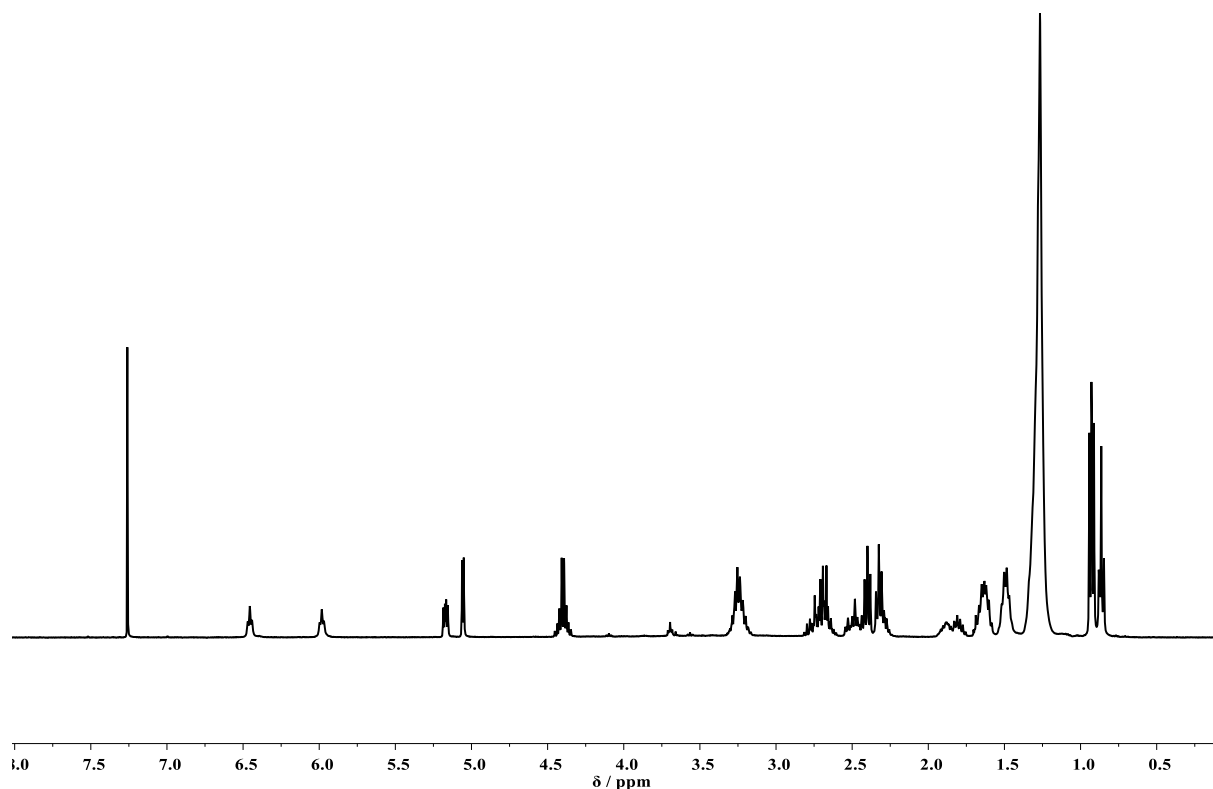
¹H NMR (400 MHz, CDCl₃): δ / ppm = 6.46 (t, *J* = 5.8 Hz, 1 H, NH¹), 5.98 (t, *J* = 5.9 Hz, 1 H, NH¹), 5.21 – 5.12 (m, 1 H, CH²), 5.06 (d, *J* = 4.4 Hz, 1 H, CH³), 4.48 – 4.32 (m, 2 H, CH²⁴), 3.34 – 3.15 (m, 4

H, CH₂⁵), 2.83 – 2.58 (m, 4 H, CH₂⁶), 2.56 – 2.20 (m, 7 H, CH⁷, CH₂⁸), 1.95 – 1.72 (m, 2 H, CH₂⁹), 1.70 – 1.55 (m, 4 H, CH₂¹⁰), 1.54 – 1.40 (m, 4 H, CH₂¹¹), 1.39 – 1.14 (m, 34 H, CH₂¹²), 0.97 – 0.90 (m, 6 H, CH₃¹³), 0.89 – 0.78 (m, 3 H, CH₃¹⁴).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 172.72, 171.32, 169.97, 169.52, 78.07, 74.73, 56.98, 39.52, 39.26, 34.43, 34.01, 31.90, 31.87, 30.62, 29.62, 29.58, 29.51, 29.41, 29.37, 29.35, 29.32, 29.29, 29.21, 29.14, 29.08, 26.97, 26.89, 25.16, 25.02, 24.88, 22.74, 18.90, 17.05, 14.18.

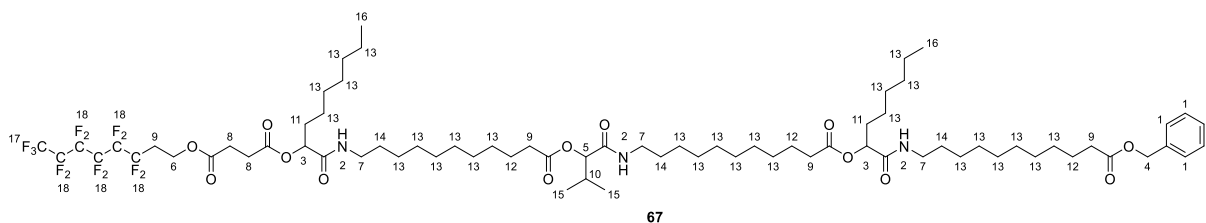
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.09 (t, J = 9.9 Hz, 3 F, CF₃¹³), -117.74 – -118.31 (m, 2 F, CF₂¹⁴), -125.91 – -126.37 (m, 2 F, CF₂¹⁴), -126.61 – -127.43 (m, 2 F, CF₂¹⁴), -127.48 – -128.13 (m, 2 F, CF₂¹⁴), -130.00 – -130.75 (m, 2 F, CF₂¹⁴). Total integral of CF₂ region normalized with respect to the CF₃¹³ group = 10.

ESI-MS [m/z]: [$M + Na$]⁺ calculated for ¹²C₄₈¹H₇₅¹⁶O₁₀¹⁴N₂¹⁹F₁₃, 1109.5106; found, 1109.5092, Δ = 1.4 mmu.



Supplementary Figure 92: ¹H-NMR of compound 66 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 274 mg of **66** (232 μmol , 1.00 eq.) was dissolved in 3.00 mL DCM and 41.9 μL heptanal **14b** (39.7 mg, 348 μmol , 1.50 eq.) and 105 mg of monomer **M1** (348 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 $\rightarrow$ 2:1) to afford product **67** as a pale highly viscous oil in a yield of 90.1% (314 mg, 209 μmol).

R_f = 0.13 in cyclohexane / ethyl acetate (2:1).

IR (ATR): ν / cm^{-1} = 3291.1 (vw), 2923.5 (s), 2852.7 (m), 1736.5 (vs), 1655.0 (vs), 1540.3 (m), 1465.1 (w), 1365.4 (w), 1235.0 (vs), 1144.9 (vs), 1005.5 (w), 842.2 (vw), 697.7 (m), 652.8 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.44 – 7.29 (m, 5 H, CH_{Ar}^1), 6.39 (t, J = 5.8 Hz, 1 H, NH^2), 6.02 (t, J = 5.9 Hz, 1 H, NH^2), 5.96 (t, J = 5.9 Hz, 1H, NH^2), 5.22 – 5.15 (m, 2 H, CH^3), 5.10 (s, 2 H, CH_2^4), 5.05 (d, J = 4.4 Hz, 1 H, CH^5), 4.49 – 4.34 (m, 2 H, CH_2^6), 3.32 – 3.14 (m, 6 H, CH_2^7), 2.83 – 2.58 (m, 4 H, CH_2^8), 2.55 – 2.23 (m, 9 H, CH^9 , CH_2^{10}), 1.96 – 1.75 (m, 4 H, CH_2^{11}), 1.75 – 1.56 (m, 8 H, CH_2^{12} , CH_2^{13}), 1.56 – 1.39 (m, 6 H, CH_2^{14}), 1.37 – 1.16 (m, 52 H, CH_2^{13}), 0.96 – 0.90 (m, 6 H, CH_3^{15}), 0.89 – 0.83 (m, 6 H, CH_2^{16}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.69, 172.66, 172.60, 171.25, 169.99, 169.74, 169.42, 136.26, 128.67, 128.29, 78.04, 74.74, 74.06, 66.20, 56.94, 39.44, 39.32, 39.28, 34.45, 34.41, 32.04, 31.93, 31.86, 31.75, 30.64, 30.57, 29.72, 29.68, 29.60, 29.58, 29.53, 29.49, 29.35, 29.32, 29.26, 29.23, 29.22, 29.13, 29.04, 26.96, 25.13, 25.09, 25.07, 25.02, 24.83, 22.73, 22.66, 18.89, 17.06, 14.17.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.09 (t, J = 9.9 Hz, 3 F, CF_3^{17}), -117.75 – -118.21 (m, 2 F, CF_2^{18}), -125.91 – -126.45 (m, 2 F, CF_2^{18}), -126.96 – -127.40 (m, 2 F, CF_2^{18}), -127.70 – -128.26 (m, 2 F, CF_2^{18}), -130.02 – -130.86 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 10.

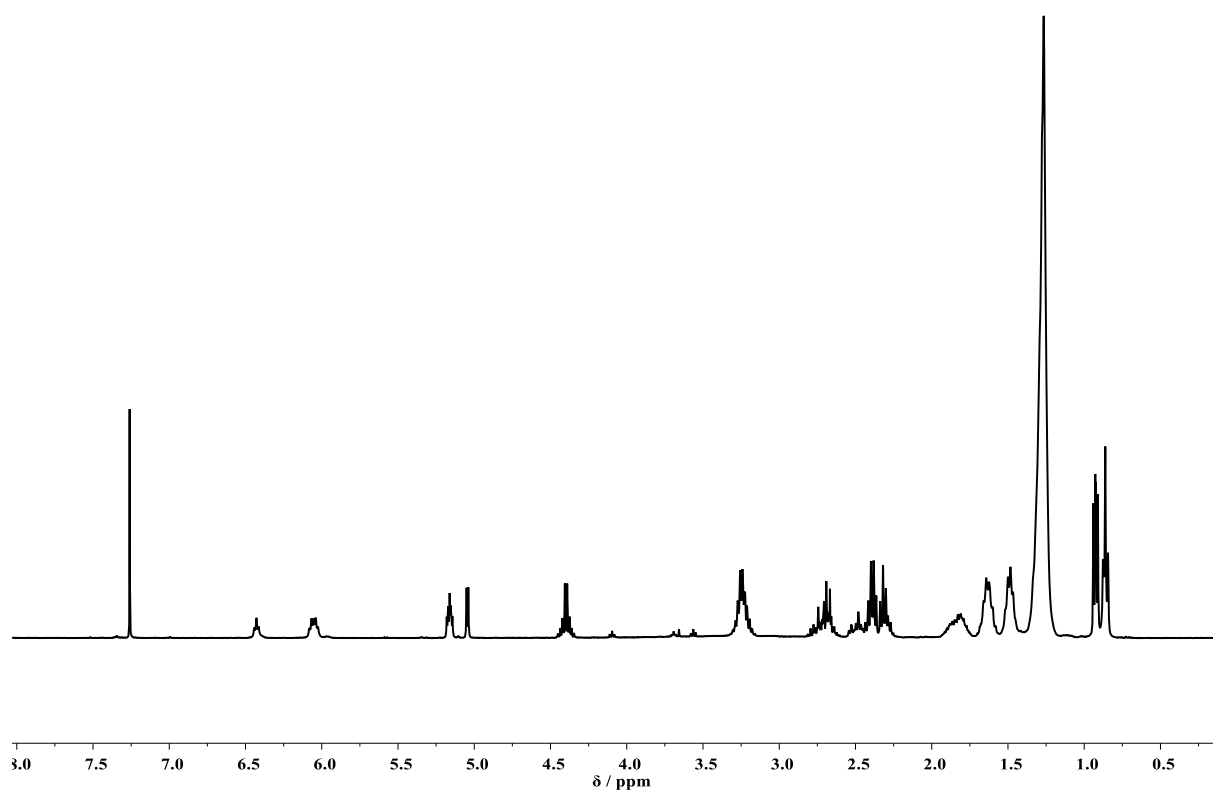
ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{74}^{1}\text{H}_{116}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_{13}$, 1524.8193; found, 1524.8176, Δ = 1.7 mmu.

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.43 (t, J = 5.8 Hz, 1 H, NH^1), 6.13 – 5.93 (m, 2 H, NH^1), 5.21– 5.12 (m, 2 H, CH_2^2), 5.04 (d, J = 4.5 Hz, 1 H, CH^3), 4.48 – 4.32 (m, 2 H, CH_2^4), 3.35 – 3.15 (m, 6 H, CH_2^5), 2.84 – 2.59 (m, 4 H, CH_2^6), 2.56 – 2.22 (m, 9 H, CH^7 , CH_2^8), 1.98 – 1.70 (m, 4 H, CH_2^9), 1.70 – 1.56 (m, 6 H, CH_2^{10}), 1.54 – 1.41 (m, 6 H, CH_2^{11}), 1.40 – 1.16 (m, 54 H, CH_2^{12}), 0.95 – 0.90 (m, 6 H, CH_3^{13}), 0.89 – 0.83 (m, 6 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 177.26, 172.80, 172.68, 172.64, 171.27, 170.10, 169.88, 169.61, 78.07, 74.73, 74.09, 56.96, 39.48, 39.35, 39.30, 34.47, 34.41, 34.07, 32.01, 31.92, 31.87, 31.75, 30.62, 29.69, 29.59, 29.55, 29.51, 29.43, 29.37, 29.34, 29.32, 29.25, 29.22, 29.14, 29.10, 29.04, 26.97, 26.96, 26.88, 25.12, 25.01, 24.94, 24.85, 22.73, 22.66, 18.88, 17.08, 14.17.

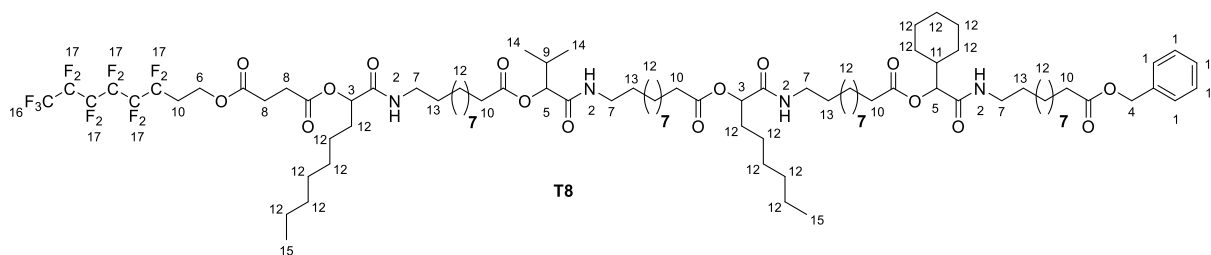
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.09 (t, J = 9.8 Hz, 3 F, CF_3^{15}), -117.60 – -118.73 (m, 2 F, CF_2^{16}), -125.73 – -126.37 (m, 2 F, CF_2^{16}), -126.86 – -127.47 (m, 2 F, CF_2^{16}), -127.73 – -128.10 (m, 2 F, CF_2^{16}), -130.03 – -130.85 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 10.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{67}\text{H}_{110}\text{O}_{13}\text{N}_3^{19}\text{F}_{13}\text{Na}$, 1434.7723; found, 1434.7705, Δ = 1.8 mmu.



Supplementary Figure 94: ^1H -NMR of compound 68 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 164 mg **68** (116 μmol , 1.00 eq.) was dissolved in 2.00 mL DCM and 21.1 μL cyclohexancarboxaldehyde **14j** (19.5 mg, 174 μmol , 1.50 eq.) and 52.5 mg of monomer **M1** (174 μmol , 1.50 eq.) were added. The mixture was stirred at room temperature for 3 days. Subsequently, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (cyclohexane / ethyl acetate 4:1 $\rightarrow$ 1:1) to afford product **T8** as a pale highly viscous oil in a yield of 75.5% (160 mg, 87.6 μmol).

R_f = 0.53 in cyclohexane / ethyl acetate (3:2).

IR (ATR): ν / cm^{-1} = 3293.48 (w), 2922.3 (s), 2851.6 (m), 1735.9 (vs), 1654.58 (vs), 1537.5 (m), 1466.3 (w), 1362.4 (w), 1236.3 (vs), 1145.2 (vs), 1009.2 (w), 809.0 (vw), 697.2 (m), 652.2 (w), 566.9 (vw), 451.0 (vw).

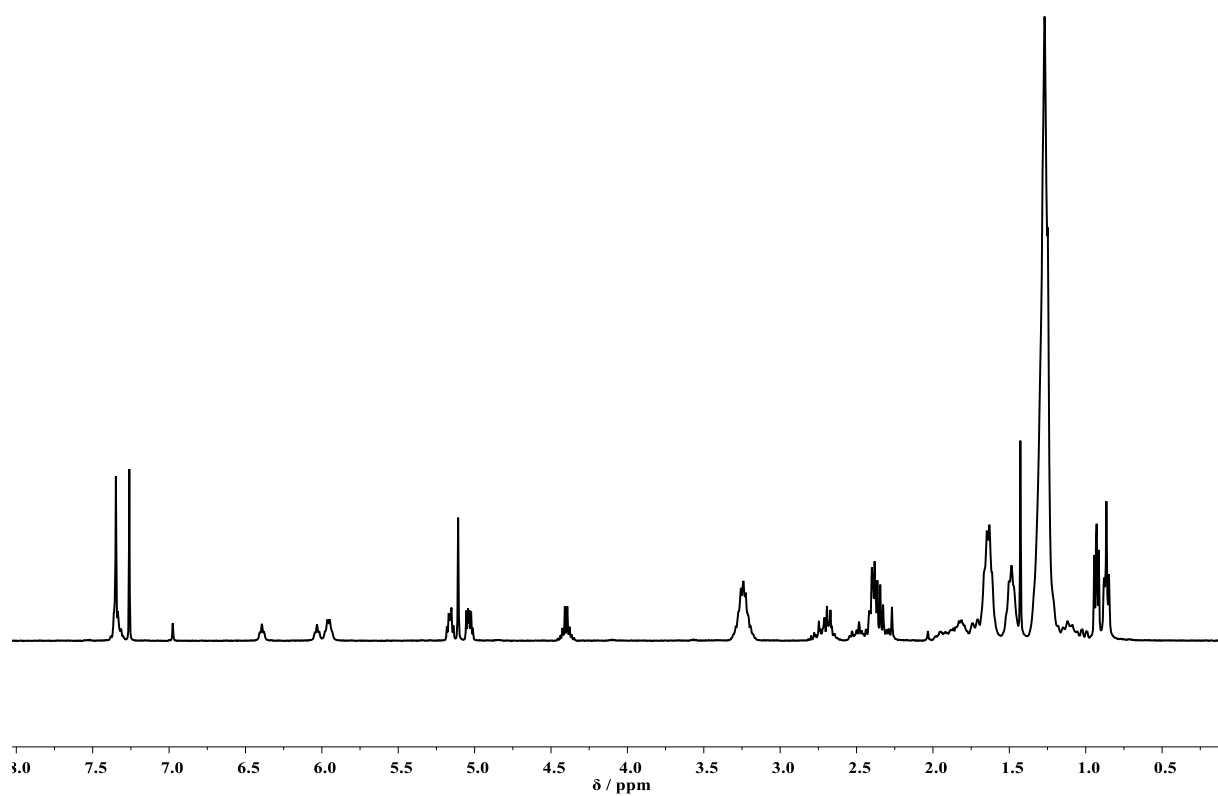
^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.30 (m, 5 H, CH_{Ar}^1), 6.39 (t, J = 5.8 Hz, 1 H, NH^2), 6.09 – 5.91 (m, 3 H, NH^2), 5.19 – 5.13 (m, 2 H, CH_2^3), 5.11 (s, 2 H, CH_2^4), 5.07 – 4.98 (m, 2 H, CH_2^5), 4.47 – 4.34 (m, 2 H, CH_2^6), 3.33 – 3.15 (m, 8 H, CH_2^7), 2.83 – 2.62 (m, 4 H, CH_2^8), 2.56 – 2.24 (m, 11 H, CH^9 , CH_2^{10}), 2.00 – 1.59 (m, 21 H, CH^{11} , CH_2^{12}), 1.54 – 1.44 (m, 8 H, CH_2^{13}), 1.38 – 1.06 (m, 68 H, CH_2^{12}), 0.97 – 0.90 (m, 6 H, CH_2^{14}), 0.90 – 0.82 (m, 6 H, CH_2^{15}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.84, 172.68, 172.62, 171.54, 171.53, 171.26, 170.00, 169.74, 169.42, 169.34, 136.26, 128.68, 128.30, 78.04, 77.75, 74.74, 74.06, 66.21, 40.11, 39.44, 39.32, 39.28, 34.46, 34.43, 32.05, 31.94, 31.87, 31.76, 30.65, 30.45, 29.85, 29.74, 29.71, 29.59, 29.54, 29.51, 29.48, 29.35, 29.33, 29.27, 29.24, 29.23, 29.14, 29.05, 27.41, 26.97, 26.21, 26.13, 26.01, 25.13, 25.10, 25.08, 25.03, 24.85, 22.74, 22.67, 18.91, 17.06, 14.19.

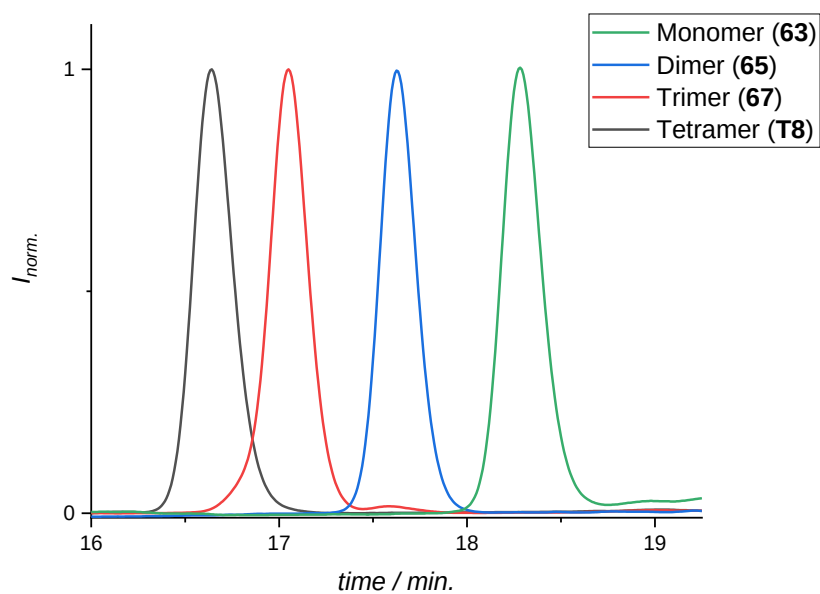
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.73 – -85.47 (m, 3 F, CF_3^{16}), -117.67 – -118.35 (m, 2 F, CF_2^{17}), -125.60 – -126.44 (m, 2 F, CF_2^{17}), -126.83 – -127.22 (m, 2 F, CF_2^{17}), -127.54 – -128.48 (m, 2 F, CF_2^{17}), -130.28 – -131.34 (m, 2 F, CF_2^{17}).

Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 10.

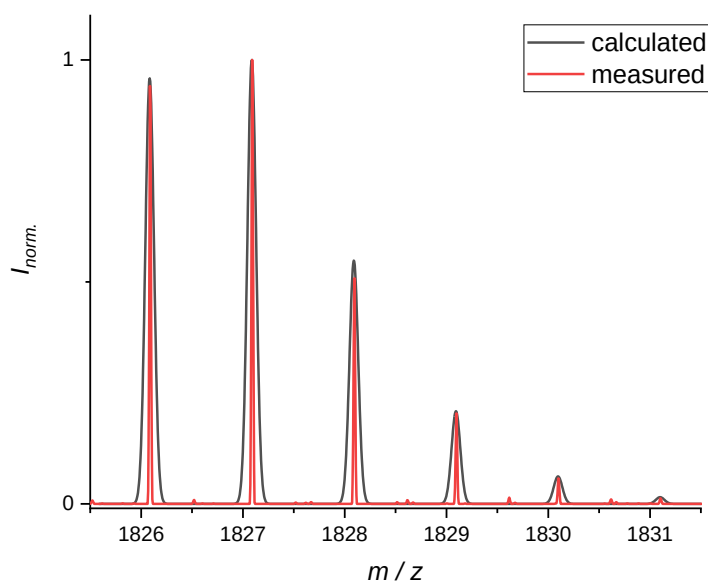
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{93}^{1}\text{H}_{149}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_{13}$, 1826.0834; found, 1826.0885
 Δ = 5.1 mmu.



Supplementary Figure 95: ^1H -NMR of compound T8 measured in CDCl_3 .



Supplementary Figure 96: SEC traces of the intermediates after each P3CR in the synthesis of product T8.



Supplementary Figure 97: High resolution ESI-MS measurement of T8. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

```

imum is 1.000000 found for mass 1827.090720
matching mass 1827.09072
cutoff 0.50000: 0 solutions (9 peaks)
cutoff 0.25000: 0 solutions (20 peaks)
cutoff 0.12500: 0 solutions (54 peaks)
cutoff 0.06250: 0 solutions (103 peaks)
cutoff 0.03125: 0 solutions (155 peaks)
cutoff 0.01562: 0 solutions (287 peaks)
cutoff 0.00781: 0 solutions (423 peaks)
cutoff 0.00391: 0 solutions (568 peaks)
cutoff 0.00195: 1 solutions (1147 peaks)
1827.09072 ≈ 447.026590 + 339.277350 + 283.214750 + 325.261700 + 323.246050 + 107.049690 (sides Octanal,
Isobutyraldehyde, Heptanal, Cyclohexancarboxaldehyde; error -2.01459)
Press ENTER to quit ...

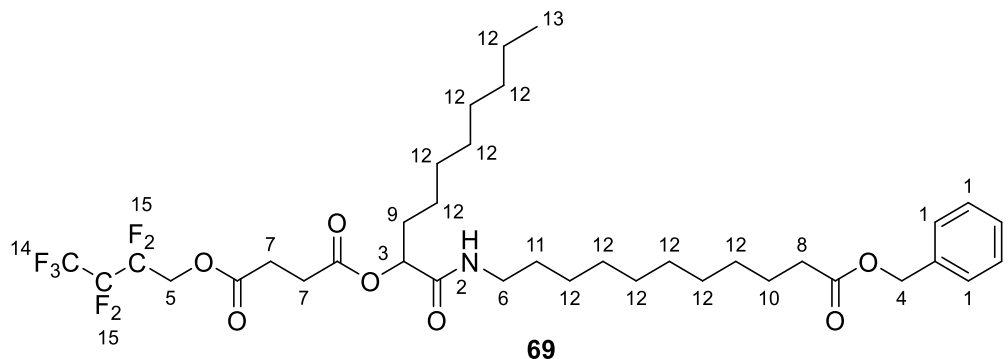
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Supplementary Figure 98: Screenshot of the automated read-out of T8.

1.3.5 Oligomer synthesis with TAG2

1.3.5.1 Synthesis of tetramer T9

Passerini reaction



In a 50 mL round bottom flask, 1.10 g of **TAG2** (3.68 mmol, 1.00 eq.) was stirred in 4.00 mL dichloromethane. Subsequently, 2.01 mL nonanal **14k** (758 mg, 5.52 mmol, 1.50 eq.) and 1.66 g of the monomer **M1** (5.52 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (9:1 → 4:1) to yield the passerini product **69** as a pale highly viscous oil (2.65 g, 3.56 mmol, 96.7%).

R_f = 0.32 in cyclohexane / ethyl acetate (3:1).

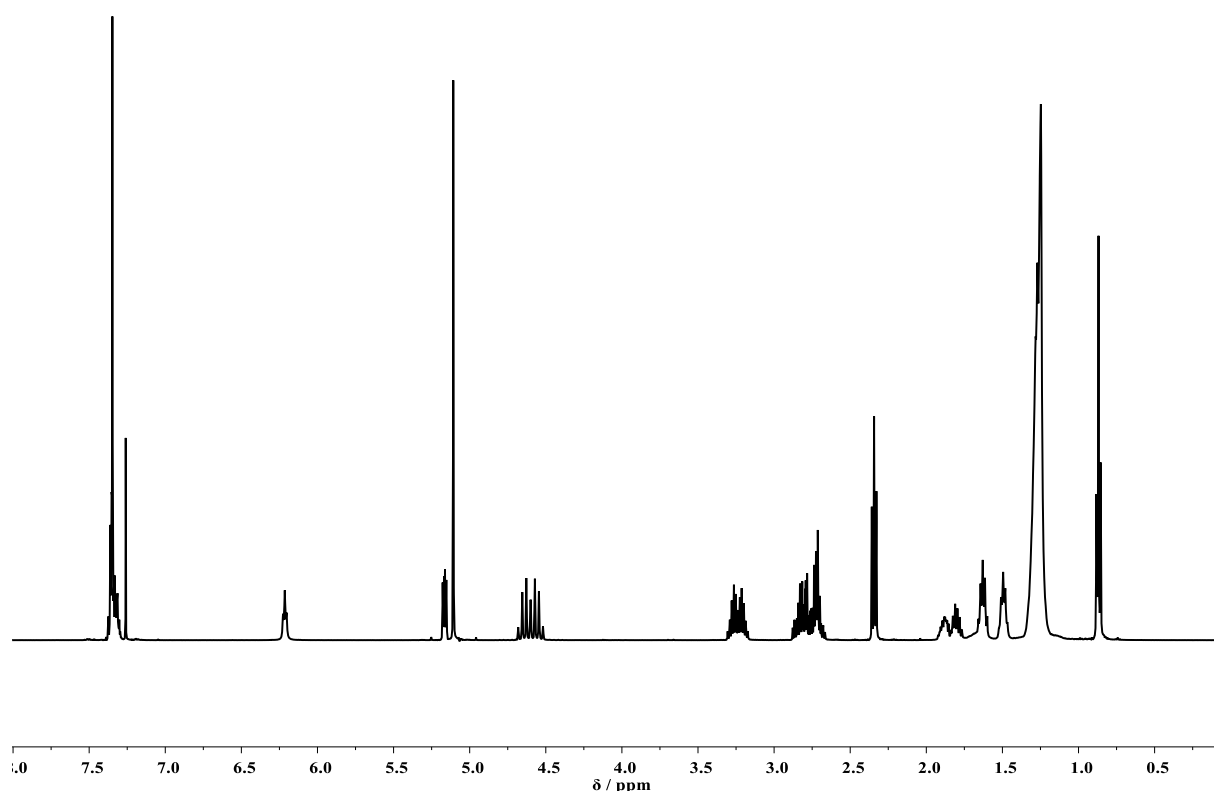
IR (ATR): ν / cm^{-1} = 3303.5 (vw), 2925.5 (m), 2854.8 (w), 1739.1 (s), 1657.5 (m), 1536.4 (w), 1456.0 (w), 1352.3 (w), 1226.4 (vs), 1144.5 (vs), 1020.1 (m), , 909.6 (w), 736.0 (m), 697.2 (m).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.42 – 7.32 (m, 5 H, CH_{Ar}^1), 6.24 (t, J = 5.8 Hz, 1 H, NH^2), 5.23 – 5.16 (m, 1 H, CH^3), 5.13 (s, 2 H, CH_2^4), 4.74 – 4.52 (m, 2 H, CH_2^5), 3.36 – 3.17 (m, 2 H, CH_2^6), 2.92 – 2.66 (m, 4 H, CH_2^7), 2.37 (t, J = 7.6 Hz, 2 H, CH_2^8), 1.96 – 1.78 (m, 2 H, CH_2^9), 1.70 – 1.61 (m, 2 H, CH_2^{10}), 1.57 – 1.47 (m, 2 H, CH_2^{11}), 1.40 – 1.21 (m, 24 H, CH_2^{12}), 0.89 (t, J = 6.9 Hz, 3 H, CH_3^{13}).

^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.70, 171.37, 170.77, 169.48, 136.14, 128.55, 128.17, 74.76, 66.07, 59.56 (t, J = 26.9 Hz), 39.32, 34.32, 31.82, 29.46, 29.42, 29.38, 29.37, 29.24, 29.21, 29.20, 29.11, 28.92, 28.66, 26.83, 24.94, 24.85, 22.64, 14.09.

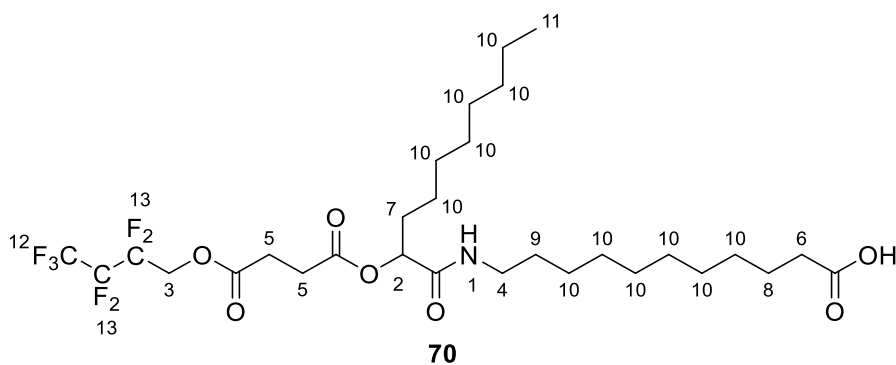
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.89 (t, J = 9.3 Hz, 3F, CF_3^{14}), -119.83 – -121.39 (m, 2 F, CF_2^{15}), -127.31 – -128.95 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{36}^{1}\text{H}_{52}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 744.3705; found, 744.3693, Δ = 1.2 mmu.



Supplementary Figure 99: ^1H -NMR of compound **69** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask, 2.08 g of **69** (3.29 mmol, 1.00 eq.) was dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Subsequently, 488 mg (20 wt.-%) palladium on activated charcoal **16** were added to the solution. The resulting mixture was purged with hydrogen gas and stirred for one day at room temperature under hydrogen atmosphere (balloon). The crude reaction mixture was filtered over celite[®] and flushed with 50 mL dichloromethane. After evaporation of the solvents and drying under reduced pressure the corresponding acid **70** was obtained as a colorless solid (2.11 g, 3.22 mol, 98.0%).

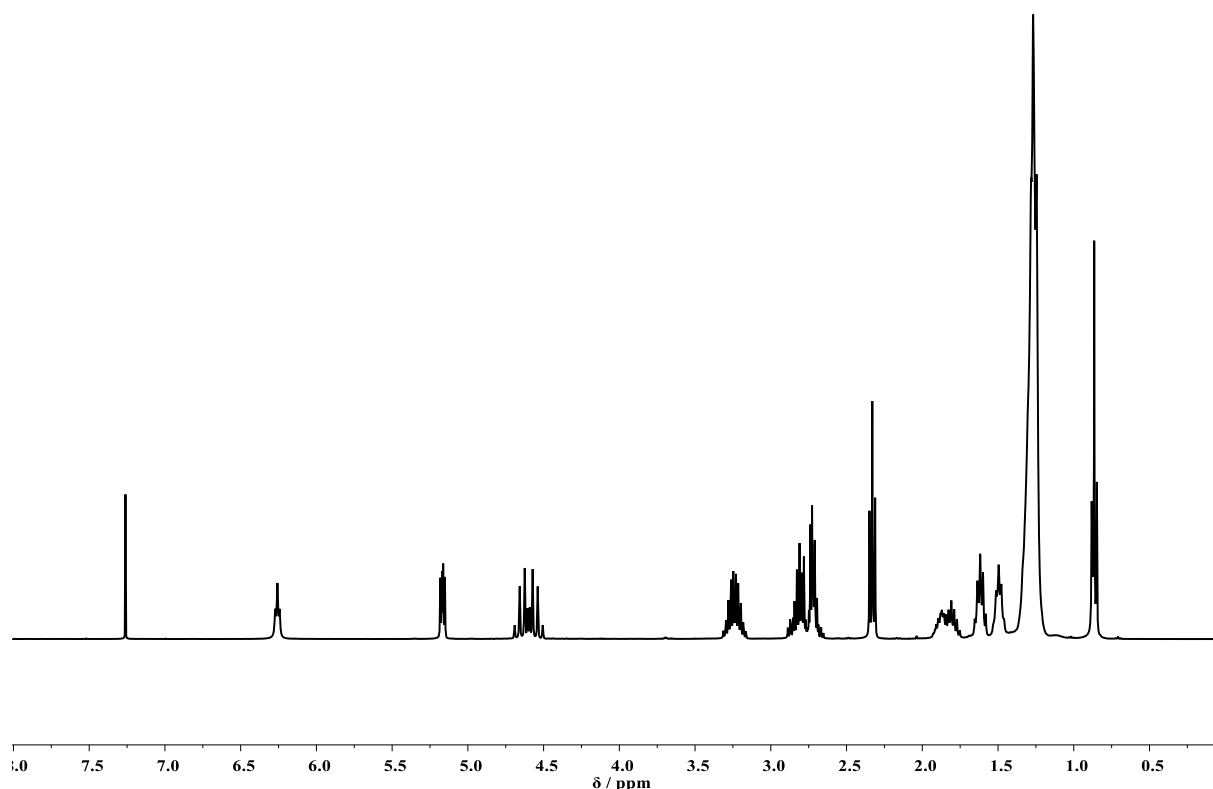
IR (ATR): ν/cm^{-1} = 3298.2 (w), 2920.6 (s), 2850.8 (s), 1744.3 (vs), 1692.7 (vs), 1651.4 (vs), 1557.3 (m), 1468.7 (w), 1412.0 (m), 1218.3 (vs), 1159.3 (vs), 1022.3 (s), 911.8 (m), 723.0 (w), 671.8 (w), 535.7 (w).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.26 (t, J = 5.8 Hz, 1H, NH^1), 5.22 – 5.09 (m, 1 H, CH^2), 4.70 – 4.49 (m, 2 H, CH_2^3), 3.34 – 3.15 (m, 2 H, CH_2^4), 2.92 – 2.64 (m, 4 H, CH_2^5), 2.33 (t, J = 7.5 Hz, 2 H, CH_2^6), 1.95 – 1.74 (m, 2 H, CH_2^7), 1.68 – 1.57 (m, 2 H, CH_2^8), 1.56 – 1.42 (m, 2 H, CH_2^9), 1.41 – 1.17 (m, 24 H, CH_2^{10}), 0.91 – 0.79 (m, 3 H, CH_3^{11}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 179.20, 171.52, 170.93, 169.77, 74.87, 59.69 (t, J = 26.8 Hz), 39.47, 34.08, 31.94, 31.92, 29.49, 29.47, 29.38, 29.35, 29.32, 29.27, 29.24, 29.10, 29.04, 28.79, 26.90, 24.97, 24.79, 22.76, 14.20.

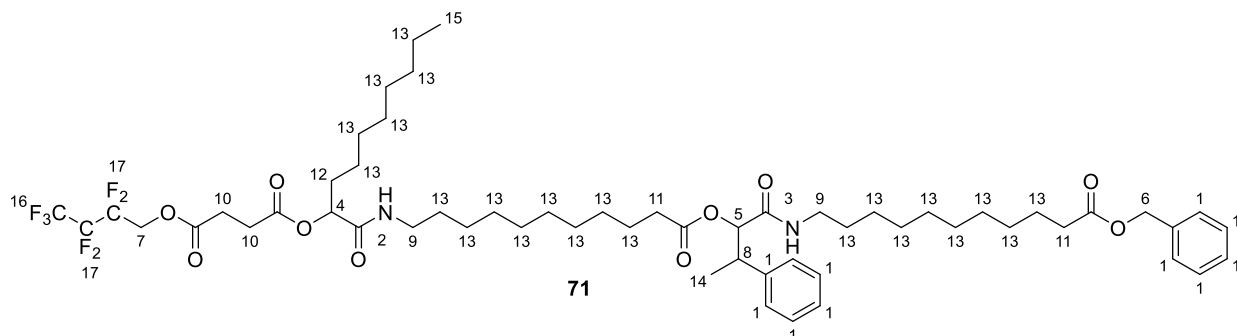
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -80.84 (t, J = 9.3 Hz, 3 F, CF_3^{12}), -120.14 – -121.45 (m, 2 F, CF_2^{13}), -127.34 – -128.12 (m, 2 F, CF_2^{13}). Total integral of CF_2 region normalized with respect to the CF_3^{12} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{29}\text{H}_{46}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 654.3235; found, 654.3219, Δ = 1.4 mmu.



Supplementary Figure 100: ^1H -NMR of compound 70 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 2.05 g of **71** (3.13 mmol, 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 629 μ L 2-phenylpropionaldehyde **14e** (630 mg, 4.70 mmol, 1.50 eq.) and 1.42 g of the monomer **M1** (4.70 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (7:1 $\rightarrow$ 1:1) to yield the passerini product **71** as a pale highly viscous oil. (3.41 g, 3.13 mmol, 99.9%).

R_f = 0.30 in cyclohexane / ethyl acetate (1:1).

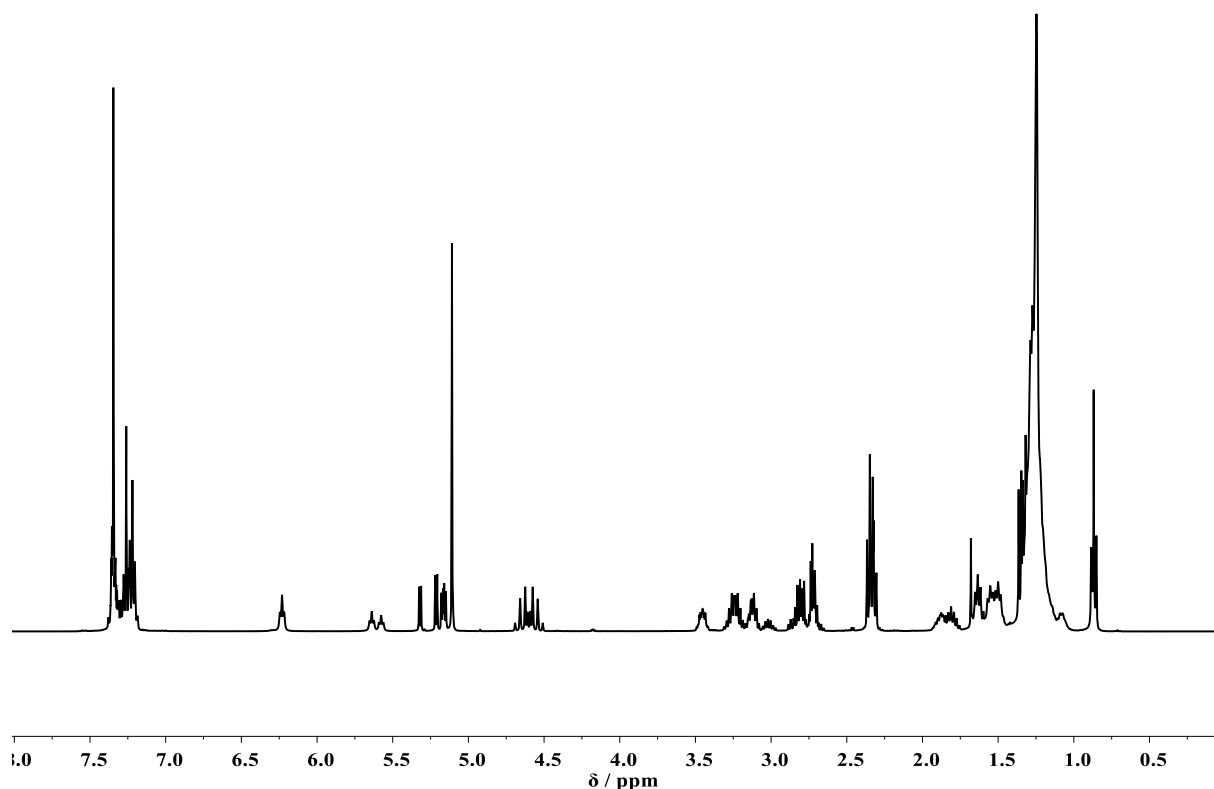
IR (ATR): ν / cm^{-1} = 3307.3 (vw), 2925.3 (s), 2854.5 (m), 1738.9 (s), 1655.6 (s), 1535.1 (w), 1496.9 (vw), 1454.8 (w), 1352.6 (w), 1226.4 (vw), 1144.0 (vs), 1020.0 (m), 909.5 (w), 735.3 (w), 698.2 (s), 534.5 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.15 (m, 10 H, CH_{Ar}^1), 6.23 (t, J = 5.8 Hz, 1 H, NH^2), 5.64 (t, J = 5.8 Hz, 0.5 H, NH^{3a}), 5.58 (t, J = 5.9 Hz, 0.5 H, NH^{3b}), 5.32 (d, J = 5.4 Hz, 0.5 H, CH^{4a}), 5.21 (d, J = 5.4 Hz, 0.5 H, CH^{4b}), 5.19 – 5.14 (m, 1 H, CH^5), 5.11 (s, 2 H, CH_2^6), 4.73 – 4.46 (m, 2 H, CH_2^7), 3.52 – 3.39 (m, 1 H, CH^8), 3.35 – 2.96 (m, 4 H, CH_2^9), 2.90 – 2.64 (m, 4 H, CH_2^{10}), 2.41 – 2.28 (m, 4 H, CH_2^{11}), 1.96 – 1.74 (m, 2 H, CH_2^{12}), 1.72 – 1.00 (m, 47 H, CH_2^{13} , CH_3^{14}), 0.91 – 0.83 (m, 3 H, CH_3^{15}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.80, 172.57, 172.42, 171.47, 170.88, 169.61, 168.82, 168.61, 141.73, 141.18, 136.26, 128.66, 128.52, 128.32, 128.28, 127.97, 127.13, 127.05, 77.85, 74.88, 66.19, 59.67 (t, J = 27.0 Hz), 41.58, 41.29, 39.43, 39.29, 39.20, 34.44, 34.35, 34.30, 31.94, 29.59, 29.55, 29.51, 29.52, 29.48, 29.47, 29.39, 29.35, 29.30, 29.23, 29.18, 29.16, 29.04, 28.78, 26.96, 26.86, 26.80, 25.06, 24.98, 24.91, 22.75, 17.62, 15.30, 14.20.

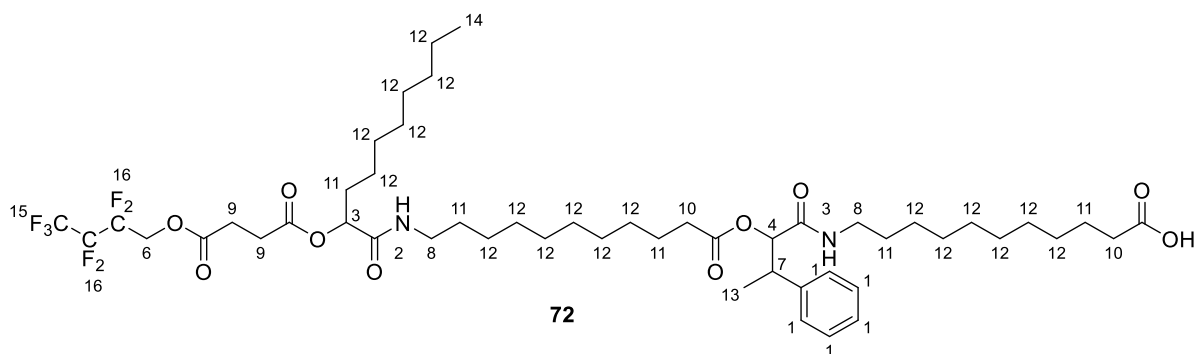
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.81 (t, J = 9.1 Hz, 3 F, CF_3), -120.24 – -120.74 (m, 2 F, CF_2), -127.46 – -127.96 (m, 2 F, CF_2). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{57}^{1}\text{H}_{83}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_7$, 1089.6009; found, 1089.5993, Δ = 1.6 mmu.



Supplementary Figure 101: ^1H -NMR of compound **71** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask, 3.26 g of **71** (2.99 mmol, 1.00 eq.) was dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Subsequently, 652 mg (20 wt.-%) palladium on activated charcoal **16** were added to the solution. The resulting mixture was purged with hydrogen gas and stirred for one day at room temperature under hydrogen atmosphere (balloon). The crude reaction mixture was filtered over celite® and flushed with 50 mL dichloromethane. After evaporation of the solvents and drying under reduced pressure the product **72** was obtained as a colorless solid (2.97 g, 2.97 mol, 99.3%).

IR (ATR): ν/cm^{-1} = 3306.6 (vw), 2924.9 (d), 2854.3 (m), 2164.0 (vw), 2111.2 (vw), 2016.9 (vw), 1741.2 (s), 1651.4 (s), 1540.4 (m), 1495.6 (vw), 1454.8 (w), 1410.5 (w), 1352.8 (w), 1226.4 (vs), 1179.0

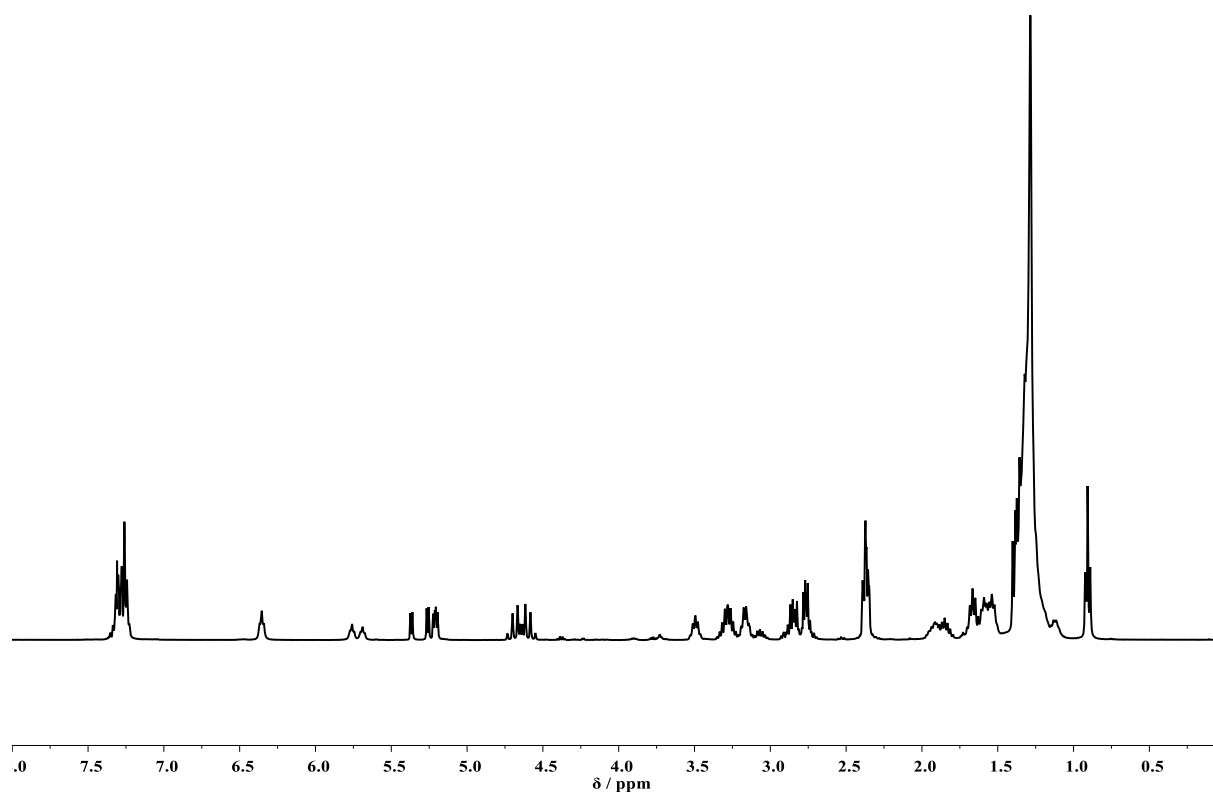
(vs), 1144.2 (vs), 1020.6 (m), 979.1 (w), 909.8 (w), 759.9 (w), 735.8 (w), 700.2 (m), 630.7 (w), 536.7 (w), 411.1 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.40 – 7.20 (m, 5 H, CH_{Ar}^1), 6.35 (t, J = 5.8 Hz, 1 H, NH^2), 5.76 (t, J = 5.8 Hz, 0.5 H, NH^{3a}), 5.69 (t, J = 5.9 Hz, 0.5 H, NH^{3b}), 5.37 (d, J = 5.3 Hz, 0.5 H, CH^{4a}), 5.26 (d, J = 5.3 Hz, 0.5 H, CH^{4b}), 5.23 – 5.14 (m, 1 H, CH^5), 4.78 – 4.53 (m, 2 H, CH_2^6), 3.56 – 3.43 (m, 1 H, CH^7), 3.38 – 3.00 (m, 4 H, CH_2^8), 2.95 – 2.68 (m, 4 H, CH_2^9), 2.43 – 2.27 (m, 4 H, CH_2^{10}), 2.03 – 1.45 (m, 10 H, CH_2^{11}), 1.44 – 1.06 (m, 39 H, CH_2^{12} , CH_3^{13}), 0.91 (t, J = 6.7 Hz, 3 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 178.45, 172.60, 172.45, 171.51, 170.92, 169.81, 168.97, 168.74, 141.66, 141.12, 128.50, 128.29, 127.95, 127.11, 127.05, 77.82, 74.82, 59.65 (t, J = 26.8 Hz), 41.54, 41.23, 39.47, 39.28, 39.19, 34.33, 34.27, 34.08, 31.91, 31.89, 29.57, 29.49, 29.46, 29.43, 29.37, 29.32, 29.25, 29.19, 29.16, 29.14, 29.11, 29.01, 28.76, 26.93, 26.79, 26.72, 24.95, 24.89, 24.84, 22.73, 17.59, 15.26, 14.18.

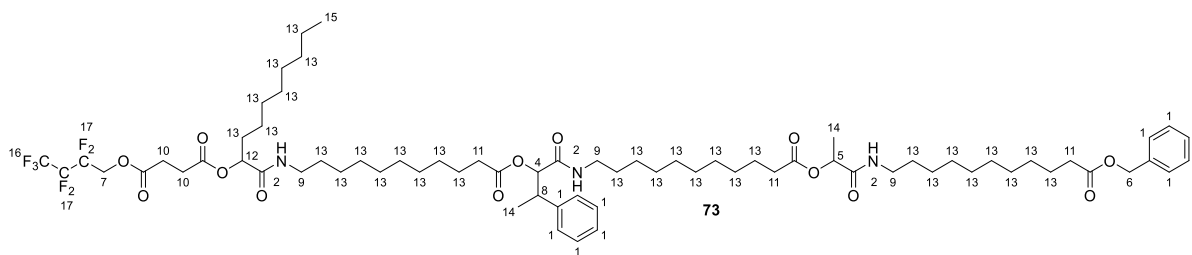
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.17 (t, J = 9.2 Hz, 3 F, CF_3^{15}), -124.68 – -125.12 (m, 2 F, CF_2^{16}), -131.78 – -132.20 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{50}^{1}\text{H}_{77}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_7$, 999.5539; found, 999.5526, Δ = 1.3 mmu.



Supplementary Figure 102: ^1H -NMR of compound 72 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 2.84 g of **72** (2.84 mmol, 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 482 μ L acetaldehyde **14f** (376 mg, 8.53 mmol, 3.00 eq.) and 1.29 g of the monomer **M1** (4.27 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 1 day. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 1:1) to yield the passerini product **73** as a pale highly viscous oil. (3.50 g, 2.60 mmol, 91.6%).

R_f = 0.60 in cyclohexane / ethyl acetate (1:1).

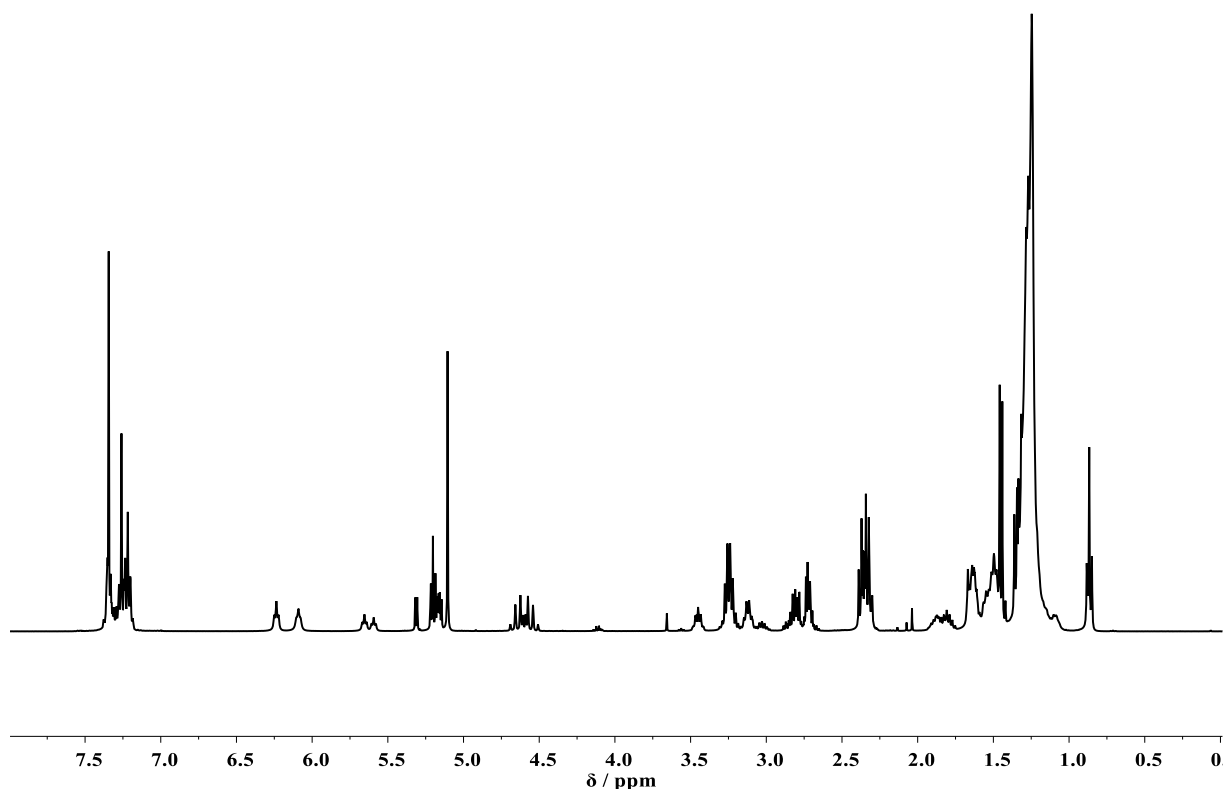
IR (ATR): ν / cm^{-1} = 3305.7 (vw), 3086.0 (vw), 2925.0 (s), 2853.9 (m), 2097.9 (vw), 1739.2 (s), 1655.6 (s), 1535.4 (m), 1497.2 (vw), 1454.8 (w), 1353.3 (w), 1226.9 (vs), 1145.6 (vs), 1020.8 (m), 909.8 (w), 736.0 (w), 699.1 (m), 538.7 (vw), 405.4 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.44 – 7.15 (m, 10 H, CH_{Ar}^1), 6.24 (t, J = 5.8 Hz, 1 H, NH^2), 6.09 (t, J = 5.8 Hz, 1 H, NH^2), 5.65 (t, J = 5.9 Hz, 0.5 H, NH^{3a}), 5.59 (t, J = 5.9 Hz, 0.5 H, NH^{3b}), 5.31 (d, J = 5.4 Hz, 0.5 H, CH^{4a}), 5.25 – 5.14 (m, 0.5 H, 2 H, CH^{4b} , CH^5), 5.11 (s, 2 H, CH_2^6), 4.72 – 4.49 (m, 2 H, CH_2^7), 3.51 – 3.39 (m, 1 H, CH^8), 3.34 – 2.97 (m, 6 H, CH_2^9), 2.90 – 2.64 (m, 4 H, CH^{10}), 2.43 – 2.26 (m, 6 H, CH_2^{11}), 1.95 – 1.73 (m, 2 H, CH_2^{12}), 1.71 – 1.05 (m, 66 H, CH_2^{13} , CH_3^{14}), 0.90 – 0.82 (m, 3 H, CH_3^{15}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.80, 172.58, 172.44, 172.38, 171.48, 170.89, 170.42, 169.62, 168.85, 168.64, 141.74, 141.21, 136.27, 128.67, 128.53, 128.32, 128.29, 127.97, 127.13, 127.05, 77.86, 74.88, 70.59, 66.19, 59.68 (t, J = 26.9 Hz), 41.58, 41.29, 39.43, 39.36, 39.29, 39.20, 34.46, 34.45, 34.36, 34.30, 31.94, 29.67, 29.59, 29.56, 29.53, 29.49, 29.47, 29.41, 29.33, 29.31, 29.28, 29.23, 29.20, 29.19, 29.16, 29.04, 28.79, 26.95, 26.86, 26.80, 25.06, 25.01, 24.98, 24.92, 22.76, 18.09, 17.63, 15.31, 14.21.

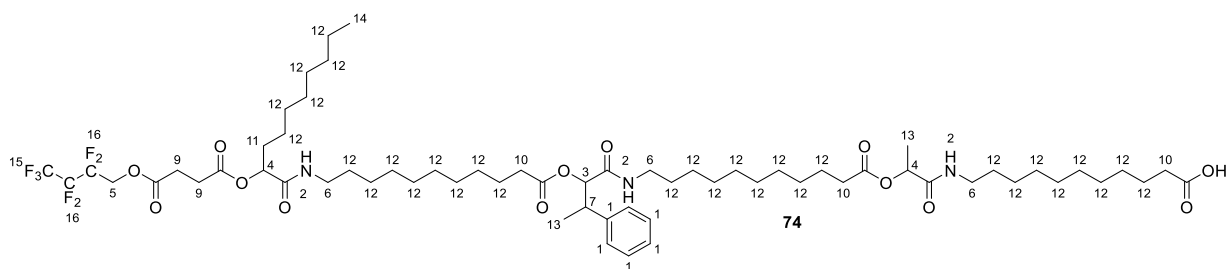
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.81 (t, J = 9.3 Hz, 3 F, CF_3^{16}), -120.19 – -120.65 (m, 2 F, CF_2^{17}), -127.59 – -127.72 (m, 2 F, CF_2^{17}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{71}^{1}\text{H}_{108}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_7$, 1344.7843; found, 1344.7813, Δ = 3.0 mmu.



Supplementary Figure 103: ^1H -NMR of compound **73** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask, 3.32 g of **73** (2.47 mmol, 1.00 eq.) was dissolved in 6.00 mL ethyl acetate and 6.00 mL THF. Subsequently, 764 mg (20 wt.-%) palladium on activated charcoal **16** were added to the solution. The resulting mixture was purged with hydrogen gas and stirred for one day at room temperature under hydrogen atmosphere (3 balloons). The crude reaction mixture was filtered over celite® and flushed with 50 mL dichloromethane. After evaporation of the solvents and drying under reduced pressure the product **74** was obtained as a colorless solid (3.08 g, 2.46 mol, 99.5%).

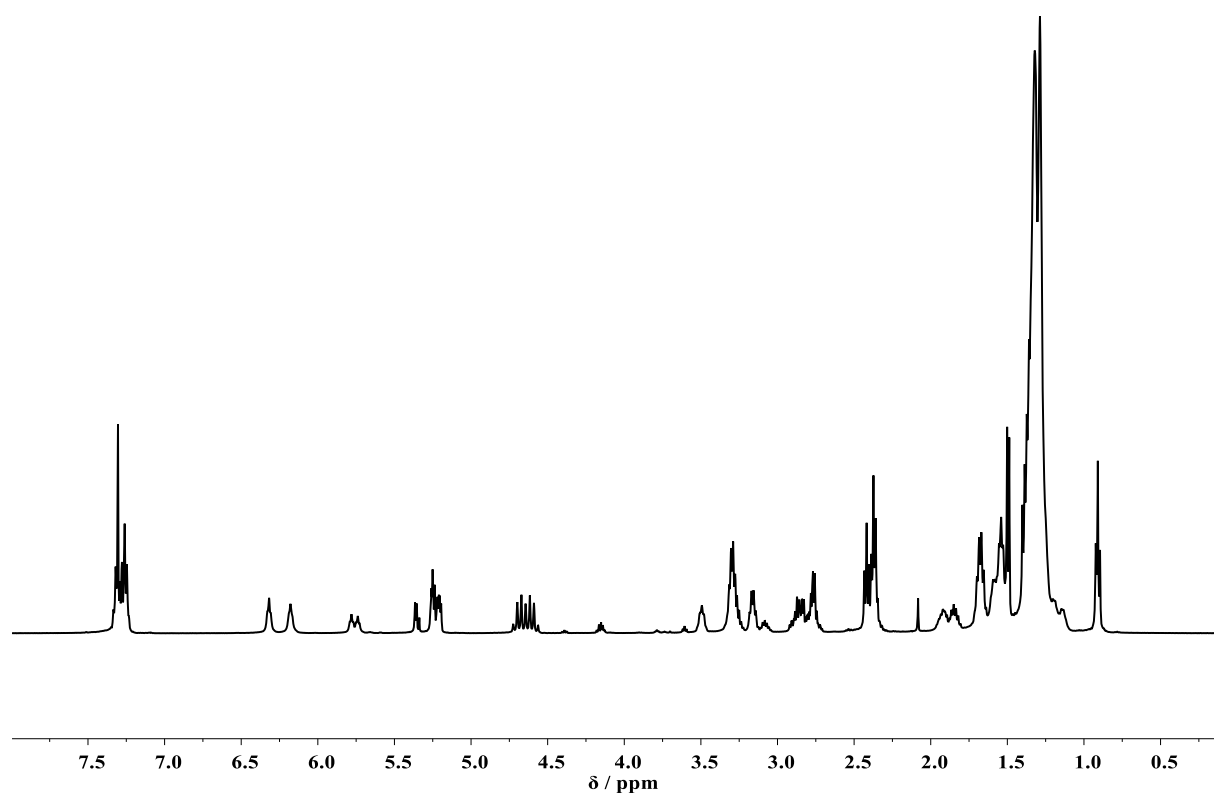
IR (ATR): ν/cm^{-1} = 3305.5 (vw), 2924.5 (s), 2854.0 (m), 1740.6 (s), 1654.0 (s), 1539.0 (m), 1454.6 (w), 1371.5 (w), 1226.7 (vs), 1145.2 (vs), 1020.8 (m), 909.9 (w), 759.8 (w), 735.7 (w), 700.3 (m), 536.7 (vw).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.25 – 7.10 (m, 5 H, CH_{Ar}^1), 6.21 (t, J = 5.9 Hz, 1 H, NH^2), 6.07 (t, J = 6.0 Hz, 1 H, NH^2), 5.76 – 5.60 (m, 0.5 H, CH^{3a}), 5.30 – 5.21 (m, 2.5 H, CH^{3b} , CH^4), 5.18 – 5.06 (m, 2 H, CH_2^5), 4.68 – 4.43 (m, 6 H, CH_2^6), 3.42 – 3.35 (m, 1 H, CH^7), 3.29 – 2.93 (m, 6 H, CH_2^8), 2.81 – 2.60 (m, 4 H, CH_2^9), 2.39 – 2.22 (m, 6 H, CH_2^{10}), 1.90 – 1.68 (m, 2 H, CH_2^{11}), 1.62 – 0.98 (m, 12H, CH_2^{12} , CH_3^{13}), 0.80 (t, J = 6.8 Hz, 3 H, CH_3^{14}).

^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 177.35, 172.71, 172.58, 172.42, 171.52, 170.93, 170.56, 169.76, 169.04, 168.82, 141.66, 141.17, 128.54, 128.31, 127.97, 127.14, 127.06, 77.88, 74.85, 70.59, 59.68 (t, J = 26.9 Hz), 41.55, 41.27, 39.47, 39.34, 39.27, 34.48, 34.35, 34.29, 33.96, 31.94, 31.92, 29.58, 29.53, 29.49, 29.43, 29.35, 29.31, 29.28, 29.22, 29.17, 29.14, 29.09, 29.03, 28.79, 26.95, 26.86, 26.85, 26.80, 25.04, 24.98, 24.96, 24.90, 24.87, 22.76, 18.06, 17.61, 15.33, 14.21.

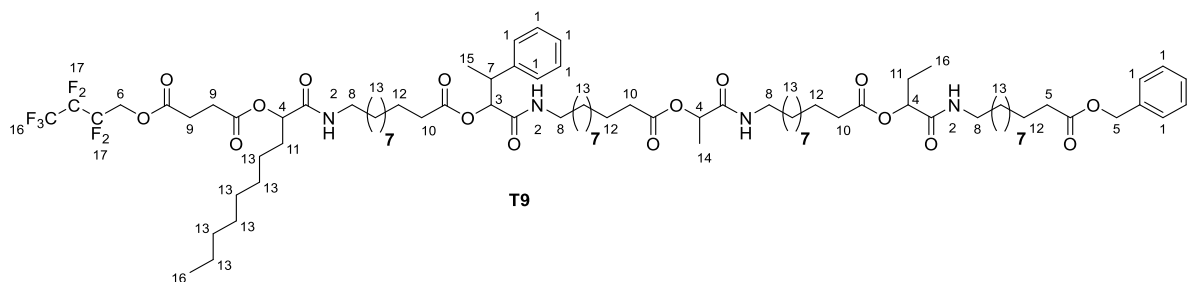
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.81 (t, J = 9.3 Hz, 3 F, CF_3^{15}), -119.20 – -121.40 (m, 2 F, CF_2^{16}), -126.52 – -130.07 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{64}^{1}\text{H}_{102}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_7$, 1254.7374; found, 1254.7351, Δ = 2.3 mmu.



Supplementary Figure 104: ^1H -NMR of compound 74 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 428 g of **74** (341 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 36.7 μL propionaldehyde **14l** (29.7 mg, 512 μmol , 3.00 eq.) and 154 mg of the monomer **M1** (512 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 1 day. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 1:1) to yield the passerini product **T9** as a pale highly viscous oil. (372 mg, 230 μmol , 67.6%).

R_f = 0.52 in cyclohexane / ethyl acetate (1:1).

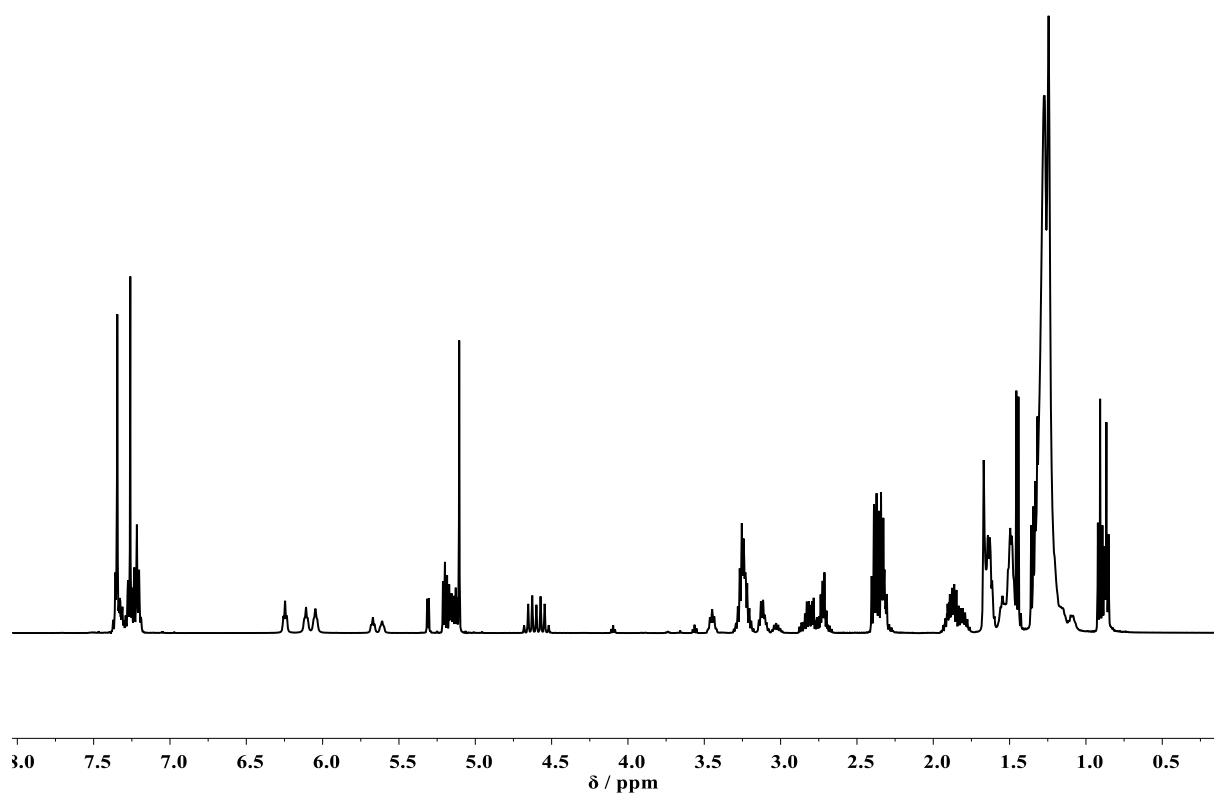
IR (ATR): ν / cm^{-1} = 3304.8 (w), 2924.6 (s), 2853.8 (m), 1738.8 (s), 1655.0 (s), 1535.6 (m), 1455.2 (w), 1373.2 (w), 1227.0 (s), 1146.1 (vs), 1020.8 (m), 735.6 (w), 699.1 (m).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.41 – 7.16 (m, 10 H, CH_{Ar}^1), 6.25 (t, J = 5.8 Hz, 1 H, NH^2), 6.11 (t, J = 5.9 Hz, 1 H, NH^2), 6.05 (t, J = 6.0 Hz, 1 H, NH^2), 5.73 – 5.56 (m, 1 H, NH^2), 5.31 (d, J = 5.4 Hz, 0.5 H, CH^{3a}), 5.24 – 5.07 (m, 5.5 H, CH^{3a} , CH^4 , CH_2^5), 4.69 – 4.51 (m, 2 H, CH_2^6), 3.49 – 3.38 (m, 1 H, CH^7), 3.32 – 2.97 (m, 8 H, CH_2^8), 2.89 – 2.66 (m, 4 H, CH_2^9), 2.43 – 2.25 (m, 8 H, CH_2^{10}), 1.95 – 1.75 (m, 4 H, CH_2^{11}), 1.71 – 1.40 (m, 19 H, $\text{CH}_2^{12,13}$, CH_3^{14}), 1.38 – 1.06 (m, 28 H, CH_2^{13} , CH_3^{15}), 0.95 – 0.84 (m, 6 H, CH_3^{16}).

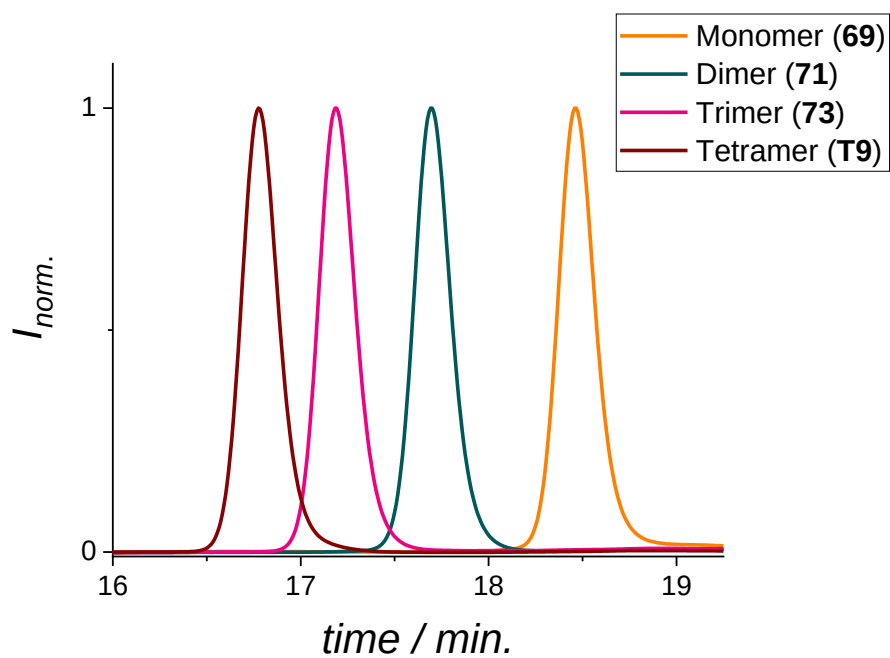
^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.83, 172.61, 172.57, 172.46, 172.41, 171.50, 170.91, 170.46, 169.75, 169.64, 168.87, 168.66, 141.72, 141.19, 136.25, 128.67, 128.53, 128.32, 128.30, 128.29, 127.97, 127.13, 127.05, 77.85, 74.93, 74.87, 70.58, 66.20, 59.67 (t, J = 26.5 Hz), 41.57, 41.28, 39.43, 39.35, 39.32, 39.29, 39.20, 34.45, 34.43, 34.35, 34.30, 31.94, 29.70, 29.68, 29.59, 29.56, 29.49, 29.47, 29.41, 29.35, 29.33, 29.28, 29.23, 29.18, 29.16, 29.04, 28.78, 26.95, 26.86, 26.80, 25.22, 25.08, 25.06, 25.00, 24.98, 24.91, 22.76, 17.62, 15.30, 14.22, 9.15.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.81 (t, J = 9.1 Hz, 3 F, CF_3^{16}), -119.77 – -123.82 (m, 2 F, CF_2^{17}), -124.53 – -130.56 (m, 2 F, CF_2^{17}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 4.

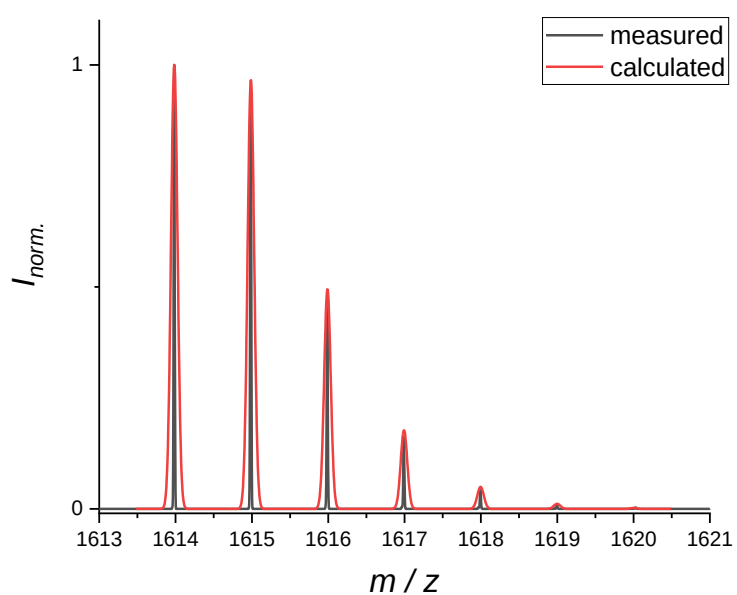
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{86}^{1}\text{H}_{135}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_7$, 1613.9834; found, 1613.9821, Δ = 1.3 mmu.



Supplementary Figure 105: ^1H -NMR of compound T9 measured in CDCl_3 .



Supplementary Figure 106: SEC traces of the intermediates after each P3CR in the synthesis of product T9.

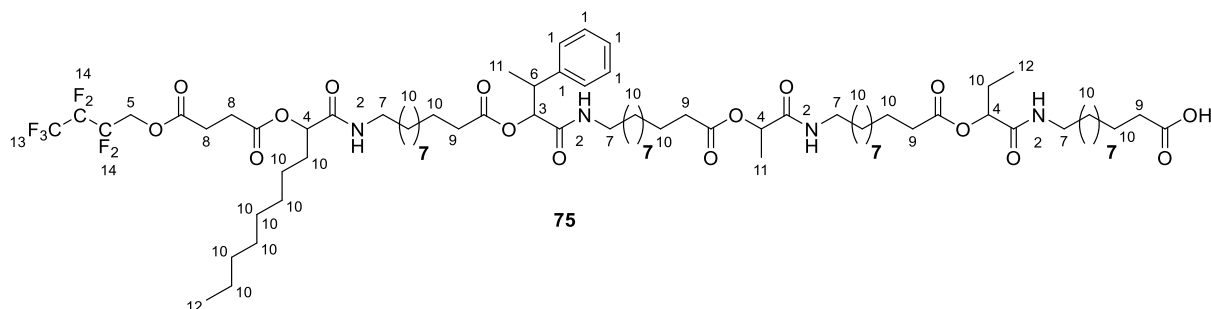


Supplementary Figure 107: High resolution ESI-MS measurement of T9. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (red).

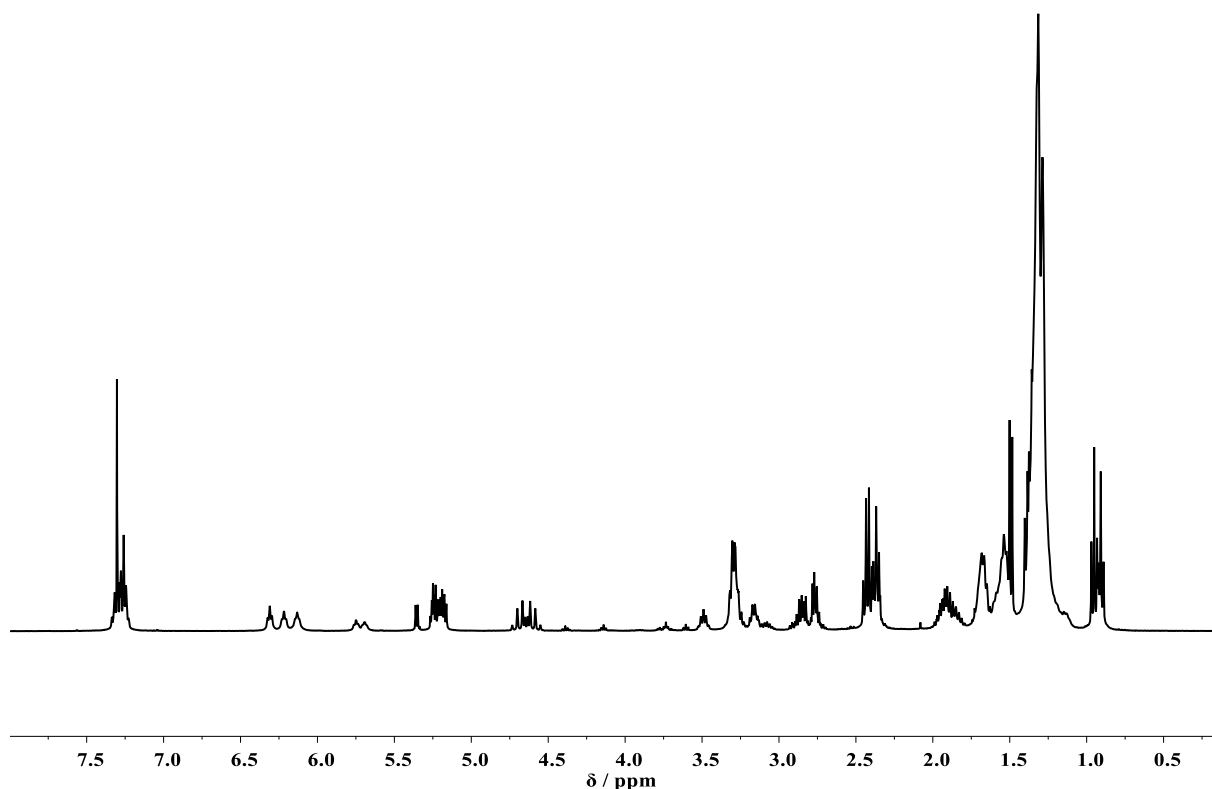
```
csv, maximum is 1.000000 found for mass 1613.982320
matching mass 1613.98232
cutoff 0.50000: 0 solutions (11 peaks)
cutoff 0.25000: 0 solutions (33 peaks)
cutoff 0.12500: 1 solutions (79 peaks)
1613.98232  $\approx$  283.020520 + 353.293000 + 345.230400 + 255.183450 + 269.199100 + 107.049690
(sides Nonanal, 2-Phenylpropionaldehyde, Acetaldehyde, Propionaldehyde; error -1.00616)
```

Supplementary Figure 108: Screenshot of the automated read-out of T9.

Deprotection

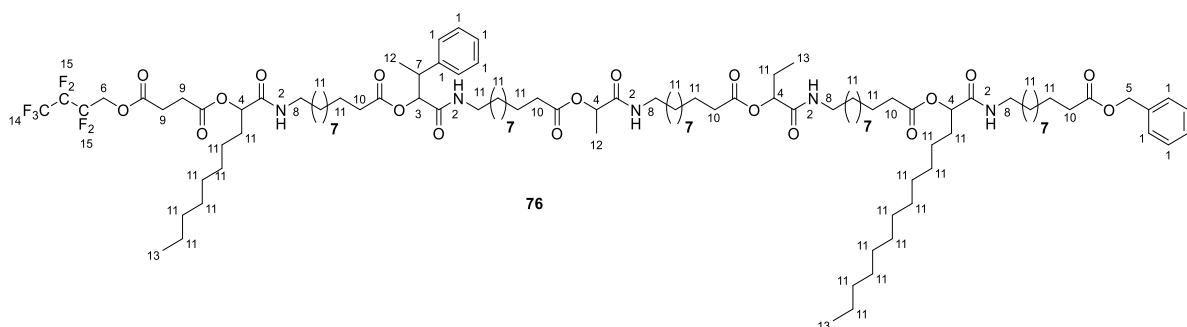


ESI-MS $[m/z]$: $[M + H]^+$ calculated for $^{12}\text{C}_{79}^{1}\text{H}_{129}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_7$, 1523.9365; found, 1523.9361, $\Delta = 0.4$ mmu.



Supplementary Figure 109: ^1H -NMR of compound **75** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 260 mg of **75** (171 μmol , 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 40.5 μL tridecanal **14d** (33.8 mg, 171 μmol , 1.00 eq.) and 51.4 mg of the monomer **M1** (171 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 1 day. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 1:1) to yield the passerini product **76** as a pale highly viscous oil. (183 mg, 90.6 μmol , 53.1%).

R_f = 0.33 in cyclohexane / ethyl acetate (1:1).

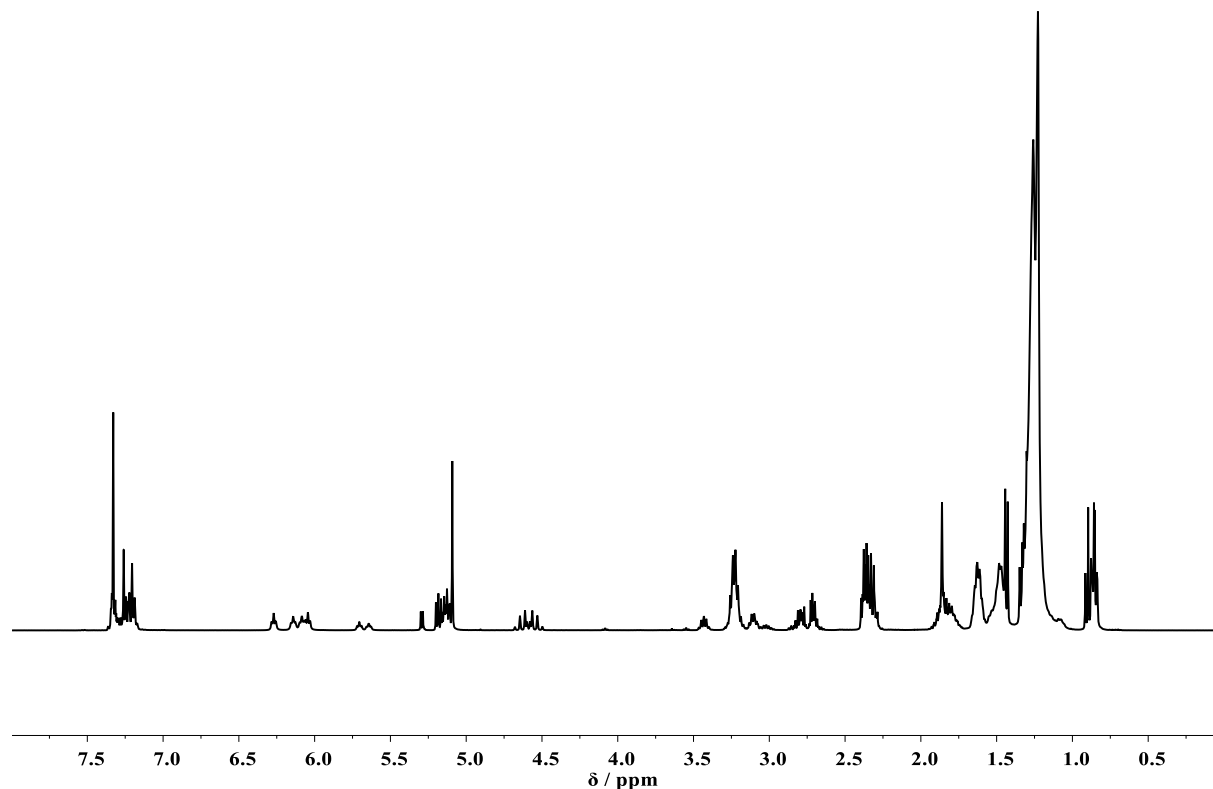
IR (ATR): ν/cm^{-1} = 2925.3 (m), 2854.3 (m), 1741.7 (w), 1649.3 (m), 1587.1 (m), 1534.1 (s), 1454.9 (m), 1337.8 (w), 1225.8 (s), 1145.7 (m), 981.3 (w), 782.1 (w), 725.8 (w), 699.6 (m), 635.1 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.39 – 7.14 (m, 10 H, CH_{Ar}^1), 6.27 (t, J = 5.8 Hz, 1 H, NH^2), 6.19 – 5.99 (m, 3 H, NH^2), 5.76 – 5.60 (m, 1 H, NH^2), 5.29 (d, J = 5.5 Hz, 0.5 H, CH^{3a}), 5.24 – 5.04 (m, 6.5 H, CH^{3a} , CH^4 , CH_2^5), 4.71 – 4.47 (m, 2 H, CH_2^6), 3.52 – 3.37 (m, 1 H, CH^7), 3.33 – 2.98 (m, 10 H, CH_2^8), 2.90 – 2.63 (m, 4 H, CH_2^9), 2.42 – 2.26 (m, 10 H, CH_2^{10}), 1.99 – 1.72 (m, 8 H, CH_2^{11}), 1.68 – 1.01 (m, 116 H, CH_2^{11} , CH_3^{12}), 0.96 – 0.80 (m, 9 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 172.38, 171.45, 170.87, 170.45, 169.97, 169.75, 169.62, 168.85, 168.64, 141.69, 141.18, 136.21, 128.62, 128.48, 128.26, 128.25, 128.23, 127.92, 127.08, 127.01, 77.81, 74.89, 74.82, 74.03, 70.52, 66.15, 59.62 (t, J = 26.7 Hz), 41.55, 41.26, 39.40, 39.31, 39.28, 39.17, 34.31, 34.25, 32.00, 31.90, 29.75, 29.72, 29.67, 29.63, 29.52, 29.43, 29.35, 29.31, 29.23, 29.19, 29.19, 29.11, 29.00, 28.74, 26.91, 26.90, 26.82, 26.76, 25.18, 25.04, 24.95, 24.86, 22.77, 22.71, 18.05, 17.59, 15.27, 14.20, 14.16, 9.12.

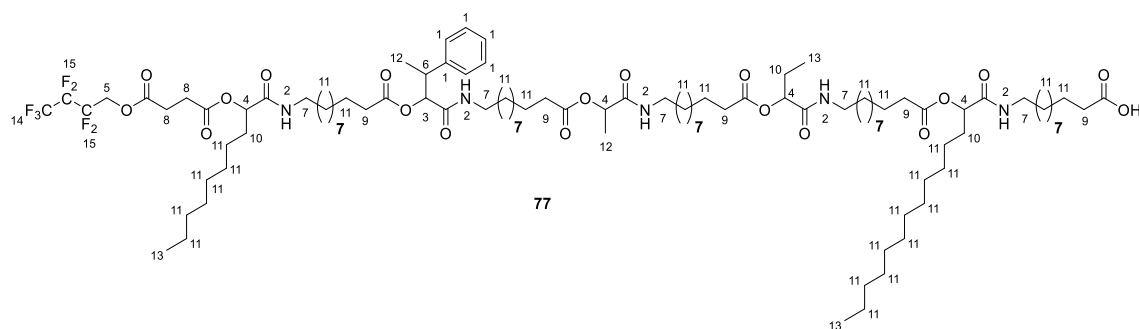
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.82 (t, J = 9.1 Hz, 3 F, CF_3^{14}), -119.33 – -121.63 (m, 2 F, CF_2^{15}), -127.21 – -128.37 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{111}^{1}\text{H}_{182}^{16}\text{O}_{19}^{14}\text{N}_5^{19}\text{F}_7$, 2023.3390; found, 2023.3392, Δ = 0.2 mmu.



Supplementary Figure 110: ^1H -NMR of compound 76 measured in CDCl_3 .

Deprotection



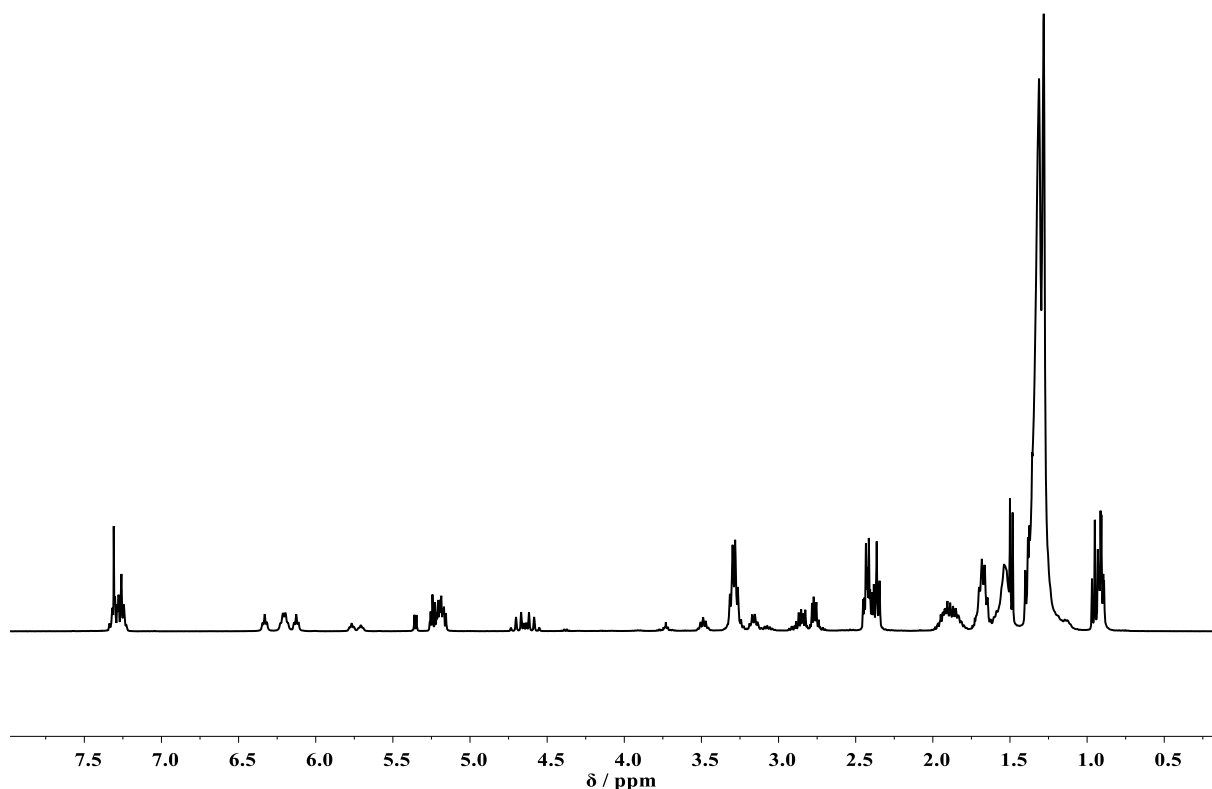
In a 25 mL round bottom flask, 77.1 mg of **76** (38.0 μmol , 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 15.4 mg (20 wt.-%) palladium on activated charcoal **16** were added to the solution. The resulting mixture was purged with hydrogen gas and stirred for one day at room temperature under hydrogen atmosphere (3 balloons). The crude reaction mixture was filtered over celite[®] and flushed with 50 mL dichloromethane. After evaporation of the solvents and drying under reduced pressure the product **77** was obtained as a colorless solid (67.2 mg, 34.7 μmol , 91.2%).

IR (ATR): ν/cm^{-1} = 3291.0 (vw), 2923.9 (s), 2853.7 (m), 1741.6 (m), 1650.2 (s), 1535.7 (s), 1456.1 (m), 1373.8 (w), 1226.7 (s), 1145.4 (s), 1021.5 (w), 980.5 (w), 781.8 (vw), 723.6 (w), 699.8 (m), 634.8 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.15 (m, 5 H, CH_{Ar}^1), 6.33 (t, J = 5.8 Hz, 1 H, NH^2), 6.26 – 6.16 (m, 2 H, NH^2), 6.13 (t, J = 5.9 Hz, 1 H, NH^2), 5.74 (dt, J = 24.0, 6.1 Hz, 1 H, NH^2), 5.35 (d, J = 5.5 Hz, 0.5 H, CH^{3a}), 5.28 – 5.14 (m, 4.5 H, CH^{3b} , CH^4), 4.75 – 4.52 (m, 2 H, CH_2^5), 3.56 – 3.43 (m, 1 H, CH^6), 3.38 – 3.01 (m, 10 H, CH_2^7), 2.95 – 2.68 (m, 4 H, CH_2^8), 2.49 – 2.30 (m, 10 H, CH_2^9), 2.00 – 1.77 (m, 6 H, CH_2^{10}), 1.75 – 1.05 (m, 118 H, CH_2^{11} , CH_3^{12}), 1.00 – 0.81 (m, 9 H, CH_3^{13}).

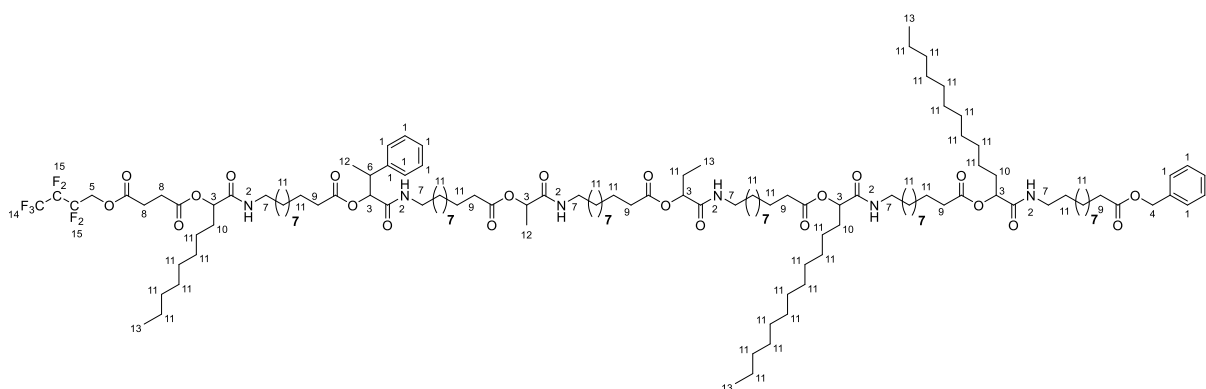
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 176.94, 172.66, 172.64, 172.49, 172.43, 171.50, 170.91, 170.59, 170.09, 169.95, 169.72, 168.96, 168.74, 141.68, 141.17, 128.52, 128.29, 127.95, 127.12, 127.04, 77.84, 77.36, 74.91, 74.84, 74.07, 70.54, 59.65 (t, J = 26.6 Hz), 41.56, 39.44, 39.37, 39.29, 39.21, 34.43, 34.40, 34.33, 34.28, 33.97, 32.03, 32.00, 31.92, 29.78, 29.76, 29.74, 29.66, 29.63, 29.58, 29.55, 29.51, 29.46, 29.45, 29.34, 29.31, 29.30, 29.26, 29.23, 29.19, 29.16, 29.14, 29.10, 29.02, 28.77, 26.94, 26.91, 26.88, 26.84, 26.78, 25.19, 25.09, 25.05, 24.98, 24.97, 24.89, 22.80, 22.74, 18.07, 17.60, 15.29, 14.24, 14.20, 9.14.

ESI-MS [m/z]: [$\text{M} + \text{H}$]⁺ calculated for $^{12}\text{C}_{104}^{1}\text{H}_{176}^{16}\text{O}_{19}^{14}\text{N}_5^{19}\text{F}_7$, 193.2921; found, 193.2935, Δ = 1.4 mmu.



Supplementary Figure 111: ^1H -NMR of compound **77** measured in CDCl_3 .

Passerini reaction



In a 10 mL round bottom flask, 56.2 mg of **77** (29.1 μmol , 1.00 eq.) was stirred in 1.00 mL DCM. Subsequently, 8.04 mg dodecanal **14h** (43.6 μmol , 1.00 eq.) and 13.1 mg of the monomer **M1** (43.6 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 1:1) to yield the passerini product **H3** as a pale highly viscous oil. (28.7 mg, 11.8 μmol , 40.5%).

$R_f = 0.46$ in cyclohexane / ethyl acetate (1:1)

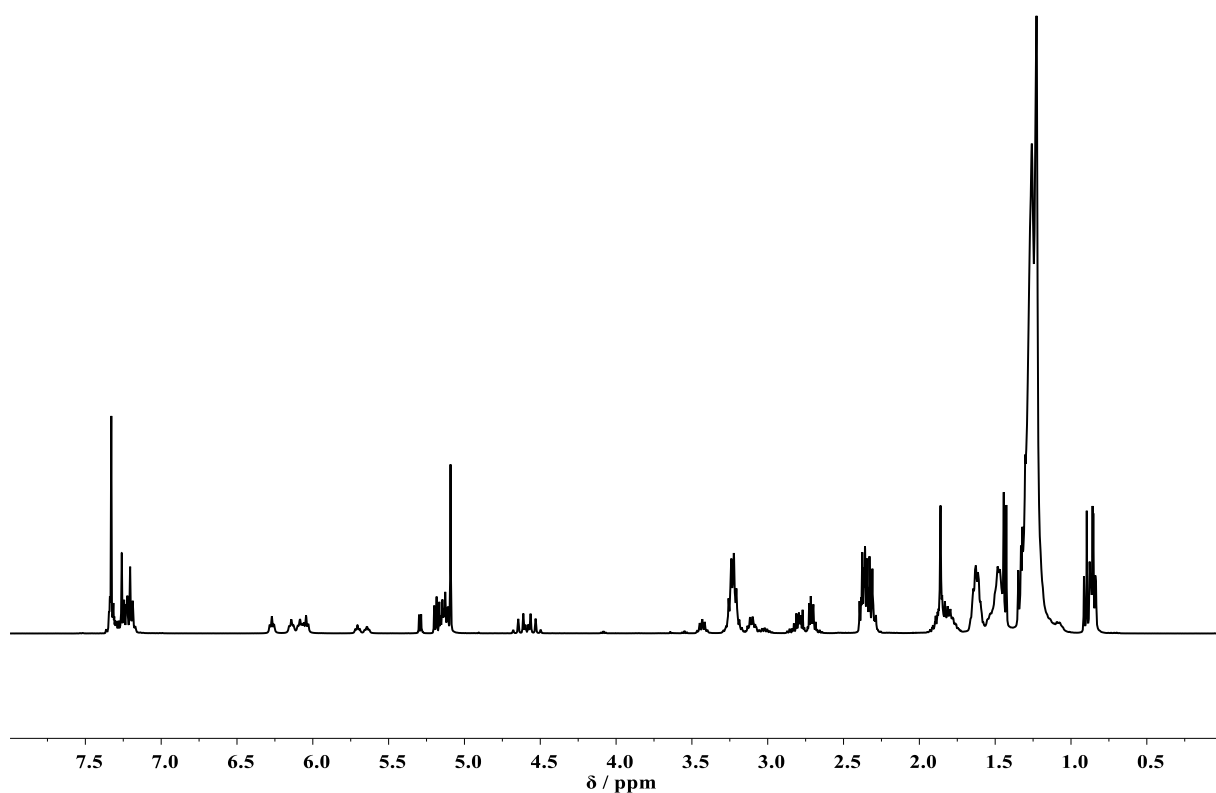
IR (ATR): $\nu / \text{cm}^{-1} = 3138.8$ (w), 2962.1 (w), 1648.2 (w), 1587.1 (m), 1535.6 (m), 1456.1 (w), 1338.2 (w), 1278.7 (w), 1224.0 (w), 1146.3 (w), 1063.5 (w), 981.8 (vw), 791.7 (vw), 726.0 (vw), 700.9 (w), 635.7 (vw).

^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 7.33 - 7.09$ (m, 10 H, CH_{Ar}^1), 6.18 (t, $J = 5.7$ Hz, 1 H, NH^2), 6.09 – 5.90 (m, 4 H, NH^2), 5.66 – 5.50 (m, 1 H, NH^2), 5.31 – 5.00 (m, 8 H, CH^3 , CH_2^4), 4.66 – 4.43 (m, 2 H, CH_2^5), 3.47 – 3.32 (m, 1 H, CH^6), 3.27 – 2.91 (m, 12 H, CH_2^7), 2.88 – 2.59 (m, 4 H, CH_2^8), 2.38 – 2.23 (m, 12 H, CH_2^9), 1.91 – 1.67 (m, 8 H, CH_2^{10}), 1.66 – 0.93 (m, 152 H, CH_2^{11} , CH_3^{12}), 0.89 – 0.71 (m, 12 H, CH_3^{13}).

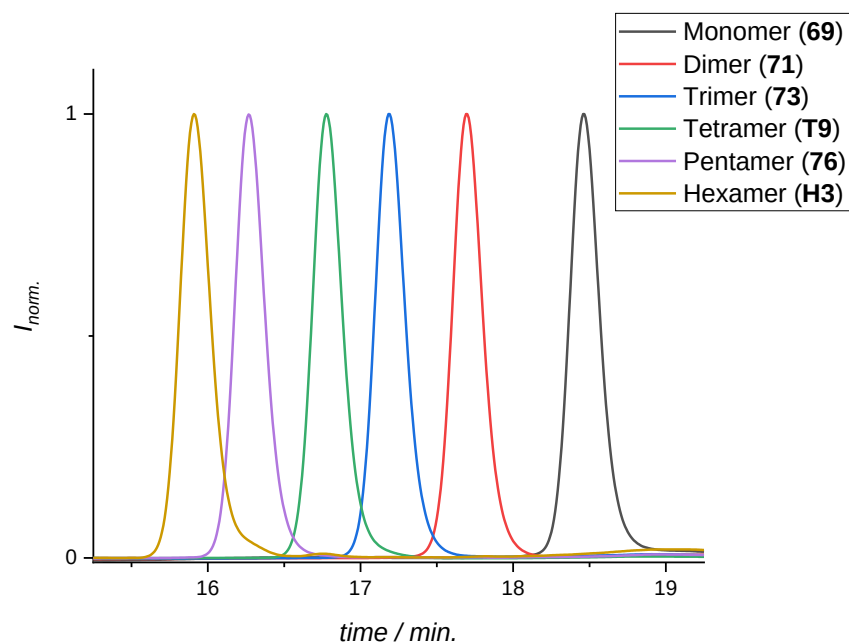
^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 173.83, 172.62, 172.43, 171.51, 170.91, 170.49, 170.02, 169.79, 169.65, 168.88, 136.27, 128.69, 128.55, 128.33, 128.31, 127.98, 77.88, 77.36, 74.95, 74.90, 74.09, 70.60, 66.22, 41.60, 39.46, 39.37, 39.34, 39.22, 34.47, 32.06, 31.96, 29.81, 29.79, 29.77, 29.72, 29.70, 29.61, 29.59, 29.50, 29.41, 29.37, 29.26, 29.06, 28.81, 27.06, 26.98, 26.88, 26.82, 25.24, 25.10, 25.02, 25.01, 24.93, 22.83, 22.78, 18.11, 15.33, 14.27, 14.23, 9.17$.

^{19}F NMR (376 MHz, CDCl_3): $\delta / \text{ppm} = -83.96 - -86.17$ (m, 3 F, CF_3^{14}), $-124.42 - -125.22$ (m, 2 F, CF_2^{15}), $-131.64 - -132.55$ (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 4.

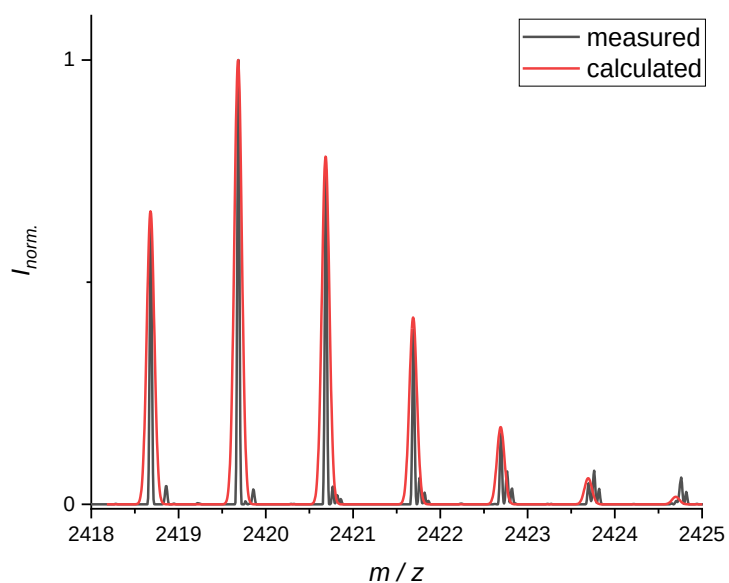
ESI-MS [m/z]: $[\text{M} + \text{H}]^+$ calculated for $^{12}\text{C}_{135}^{1}\text{H}_{227}^{16}\text{O}_{22}^{14}\text{N}_6^{19}\text{F}_7$, 2418.6789; found, 2418.6818, $\Delta = 2.9$ mmu.



Supplementary Figure 112: ^1H -NMR of compound H3 measured in CDCl_3 .



Supplementary Figure 113: SEC traces of the intermediates after each P3CR in the synthesis of product H3.



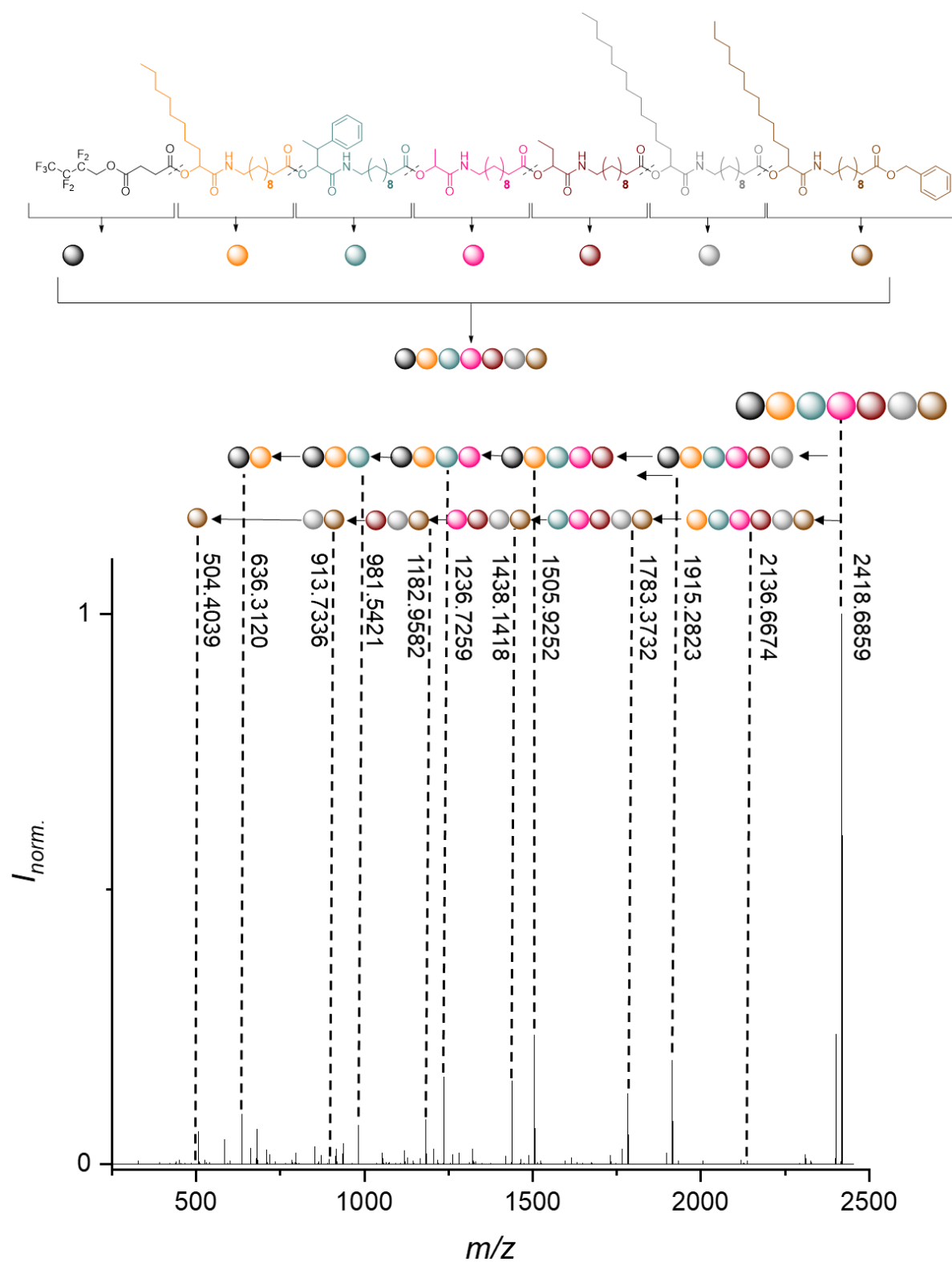
Supplementary Figure 114: High resolution ESI-MS measurement of H3. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (red).

```

matching mass 2418.68173
cutoff 0.50000: 0 solutions (7 peaks)
cutoff 0.25000: 0 solutions (12 peaks)
cutoff 0.12500: 0 solutions (34 peaks)
cutoff 0.06250: 0 solutions (68 peaks)
cutoff 0.03125: 0 solutions (117 peaks)
cutoff 0.01562: 0 solutions (217 peaks)
cutoff 0.00781: 0 solutions (328 peaks)
cutoff 0.00391: 1 solutions (513 peaks)
2418.68173 ≈ 283.020520 + 353.293000 + 345.230400 + 255.183450 + 269.199100 + 409.355600 + 395.339950 + 107.049690 (sides
Nonanal, 2-Phenylpropionaldehyde, Acetaldehyde, Propionaldehyde, Tridecanal, Dodecanal; error -1.01002)
Press ENTER to quit ...

```

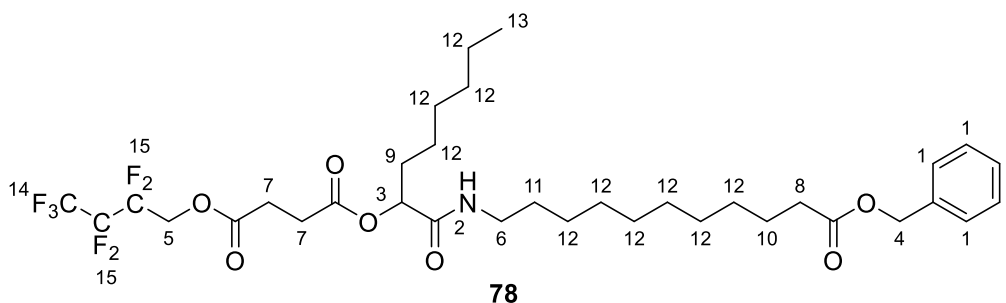
Supplementary Figure 115: Screenshot of the automated read-out of H3.



Supplementary Figure 116: Read-out of the sequence-defined hexamer H2. Read-out of the hexamer H3 via tandem ESI-MS/MS with an NCE of 17. In the spectrum, the read-out from both ends of the oligomer using the fragmentation next to the carbonyl are shown.

1.3.5.3 Synthesis of tetramer T10

Passerini reaction



In a 50 mL round bottom flask 500 mg, **TAG2** (1.67 mmol, 1.00 eq.) was stirred in 5.00 mL DCM. Subsequently, 372 μ L heptanal **14b** (321 mg, 2.50 mmol, 1.50 eq.) and 754 mg of the monomer **M1** (2.50 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 $\rightarrow$ 4:1) to yield the passerini product **78** as a pale highly viscous oil. (1.04 g, 1.46 mmol, 87.4%).

R_f = 0.38 in cyclohexane / ethyl acetate (3:1).

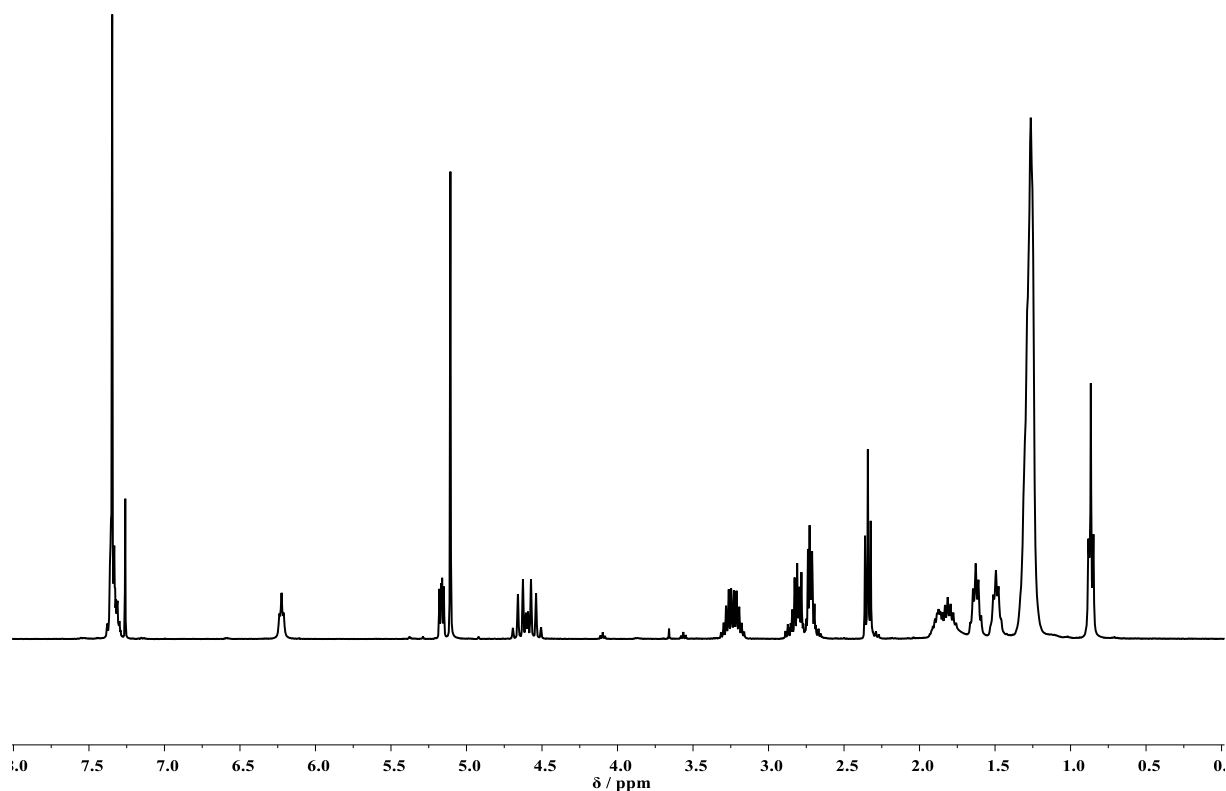
IR (ATR): ν / cm^{-1} = 3306.1 (vw), 2927.1 (m), 2856.0 (w), 1738.6 (s), 1657.5 (m), 1536.5 (w), 1456.0 (w), 1352.2 (w), 1226.3 (vs), 1144.2 (vs), 1019.9 (m), 909.7 (w), 735.9 (m), 697.2 (m).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.29 (m, 5 H, CH_{Ar}^1), 6.22 (t, J = 5.8 Hz, 1 H, NH^2), 5.19 – 5.14 (m, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 4.71 – 4.48 (m, 2 H, CH_2^5), 3.32 – 3.11 (m, 2 H, CH_2^6), 2.94 – 2.64 (m, 4 H, CH_2^7), 2.34 (t, J = 7.6 Hz, 2 H, CH_2^8), 1.95 – 1.76 (m, 2 H, CH_2^9), 1.67 – 1.57 (m, 2 H, CH_2^{10}), 1.54 – 1.43 (m, 2 H, CH_2^{11}), 1.39 – 1.13 (m, 20 H, CH_2^{12}), 0.87 (t, J = 6.6 Hz, 3 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 174.58, 172.23, 171.64, 170.37, 137.03, 129.42, 129.04, 75.64, 66.95, 60.45, 40.21, 35.21, 32.70, 32.49, 30.34, 30.30, 30.24, 30.13, 30.09, 29.99, 29.81, 29.77, 29.55, 27.72, 25.83, 25.69, 23.42, 14.90.

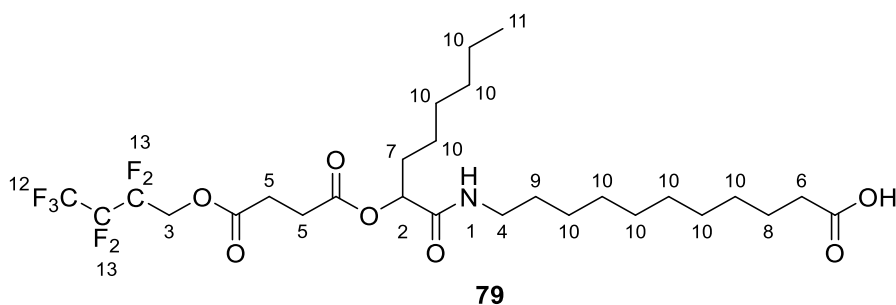
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.54 – -86.48 (m, 3 F, CF_3^{14}), -124.50 – -126.45 (m, 2 F, CF_2^{15}), -131.22 – -133.88 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{34}^{1}\text{H}_{48}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 716.3392; found, 716.3371, Δ = 2.1 mmu.



Supplementary Figure 117: ^1H -NMR of compound **78** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 995 mg of **78** (1.39 mmol, 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 199 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **79** was obtained as a pale highly viscous oil in a yield of 96.4% (835 mg, 1.34 mmol).

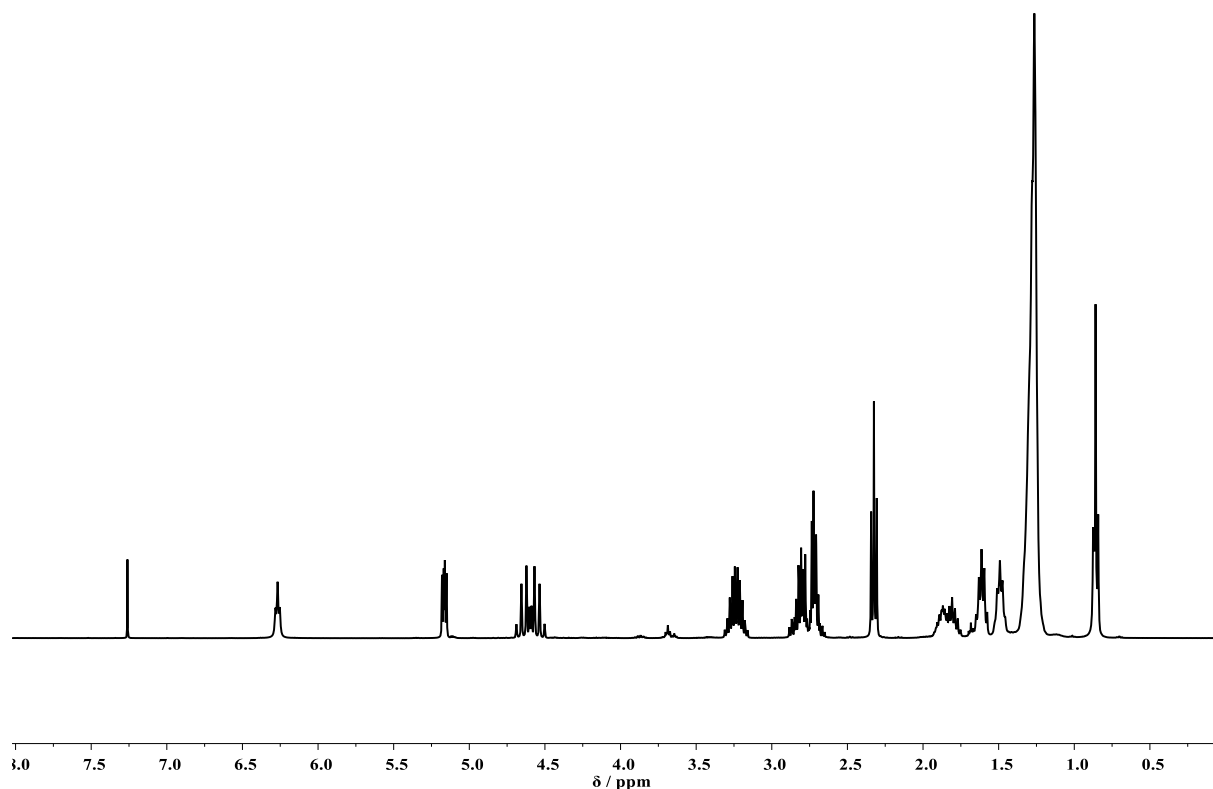
IR (ATR): ν/cm^{-1} = 2926.9 (m), 2856.3 (m), 1743.1 (s), 1652.0 (m), 1542.6 (w), 1352.4 (w), 1226.0 (vs), 1179.7 (vs), 1144.2 (vs), 1020.0 (m), 909.4 (w), 735.9 (w), 628.5 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.27 (t, J = 5.8 Hz, 1 H, NH^1), 5.22 – 5.10 (m, 1 H, CH^2), 4.71 – 4.49 (m, 2 H, CH^3), 3.31 – 3.13 (m, 2 H, CH_2^4), 2.93 – 2.63 (m, 4 H, CH_2^5), 2.32 (t, J = 7.5 Hz, 2 H, CH_2^6), 2.00 – 1.74 (m, 2 H, CH_2^7), 1.69 – 1.56 (m, 2 H, CH_2^8), 1.54 – 1.43 (m, 2 H, CH_2^9), 1.39 – 1.16 (m, 20 H, CH_2^{10}), 0.98 – 0.80 (m, 3 H, CH_3^{11}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 178.91, 171.52, 170.93, 169.78, 74.88, 59.70 (t, J = 26.8 Hz), 39.48, 34.12, 31.92, 31.73, 29.47, 29.37, 29.26, 29.22, 29.10, 29.05, 29.01, 28.80, 26.90, 24.92, 24.84, 22.66, 14.14. 179.16, 171.69, 169.77, 75.53, 44.09, 43.62, 39.41, 34.18, 31.22, 29.57, 29.46, 29.36, 29.23, 29.10, 27.46, 26.92, 24.83, 22.35, 22.00, 11.71, 11.68.

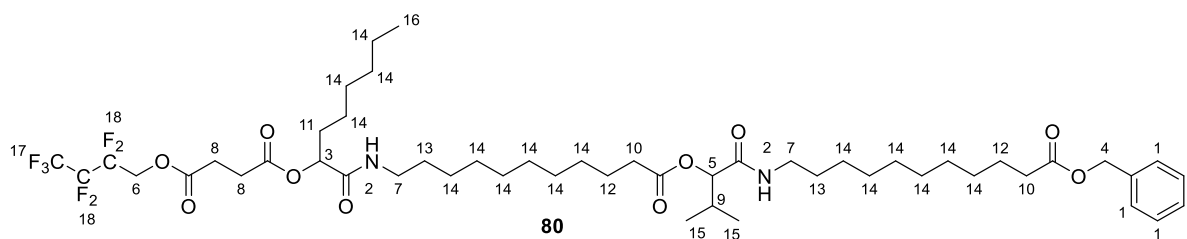
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -80.85 (t, J = 9.2 Hz, 3 F, CF_3^{12}), -120.39 – -120.91 (m, 2 F, CF_2^{13}), -127.07 – -129.04 (m, 2 F, CF_2^{13}). Total integral of CF_2 region normalized with respect to the CF_3^{12} group = 4.

ESI-MS [m/z]: $[\text{M} + \text{Na}]^+$ calculated for $^{12}\text{C}_{27}^{1}\text{H}_{42}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 648.2742; found, 648.2729, Δ = 1.3 mmu.



Supplementary Figure 118: ^1H -NMR of compound 79 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 794 mg of **79** (1.27 mmol, 1.00 eq.) was stirred in 4.00 mL DCM. Subsequently, 174 μ L isobutyraldehyde **14c** (137 mg, 1.90 mmol, 1.50 eq.) and 577 mg of the monomer **M1** (1.90 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 2:1) to yield the passerini product **80** as a pale highly viscous oil. (1.12 g, 1.12 mol, 88.2%).

R_f = 0.21 in cyclohexane / ethyl acetate (2:1).

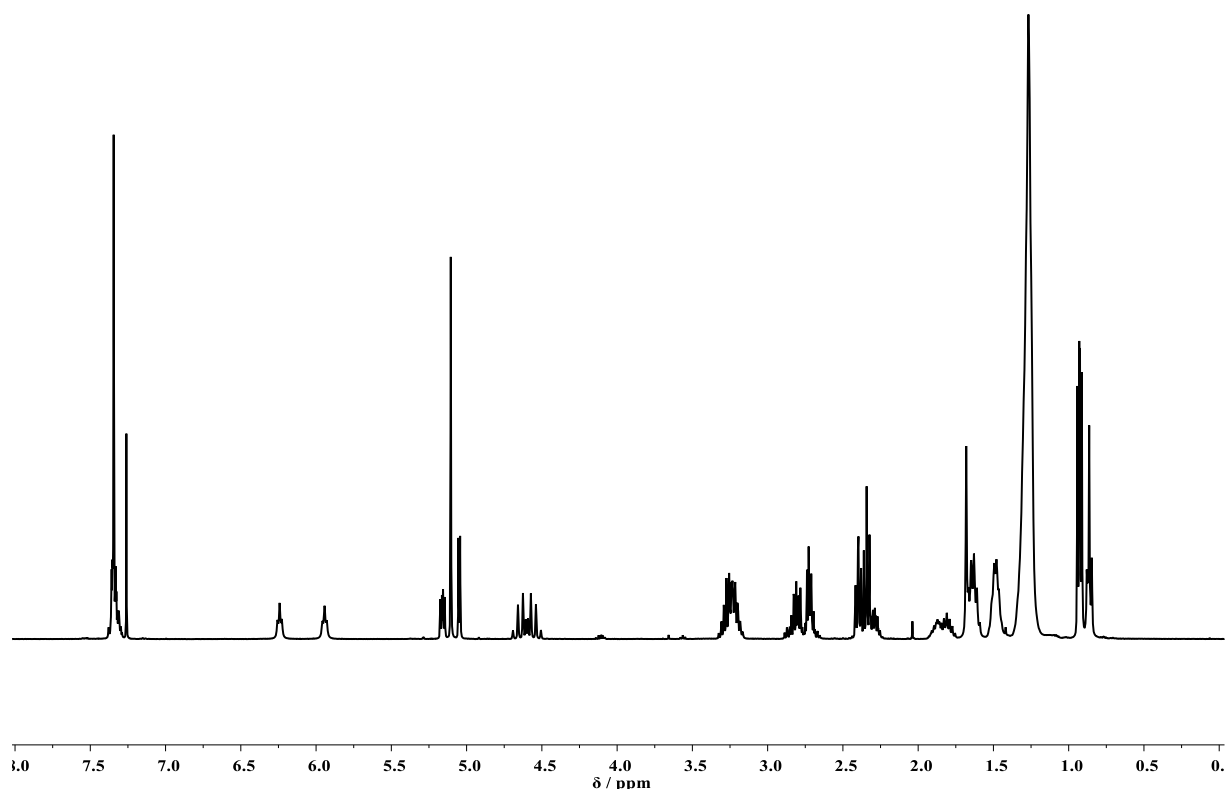
IR (ATR): ν / cm^{-1} = 3308.0 (vw), 2926.1 (m), 2854.9 (w), 1738.8 (s), 1655.3 (s), 1534.8 (m), 1457.1 (w), 1352.5 (w), 1226.6 (vs), 1144.7 (vs), 1019.3 (m), 909.9 (w), 735.7 (w), 697.3 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.36 – 7.21 (m, 5 H, CH_{Ar}^1), 6.18 (t, J = 5.8 Hz, 1 H, NH^2), 5.88 (t, J = 5.9 Hz, 1 H, NH^2), 5.13 – 5.07 (m, 1 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.99 (d, J = 4.4 Hz, 1 H, CH^5), 4.66 – 4.43 (m, 2 H, CH_2^6), 3.30 – 3.09 (m, 4 H, CH^7), 2.83 – 2.59 (m, 4 H, CH_2^8), 2.39 – 2.19 (m, 5 H, CH^9 , CH_2^{10}), 1.90 – 1.69 (m, 2 H, CH_2^{11}), 1.67 – 1.58 (m, 4 H, CH_2^{12}), 1.49 – 1.35 (m, 4 H, CH_2^{13}), 1.29 – 1.10 (m, 32 H, CH_2^{14}), 0.92 – 0.84 (m, 6 H, CH_3^{15}), 0.83 – 0.77 (m, 3 H, CH_3^{16}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.68, 171.49, 170.89, 169.63, 169.40, 136.26, 128.67, 128.28, 78.05, 74.88, 66.20, 59.68 (t, J = 26.8 Hz), 39.43, 39.29, 34.45, 34.42, 31.94, 31.72, 30.65, 29.71, 29.58, 29.55, 29.54, 29.49, 29.46, 29.33, 29.25, 29.23, 29.04, 29.01, 28.79, 26.96, 26.95, 25.13, 25.07, 24.93, 22.65, 18.90, 17.07, 14.14.

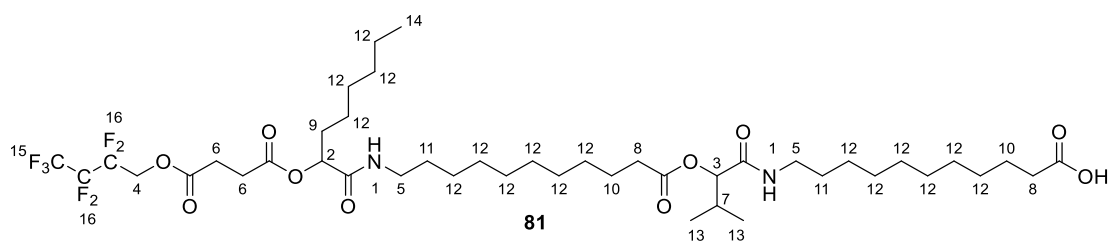
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.16 (t, J = 9.3 Hz, 3 F, CF_3^{17}), -124.27 – -125.33 (m, 2 F, CF_2^{18}), -131.44 – -132.73 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{50}^{1}\text{H}_{77}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_7$, 1021.5359; found, 1021.5337, Δ = 2.2 mmu.



Supplementary Figure 119: ^1H -NMR of compound **80** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.03 g of **80** (1.03 mmol, 1.00 eq.) were dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Afterwards, 206 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **81** was obtained as a pale highly viscous oil in a yield of 98.1% (918 mg, 1.01 mmol).

IR (ATR): ν/cm^{-1} = 3305.8 (vw), 2926.4 (s), 2855.3 (m), 1741.5 (s), 1652.3 (s), 1540.2 (m), 1463.6 (w), 1353.0 (w), 1226.3 (vs), 1144.1 (vs), 1019.3 (m), 909.7 (w), 735.6 (w), 627.5 (vw).

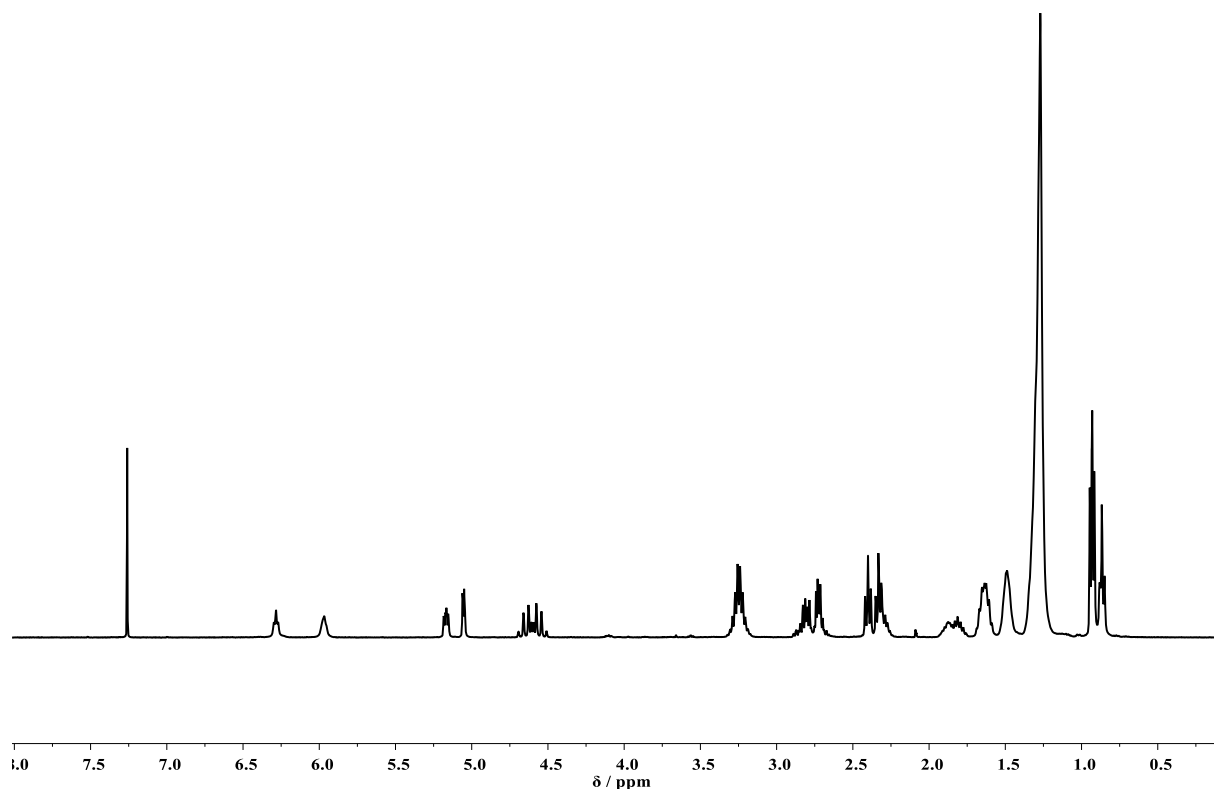
^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.22 (t, J = 5.8 Hz, 1 H, NH^1), 5.97 – 5.86 (m, 1 H, NH^2), 5.13 – 5.06 (m, 1 H, CH^2), 5.01 – 4.96 (m, 1 H, CH^3), 4.64 – 4.43 (m, 2 H, CH_2^4), 3.30 – 3.09 (m, 4 H,

CH₂⁵), 2.85 – 2.59 (m, 4 H, CH₂⁶), 2.37 – 2.17 (m, 5 H, CH⁷, CH₂⁸), 1.90 – 1.68 (m, 2 H, CH₂⁹), 1.64 – 1.50 (m, 4 H, CH₂¹⁰), 1.48 – 1.35 (m, 4 H, CH₂¹¹), 1.33 – 1.07 (m, 32 H, CH₂¹²), 0.89 – 0.84 (m, 6 H, CH₃¹³), 0.83 – 0.75 (m, 3 H, CH₃¹⁴).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 172.71, 171.53, 170.94, 169.83, 169.51, 78.08, 74.87, 59.70 (t, J = 26.9 Hz), 39.51, 39.28, 34.43, 34.00, 33.96, 31.91, 31.72, 30.62, 29.60, 29.52, 29.51, 29.43, 29.42, 29.36, 29.35, 29.28, 29.21, 29.20, 29.09, 29.05, 29.00, 28.80, 26.95, 26.90, 25.16, 24.93, 24.85, 22.66, 18.90, 17.07, 14.14.

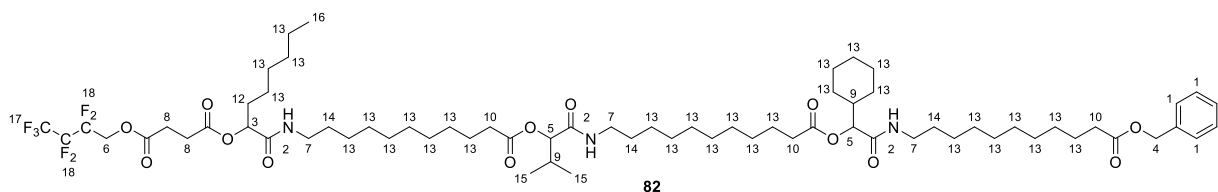
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -84.58 – -86.46 (m, 3 F, CF₃¹⁵), -124.16 – -125.27 (m, 2 F, CF₂¹⁶), -131.44 – -132.90 (m, 2 F, CF₂¹⁶). Total integral of CF₂ region normalized with respect to the CF₃¹⁵ group = 4.

ESI-MS [m/z]: [M + Na]⁺ calculated for ¹²C₄₃¹H₇₁¹⁶O₁₀¹⁴N₂¹⁹F₇, 931.4889; found, 931.4871, Δ = 1.8 mmu.



Supplementary Figure 120: ¹H-NMR of compound 81 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 831 mg **81** (895 μmol , 1.00 eq.) was stirred in 4.00 mL DCM. Subsequently, 163 μL cyclohexanecarboxaldehyde **14j** (151 mg, 1.34 mmol, 1.50 eq.) and 407 mg of the monomer **M1** (1.34 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **82** as a pale highly viscous oil. (880 mg, 665 μmol , 74.3%).

R_f = 0.13 in cyclohexane / ethyl acetate (2:1).

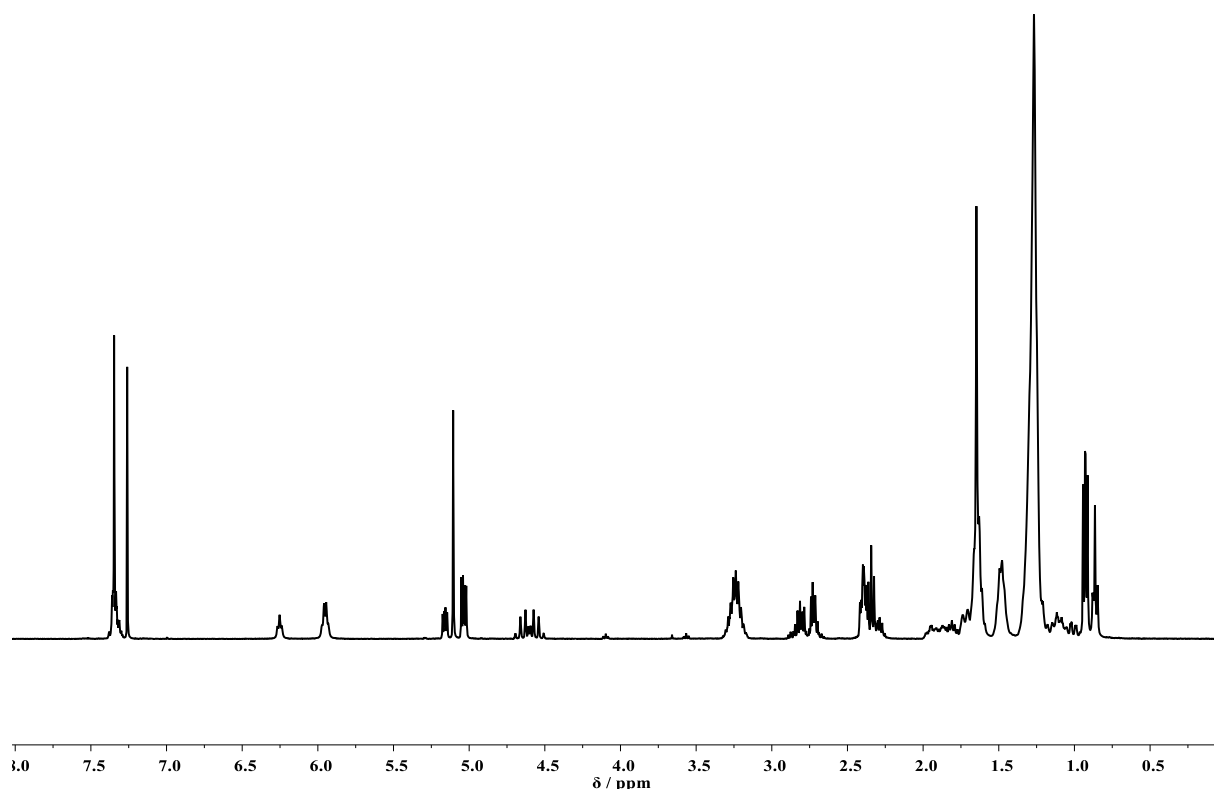
IR (ATR): ν / cm^{-1} = 3306.2 (vw), 2925.2 (s), 2853.8 (m), 1738.9 (s), 1654.4 (s), 1534.8 (m), 1454.6 (w), 1352.8 (w), 1226.9 (s), 1145.7 (vs), 1019.3 (m), 735.6 (w), 697.4 (w).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.28 (m, 5 H, CH_{Ar}^1), 6.25 (t, J = 5.8 Hz, 1 H, NH^2), 6.02 – 5.90 (m, 2 H, NH^2), 5.19 – 5.14 (m, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 5.08 – 5.00 (m, 2 H, CH_2^5), 4.72 – 4.50 (m, 2 H, CH_2^6), 3.34 – 3.16 (m, 6 H, CH_2^7), 2.90 – 2.65 (m, 4 H, CH_2^8), 2.43 – 2.24 (m, 7 H, CH^9 , CH_2^{10}), 2.01 – 1.77 (m, 3 H, CH^{11} , CH_2^{12}), 1.76 – 1.58 (m, 12 H, CH_2^{13}), 1.56 – 1.41 (m, 6 H, CH^{14}), 1.37 – 1.04 (m, 48 H, CH_2^{13}), 0.96 – 0.90 (m, 6 H, CH_3^{15}), 0.90 – 0.82 (m, 3 H, CH_3^{16}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.83, 172.70, 172.69, 171.51, 170.91, 169.65, 169.43, 169.35, 136.26, 128.68, 128.29, 78.06, 77.76, 74.88, 66.21, 59.69, 40.12, 39.44, 39.29, 34.46, 34.43, 31.94, 31.73, 30.65, 29.72, 29.72, 29.58, 29.55, 29.50, 29.48, 29.35, 29.31, 29.26, 29.24, 29.05, 29.02, 28.80, 27.43, 26.98, 26.97, 26.21, 26.13, 26.02, 25.13, 25.08, 24.94, 22.66, 18.91, 17.08, 14.15.

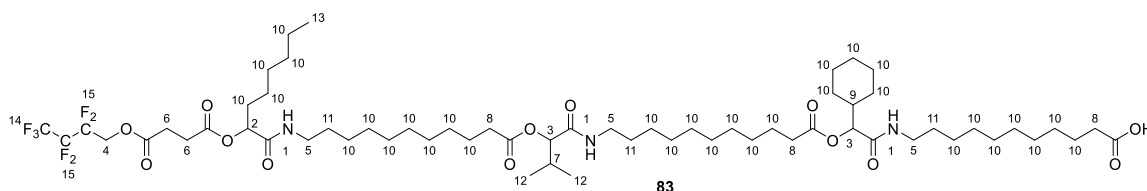
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.15 (t, J = 9.2 Hz, 3 F, CF_3^{17}), -124.51 – -125.62 (m, 2 F, CF_2^{18}), -131.79 – -133.84 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$]⁺ calculated for $^{12}\text{C}_{69}^{1}\text{H}_{110}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_7$, 1322.8000; found, 1322.7981, Δ = 1.9 mmu.



Supplementary Figure 121: ^1H -NMR of compound **82** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 829 mg of **82** (627 μmol , 1.00 eq.) were dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Afterwards, 166 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **83** was obtained as a pale highly viscous oil in a quant. yield. (772 mg, 627 mmol).

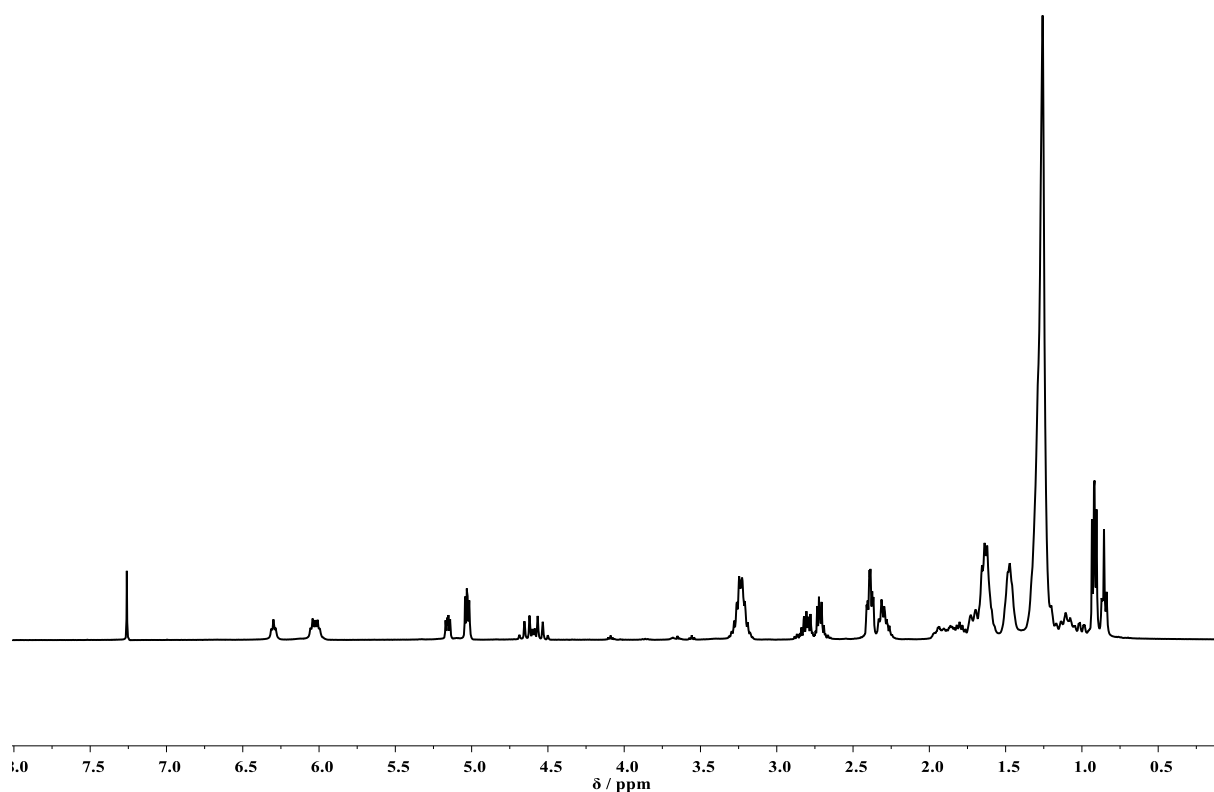
IR (ATR): ν/cm^{-1} = 3294.0 (vw), 2925.3 (s), 2854.1 (m), 1740.3 (s), 1651.1 (s), 1538.6 (m), 1452.6 (w), 1370.2 (w), 1226.3 (vs), 1145.1 (vs), 1019.1 (w), 909.9 (w), 735.4 (w).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.24 (t, J = 5.8 Hz, 1 H, NH^1), 6.06 – 5.88 (m, 2 H, NH^1), 5.14 – 5.07 (m, 1 H, CH^2), 5.03 – 4.92 (m, 2 H, CH^3), 4.70 – 4.39 (m, 2 H, CH_2^4), 3.26 – 3.08 (m, 6 H, CH_2^5), 2.84 – 2.58 (m, 4 H, CH_2^6), 2.39 – 2.16 (m, 7 H, CH^7 , CH_2^8), 1.94 – 1.50 (m, 15 H, CH^9 , CH_2^{10}),

1.48 – 1.33 (m, 6 H, CH₂¹¹), 1.33 – 0.94 (m, 48 H, CH₂¹⁰), 0.91 – 0.83 (m, 6 H, CH₃¹²), 0.83 – 0.77 (m, 3 H, CH₃¹³).

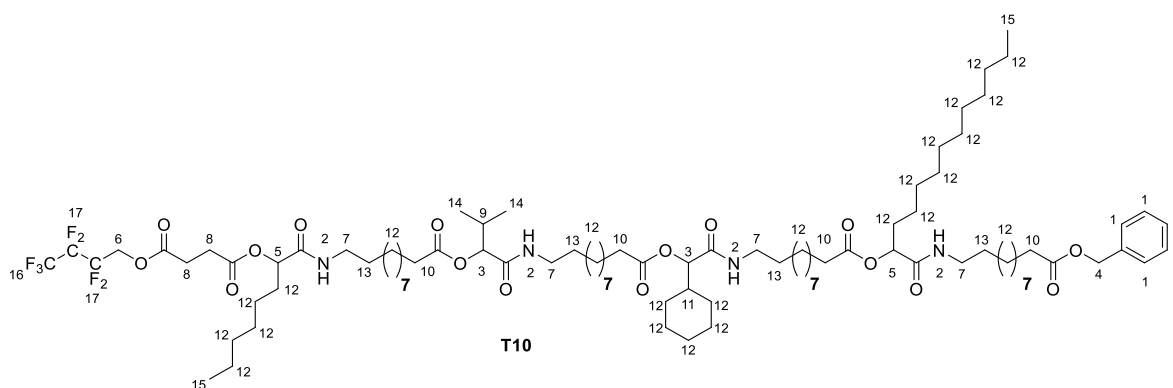
¹³C NMR (101 MHz, CDCl₃): δ / ppm = 172.77, 172.71, 171.52, 170.92, 169.77, 169.59, 169.45, 78.03, 77.74, 74.82, 59.65 (t, J = 27.0 Hz), 40.05, 39.45, 39.32, 39.25, 34.40, 34.08, 31.91, 31.70, 30.61, 29.67, 29.56, 29.49, 29.46, 29.34, 29.31, 29.29, 29.24, 29.21, 29.11, 29.02, 28.99, 28.77, 27.39, 26.94, 26.92, 26.90, 26.17, 26.10, 25.98, 25.12, 25.11, 24.90, 22.64, 18.87, 17.06, 14.13.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₆₂¹H₁₀₄¹⁶O₁₃¹⁴N₃¹⁹F₇, 1232.7530; found, 1232.7502, Δ = 2.8 mmu.



Supplementary Figure 122: ¹H-NMR of compound 83 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 686 mg of **83** (557 μmol , 1.00 eq.) was stirred in 4.00 mL DCM. Subsequently, 154 mg dodecanal (835 μmol , 1.50 eq.) and 252 mg of the monomer **M1** (835 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 1 day. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **T10** as a pale highly viscous oil. (707 mg, 412 μmol , 74.0%).

$R_f = 0.66$ in cyclohexane / ethyl acetate (1:1).

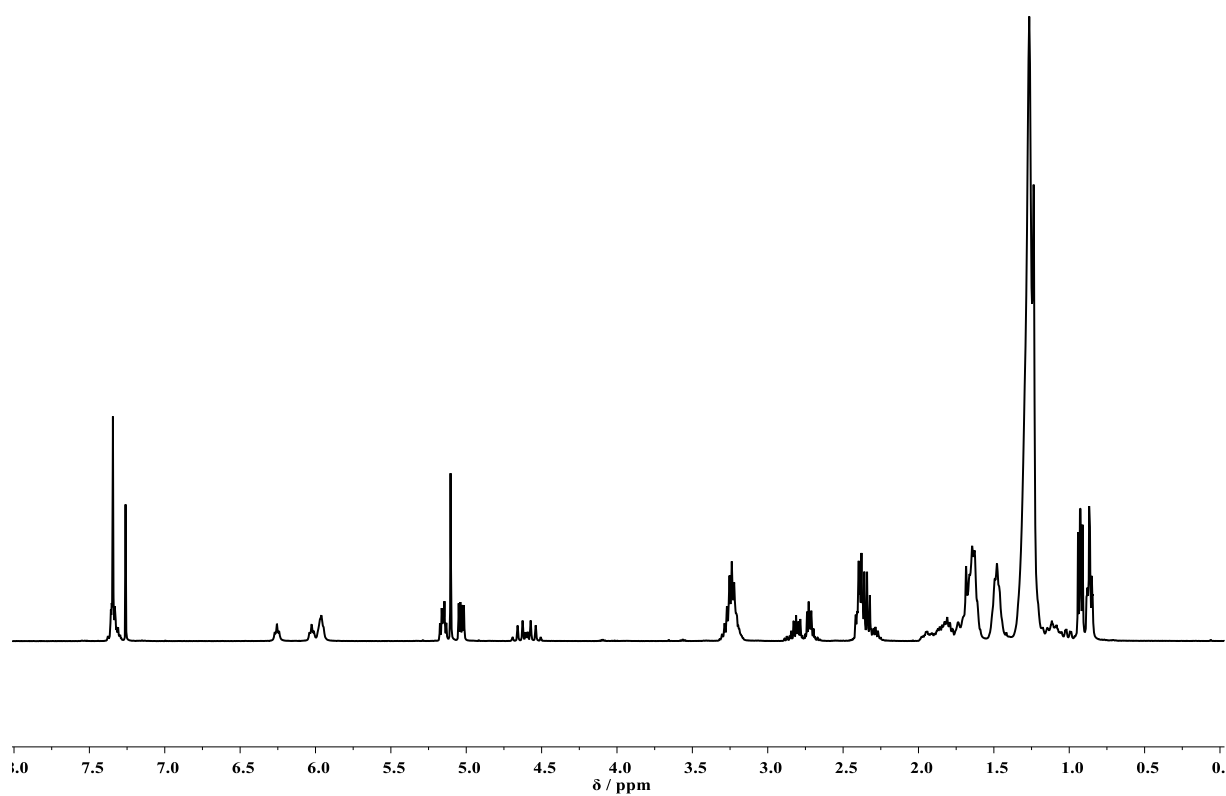
IR (ATR): $\nu / \text{cm}^{-1} = 3290.4$ (vw), 2920.8 (m), 2851.4 (w), 1736.9 (m), 1655.8 (m), 1557.1 (w), 1466.8 (vw), 1377.1 (vw), 1228.5 (w), 1205.6 (w), 1174.5 (m), 1019.8 (vw), 722.6 (vw), 696.6 (vw).

^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 7.41 - 7.28$ (m, 5 H, CH_{Ar}^1), 6.26 (t, $J = 5.8$ Hz, 1 H, NH^2), 6.06 – 5.93 (m, 3 H, NH^2), 5.19 – 5.13 (m, 2 H, CH^3), 5.10 (s, 2 H, CH_2^4), 5.07 – 4.99 (m, 2 H, CH^5), 4.72 – 4.48 (m, 2 H, CH_2^6), 3.34 – 3.14 (m, 8 H, CH_2^7), 2.90 – 2.65 (m, 4 H, CH_2^8), 2.43 – 2.24 (m, 9 H, CH^9 , CH_2^{10}), 2.00 – 1.58 (m, 19 H, CH^{11} , CH_2^{12}), 1.54 – 1.43 (m, 8 H, CH_2^{13}), 1.37 – 1.04 (m, 78 H, CH_2^{12}), 0.95 – 0.90 (m, 6 H, CH_3^{14}), 0.89 – 0.83 (m, 6 H, CH_3^{15}).

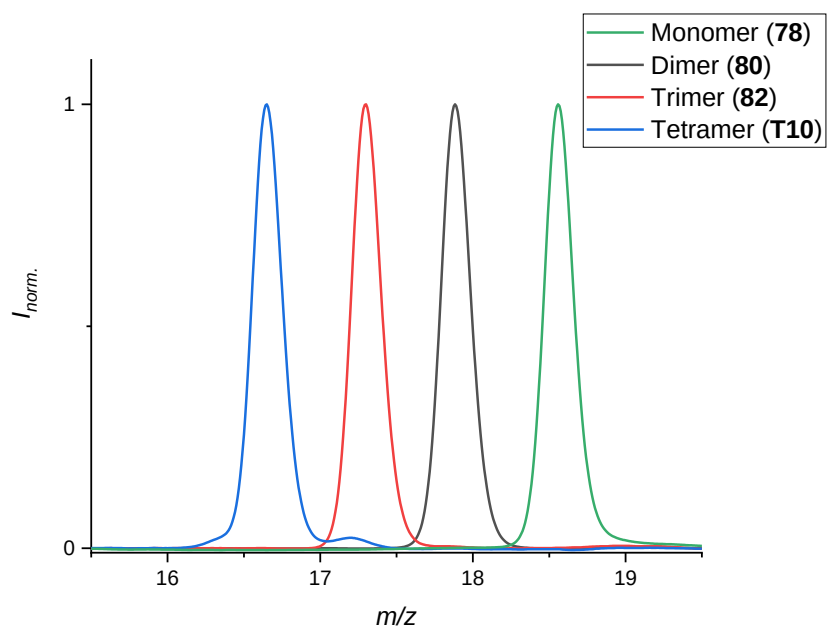
^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 173.82, 172.69, 172.60, 171.50, 170.90, 169.98, 169.63, 169.41, 169.35, 136.24, 128.67, 128.28, 78.03, 77.74, 74.86, 74.06, 66.20, 59.66, 40.10, 39.42, 39.32, 39.27, 34.44, 32.04, 31.93, 31.72, 30.64, 29.75, 29.72, 29.68, 29.67, 29.54, 29.49, 29.49, 29.34, 29.31, 29.26, 29.24, 29.04, 29.01, 28.79, 27.41, 26.96, 26.95, 26.20, 26.12, 26.01, 25.12, 25.07, 24.93, 24.89, 22.81, 22.65, 18.91, 17.07, 14.25, 14.15.$

^{19}F NMR (376 MHz, CDCl_3): $\delta / \text{ppm} = -83.46 - -86.58$ (m, 3 F, CF_3^{16}), $-123.51 - -126.45$ (m, 2 F, CF_2^{16}), $-131.44 - -133.84$ (m, 2 F, CF_2^{17}). Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 4.

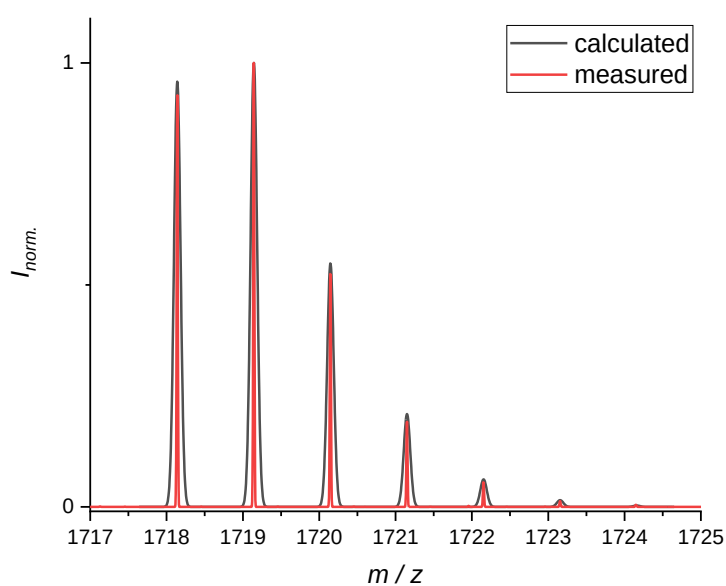
ESI-MS [m/z]: $[\text{M} + \text{H}]^+$ calculated for $^{12}\text{C}_{93}^{1}\text{H}_{155}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_7$, 1718.1399; found, 1718.1400, $\Delta = 0.1$ mmu.



Supplementary Figure 123: $^1\text{H-NMR}$ of compound T10 measured in CDCl_3 .



Supplementary Figure 124: SEC traces of the intermediates after each P3CR in the synthesis of product T10.



Supplementary Figure 125: High resolution ESI-MS measurement of T10. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

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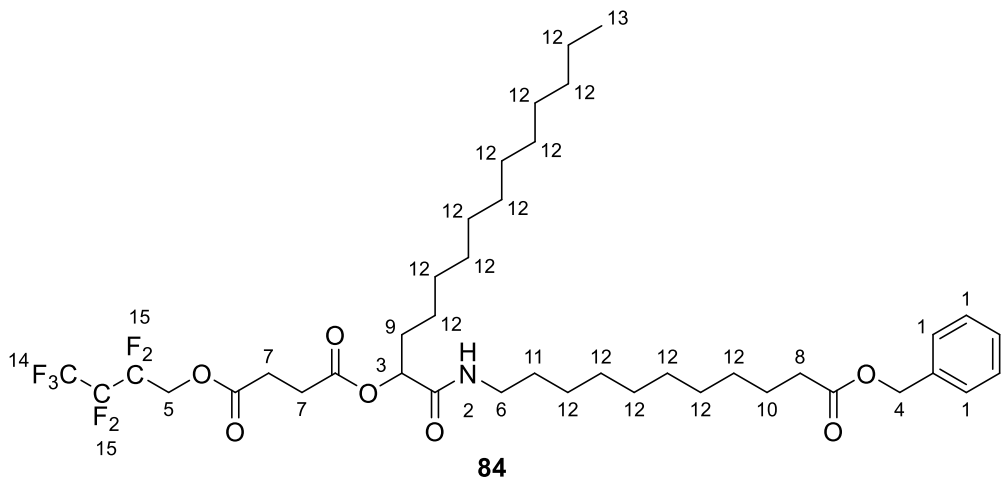
matching mass 1741.12135
cutoff 0.50000: 0 solutions (14 peaks)
cutoff 0.25000: 0 solutions (55 peaks)
cutoff 0.12500: 0 solutions (113 peaks)
cutoff 0.06250: 0 solutions (186 peaks)
cutoff 0.03125: 2 solutions (280 peaks)
cutoff 0.04688: 0 solutions (222 peaks)
cutoff 0.03906: 0 solutions (250 peaks)
cutoff 0.03516: 0 solutions (262 peaks)
cutoff 0.03320: 1 solutions (275 peaks)
1741.12135 ≈ 299.015430 + 325.261700 + 283.214750 + 323.246050 + 395.339950 + 91.054780 (sides Heptanal,
Isobutyraldehyde, Cyclohexancarboxaldehyde, Dodecanal; error -23.98869)
Press ENTER to quit ...

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Supplementary Figure 126: Screenshot of the automated read-out of T10, sodium trifluoroacetate was used as additive during the measurement.

1.3.5.4 Synthesis of tetramer T11

Passerini reaction



In a 50 mL round bottom flask, 500 mg **TAG2** (1.67 mmol, 1.00 eq.) was stirred in 2.00 mL DCM. Subsequently, 593 μ L tridecanal **14d** (496 mg, 2.50 mmol, 1.50 eq.) and 754 mg of the monomer **M1** (2.50 mmol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (7:1 $\rightarrow$ 5:1) to yield the passerini product **84** as a pale highly viscous oil. (1.03 g, 1.30 mmol, 78.0%).

R_f = 0.45 in cyclohexane / ethyl acetate (3:1).

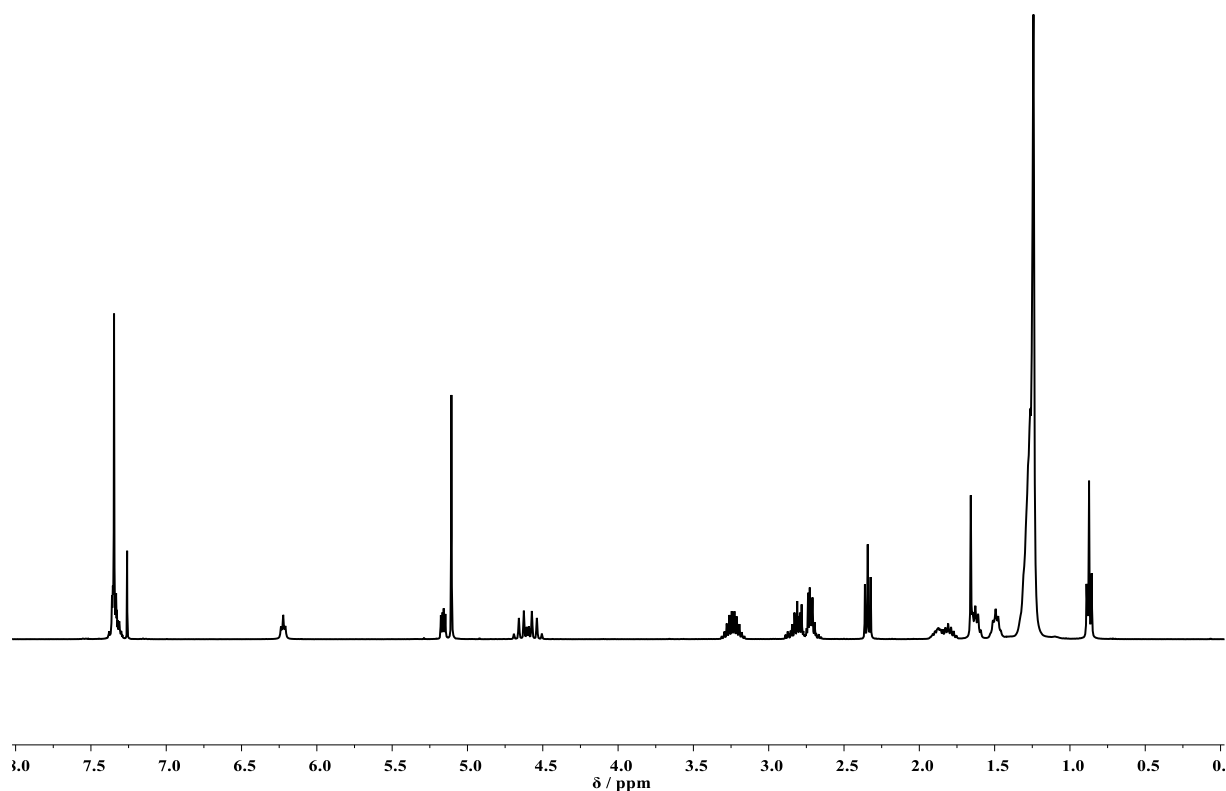
IR (ATR): ν / cm^{-1} = 3305.5 (vw), 2924.2 (s), 2853.9 (m), 1739.8 (s), 1656.6 (m), 1535.6 (w), 1456.5 (w), 1352.2 (w), 1226.6 (vs), 1144.2 (vs), 1019.9 (m), 909.7 (w), 735.7 (m), 696.9 (m).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.44 – 7.30 (m, 5 H, CH_{Ar}^1), 6.22 (t, J = 5.8 Hz, 1 H, NH^2), 5.19 – 5.13 (m, 1 H, CH^3), 5.11 (s, 2 H, CH_2^4), 4.73 – 4.49 (m, 2 H, CH_2^5), 3.34 – 3.15 (m, 2 H, CH_2^6), 2.91 – 2.66 (m, 4 H, CH_2^7), 2.34 (t, J = 7.6 Hz, 2 H, CH_2^8), 1.95 – 1.74 (m, 2 H, CH_2^9), 1.68 – 1.57 (m, 2 H, CH_2^{10}), 1.54 – 1.44 (m, 2 H, CH_2^{11}), 1.36 – 1.15 (m, 32 H, CH_2^{12}), 0.92 – 0.83 (m, 3 H, CH_3^{13}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 171.48, 170.89, 169.62, 136.27, 128.67, 128.29, 74.90, 66.19, 59.69 (t, J = 27.1 Hz), 39.45, 34.45, 32.05, 31.95, 29.78, 29.77, 29.75, 29.68, 29.58, 29.56, 29.54, 29.48, 29.37, 29.33, 29.24, 29.04, 28.79, 26.96, 25.06, 25.00, 22.82, 14.24.

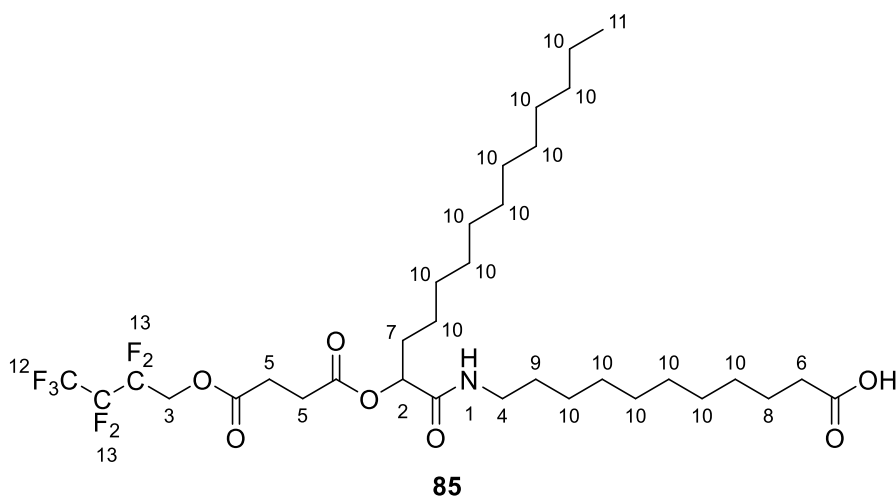
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.16 (t, J = 9.2, 3 F, CF_3^{14}), -123.69 – -125.74 (m, 2 F, CF_2^{15}), -131.26 – -133.08 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 4.

ESI-MS [m/z]: $[\text{M} + \text{Na}]^+$ calculated for $^{12}\text{C}_{40}^{1}\text{H}_{60}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 822.4150; found, 822.4133, Δ = 1.7 mmu.



Supplementary Figure 127: ^1H -NMR of compound **84** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 1.03 g of **84** (1.28 mmol, 1.00 eq.) were dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Afterwards, 103 mg (10 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under

reduced pressure. The product **85** was obtained as a pale highly viscous oil in a yield of 98.4% (894 mg, 1.26 mmol).

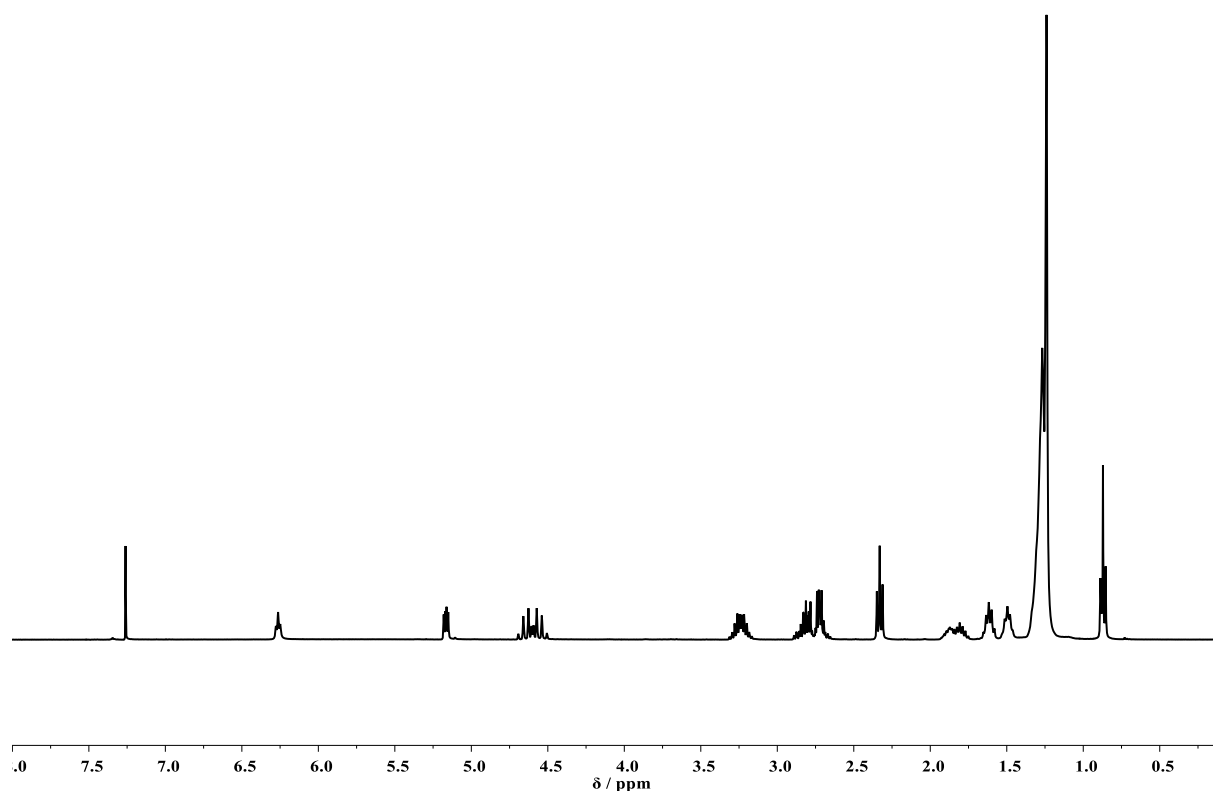
IR (ATR): ν/cm^{-1} = 3293.4 (vw), 2918.0 (s), 2851.6 (s), 1736.1 (vs), 1694.9 (s), 1657.2 (vs), 1560.9 (w), 1470.0 (w), 1419.7 (w), 1343.8 (m), 1278.1 (m), 1220.9 (vs), 1176.8 (vs), 1131.7 (vs), 1021.9 (m), 929.3 (m), 800.9 (w), 722.1 (w), 678.8 (w), 624.1 (w), 528.8 (w), 462.8 (vw).

^1H NMR (400 MHz, CDCl_3): δ/ppm = 6.26 (t, J = 5.8 Hz, 1 H, NH^1), 5.21 – 5.13 (m, 1 H, CH^2), 4.75 – 4.48 (m, 2 H, CH_2^3), 3.35 – 3.15 (m, 2 H, CH_2^4), 2.91 – 2.64 (m, 4 H, CH_2^5), 2.33 (t, J = 7.5 Hz, 2 H, CH_2^6), 1.94 – 1.73 (m, 2 H, CH_2^7), 1.71 – 1.57 (m, 2 H, CH_2^8), 1.54 – 1.42 (m, 2 H, CH_2^9), 1.38 – 1.14 (m, 32 H, CH_2^{10}), 0.91 – 0.83 (m, 3 H, CH_3^{11}).

^{13}C NMR (101 MHz, CDCl_3): δ/ppm = 179.82, 172.29, 171.70, 170.54, 75.64, 60.46 (t, J = 26.9 Hz), 40.24, 34.86, 32.81, 32.69, 30.54, 30.54, 30.52, 30.45, 30.32, 30.24, 30.13, 30.03, 29.99, 29.86, 29.81, 29.55, 27.66, 25.76, 25.58, 23.58, 15.00.

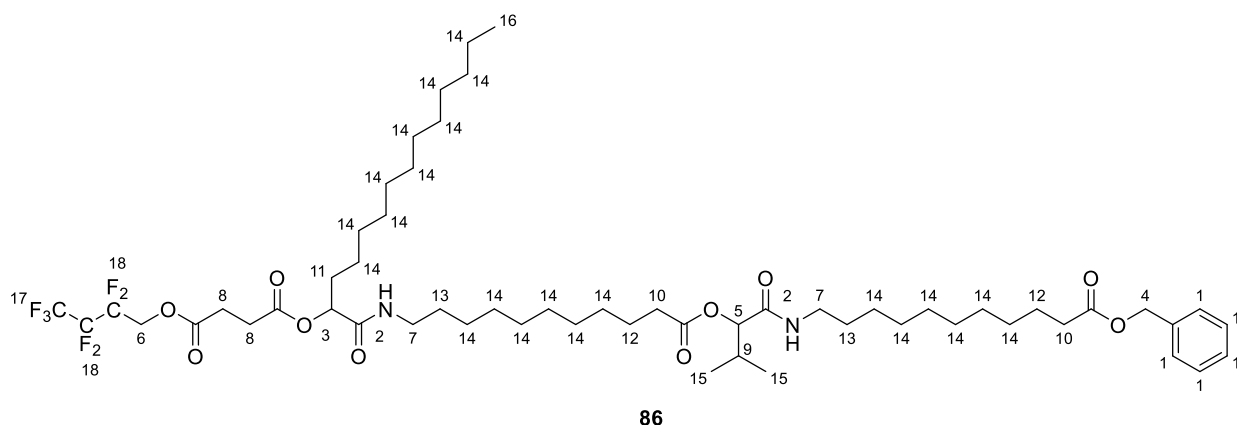
^{19}F NMR (376 MHz, CDCl_3): δ/ppm = -85.17 (t, J = 9.2 Hz, 3 F, CF_3^{12}), -124.45 – -128.85 (m, 2 F, CF_2^{13}), -131.44 – -136.02 (m, 2 F, CF_2^{13}). Total integral of CF_2 region normalized with respect to the CF_3^{12} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{33}^{1}\text{H}_{54}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 710.3861; found, 710.3848, Δ = 1.3 mmu.



Supplementary Figure 128: ^1H -NMR of compound **85** measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 420 mg **85** (592 μmol , 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 81.1 μL isobutyraldehyde **14c** (64.0 mg, 888 μmol , 1.50 eq.) and 268 mg of the monomer **M1** (888 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 1:1) to yield the passerini product **86** as a pale highly viscous oil. (618 g, 571 μmol , 96.4%).

R_f = 0.36 in cyclohexane / ethyl acetate (2:1).

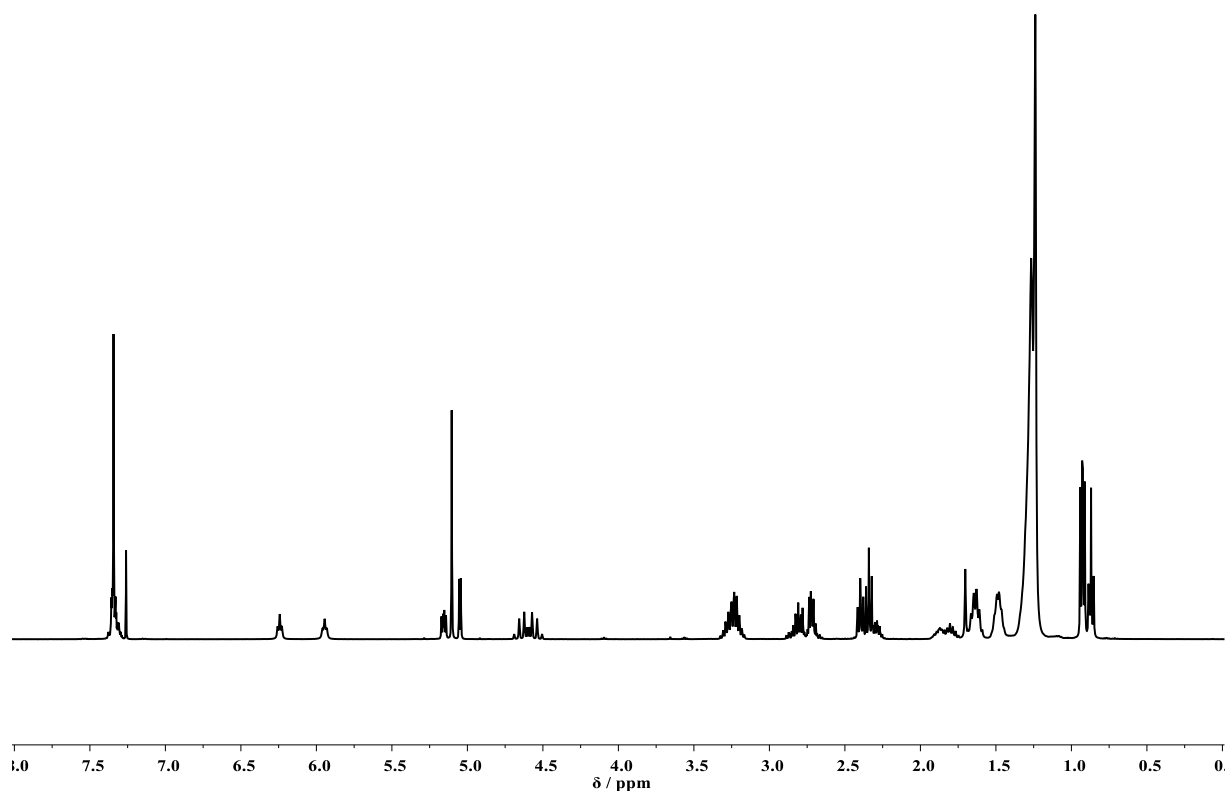
IR (ATR): ν / cm^{-1} = 3306.9 (w), 2917.5 (s), 2850.1 (s), 1732.5 (vs), 1656.2 (vs), 1544.3 (m), 1467.2 (w), 1312.7 (w), 1228.4 (vs), 1148.4 (vs), 1020.4 (m), 979.6 (m), 913.5 (m), 800.8 (vw), 735.0 (m), 696.5 (m), 536.6 (vw), 474.9 (vw), 422.4 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 7.43 – 7.28 (m, 5 H, $\text{CH}_{\text{Ar}}^{17}$), 6.24 (t, J = 5.8 Hz, 1 H, NH^{21}), 5.95 (t, J = 5.9 Hz, 1 H, NH^{21}), 5.19 – 5.13 (m, 1 H, CH^3), 5.10 (s, 2 H, CH^4), 5.05 (d, J = 4.4 Hz, 1 H, CH^5), 4.71 – 4.49 (m, 2 H, CH_2^6), 3.36 – 3.14 (m, 4 H, CH_2^7), 2.89 – 2.65 (m, 4 H, CH_2^8), 2.44 – 2.22 (m, 5 H, CH^9 , CH_2^{10}), 1.94 – 1.73 (m, 2 H, CH_2^{11}), 1.69 – 1.57 (m, 4 H, CH_2^{12}), 1.54 – 1.43 (m, 4 H, CH_2^{13}), 1.36 – 1.20 (m, 44 H, CH^{14}), 0.96 – 0.90 (m, 6 H, CH_3^{15}), 0.89 – 0.83 (m, 3 H, CH_2^{16}).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.81, 172.66, 171.48, 170.89, 169.63, 169.39, 136.27, 128.66, 128.28, 78.05, 74.88, 66.19, 59.67 (t, J = 27.0 Hz), 39.43, 39.28, 34.44, 34.42, 32.04, 31.94, 30.65, 29.76, 29.74, 29.71, 29.67, 29.58, 29.55, 29.49, 29.47, 29.36, 29.33, 29.26, 29.23, 29.04, 28.79, 26.96, 26.95, 25.13, 25.06, 25.00, 22.81, 18.90, 17.06, 14.23.

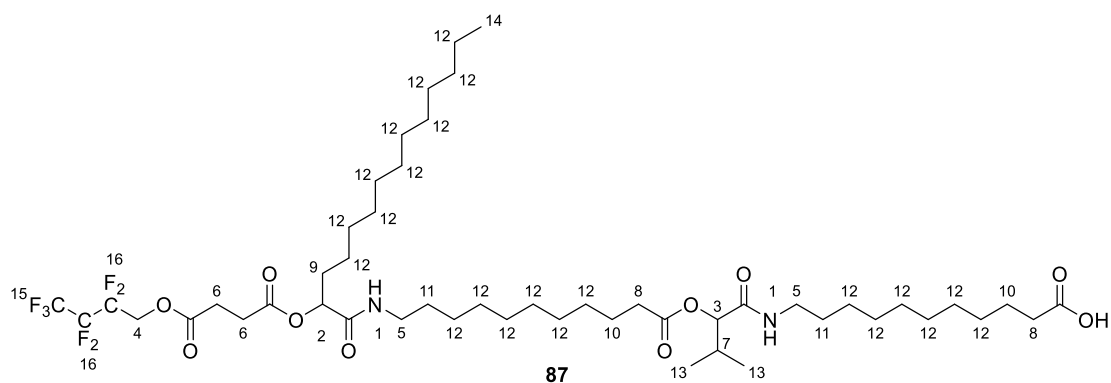
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.16 (t, J = 9.2 Hz, 3 F, CF_3^{17}), -124.27 – -125.74 (m, 2 F, CF_2^{18}), -131.26 – -133.08 (m, 2 F, CF_2^{18}). Total integral of CF_2 region normalized with respect to the CF_3^{17} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{56}^{1}\text{H}_{89}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_7$, 1083.6478; found, 1083.6459, Δ = 1.9 mmu.



Supplementary Figure 129: ^1H -NMR of compound **86** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 537 mg of **86** (496 μmol , 1.00 eq.) were dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Afterwards, 107 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **87** was obtained as a pale highly viscous oil in a yield of 98.2% (484 mg, 487 μmol).

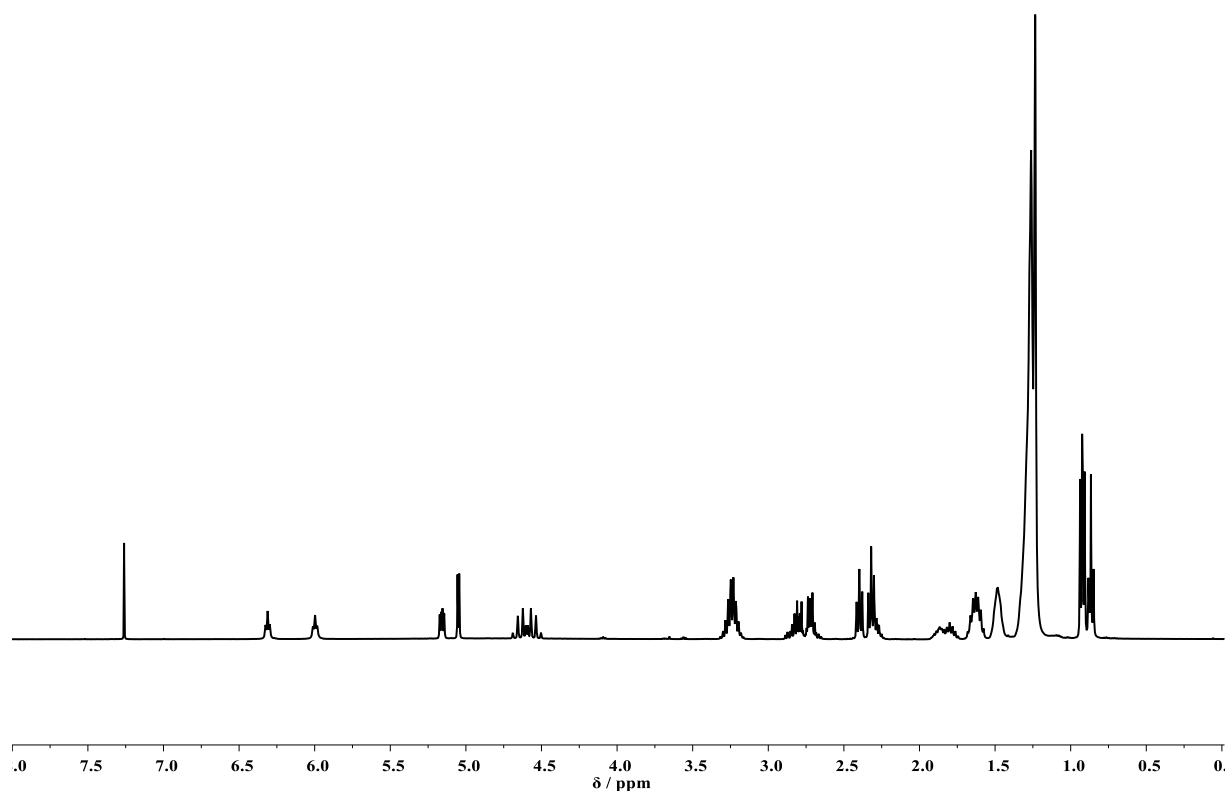
IR (ATR): $\nu / \text{cm}^{-1} = 3324.9$ (vw), 2920.4 (s), 2850.9 (s), 1741.3 (vs), 1702.3 (m), 1650.7 (vs), 1540.1 (m), 1466.9 (w), 1433.6 (w), 1354.3 (w), 1291.7 (m), 1228.4 (vs), 1145.5 (vs), 1020.8 (m), 955.5 (w), 721.0 (m), 658.5 (w), 534.0 (vw), 473.2 (vw), 403.9 (vw).

^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 6.31$ (t, $J = 5.8$ Hz, 1 H, NH^1), 6.00 (t, $J = 5.8$ Hz, 1 H, NH^1), 5.20 – 5.13 (m, 1 H, CH^2), 5.05 (d, $J = 4.4$ Hz, 1 H, CH^3), 4.72 – 4.49 (m, 2 H, CH_2^4), 3.36 – 3.14 (m, 4 H, CH_2^5), 2.92 – 2.64 (m, 4 H, CH_2^6), 2.45 – 2.24 (m, 5 H, CH^7 , CH_2^8), 1.95 – 1.71 (m, 2 H, CH_2^9), 1.68 – 1.56 (m, 4 H, CH_2^{10}), 1.54 – 1.40 (m, 4 H, CH_2^{11}), 1.40 – 1.14 (m, 44 H, CH_2^{12}), 0.95 – 0.89 (m, 6 H, CH_3^{13}), 0.89 – 0.84 (m, 3 H, CH_3^{14}).

^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 178.15$, 172.71, 171.54, 170.96, 169.84, 169.53, 78.05, 74.85, 59.68 (t, $J = 26.7$ Hz), 39.49, 39.28, 34.41, 34.08, 32.04, 31.91, 30.61, 29.78, 29.77, 29.74, 29.67, 29.59, 29.55, 29.50, 29.47, 29.44, 29.34, 29.33, 29.27, 29.22, 29.10, 29.03, 28.78, 26.94, 26.90, 25.14, 24.99, 24.87, 22.81, 18.89, 17.05, 14.23.

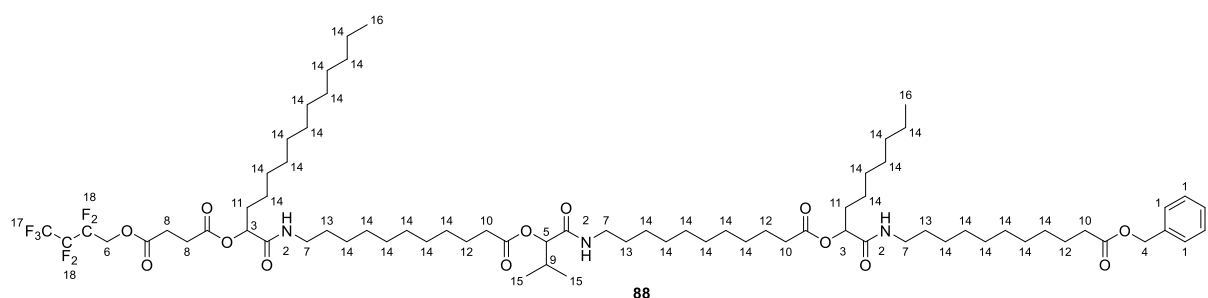
^{19}F NMR (376 MHz, CDCl_3): $\delta / \text{ppm} = -85.16$ (t, $J = 9.2$ Hz, 3 F, CF_3^{15}), -123.16 – -126.45 (m, 2 F, CF_2^{16}), -130.67 – -138.42 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{49}\text{H}_{83}^{16}\text{O}_{10}\text{N}_2^{19}\text{F}_7^{23}\text{Na}$, 1015.5828; found, 1015.5812, $\Delta = 1.6$ mmu.



Supplementary Figure 130: ^1H -NMR of compound 87 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 403 mg of **87** (406 μmol , 1.00 eq.) was stirred in 4.00 mL dichloromethane. Subsequently, 95.2 μL octanal **14i** (78.1 mg, 609 μmol , 1.50 eq.) and 184 mg of the monomer **M1** (609 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (6:1 $\rightarrow$ 4:1) to yield the passerini product **88** as a pale highly viscous oil. (430 mg, 302 μmol , 74.4%).

R_f = 0.53 in cyclohexane / ethyl acetate (2:1).

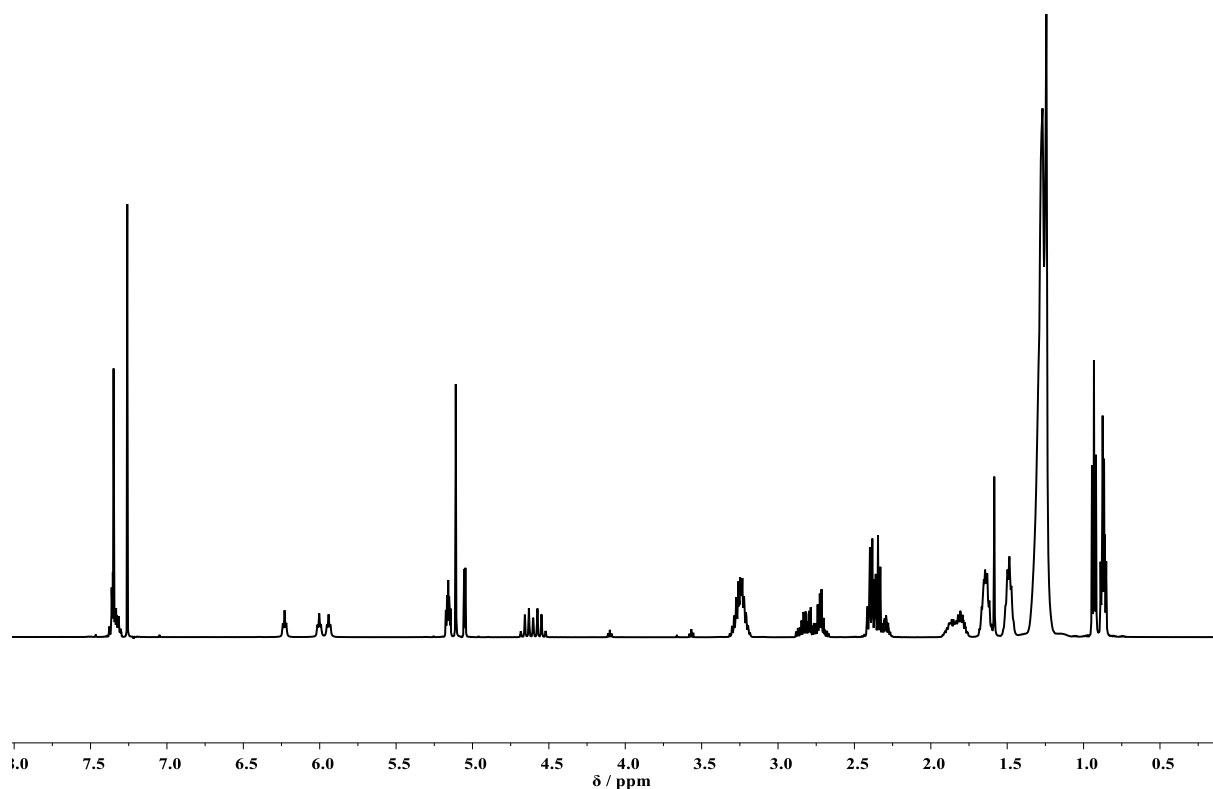
IR (ATR): ν / cm^{-1} = 3300.5 (vw), 2919.6 (w), 2850.9 (w), 2367.7 (vw), 2358.7 (vw), 2339.6 (vw), 2123.3 (vw), 1739.2 (w), 1655.9 (w), 1556.2 (vw), 1466.6 (vw), 1366.9 (vw), 1301.3 (vw), 1225.7 (w), 1164.1 (w), 1118.0 (w), 1019.5 (vw), 912.3 (vw), 803.3 (vw), 738.2 (vw), 696.7 (vw), 417.8 (vw).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.35 – 7.21 (m, 5 H, CH_{Ar}^1), 6.16 (t, J = 5.8 Hz, 1 H, NH^2), 5.94 (t, J = 5.9 Hz, 1 H, NH^2), 5.88 (t, J = 5.9 Hz, 1 H, NH^2), 5.12 – 5.07 (m, 2 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.98 (d, J = 4.4 Hz, 1 H, CH^5), 4.68 – 4.43 (m, 2 H, CH_2^6), 3.32 – 3.10 (m, 6 H, CH_2^7), 2.85 – 2.60 (m, 4 H, CH_2^8), 2.37 – 2.18 (m, 7 H, CH^9 , CH_2^{10}), 1.91 – 1.67 (m, 4 H, CH_2^{11}), 1.66 – 1.54 (m, 6 H, CH_2^{12}), 1.48 – 1.37 (m, 6 H, CH_2^{13}), 1.32 – 1.11 (m, 66 H, CH^{14}), 0.87 (t, J = 6.5 Hz, 6 H, CH_3^{15}), 0.83 – 0.74 (m, 6 H, CH_3^{16}).

^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.83, 172.69, 172.60, 171.52, 170.91, 169.98, 169.63, 169.41, 136.27, 128.69, 128.30, 78.05, 74.89, 74.08, 66.21, 59.69 (t, J = 26.9 Hz), 39.44, 39.33, 39.28, 34.46, 34.43, 32.06, 31.95, 31.87, 30.66, 29.80, 29.78, 29.76, 29.75, 29.70, 29.60, 29.57, 29.50, 29.36, 29.33, 29.28, 29.25, 29.05, 28.80, 26.98, 25.14, 25.11, 25.08, 25.02, 24.90, 22.83, 22.76, 18.92, 17.08, 14.26, 14.22.

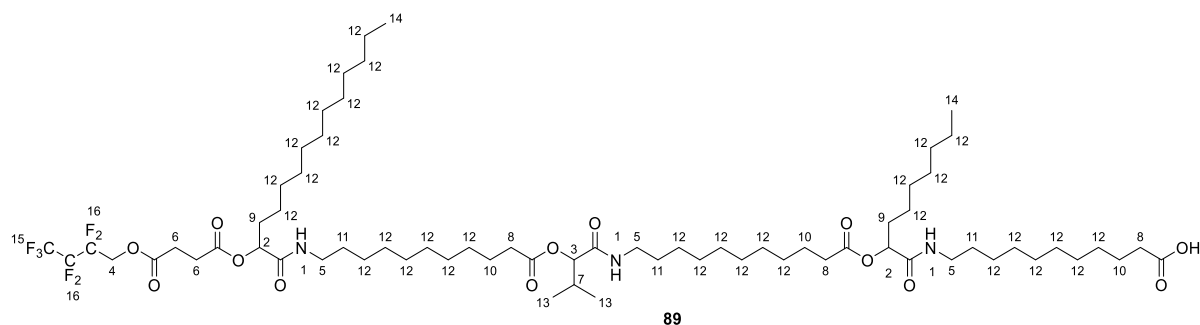
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -84.05 – -85.87 (m, 3 F, CF_3^{14}), -123.33 – -127.03 (m, 2 F, CF_2^{15}), -131.26 – -133.96 (m, 2 F, CF_2^{15}). Total integral of CF_2 region normalized with respect to the CF_3^{14} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{76}^{1}\text{H}_{126}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_7$, 1422.9252; found, 1422.9239, Δ = 1.3 mmu.



Supplementary Figure 131: ^1H -NMR of compound **88** measured in CDCl_3 .

Deprotection



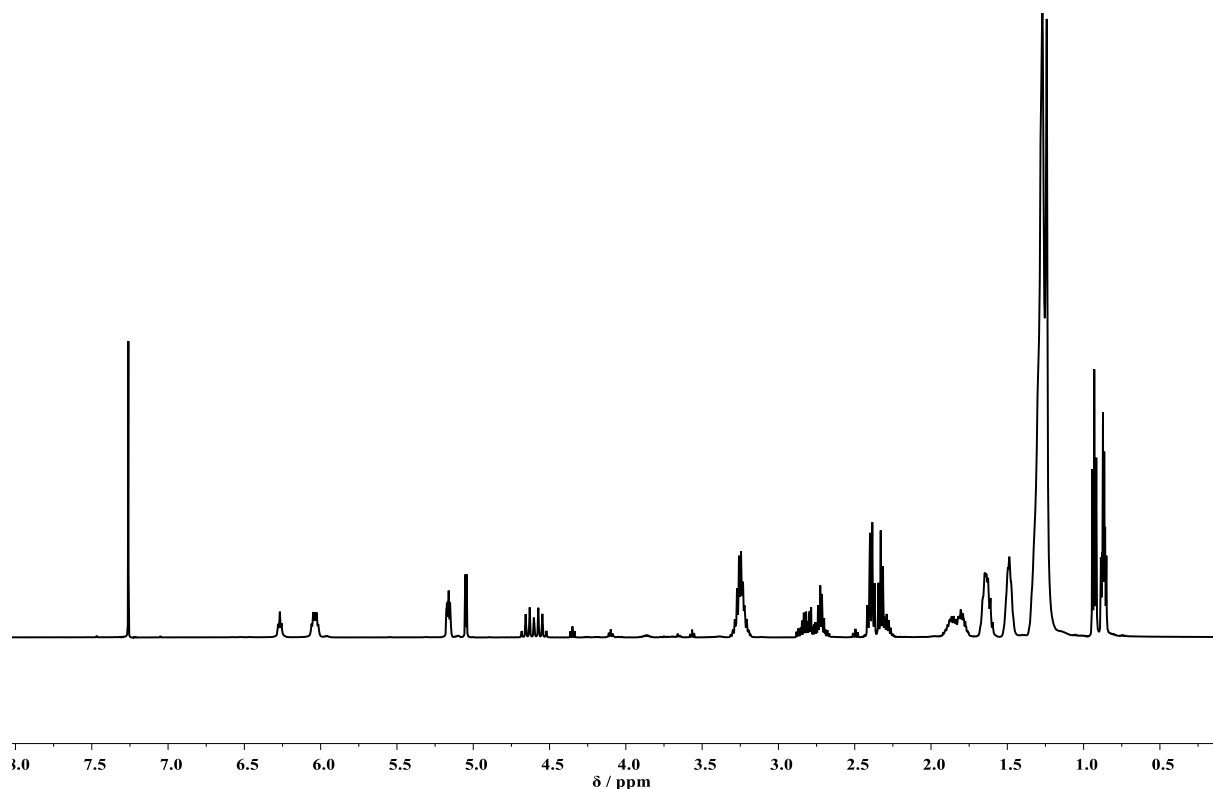
In a 50 mL round bottom flask, 363 mg of **88** (255 μmol , 1.00 eq.) were dissolved in 5.00 mL ethyl acetate and 5.00 mL THF. Afterwards, 166 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **89** was obtained as a pale highly viscous oil in a yield of 97.3% (331 mg, 249 μmol).

IR (ATR): ν / cm^{-1} = 3274.6 (vw), 2919.2 (vs), 2850.9 (s), 1740.1 (vs), 1654.7 (vs), 1545.2 (m), 1466.5 (w), 1365.9 (w), 1227.7 (vs), 1146.3 (vs), 1020.3 (m), 911.5 (w), 721.6 (w), 535.5 (vw), 474.0 (vw), 407.2 (vw).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 6.20 (t, J = 5.8 Hz, 1 H, NH^1), 6.03 – 5.93 (m, 2 H, NH^1), 5.14 – 5.07 (m, 2 H, CH^2), 4.98 (d, J = 4.5 Hz, 1 H, CH^3), 4.67 – 4.43 (m, 2 H, CH_2^4), 3.28 – 3.12 (m, 6 H, CH_2^5), 2.85 – 2.60 (m, 4 H, CH_2^6), 2.37 – 2.18 (m, 7 H, CH^7 , CH_2^8), 1.91 – 1.68 (m, 4 H, CH_2^9), 1.64 – 1.50 (m, 6 H, CH_2^{10}), 1.48 – 1.37 (m, 6 H, CH_2^{11}), 1.33 – 1.06 (m, 66 H, CH_2^{12}), 0.87 (t, J = 6.4 Hz, 6 H, CH_3^{13}), 0.83 – 0.76 (m, 6 H, CH_3^{14}).

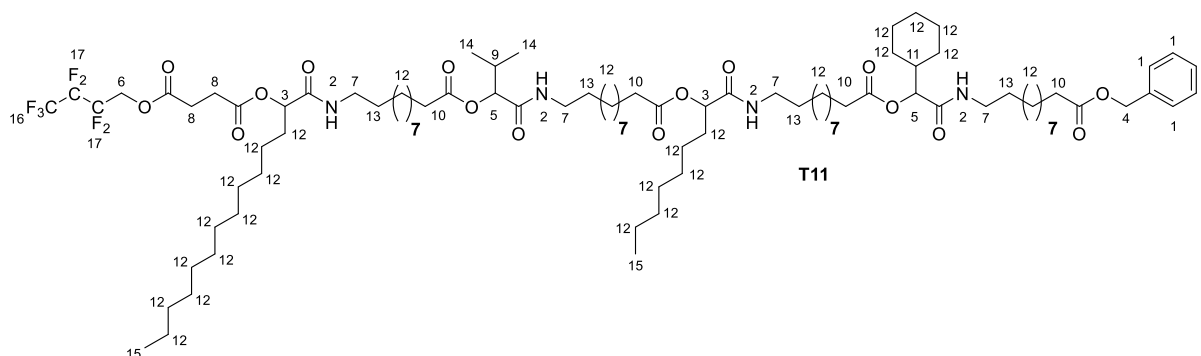
^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 177.05, 172.80, 172.63, 171.54, 170.93, 170.08, 169.76, 169.61, 78.07, 74.87, 74.09, 59.69 (t, J = 26.9 Hz), 39.47, 39.35, 39.29, 34.47, 34.42, 33.91, 32.05, 32.01, 31.93, 31.87, 30.62, 29.79, 29.78, 29.75, 29.70, 29.69, 29.60, 29.58, 29.56, 29.52, 29.51, 29.49, 29.43, 29.38, 29.37, 29.33, 29.26, 29.24, 29.21, 29.08, 29.04, 28.79, 26.97, 26.94, 26.88, 25.13, 25.12, 25.01, 24.90, 24.88, 22.82, 22.75, 18.89, 17.09, 14.25, 14.21.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{70}^{1}\text{H}_{120}^{16}\text{O}_{11}^{14}\text{N}_3^{35}\text{Cl}$, 1214.8684; found, 1214.8655, Δ = 2.9 mmu.



Supplementary Figure 132: ^1H -NMR of compound 89 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 281 mg of **89** (211 μmol , 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 38.3 μL cyclohexancarboxaldehyde **14j** (35.5 mg, 316 μmol , 1.50 eq.) and 95.3 mg of the monomer **M1** (316 μmol , 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite[®] and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **T11** as a pale highly viscous oil. (331 mg, 190 μmol , 90.0%).

R_f = 0.46 in cyclohexane / ethyl acetate (2:1).

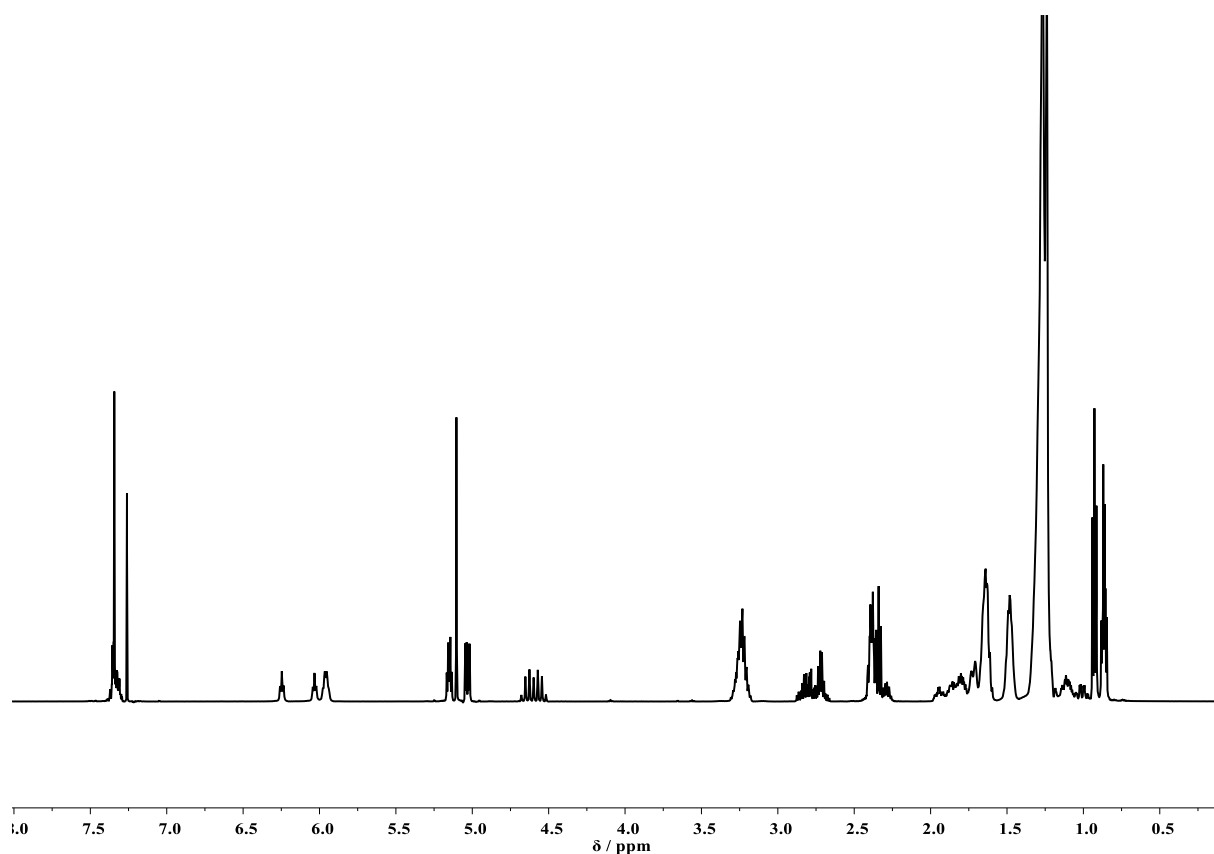
IR (ATR): ν / cm^{-1} = 3302.4 (w), 2920.6 (vs), 2851.2 (s), 1735.2 (vs), 1655.3 (vs), 1555.1 (m), 1466.2 (m), 1377.7 (w), 1228.1 (vs), 1207.0 (vs), 1172.6 (vs), 1020.5 (w), 722.7 (w), 696.5 (m).

^1H NMR (500 MHz, CDCl_3): δ / ppm = 7.35 – 7.22 (m, 5 H, CH_{Ar}^1), 6.19 (t, J = 5.8 Hz, 1 H, NH^2), 5.97 (t, J = 5.9 Hz, 1 H, NH^2), 5.93 – 5.81 (m, 2 H, NH^2), 5.12 – 5.07 (m, 2 H, CH^3), 5.04 (s, 2 H, CH_2^4), 4.98 (d, J = 4.4 Hz, 1 H, CH^5), 4.96 (d, J = 4.6 Hz, 1 H, CH^5), 4.65 – 4.43 (m, 2 H, CH_2^6), 3.29 – 3.09 (m, 8 H, CH_2^7), 2.84 – 2.60 (m, 4 H, CH_2^8), 2.41 – 2.18 (m, 9 H, $\text{CH}^9, \text{CH}_2^{10}$), 1.95 – 1.52 (m, 21 H, $\text{CH}^{11}, \text{CH}_2^{12}$), 1.48 – 1.36 (m, 8 H, CH_2^{13}), 1.30 – 0.94 (m, 18 H, CH_2^{12}), 0.87 (t, J = 6.5 Hz, 6 H, CH_3^{14}), 0.85 – 0.76 (m, 6 H, CH_3^{15}).

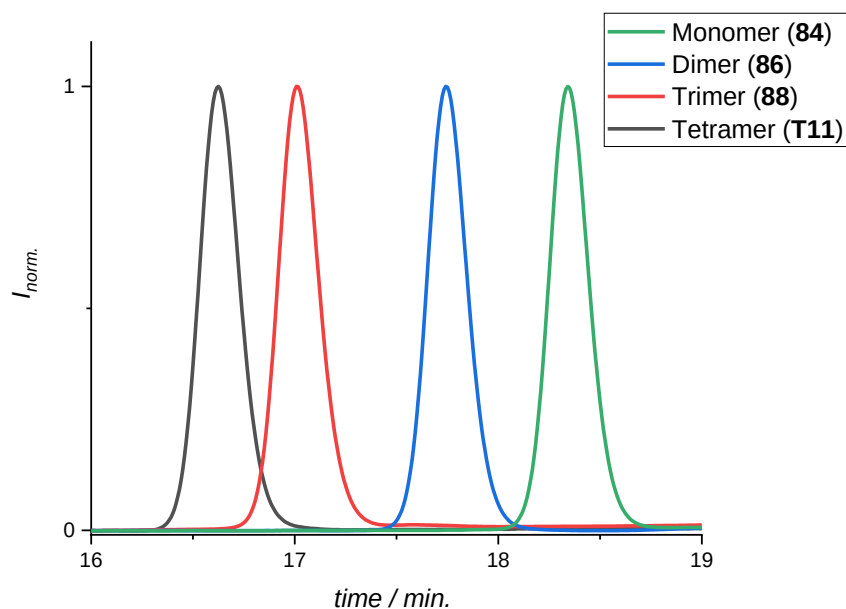
^{13}C NMR (126 MHz, CDCl_3): δ / ppm = 173.80, 172.67, 172.66, 172.60, 171.49, 170.89, 169.98, 169.62, 169.40, 169.32, 136.24, 128.66, 128.28, 128.27, 78.03, 77.74, 74.86, 74.05, 66.19, 59.66 (t, J = 27.0 Hz), 40.10, 39.43, 39.31, 39.27, 34.44, 34.41, 32.04, 31.94, 31.86, 30.64, 29.78, 29.77, 29.74, 29.72, 29.70, 29.67, 29.58, 29.57, 29.55, 29.54, 29.51, 29.49, 29.47, 29.36, 29.34, 29.32, 29.26, 29.23, 29.03, 28.78, 27.41, 26.97, 26.95, 26.20, 26.12, 26.01, 25.12, 25.09, 25.07, 25.01, 24.89, 22.81, 22.74, 18.90, 17.07, 14.25, 14.21.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.14 (t, J = 9.2 Hz, 3 F, CF_3^{16}), -124.10 – -125.56 (m, 2 F, CF_2^{17}), -131.03 – -133.61 (m, 2 F, CF_2^{17}). Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 4.

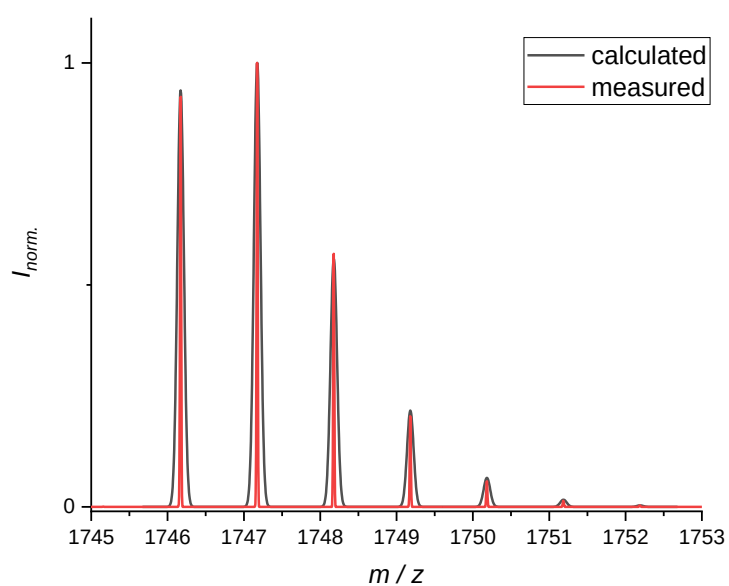
ESI-MS [m/z]: [$\text{M} + \text{H}$]⁺ calculated for $^{12}\text{C}_{95}^{1}\text{H}_{159}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_7$, 1746.1712; found, 1746.1708, Δ = 0.4 mmu.



Supplementary Figure 133: ^1H -NMR of compound T11 measured in CDCl_3 .



Supplementary Figure 134: SEC traces of the intermediates after each P3CR I the synthesis of product T11.



Supplementary Figure 135: High resolution ESI-MS measurement of T11. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

```

matching mass 1747.17426
cutoff 0.50000: 0 solutions (16 peaks)
cutoff 0.25000: 0 solutions (42 peaks)
cutoff 0.12500: 0 solutions (106 peaks)
cutoff 0.06250: 0 solutions (216 peaks)
cutoff 0.03125: 0 solutions (394 peaks)
cutoff 0.01562: 0 solutions (654 peaks)
cutoff 0.00781: 1 solutions (1071 peaks)
1747.17426 = 283.020520 + 409.355600 + 283.214750 + 339.277350 + 323.246050 + 107.049690 (sides Tridecanal,
Isobutyraldehyde, Octanal, Cyclohexancarboxaldehyde; error -2.01030)
Press ENTER to quit ...

```

Supplementary Figure 136: Screenshot of the automated read-out of T11.

Passerini reaction

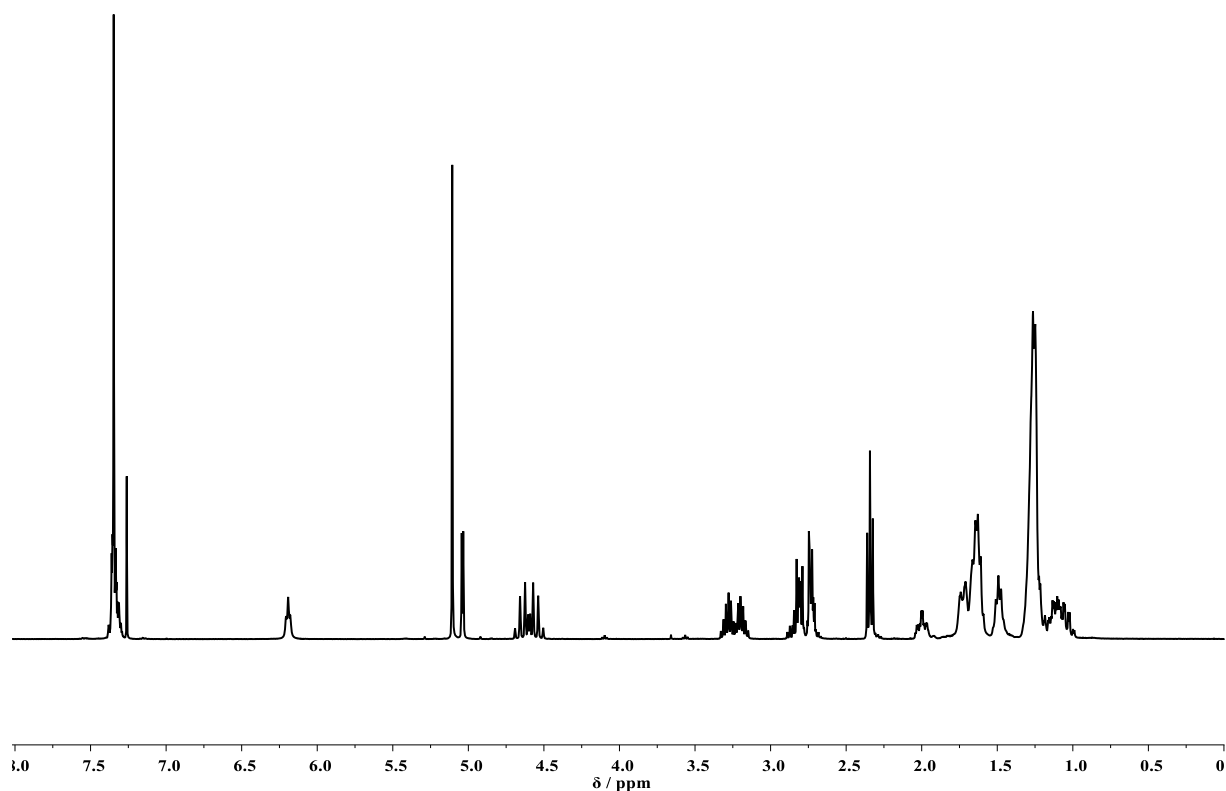


$R_f = 0.47$ in cyclohexane / ethyl acetate (3:1).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.46 – 7.29 (m, 5 H, CH_{Ar}¹), 6.19 (t, *J* = 5.8 Hz, 1 H, NH²), 5.11 (s, 2 H, CH₂³), 5.04 (d, *J* = 4.0 Hz, 1 H, CH⁴), 4.74 – 4.46 (m, 2 H, CH₂⁵), 3.35 – 3.12 (m, 2 H, CH₂⁶), 2.91 – 2.66 (m, 4 H, CH₂⁷), 2.34 (t, *J* = 7.6 Hz, 2 H, CH₂⁸), 2.07 – 1.92 (m, 1 H, CH₂⁹), 1.80 – 1.57 (m, 8 H, CH₂¹⁰), 1.55 – 1.42 (m, 2 H, CH₂¹¹), 1.37 – 0.96 (m, 16 H, CH₂¹⁰).

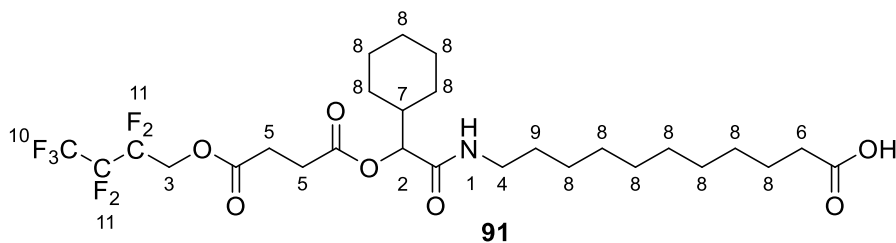
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.16 (t, J = 9.2 Hz, 3 F, CF₃¹²), -124.49 – -125.85 (m, 2 F, CF₂¹³), -131.00 – -132.82 (m, 2 F, CF₂¹³). Total integral of CF₂ region normalized with respect to the CF₃¹³ group = 4.

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Supplementary Figure 137: ^1H -NMR of compound **90** measured in CDCl_3 .

Deprotection



In a 50 mL round bottom flask, 625 mg of **90** (876 μmol , 1.00 eq.) were dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Afterwards, 125 mg (20 wt%) palladium on activated charcoal **16** were added. Subsequently, the mixture was purged with hydrogen (3 balloons) and stirred under hydrogen atmosphere overnight. The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **91** was obtained as a pale highly viscous oil in a yield of 99.6% (544 mg, 872 μmol).

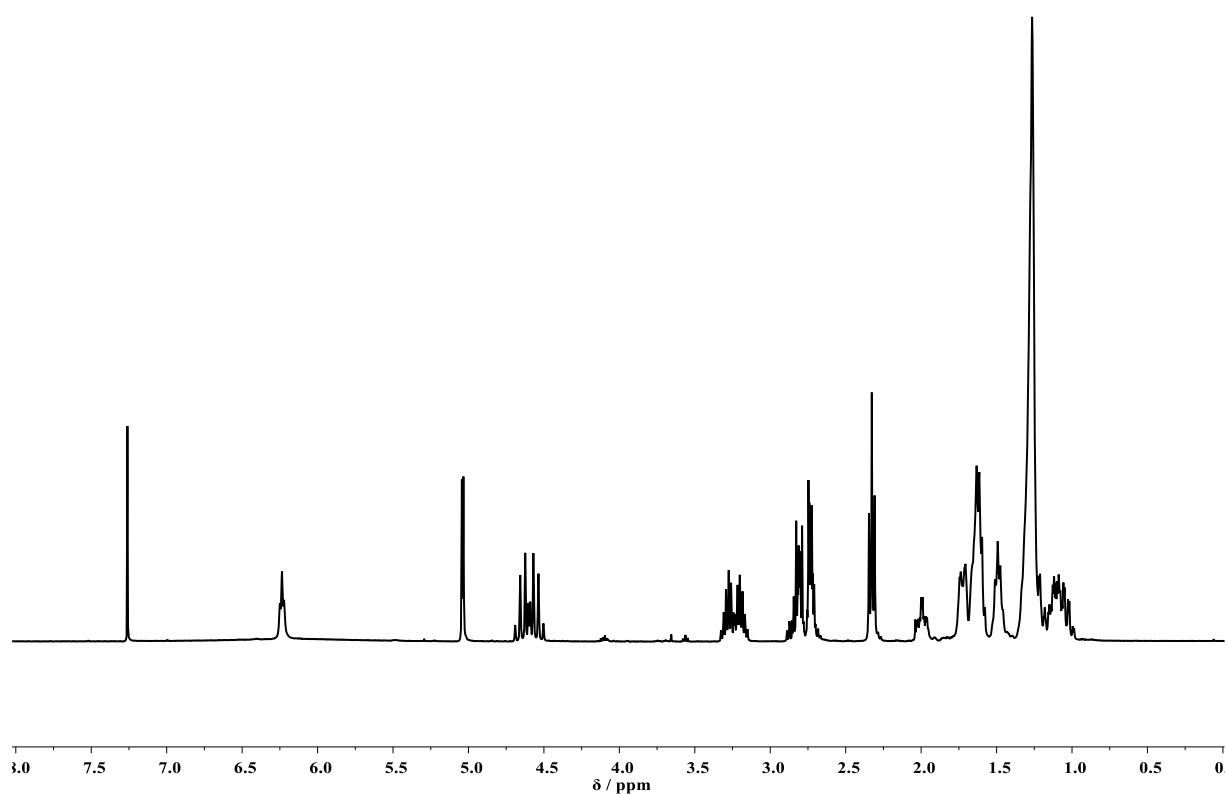
IR (ATR): ν/cm^{-1} = 3313.2 (w), 2926.8 (s), 2853.3 (m), 1765.1 (s), 1736.3 (vs), 1686.1 (vs), 1655.2 (vs), 1552.0 (s), 1447.0 (w), 1381.9 (w), 1352.7 (m), 1298.0 (m), 1217.5 (vs), 1144.9 (vs), 1115.9 (vs), 1084.8 (m), 1023.4 (w), 984.8 (s), 955.5 (m), 912.4 (m), 872.9 (w), 843.8 (vw), 784.1 (w), 737.0 (vs), 671.5 (w), 573.5 (w), 540.4 (w), 451.3 (w), 381.1 (vw).

^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.17 (t, J = 5.8 Hz, 1 H, NH^1), 4.98 (d, J = 4.1 Hz, 1 H, CH^2), 4.68 – 4.41 (m, 2 H, CH_2^3), 3.31 – 3.07 (m, 2 H, CH_2^4), 2.84 – 2.59 (m, 4 H, CH_2^5), 2.27 (t, J = 7.5 Hz, 2 H, CH_2^6), 2.00 – 1.87 (m, 1 H, CH^7), 1.73 – 1.51 (m, 6 H, CH_2^8), 1.47 – 1.37 (m, 2 H, CH_2^9), 1.30 – 0.90 (m, 18 H, CH_2^8).

^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 179.13, 171.58, 170.98, 169.10, 78.56, 59.71 (t, J = 27.0 Hz), 39.88, 39.42, 34.12, 29.47, 29.40, 29.35, 29.23, 29.22, 29.09, 28.99, 28.79, 27.12, 26.91, 26.13, 26.00, 24.81.

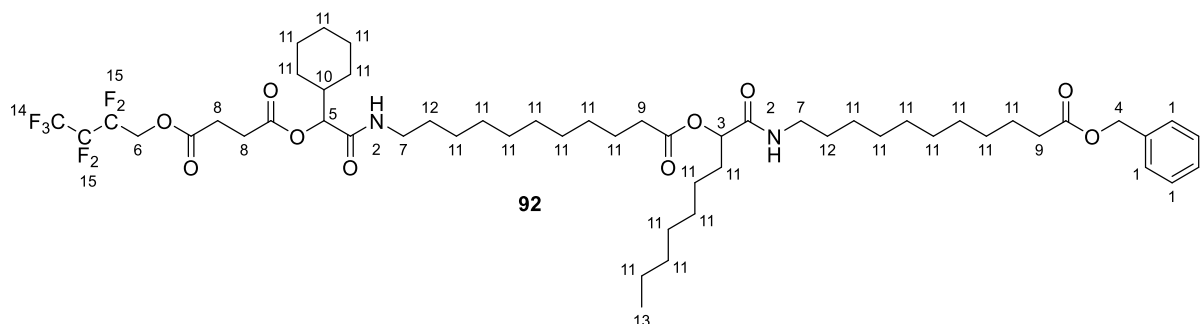
^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.18 (t, J = 9.2 Hz, 3 F, CF_3^{10}), -124.03 – -125.46 (m, 2 F, CF_2^{11}), -131.58 – -132.63 (m, 2 F, CF_2^{11}). Total integral of CF_2 region normalized with respect to the CF_3^{10} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{27}^{1}\text{H}_{40}^{16}\text{O}_7^{14}\text{N}^{19}\text{F}_7$, 624.2766; found, 624.2752, Δ = 1.4 mmu.



Supplementary Figure 138: ^1H -NMR of compound 91 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 419 mg of **91** (671 μ mol, 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 194 μ L octanal **14i** (160 mg, 1.25 mmol, 1.85 eq.) and 374 mg of the monomer **M1** (1.25 mol, 1.85 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (4:1 $\rightarrow$ 2:1) to yield the passerini product **92** as a pale highly viscous oil. (663 mg, 927 μ mol, 91.8%).

R_f = 0.32 in cyclohexane / ethyl acetate (2:1).

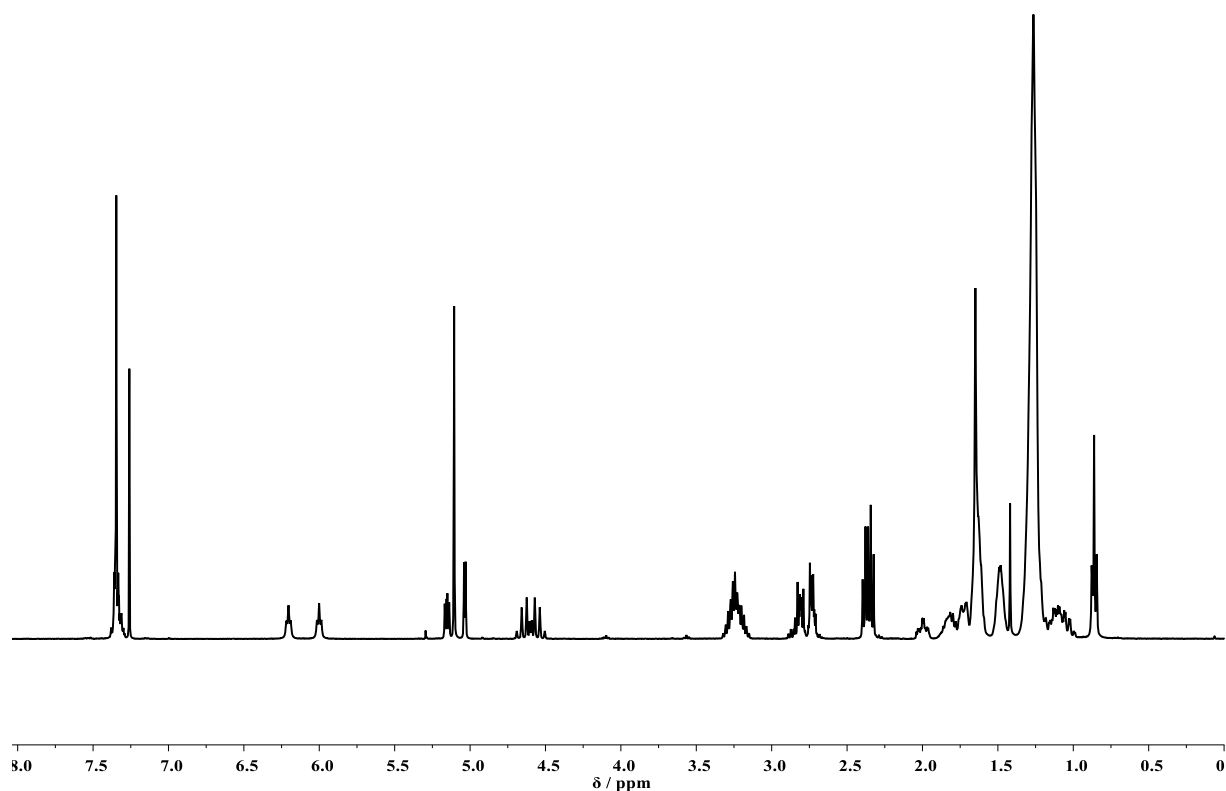
IR (ATR): ν / cm^{-1} = 3293.7 (w), 2918.5 (s), 2850.5 (s), 1728.6 (vs), 1679.6 (m), 1651.3 (vs), 1533.4 (m), 1466.9 (w), 1320.5 (m), 1227.7 (vs), 1158.9 (vs), 1021.9 (m), 957.0 (w), 909.9 (w), 803.6 (vw), 735.6 (w), 720.1 (w), 697.8 (m), 628.5 (w), 539.8 (w), 449.2 (vw), 383.7 (vw).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.45 – 7.28 (m, 5 H, CH_{Ar}¹), 6.20 (t, J = 5.8 Hz, 1 H, NH²), 6.00 (t, J = 5.8 Hz, 1 H, NH²), 5.19 – 5.13 (m, 1 H, CH³), 5.11 (s, 2 H, CH₂⁴), 5.03 (d, J = 4.1 Hz, 1 H, CH⁵), 4.72 – 4.48 (m, 2 H, CH₂⁶), 3.36 – 3.13 (m, 4 H, CH₂⁷), 2.90 – 2.66 (m, 4 H, CH₂⁸), 2.44 – 2.30 (m, 4 H, CH₂⁹), 2.08 – 1.93 (m, 1 H, CH¹⁰), 1.90 – 1.56 (m, 14 H, CH₂¹¹), 1.56 – 1.44 (m, 4 H, CH₂¹²), 1.38 – 0.98 (m, 36 H, CH₂¹¹), 0.90 – 0.83 (m, 3 H, CH₃¹³).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.83, 172.59, 171.55, 170.93, 169.99, 168.96, 136.26, 128.68, 128.29, 78.58, 74.07, 66.21, 59.84 (t, J = 27.0 Hz), 39.91, 39.39, 39.33, 34.46, 32.04, 31.86, 29.69, 29.60, 29.58, 29.57, 29.49, 29.42, 29.35, 29.33, 29.24, 29.23, 29.00, 28.80, 27.14, 27.05, 26.97, 26.15, 26.02, 25.09, 25.08, 24.88, 22.74, 14.20.

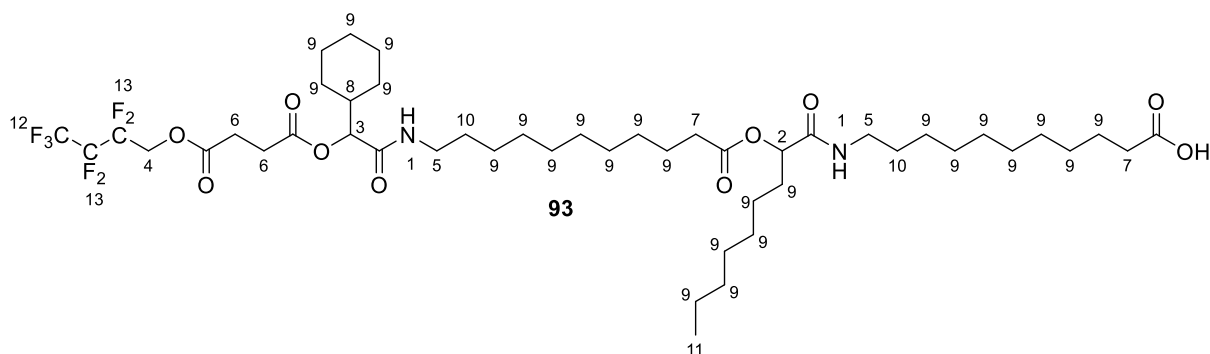
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.15 (t, J = 9.7 Hz, 3 F, CF₃¹⁴), -124.10 – -125.74 (m, 2 F, CF₂¹⁵), -130.32 – -133.43 (m, 2 F, CF₂¹⁵). Total integral of CF₂ region normalized with respect to the CF₃¹⁴ group = 4.

ESI-MS [m/z]: [$M + H$]⁺ calculated for ¹²C₅₄¹H₈₃¹⁶O₁₀¹⁴N₂¹⁹F₇, 1053.6009; found, 1053.6000, Δ = 0.9 mmu.



Supplementary Figure 139: ^1H -NMR of compound **92** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask, 497 mg of **92** (472 μmol , 1.00 eq.) was dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Subsequently, 99.4 mg (20 wt.-%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 1 day at room temperature under hydrogen atmosphere (3 balloons). The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **93** was obtained as a yellow high viscous oil. (429 mg, 445 μmol , 94.4%).

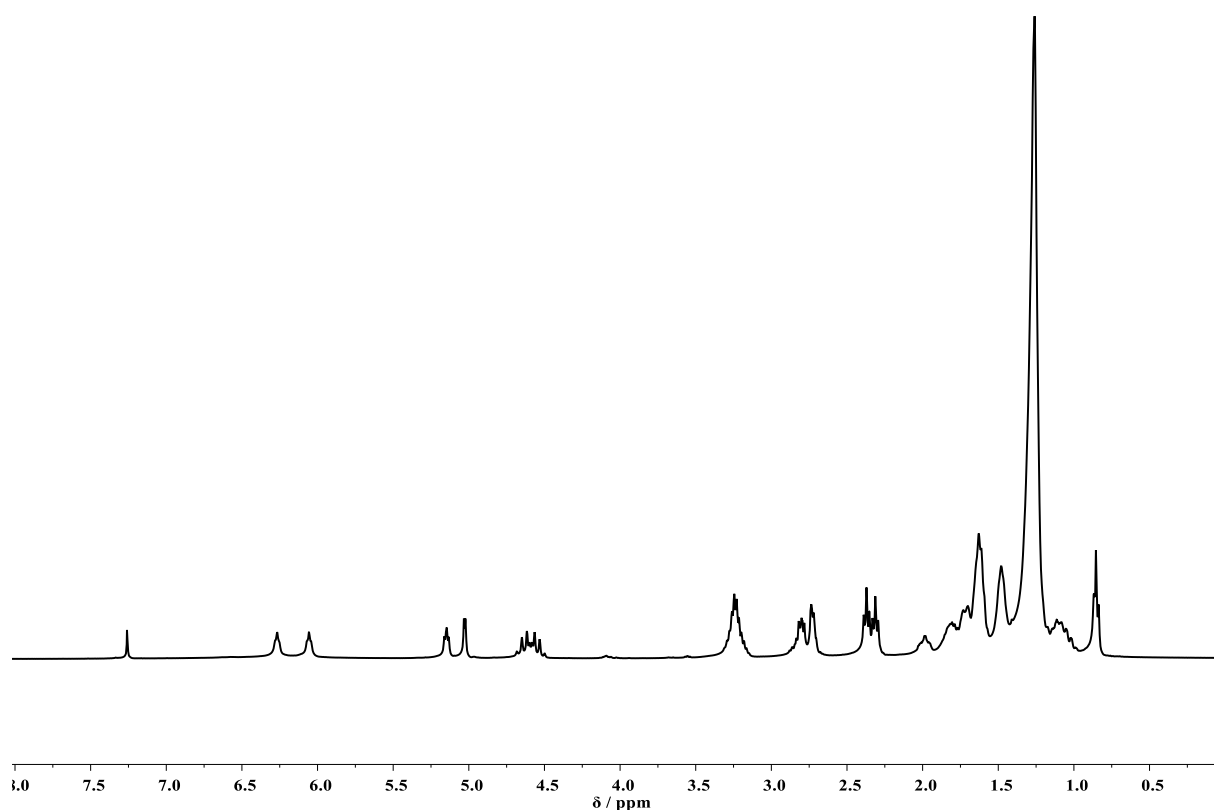
IR (ATR): $\nu / \text{cm}^{-1} = 3316.2$ (vw), 2927.8 (w), 2855.4 (vw), 2360.7 (w), 2343.5 (vw), 2328.7 (vw), 2154.8 (vw), 1743.0 (w), 1656.5 (vw), 1544.0 (vw), 1453.7 (vw), 1354.3 (vw), 1229.6 (w), 1181.7 (vw), 1146.8 (w), 1020.7 (vw), 736.0 (vw), 443.1 (vw), 418.4 (vw).

^1H NMR (400 MHz, CDCl_3): $\delta / \text{ppm} = 6.29$ (t, $J = 6.0$ Hz, 1 H, NH^1), 6.07 (t, $J = 6.0$ Hz, 1 H, NH^1), 5.16 (t, $J = 6.1$ Hz, 1 H, CH^2), 5.05 (d, $J = 4.2$ Hz, 1 H, CH^3), 4.76 – 4.47 (m, 2 H, CH_2^4), 3.41 – 3.12 (m, 4 H, CH_2^5), 2.93 – 2.69 (m, 4 H, CH_2^6), 2.48 – 2.28 (m, 4 H, CH_2^7), 2.10 – 1.95 (m, 1 H, CH^8), 1.92 – 0.99 (m, 54 H, CH_2^9), 0.87 (t, $J = 6.6$ Hz, 3 H, CH_3^{10}).

^{13}C NMR (101 MHz, CDCl_3): $\delta / \text{ppm} = 178.20, 172.61, 171.54, 170.96, 170.11, 169.12, 78.57, 74.08, 59.71$ (t, $J = 27.1$ Hz), 39.89, 39.44, 39.33, 34.45, 34.13, 32.01, 31.84, 29.59, 29.53, 29.48, 29.38, 29.35, 29.31, 29.25, 29.20, 29.13, 28.99, 28.79, 27.17, 26.96, 26.90, 26.13, 26.00, 25.10, 24.89, 22.72, 14.16.

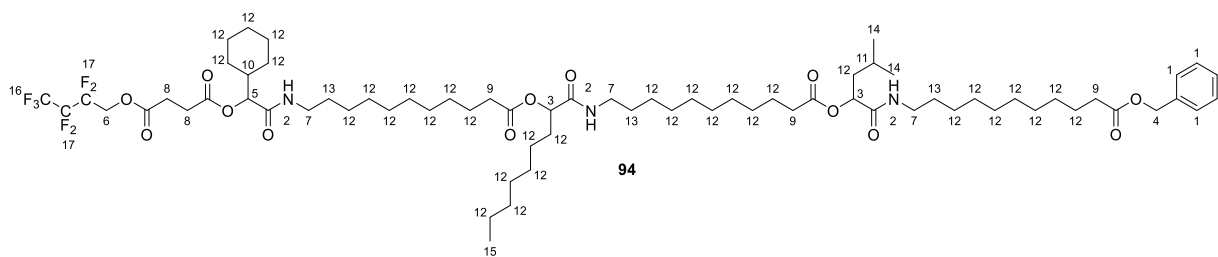
^{19}F NMR (376 MHz, CDCl_3): $\delta / \text{ppm} = -84.58$ – -85.52 (m, 3 F, CF_3^{11}), -124.10 – -125.92 (m, 2 F, CF_2^{12}), -130.67 – -133.43 (m, 2 F, CF_2^{12}). Total integral of CF_2 region normalized with respect to the CF_3^{11} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{Na}$] $^+$ calculated for $^{12}\text{C}_{47}\text{H}_{77}^{16}\text{O}_{10}^{14}\text{N}_2^{19}\text{F}_7^{23}\text{Na}$, 985.5359; found, 985.5341, $\Delta = 1.8$ mmu.



Supplementary Figure 140: ^1H -NMR of compound 93 measured in CDCl_3 .

Passerini reaction



In a 50 mL round bottom flask, 361 mg of **94** (375 μ mol, 1.00 eq.) was stirred in 4.00 mL dichloromethane. Subsequently, 60.5 μ L 3-methylbutyraldehyde **14g** (48.4 mg, 562 μ mol, 1.50 eq.) and 169 mg of the monomer **M1** (562 μ mol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified via column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (5:1 $\rightarrow$ 2:1) to yield the passerini product **94** as a pale highly viscous oil. (377 mg, 279 μ mol, 74.5%).

R_f = 0.30 in cyclohexane / ethyl acetate (2:1).

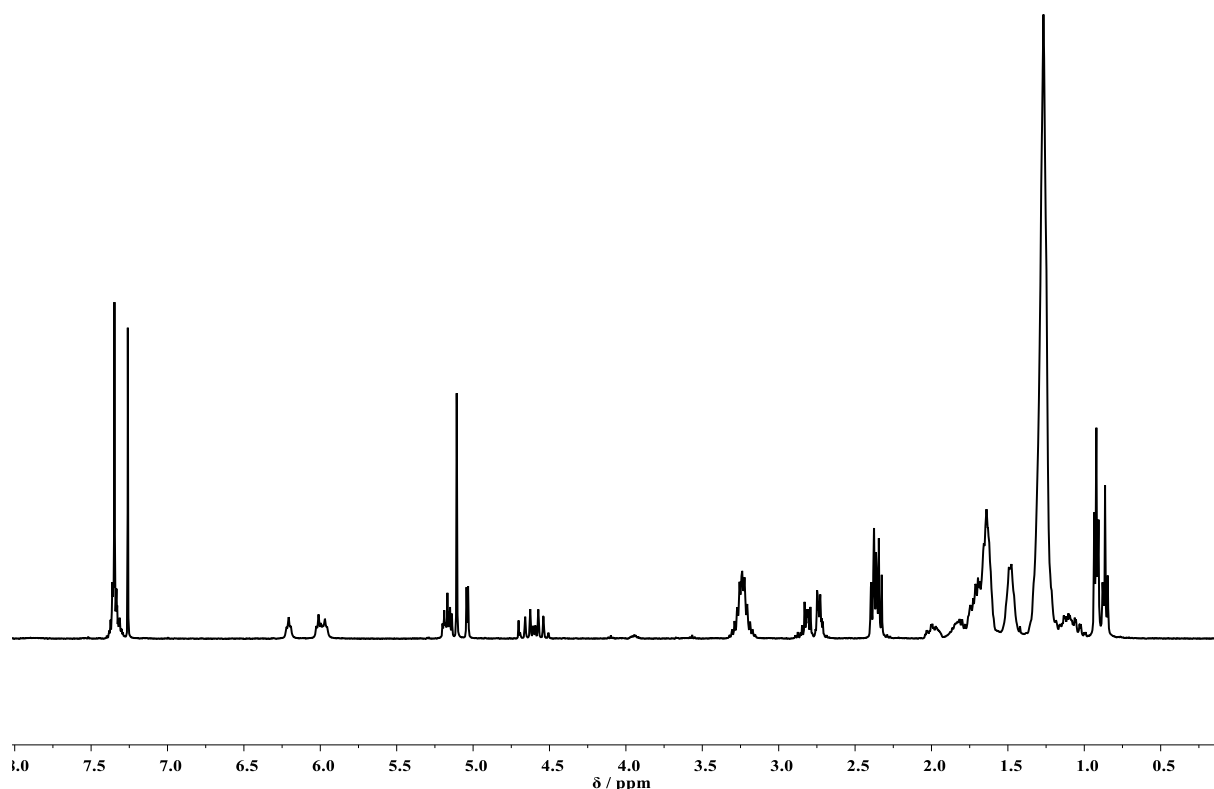
IR (ATR): ν / cm^{-1} = 3307.8 (vw), 2926.3 (w), 2854.6 (w), 1740.3 (w), 1654.7 (w), 1537.7 (w), 1454.8 (vw), 1353.3 (vw), 1227.3 (m), 1144.9 (m), 1020.0 (vw), 910.7 (vw), 735.7 (vw), 697.4 (vw), 453.0 (vw), 431.1 (vw).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ / ppm = 7.44 – 7.28 (m, 5 H, CH_{Ar}^1), 6.21 (t, J = 5.8 Hz, 1 H, NH^2), 6.07 – 5.91 (m, 2 H, NH^2), 5.26 – 5.14 (m, 2 H, CH^3), 5.11 (s, 2 H, CH_2^4), 5.04 (d, J = 4.0 Hz, 1 H, CH^5), 4.74 – 4.45 (m, 2 H, CH_2^6), 3.35 – 3.14 (m, 6 H, CH_2^7), 2.91 – 2.68 (m, 4 H, CH_2^8), 2.44 – 2.30 (m, 6 H, CH_2^9), 2.08 – 1.91 (m, 1 H, CH^{10}), 1.90 – 1.56 (m, 17 H, CH^{11} , CH_2^{12}), 1.56 – 1.38 (m, 6 H, CH_2^{13}), 1.38 – 0.99 (m, 50 H, CH_2^{12}), 0.92 (t, J = 5.7 Hz, 6 H, CH_3^{14}), 0.89 – 0.79 (m, 3 H, CH_3^{15}).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ / ppm = 173.82, 172.77, 172.60, 171.55, 170.93, 170.34, 170.00, 168.95, 136.27, 128.68, 128.30, 78.58, 74.07, 72.78, 66.21, 59.71, 40.99, 39.91, 39.39, 39.37, 39.32, 34.46, 32.05, 31.86, 30.23, 29.70, 29.66, 29.59, 29.57, 29.50, 29.48, 29.43, 29.34, 29.24, 29.00, 28.81, 27.14, 26.97, 26.94, 26.15, 26.02, 25.09, 25.08, 25.06, 24.90, 24.69, 23.82, 23.27, 22.74, 21.94, 14.20.

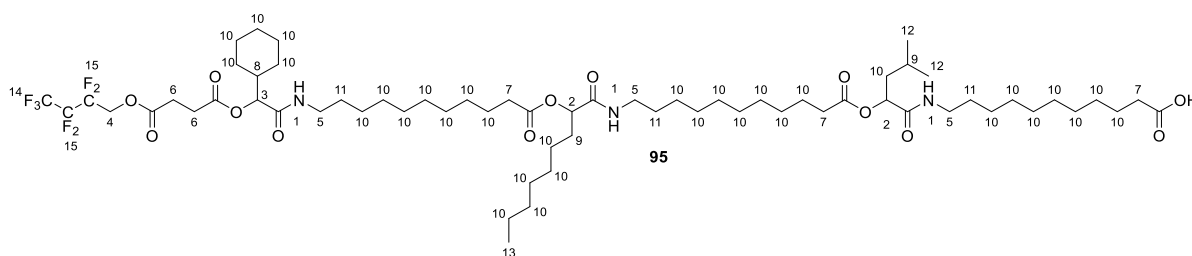
$^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ / ppm = -85.14 (t, J = 9.5 Hz, 3 F, CF_3^{16}), -124.79 – -124.91 (m, 2 F, CF_2^{17}), -131.94 – -132.04 (m, 2 F, CF_2^{17}). Total integral of CF_2 region normalized with respect to the CF_3^{16} group = 4.

ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{71}^{1}\text{H}_{114}^{16}\text{O}_{13}^{14}\text{N}_3^{19}\text{F}_7$, 1350.8313; found, 1350.8312, Δ = 0.1 mmu.



Supplementary Figure 141: ^1H -NMR of compound **94** measured in CDCl_3 .

Deprotection



In a 25 mL round bottom flask, 335 mg of **94** (248 μmol , 1.00 eq.) was dissolved in 4.00 mL ethyl acetate and 4.00 mL THF. Subsequently, 84.6 mg (20 wt.-%) palladium on activated charcoal **16** was added to the solution. The resulting mixture was purged with hydrogen gas and stirred for 1 day at room temperature under hydrogen atmosphere (3 balloons). The heterogeneous catalyst was filtered off and the solvent was evaporated under reduced pressure. The product **95** was obtained as a yellow high viscous oil (308 mg, 244 μmol , 98.5%).

IR (ATR): ν/cm^{-1} = 3309.2, 2925.5, 2854.6, 2036.6, 1987.3, 1742.0, 1654.5, 1540.1, 1465.2, 1369.3, 1227.8, 1145.9, 1021.0, 910.8, 735.9, 472.7, 422.0.

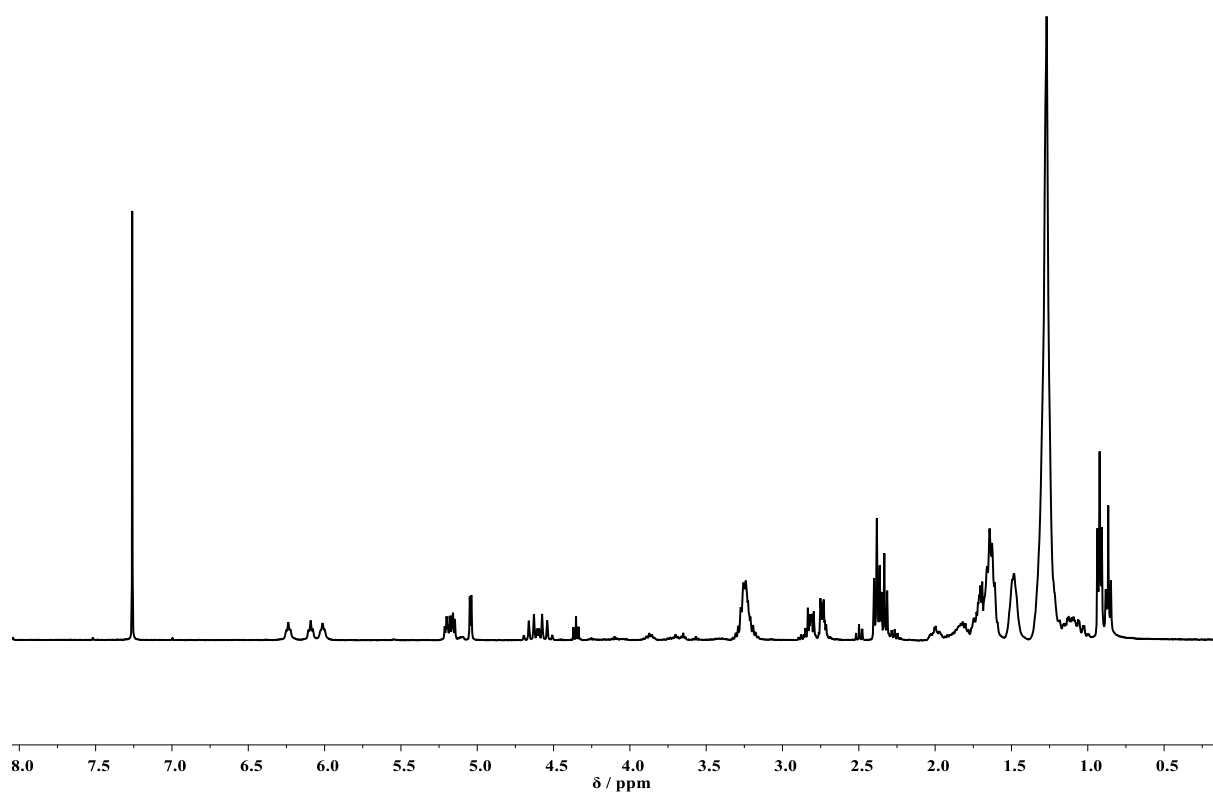
^1H NMR (400 MHz, CDCl_3): δ / ppm = 6.28 – 6.17 (m, 1 H, NH^1), 6.11 – 6.07 (m, 1 H, NH^1), 6.03 – 5.97 (m, 1 H, NH^1), 5.24 – 5.11 (m, 2 H, CH^2), 5.04 (d, J = 4.0 Hz, 1 H, CH^3), 4.71 – 4.48 (m, 2 H, CH_2^4), 3.33 – 3.15 (m, 6 H, CH_2^5), 2.91 – 2.67 (m, 4 H, CH_2^6), 2.43 – 2.29 (m, 6 H, CH_2^7), 2.04 – 1.94

(m, 1 H, CH⁸), 1.93 – 1.59 (m, 17 H, CH⁹, CH₂¹⁰), 1.56 – 1.42 (m, 6 H, CH₂¹¹), 1.34 – 0.90 (m, 50 H, CH₂¹⁰), 0.92 (t, *J* = 5.7 Hz, 6 H, CH₃¹²), 0.87 (t, *J* = 6.8 Hz, 3 H, CH₃¹³).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 176.62, 172.82, 172.72, 171.59, 170.96, 170.43, 170.21, 169.08, 78.56, 74.07, 72.80, 40.93, 39.89, 39.42, 39.32, 34.45, 33.85, 32.01, 31.87, 29.67, 29.61, 29.60, 29.55, 29.52, 29.51, 29.42, 29.38, 29.34, 29.32, 29.29, 29.27, 29.23, 29.18, 29.05, 29.00, 28.81, 27.13, 26.97, 26.84, 26.15, 26.02, 25.10, 25.09, 24.89, 24.69, 23.27, 22.75, 21.92, 14.21.

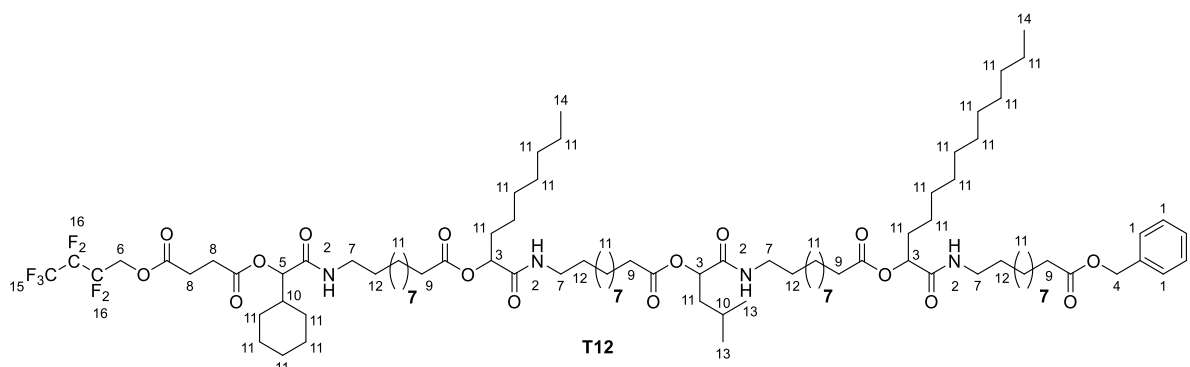
¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.14 (t, *J* = 9.6 Hz, 3 F, CF₃¹⁴), -124.79 – -124.90 (m, 2 F, CF₂¹⁵), -131.90 – -132.10 (m, 2 F, CF₂¹⁵). Total integral of CF₂ region normalized with respect to the CF₃¹⁴ group = 4.

ESI-MS [*m/z*]: [M + H]⁺ calculated for ¹²C₆₄¹H₁₀₈¹⁶O₁₃¹⁴N₃¹⁹F₇, 1260.7843; found, 1260.7826, Δ = 1.7 mmu



Supplementary Figure 142: ¹H-NMR of compound 95 measured in CDCl₃.

Passerini reaction



In a 50 mL round bottom flask, 264 mg of **95** (210 μ mol, 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 57.9 mg dodecanal **14h** (314 μ mol, 1.50 eq.) and 94.7 mg of the monomer **M1** (314 μ mol, 1.50 eq.) were added. The resulting reaction mixture was stirred at room temperature for 2 days. Afterwards, the crude mixture was dried under reduced pressure. The residue was adsorbed onto celite® and purified *via* column chromatography on silica gel eluting with a gradual solvent mixture of ethyl acetate and cyclohexane (3:1 $\rightarrow$ 2:1) to yield the passerini product **T12** as a pale highly viscous oil. (292 mg, 167 μ mol, 79.7%).

R_f = 0.68 in cyclohexane / ethyl acetate (1:1).

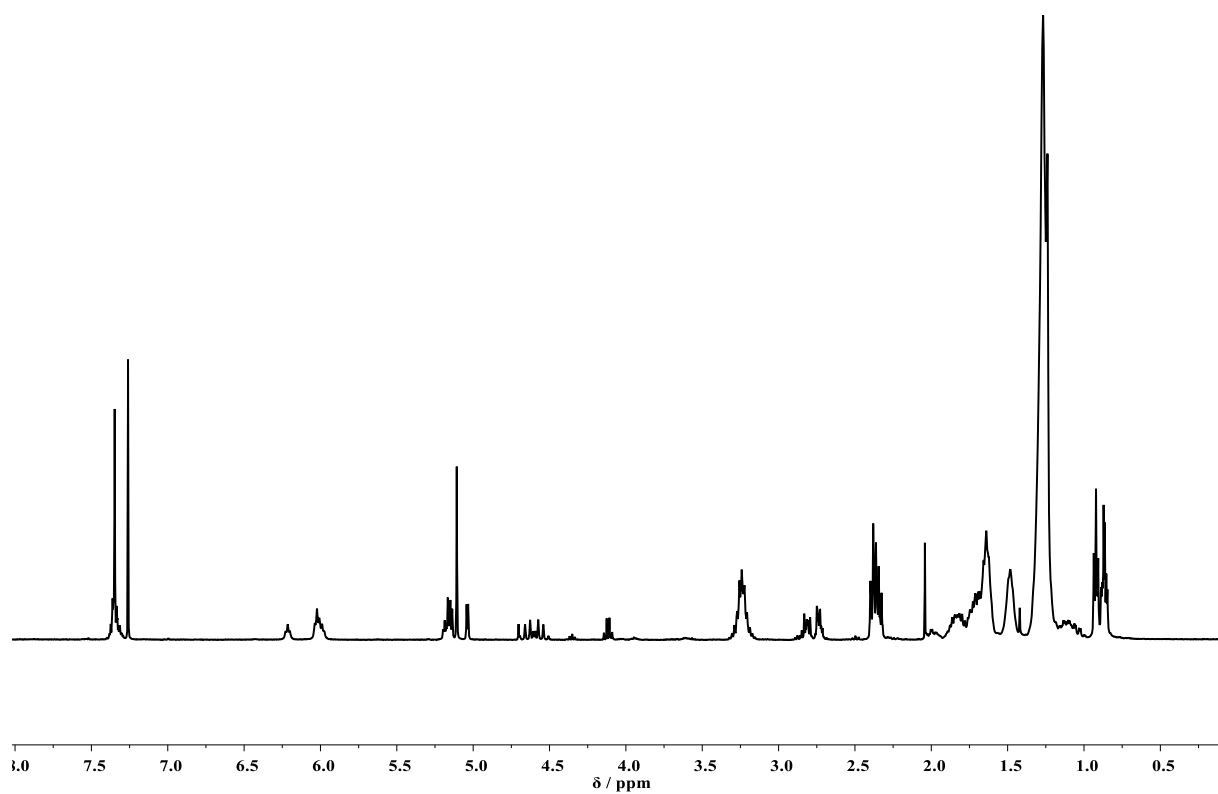
IR (ATR): ν / cm^{-1} = 3302.0, 2922.6, 2852.3, 2165.9, 1739.0, 1656.3, 1540.6, 1466.3, 1369.9, 1228.7, 1171.8, 1022.2, 722.6, 697.9 (vw).

^1H -NMR (400 MHz, CDCl_3): δ / ppm = 7.41 – 7.28 (m, 5 H, CH_{Ar}^1), 6.21 (t, J = 5.9 Hz, 1 H, NH^2), 6.08 – 5.93 (m, 3 H, NH^2), 5.22 – 5.13 (m, 3 H, CH^3), 5.11 (s, 2 H, CH_2^4), 5.04 (d, J = 4.1 Hz, 1 H, CH^5), 4.72 – 4.46 (m, 2 H, CH_2^6), 3.34 – 3.14 (m, 8 H, CH_2^7), 2.91 – 2.68 (m, 4 H, CH_2^8), 2.43 – 2.29 (m, 8 H, CH_2^9), 2.03 – 1.57 (m, 26 H, CH^{10} , CH_2^{11}), 1.55 – 1.43 (m, 8 H, CH_2^{12}), 1.38 – 1.00 (m, 76 H, CH_2^{11}), 0.92 (t, J = 5.8 Hz, 6 H, CH_3^{13}), 0.90 – 0.84 (m, 6 H, CH_3^{14}).

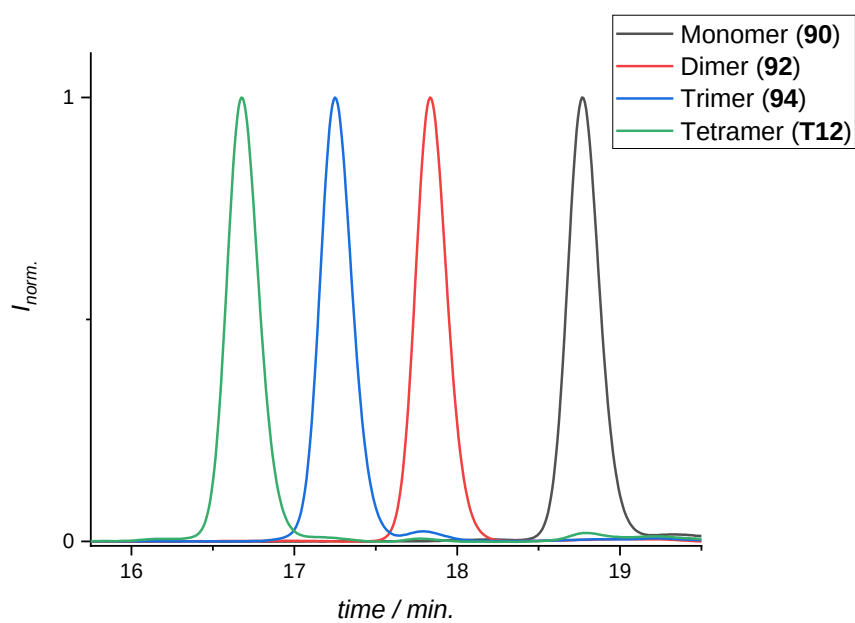
^{13}C NMR (101 MHz, CDCl_3): δ / ppm = 173.82, 172.79, 172.61, 171.56, 170.93, 170.36, 170.01, 169.99, 168.96, 136.26, 128.68, 128.30, 78.58, 74.07, 72.77, 66.21, 42.13, 40.99, 39.91, 39.39, 39.36, 39.33, 34.46, 32.05, 31.86, 29.76, 29.71, 29.68, 29.60, 29.58, 29.51, 29.48, 29.43, 29.40, 29.35, 29.24 (d, J = 1.9 Hz), 29.00, 28.81, 27.15, 26.97, 26.94, 26.15, 26.02, 25.10, 25.08, 25.06, 24.90, 24.69, 23.27, 22.82, 22.75, 21.93, 14.26, 14.21.

^{19}F NMR (376 MHz, CDCl_3): δ / ppm = -85.14 (t, J = 9.6 Hz, 3 F, CF_3^{15}), -123.51 – -127.56 (m, 2 F, CF_2^{16}), -130.32 – -134.20 (m, 2 F, CF_2^{16}). Total integral of CF_2 region normalized with respect to the CF_3^{15} group = 4.

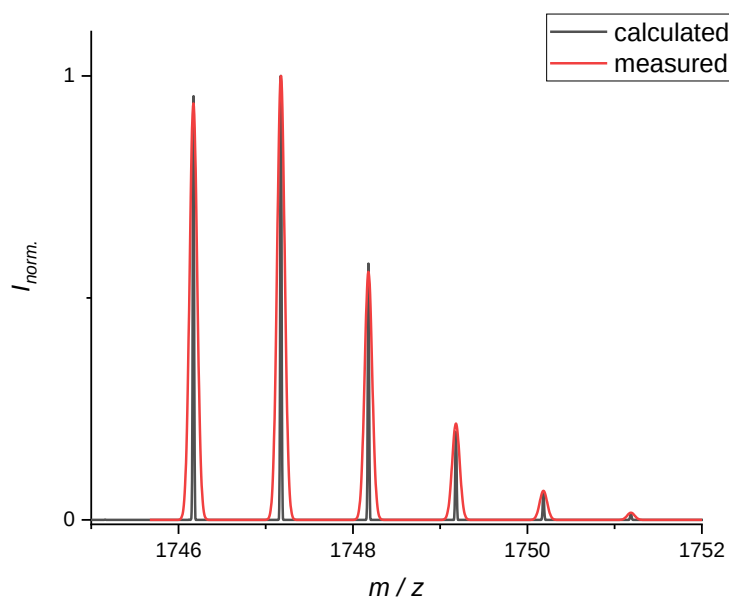
ESI-MS [m/z]: [$\text{M} + \text{H}$] $^+$ calculated for $^{12}\text{C}_{95}^{1}\text{H}_{159}^{16}\text{O}_{16}^{14}\text{N}_4^{19}\text{F}_7$, 1746.1712; found, 1746.1712, Δ = 0.0 mmu.



Supplementary Figure 143: ^1H -NMR of compound T12 measured in CDCl_3 .



Supplementary Figure 144: SEC traces of the intermediates after each P3CR in the synthesis of product T12.



Supplementary Figure 145: High resolution ESI-MS measurement of T12. The observed isotopic pattern is compared with the calculated isotopic pattern obtained from mMass (black).

```
found 22108 values in C:\Users\Maxi\bwSyncShare\Dennis\Daten für Programm\LFMF 015 nce 18.csv,
maximum is 1.000000 found for mass 1746.171390
matching mass 1746.17139
cutoff 0.50000: 0 solutions (10 peaks)
cutoff 0.25000: 0 solutions (30 peaks)
cutoff 0.12500: 0 solutions (66 peaks)
cutoff 0.06250: 0 solutions (128 peaks)
cutoff 0.03125: 0 solutions (206 peaks)
cutoff 0.01562: 1 solutions (367 peaks)
1746.17139  $\approx$  283.020520 + 323.246050 + 339.277350 + 297.230400 + 395.339950 + 107.049690 (sides
Cyclohexancarboxaldehyde, Octanal, 3-Methylbutanal, Dodecanal; error -1.00743)
Press ENTER to quit ...
```

Supplementary Figure 146: Screenshot of the automated read-out of T12.

1.3.6 Equations

$$[M_{Molecule} + H]^+ = [(M_{Start} + n * (M_{Backbone}) + \sum_{i=1}^{i=n} M_{Sidechain}^i + M_{End} + y * M(H)) + H]^+$$

(Supplementary Equation 1)

n = number of repeating units,

$$y = (n-1)$$

$$M_{Start} = M(\text{Tag X})$$

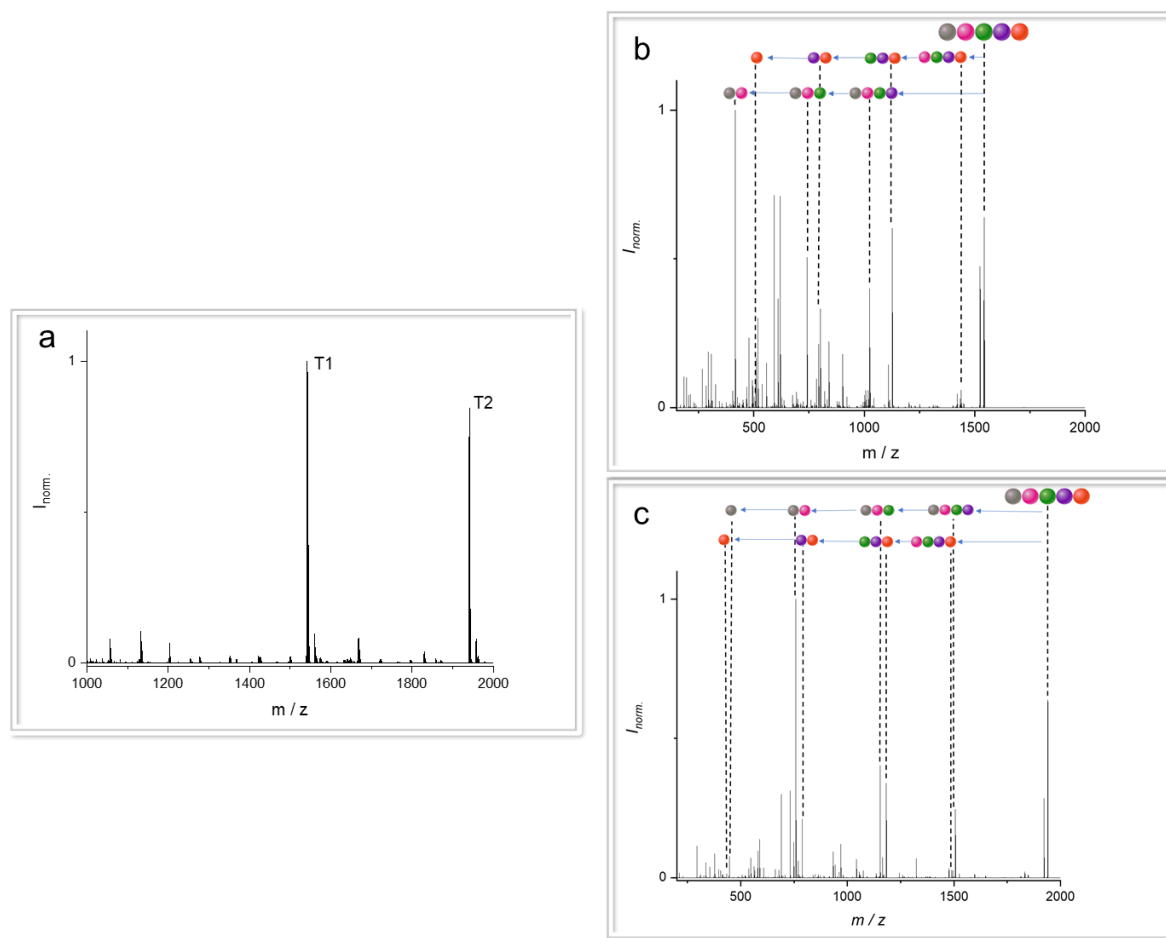
$$M_{End} = M(C_7H_7)$$

$$M_{Backbone} = (M(\text{monomer } \mathbf{M1})) - M(C_7H_7)$$

$$M_{Sidechain} = M(\mathbf{2a}) \text{ or } M(\mathbf{2b}) \text{ or } M(\mathbf{2c}) \text{ or } M(\mathbf{2d}) \text{ or } M(\mathbf{2e}) \text{ or } M(\mathbf{2f}) \text{ or } M(\mathbf{2g}) \text{ or } M(\mathbf{2h}) \text{ or } M(\mathbf{2i}) \text{ or } M(\mathbf{2j}) \text{ or } M(\mathbf{2k}) \text{ or } M(\mathbf{2l})$$

$M_{Backbone}$ is calculated with the mass of the monomer, which incorporates the protected acid (benzyl ester); however, in the iterative cycle, the benzyl ester is deprotected and further converted as the free acid compound. In order to take this into consideration in the formula, y is introduced as additional summand.

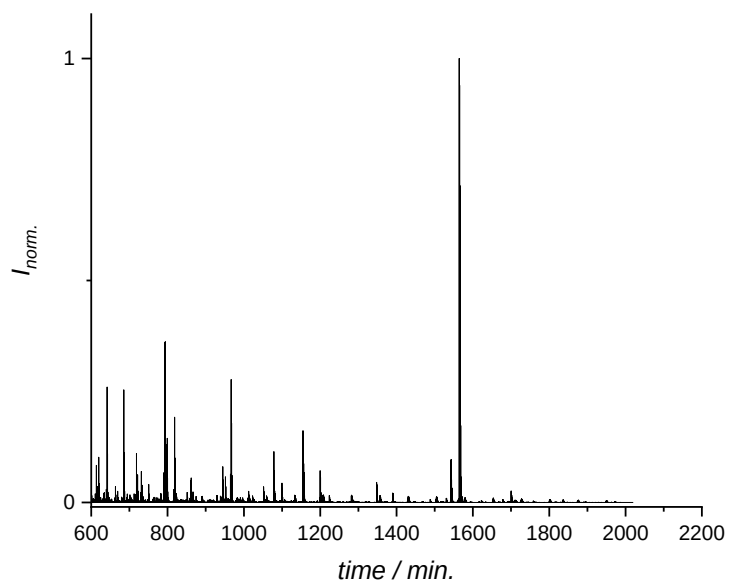
1.3.7 Tetramer mixture



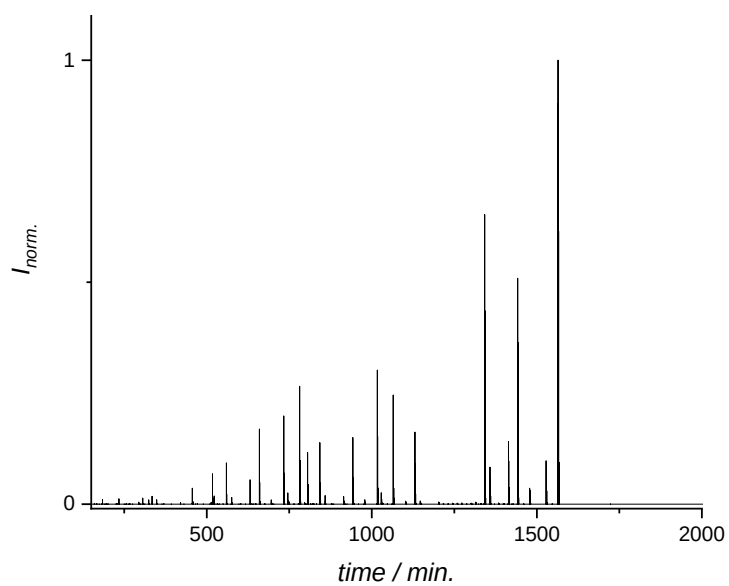
Supplementary Figure 147: Read-out of a mixture of two tetramers. a. ESI-MS spectrum of a mixture of two different tetramers **T1** and **T5** that was used for subsequent tandem ESI-MS/MS fragmentation. For the fragmentation, one of the respective molecule peaks was chosen at a time. b. fragmentation and read-out of tetramer **T1**. c. fragmentation and read-out of tetramer **T5**.

1.3.8 MS and MS/MS Data's

Tetramer T1:

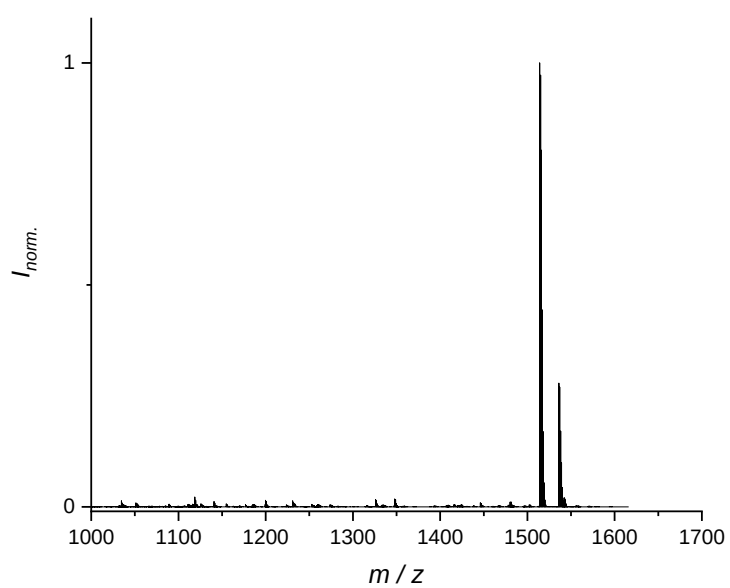


Supplementary Figure 148: ESI-MS spectra of T1, $[M+H]^+$ and $[M+Na]^+$ are visible.

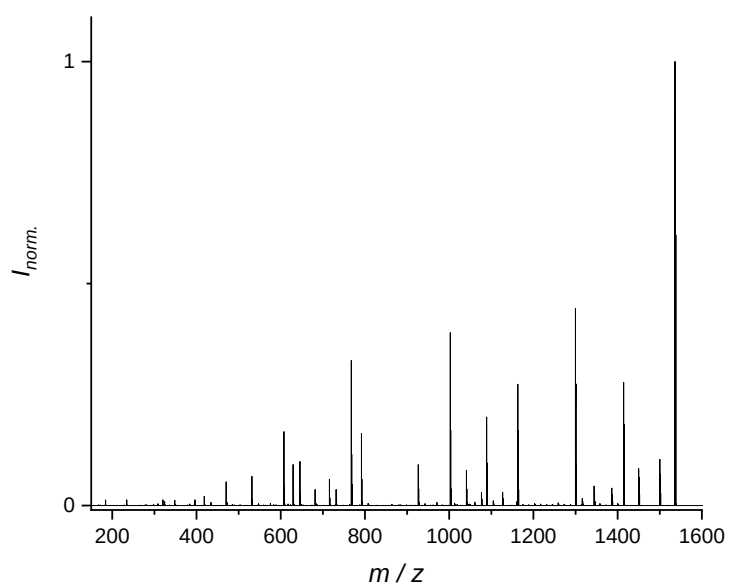


Supplementary Figure 149: ESI-MS/MS spectra of T1 with NCE 35.

Tetramer T2:

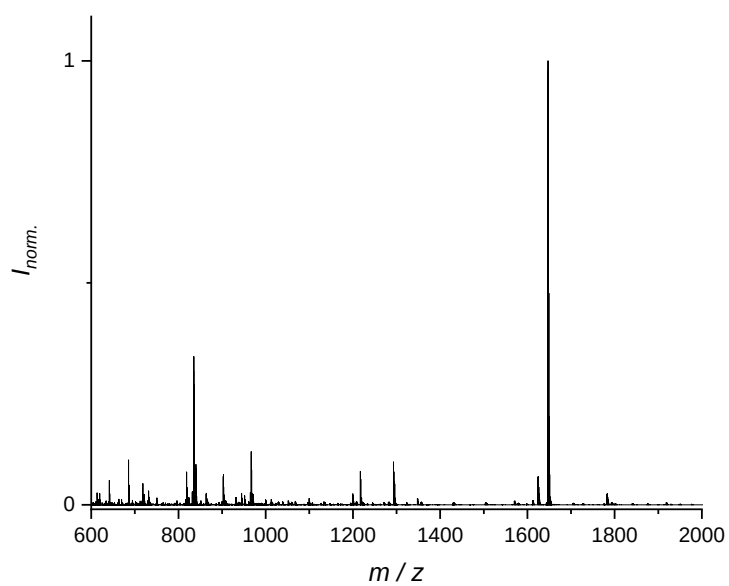


Supplementary Figure 150: ESI-MS spectra of T2, $[M+H]^+$ and $[M+Na]^+$ are visible.

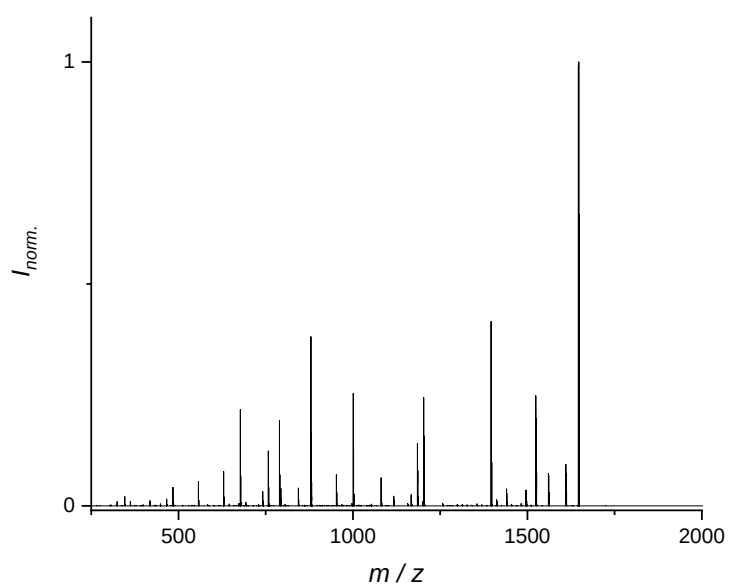


Supplementary Figure 151: ESI-MS/MS spectra of T2 with NCE 35.

Tetramer T3:

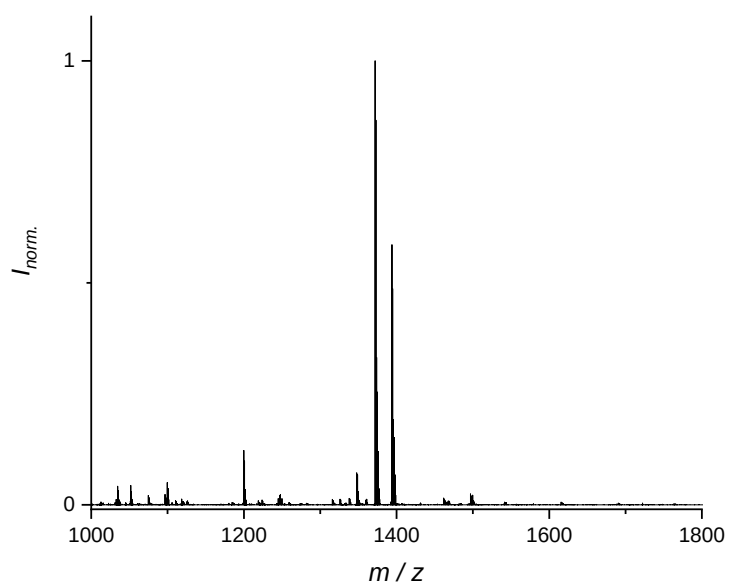


Supplementary Figure 152: ESI-MS spectra of T3, $[M+H]^+$ and $[M+Na]^+$ and $[M+Na]^{2+}$ are visible.

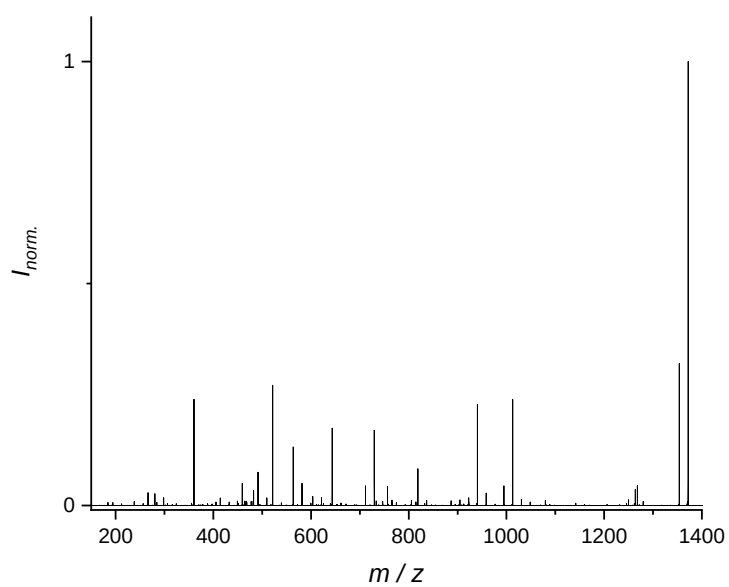


Supplementary Figure 153: ESI-MS/MS spectra of T3 with NCE 35.

Tetramer T4

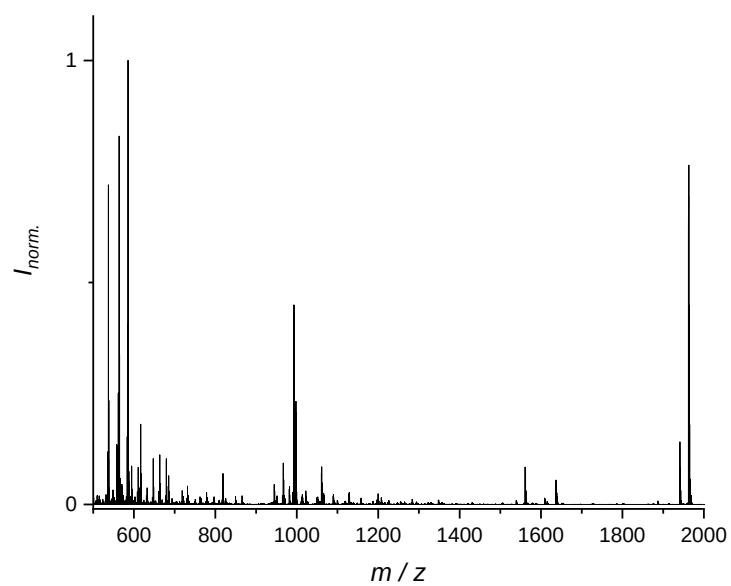


Supplementary Figure 154: ESI-MS spectra of T4, $[M+H]^+$ and $[M+Na]^+$ are visible.

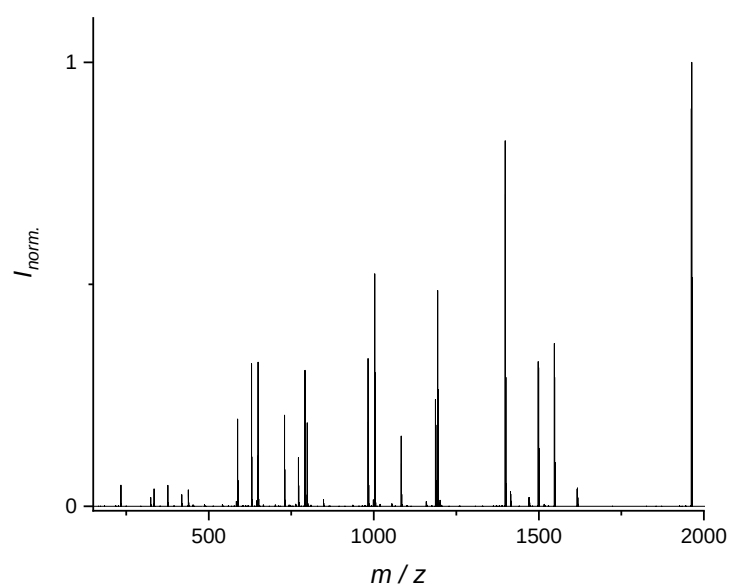


Supplementary Figure 155: ESI-MS/MS spectra of T4 with NCE 18.

Tetramer T5

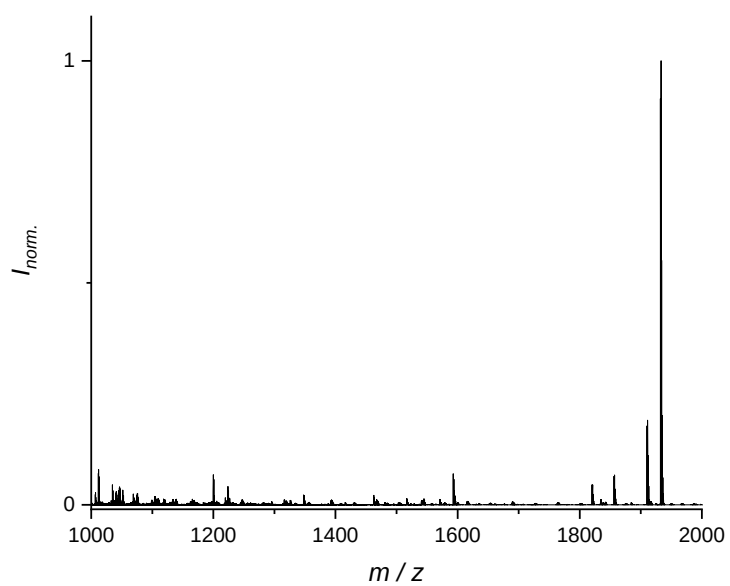


Supplementary Figure 156: ESI-MS spectra of T5, $[M+H]^+$ and $[M+Na]^+$ and $[M+Na]^{2+}$ are visible.

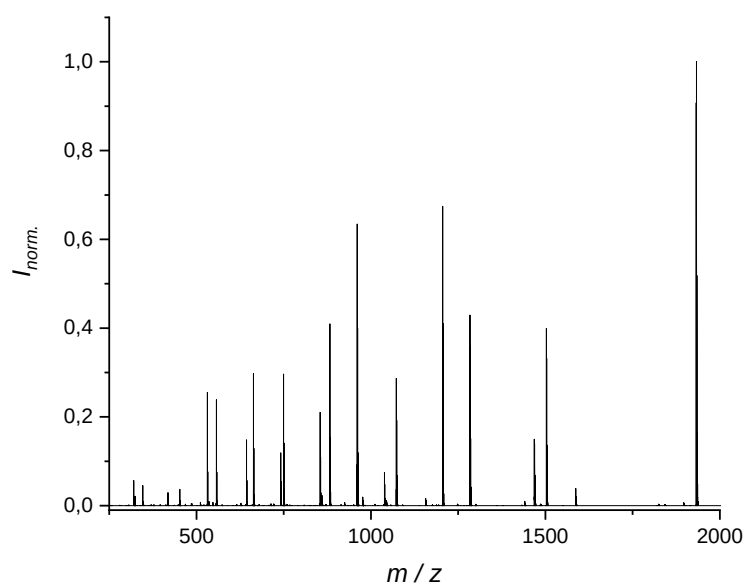


Supplementary Figure 157: ESI-MS/MS spectra of T5 with NCE 35.

Tetramer T6

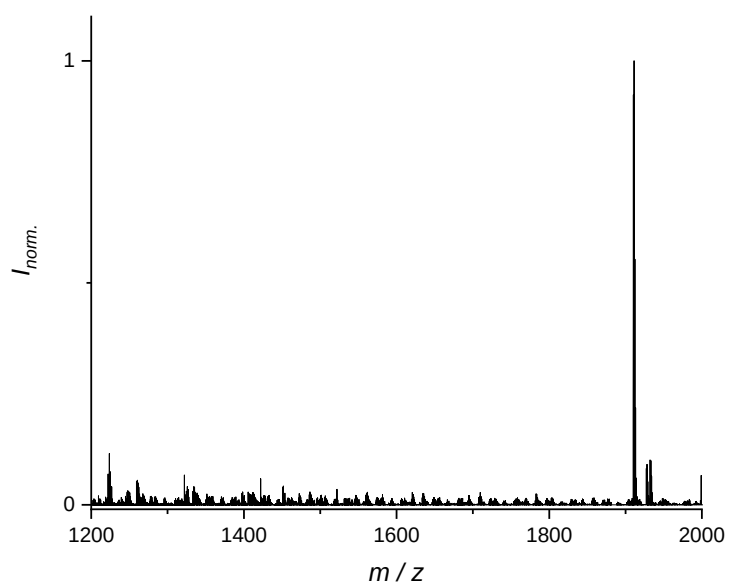


Supplementary Figure 158: ESI-MS spectra of T5, [M+H]⁺ and [M+Na]⁺ are visible.

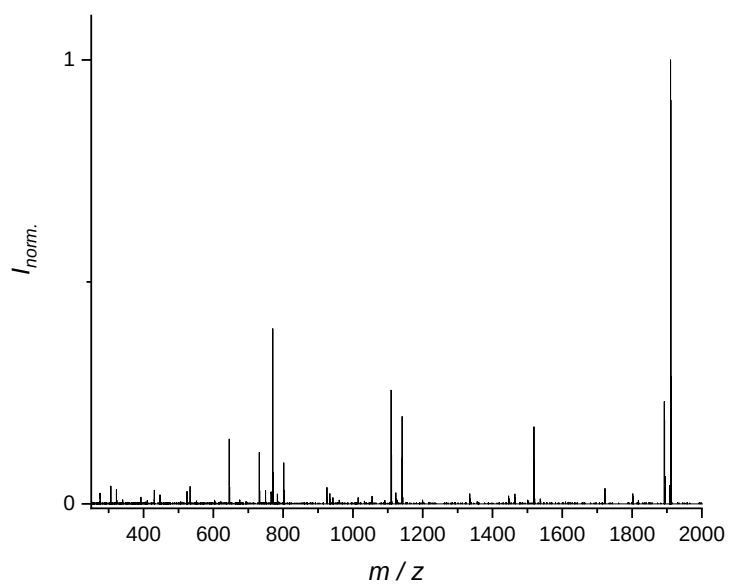


Supplementary Figure 159: ESI-MS/MS spectra of T6 with NCE 35.

Tetramer T7

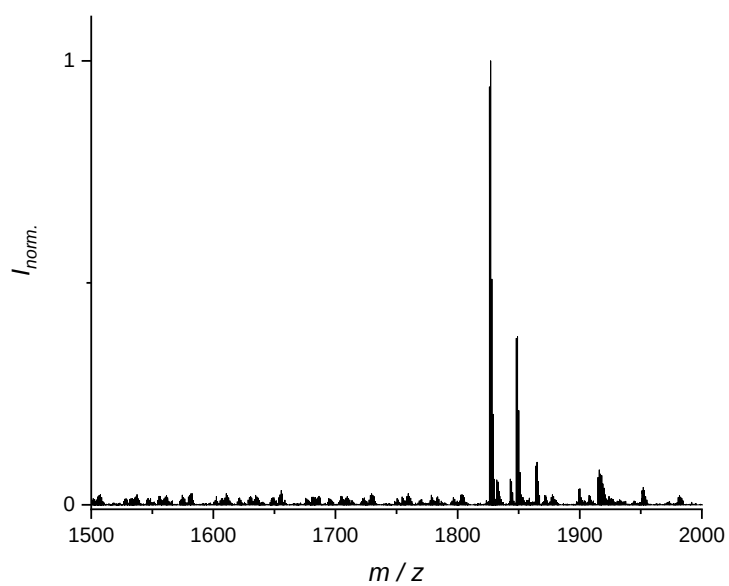


Supplementary Figure 160: ESI-MS spectra of T7, $[M+H]^+$ and $[M+Na]^+$ are visible.

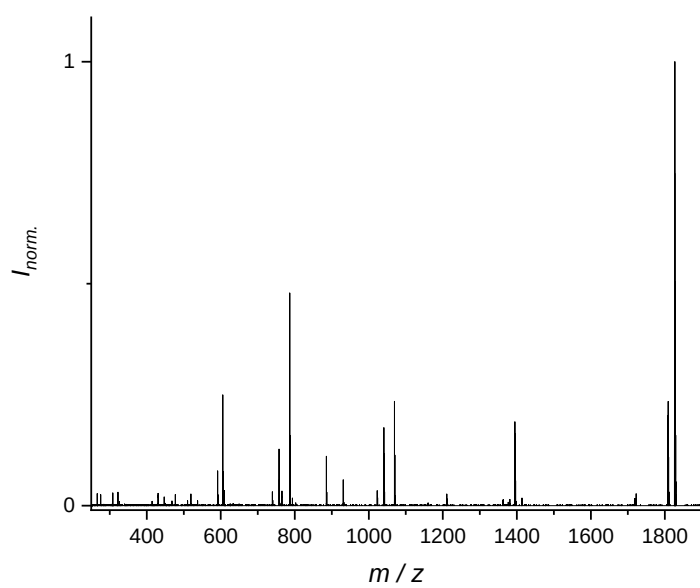


Supplementary Figure 161: ESI-MS/MS spectra of T7 with NCE 17.

Tetramer T8

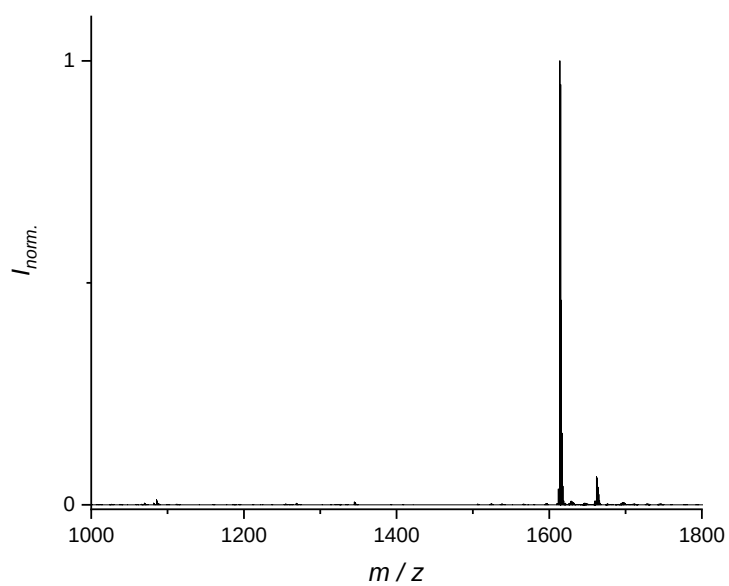


Supplementary Figure 162: ESI-MS spectra of T8, $[M+H]^+$ and $[M+Na]^+$ are visible.

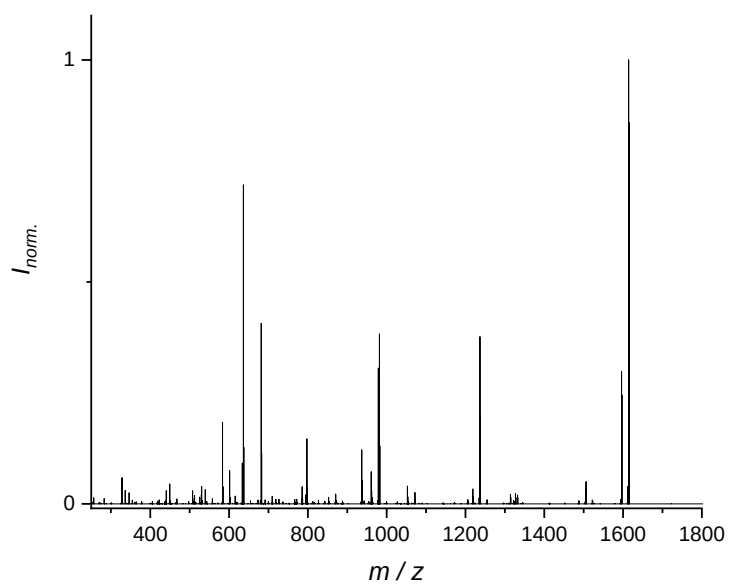


Supplementary Figure 163: ESI-MS/MS spectra of T8 with NCE 17.

Tetramer 9

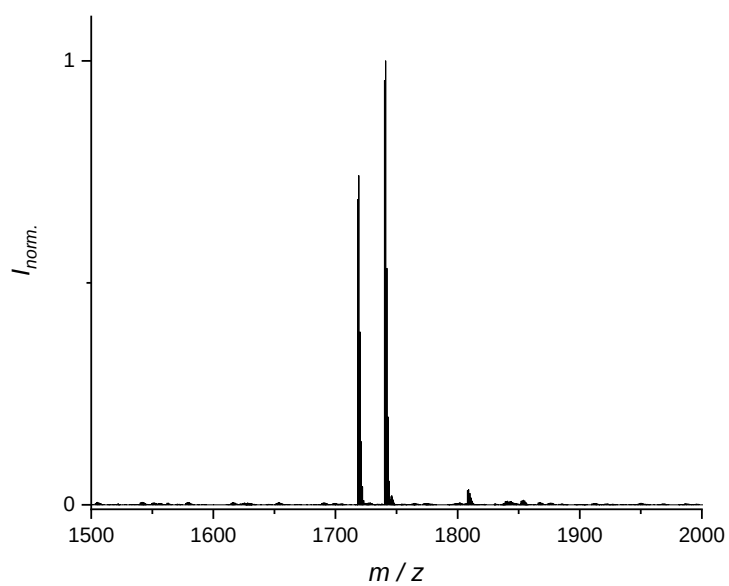


Supplementary Figure 164: ESI-MS spectra of T9, $[M+H]^+$ and $[M+Na]^+$ are visible.

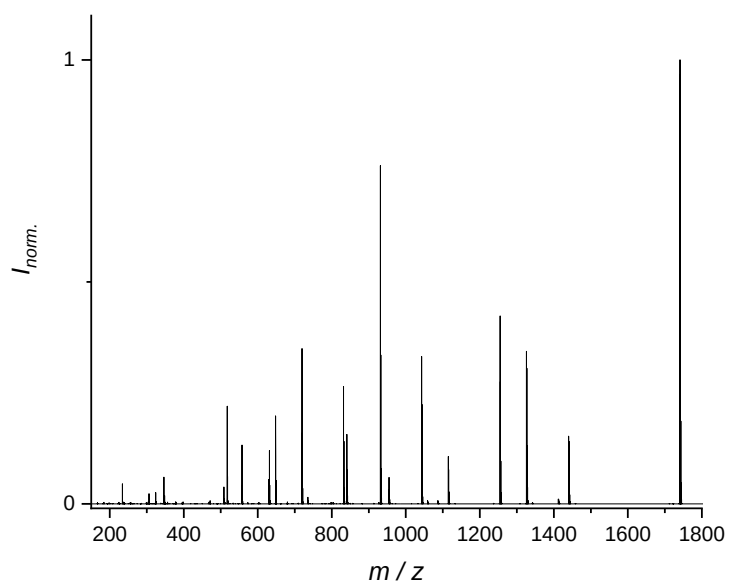


Supplementary Figure 165: ESI-MS/MS spectra of T9 with NCE 17.

Tetramer T10

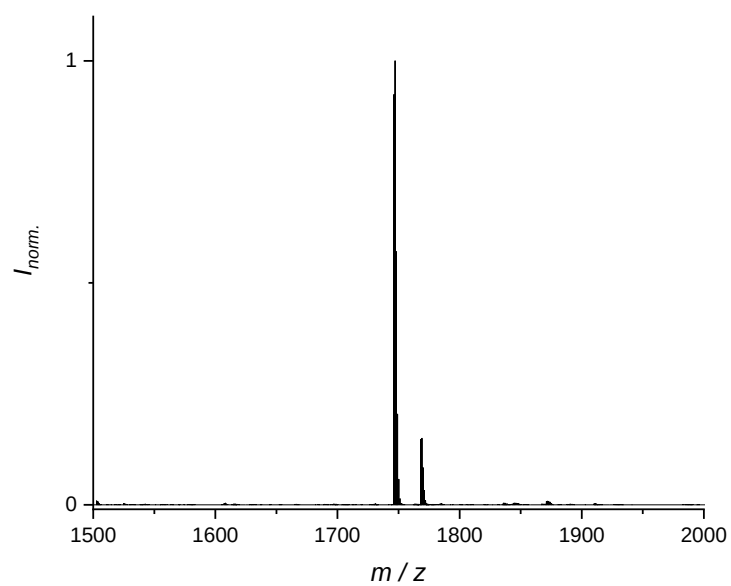


Supplementary Figure 166: ESI-MS spectra of T10, $[M+H]^+$ and $[M+Na]^+$ are visible.

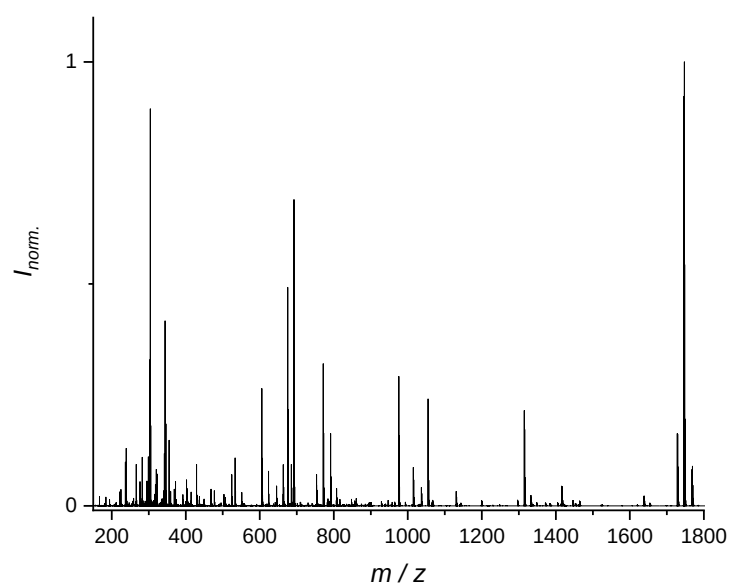


Supplementary Figure 167: ESI-MS/MS spectra of T10 with NCE 35.

Tetramer T11

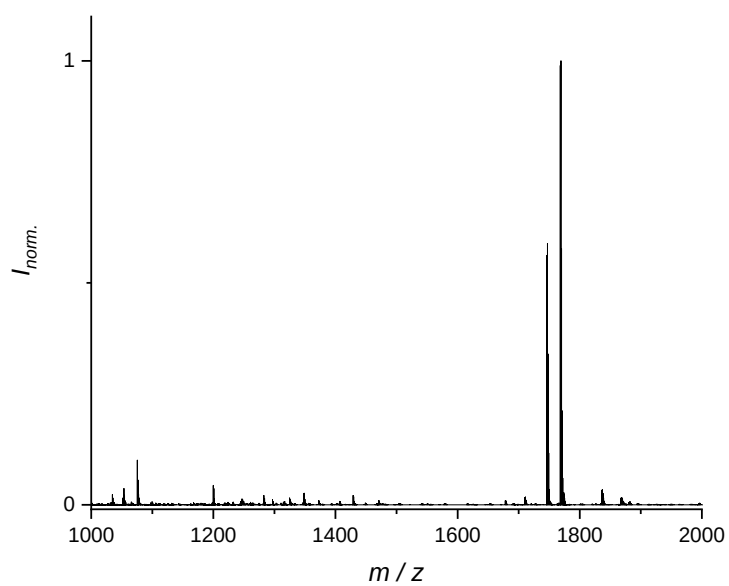


Supplementary Figure 168: ESI-MS spectra of T11, $[M+H]^+$ and $[M+Na]^+$ are visible.

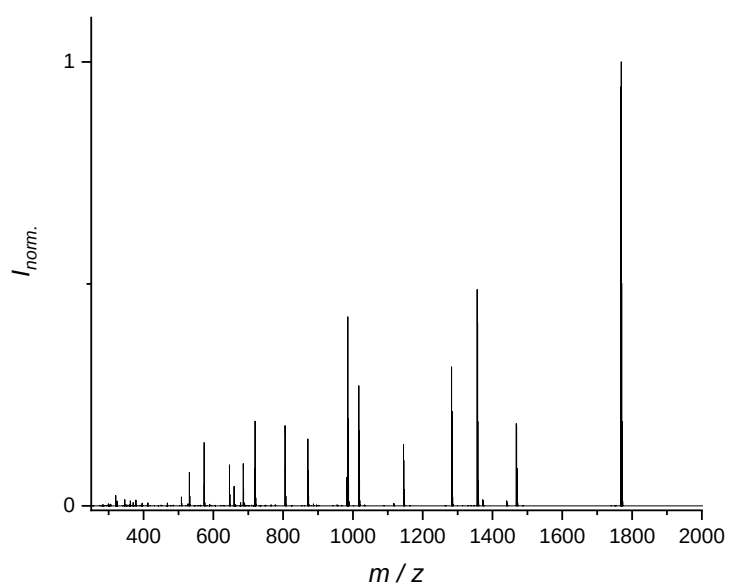


Supplementary Figure 169: ESI-MS/MS spectra of T11 with NCE 17.

Tetramer T12



Supplementary Figure 170: ESI-MS spectra of T12, $[M+H]^+$ and $[M+Na]^+$ are visible.



Supplementary Figure 171: ESI-MS/MS spectra of T12 with NCE 35.

1.4 Supplementary References

1. Solleder, S. C., Zengel, D., Wetzel, K. S. & Meier, M. A. R. A scalable and high-yield strategy for the synthesis of sequence-defined macromolecules. *Angew. Chemie - Int. Ed.* **55**, 1204–1207 (2016).