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), isobutyaldehyde 14c (98%, Sigma-Aldrich), 3-methylbutyaldehyde 14g (≥ 98%, VWR), cyclohexancarboxaldehyde 14j (98%), heptanal 14b (≥ 95%,Sigma-Aldrich), octanal 14i (99%, Sigma-Aldrich), dodecanal 14h (≥ 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, 1H,1H,2H,2H-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 (≥ 99%, Carl Roth), DMSO-d6 (≥ 99.8%, Euriso-top), MeOH-d4 (≥ 99.8%, Euriso-top), CDC13 (≥ 99.8%, Euriso-top), dichloromethane (DCM, HPLC grade ≥ 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**

\(^1\)H, \(^{19}\)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 \(^1\)H NMR, at 376 MHz for \(^{19}\)F and 101 MHz for \(^{13}\)C NMR. \(^1\)H spectra were recorded on a Bruker Avance 300 NMR instrument at 300 MHz for \(^1\)H NMR or on a Bruker AVANCE DRX at 500 MHz for \(^1\)H NMR and 126 MHz for \(^{13}\)C NMR. CDCl\(_3\) or CD\(_3\)OD were used as solvents. Chemical shifts are presented in parts per million (δ) relative to the resonance signal at 7.26 ppm (\(^1\)H, CDCl\(_3\)) and 77.16 ppm (\(^{13}\)C, CDCl\(_3\)) or 3.31 ppm (\(^1\)H, CD\(_3\)OD) and 49.00 ppm (\(^{13}\)C, CD\(_3\)OD), 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 (LCYCLE20AD), 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, ≥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 [M]\(^+\), peaks of pseudo molecules [M+H]\(^+\) and [M+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

\[
\begin{align*}
\text{H}_3\text{N} & \hspace{1cm} \text{4} \\
\text{Cl} & \hspace{1cm} \text{O}
\end{align*}
\]

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).

\(^1\)H-NMR (300 MHz, CDOD\(_3\)): \(\delta / \text{ppm} = 7.53 – 6.77 \text{ (m, 5 H, } \text{CH}_\text{Ar})\), 5.08 (s, 2 H, CH\(_2\)), 3.03 – 2.71 (m, 2 H, CH\(_2\)), 2.39 – 2.08 (m, 2 H, CH\(_2\)), 1.76 – 1.45 (m, 4 H, CH\(_2\)), 1.42 – 1.02 (m, 12 H, CH\(_2\)). \(^1\)H-NMR was in accordance to the literature.¹

1.3.1.2 N-Formylation

\[
\begin{align*}
\text{H} & \hspace{1cm} \text{6} \\
\text{N} & \hspace{1cm} \text{O}
\end{align*}
\]

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).

\(^1\)H-NMR (300 MHz, CDCl\(_3\)): \(\delta / \text{ppm} = 8.01 \text{ (s, 1 H, CH)}, 7.38 – 7.08 \text{ (m, 5 H, CH}_\text{Ar}\)), 5.03 (s, 2 H, CH\(_2\)), 4.52 (s, 1 H, NH), 3.31 – 3.18 (m, 2 H, CH\(_2\)), 2.26 (t, \(J = 7.6 \text{ Hz, } 2 \text{ H, CH}_2\)), 1.67 – 1.30 (m, 4 H, CH\(_2\)), 1.18 (s, 12 H, CH\(_2\)). \(^1\)H-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 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).

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ / ppm = 7.47 – 7.03 (m, 5 H, CH$_{Ar}$), 5.00 (s, 2 H, CH$_2$), 3.24 (s, 2 H, CH$_2$), 2.33 – 2.13 (m, 2 H, CH$_2$), 1.62 – 1.47 (m, 4 H, CH$_2$), 1.36 – 1.31 (m, 12 H, CH$_2$). $^1$H-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 µL 1H,1H,2H,2H-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 µmol, 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 × 60 mL). The organic layer was washed with water (3 × 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).

Rₐ = 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, OH), 4.41 (t, J = 6.5 Hz, 2 H, CH₂), 2.76 – 2.59 (m, 4 H, CH₂), 2.56 – 2.38 (m, 2 H, CH₂).

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, CF₅), -117.80 – -118.24 (m, 2 F, CF₂), 125.96 – 126.62 (m, 2 F, CF₂), -126.68 – -127.49 (m, 2 F, CF₂), -127.68 – -128.41 (m, 2 F, CF₂), -130.13 – -130.91 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₅ group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for 12C₁₂¹H₉¹⁶O₄¹⁹F₁₃, 465.0366; found, 465.0354, Δ = 1.2 mmu.
Supplementary Figure 1: $^1$H-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 succin anhydride 11 (5.75 mmol, 1.15 eq.) and 48.9 mg DMAP 12 (400 µmol, 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 × 60 mL). The organic layer was washed with water (3 × 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, CH₂), 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, CF₃), -123.85 – -126.58 (m, 2 F, CF₂), -131.47 – -134.72 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + Na]⁺ calculated for ¹²C₈H₁₇O₁₆F₇, 323.0125; found, 323.0117, Δ = 0.8 mmu.
Supplementary Figure 2: $^1$H-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 µL 4-chlorobutyric acid TAG3 (254 mg, 2.07 mmol, 1.00 eq.) was stirred in 2.00 mL DCM, subsequently 328 µL 2-ethybutanal 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 → 6:1) to yield product 15 as a yellow, highly viscous oil. (992 mg, 1.88 mmol, 90.8%).

Rf: 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, CDCl₃): δ / ppm = 7.40 – 7.28 (m, 5 H, CHAr), 6.03 (t, J = 5.9 Hz, 1 H, NH₂), 5.28 (d, J = 3.8 Hz, 1 H, CH₂), 5.10 (s, 2 H, CH₂), 3.68 – 3.50 (m, 2 H, CH₂), 3.36 – 3.15 (m, 2 H, CH₂), 2.60 (td, J = 7.1, 2.5 Hz, 2 H, CH₂), 2.33 (t, J = 7.5 Hz, 2 H, CH₂), 2.18 – 2.07 (m, 2 H, CH₂), 1.88 – 1.77 (m, 1 H, CH₁), 1.69 – 1.33 (m, 2 H, CH₂), 1.53 – 1.13 (m, 18 H, CH₂), 0.95 – 0.86 (m, 6 H, CH₃).

¹³C NMR (101 MHz, CDCl₃): 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]: [M+H]⁺ calculated for ¹²C₂⁹H₄⁶O₅¹⁴N⁻¹⁵Cl: 524.3137; found: 524.3126; Δ = 1.1 mmu.
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, CDCl₃): δ / ppm = 5.97 (t, J = 5.9 Hz, 1 H, NH¹), 5.23 (d, J = 3.8 Hz, 1 H, CH²), 3.62 – 3.52 (m, 2 H, CH₃), 3.30 – 3.11 (m, 2 H, CH₂), 2.56 (td, J = 7.1, 2.3 Hz, 2 H, CH₂), 2.27 (t,
$J = 7.5$ Hz, 2 H, CH$_6^6$), 2.13 – 2.01 (m, 2 H, CH$_2^5$), 1.83 – 1.72 (m, 1 H, CH$_3^6$), 1.60 – 1.51 (m, 2 H, CH$_2^7$), 1.47 – 1.09 (m, 18 H, CH$_2^{10}$), 0.91 – 0.79 (m, 6 H, CH$_2^{11}$).

$^1$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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 $^{12}$C$_{22}$H$_{40}$O$_5$N$_3$Cl, 434.2668; found, 434.2659, $\Delta = 0.9$ mmu.

Supplementary Figure 4: $^1$H-NMR of compound 17 measured in CDCl$_3$.

Passerini reaction

In a 50 mL round bottom flask, 313 mg 17 (722 µmol, 1.00 eq.) was stirred in 2.00 mL DCM, subsequently 151 µL 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%).

Rf: 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, CH₆¹), 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, CH⁵), 3.62 (t, J = 6.2 Hz, 2 H, CH⁶), 3.33 – 3.17 (m, 4 H, CH⁷), 2.61 (td, J = 7.1, 2.7 Hz, 2 H, CH⁸), 2.41 – 2.30 (m, 4 H, CH⁹), 1.90 – 1.74 (m, 3 H, CH¹₀, CH¹₁), 1.68 – 1.57 (m, 4 H, CH¹₂), 1.54 – 1.15 (m, 40H, CH¹³), 0.96 – 0.82 (m, 9 H, CH¹⁴).

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 12C₄₈H₆¹O₈¹⁴N₂³⁵Cl: 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), 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, CDCl₃): δ / ppm = 6.15 – 6.02 (m, 2 H, NH¹), 5.28 (d, J = 3.9 Hz, 1 H, CH²), 5.21 – 5.10 (m, 1 H, CH³), 3.61 (t, J = 6.1 Hz, 2 H, CH₄), 3.33 – 3.15 (m, 4 H, CH₂⁵), 2.61 (td, J = 7.1, 2.8 Hz, 2 H, CH₂⁶), 2.37 (t, J = 7.5 Hz, 2 H, CH₂⁷), 2.31 (t, J = 7.5 Hz, 2 H, CH₂⁸), 2.18 – 2.05 (m, 2 H, CH₂⁹), 1.88 – 1.74 (m, 3 H, CH³, CH₂¹⁰), 1.69 – 1.54 (m, 4 H, CH₂¹¹), 1.52 – 1.14 (m, 40 H, CH₂¹²), 0.95 – 0.81 (m, 9 H, CH₃¹³).

¹³C NMR (101 MHz, CDCl₃): 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, 24.63, 22.33, 21.97, 14.15, 11.67, 11.65.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹⁵C₄₁H₅₁O₇¹⁴N₂⁵Cl, 759.5285; found, 759.5267, Δ = 1.8 mmu.
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 → 2:1) to yield the passerini product 20 as a yellow highly viscous oil. (460 mg, 410 μmol, 89.1%).

Rf: 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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 7.35 – 7.23 (m, 5 H, CH$_3^1$), 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$_3^8$), 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$_3$): $\delta$ / 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]: [M+Na]$^+$ calculated for $^{13}$C$_6$H$_{110}$O$_{11}$N$_3$Cl: 1154.7721; found: 1154.7698; $\Delta$ = 2.3 mmu.

Supplementary Figure 7: $^1$H-NMR of compound 20 measured in CDCl$_3$. 

![Supplementary Figure 7: $^1$H-NMR of compound 20 measured in CDCl$_3$.](image-url)
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, CDCl₃): δ / ppm = 6.08 (t, J = 5.9 Hz, 1 H, NH¹), 6.06 – 5.98 (m, 2 H, NH¹), 5.29 (d, J = 3.8 Hz, 1 H, CH²), 5.18 – 5.13 (m, 1 H, CH³), 5.05 (d, J = 4.5 Hz, 1 H, CH⁴), 3.62 (t, J = 6.2 Hz, 2 H, CH₂⁵), 3.34 – 3.18 (m, 6 H, CH₃⁵), 2.62 (td, J = 7.1, 2.6 Hz, 2 H, CH₂⁷), 2.44 – 2.25 (m, 7 H, CH²⁸,CH₃⁹), 2.18 – 2.08 (m, 2, CH₂¹⁰), 1.94 – 1.74 (m, 3 H, CH¹¹, CH₂¹²), 1.71 – 1.57 (m, 6 H, CH₃¹³), 1.37 – 1.14 (m, 54 H, CH₂¹⁴), 0.98 – 0.82 (m, 15 H, CH₃¹⁵).

¹³C NMR (101 MHz, CDCl₃): 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]: [M + H]⁺ calculated for 12C₅⁷H₁₀₄O₁⁴N₃Cl, 1042.7432; found, 1042.7412, Δ = 2.0 mmu.
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 → 1:1) to yield the passerini product T1 as a yellow highly viscous oil. (981 mg, 635 µmol, 96.4%).
Rf: 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, CDCl₃): δ / ppm = 7.43 – 7.29 (m, 5 H, CH₁⁻⁸), 6.08 – 5.93 (m, 4 H, NH²), 5.29 (d, J = 3.8 Hz, 1 H, CH³), 5.17 – 5.12 (m, 2 H, CH⁵), 5.11 (s, 2 H, CH⁶), 5.04 (d, J = 4.5 Hz, 1 H, CH⁹), 3.63 (t, J = 6.2 Hz, 2 H, CH₁⁵), 3.33 – 3.17 (m, 8 H, CH₂⁸), 2.68 – 2.56 (m, 2 H, CH₂⁹), 2.43 – 2.26 (m, 9 H, CH₁⁰, CH₂¹¹), 2.18 – 2.08 (m, 2 H, CH₁²), 1.91 – 1.74 (m, 5 H, CH¹³, CH₂¹⁴), 1.69 – 1.58 (m, 12 H, CH₂¹⁵), 1.54 – 1.16 (m, 84 H, CH₂¹⁶), 0.96 – 0.82 (m, 18 H, CH₂¹⁷).

¹³C NMR (126 MHz, CDCl₃): 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]: [M+Na]⁺ calculated for ¹²C₈₉H₁₅₇O₁₄N₄Cl: 1564.1277; found: 1564.1282; Δ = 0.5 mmu.

Supplementary Figure 9: ¹H-NMR of compound T1 measured in CDCl₃.
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).
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 I6 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, CDCl₃): δ/ppm = 6.14 – 5.98 (m, 4 H, NH¹), 5.29 (d, J = 3.8 Hz, 1 H, CH²), 5.19 – 5.11 (m, 2 H, CH³), 5.04 (d, J = 4.5 Hz, 1 H, CH⁴), 3.62 (t, J = 6.2 Hz, 2 H, CH₅), 3.33 – 3.16 (m, 8 H, CH₂⁶), 2.68 – 2.57 (m, 2 H, CH⁷), 2.50 – 2.23 (m, 9 H, CH⁸, CH₉), 2.21 – 2.06 (m, 2 H, CH₁₀), 1.94 – 1.73 (m, 5 H, CH¹⁰, CH₁²), 1.73 – 1.56 (m, 8 H, CH₁³), 1.57 – 1.17 (m, 88 H, CH₁⁴), 0.98 – 0.82 (m, 18 H, CH₁⁵).

¹³C NMR (101 MHz, CDCl₃): 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]: [M + H]⁺ calculated for ¹²C₈₂¹H₁₅₁⁶O₁⁴N₄³Cl, 1452.0988; found, 1452.0990, Δ = 0.2 mmu.
Supplementary Figure 13: $^1$H-NMR of compound 22 measured in CDCl₃.

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 → 1:1) to yield the passerini product 23 as a yellow highly viscous oil (911 mg, 482 µmol, 93.2%).

Rf: 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), $1311.6$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 7.44 – 7.16$ (m, 10 H, CH$_{1}$), $6.12 – 5.93$ (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$_{6}$), $5.17 – 5.12$ (m, 2 H, CH$_{7}$), $5.10$ (s, 2 H, CH$_{2}$), $5.04$ (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$_{10}$), $3.34 – 2.95$ (m, 2 H, CH$_{2}$), $2.69 – 2.55$ (m, 2 H, CH$_{11}$), $2.52 – 2.22$ (m, 11 H, CH$_{12}$), $1.96 – 1.72$ (m, 5 H, CH$_{13}$, CH$_{17}$), $1.72 – 1.04$ (m, 115 H, CH$_{14}$, CH$_{19}$), $0.97 – 0.82$ (m, 18 H, CH$_{20}$).

$^{13}$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, 29.65, 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, 26.95, 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]: [M+H]$^+$ calculated for $^{12}$C$_{110}^{1}$H$_{188}^{16}$O$_{17}^{14}$N$_{35}^{35}$Cl: 1887.3762; found 1887.3793; $\Delta = 3.1$ mmu.
Supplementary Figure 14: $^1$H-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): $\nu$ / 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), 699.8 (m), 653.9 (w), 538.2 (vw).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 7.34 – 7.15 (m, 5 H, CH$_{Ar}$), 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$_{6b}$), 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$_{8}$), 3.52 – 3.40 (m, 1 H, CH$_{9}$), 3.35 – 2.97 (m, 10 H, CH$_{2}$), 2.68 – 2.56 (m, 2 H, CH$_{10}$), 2.44 – 2.23 (m, 11 H, CH$_{11}$, CH$_{12}$), 2.18 – 2.08 (m, 2 H, CH$_{13}$), 1.93 – 1.73 (m, 5 H, CH$_{14}$, CH$_{15}$), 1.71 – 1.04 (m, 115 H, CH$_{16}$, CH$_{17}$), 0.99 – 0.82 (m, 18 H, CH$_{18}$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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, 1j5.31, 14.26, 14.18, 11.73, 11.71.

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

Supplementary Figure 15: $^1$H-NMR of compound 24 measured in CDCl$_3$. 
Passerini reaction

In a 25 mL round bottom flask, 641 mg \( \text{24} \) (356 \( \mu \text{mol}, 1.00 \text{eq.} \)) was stirred in 3.00 mL DCM. Subsequently, 59.8 \( \mu \text{L} \) acetaldehyde \( \text{14f} \) (47.1 mg, 1.07 mmol, 3.00 eq.) and 161 mg of the monomer \( \text{M1} \) (535 \( \mu \text{mol}, 1.50 \text{eq.} \)) 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\textsuperscript{®} 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 \( \text{H1} \) as a pale highly viscous oil. (433.1 mg, 626 \( \mu \text{mol}, 56.7\% \)).

\( \text{Rf} = 0.39 \) in cyclohexane / ethyl acetate (1:1).

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

\( ^{1} \text{H NMR (400 MHz, CDCl}_3) \): \( \delta / \text{ppm} \) = 7.46 – 7.13 (m, 10 H, CH\text{Ar}), 6.20 – 5.92 (m, 5 H, NH\text{2}), 5.75 – 5.59 (m, 1 H, NH\text{2}), 5.34 – 5.08 (m, 7 H, CH\text{3}, CH\text{5}), 5.04 (d, \( J = 4.5 \text{ Hz} \), 1 H, CH\text{3}), 3.69 – 3.58 (m, 2 H, CH\text{2}), 3.49 – 3.39 (m, 1 H, CH\text{6}), 3.34 – 2.97 (m, 12 H, CH\text{2}), 2.66 – 2.57 (m, 2 H, CH\text{2}), 2.45 – 2.23 (m, 13 H, CH\text{2}, CH\text{3}), 2.19 – 2.07 (m, 2 H, CH\text{1}), 1.92 – 1.05 (m, 138 H, CH\text{1}, CH\text{3}), 0.99 – 0.82 (m, 18 H, CH\text{3}).

\( ^{13} \text{C NMR (101 MHz, CDCl}_3) \): \( \delta / \text{ppm} \) = 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 [\( m/z \): [M + H]\textsuperscript{+} calculated for \( ^{12} \text{C}_124^{16} \text{H}_{213}^{16} \text{O}_{20}^{14} \text{N}_6^{35} \text{Cl}, 2142.5596; \) found, 2142.5607, \( \Delta = 1.1 \text{ mmu.} \)
Supplementary Figure 16: $^1$H-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).

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.
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 → 6:1) to afford product 25 as a high viscous oil in a yield of 78.9% (258 mg, 480 µmol).

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, CDCl₃): δ / ppm = 7.42 – 7.29 (m, 5 H, CHAr), 6.01 (t, J = 5.9 Hz, 1 H, NH₂), 5.18 – 5.14 (m, 1 H, CH₃), 5.11 (s, 2 H, CH₂), 3.62 (td, J = 6.3, 1.4 Hz, 2 H, CH₂), 3.36 – 3.17 (m, 2 H, CH₂), 2.61 (td, J = 7.1, 1.5 Hz, 2 H, CH₂), 2.35 (t, J = 7.5 Hz, 2 H, CH₂), 1.93 – 1.74 (m, 2 H, CH₂), 1.69 – 1.59 (m, 2 H, CH₂), 1.54 – 1.44 (m, 2 H, CH₂), 1.40 – 1.13 (m, 20 H, CH₃), 0.91 – 0.83 (m, 3 H, CH₃).

13C NMR (101 MHz, CDCl₃): 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, 25.07, 24.86, 22.66, 14.17.

ESI-MS [m/z]: [M + H]⁺ calculated for 13C₃₀H₄₈O₅NCl, 538.3294; found, 538.3282, Δ = 1.2 mmu.
Supplementary Figure 21: $^1$H-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): $\nu/\text{cm}^{-1}$ = 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).
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta / \text{ppm} = 6.11 - 6.01 (m, 1 \text{ H, NH})\), 5.20 – 5.11 (m, 1 \text{ H, CH})\(^2\), 3.62 (t, \(J = 6.1 \text{ Hz, 2 H, CH}_2\)), 3.35 – 3.17 (m, 2 \text{ H, CH}_2\)), 2.60 (t, \(J = 6.6 \text{ Hz, 2 H, CH}_2\)), 2.36 – 2.28 (m, 2 \text{ H, CH}_2\)), 2.19 – 2.06 (m, 2 \text{ H, CH}_2\)), 1.92 – 1.75 (m, 2 \text{ H, CH}_2\)), 1.67 – 1.56 (m, 2 \text{ H, CH}_2\)), 1.56 – 1.43 (m, 2 \text{ H, CH}_2\(^{10}\)), 1.38 – 1.12 (m, 20 \text{ H, CH}_2\(^{11}\)), 0.92 – 0.81 (m, 3 \text{ H, CH}_3\(^{12}\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta / \text{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]: [M + Na]\(^+\) calculated for \(^{12}\)C\(^2\)H\(_4\)\(^{16}\)O\(_3\)\(^{14}\)N\(^{15}\)Cl, 470.2644; found, 470.2639, \(\Delta = 0.5 \text{ mmu.}\)

Supplementary Figure 22: \(^1\)H-NMR of compound 26 measured in CDCl\(_3\).

Passerini reaction

![Passerini reaction](image)

In a 50 mL round bottom flask, 172 mg 26 (384 \(\mu\)mol, 1.00 eq.) was dissolved in 2.00 mL DCM and 62.1 \(\mu\)L 3-methylbutanal 14g (49.7 mg, 577 \(\mu\)mol, 1.50 eq.) and 174 mg of monomer M1 (577 \(\mu\)mol,
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 → 2:1) to afford product 27 as a high viscous oil in a yield of 70.6% (227 mg, 271 µmol).

\[ R_f = 0.39 \text{ in cyclohexane / ethyl acetate (2:1).} \]

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \[ \delta / \text{ppm} = 7.37 \text{– 7.21 (m, 5 H, CH}_2\text{Ar}}, 5.98 \text{– 5.91 (m, 1 H, NH}_2\text{)}, 5.90 \text{– 5.81 (m, 1 H, NH}_2\text{)}, 5.16 \text{– 5.06 (m, 2 H, CH}\_2\text{)}, 5.04 \text{ (s, 2 H, CH}_2\text{)}, 3.56 \text{ (t, } J = 5.7 \text{ Hz, 2 H, CH}_2\text{)}, 3.26 \text{– 3.11 (m, 4 H, CH}_2\text{)}, 2.58 \text{– 2.49 (m, 2 H, CH}_2\text{)}, 2.35 \text{– 2.24 (m, 4 H, CH}_2\text{)}, 2.11 \text{– 2.00 (m, 2 H, CH}_2\text{)}, 1.85 \text{– 1.52 (m, 9 H, CH}(10, 11), 1.47 \text{– 1.36 (m, 4 H, CH}_2\text{)}, 1.31 \text{– 1.12 (m, 32 H, CH}_2\text{)}, 0.86 \text{ (t, } J = 5.6 \text{ Hz, 6 H, CH}_3\text{)}.

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \[ \delta / \text{ppm} = 173.84, 172.78, 171.61, 170.34, 169.78, 128.69, 128.31, 74.49, 72.80, 66.22, 44.09, 40.99, 39.38, 34.47, 34.45, 32.07, 31.74, 31.26, 29.67, 29.58, 29.49, 29.35, 29.25, 29.24, 29.04, 27.51, 26.96, 26.95, 25.08, 24.88, 24.70, 23.28, 22.67, 21.95, 14.18. \]

ESI-MS [m/z]: [M + H]⁺ calculated for \(^{12}\)C\(_4\)H\(_{79}\)O\(_8\)N\(_2\)Cl, 835.5598; found, 835.5588, \(\Delta = 1.0 \text{ mmu.} \]

Supplementary Figure 23: \(^1\)H-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 of 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 mmol).

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, CDCl₃): δ / ppm = 6.12 – 6.03 (m, 1 H, NH¹), 5.98 (t, J = 5.8 Hz, 1 H, NH¹), 5.16 – 5.07 (m, 2 H, CH₂), 3.62 – 3.52 (m, 2 H, CH₃), 3.24 – 3.13 (m, 4 H, CH₂), 2.59 – 2.50 (m, 2 H, CH₂), 2.36 – 2.22 (m, 4 H, CH₂), 2.11 – 2.01 (m, 2 H, CH₂), 1.85 – 1.69 (m, 2 H, CH₂), 1.68 – 1.50 (m, 7 H, CH⁹, CH₁⁵), 1.50 – 1.34 (m, 4 H, CH₂), 1.31 – 1.13 (m, 32 H, CH₁¹), 0.86 (t, J = 5.8 Hz, 6 H, CH₂), 0.83 – 0.77 (m, 3 H, CH₁³).

13C NMR (101 MHz, CDCl₃): 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]: [M + H]^+ calculated for C₄₀H₃₀O₈N₂Cl²⁺, 745.5128; found, 745.5113, Δ = 1.5 mmu.
Supplementary Figure 24: $^1$H-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 → 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): $\tilde{\nu} / \text{cm}^{-1} = 3294.1$ (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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 7.36 – 7.23 (m, 5 H, CH$_{Ar}$), 6.04 – 5.88 (m, 3 H, NH$_2$), 5.16 – 5.05 (m, 3 H, CH$_3$), 5.04 (s, 2 H, CH$_2$), 3.62 – 3.53 (m, 2 H, CH$_2$), 3.27 – 3.12 (m, 6 H, CH$_3$), 2.59 – 2.50 (m, 2 H, CH$_2$), 2.34 – 2.24 (m, 6 H, CH$_3$), 2.12 – 2.01 (m, 2 H, CH$_2$), 1.84 – 1.67 (m, 4 H, CH$_2$), 1.64 – 1.51 (m, 9 H, CH$_3$), 1.47 – 1.37 (m, 6 H, CH$_2$), 1.30 – 1.14 (m, 62 H, CH$_3$), 0.86 (t, $J$ = 5.8 Hz, 6 H, CH$_3$), 0.83 – 0.77 (m, 6 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / ppm = 173.82, 172.78, 172.61, 171.61, 170.36, 169.99, 169.78, 169.71, 146.23, 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, 22.61, 22.65, 21.91, 14.25, 14.16.

ESI-MS [m/z]: [M + H]$^+$ calculated for $^{13}$C$_7$H$_{12}$O$_{11}$N$_3$Cl, 1230.8997; found, 1230.8976, $\Delta$ = 2.1 mmu.

Supplementary Figure 25: $^1$H-NMR of compound 29 measured in CDCl$_3$. 

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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 mmol).

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

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.10 – 5.95$ (m, 3 H, NH$_1$), 5.18 – 5.01 (m, 3 H, CH$_2$), 3.61 – 3.49 (m, 2 H, CH$_2$), 3.25 – 3.12 (m, 6 H, CH$_2$), 2.60 – 2.50 (m, 2 H, CH$_2$), 2.36 – 2.20 (m, 6 H, CH$_2$), 2.13 – 2.00 (m, 2 H, CH$_2$), 1.85 – 1.67 (m, 4 H, CH$_2$), 1.67 – 1.50 (m, 9 H, CH, CH$_2$), 1.48 – 1.37 (m, 6 H, CH$_2$), 1.30 – 1.13 (m, 22 H, CH$_2$), 0.86 (t, $J = 5.9$ Hz, 6 H, CH$_3$), 0.84 – 0.77 (m, 6 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta / \text{ppm} = 177.57, 172.86, 172.62, 171.63, 170.50, 170.09, 169.90, 169.44, 174.08, 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]: [M + H]$^+$ calculated for $^{12}$C$_{68}$H$_{118}$O$_{11}$N$_3$Cl$^{2+}$, 1140.8528; found, 1140.8505, $\Delta = 2.3$ mmu.
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 → 2:1) to afford product T2 as a high viscous oil in a yield of 70.7% (58.2 mg, 38.2 µmol).

Rf = 0.53 in cyclohexane / ethyl acetate (2:1).
IR (ATR): \( \nu / \text{cm}^{-1} = 3293.2541 \) (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).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.35 – 7.23 \) (m, 5 H, CH\(_2\)\(_{\text{Ar}}\)), 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\(_3\)), 3.56 (t, \( J = 6.1 \) Hz, 2 H, CH\(_2\)\(_4\)), 3.27 – 3.09 (m, 8 H, CH\(_2\)\(_3\)), 2.60 – 2.50 (m, 2 H, CH\(_2\)\(_8\)), 2.38 – 2.18 (m, 9 H, CH\(_3\), CH\(_2\)\(_6\)), 2.11 – 2.02 (m, 2 H, CH\(_2\)\(_{11}\)), 1.85 – 1.51 (m, 15 H, CH\(_2\)\(_{12}\), 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\(_3\)): \( \delta / \text{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 \(^{12}\)C\(_{87}\)\(^{1}\)H\(_{15}\)\(^{16}\)O\(_{14}\)N\(_{35}\)Cl, 1514.1145; found, 1514.1137, \( \Delta = 0.8 \) mmu.

Supplementary Figure 27: \(^1\)H-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).
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 µL 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 → 6:1) to yield the passerini product 31 as a yellow highly viscous oil. (675 mg, 1.22 mmol, 86.2%).

Rf = 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, CDCl3): δ/ppm = 7.41 – 7.27 (m, 5 H, CHAr¹), 6.09 (t, J = 5.9 Hz, 1 H, NH²), 5.18 – 5.12 (m, 1 H, CH³), 5.09 (s, 2 H, CH²), 3.60 (td, J = 6.3, 1.2 Hz, 2 H, CH²), 3.32 – 3.16 (m, 2 H, CH²), 2.59 (td, J = 7.1, 1.7 Hz, 2 H, CH²), 2.33 (t, J = 7.5 Hz, 2 H, CH³), 2.16 – 2.06 (m, 2 H, CH²), 1.95 – 1.73 (m, 2 H, CH²), 1.66 – 1.56 (m, 2 H, CH²), 1.52 – 1.45 (m, 2 H, CH²), 1.37 – 1.14 (m, 22 H, CH(CH₃)²), 0.92 – 0.81 (m, 3 H, CH(CH₃)²).

13C NMR (101 MHz, CDCl3): 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]: [M+H]+ calculated for 12C₃₁H₅₁O₁₆N₁₄Cl, 552.3450; found: 552.3438; Δ = 1.2 mmu.
Supplementary Figure 31: $^1$H-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): $\nu$ / 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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/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$_2$), 3.28 – 3.11 (m, 2 H, CH$_2$), 2.62 – 2.49 (m, 2 H, CH$_2$), 2.26 (t, $J = 7.5$ Hz, 2 H, CH$_2$), 2.13 – 2.01 (m, 2 H, CH$_2$), 1.86 – 1.69 (m, 2 H, CH$_2$), 1.61 – 1.50 (m, 2 H, CH$_2$), 1.47 – 1.38 (m, 2 H, CH$_2$), 1.32 – 1.13 (m, 22 H, CH$_2$), 0.84 – 0.76 (m, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/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]: [M + H]$^+$ calculated for $^{12}$C$_{24}$H$_{44}$O$_5$N$^{35}$Cl, 462.2981; found, 462.2971, $\Delta = 1.0$ mmu.

Supplementary Figure 32: $^1$H-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 3.0 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 → 4:1) to yield the passerini product 33 as a yellow highly viscous oil. (1.65 g, 755 µmol, 92.6%).

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

IR (ATR): υ / cm⁻¹ = 3304.4 (w), 2922.2 (s), 2852.3 (m), 1737.3 (s), 1536.8 (m), 1456.1 (w), 1376.6 (w), 1166.4 (m), 723.0 (w), 696.9 (w).

¹H NMR (400 MHz, CDCl₃): δ / ppm = 7.41 – 7.29 (m, 5 H, CHAr¹), 6.08 – 5.92 (m, 2 H, NH₂), 5.21 – 5.14 (m, 2 H, CH₃), 5.11 (s, 2 H, CH₄), 3.66 – 3.59 (m, 2 H, CH₂), 3.32 – 3.19 (m, 4 H, CH₂), 2.61 (td, J = 7.1, 1.7 Hz, 2 H, CH₂), 2.41 – 2.31 (m, 4 H, CH₂), 1.92 – 1.73 (m, 4 H, CH₂), 1.69 – 1.57 (m, 8 H, CH₂), 1.54 – 1.42 (m, 4 H, CH₂), 1.36 – 1.19 (m, 48 H, CH₂), 0.91 – 0.83 (m, 6 H, CH₃).

¹³C NMR (101 MHz, CDCl₃): 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]: [M+H]⁺ calculated for 12C₅₅¹H₉₅¹⁶O₈¹⁴N₂³⁵Cl, 947.6850; found: 947.6823; Δ = 1.8 mmu.
Supplementary Figure 33: $^1$H-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): $\nu / \text{cm}^{-1} = 3291.2$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.04$ (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$_2$), 3.25 – 3.10 (m, 4 H, CH$_2$), 2.55 (td, $J = 7.1$, 1.9 Hz, 2 H, CH$_2$), 2.32 (t, $J = 7.5$ Hz, 2 H, CH$_2$), 2.27 (t, $J = 7.5$ Hz, 2 H, CH$_2$), 2.11 – 2.00 (m, 2 H, CH$_2$), 1.87 – 1.65 (m, 4 H, CH$_2$), 1.65 – 1.49 (m, 4 H, CH$_2$), 1.50 – 1.31 (m, 4 H, CH$_2$), 1.32 – 0.98 (m, 52 H, CH$_2$), 0.84 – 0.74 (m, 6 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta / \text{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]: [M + H]$^+$ calculated for $^{12}$C$_{48}$H$_{89}$O$_8$N$_2$Cl, 857.6380 found, 857.6366, $\Delta = 1.4$ mmu.

Supplementary Figure 34: $^1$H-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 2.0 mL DCM. Subsequently, 286 µL cyclohexancarboxaldehyde 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 → 2:1) to yield the passerini product 35 as a yellow highly viscous oil. (1.88 g, 1.48 mmol, 93.7%).

Rf: 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, CHAr), 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, CH₂), 5.02 (d, J = 4.6 Hz, 1 H, CH₂), 3.67 – 3.58 (m, 2 H, CH₂), 3.32 – 3.16 (m, 6 H, CH₂), 2.61 (td, J = 7.1, 1.9 Hz, 2 H, CH₃), 2.44 – 2.29 (m, 6 H, CH₃), 2.19 – 2.07 (m, 2 H, CH₂), 2.00 – 1.58 (m, 17 H, CH₁¹, CH₂¹₂), 1.54 – 1.42 (m, 6 H, CH₂¹₁), 1.39 – 1.05 (m, 68 H, CH₂¹₂), 0.91 – 0.82 (m, 6 H, CH₂¹₄).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 173.81, 172.67, 172.60, 171.61, 170.00, 169.77, 169.33, 166.32, 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, 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 C₇₄H₁₂₅O₁₁N₃Cl, 1292.9130; found: 1292.9134; Δ = 0.4 mmu.
Supplementary Figure 35: $^1$H-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): $\nu / \text{cm}^{-1} = 3292.4$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.06 – 5.97$ (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$_2$), 3.24 – 3.09 (m, 6 H, CH$_2$), 2.55 (td, $J = 7.1$, 1.8 Hz, 2 H, CH$_2$), 2.36 – 2.22 (m, 6 H, CH$_2$), 2.12 – 2.01 (m, 2 H, CH$_2$), 1.93 – 1.51 (m, 15 H, CH$_3$, CH$_2$), 1.50 – 1.38 (m, 6 H, CH$_2$), 1.32 – 0.93 (m, 70 H, CH$_2$), 0.85 – 0.74 (m, 6 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta / \text{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 $[m/z]$: [M + H]$^+$ calculated for $^{12}$C$_{67}$H$_{122}$O$_{11}$N$_3$Cl, 1180.8841 found, 1180.8837, $\Delta = 0.4$ mmu.

Supplementary Figure 36: $^1$H-NMR of compound 36 measured in CDCl$_3$. 
Passerini reaction

In a 50 mL round bottom flask, 415 mg 36 (351 mol, 1.00 eq.) was stirred in 2.0 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 → 2:1) to yield the passerini product T3 as a yellow highly viscous oil. (527 mg, 323 µmol, 92.0%).

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

IR (ATR): \( \nu / \text{cm}^{-1} = 3291.6 \) (w), 2920.0 (vs), 2851.1 (s), 1736.4 (vs), 1654.9 (s), 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).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.44 - 7.31 \) (m, 5 H, CH\(_4\)), 6.10 – 5.99 (m, 3 H, NH\(^2\)), 5.97 – 5.87 (m, 1 H, NH\(^3\)), 5.18 – 5.13 (m, 3 H, CH\(^3\)), 5.11 (s, 2 H, CH\(^5\)), 5.02 (d, \( J = 4.6 \) Hz, 1 H, CH\(^3\)), 3.67 – 3.56 (m, 2 H, CH\(^7\)), 3.33 – 3.16 (m, 8 H, CH\(_2\)), 2.67 – 2.56 (m, 2 H, CH\(^8\)), 2.44 – 2.29 (m, 8 H, CH\(_2\)), 2.19 – 2.10 (m, 2 H, CH\(^8\)), 2.01 – 1.58 (m, 23 H, CH\(_{10}\)), 1.54 – 1.44 (m, 8 H, CH\(_{12}\)), 1.38 – 0.97 (m, 88 H, CH\(_{12}\)), 0.94 – 0.80 (m, 9 H, CH\(_{14}\)).

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta / \text{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, 29.20, 27.50, 27.43, 26.99, 26.96, 26.97, 26.21, 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 \(^{12}\)C\(_{36}\)H\(_{167}\)O\(_{14}\)N\(_4\)Cl, 1646.2060; found: 1646.2066; \( \Delta = 0.6 \) mmu.
Supplementary Figure 37: $^1$H-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).

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 µL 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 → 2:1) to yield the passerini product 37 as a pale highly viscous oil with 92.3% (441 mg, 941 µmol).

R<sub>f</sub> = 0.16 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν/ cm<sup>−1</sup> = 3317.5 (vw), 2926.7 (w), 2854.4 (w), 1734.8 (s), 1660.0 (m), 1583.4 (w), 1498.1 (vw), 1454.9 (w), 1373.5 (w), 1298.4 (w), 1166.8 (m), 1144.5 (s), 1097.3 (w), 1031.5 (vv), 878.2 (vv), 787.6 (sv), 735.8 (w), 697.2 (m), 648.5 (vw), 432.2 (w).

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

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 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]: [M + H]<sup>+</sup> calculated for <sup>12</sup>C<sub>25</sub>H<sub>38</sub>O<sub>3</sub>N<sub>15</sub>Cl, 468.2511; found, 468.2511, Δ = 0.0 mmu.
Supplementary Figure 41: $^1$H-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$^\circledR$ 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): $\nu$ / 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).
$^1\text{H NMR}$ (300 MHz, CDCl$_3$): $\delta$ / ppm = 6.26 – 5.72 (m, 1 H, NH$^1$), 5.27 – 5.06 (m, 1 H, CH$^5$), 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$_3^8$, CH$_3^9$).

$^{13}\text{C NMR}$ (126 MHz, CDCl$_3$): $\delta$ / 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]: [M + H]$^+$ calculated for $^{12}\text{C}_{18}^{1}\text{H}_{33}^{16}\text{O}_{5}^{14}\text{N}_{35}^{15}\text{Cl}$, 378.2042; found, 378.2030, $\Delta = 1.2$ mmu.

Supplementary Figure 42: $^1\text{H-NMR}$ 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$^\circledR$ 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 \mu\text{mol}).

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

IR (ATR): v / 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).

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

\(^{13}\)C NMR (101 MHz, CDCl\text{3}): \delta / 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]: [M + H]^+ calculated for \(^{12}\)C\text{41}^{1}\text{H}_{67}^{16}\text{O}_{8}^{35}\text{N}_{2}^{35}\text{Cl}, 751.4659; found, 751.4636, \Delta = 2.3 \text{ mmu}.

Supplementary Figure 43: \(^1\)H-NMR of compound 39 measured in CDCl\text{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, CH²), 3.42 – 3.08 (m, 4 H, CH²), 2.65 – 2.43 (m, 2 H, CH²), 2.40 – 2.16 (m, 5 H, CH⁶, CH¹⁺), 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 ¹²C₃₄H₆₁¹⁶O₈¹⁴N₂³⁵Cl; 661.4189 found, 661.4197, Δ = 0.8 mmu.
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 → 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, CDCl₃): δ / ppm = 7.42 – 7.29 (m, 5 H, CHAr₁), 6.11 (s, 1 H, NH₂), 5.96 (d, J = 6.3 Hz, 2 H, NH²), 5.26 – 5.16 (m, 2 H, CH₁), 5.11 (s, 2 H, CH₂), 5.05 (d, J = 4.4 Hz, 1 H, CH₃), 3.63 (td, J = 6.2, 1.6 Hz, 2 H, CH₂), 3.32 – 3.15 (m, 6 H, CH₂), 2.60 (td, J = 7.1, 3.0 Hz, 2 H, CH₂), 2.47 – 2.23
(m, 7 H, CH\textsubscript{9}, CH\textsubscript{2}\textsuperscript{10}), 2.21 – 2.08 (m, 2 H, CH\textsubscript{2}\textsuperscript{11}), 1.86 – 1.59 (m, 9 H, CH\textsubscript{12}, CH\textsubscript{2}\textsuperscript{13}), 1.55 – 1.42 (m, 9 H, CH\textsubscript{2}\textsuperscript{14}, CH\textsubscript{3}\textsuperscript{15}), 1.36 – 1.15 (m, 36 H, CH\textsubscript{2}\textsuperscript{16}), 1.07 – 0.57 (m, 12 H, CH\textsubscript{3}\textsuperscript{17}).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ / ppm = 173.83, 172.78, 172.70, 171.40, 170.34, 170.24, 169.42, 169.1, 168.69, 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]\textsuperscript{+} calculated for \textsuperscript{12}C\textsubscript{58}H\textsubscript{98}O\textsubscript{11}N\textsubscript{3}Cl, 1048.6963; found, 1048.6944, Δ = 1.9 mmu.

Supplementary Figure 45: \textsuperscript{1}H-NMR of compound 41 measured in CDCl\textsubscript{3}. 
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, NH₃), 6.09 – 5.98 (m, 2 H, NH₃), 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, CH₂⁴), 3.32 – 3.17 (m, J = 6.1 Hz, 6 H, CH₂), 2.59 (td, J = 7.1, 3.2 Hz, 2 H, CH₂⁵), 2.44 – 2.23 (m, 7 H, CH₂⁷, CH₂⁸), 2.19 – 2.06 (m, 2 H, CH₂⁹), 1.74 – 1.56 (m, 9 H, CH¹⁰, CH₁¹), 1.54 – 1.40 (m, 9 H, CH₁², CH₁₃), 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 C₅₁H₉₂O₁₆N₃³⁵Cl, 958.6493; found, 958.6476, Δ = 1.7 mmu.
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 cyclohexancarboxaldehyde 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 → 0:1) to yield the passeri product T4 with 88.5% (65.4 mg, 48 µmol). Rf = 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), 1453.5 (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).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$/ppm = 7.40 – 7.28 (m, 5 H, CH$_2$), 6.15 (t, $J$ = 6.0 Hz, 1 H, NH$^2$), 6.06 – 5.90 (m, 3 H, NH$^3$), 5.25 – 5.13 (m, 2 H, CH$^3$), 5.10 (s, 2 H, CH$_2$), 5.05 – 4.98 (m, 2 H, CH$^5$), 3.67 – 3.57 (m, 2 H, CH$_2$), 3.35 – 3.14 (m, 8 H, CH$_2$), 2.66 – 2.53 (m, 2 H, CH$_2$), 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$_3^{13}$), 1.56 – 1.38 (m, 12 H, CH$^{14}$, CH$^{15}$, CH$_2^{16}$), 1.35 – 1.05 (m, 50 H, CH$_2$), 0.98 – 0.88 (m, 12 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/ppm = 173.73, 172.72, 172.64, 171.35, 170.31, 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 [$m/z$]: [M + H]$^+$ calculated for $^{12}$C$_7$H$_{33}$O$_4$N$_3$Cl, 1371.9423; found, 1371.9403, $\Delta$ = 2.0 mmu.

Supplementary Figure 47: $^1$H-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 mMасс (red).
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**

![Chemical structure](image)

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 µL 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 → 5:1) to yield the Passerini product 43 as a pale highly viscous oil. (2.16 g, 2.49 mmol, 96.3%).

Rf = 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), 1351.1 (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, CDCl₃): δ/ppm = 7.41 – 7.20 (m, 5 H, CH₆), 6.39 (t, J = 5.8 Hz, 1 H, NH₂), 5.25 (d, J = 3.1 Hz, 1 H, CH³), 5.04 (s, 2 H, CH₂), 4.47 – 4.18 (m, 2 H, CH₂), 3.34 – 3.05 (m, 2 H, CH₂), 2.81 – 2.54 (m, 2 H, CH₂), 2.50 – 2.33 (m, 4 H, CH₂), 2.27 (t, J = 7.5 Hz, 2 H, CH₂), 1.85 (td, J = 5.0, 3.0 Hz, 1 H, CH⁶), 1.61 – 1.52 (m, 2 H, CH₁), 1.50 – 1.35 (m, 4 H, CH₂), 1.29 – 1.04 (m, 14 H, CH₂), 0.85 (t, J = 7.3, 3 H, CH₃), 0.83 (t, J = 7.3, 3 H, CH₃).

13C NMR (101 MHz, CDCl₃): 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.

19F NMR (376 MHz, CDCl₃): δ/ppm = -84.73 – -85.64 (m, 3 F, CF₃), -117.60 – -119.25 (m, 2 F, CF₂), -126.03 – -126.50 (m, 2 F, CF₂), -126.75 – -127.62 (m, 2 F, CF₂), -127.46 – -128.50 (m, 2 F, CF₂), -130.04 – -131.52 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + Na]⁺ calculated for 12C₃H₄₈16O₇¹⁴N¹⁹F₁₃, 888.3115; found, 888.3144, Δ = 2.9 mmu.
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): $\nu / \text{cm}^{-1} = 2928.2$ (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), 1066.9 (m), 841.9 (w), 808.8 (w), 732.4 (w), 697.7 (w), 651.4 (w), 530.7 (w).

$^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.51 (t, J = 5.8 \text{ Hz}, 1 \text{ H}, \text{NH})$, 5.32 (d, $J = 3.1 \text{ Hz}$, 1 H, CH$_2$), 4.48 – 4.28 (m, 2 H, CH$_2$), 3.39 – 3.11 (m, 2 H, CH$_2$), 2.87 – 2.60 (m, 4 H, CH$_3$), 2.59 – 2.40 (m, 2
H, CH₃), 2.33 (t, J = 7.5 Hz, 2H, CH₂), 1.97 – 1.86 (m, 1H, CH₃), 1.72 – 1.56 (m, 2H, CH₂), 1.58 – 1.38 (m, 4H, CH₂), 1.39 – 1.14 (m, 14H, CH₂), 0.99 – 0.79 (m, 6H, CH₃).

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, 3F, CF₃), -117.83 – -118.35 (m, 3F, CF₃), -126.02 – -126.56 (m, 2F, CF₂), -126.73 – -127.51 (m, 2F, CF₂), -127.64 – -128.11 (m, 2F, CF₂), -130.37 – -130.95 (m, 2F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + H]+ calculated for ¹²C₃₀¹H₄₂¹⁶O₇¹⁹F₁₃, 776.2826; found, 776.2811, Δ = 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).

Rf = 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), 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, CDCl₃): δ/ppm = 7.48 – 7.27 (m, 5 H, CHAr), 6.47 (t, J = 5.8 Hz, 1 H, NH₂), 6.00 (t, J = 5.8 Hz, 1 H, NH₂), 5.31 (d, J = 3.1 Hz, 1 H, CH), 5.17 – 5.13 (m, 1 H, CH₂), 5.11 (s, 2 H, CH₂), 4.47 – 4.33 (m, 2 H, CH₂), 3.34 – 3.15 (m, 4 H, CH₂), 2.85 – 2.61 (m, 4 H, CH₂), 2.58 – 2.40 (m, 2 H, CH₂), 2.41 – 2.30 (m, 4 H, CH₂), 1.97 – 1.73 (m, 3 H, CH₁₁, CH₁₂), 1.70 – 1.58 (m, 6 H, CH₂₁₃), 1.57 – 1.38 (m, 6 H, CH₂₁₃), 1.36 – 1.10 (m, 42 H, CH₂₁₃), 0.96 – 0.80 (m, 9 H, CH₁₄).

13C NMR (101 MHz, CDCl₃): 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.

19F NMR (376 MHz, CDCl₃): δ/ppm = -84.73 – -85.52 (m, 3 F, CF₃), -117.70 – -118.32 (m 2 F, CF₂₁⁴), -125.97 – -126.42 (m 2 F, CF₂₁⁴), -126.99 – -127.39 (m 2 F, CF₂₁⁴), -127.77 – -128.04 (m 2 F, CF₂₁⁴), -130.30 – -130.60 (m 2 F, CF₂₁⁴). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for C₆₁H₇₁O₁⁰¹⁴N₂¹⁹F_{1₃}, 1261.6695 found, 1261.6692, Δ = 0.3 mmu.
Supplementary Figure 53: $^1$H-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): $\nu / \text{cm}^{-1}$ = 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 (s), 1007.1 (w), 841.9 (vw), 808.5 (w), 697.6 (w), 651.5 (w).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.54$ (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$_2$), 3.36 – 3.14 (m, 4 H, CH$_2$), 2.81 – 2.62 (m, 4 H, CH$_2$), 2.55 – 2.44 (m, 2 H, CH$_2$), 2.43 – 2.19 (m, 4 H, CH$_2$), 1.97 – 1.75 (m, 3 H, CH$_9$, CH$_2$), 1.71 – 1.58 (m, 4 H, CH$_1$), 1.56 – 1.40 (m, 6 H, CH$_2$), 1.37 – 1.15 (m, 44 H, CH$_2$), 0.96 – 0.82 (m, 9 H, CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta / \text{ppm} = 177.43$, 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$_3$): $\delta / \text{ppm} = -85.09$ (t, $J = 9.7$ Hz, 3 F, CF$_3$), -117.79 – -118.40 (m, 2 F, CF$_2$), -125.89 – -126.53 (m, 2 F, CF$_2$), -126.69 – -127.45 (m, 2 F, CF$_2$), -127.74 – -128.14 (m, 2 F, CF$_2$), -130.00 – -130.81 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

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

Supplementary Figure 54: $^1$H-NMR of compound 46 measured in CDCl$_3$. 

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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 µL 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 → 2:1) to afford product 47 as a white solid in a yield of 91.9% (1.99 g, 1.24 mmol).

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

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.39 – 7.29 \text{ (m, 5 H, CH}\_\text{Ar}), 6.47 \text{ (t, } J = 5.7 \text{ Hz, 1 H, NH}^2), 6.07 – 5.98 \text{ (m, 2 H, NH}^2), 5.31 \text{ (d, } J = 3.1 \text{ Hz, 1 H, CH}\^3), 5.17 – 5.13 \text{ (m, 2 H, CH}\^4), 5.11 \text{ (s, 2 H, CH}\^5), 4.46 – 4.34 \text{ (m, 2 H, CH}\_\text{2}), 3.35 – 3.14 \text{ (m, 6 H, CH}\_\text{2}), 2.85 – 2.62 \text{ (m, 4 H, CH}\_\text{2}), 2.57 – 2.42 \text{ (m, 2 H, CH}\_\text{2}), 2.42 – 2.30 \text{ (m, 6 H, CH}\_\text{2}), 1.95 – 1.75 \text{ (m, 5 H, CH}\_\text{2}, \text{ CI}^2), 1.70 – 1.58 \text{ (m, 6 H, CH}\_\text{2}), 1.54 – 1.40 \text{ (m, 8 H, CH}\_\text{2}), 1.38 – 1.15 \text{ (m, 68 H, CH}\_\text{2}), 0.98 – 0.79 \text{ (m, 12 H, CH}\_\text{3}).\)

\(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{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.

\(^19\)F NMR (376 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = -84.62 – -85.83 \text{ (m, 3 F, CF}_3^{16}, -117.63 – -118.90 \text{ (m, 2 F, CF}_2^{17}), -126.02 – -126.52 \text{ (m, 2 F, CF}_2^{17}), -126.81 – -127.48 \text{ (m, 2 F, CF}_2^{17}), -127.63 – -128.33 \text{ (m, 2 F, CF}_2^{17}), -130.01 – -131.02 \text{ (m, 2 F, CF}_2^{17}).\) Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 10.

ESI-MS \([m/z]\): [M + Na]\(^+\) calculated for \(^{12}\)C\(_8\)\(^2\)H\(_{112}\)^{16}O\(_3\)^{14}N\(_3\)^{19}F\(_{13}\), 1636.9445; found, 1636.9430, \( \Delta = 1.5 \text{ mmu}.\)
Supplementary Figure 55: $^1$H-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): $\nu / \text{cm}^{-1} = 3297.8$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 6.49 – 6.39 (m, 1 H, NH$^1$), 6.06 – 5.94 (m, 2 H, NH$^3$), 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$_2$), 3.28 – 3.09 (m, 6 H, CH$_2$), 2.79 – 2.55 (m, 4 H, CH$_2$), 2.51 – 2.37 (m, 2 H, CH$_2$), 2.36 – 2.20 (m, 6 H, CH$_2$), 1.92 – 1.67 (m, 5 H, CH$^6$, 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$_2^{13}$), 0.89 – 0.76 (m, 12 H, CH$_3^{13}$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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$_3$): $\delta$ / 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]: [M + Na]$^+$ calculated for $^{12}$C$_{75}$H$_{126}$O$_{13}$F$_{13}$N$_3$: 1546.8975; found, 1546.8952, $\Delta = 2.3$ mmu.

Supplementary Figure 56: $^1$H-NMR of compound 48 measured in CDCl$_3$. 

![1H-NMR Spectrum](image-url)
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 μL 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 → 1:1) to afford product T5 as a white solid in a yield of 94.6% (2.06 g, 1.06 mmol).

Rf = 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), 1145.3 (vs), 697.1 (w), 651.1 (w), 396.3 (vw).

1H NMR (500 MHz, CDCl₃): δ/ ppm = 7.45 – 7.28 (m, 5 H, CHAr), 6.47 (t, J = 5.8 Hz, 1 H, NH²), 6.06 – 5.96 (m, 3 H, NH²), 5.31 (d, J = 3.2 Hz, 1 H, CH²), 5.17 – 5.13 (m, 3 H, CH²), 5.10 (s, 2 H, CH₂), 4.47 – 4.33 (m, 2 H, CH₂), 3.33 – 3.14 (m, 8 H, CH₂), 2.82 – 2.60 (m, 4 H, CH₂), 2.56 – 2.41 (m, 2 H, CH₂), 2.42 – 2.30 (m, 8 H, CH₂), 1.96 – 1.74 (m, 7 H, CH₁¹, CH₁²), 1.71 – 1.59 (m, 12 H, CH₁³), 1.55 – 1.40 (m, 14 H, CH₁³), 1.38 – 1.11 (m, 80 H, CH₂), 0.96 – 0.82 (m, 15 H, CH₁⁴).

13C NMR (126 MHz, CDCl₃): 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.

19F NMR (376 MHz, CDCl₃): δ/ ppm = -80.74 (t, J = 10.0 Hz, 3 F, CF₂), -113.42 – -113.95 (m, 2 F, CF₂), -121.56 – -122.14 (m, 2 F, CF₂), -122.38 – -123.21 (m, 2 F, CF₂), -123.25 – -123.72 (m, 2 F, CF₂), -125.70 – -126.66 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + Na]+ calculated for C₁₀₁H₁₆⁷F₁₃¹⁴N₄₁⁶O₁₆, 1962.2062; found, 1962.2090, Δ = 2.8 mmu.
Supplementary Figure 57: $^1$H-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).

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

\(^1H\) NMR (400 MHz, CDCl\(_3\)):\(\delta/\text{ppm} = 6.43 \text{ (t, } J = 5.8 \text{ Hz, } 1 \text{ H, NH}^1), 6.09 - 5.94 \text{ (m, } 3 \text{ H, NH}^1), 5.25 \text{ (d, } J = 3.2 \text{ Hz, } 1 \text{ H, CH}^2), 5.14 - 5.05 \text{ (m, } 3 \text{ H, CH}^3), 4.43 - 4.24 \text{ (m, } 2 \text{ H, CH}_2^2), 3.30 - 3.05 \text{ (m, } 8 \text{ H, CH}_2^5), 2.78 - 2.54 \text{ (m, } 4 \text{ H, CH}_2^6), 2.51 - 2.16 \text{ (m, } 10 \text{ H, CH}_2^7), 1.91 - 1.66 \text{ (m, } 7 \text{ H, CH}^8, \text{ CH}_2^9), 1.65 - 1.51 \text{ (m, } 8 \text{ H, CH}_2^{10}), 1.49 - 0.98 \text{ (m, } 101 \text{ H, CH}_2^{11}), 0.92 - 0.74 \text{ (m, } 15 \text{ H, CH}_2^{12})\).

\(^{13}C\) NMR (101 MHz, CDCl\(_3\)):\(\delta/\text{ppm} = 177.11, 172.86, 172.68, 172.62, 171.24, 170.17, 170.11, 170.07, 169.72, 75.75, 74.07, 74.05, 56.98, 43.34, 34.43, 33.97, 32.03, 31.95, 31.75, 30.57, 29.74, 29.67, 29.61, 29.56, 29.51, 29.48, 29.46, 29.36, 29.35, 29.24, 29.18, 29.13, 29.10, 29.03, 26.96, 26.89, 25.11, 25.08, 24.89, 24.84, 22.80, 22.77, 22.65, 22.54, 22.15, 14.23, 14.16, 11.85, 11.72\).

\(^{19}F\) NMR (376 MHz, CDCl\(_3\)):\(\delta/\text{ppm} = -80.74 \text{ (t, } J = 9.9 \text{ Hz, } 3 \text{ F, CF}_2^{13}), -113.52 - -113.84 \text{ (m, } 2 \text{ F, CF}_2^{14}), -121.68 - -121.98 \text{ (m, } 2 \text{ F, CF}_2^{14}), -122.48 - -122.99 \text{ (m, } 2 \text{ F, CF}_2^{14}), -123.39 - -123.65 \text{ (m, } 2 \text{ F, CF}_2^{14}), -125.48 - -126.44 \text{ (m, } 2 \text{ F, CF}_2^{14})\). Total integral of CF\(_2\) region normalized with respect to the CF\(_2^{14}\) group = 10.

ESI-MS [m/z]: [M + H]^+ calculated for \(^{13}C_{94}H_{161}O_{16}N_{4}^{19}F_{13}\), 1850.1773; found, 1850.1772, \(\Delta = 0.1 \text{ mmu}\).
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 14I (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 → 1:1) to yield the passerini product 50 as a pale highly viscous oil. (1.39 g, 626 µmol, 90.7%).

Rf = 0.61 in cyclohexane / ethyl acetate (3:2).
IR (ATR): $\nu / \text{cm}^{-1} = 3304.8$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 7.39 – 7.23$ (m, 5 H, CH$_A$), 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$^5$), 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$_2^{12}$).

$^{13}$C NMR (101MHz, CDCl$_3$): $\delta / \text{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, 131.94, 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$_3$): $\delta / \text{ppm} = -80.64 – -81.03$ (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 [$m/z$]: [M + H]$^+$ calculated for $^{12}$C$_{116}$H$_{194}$O$_{19}$N$_{19}$F$_{13}$, 2209.4233; found, 2209.4261, $\Delta = 2.8$ mmu.

Supplementary Figure 62: $^1$H-NMR of compound 50 measured in CDCl$_3$. 

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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), 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, CDCl₃): δ / ppm = 6.49 (t, J = 5.8 Hz, 1 H, NH¹), 6.17 – 5.99 (m, 4 H, NH¹), 5.31 (d, J = 3.2 Hz, 1 H, CH₂), 5.16 – 5.08 (m, 4 H, CH₂), 4.49 – 4.30 (m, 2 H, CH₂), 3.35 – 3.14 (m, 10 H, CH₂), 2.84 – 2.58 (m, 4 H, CH₂), 2.55 – 2.25 (m, 12 H, CH²), 1.98 – 1.72 (m, 9 H, CH³, CH²), 1.70 – 1.56 (m, 10 H, CH₄), 1.53 – 1.12 (m, 127 H, CH²), 0.96 – 0.82 (m, 18 H, CH₃).

¹³C NMR (101 MHz, CDCl₃): δ / ppm = 13C 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, 29.32, 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.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -80.56 – -80.94 (m, 3 F, CF₃), -113.44 – -113.80 (m, 2 F, CF₂), -121.63 – -122.01 (m), -122.60 – -123.02 (m), -123.25 – -123.84 (m), -125.82 – -126.33 (m). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₁₀⁹¹⁹H₁₈₈¹⁶O₁⁰¹⁴N₅¹⁹F₁₃, 2119.3764; found, 2119.3829, Δ = 6.5 mmu.
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 → 1:2) to afford product H2 as a white solid in a yield of 83.8% (863 mg, 347 µmol).

R<sub>f</sub> = 0.71 in cyclohexane / ethyl acetate (1:1).

IR (ATR): ν / cm<sup>-1</sup> = 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).

Supplementary Figure 63: <sup>1</sup>H-NMR of compound 51 measured in CDCl<sub>3</sub>.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 7.43 – 7.31 (m, 5 H, CH$_2$), 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$_2$), 3.38 – 3.16 (m, 12 H, CH$_2$), 2.84 – 2.61 (m, 4 H, CH$_2$), 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$_3$): $\delta$ / 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$_3$): $\delta$ / 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$_3$ group = 10.

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

Supplementary Figure 64: $^1$H-NMR of compound H2 measured in CDCl$_3$. 

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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).
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 flaks, 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).

**IR (ATR):** $\nu / \text{cm}^{-1} = 2925.0$ (m), 2854.4 (w), 1738.1 (s), 1658.1 (w), 1535.5 (w), 1457.7 (w), 1359.5 (w), 1235.3 (vs), 1208.9 (m), 1005.2 (w), 842.0 (vw), 808.9 (vw), 732.4 (w), 697.2 (m), 651.2 (w).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 7.41 – 7.28$ (m, 5 H, CH$_3^1$), 6.37 (t, $J = 5.8$ Hz, 1 H, NH$_2$), 5.19 – 5.15 (m, 1 H, CH$_2$), 5.11 (s, 2 H, CH$_2^3$), 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$_3^{10}$), 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$_3$): $\delta / \text{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, 29.76, 29.69, 29.60, 28.98, 28.93, 29.49, 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$_3$): $\delta / \text{ppm} = -83.76$ – $-86.21$ (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]: [M + H]$^+$ calculated for $^{12}$C$_{43}$H$_{60}$O$_7$N$^{19}$F$_{13}$, 950.4235; found, 950.4210, $\Delta = 2.5$ mmu.
Supplementary Figure 69: $^1$H-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): \( \nu / \text{cm}^{-1} = 3291.4 \text{ (w)}, 2913.2 \text{ (vs)}, 2847.8 \text{ (s)}, 1740.8 \text{ (vs)}, 1695.6 \text{ (s)}, 1659.5 \text{ (vs)}, 1566.4 \text{ (m)}, 1469.3 \text{ (m)}, 1414.0 \text{ (w)}, 1367.0 \text{ (m)}, 1188.8 \text{ (vs)}, 1162.5 \text{ (vs)}, 1141.8 \text{ (vs)}, 1080.1 \text{ (s)}, 905.0 \text{ (w)}, 839.7 \text{ (w)}, 808.4 \text{ (w)}, 732.6 \text{ (m)}, 698.7 \text{ (s)}, 651.0 \text{ (m)}, 565.9 \text{ (w)}, 529.5 \text{ (w)}, 460.5 \text{ (w)}.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 6.41 \text{ (t, } J = 5.8 \text{ Hz, 1 H, CH}\(^2\)), 4.50 – 4.31 \text{ (m, 2 H, CH}\(^3\)), 3.33 – 3.14 \text{ (m, 2 H, CH}\(^3\)), 2.84 – 2.60 \text{ (m, 4 H, CH}\(^2\)), 2.56 – 2.40 \text{ (m, 2 H, CH}\(^2\)), 2.33 \text{ (t, } J = 7.5 \text{ Hz, 2 H, CH}\(^2\)), 1.96 – 1.74 \text{ (m, 2 H, CH}\(^2\)), 1.67 – 1.56 \text{ (m, 2 H, CH}\(^2\)), 1.54 – 1.45 \text{ (m, 2 H, CH}\(^2\)), 1.39 – 1.17 \text{ (m, 30 H, CH}\(^3\)), 0.87 \text{ (t, } J = 6.7 \text{ Hz, 3 H, CH}\(^3\)).

\(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{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\(_3\)): \( \delta / \text{ppm} = -84.77 – -85.47 \text{ (m, 3 F, CF}_2^{(12)}\)), -117.91 – -118.15 \text{ (m, 2 F, CF}_2^{(13)}\)), -126.04 – -126.37 \text{ (m, 2 F, CF}_2^{(12)}\)), -127.07 – -127.35 \text{ (m, 2 F, CF}_2^{(13)}\)), -127.78 – -128.08 \text{ (m, 2 F, CF}_2^{(13)}\)), -130.31 – -130.62 \text{ (m, 2 F, CF}_2^{(13)}\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 10.

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

Supplementary Figure 70: \(^1\)H-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 µL 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 → 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): \( \nu/ \text{cm}^{-1} = 3285.3 \text{ (vw)}, 2919.4 \text{ (s)}, 2850.8 \text{ (m)}, 1737.6 \text{ (vs)}, 1652.4 \text{ (s)}, 1552.7 \text{ (w)}, 1466.8 \text{ (w)}, 1362.9 \text{ (vs)}, 1082.8 \text{ (m)}, 1005.2 \text{ (w)}, 842.4 \text{ (v)}, 809.6 \text{ (v)}, 697.3 \text{ (s)}, 652.3 \text{ (w)}, 567.2 \text{ (v)}, 455.5 \text{ (v)}.\)

1H NMR (400 MHz, CDCl_3): \( \delta/ \text{ppm} = 7.36 - 7.22 \text{ (m, 5 H, CH}_2\text{Ar}), 6.32 \text{ (t, } J = 5.8 \text{ Hz, 1 H, NH}_2\text{)}, 5.86 \text{ (t, } J = 5.9 \text{ Hz, 1 H, NH}_2\text{)}, 5.12 - 5.07 \text{ (m, 1 H, CH}_3\text{)}, 5.04 \text{ (s, 2 H, CH}_2\text{)}, 4.97 \text{ (d, } J = 4.6 \text{ Hz, 1 H, CH}_3\text{)}, 4.43 - 4.25 \text{ (m, 2 H, CH}_2\text{)}, 3.25 - 3.06 \text{ (m, 4 H, CH}_2\text{)}, 2.78 - 2.55 \text{ (m, 4 H, CH}_2\text{)}, 2.51 - 2.21 \text{ (m, 6 H, CH}_2\text{)}, 1.95 - 1.51 \text{ (m, 13 H, CH}_2\text{), 1.47 - 1.37 \text{ (m, 4 H, CH}_2\text{), 1.30 - 0.93 \text{ (m, 46 H, CH}_2\text{), 0.84 - 0.76 \text{ (m, 3 H, CH}_3\text{).}}\)

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

19F NMR (376 MHz, CDCl_3): \( \delta/ \text{ppm} = -84.31 - -85.80 \text{ (m, 3 F, CF}_3\text{), -117.77 - -118.47 \text{ (m, 2 F, CF}_2\text{)}, -125.71 - -126.57 \text{ (m, 2 F, CF}_2\text{)}, -126.86 - -127.43 \text{ (m, 2 F, CF}_2\text{)}, -127.48 - -128.34 \text{ (m, 2 F, CF}_2\text{)}, -129.95 - -130.75 \text{ (m, 2 F, CF}_2\text{)}. \) Total integral of CF_2 region normalized with respect to the CF_3 group = 10.

ESI-MS [m/z]: [M + 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, \( \Delta = 1.5 \text{ mmu} \).
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): $\nu$ / 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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / 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$_2$), 3.31 – 3.15 (m, 4 H, CH$_2$), 2.81 – 2.58 (m, 4 H, CH$_2$), 2.56 – 2.28 (m, 6 H, CH$_2$), 2.00 – 1.56 (m, 13 H, CH$^8$, CH$_2$), 1.55 – 1.42 (m, 4 H, CH$_2$), 1.37 – 0.97 (m, 46 H, CH$_2$), 0.93 – 0.82 (m, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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$_3$): $\delta$ / ppm = -85.10 (t, $J$ = 9.8 Hz, 3 F, CF$_3$), -117.60 – -118.27 (m, 2 F, CF$_2$), -125.80 – -126.54 (m, 2 F, CF$_2$), -126.84 – -127.47 (m, 2 F, CF$_3$), -127.62 – -128.11 (m, 2 F, CF$_3$), -130.25 – -130.87 (m, 2 F, CF$_3$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

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

**Supplementary Figure 72:** $^1$H-NMR of compound 54 measured in CDCl$_3$. 

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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 → 2:1) to afford product 55 as a pale highly viscous oil in a yield of 86.2% (1.20 g, 764 µmol).

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

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

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.35 – 7.22 \text{ (m, 5 H, CH}_2\text{Ar)}), 6.33 \text{ (t, } J = 5.8 \text{ Hz, 1 H, NH})\), 5.97 – 5.82 \text{ (m, 2 H, NH})\), 5.15 – 5.06 (m, 2 H, CH\(_3\))\), 5.04 \text{ (s, 2 H, CH})\(_2\)\), 4.96 (d, \( J = 4.6 \text{ Hz, 1 H, CH})\(_3\))\), 4.42 – 4.25 \text{ (m, 2 H, CH})\(_4\)\), 3.25 – 3.07 \text{ (m, 6 H, CH})\(_7\)\), 2.76 – 2.53 \text{ (m, 4 H, CH})\(_8\)\), 2.50 – 2.23 \text{ (m, 8 H, CH})\(_9\)\), 1.95 – 1.51 \text{ (m, 16 H, CH})\(_{10}\)\), 1.48 – 1.35 \text{ (m, 6 H, CH})\(_{12}\)\), 1.32 – 0.96 \text{ (m, 60 H, CH})\(_{11}\)\), 0.86 \text{ (t, } J = 5.7 \text{ Hz, 6 H, CH})\(_{13}\)\), 0.81 \text{ (t, } J = 6.8 \text{ Hz, 3 H, CH})_{14}\).

\(^13\)C NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 173.82, 172.77, 172.67, 172.65, 171.25, 170.34, 169.74, 169.36, 169.36, 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 \text{ (t, } J = 21.7 \text{ 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\(_3\)): \( \delta / \text{ppm} = -85.09 \text{ (t, } J = 9.9 \text{ Hz, 3 F, CF})_3\text{)}}\), -117.70 – 118.56 \text{ (m, 2 F, CF})_2\text{)}}\), -126.00 – 126.49 \text{ (m, 2 F, CF})_2\text{)}}\), -126.86 – 127.42 \text{ (m, 2 F, CF})_2\text{)}}\), -127.72 – 127.97 \text{ (m, 2 F, CF})_2\text{)}}\), -130.25 – 130.99 \text{ (m, 2 F, CF})_2\text{)}}\). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 10.

ESI-MS \([m/z]\): [M + H\(^+\)] calculated for \(^{13}\)C\(_7\)H\(_{12}\)O\(_3\)N\(_2\)F\(_{13}\), 1570.8999; found, 1570.8988, \( \Delta = 1.1 \text{ mmu} \).
Supplementary Figure 73: $^1$H-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): $\nu$ / 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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 6.43 (t, $J = 5.8$ Hz, 1 H, NH$^1$), 6.09 – 5.99 (m, 2 H, NH$^4$), 5.23 – 5.13 (m, 2 H, CH$^3$), 5.02 (d, $J = 4.7$ Hz, 1 H, CH$^3$), 4.46 – 4.33 (m, 2 H, CH$^2$), 3.35 – 3.16 (m, 6 H, CH$_2$), 2.82 – 2.59 (m, 4 H, CH$_2$), 2.55 – 2.28 (m, 8 H, CH$_2$), 2.00 – 1.56 (m, 16 H, CH$_3$, CH$_2$), 1.54 – 1.41 (m, 6 H, CH$_2$), 1.38 – 1.01 (m, 60 H, CH$_3$), 0.91 (t, $J = 5.8$ Hz, 6 H, CH$_3$), 0.89 – 0.83 (m, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/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$_3$): $\delta$/ppm = -85.10 (t, $J = 9.8$ Hz, 3 F, CF$_3$), -117.52 – -118.47 (m, 2 F, CF$_2$)$_2$, -125.86 – -126.49 (m, 2 F, CF$_2$)$_2$, -126.92 – -127.34 (m, 2 F, CF$_2$)$_2$, -127.44 – -128.06 (m, 2 F, CF$_2$)$_2$, -130.27 – -130.61 (m, 2 F, CF$_2$)$_2$. Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

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

Supplementary Figure 74: $^1$H-NMR of compound 56 measured in CDCl$_3$. 

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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 → 1:1) to afford product T6 as a white solid in a yield of 89.4% (1.46 g, 763 µmol).

IR (ATR): v / cm$^{-1}$ = 3302.5 ν(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), 1365.9 (w), 1237.8 (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).

$^1$H NMR (400 MHz, CDCl$_3$): δ / ppm = 7.41 – 7.28 (m, 5 H, CH$_n$), 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$_2$), 5.02 (d, J = 4.6 Hz, 1 H, CH$_3$), 4.47 – 4.32 (m, 2 H, CH$_2$), 3.32 – 3.14 (m, 8 H, CH$_3$), 2.85 – 2.59 (m, 4 H, CH$_2$), 2.58 – 2.27 (m, 10 H, CH$_2$), 1.99 – 1.57 (m, 22 H, CH$_3$), 1.55 – 1.40 (m, 8 H, CH$_2$), 1.36 – 1.03 (m, 80 H, CH$_2$), 0.92 (t, J = 5.8 Hz, 6 H, CH$_3$), 0.89 – 0.80 (m, 6 H, CH$_3$).

$^{13}$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$_3$), -117.86 – -118.51 (m, 2 F, CF$_2$), -125.81 – -126.56 (m, 2 F, CF$_2$), -126.89 – -127.43 (m, 2 F, CF$_2$), -127.81 – -128.18 (m, 2 F, CF$_2$), -130.22 – -130.82 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

ESI-MS [m/z]: [M + Na]$^+$ calculated for $^{12}$C$_{99}$H$_{161}$O$_{16}$N$_4$F$_{13}$, 1932.1592; found, 1932.1591 Δ = 0.1 mmu.
Supplementary Figure 75: $^1$H-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).

Supplementary Figure 78: Screenshot of the automated read-out of T6, sodium trifluoroacetate was used as additive during the measurement.
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 → 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): $\nu / \text{cm}^{-1} = 2927.3$ (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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 7.43 - 7.30$ (m, 5 H, CH$_{ar}$), 6.34 (t, $J = 5.7$ Hz, 1 H, NH$^2$), 5.11 (s, 2 H, CH$_2$), 5.05 (d, $J = 3.9$ Hz, 1 H, CH$_2$), 4.47 - 4.33 (m, 2 H, CH$_2$), 3.35 - 3.13 (m, 2 H, CH$_2$), 2.83 - 2.62 (m, 4 H, CH$_2$), 2.56 - 2.40 (m, 2 H, CH$_2$), 2.34 (t, $J = 7.6$ Hz, 2 H, CH$_2$), 2.08 - 1.96 (m, 1 H, CH$_2$), 1.79 - 1.58 (m, 8 H, CH$_2$), 1.55 - 1.47 (m, 2 H, CH$_2$), 1.35 - 0.96 (m, 16 H, CH$_2$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta / \text{ppm} = 173.82$, 172.69, 171.24, 169.03, 163.26, 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$_3$): $\delta / \text{ppm} = -84.01 - -86.07$ (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]: [M + H]$^+$ calculated for $^{12}$C$_{38}$H$_{48}$O$_{14}$N$^{19}$F$_{13}$, 878.3296; found, 878.3271, $\Delta = 2.5$ mmu.
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): $\nu / \text{cm}^{-1} = 2927.4$ (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), 1033.7 (w), 842.5 (w), 808.9 (w), 732.4 (w), 697.6 (m), 651.3 (w), 566.3 (w), 531.4 (w).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 6.38 (t, $J = 5.8$ Hz, 1 H, NH), 5.05 (d, $J = 3.9$ Hz, 1 H, CH$^2$), 4.49 – 4.32 (m, 2 H, CH$_2$), 3.38 – 3.12 (m, 2 H, CH$_2$), 2.84 – 2.62 (m, 4 H, CH$_2$), 2.57 – 2.40 (m, 2 H, CH$_2$), 2.33 (t, $J = 7.5$ Hz, 2 H, CH$_2$), 2.11 – 1.94 (m, 1 H, CH$^3$), 1.78 – 1.68 (m, 2 H, CH$_2$), 1.68 – 1.54 (m, 4 H, CH$_2$), 1.56 – 1.43 (m, 2 H, CH$_2$), 1.37 – 0.96 (m, 18 H, CH$_2$).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ / 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$_3$): $\delta$ / ppm = -85.12 (t, $J = 9.9$ Hz, 3 F, CF$_3$), -117.58 – -118.68 (m, 2 F, CF$_2$), -125.95 – -126.43 (m, 2 F, CF$_2$), -127.08 – -127.31 (m, 2 F, CF$_2$), -127.70 – -128.07 (m, 2 F, CF$_2$), -130.32 – -131.42 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

ESI-MS [$m/z$]: [M + H]$^+$ calculated for $^{12}$C$_31^{1}$H$_{42}^{16}$O$_2^{14}$N$^{19}$F$_{13}$, 788.2826; found, 788.2803, $\Delta = 2.3$ mmu.

Supplementary Figure 80: $^1$H-NMR of compound 58 measured in CDCl$_3$. 

![Supplementary Figure 80: $^1$H-NMR of compound 58 measured in CDCl$_3$.](image-url)
Passerini reaction

In a 50 mL round bottom flask, 338 mg of 58 (429 µmol, 1.00 eq.) was stirred in 2.0 mL DCM. Subsequently, 101 µL octanal 14i (109 mg, 644 µmol, 1.50 eq.) and 194 mg of the monomer M1 (644 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 → 5:1) to yield the passerini product 59 as a pale highly viscous oil. (420 mg, 344 µmol, 80.2%).

Rf = 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, CDCl₃): δ / ppm = 7.41 – 7.28 (m, 5 H, CH₁), 6.35 (t, J = 5.8 Hz, 1 H, NH₂), 6.00 (t, J = 5.9 Hz, 1 H, NH₂), 5.18 – 5.13 (m, 1 H, CH₃), 5.10 (s, 2 H, CH₂), 5.04 (d, J = 3.9 Hz, 1 H, CH₅), 4.48 – 4.33 (m, 2 H, CH₂), 3.33 – 3.15 (m, 4 H, CH₂), 2.79 – 2.64 (m, 4 H, CH₂), 2.54 – 2.41 (m, 2 H, CH₂), 2.41 – 2.31 (m, 4 H, CH₂), 2.08 – 1.96 (m, 1 H, CH¹), 1.90 – 1.57 (m, 12 H, CH₁²), 1.55 – 1.43 (m, 4 H, CH₁³), 1.36 – 0.99 (m, 38 H, CH₂), 0.91 – 0.82 (m, 3 H, CH₁⁴).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.01 – -85.18 (m, 3 F, CF₂¹⁵), -117.85 – -118.19 (m, 2 F, CF₂¹⁶), -126.01 – -126.38 (m, 2 F, CF₂¹⁶), -127.05 – -127.36 (m, 2 F, CF₂¹⁶), -127.74 – -128.06 (m, 2 F, CF₂¹⁶), -130.32 – -130.63 (m, 2 F, CF₂¹⁶). Total integral of CF₂ region normalized with respect to the CF₂¹⁵ group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₅₅H₄₅O₁₀⁴F₁₃N₂¹⁹F₁₃, 1217.6069; found, 1217.6050, Δ = 1.9 mmu.
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): $\nu / \text{cm}^{-1} = 2917.1$ (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), 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).

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.42$ (t, $J = 5.8$ Hz, 1 H, NH$^1$), 6.04 (t, $J = 5.8$ Hz, 1 H, NH$^2$), 5.19 – 5.12 (m, 1 H, CH$^3$), 5.04 (d, $J = 3.9$ Hz, 1 H, CH$^4$), 4.49 – 4.33 (m, 2 H, CH$_2^5$), 3.34 – 3.13 (m, 4
H, CH₂, 2.83 – 2.62 (m, 4 H, CH₂), 2.55 – 2.27 (m, 6 H, CH₂), 2.06 – 1.96 (m, 1 H, CH), 1.91 – 1.55 (m, 12 H, CH₂), 1.54 – 1.42 (m, 4 H, CH₂), 1.38 – 0.98 (m, 38 H, CH₂), 0.89 – 0.83 (m, 3 H, CH₃).

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, 40.07, 35.22, 34.79, 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, CF₃), -117.41 – -118.41 (m, 2 F, CF₂), -125.94 – -126.53 (m, 2 F, CF₂), -126.87 – -127.33 (m, 2 F, CF₂), -127.67 – -128.39 (m, 2 F, CF₂), -130.26 – -130.98 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₅₁H₇₉O₁₆N₂¹⁹F₁₃, 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 2.0 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 → 2:1) to yield the passerini product 61 as a pale highly viscous oil. (255 mg, 157 µmol, 70.1%).

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

IR (ATR): \( \nu / \text{cm}^{-1} = 3292.0 \text{ (w)}, 2917.4 \text{ (vs)}, 2850.3 \text{ (s)}, 1737.0 \text{ (vs)}, 1654.5 \text{ (vs)}, 1556.9 \text{ (m)}, 1466.7 \text{ (w)}, 1362.8 \text{ (w)}, 1263.8 \text{ (vs)}, 1082.6 \text{ (m)}, 1007.7 \text{ (w)}, 809.0 \text{ (vw)}, 696.6 \text{ (m)}, 652.3 \text{ (w)}, 566.2 \text{ (vw)}, 529.3 \text{ (vw)}, 440.8 \text{ (vw)}.\)

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

\( ^{13}C \text{ NMR (101 MHz, CDCl}_{3}\): } \delta / \text{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.

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

ESI-MS \([m/z] \): } [M + Na]^{+} \text{ calculated for } ^{12}C_{39}^{1}H_{33}^{16}O_{15}^{14}N_{9}^{5}F_{13}, 1648.9445; \text{ found, } 1648.9487, \Delta = 4.2 \text{ mmu.}
Supplementary Figure 83: $^1$H-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), 1288.2 (m), 1204.7 (m), 1146.3 (m), 1120.5 (w), 809.9 (vw), 721.8 (vw), 653.6 (vw).

¹H NMR (400 MHz, CDCl₃): δ/ppm = 6.39 (t, J = 5.8 Hz, 1 H, NH¹), 6.15 – 6.00 (m, 2 H, NH¹), 5.21 – 5.10 (m, 2 H, CH²), 5.04 (d, J = 3.8 Hz, 1 H, CH³), 4.49 – 4.31 (m, 2 H, CH²), 3.33 – 3.12 (m, 6 H, CH₂⁴), 2.82 – 2.65 (m, 4 H, CH₂⁶), 2.57 – 2.26 (m, 8 H, CH₂⁷), 2.06 – 1.96 (m, 1 H, CH⁹), 1.90 – 1.56 (m, 14 H, CH₂¹⁰), 1.54 – 1.43 (m, 6 H, CH₂¹¹), 1.43 – 1.03 (m, 72 H, CH₂¹²), 0.95 – 0.80 (m, 6 H, CH₃¹³).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ/ppm = -83.45 – -86.27 (m, 3 F, CF₃¹³), -117.14 – -118.77 (m, 2 F, CF₂¹⁴), -125.77 – -126.36 (m, 2 F, CF₂¹⁴), -126.88 – -127.40 (m, 2 F, CF₂¹⁴), -127.40 – -128.01 (m, 2 F, CF₂¹⁴), -130.23 – -131.00 (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 ¹²C₇₆H₁₂₆O₁₆N₃¹⁹F₁₃, 1536.9156; found, 1536.9133, Δ = 2.3 mmu.
Passerini reaction

In a 50 mL round bottom flask, 118 mg of 62 (77.0 µmol, 1.00 eq.) was stirred in 2.0 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 → 1:1) to yield the passerini product T7 as a pale highly viscous oil. (45.5 mg, 23.9 µmol, 31.0%).

Rf = 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, CDCl3): δ / ppm = 7.42 – 7.29 (m, 5 H, CHAr), 6.44 – 6.30 (m, 1 H, NH2), 6.11 – 5.92 (m, 3 H, NH2), 5.19 – 5.09 (m, 2 H, CH5), 5.08 – 5.02 (m, 2 H, CH5), 4.49 – 4.34 (m, 2 H, CH5), 3.37 – 3.15 (m, 8 H, CH2), 2.82 – 2.63 (m, 4 H, CH2), 2.57 – 2.44 (m, 2 H, CH3), 2.44 – 2.24 (m, 9 H, CH10, CH14), 2.10 – 1.96 (m, 1 H, CH12), 1.90 – 1.57 (m, 20 H, CH213, CH214), 1.55 – 1.44 (m, 8 H, CH215), 1.37 – 1.02 (m, 80, CH214), 0.97 – 0.82 (m, 12 H, CH316).

13C NMR (101 MHz, CDCl3): δ / ppm = 173.83, 172.71, 172.71, 172.61, 171.25, 170.01, 169.40, 169.06, 169.06, 169.06, 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.

19F NMR (376 MHz, CDCl3): δ / ppm = -83.70 – -85.90 (m, 3 F, CF317), -117.79 – -118.30 (m, 2 F, CF318), -125.87 – -126.56 (m, 2 F, CF318), -127.01 – -127.46 (m, 2 F, CF318), -127.81 – -128.10 (m, 2 F, CF318), -130.33 – -130.97 (m, 2 F, CF318). Total integral of CF2 region normalized with respect to the CF317 group = 10.

ESI-MS [m/z]: [M + H]⁺ calculated for 12C99H16116O1614N4F13, 1910.1773; found, 1910.1826, Δ = 5.3 mmu.
Supplementary Figure 85: $^1$H-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).

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 flask, 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 → 5:1) to afford product 63 as a yellow oil in a yield of 97.1% (560 mg, 627 µmol).

R<sub>t</sub> = 0.40 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν/cm<sup>-1</sup> = 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).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 7.43 – 7.28 (m, 5 H, CH<sub>Ar</sub>), 6.37 (t, J = 5.8 Hz, 1 H, NH), 5.17 (q, J = 7.6, 4.3 Hz, 1 H, CH<sub>3</sub>), 5.11 (s, 2 H, CH<sub>2</sub>), 4.47 – 4.33 (m, 2 H, CH<sub>2</sub>), 3.34 – 3.14 (m, 2 H, CH<sub>2</sub>), 2.85 – 2.60 (m, 2 H, CH<sub>2</sub>), 2.55 – 2.40 (m, 4 H, CH<sub>2</sub>), 2.34 (t, J = 7.6 Hz, 2 H, CH<sub>2</sub>), 1.95 – 1.74 (m, 2 H, CH<sub>3</sub>), 1.69 – 1.58 (m, 4 H, CH<sub>2</sub>), 1.55 – 1.43 (m, 2 H, CH<sub>2</sub>), 1.38 – 1.21 (m, 20 H, CH<sub>2</sub>), 0.86 (t, J = 7.0 Hz, 3 H, CH<sub>3</sub>)

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): 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.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ/ppm = -83.86 – -86.34 (m, 3 F, CF<sub>3</sub>), -117.65 – -118.28 (m, 2 F, CF<sub>2</sub>), -125.99 – -126.38 (m, 2 F, CF<sub>2</sub>), -127.05 – -127.38 (m, 2 F, CF<sub>2</sub>), -127.71 – -128.09 (m, 2 F, CF<sub>2</sub>), -130.31 – -130.71 (m, 2 F, CF<sub>2</sub>). Total integral of CF<sub>2</sub> region normalized with respect to the CF<sub>3</sub> group = 10.

ESI-MS [m/z]: [M + H]<sup>+</sup> calculated for <sup>12</sup>C<sub>39</sub>H<sub>52</sub>O<sub>7</sub>N<sub>19</sub>F<sub>13</sub>, 894.3609; found, 894.3597, Δ = 1.2 mnu.
Supplementary Figure 89: $^1$H-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): $\nu$/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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/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$_2$), 3.34 – 3.02 (m, 2 H, CH$_2$), 2.77 – 2.54 (m, 4 H, CH$_2$), 2.49 – 2.35 (m, 2 H, CH$_2$), 2.30 – 2.23 (m, 2 H, CH$_2$), 1.90 – 1.67 (m, 2 H, CH$_2$), 1.61 – 1.49 (m, 2 H, CH$_2$), 1.49 – 1.39 (m, 2 H, CH$_2$), 1.34 – 1.14 (m, 22 H, CH$_2$), 0.80 (t, $J = 6.7$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/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$_3$): $\delta$/ppm = -85.01 – -85.29 (m, 3 F, CF$_3$), -117.90 – -118.20 (m, 2 F, CF$_2$), -125.96 – -126.43 (m, 2 F, CF$_2$), -126.99 – -127.42 (m, 2 F, CF$_2$), -127.82 – -128.11 (m, 2 F, CF$_2$), -130.29 – -130.76 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

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

Supplementary Figure 90: $^1$H-NMR of compound 64 measured in CDCl$_3$. 

Supplementary Figure 90: $^1$H-NMR of compound 64 measured in CDCl$_3$. 

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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 → 1:1) to afford product 65 as a pale highly viscous oil in a yield of 96.5% (555 mg, 496 µmol).

R<sub>f</sub> = 0.20 in cyclohexane / ethyl acetate (3:1).

IR (ATR): ν / cm<sup>-1</sup> = 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), 1099.0 (m), 841.8 (w), 809.6 (vw), 732.3 (w), 697.3 (m), 652.0 (w), 567.3 (vw).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ / ppm = 7.41 – 7.28 (m, 5 H, CH<sub>Ar</sub>), 6.39 (t, J = 5.8 Hz, 1 H, NH), 5.94 (t, J = 5.9 Hz, 1 H, NH<sup>2</sup>), 5.20 – 5.14 (m, 1 H, CH<sup>3</sup>), 5.11 (s, 2 H, CH<sup>4</sup>), 5.05 (d, J = 4.4 Hz, 1 H, CH<sup>5</sup>), 4.46 – 4.34 (m, 2 H, CH<sup>6</sup>), 3.36 – 3.15 (m, 4 H, CH<sup>7</sup>), 2.83 – 2.60 (m, 4 H, CH<sup>8</sup>), 2.56 – 2.24 (m, 7 H, CH<sup>9</sup>, CH<sub>2</sub>), 1.97 – 1.74 (m, 2 H, CH<sub>2</sub>), 1.72 – 1.61 (m, 4 H, CH<sub>2</sub>), 1.55 – 1.45 (m, 4 H, CH<sub>2</sub>), 1.38 – 1.20 (m, 34 H, CH<sub>2</sub>), 0.95 – 0.90 (m, 6 H, CH<sub>2</sub>), 0.89 – 0.84 (m, 3 H, CH<sub>2</sub>).

<sup>1</sup>3C NMR (101 MHz, CDCl<sub>3</sub>): 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.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ / ppm = -84.77 – -85.55 (m, 3 F, CF<sub>2</sub>), -117.72 – -118.51 (m, 2 F, CF<sub>2</sub>), -126.00 – -126.49 (m, 2 F, CF<sub>2</sub>), -126.94 – -127.43 (m, 2 F, CF<sub>2</sub>), -127.58 – -128.18 (m, 2 F, CF<sub>2</sub>), -129.96 – -130.99 (m, 2 F, CF<sub>2</sub>). Total integral of CF<sub>2</sub> region normalized with respect to the CF<sub>3</sub> group = 10.

ESI-MS [m/z]: [M + Na]<sup>+</sup> calculated for <sup>12</sup>C<sub>55</sub>H<sub>81</sub>O<sub>10</sub>N<sub>2</sub>F<sub>13</sub>, 1199.5576; found, 1199.5555, Δ = 2.1 mmu.
Supplementary Figure 91: $^1$H-NMR of compound 65 measured in CDCl$_3$.

**Deprotection**

In a 25 mL round bottom flask, 505 mg of 65 (429 µmol, 1.00 eq.) was dissolved in 2.00 mL ethyl acetate and 2.00 mL THF. Subsequently, 101 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 66 was obtained as a yellow highly viscous oil in a yield of 97.4%, (445 mg, 418 µmol).

IR (ATR): $\nu / \text{cm}^{-1} = 3304.8$ (vw), 2925.6 (m), 2854.6 (m), 1738.4 (s), 1654.9 (s), 1540.6 (w), 1464.3 (w), 1365.1 (w), 1235.0 (vs), 1144.6 (vs), 1070.2 (w), 841.4 (vw), 808.8 (w), 697.7 (w), 651.2 (w).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 6.46$ (t, $J = 5.8$ Hz, 1 H, NH$_1$), 5.98 (t, $J = 5.9$ Hz, 1 H, NH$_1$), 5.21 – 5.12 (m, 1 H, CH$_2$), 5.06 (d, $J = 4.4$ Hz, 1 H, CH$_3$), 4.48 – 4.32 (m, 2 H, CH$_2$), 3.34 – 3.15 (m, 4
H, CH₂, 2.83 – 2.58 (m, 4 H, CH₂), 2.56 – 2.20 (m, 7 H, CH₂, CH₂), 1.95 – 1.72 (m, 2 H, CH₂), 1.70 – 1.55 (m, 4 H, CH₂), 1.54 – 1.40 (m, 4 H, CH₂), 1.39 – 1.14 (m, 3 H, CH₃), 0.97 – 0.90 (m, 6 H, CH₃), 0.89 – 0.78 (m, 3 H, CH₃).

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, CF₃), -117.74 – -118.31 (m, 2 F, CF₂), -125.91 – -126.37 (m, 2 F, CF₂), -126.61 – -127.43 (m, 2 F, CF₂), -127.48 – -128.13 (m, 2 F, CF₂), -130.00 – -130.75 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 10.

ESI-MS [m/z]: [M + Na]⁺ calculated for C₄₈H₇₅O₁₀N₂F₁₃, 1109.5106; found, 1109.5092, Δ = 1.4 mmu.

Supplementary Figure 92: ¹H-NMR of compound 66 measured in CDCl₃.
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 → 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): $\tilde{\nu}$/ 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), 1144.9 (vs), 1005.5 (w), 842.2 (vw), 697.7 (m).  

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$/ ppm = 7.44 – 7.29 (m, 5 H, CH$_{Ar}$), 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$_2$), 5.05 (d, $J$ = 4.4 Hz, 1H, CH$_3$), 4.49 – 4.34 (m, 2 H, CH$_2$), 3.32 – 3.14 (m, 6 H, CH$_2$), 2.83 – 2.58 (m, 4 H, CH$_2$), 2.55 – 2.23 (m, 9 H, CH$_3$), 1.96 – 1.75 (m, 4 H, CH$_2$), 1.75 – 1.56 (m, 8 H, CH$_2$), 1.56 – 1.39 (m, 6 H, CH$_2$), 1.37 – 1.16 (m, 52 H, CH$_2$), 0.96 – 0.90 (m, 6 H, CH$_3$), 0.89 – 0.83 (m, 6 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/ ppm = 173.82, 172.69, 172.66, 172.60, 171.25, 169.99, 169.74, 169.42, 169.42, 169.26, 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$_3$): $\delta$/ ppm = -85.09 (t, $J$ = 9.9 Hz, 3 F, CF$_3$), -117.75 – -118.21 (m, 2 F, CF$_2$), -125.91 – -126.45 (m, 2 F, CF$_2$), -126.96 – -127.40 (m, 2 F, CF$_2$), -127.70 – -128.26 (m, 2 F, CF$_2$), -130.02 – -130.86 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 10.

ESI-MS [m/z]: [M + Na]$^+$ calculated for $^{12}$C$_{74}$H$_{116}$O$_{13}$N$_{3}$F$_{13}$, 1524.8193; found, 1524.8176, $\Delta$ = 1.7 mmu.
Supplementary Figure 93: ^1^H-NMR of compound 67 measured in CDCl₃.

**Deprotection**

In a 25 mL round bottom flask, 225 mg of 67 (150 µmol, 1.00 eq.) was dissolved in 3.00 mL ethyl acetate and 3.00 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 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 68 was obtained as a pale highly viscous oil in a yield of 95.3%. (201 mg, 143 µmol).

IR (ATR): v/ cm⁻¹ = 3290.0 (vw), 2922.6 (m), 2852.3 (m), 2335.9 (vw), 1737.7 (s), 1655.3 (s), 1554.2 (w), 1466.3 (w), 1366.0 (w), 1235.6 (s), 1144.9 (vs), 1008.2 (w), 842.6 (vw), 809.8 (vw), 698.5 (w), 652.2 (w), 567.4 (vw).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 6.43 (t, $J$ = 5.8 Hz, 1 H, NH$^1$), 6.13 – 5.93 (m, 2 H, NH$^4$), 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$_2^3$), 3.35 – 3.15 (m, 6 H, CH$_2^5$), 2.84 – 2.59 (m, 4 H, CH$_2^8$), 2.56 – 2.22 (m, 9 H, CH$^2$, 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$_3$): $\delta$/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$_3$): $\delta$/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]: [M + Na]$^+$ calculated for $^{12}$C$_6$H$_{10}$O$_3$N$_3$F$_{13}$Na, 1434.7723; found, 1434.7705, $\Delta$ = 1.8 mmu.

Supplementary Figure 94: $^1$H-NMR of compound 68 measured in CDCl$_3$. 

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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 → 1:1) to afford product T8 as a pale highly viscous oil in a yield of 75.5% (160 mg, 87.6 µmol).

**IR (ATR):** ν / cm⁻¹ = 3293.4 8 (w), 2922.3 (s), 2851.6 (m), 1735.9 (vs), 1654.5 8 (vs), 1537.5 (m), 1466.3 (w), 1362.4 (w), 1236.3 (vs), 1145.2 (vs), 100 9.2 (w), 809.0 (vw), 697.2 (m), 652.2 (w), 566.9 (vw), 451.0 (vw).

**H NMR (400 MHz, CDCl₃):** δ / ppm = 7.41 – 7.30 (m, 5 H, CHAr¹), 6.39 (t, J = 5.8 Hz, 1 H, NH²), 6.09 – 5.91 (m, 3 H, NH³), 5.19 – 5.13 (m, 2 H, CH₂⁴), 5.11 (s, 2 H, CH₂⁵), 5.07 – 4.98 (m, 2 H, CH₂⁵), 4.47 – 4.34 (m, 2 H, CH₂⁶), 3.33 – 3.15 (m, 8 H, CH₂⁷), 2.83 – 2.62 (m, 4 H, CH₂⁸), 2.56 – 2.24 (m, 11 H, CH₂⁹, CH₂¹⁰), 2.00 – 1.59 (m, 21 H, CH¹¹, CH₁²), 1.54 – 1.44 (m, 8 H, CH₁³), 1.38 – 1.06 (m, 68 H, CH₂¹⁵), 0.97 – 0.90 (m, 6 H, CH₂¹⁶), 0.90 – 0.82 (m, 6 H, CH₂¹⁵).

**C NMR (101 MHz, CDCl₃):** 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.

**F NMR (376 MHz, CDCl₃):** δ / ppm = -84.73 – -85.47 (m, 3 F, CF₃¹⁶), -117.67 – -118.35 (m, 2 F, CF₂¹⁶), -125.60 – -126.44 (m, 2 F, CF₂¹⁷), -126.83 – -127.22 (m, 2 F, CF₂¹⁷), -127.54 – -128.48 (m, 2 F, CF₂¹⁷), -130.28 – -131.34 (m, 2 F, CF₂¹⁷).

Total integral of CF₂ region normalized with respect to the CF₃¹⁶ group = 10.

**ESI-MS [m/z]:** [M + H]⁺ calculated for 1²C₉₉¹H₁₄⁹₁⁶O₁₆¹⁴N₄¹⁹F₁₃, 1826.0834; found, 1826.0885 Δ = 5.1 mmu.
Supplementary Figure 95: $^1$H-NMR of compound T8 measured in CDCl3.

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).

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\text{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 (w), 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).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ/ ppm = 7.42 – 7.32 (m, 5 H, CH\text{Ar}), 6.24 (t, J = 5.8 Hz, 1 H, NH\text{2}), 5.23 – 5.16 (m, 1 H, CH\text{3}), 5.13 (s, 2 H, CH\text{2}), 4.74 – 4.52 (m, 2 H, CH\text{2}), 3.36 – 3.17 (m, 2 H, CH\text{2}), 2.92 – 2.66 (m, 4 H, CH\text{2}), 2.37 (t, J = 7.6 Hz, 2 H, CH\text{2}), 1.96 – 1.78 (m, 2 H, CH\text{2}), 1.70 – 1.61 (m, 2 H, CH\text{2}), 1.57 – 1.47 (m, 2 H, CH\text{2}), 1.40 – 1.21 (m, 24 H, CH\text{2}), 0.89 (t, J = 6.9 Hz, 3 H, CH\text{3}).

\(^13\)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\text{3}), -119.83 – -121.39 (m, 2 F, CF\text{2}), -127.31 – -128.95 (m, 2 F, CF\text{2}). Total integral of CF\text{2} region normalized with respect to the CF\text{3} group = 4.

ESI-MS [m/z]: [M + H]\(^+\) calculated for \(^{12}\)C\text{36}\(^{1}\)H\text{52}\(^{16}\)O\text{7}\(^{14}\)N\text{19}\(^{13}\)F\text{7}, 744.3705; found, 744.3693, Δ = 1.2 mmu.
Supplementary Figure 99: $^1$H-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$^\circledR$ 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, CDCl₃): δ ppm = 6.26 (t, J = 5.8 Hz, 1 H, NH¹), 5.22 – 5.09 (m, 1 H, CH²), 4.70 – 4.49 (m, 2 H, CH₂³), 3.34 – 3.15 (m, 2 H, CH₂⁴), 2.92 – 2.64 (m, 4 H, CH₂⁵), 2.33 (t, J = 7.5 Hz, 2 H, CH₂⁶), 1.95 – 1.74 (m, 2 H, CH₂⁷), 1.68 – 1.57 (m, 2 H, CH₂⁸), 1.56 – 1.42 (m, 2 H, CH₂⁹), 1.41 – 1.17 (m, 24 H, CH₂¹⁰), 0.91 – 0.79 (m, 3 H, CH₃¹¹).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ ppm = -80.84 (t, J = 9.3 Hz, 3 F, CF₃¹²), -120.14 – -121.45 (m, 2 F, CF₂¹³), -127.34 – -128.12 (m, 2 F, CF₂¹³). Total integral of CF₂ region normalized with respect to the CF₃¹² group = 4.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₂₀¹⁶H₄₆¹⁶O₇¹⁴N¹⁹F₇, 654.3235; found, 654.3219, Δ = 1.4 mmu.

Supplementary Figure 100: ¹H-NMR of compound 70 measured in CDCl₃.
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 µL 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 → 1:1) to yield the passerini product 71 as a pale highly viscous oil. (3.41 g, 3.13 mmol, 99.9%).

Rf = 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, CDCl₃): δ / ppm = 7.43 – 7.15 (m, 10 H, CHAr), 6.23 (t, J = 5.8 Hz, 1 H, NH₂), 5.64 (t, J = 5.8 Hz, 0.5 H, NH₁a), 5.58 (t, J = 5.9 Hz, 0.5 H, NH₂b), 5.32 (d, J = 5.4 Hz, 0.5 H, CH₁b), 5.21 (d, J = 5.4 Hz, 0.5 H, CH₁b), 5.19 – 5.14 (m, 1 H, CH₁), 5.11 (s, 2 H, CH₂₆), 4.73 – 4.46 (m, 2 H, CH₂₇), 3.52 – 3.39 (m, 1 H, CH₈), 3.35 – 2.96 (m, 4 H, CH₂₉), 2.90 – 2.64 (m, 4 H, CH₅), 2.41 – 2.28 (m, 4 H, CH₇), 1.96 – 1.74 (m, 2 H, CH₁₂), 1.72 – 1.00 (m, 47 H, CH₁₃, CH₃₁₄), 0.91 – 0.83 (m, 3 H, CH₃₁₅).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -80.81 (t, J = 9.1 Hz, 3 F, CF₁), -120.24 – -120.74 (m, 2 F, CF₂), -127.46 – -127.96 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃¹⁴ group = 4.

ESI-MS [m/z]: [M + H]^+ calculated for ¹²C₅₇H₆₇O₁₆N₂₁₉F₇, 1089.6009; found, 1089.5993, Δ = 1.6 mmu.
Supplementary Figure 101: $^1$H-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$^\circledR$ 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): $\nu$ / 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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / ppm = 7.40 – 7.20 (m, 5 H, CH$_5^1$), 6.35 (t, $J$ = 5.8 Hz, 1 H, NH$^2$), 5.76 (t, $J$ = 5.8 Hz, 0.5 H, NH$^{1b}$), 5.69 (t, $J$ = 5.9 Hz, 0.5 H, NH$^{1b}$), 5.37 (d, $J$ = 5.3 Hz, 0.5 H, CH$^4$), 5.26 (d, $J$ = 5.3 Hz, 0.5 H, CH$^{1b}$), 5.23 – 5.14 (m, 1 H, CH$^3$), 4.78 – 4.53 (m, 2 H, CH$_2^2$), 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$_2^8$), 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$_3$): $\delta$ / 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$_3$): $\delta$ / 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 [$m/z$]: [M + H]$^+$ calculated for $^{12}$C$_{50}^{16}$H$_{77}^{16}$O$_{10}^{14}$N$_2^{19}$F$_7$, 999.5539; found, 999.5526, $\Delta$ = 1.3 mmu.

Supplementary Figure 102: $^1$H-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 µL 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 → 1:1) to yield the passerini product 73 as a pale highly viscous oil. (3.50 g, 2.60 mmol, 91.6%).

Rf = 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, CDCl₃): δ/ ppm = 7.44 – 7.15 (m, 10 H, CH₆), 6.24 (t, J = 5.8 Hz, 1 H, NH²), 6.09 (t, J = 5.8 Hz, 1 H, NH²), 5.65 (t, J = 5.9 Hz, 0.5 H, NH³), 5.59 (t, J = 5.9 Hz, 0.5 H, NH³b), 5.31 (d, J = 5.4 Hz, 0.5 H, CH₄α), 5.25 – 5.14 (m, 0.5 H, 2 H, CH₄b, CH₄), 5.11 (s, 2 H, CH₃), 4.72 – 4.49 (m, 2 H, CH₂), 3.51 – 3.39 (m, 1 H, CH), 3.34 – 2.97 (m, 6 H, CH₂), 2.90 – 2.64 (m, 4 H, CH₁⁰), 2.43 – 2.26 (m, 6 H, CH₂₁), 1.95 – 1.73 (m, 2 H, CH₂), 1.7 – 1.05 (m, 66 H, CH₃, CH₂), 0.90 – 0.82 (m, 3 H, CH₃, CH₃).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ/ ppm = -80.81 (t, J = 9.3 Hz, 3 F, CF₃₁⁶), -120.19 (m, 2 F, CF₂), -127.59 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + H]⁺ calculated for 12C₇₁H₁₀₈O₁₃N₁₄F₇, 1344.7843; found, 1344.7813, Δ = 3.0 mmu.
Supplementary Figure 103: $^1$H-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): $\nu$ / 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).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ / ppm = 7.25 – 7.10 (m, 5 H, CH$_{Ar}$), 6.21 (t, $J = 5.9$ Hz, 1 H, NH), 5.67 (t, $J = 6.0$ Hz, 1 H, NH), 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$_{2}$), 4.68 – 4.43 (m, 6 H, CH$_{2}$), 3.42 – 3.35 (m, 1 H, CH$_{7}$), 3.29 – 2.93 (m, 6 H, CH$_{2}$), 2.81 – 2.60 (m, 4 H, CH$_{2}$), 2.39 – 2.22 (m, 6 H, CH$_{2}$), 1.90 – 1.68 (m, 2 H, CH$_{11}$), 1.62 – 0.98 (m, 12H, CH$_{2}$, CH$_{3}$), 0.80 (t, $J = 6.8$ Hz, 3 H, CH$_{3}$).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ / 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$_3$): $\delta$ / ppm = -80.81 (t, $J = 9.3$ Hz, 3 F, CF$_3$), -119.20 – -121.40 (m, 2 F, CF$_2$), -126.52 – -130.07 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 4.

ESI-MS [m/z]: [M + H]$^+$ calculated for $^{12}$C$_6$$^{14}$H$^{16}$O$_3$$^{15}$N$^9$F$_7$, 1254.7374; found, 1254.7351, $\Delta = 2.3$ mmu.

Supplementary Figure 104: $^1$H-NMR of compound 74 measured in CDCl$_3$. 

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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 → 1:1) to yield the passerini product T9 as a pale highly viscous oil. (372 mg, 230 µmol, 67.6%).

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

\(^1\)H NMR (500 MHz, CDCl₃): \( \delta / \text{ppm} = 7.41 – 7.16 \text{ (m, 10 H, CH}_2\text{Ar}) \), 6.25 (t, \( J = 5.8 \text{ Hz, 1 H, NH}_2 \)), 6.11 (t, \( J = 5.9 \text{ Hz, 1 H, NH}_2 \)), 6.05 (t, \( J = 6.0 \text{ Hz, 1 H, NH}_2 \)), 5.73 – 5.56 (m, 1 H, NH\(^2\)), 5.31 (d, \( J = 5.4 \text{ Hz, 0.5 H, CH}_3\text{a} \)), 5.24 – 5.07 (m, 5.5 H, CH\(^2\text{a}, CH^1, CH^5 \)), 4.69 – 4.51 (m, 2 H, CH\(^2\)), 3.49 – 3.38 (m, 1 H, CH\(^7\)), 3.32 – 2.97 (m, 8 H, CH\(^2\)), 2.89 – 2.66 (m, 4 H, CH\(^2\)), 2.43 – 2.25 (m, 8 H, CH\(^10\)), 1.95 – 1.75 (m, 4 H, CH\(^3\)), 1.71 – 1.40 (m, 19 H, CH\(^{12-13}\), CH\(^{14}\)), 1.38 – 1.06 (m, 28 H, CH\(^2\)), 0.95 – 0.84 (m, 6 H, CH\(^16\)).

\(^{13}\)C NMR (126 MHz, CDCl₃): \( \delta / \text{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, \( J = 26.5 \text{ Hz, 11 F, CF}_3\)), 41.57, 41.28, 39.43, 39.35, 39.32, 39.29, 39.20, 34.45, 34.43, 34.35, 34.30, 31.94, 29.97, 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, CDCl₃): \( \delta / \text{ppm} = -80.81 \text{ (t, } J = 9.1 \text{ Hz, 3 F, CF}_3\)), -119.77 – 123.82 (m, 2 F, CF\(^2\)), -124.53 – 130.56 (m, 2 F, CF\(^2\)). Total integral of CF\(^2\) region normalized with respect to the CF\(^3\) group = 4.

ESI-MS \([m/z]\): \([M + H]^+ \) calculated for \(^{12}\)C\(^{86}\)H\(^{133}\)O\(^{16}\)N\(_4^{19}\)F\(_7\), 1613.9834; found, 1613.9821, \( \Delta = 1.3 \text{ mmu}. \)
Supplementary Figure 105: $^1$H-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).

Supplementary Figure 108: Screenshot of the automated read-out of T9.
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1.3.5.2 Synthesis of hexamer H3

Deprotection

In a 25 mL round bottom flask, 323 mg of T9 (200 µmol, 1.00 eq.) was dissolved in 3.00 mL ethyl acetate and 3.00 mL THF. Subsequently, 64.5 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 75 was obtained as a colorless solid (296 mg, 1940 µmol, 97.1%).

IR (ATR): \(\tilde{\nu}/\text{cm}^{-1} = 3300.1 \text{ (vw)}, 2926.1 \text{ (w)}, 2854.6 \text{ (vw)}, 1741.9 \text{ (w)}, 1655.1 \text{ (w)}, 1541.6 \text{ (vw)}, 1457.2 \text{ (vw)}, 1228.3 \text{ (w)}, 1147.3 \text{ (vw)}, 700.5 \text{ (vw)}, 426.6 \text{ (vw)}.\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = 7.38 – 7.18 \text{ (m, 5 H, CH}_2\text{Ar}_1\), 6.31 (t, \(J = 5.9 \text{ Hz}, 1 \text{ H, NH}_2\), 6.22 (t, \(J = 5.9 \text{ Hz}, 1 \text{ H, NH}_2\), 6.13 (t, \(J = 6.0 \text{ Hz}, 1 \text{ H, NH}_2\), 5.81 – 5.61 (m, 1 H, NH\(^2\)), 5.36 (d, \(J = 5.5 \text{ Hz}, 0.5 \text{ H, CH}_3\)), 5.29 – 5.12 (m, 3.5 H, CH\(^{10}\), CH\(^{11}\)), 4.79 – 4.51 (m, 2 H, CH\(^5\)), 3.61 – 3.43 (m, 1 H, CH\(^6\)), 3.38 – 2.99 (m, 8 H, CH\(_2\)), 2.95 – 2.67 (m, 4 H, CH\(_2\)), 2.48 – 2.26 (m, 8 H, CH\(_3\)), 2.02 – 1.07 (m, 86 H, CH\(_2\)), 1.04 – 0.82 (m, 6 H, CH\(_3\)).\)

\(^13\)C NMR (126 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = 176.95, 172.65, 172.61, 172.51, 172.48, 171.52, 170.93, 170.66, 169.86, 169.74, 168.99, 168.77, 141.69, 141.18, 128.54, 128.31, 127.97, 127.14, 127.07, 77.85, 74.95, 74.86, 70.56, 59.67 (t, \(J = 26.9 \text{ Hz}, 1 \text{ H, CH}_2\)), 41.57, 41.27, 39.46, 39.41, 39.30, 39.23, 34.44, 34.35, 34.29, 33.94, 31.93, 29.64, 29.57, 29.53, 29.49, 29.41, 29.35, 29.33, 29.26, 29.23, 29.20, 29.08, 29.03, 28.78, 26.95, 26.94, 26.86, 26.79, 25.18, 25.11, 24.98, 24.90, 22.76, 20.07, 17.62, 15.30, 14.21, 9.15.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta/\text{ppm} = -80.81 \text{ (t, } J = 9.2 \text{ Hz, 3 F, CF}_3\)), -117.22 – -122.54 (m, 2 F, CF\(_2\)), -125.88 – -129.43 (m, 2 F, CF\(_2\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 4.

ESI-MS [m/z]: [M + H]\(^+\) calculated for \(^{12}\)C\(_{79}\)H\(_{129}\)O\(_{16}\)N\(_{4}\)F\(_7\), 1523.9365; found, 1523.9361, \(\Delta = 0.4 \text{ mmu.}\)
Supplementary Figure 109: $^1$H-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 → 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): \( v / \text{cm}^{-1} \) = 2925.3 (m), 2854.3 (m), 1741.7 (w), 1649.3 (m), 1587.1 (m), 1534.1 (s), 1454.9 (m), 1378.8 (w), 1225.8 (s), 1145.7 (m), 981.3 (w), 782.1 (w), 725.8 (w), 699.6 (m), 635.1 (w).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.39 - 7.14 \) (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\(_{18}\)), 5.24 - 5.04 (m, 6.5 H, CH\(_{3a}\), CH\(_4\), CH\(_2\)), 4.71 - 4.47 (m, 2 H, CH\(_2\)), 3.52 - 3.37 (m, 1 H, CH\(_7\)), 3.33 - 2.98 (m, 10 H, CH\(_3\)), 2.90 - 2.63 (m, 4 H, CH\(_2\)), 2.42 - 2.26 (m, 10 H, CH\(_3\)), 1.99 - 1.72 (m, 8 H, CH\(_2\)), 1.68 - 1.01 (m, 116 H, CH\(_2\), CH\(_3\)), 0.96 - 0.80 (m, 9 H, CH\(_3\)),

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{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\(_3\)): \( \delta / \text{ppm} = -80.82 \) (t, \( J = 9.1 \) Hz, 3 F, CF\(_3\)), -119.33 - -121.63 (m, 2 F, CF\(_2\)), -127.21 - -128.37 (m, 2 F, CF\(_2\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 4.

ESI-MS \( [m/z] \): [M + H]^+ calculated for \(^{12}\)C\(_{111}\)\(^{1}\)H\(_{182}\)\(^{16}\)O\(_{19}\)\(^{14}\)N\(_{5}\)\(^{19}\)F\(_{7}\), 2023.3390; found, 2023.3392, \( \Delta = 0.2 \) mmu.

Supplementary Figure 110: \(^1\)H-NMR of compound 76 measured in CDCl\(_3\).
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): \( \nu / \text{cm}^{-1} = 3291.0 \text{ (vw)}, 2923.9 \text{ (s)}, 2853.7 \text{ (m)}, 1741.6 \text{ (m)}, 1650.2 \text{ (s)}, 1535.7 \text{ (s)}, 1456.1 \text{ (m)}, 1373.8 \text{ (w)}, 1226.7 \text{ (s)}, 1145.4 \text{ (s)}, 1021.5 \text{ (w)}, 980.5 \text{ (w)}, 781.8 \text{ (vw)}, 723.6 \text{ (w)}, 699.8 \text{ (m)}, 634.8 \text{ (w)}. \)

\(^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 7.41 – 7.15 \text{ (m, 5 H, CH}_\text{Ar}\text{)}, 6.33 (t, J = 5.8 Hz, 1 H, NH\text{2}), 6.26 – 6.16 \text{ (m, 2 H, NH\text{2})}, 6.13 (t, J = 5.9 Hz, 1 H, NH\text{2}), 5.74 (dt, J = 24.0, 6.1 Hz, 1 H, NH\text{2}), 5.35 (d, J = 5.5 Hz, 0.5 H, CH\text{3a}), 5.28 – 5.14 \text{ (m, 4.5 H, CH\text{3b}, CH\text{4})}, 4.75 – 4.52 \text{ (m, 2 H, CH\text{5})}, 3.56 – 3.43 \text{ (m, 1 H, CH\text{6})}, 3.38 – 3.01 \text{ (m, 10 H, CH\text{7})}, 2.95 – 2.68 \text{ (m, 4 H, CH\text{8})}, 2.49 – 2.30 \text{ (m, 10 H, CH\text{9})}, 2.00 – 1.77 \text{ (m, 6 H, CH\text{10})}, 1.75 – 1.05 \text{ (m, 118 H, CH\text{11}, CH\text{12})}, 1.00 – 0.81 \text{ (m, 9 H, CH\text{13})}.

\(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{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\]): [M + H]^+ calculated for \(^{12}C_{104}^{1}H_{176}^{16}O_{19}^{14}N_{5}^{19}F_{7}\), 193.2921; found, 193.2935, \(\Delta = 1.4 \text{ mmu}\).
Supplementary Figure 11: $^1$H-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 → 1:1) to yield the passerini product H3 as a pale highly viscous oil. (28.7 mg, 11.8 µmol, 40.5%).
$R_t = 0.46$ 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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta / \text{ppm} = 7.33 – 7.09$ (m, 10 H, CH$_{\text{Ar}}^{1}$), 6.18 (t, $J = 5.7$ Hz, 1 H, NH$_2^{2}$), 6.09 – 5.90 (m, 4 H, NH$_2^{2}$), 5.66 – 5.50 (m, 1 H, NH$_2^{2}$), 5.31 – 5.00 (m, 8 H, CH$_3^{1}$, CH$_2^{4}$), 4.66 – 4.43 (m, 2 H, CH$_2^{5}$), 3.47 – 3.32 (m, 1 H, CH$_6^{5}$), 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$_{11}$, CH$_{12}$), 0.89 – 0.71 (m, 12 H, CH$_{13}$).

$^{13}$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, 168.60, 168.60, 168.33, 168.31, 167.98, 167.88, 167.36, 167.95, 167.90, 167.09, 167.06, 166.22, 141.60, 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$_3$ group = 4.

ESI-MS [m/z]: [M + H]$^+$ calculated for $^{12}$C$_{135}$H$_{227}$^{16}O$_{22}$^{14}N$_6^{19}$F$_7$, 2418.6789; found, 2418.6818, $\Delta = 2.9$ mmu.
Supplementary Figure 112: $^1$H-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).

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 µL 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 → 4:1) to yield the passerini product 78 as a pale highly viscous oil. (1.04 g, 1.46 mmol, 87.4%).

Rf = 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, CDCl₃): δ/ ppm = 7.41 – 7.29 (m, 5 H, CHAr), 6.22 (t, J = 5.8 Hz, 1 H, NH²), 5.19 – 5.14 (m, 1 H, CH³), 5.11 (s, 2 H, CH₄), 4.71 – 4.48 (m, 2 H, CH₅), 3.32 – 3.11 (m, 2 H, CH₆), 2.94 – 2.64 (m, 4 H, CH₇), 2.34 (t, J = 7.6 Hz, 2 H, CH₈), 1.95 – 1.76 (m, 2 H, CH₉), 1.67 – 1.57 (m, 2 H, CH₁₀), 1.54 – 1.43 (m, 2 H, CH₁¹), 1.39 – 1.13 (m, 20 H, CH₁²), 0.87 (t, J = 6.6 Hz, 3 H, CH₃¹³).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ/ ppm = -84.54 – -86.48 (m, 3 F, CF₃¹⁴), -124.50 – -126.45 (m, 2 F, CF₂¹⁴), -131.22 – -133.88 (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 C₃₄H₄₃O₁₄N₁₉F₇: 716.3392; found, 716.3371, Δ = 2.1 mpu.

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Supplementary Figure 117: $^1$H-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): $\nu$ / 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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / 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$_3$): $\delta$ / 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$_3$): $\delta$ / 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]: [M + Na]$^+$ calculated for $^{12}$C$_7^{15}$H$_{42}$O$_7^{14}$N$^{19}$F$_7$, 648.2742; found, 648.2729, $\Delta$ = 1.3 mmu.

Supplementary Figure 118: $^1$H-NMR of compound 79 measured in CDCl$_3$. 

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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 µL 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 → 2:1) to yield the passerini product 80 as a pale highly viscous oil. (1.12 g, 1.12 mol, 88.2%).

Rf = 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, CDCl₃): δ/ppm = 7.36 – 7.21 (m, 5 H, CHAr₁), 6.18 (t, J = 5.8 Hz, 1 H, NH₂), 5.88 (t, J = 5.9 Hz, 1 H, NH²), 5.13 – 5.07 (m, 1 H, CH₃), 5.01 (s, 2 H, CH₂), 4.99 (d, J = 4.4 Hz, 1 H, CH₅), 4.66 – 4.43 (m, 2 H, CH₆), 3.30 – 3.09 (m, 4 H, CH₇), 2.83 – 2.59 (m, 4 H, CH₂), 2.39 – 2.19 (m, 5 H, CH₉, CH₂₁₀), 1.90 – 1.69 (m, 2 H, CH₂¹¹), 1.67 – 1.58 (m, 4 H, CH₂¹²), 1.49 – 1.35 (m, 4 H, CH₂¹³), 1.29 – 1.10 (m, 32 H, CH₂¹⁴), 0.92 – 0.84 (m, 6 H, CH₁⁵), 0.83 – 0.77 (m, 3 H, CH₂¹⁶).

¹³C NMR (101 MHz, CDCl₃): 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, 28.79, 26.96, 26.95, 25.13, 25.07, 24.93, 22.65, 18.90, 17.07, 14.14.

¹⁹F NMR (376 MHz, CDCl₃): δ/ppm = -85.16 (t, J = 9.3 Hz, 3 F, CF₃¹⁷), -124.27 – -125.33 (m, 2 F, CF₂¹⁸), -131.44 – -132.73 (m, 2 F, CF₂¹⁸). Total integral of CF₂ region normalized with respect to the CF₃¹⁷ group = 4.

ESI-MS [m/z]: [M + Na]⁺ calculated for ¹²C₃₀¹⁷H₇₇¹⁶O₁₀¹⁴N₂¹⁹F₇, 1021.5359; found, 1021.5337, Δ = 2.2 mmu.
Supplementary Figure 119: ^1^H-NMR of compound 80 measured in CDCl₃.

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 (m), 1540.2 (s), 1463.6 (w), 1353.0 (w), 1226.3 (vs), 1144.1 (vs), 1019.3 (m), 909.7 (w), 735.6 (w), 627.5 (vw).

^1^H NMR (400 MHz, CDCl₃): 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, CH₂^4^), 3.30 – 3.09 (m, 4 H,
CH₂), 2.85 – 2.59 (m, 4 H, CH₆), 2.37 – 2.17 (m, 5 H, CH⁷, CH₈), 1.90 – 1.68 (m, 2 H, CH₉), 1.64 – 1.50 (m, 4 H, CH₁₀), 1.48 – 1.35 (m, 4 H, CH₁¹), 1.33 – 1.07 (m, 32 H, CH₁²), 0.89 – 0.84 (m, 6 H, CH₂¹³), 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 ¹²C₄³H₇¹⁶O₁₀¹⁴N₂¹⁹F₇, 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 → 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): \( \nu / \text{cm}^{-1} = 3306.2 \) (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).

\( ^1H \text{NMR} (400 \text{ MHz, CDCl}_3): \delta / \text{ppm} = 7.43 – 7.28 \) (m, 5 H, CH\(_{\text{Ar}}\)), 6.25 (t, \( J = 5.8 \) Hz, 1 H, NH\(_2\)), 6.02 – 5.90 (m, 2 H, NH\(_2\)), 5.11 (s, 2 H, CH\(_2\)), 5.19 – 5.14 (m, 1 H, CH\(_3\)), 5.11 (s, 2 H, CH\(_2\)), 5.08 – 5.00 (m, 2 H, CH\(_2\)), 4.72 – 4.50 (m, 2 H, CH\(_2\)), 3.34 – 3.16 (m, 6 H, CH\(_2\)), 2.90 – 2.65 (m, 4 H, CH\(_2\)), 2.43 – 2.24 (m, 7 H, CH\(_9\), CH\(_2\)), 2.01 – 1.77 (m, 3 H, CH\(_{11}\), CH\(_2\)), 1.76 – 1.58 (m, 12 H, CH\(_{13}\)), 1.56 – 1.41 (m, 6 H, CH\(_{14}\)), 1.37 – 1.04 (m, 48 H, CH\(_{15}\)), 0.96 – 0.90 (m, 6 H, CH\(_{16}\)), 0.90 – 0.82 (m, 3 H, CH\(_{17}\)).

\( ^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3): \delta / \text{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, 25.85, 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.

\( ^{19}F \text{NMR} (376 \text{ MHz, CDCl}_3): \delta / \text{ppm} = -85.15 \) (t, \( J = 9.2 \) Hz, 3 F, CF\(_3\)), -124.51 – -125.62 (m, 2 F, CF\(_2\)), -131.79 – -133.84 (m, 2 F, CF\(_2\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 4.

ESI-MS [m/z]: [M + H]\(^+\) calculated for \(^{12}C_6^{19}H_{110}^{16}O_{13}^{14}N_3^{19}F_7\), 1322.8000; found, 1322.7981, \( \Delta = 1.9 \) mmu.
Supplementary Figure 121: ¹H-NMR of compound 82 measured in CDCl₃.

**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): $\nu$ / 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, CDCl₃): $\delta$ / ppm = 6.24 (t, $J = 5.8$ Hz, 1 H, NH¹), 6.06 – 5.88 (m, 2 H, NH²), 5.14 – 5.07 (m, 1 H, CH¹), 5.03 – 4.92 (m, 2 H, CH²), 4.70 – 4.39 (m, 2 H, CH₂⁴), 3.26 – 3.08 (m, 6 H, CH₂⁵), 2.84 – 2.58 (m, 4 H, CH₂⁶), 2.39 – 2.16 (m, 7 H, CH⁷, CH₂⁸), 1.94 – 1.50 (m, 15 H, CH⁹, CH₂¹⁰),
1.48 – 1.33 (m, 6 H, CH2\textsuperscript{11}), 1.33 – 0.94 (m, 48 H, CH2\textsuperscript{10}), 0.91 – 0.83 (m, 6 H, CH3\textsuperscript{12}), 0.83 – 0.77 (m, 3 H, CH3\textsuperscript{13}).

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \(\delta / \text{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]\textsuperscript{+} calculated for \textsuperscript{12}C\textsubscript{62}H\textsubscript{104}O\textsubscript{13}N\textsubscript{3}F\textsubscript{7}, 1232.7530; found, 1232.7502, \(\Delta = 2.8\) mmu.

Supplementary Figure 122: \textsuperscript{1}H-NMR of compound 83 measured in CDCl\textsubscript{3}.

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 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 → 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): ν / 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, CDCl₃): δ / ppm = 7.41 – 7.28 (m, 5 H, CH₆Ar), 6.26 (t, J = 5.8 Hz, 1 H, NH₂), 6.06 – 5.93 (m, 3 H, NH₃), 5.19 – 5.13 (m, 2 H, CH₂), 5.10 (s, 2 H, CH₂), 5.07 – 4.99 (m, 2 H, CH₂), 4.72 – 4.48 (m, 2 H, CH₂), 3.34 – 3.14 (m, 8 H, CH₂), 2.90 – 2.65 (m, 4 H, CH₂), 2.43 – 2.24 (m, 9 H, CH₃), 2.00 – 1.58 (m, 19 H, CH₉), 1.54 – 1.43 (m, 8 H, CH₂), 1.37 – 1.04 (m, 78 H, CH₂), 0.95 – 0.90 (m, 6 H, CH₃), 0.89 – 0.83 (m, 6 H, CH₃).

¹³C NMR (101 MHz, CDCl₃): δ / 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, 26.92, 26.12, 26.01, 25.12, 25.07, 24.93, 24.89, 22.81, 22.65, 18.91, 17.07, 14.25, 14.15.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -83.46 – -86.58 (m, 3 F, CF₃), -123.51 – -126.45 (m, 2 F, CF₂), -131.44 – -133.84 (m, 2 F, CF). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + H]+ calculated for ²⁵C₉₃H₅₅O₁₆N₄F₇, 1718.1399; found, 1718.1400, Δ = 0.1 mmu.

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Supplementary Figure 123: $^1$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).

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 µL 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 → 5:1) to yield the passerini product 84 as a pale highly viscous oil. (1.03 g, 1.30 mmol, 78.0%).

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

IR (ATR): $\nu$/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).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$/ppm = 7.44 – 7.30 (m, 5 H, CH$_2$Ar), 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$_2$), 4.73 – 4.49 (m, 2 H, CH$_2$), 3.34 – 3.15 (m, 2 H, CH$_2$), 2.91 – 2.66 (m, 4 H, CH$_2$), 2.34 (t, $J = 7.6$ Hz, 2 H, CH$_2$), 1.95 – 1.74 (m, 2 H, CH$_2$), 1.68 – 1.57 (m, 2 H, CH$_2$), 1.54 – 1.44 (m, 2 H, CH$_2$), 1.36 – 1.15 (m, 32 H, CH$_2$), 0.92 – 0.83 (m, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$/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$_3$): $\delta$/ppm = -85.16 (t, $J = 9.2$, 3 F, CF$_3$), -123.69 – -125.74 (m, 2 F, CF$_2$), -131.26 – -133.08 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 4.

ESI-MS [m/z]: [M + Na]$^+$ calculated for $^{12}$C$_{40}$H$_{60}$O$_7$N$^{19}$F$_7$, 822.4150; found, 822.4133, $\Delta = 1.7$ mmu.
Supplementary Figure 127: $^1$H-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): \( \nu / \text{cm}^{-1} = 3293.4 \) (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).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 6.26 \) (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\(^3\)), 3.35 – 3.15 (m, 2 H, CH\(^4\)), 2.91 – 2.64 (m, 4 H, CH\(^5\)), 2.33 (t, \( J = 7.5 \) Hz, 2 H, CH\(^6\)), 1.94 – 1.73 (m, 2 H, CH\(^7\)), 1.71 – 1.57 (m, 2 H, CH\(^8\)), 1.54 – 1.42 (m, 2 H, CH\(^9\)), 1.38 – 1.14 (m, 32 H, CH\(^{10}\)), 0.91 – 0.83 (m, 3 H, CH\(^{11}\)).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 179.82, 172.29, 171.70, 170.54, 75.64, 60.46 \) (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\(_3\)): \( \delta / \text{ppm} = -85.17 \) (t, \( J = 9.2 \) Hz, 3 F, CF\(_3\)), -124.45 – -128.85 (m, 2 F, CF\(^2\)), -131.44 – -136.02 (m, 2 F, CF\(^3\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 4.

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

Supplementary Figure 128: \(^1\)H-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 → 1:1) to yield the passerini product 86 as a pale highly viscous oil. (618 g, 571 µmol, 96.4%).

Rf = 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), 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, CDCl₃): δ / ppm = 7.43 – 7.28 (m, 5 H, CH₉), 6.24 (t, J = 5.8 Hz, 1 H, NH₂), 5.95 (t, J = 5.9 Hz, 1 H, NH₂), 5.19 – 5.13 (m, 1 H, CH₃), 5.05 (d, J = 4.4 Hz, 1 H, CH₃), 4.71 – 4.49 (m, 2 H, CH₂), 3.36 – 3.14 (m, 4 H, CH₂), 2.89 – 2.65 (m, 4 H, CH₂), 2.44 – 2.22 (m, 5 H, CH₂, CH₃), 1.94 – 1.73 (m, 2 H, CH₂), 1.69 – 1.57 (m, 4 H, CH₂), 1.54 – 1.43 (m, 4 H, CH₂), 1.36 – 1.20 (m, 44 H, CH₂), 0.96 – 0.90 (m, 6 H, CH₃), 0.89 – 0.83 (m, 3 H, CH₃).

¹³C NMR (101 MHz, CDCl₃): 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.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.16 (t, J = 9.2 Hz, 3 F, CF₃), -124.27 – -125.74 (m, 2 F, CF₂), -131.26 – -133.08 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₅₆¹⁵H₈⁹¹⁶O₁⁰¹⁴N₂¹⁹F₇, 1083.6478; found, 1083.6459, Δ = 1.9 mmu.
Supplementary Figure 129: $^1$H-NMR of compound 86 measured in CDCl₃.

De-protection

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).

$^1$H 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$_2$), 3.36 – 3.14 (m, 4 H, CH$_2$), 2.92 – 2.64 (m, 4 H, CH$_2$), 2.45 – 2.24 (m, 5 H, CH$_7$, CH$_3$), 1.95 – 1.71 (m, 2 H, CH$_2$), 1.68 – 1.56 (m, 4 H, CH$_10$), 1.54 – 1.40 (m, 4 H, CH$_{11}$), 1.40 – 1.14 (m, 44 H, CH$_{12}$), 0.95 – 0.89 (m, 6 H, CH$_{13}$), 0.89 – 0.84 (m, 3 H, CH$_{14}$).

$^{13}$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$_3$), -123.16 – -126.45 (m, 2 F, CF$_2$), -130.67 – -138.42 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group = 4.

ESI-MS [m/z]: [M + H]$^+$ calculated for $^{12}$C$_{49}$H$_{83}$O$_{16}$N$_2$F$_{7}$Na, 1015.5828; found, 1015.5812, $\Delta = 1.6$ mmu.

Supplementary Figure 130: $^1$H-NMR of compound 87 measured in CDCl$_3$. 

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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 → 4:1) to yield the passerini product 88 as a pale highly viscous oil. (430 mg, 302 µmol, 74.4%).

Rf = 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), 1466.6 (vw), 1366.9 (vw), 1301.3 (vw), 1257.5 (w), 1164.1 (w), 1118.0 (w), 1019.5 (vw), 912.3 (vw), 696.7 (vw), 417.8 (vw).

1H NMR (500 MHz, CDCl₃): δ/ppm = 7.35 – 7.21 (m, 5 H, CHAr₁), 6.16 (t, J = 5.8 Hz, 1 H, NH₂), 5.94 (t, J = 5.9 Hz, 1 H, NH₂), 5.88 (t, J = 5.9 Hz, 1 H, NH₂), 5.12 – 5.07 (m, 2 H, CH₃), 5.04 (s, 2 H, CH₂), 4.98 (d, J = 4.4 Hz, 1 H, CH₂), 4.68 – 4.43 (m, 2 H, CH₂), 3.32 – 3.10 (m, 6 H, CH₂), 2.85 – 2.60 (m, 4 H, CH₂), 2.37 – 2.18 (m, 7 H, CH₃, CH₂), 1.91 – 1.67 (m, 4 H, CH₂), 1.66 – 1.54 (m, 6 H, CH₂), 1.48 – 1.37 (m, 6 H, CH₂), 1.32 – 1.11 (m, 6 H, CH₂), 0.87 (t, J = 6.5 Hz, 6 H, CH₃), 0.83 – 0.74 (m, 6 H, CH₃).

13C NMR (126 MHz, CDCl₃): 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.

19F NMR (376 MHz, CDCl₃): δ/ppm = -84.05 – -85.87 (m, 3 F, CF₂₁₄), -123.33 – -127.03 (m, 2 F, CF₂₁₅), -131.26 – -133.96 (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 12C₇₆H₁₂₆O₁₃¹⁴N₃¹⁹F₇, 1422.9252; found, 1422.9239, Δ = 1.3 mmu.
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): $\nu$ / 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).
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ / 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$_3$), 4.98 (d, $J = 4.5$ Hz, 1 H, CH$^3$), 4.67 – 4.43 (m, 2 H, CH$_2^3$), 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$_3$): $\delta$ / 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, 29.60, 29.68, 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, 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]: [M + H]$^+$ calculated for $^{12}$C$_{70}$H$_{120}$O$_{11}$N$_3$Cl, 1214.8684; found, 1214.8655, $\Delta$ = 2.9 mmu.

Supplementary Figure 132: $^1$H-NMR of compound 89 measured in CDCl$_3$. 

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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 → 2:1) to yield the passerini product T11 as a pale highly viscous oil. (331 mg, 190 µmol, 90.0%).

Rf = 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), 1172.6 (vs), 1020.5 (w), 722.7 (w), 696.5 (m).

¹H NMR (500 MHz, CDCl₃): δ / ppm = 7.35 – 7.22 (m, 5 H, CHAr), 6.19 (t, J = 5.8 Hz, 1 H, NH₂), 5.97 (t, J = 5.9 Hz, 1 H, NH₂), 5.93 – 5.81 (m, 2 H, NH₂), 5.12 – 5.07 (m, 2 H, CH₃), 5.04 (s, 2 H, CH₂), 4.98 (d, J = 4.4 Hz, 1 H, CH²), 4.96 (d, J = 4.6 Hz, 1 H, CH²), 4.65 – 4.43 (m, 2 H, CH₂), 3.29 – 3.09 (m, 8 H, CH₂), 2.84 – 2.60 (m, 4 H, CH₂), 2.41 – 2.18 (m, 9 H, CH³CH₂), 1.95 – 1.52 (m, 21 H, CH₁₁, CH₁₂), 1.48 – 1.36 (m, 8 H, CH₂), 1.30 – 0.94 (m, 18 H, CH₂), 0.87 (t, J = 6.5 Hz, 6 H, CH₃), 0.85 – 0.76 (m, 6 H, CH₃).

¹³C NMR (126 MHz, CDCl₃): δ / ppm = 173.80, 172.67, 172.66, 172.60, 171.49, 170.89, 169.98, 169.62, 169.40, 169.32, 163.24, 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.

¹⁹F NMR (376 MHz, CDCl₃): δ / ppm = -85.14 (t, J = 9.2 Hz, 3 F, CF₃), -124.10 – -125.56 (m, 2 F, CF₂), -131.03 – -133.61 (m, 2 F, CF₂). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + H]⁺ calculated for ¹²C₉₅¹H₁₅₉¹⁶O₁₆¹⁴N₁⁴F₇, 1746.1712; found, 1746.1708, Δ = 0.4 mmu.
Supplementary Figure 133: $^1$H-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).

Supplementary Figure 136: Screenshot of the automated read-out of T11.
Synthesis of tetramer T12
Passerini reaction

In a 50 mL round bottom flask, 304 mg TAG2 (1.01 mmol, 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 204 µL cyclohexancarboxaldehyde 14j (170 mg, 1.52 mmol, 1.50 eq.) and 458 mg of the monomer M1 (1.52 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 (7:1 → 5:1) to yield the passerini product 90 as a pale highly viscous oil. (663 mg, 927 µmol, 91.8%).

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

IR (ATR): ν/cm⁻¹ = 3306.8 (vw), 2927.0 (m), 2854.6 (w), 1737.7 (s), 1655.8 (m), 1534.5 (w), 1452.0 (w), 1351.8 (w), 1226.0 (vs), 1142.5 (vs), 1019.7 (m), 910.1 (m), 735.9 (m), 697.2 (m).

¹H NMR (400 MHz, CDCl₃): δ/ppm = 7.46 – 7.29 (m, 5 H, CH₆₁), 6.19 (t, J = 5.8 Hz, 1 H, NH²), 5.11 (s, 2 H, CH₂ª), 5.04 (d, J = 4.0 Hz, 1 H, CH³), 4.74 – 4.46 (m, 2 H, CH₂ª), 3.35 – 3.12 (m, 2 H, CH₂ª), 2.91 – 2.66 (m, 4 H, CH₂ª), 2.34 (t, J = 7.6 Hz, 2 H, CH₂ª), 2.07 – 1.92 (m, 1 H, CH₂ª), 1.80 – 1.57 (m, 8 H, CH₂ª), 1.55 – 1.42 (m, 2 H, CH₂ª), 1.37 – 0.96 (m, 16 H, CH₂ª).

¹³C NMR (101 MHz, CDCl₃): δ/ppm = 173.83, 171.54, 170.93, 168.95, 136.27, 128.67, 128.29, 78.58, 66.19, 59.71 (t, J = 27.1 Hz), 39.91, 39.40, 34.45, 29.57, 29.56, 29.47, 29.42, 29.33, 29.23, 29.00, 28.80, 27.14, 26.97, 26.15, 26.01, 25.06.

¹⁹F NMR (376 MHz, CDCl₃): δ/ppm = -85.16 (t, J = 9.2 Hz, 3 F, CF₁³), -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.

ESI-MS [m/z]: [M + H]+ calculated for ¹²C₃₄H₄₆O₇N¹⁹F₇, 714.3235; found, 714.3226, Δ = 0.9 mmu.
Supplementary Figure 137: ¹H-NMR of compound 90 measured in CDCl₃.

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).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ / 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$_2^{10}$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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, 29.09, 28.99, 28.79, 27.12, 26.91, 26.13, 26.00, 24.81.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ / 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]: [M + H]$^+$ calculated for $^{12}$C$_{27}$H$_{40}$O$_7$N$_{19}$F$_7$, 624.2766; found, 624.2752, $\Delta = 1.4$ mmu.

Supplementary Figure 138: $^1$H-NMR of compound 91 measured in CDCl$_3$. 

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Passerini reaction

In a 50 mL round bottom flask, 419 mg of 91 (671 µmol, 1.00 eq.) was stirred in 3.00 mL dichloromethane. Subsequently, 194 µL 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 → 2:1) to yield the passerini product 92 as a pale highly viscous oil. (663 mg, 927 µmol, 91.8%).

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

IR (ATR): /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), 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).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): / ppm = 7.45 – 7.28 (m, 5 H, CH\(_{Ar}\)), 6.20 (t, J = 5.8 Hz, 1 H, NH\(_2\)), 6.00 (t, J = 5.8 Hz, 1 H, NH\(_2\)), 5.19 – 5.13 (m, 1 H, CH\(_3\)), 5.11 (s, 2 H, CH\(_2\)), 5.03 (d, J = 4.1 Hz, 1 H, CH\(_3\)), 4.72 – 4.48 (m, 2 H, CH\(_2\)), 3.36 – 3.13 (m, 4 H, CH\(_2\)), 2.90 – 2.66 (m, 4 H, CH\(_2\)), 2.44 – 2.30 (m, 4 H, CH\(_2\)), 2.08 – 1.93 (m, 1 H, CH\(_3\)), 1.90 – 1.56 (m, 14 H, CH\(_2\)), 1.56 – 1.44 (m, 4 H, CH\(_2\)), 1.38 – 0.98 (m, 36 H, CH\(_3\)), 0.90 – 0.83 (m, 3 H, CH\(_3\)).

\(^13\)C NMR (101 MHz, CDCl\(_3\)): / 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.

\(^19\)F NMR (376 MHz, CDCl\(_3\)): / ppm = -85.15 (t, J = 9.7 Hz, 3 F, CF\(_3\)), -124.10 – -125.74 (m, 2 F, CF\(_3\)), -130.32 – -133.43 (m, 2 F, CF\(_3\)). Total integral of CF\(_2\) region normalized with respect to the CF\(_3\) group = 4.

ESI-MS [m/z]: [M + H]\(^+\) calculated for \(^{12}\)C\(_{54}\)^{1}\(^3\)H\(_8\)^{16}\(^{15}\)O\(_{10}\)^{14}\(^{19}\)F\(_7\), 1053.6009; found, 1053.6000, Δ = 0.9 mmu.
Supplementary Figure 139: $^1$H-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 viscos 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).

$^1$H 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$_2$), $3.41 - 3.12$ (m, 4 H, CH$_2$), $2.93 - 2.69$ (m, 4 H, CH$_2$), $2.48 - 2.28$ (m, 4 H, CH$_2$), $2.10 - 1.95$ (m, 1 H, CH$_3$), $1.92 - 0.99$ (m, 54 H, CH$_2$), $0.87$ (t, $J = 6.6$ Hz, 3 H, CH$_3$).

$^{13}$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$_3$), -124.10 - -125.92 (m, 2 F, CF$_2$), -130.67 - -133.43 (m, 2 F, CF$_2$). Total integral of CF$_2$ region normalized with respect to the CF$_3$ group $= 4$.

ESI-MS [$m/z$]: [M + Na]$^+$ calculated for $^{12}$C$_{47}$H$_{77}$O$_{10}$N$_4^{19}$F$_7$Na, 985.5359; found, 985.5341, $\Delta = 1.8$ mmu.

Supplementary Figure 140: $^1$H-NMR of compound 93 measured in CDCl$_3$.  

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Passerini reaction

In a 50 mL round bottom flask, 361 mg of 94 (375 µmol, 1.00 eq.) was stirred in 4.00 mL dichloromethane. Subsequently, 60.5 µL 3-methylbutyraldehyde 14g (48.4 mg, 562 µmol, 1.50 eq.) and 169 mg of the monomer M1 (562 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 → 2:1) to yield the passerini product 94 as a pale highly viscous oil. (377 mg, 279 µmol, 74.5%).

Rf = 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).

1H-NMR (400 MHz, CDCl₃): δ / ppm = 7.44 – 7.28 (m, 5 H, CHAr), 6.21 (t, J = 5.8 Hz, 1 H, NH₂), 6.07 – 5.91 (m, 2 H, NH₂), 5.26 – 5.14 (m, 2 H, CH₂), 5.11 (s, 2 H, CH₂), 5.04 (d, J = 4.0 Hz, 1 H, CH₃), 4.74 – 4.45 (m, 2 H, CH₂), 3.35 – 3.14 (m, 6 H, CH₂), 2.91 – 2.68 (m, 4 H, CH₂), 2.44 – 2.30 (m, 6 H, CH₂), 2.08 – 1.91 (m, 1 H, CH₃), 1.90 – 1.56 (m, 17 H, CH₁³), 1.56 – 1.38 (m, 6 H, CH₂), 1.38 – 0.99 (m, 50 H, CH₂), 0.92 (t, J = 5.7 Hz, 6 H, CH₃), 0.89 – 0.79 (m, 3 H, CH₃).

13C NMR (101 MHz, CDCl₃): 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.

19F NMR (376 MHz, CDCl₃): δ / ppm = -85.14 (t, J = 9.5 Hz, 3 F, CF₃), -124.79 – -124.91 (m, 2 F, CF₃), -131.94 – -132.04 (m, 2 F, CF₃). Total integral of CF₂ region normalized with respect to the CF₃ group = 4.

ESI-MS [m/z]: [M + H]⁺ calculated for 12C₇₁H₁₁₄¹⁶O₁₃¹⁴N₁⁹F₇, 1350.8313; found, 1350.8312, Δ = 0.1 mmu.
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): \( \nu / \text{cm}^{-1} = 3309.2, 2925.5, 2854.6, 2036.6, 1987.3, 1879.2, 1654.5, 1540.1, 1465.2, 1369.3, 1227.8, 1145.9, 1021.0, 910.8, 735.9, 472.7, 422.0 \).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta / \text{ppm} = 6.28 - 6.17 (\text{m, } 1 \text{ H, NH})^1, 6.11 - 6.07 (\text{m, } 1 \text{ H, NH})^1, 6.03 - 5.97 (\text{m, } 1 \text{ H, NH})^1, 5.24 - 5.11 (\text{m, } 2 \text{ H, CH}^2), 5.04 (\text{d, } J = 4.0 \text{ Hz, } 1 \text{ H, CH})^1, 4.71 - 4.48 (\text{m, } 2 \text{ H, CH}^2), 3.33 - 3.15 (\text{m, } 6 \text{ H, CH}^3), 2.91 - 2.67 (\text{m, } 4 \text{ H, CH}^6), 2.43 - 2.29 (\text{m, } 6 \text{ H, CH}^7), 2.04 - 1.94 \)
(m, 1 H, CH$^8$), 1.93 – 1.59 (m, 17 H, CH$^9$, CH$_2$$^{10}$), 1.56 – 1.42 (m, 6 H, CH$_2$$^{11}$), 1.34 – 0.90 (m, 50 H, CH$_2$$^{10}$), 0.92 (t, $J = 5.7$ Hz, 6 H, CH$_1$$^{12}$), 0.87 (t, $J = 6.8$ Hz, 3 H, CH$_1$$^{13}$).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ / 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.

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ / ppm = -85.14 (t, $J = 9.6$ Hz, 3 F, CF$_3$$^{14}$), -124.79 – -124.90 (m, 2 F, CF$_2$$^{15}$), -131.90 – -132.10 (m, 2 F, CF$_2$$^{15}$). Total integral of CF$_2$ region normalized with respect to the CF$_3$$^{14}$ group = 4.

ESI-MS [m/z]: [M + H]$^+$ calculated for $^{12}$C$_{64}$$^{1}$$H_{108}$$^{16}$O$_{13}$$^{14}$N$_3$$^{19}$F$_7$, 1260.7843; found, 1260.7826, $\Delta = 1.7$ mmu

Supplementary Figure 142: $^1$H-NMR of compound 95 measured in CDCl$_3$. 
Passerini reaction

In a 50 mL round bottom flask, 264 mg of 95 (210 µmol, 1.00 eq.) was stirred in 3.00 mL DCM. Subsequently, 57.9 mg dodecanal 14h (314 µmol, 1.50 eq.) and 94.7 mg of the monomer M1 (314 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 → 2:1) to yield the passerini product T12 as a pale highly viscous oil. (292 mg, 167 µmol, 79.7%).

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

IR (ATR): \( \nu / \text{cm}^{-1} = 3302.0, 2922.6, 2852.3, 2165.9, 1739.0, 1656.3, 1540.6, 1466.3, 1369.9, 1228.7, 1171.8, 1022.6, 697.9 \) (vw).

\(^1H\)-NMR (400 MHz, CDCl₃): \( \delta / \text{ppm} = 7.41 – 7.28 \) (m, 5 H, CHAr), 6.21 (t, \( J = 5.9 \) Hz, 1 H, NH), 6.08 – 5.93 (m, 3 H, NH²), 5.22 – 5.13 (m, 3 H, CH³), 5.11 (s, 2 H, CH²), 5.04 (d, \( J = 4.1 \) Hz, 1 H, CH³), 4.72 – 4.46 (m, 2 H, CH⁶), 3.34 – 3.14 (m, 8 H, CH²), 2.91 – 2.68 (m, 4 H, CH³), 2.43 – 2.29 (m, 8 H, CH₃), 2.03 – 1.57 (m, 26 H, CH), 1.55 – 1.43 (m, 8 H, CH₂), 1.38 – 1.00 (m, 76 H, CH₂), 0.92 (t, \( J = 5.8 \) Hz, 6 H, CH₁³), 0.90 – 0.84 (m, 6 H, CH₁⁴).

\(^13C\)-NMR (101 MHz, CDCl₃): \( \delta / \text{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.

\(^19F\)-NMR (376 MHz, CDCl₃): \( \delta / \text{ppm} = -85.14 \) (t, \( J = 9.6 \) Hz, 3 F, CF₃¹⁵), -123.51 – -127.56 (m, 2 F, CF₂¹⁶), -130.32 – -134.20 (m, 2 F, CF₂¹⁶). Total integral of CF₂ region normalized with respect to the CF₃¹⁵ group = 4.

ESI-MS \([m/z]\): [M + H]⁺ calculated for \(^{12}C⁹¹H_{159}^{16}O_{16}^{14}N_{4}^{19}F_{7} \), 1746.1712; found, 1746.1712, \( \Delta = 0.0 \) mmu.

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Supplementary Figure 143: $^1$H-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.

Monomer (90)  
Dimer (92)  
Trimer (94)  
Tetramer (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).

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

\[
[M_{\text{Molecule}} + H]^+ = \left( M_{\text{Start}} + n \cdot M_{\text{Backbone}} + \sum_{i=1}^{n} M_{\text{Sidechain}} + M_{\text{End}} + y \cdot M(H) \right) + H
\]

(Supplementary Equation 1)

n = number of repeating units,
y = (n - 1)
\(M_{\text{Start}} = M \text{ (Tag X)}\)
\(M_{\text{End}} = M \text{ (C}_7\text{H}_7)\)
\(M_{\text{Backbone}} = (M \text{ (monomer M1)}) - M\text{(C}_7\text{H}_7)\)
\(M_{\text{Sidechain}} = M \text{ (2a)} \text{ or } M \text{ (2b)} \text{ or } M \text{ (2c)} \text{ or } M \text{ (2d)} \text{ or } M \text{ (2e)} \text{ or } M \text{ (2f)} \text{ or } M \text{ (2g)} \text{ or } M \text{ (2h)} \text{ or } M \text{ (2i)} \text{ or } M \text{ (2j)} \text{ or } M \text{ (2k)} \text{ or } M \text{ (2l)}\)

\(M_{\text{Backbone}}\) 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.
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).