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**Supplementary methods**

**General information**

Unless stated otherwise, reactions were performed without special precautions like drying or N$_2$/Argon atmosphere. Dried CH$_2$Cl$_2$ and CH$_3$CN were obtained by distilling these solvents with CaH$_2$ as drying agent. Dried THF and Et$_2$O were obtained by distillation with sodium. All dried solvents were stored under N$_2$ atmosphere. Dry DMF on 4 Å molecular sieves was obtained from Sigma-Aldrich and stored under N$_2$ atmosphere. Reagents were purchased with the highest purity (usually >98%) from Sigma Aldrich and Fluorochem and used as received. Grubbs 2$^{nd}$ generation catalyst was purchased from AK Scientific and TBTA was purchased from TCI Europe. Reactions were monitored with thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254). SiliFlash® P60 (particle size 40-63 µm) was used for silica column chromatography. NMR spectra were recorded on Bruker DRX-500, 400 and 300 MHz instruments and calibrated on residual undeuterated solvent signals as internal standard. The $^1$H-NMR multiplicities were abbreviated as followed: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. High resolution mass spectra (HRMS) were recorded on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). FD/FI probe equipped with FD Emitter, Carbotec or Linden (Germany), FD 10 µm. Current rate 51.2 mA/min over 1.2 min machine using field desorption (FD) as ionization method. Depending on the molecule, either the (M)$^+$ or (M+H)$^+$ were observed; often the (M+Na)$^+$ signal was also observed. Melting points were recorded on a Wagner & Munz Polytherm A melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FTIR machine. 2,7-diiodofluorene$^1$ and 3,3,3-tris(tert-butylphenyl)propionic acid$^2$ were synthesized according to literature procedures. For the purification of quasi-rotaxane 3, a Waters Prep 100 SFC UV directed system was used; Column: Waters Viridis Prep Silica 2-EP, OBD (100x19 mm, 5 µm), Flow: 70 mL/min, Column temp: 35°C; ABPR: 120 bar; Eluent A: CO$_2$, Eluent B: 20 mM Ammonia in EtOH, Isocratic: 18% B for 10 min, Injection: Sandwich 100 µL methanol, Collection: Based on PDA TIC.
Synthetic procedures

4.18 g 2,7-diiodofluorene\(^1\) (10 mmol) was dissolved in 60 mL dry DMF, under N\(_2\) atmosphere and cooled to 0 °C. After cooling, 880 mg NaH (60% w/w in mineral oil, 22 mmol, 2.2 equiv) was added; the suspension was stirred for 5 minutes and then 3.25 mL tert-butyl bromoacetate (22 mmol, 2.2 equiv) was added dropwise. The reaction was stirred for 1h at 0 °C and overnight at room temperature, and then concentrated in vacuo. The residue was partitioned between 100 mL EtOAc and 50 mL 1M HCl. The water layer was extracted with 2 x 50 mL EtOAc and the combined organic layers were washed with 2 x 50 mL H\(_2\)O, 50 mL brine, dried over MgSO\(_4\) and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (PE:EtOAc 30:1 → 25:1 → 20:1) to give compound 13 (5.44 g, 8.42 mmol, 84%) as a yellow solid. Melting point: 110-115 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)): δ 7.88 (s, 2H), 7.70 (d, 2H), 7.42 (d, 2H), 2.93 (s, 4H), 1.13 (s, 18H); \(^13\)C-NMR (75 MHz, CDCl\(_3\)) δ 168.80, 150.16, 139.26, 136.98, 133.38, 121.61, 92.90, 80.77, 50.69, 44.09, 27.68; IR (cm\(^{-1}\)): 2977, 2925, 1717, 1367, 1142

Compound 14

4.35 g 13 (6.73 mmol) and 1.55 mL propargylalcohol (26.93 mmol, 4 equiv) were dissolved in 60 mL dry THF/NEt\(_3\) 1:1 and the mixture was degassed with three vacuum/N\(_2\) cycles. After degassing, 189 mg Pd(PPh\(_3\))\(_2\)Cl\(_2\) (0.269 mmol, 0.04 equiv) and 102 mg CuI (0.538 mmol, 0.08 equiv) were added. The reaction was stirred overnight at room temperature and concentrated in vacuo. The residue was partitioned between 50 mL EtOAc and 50 mL 1M HCl. The water layer was extracted with 2 x 25 mL EtOAc and the combined organic layers were washed with 25 mL brine, dried over MgSO\(_4\) and concentrated in vacuo. The residue was purified by column chromatography (PE:EtOAc 5:2 → 2:1 → 1:1) to give 14 (2.88 g, 5.73 mmol, 85%) as a beige solid. Melting point: 175-178 °C (dec.); \(^1\)H-NMR (300 MHz, CDCl\(_3\)); δ = 7.64-7.61 (m, 4H), 7.46 (d, 2H), 4.53 (s, 4H), 2.94 (s, 4H), 2.04 (bs, 2H), 1.03 (s, 18H); \(^13\)C-NMR (75 MHz, CDCl\(_3\)) δ = 168.91, 148.79, 140.36, 131.62, 127.47, 121.69, 120.02, 87.88, 86.21, 80.66, 51.77, 50.50, 44.63, 27.55; IR (cm\(^{-1}\)): 3504, 2978, 1697, 1468, 1347, 1151

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Compound 15

2.98 g of 14 (5.92 mmol) was dissolved in 50 mL THF/EtOH 1:1 and 15 mL of a slurry of Raney nickel in H₂O was added. The mixture was degassed by 5 cycles of vacuum/H₂ and the mixture was stirred overnight at 60 °C under H₂ atmosphere. After completion, the mixture was purged with N₂ gas for 15 minutes, and then filtered over Celite. The filtrate was washed with 2 x 10 mL EtOAc and the combined organic layers were concentrated in vacuo. The remaining water layer was partitioned with 20 mL EtOAc and separated. The water layer was extracted with 2 x 10 mL EtOAc and the combined organic layers were washed with 20 mL brine, dried over MgSO₄ and concentrated in vacuo to give 15 (2.91 g, 5.69 mmol, 96%) as a viscous yellow oil and was used without further purification. 

\[
\text{H-NMR (300 MHz, CDCl₃) } \delta 7.55 (d, 2H), 7.35 (s, 2H), 7.16 (d, 2H), 3.66 (t, 4H), 2.93 (s, 4H), 2.78 (t, 4H), 2.16 (bs, 2H), 1.94 (quint, 4H), 1.01 (s, 18H); \text{C-NMR (75 MHz, CDCl₃) } \delta 169.62, 148.52, 140.68, 138.57, 127.89, 124.27, 119.37, 80.21, 61.84, 50.34, 44.97, 34.43, 32.35, 27.51; \text{IR (cm}^{-1}): 3394, 2977, 2932, 1718, 1471, 1367, 1155
\]

Compound 16

2.77 g of 15 (5.43 mmol) and 2.50 mL Et₃N (17.92 mmol, 3.3 equiv) were dissolved in 25 mL dry THF under N₂ atmosphere, cooled to 0 °C and 1.27 mL methanesulfonyl chloride (16.29 mmol, 3 equiv) was added dropwise. The icebath was removed and the reaction was stirred overnight at room temperature, and was subsequently quenched with 5 mL H₂O and stirred for 15 min. The mixture was diluted with 50 mL Et₂O and 50 mL H₂O. The water layer was extracted with 25 mL Et₂O and the combined organic layers were washed with 25 mL 1M HCl, 25 mL brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography (PE/EtOAc 4:2 → 3:2 → 2:2) to give 16 (3.04 g, 4.56 mmol, 84%) as a yellow solid. Melting point: 96-100 °C; 

\[
\text{H-NMR (300 MHz, CDCl₃) } \delta 7.57 (d, 2H), 7.34 (s, 2H), 7.16 (d, 2H), 4.25 (t, 4H), 3.03 (s, 6H), 2.93 (s, 4H), 2.82 (t, 4H), 2.10 (quint, 4H), 0.99 (s, 18H); \text{C-NMR (75 MHz, CDCl₃) } \delta 169.18, 148.77, 139.16, 138.83, 127.95, 124.14, 119.60, 80.01, 69.22, 50.38, 44.86, 37.26, 31.72, 30.98, 27.43; \text{IR (cm}^{-1}): 2974, 2932, 1714, 1353, 1171
\]
Compound 17

3.21 g 16 (4.81 mmol) was dissolved in 30 mL HCO$_2$H and stirred overnight at room temperature. The mixture was concentrated in vacuo and dried thoroughly on a high vacuum pump to give 17 (2.66 g 4.80 mmol, quant) as a thick yellow oil. $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.62 (d, 2H), 7.37 (s, 2H), 7.20 (d, 2H), 4.21 (t, 4H), 3.08 (s, 4H), 3.00 (s, 6H), 2.81 (t, 4H), 2.09 (quint, 4H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 175.94, 148.63, 139.64, 138.01, 128.60, 124.03, 120.24, 69.08, 49.03, 41.46, 37.36, 31.61, 30.67; IR (cm$^{-1}$): 3028, 2940, 1708, 1346, 1170

Compound 18

2.66 g 17 (4.79 mmol) and 1.24 g NaN$_3$ (19.18 mmol, 4 equiv) were dissolved in 20 mL DMF and stirred overnight at 70 °C. The mixture was cooled to room temperature and diluted with 40 mL Et$_2$O and 40 mL 1M HCl. The water layer was extracted with 20 mL Et$_2$O and the combined organic layers were washed with 30 mL brine, dried over MgSO$_4$ and concentrated in vacuo. The product was dried further on a high vacuum pump to give 18 (1.94 g, 4.32 mmol, 90%) as a yellow solid. Melting point: 101-104 °C; $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.62 (d, 2H), 7.39 (s, 2H), 7.20 (d, 2H), 3.27 (t, 4H), 3.10 (s, 4H), 2.77 (t, 4H), 1.92 (quint, 4H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 176.79, 148.82, 140.31, 137.88, 128.56, 124.08, 120.11, 50.57, 48.89, 41.23, 33.02, 30.62; IR (cm$^{-1}$): 2933, 2858, 2095, 1695, 1261, 1196

Compound 19

For the synthesis of bis-OSu ester 19 the protocol of Brunckova et al was used. 3: 1.93 g 18 (4.30 mmol) was dissolved in 40 mL dry CH$_2$Cl$_2$ under N$_2$ atmosphere and cooled to 0 °C, after which 3.47 mL pyridine (43 mmol, 10 equiv) and 2.03 g N-hydroxysuccinimide (17.63 mmol, 4.1 equiv) were added, followed by dropwise addition of 2.39 mL TFAA (17.20 mmol, 4 equiv). The mixture was stirred overnight at room temperature and quenched by addition of 20 mL 1M HCl and stirred for 15 min. The water layer was extracted with 2 x 10 mL CH$_2$Cl$_2$ and the combined organic layers were washed with 20 mL 1M HCl and 2 x 20 mL NaHCO$_3$, dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography (PE/EtOAc 3:2 → 2:3 → 2:4). The product was dried on a high vacuum pump to give 19 (2.47 g, 3.85 mmol, 90%) as a colorless foam. $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.65 (d, 2H), 7.50 (d, 2H), 2.82-2.78 (m, 12H), 1.97 (quint, 4H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ
169.00, 165.92, 147.13, 140.84, 137.72, 129.09, 124.17, 120.11, 50.56, 48.59, 38.30, 32.87, 30.39, 25.60; IR (cm\(^{-1}\)): 2944, 2865, 2094, 1814, 1784, 1734, 1162, 1061

Compound 20

6.01 mL 10-undecyl alcohol (30.0 mmol), 7.87 g PPh\(_3\) (30.0 mmol, 1 equiv) and 4.41 g phthalimide (30.0 mmol, 1 equiv) were dissolved in 150 mL dry THF under N\(_2\) atmosphere and cooled to 0 °C, followed by dropwise addition of 5.91 mL DIAD (30.0 mmol, 1 equiv). The reaction was stirred overnight at room temperature and the mixture was concentrated in vacuo and loaded on silica. The dry-loaded product was purified by column chromatography (PE/EtOAc 30:1 \(\rightarrow\) 25:1) to give a slightly yellow oil, which slowly crystallized to give 20 (7.38 g, 24.6 mmol, 82%) as a waxy solid. Melting point: 39-40 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.82 (m, 2H), 7.71 (m, 2H), 5.81 (m, 1H), 4.95 (dd, 2H), 3.67 (t, 2H), 2.02 (q, 2H), 1.67 (quint, 2H), 1.33-1.27 (m, 12H); \(^1^3\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.52, 139.27, 133.89, 132.26, 123.21, 114.19, 38.14, 33.87, 29.49, 29.45, 29.15, 28.97, 28.67, 26.93; IR (cm\(^{-1}\)): 2916, 2848, 1693, 1398, 1052

Compound 21

7.31 g 20 (24.4 mmol) was dissolved in 100 mL THF/EtOH 1:1 and 2.57 mL methylhydrazine (48.9 mmol, 2 equiv) was added. The mixture was stirred overnight at 70 °C and the mixture was concentrated in vacuo and to the residue was added 100 mL Et\(_2\)O. The precipitate was filtered off and washed with Et\(_2\)O. The combined organic layers were concentrated in vacuo and the crude product was purified by Kugelrohr distillation (0.02 mbar, 90-110 °C) to give 21 (3.66 g, 21.6 mmol, 88%) as a clear colorless oil. \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.78 (m, 1H), 4.93 (dd, 2H), 2.65 (t, 2H), 2.02 (q, 2H), 1.40-1.26 (m, 16H); \(^1^3\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 139.23, 114.14, 42.31, 33.92, 33.85, 29.62, 29.54, 29.49, 29.17, 28.97, 26.93; IR (cm\(^{-1}\)): 3333, 2920, 2852, 1568, 1487
Compound 22

1.02 g 21 (6.00 mmol) and 913 mg 2-hydroxy-4-methoxybenzaldehyde (6.00 mmol, 1 equiv) were dissolved in 30 mL absolute CH₂OH and stirred overnight at room temperature. The mixture was cooled to 0 °C and 454 mg NaBH₄ (12.0 mmol, 2 equiv) was added in one portion. The reaction was stirred for 1 h at 0 °C, 1 h at room temperature and then concentrated in vacuo. The residue was partitioned between 40 mL EtOAc and 20 mL NaHCO₃. The water layer was extracted with 2 x 10 mL EtOAc and the combined organic layers were washed with 20 mL brine, dried over MgSO₄ and concentrated in vacuo to give 22 (1.77 g, 5.78 mmol, 96%) as a faint yellow oil, which was used without further purification. ¹H-NMR (300 MHz, CDCl₃) δ 6.88 (d, 1H), 6.44 (s, 1H), 6.35 (s, 1H), 5.82 (m, 1H), 4.97 (dd, 2H), 3.95 (s, 2H), 3.78 (s, 3H), 2.68 (t, 2H), 2.06 (q, 2H), 1.54 (quint, 2H), 1.39-1.30 (m, 12H); ¹³C-NMR (75 MHz, CDCl₃) δ 160.46, 159.62, 139.34, 128.78, 115.05, 114.25, 104.89, 102.02, 55.34, 52.28, 48.73, 33.92, 29.68, 29.60, 29.53, 29.21, 29.03, 27.25; IR (cm⁻¹): 2923, 2852, 1622, 1590, 1510, 1456, 1157

Compound 5

1.80 g 19 (2.80 mmol), 1.76 g 22 (5.75 mmol, 2.05 equiv) and 0.93 mL Et₃N (6.71 mmol, 2.4 equiv) were dissolved in 17 mL dry CH₂Cl₂ and the mixture was stirred for 3 days at room temperature. The reaction mixture was washed with 10 mL 1M HCl and the water layer was extracted with 10 mL CH₂Cl₂. The combined organic layers were washed with 10 mL NaHCO₃, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography (PE/EtOAc 6:1 → 5:1) to give a colorless oil, which slowly crystallized to give 5 (2.10 g, 2.05 mmol, 73%) as a colorless waxy solid. Melting point: 81-82 °C; ¹H-NMR (300 MHz, CDCl₃) δ 10.15 (s, 2H), 7.60 (d, 2H), 7.28 (s, 2H), 7.13 (d, 2H), 6.96 (d, 2H), 6.54 (s, 2H), 6.38 (d, 2H), 5.83 (m, 2H), 4.99 (dd, 4H), 4.39 (bs, 4H), 3.82 (s, 6H), 3.18 (m, 8H), 2.90 (t, 4H), 2.43 (t, 4H), 2.08 (q, 4H), 1.73 (quint, 4H), 1.46-1.12 (m, 30H); ¹³C-NMR (75 MHz, CDCl₃) δ 173.56, 161.50, 157.82, 150.09, 140.53, 139.22, 137.30, 132.29, 128.11, 124.23, 119.87, 114.95, 114.24, 105.19, 102.66, 55.31, 50.88, 50.67, 47.51, 46.23, 37.80, 33.85, 32.82, 30.53, 29.43, 29.12, 28.95, 27.77, 26.69; IR (cm⁻¹): 2925, 2854, 2094, 1595, 1466, 1158
Compound 23

1.86 mL 4-pentyn-1-ol (20.0 mmol) and 3.33 mL Et₃N (24.0 mmol, 1.2 equiv) were dissolved in 40 mL dry THF and cooled to 0 °C and 1.70 mL methanesulfonyl chloride (22.0 mmol, 1.1 equiv) was added dropwise. The icebath was removed and the reaction was stirred overnight at room temperature and was then quenched with 20 mL H₂O and stirred for 15 min. The mixture was diluted with 40 mL Et₂O and 20 mL 1M HCl and the water layer was extracted with 2 x 20 mL Et₂O. The combined organic layers were washed with 40 mL brine, dried over MgSO₄ and concentrated in vacuo to give 23 (3.11 g, 19.18 mmol, 96%) as a slightly yellow oil, which was used without further purification. ¹H-NMR (300 MHz, CDCl₃) δ 4.37 (t, 2H), 3.05 (s, 3H), 2.38 (dt, 2H), 2.03 (t, 1H), 1.98 (quint, 2H); ¹³C-NMR (75 MHz, CDCl₃) δ 82.21, 69.92, 68.38, 37.37, 27.87, 14.79; IR (cm⁻¹): 3287, 3029, 2940, 1346, 1331, 1168

Compound 24

5.70 g dimethyl-2,5-dioxocyclohexane-1,4-dicarboxylate (25.0 mmol) was suspended in 25 mL AcOH and heated to 80 °C and 3.41 g N-chlorosuccinimide (25.5 mmol, 1.02 equiv) was added portionwise over 30 minutes. The reaction was stirred at 80 °C for 90 minutes and was then cooled to room temperature and diluted with 25 mL H₂O. The solid was filtered and washed with 2 x 25 mL H₂O, 2 x 5 mL CH₃OH and dried on air and vacuum to give 24 (5.43 g, 24.0 mmol, 96%) as a yellow powder. Melting point: 173-175 °C; ¹H-NMR (300 MHz, CDCl₃) δ 10.05 (s, 2H), 7.45 (s, 2H), 3.97 (s, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 169.57, 152.99, 118.40, 117.84, 52.88; IR (cm⁻¹): 3234, 2957, 1672, 1440, 1328, 1193, 1172

Compound 6b

2.93 g 23 (18.0 mmol, 2.4 equiv), 1.70 g 24 (7.52 mmol, 1.0 equiv), 2.49 g K₂CO₃ (18.0 mmol, 2.4 equiv) and 124 mg KI (0.75 mmol, 0.1 equiv) were dissolved in 50 mL dry DMF and stirred overnight at 80 °C. The mixture was cooled to room temperature, concentrated in vacuo and to the residue was added EtOAc and the suspension was filtered. The filter cake was washed with EtOAc and the combined organic layers were washed with 2 x 20 mL H₂O and 20 mL brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography (PE/EtOAc 4:1) to give 6b (2.11 g, 5.89 mmol, 78%) as a slightly yellow solid.

Note: the product is slightly contaminated (see ¹H-NMR spectrum at page 51) with the methyl-pentynol-ester. This has no consequence for the next step
(saponification). Melting point: 89-93 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42 (s, 2H), 4.14 (t, 4H), 3.92 (s, 6H), 2.47 (dt, 4H), 2.06 (quint, 4H), 1.98 (t, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.15, 151.92, 124.59, 117.04, 83.57, 69.04, 68.16, 52.46, 28.33, 15.18; IR (cm\(^{-1}\)): 3299, 2884, 2116, 1725, 1504, 1408, 1201

Compound 25

1.44 g \(6b\) (4.02 mmol) was dissolved in 30 mL THF/CH\(_2\)OH/H\(_2\)O 2:1:1 and 901 mg KOH (15.1 mmol, 4 equiv) was added. The mixture was stirred overnight at room temperature and was acidified with 3 mL 37% HCl and stirred for 15 minutes. The mixture was diluted with 20 mL H\(_2\)O and 20 mL EtOAc. The water layer was extracted with 3 x 20 mL EtOAc and the combined organic layers were washed with 20 mL brine, dried over MgSO\(_4\) and concentrated \textit{in vacuo} to give 24 (1.30 g, 3.94 mmol, 98%) as a faint yellow solid. Melting point: 175-178 °C; Yield: \(^1\)H-NMR (300 MHz, CD\(_2\)OD) \(\delta\) 7.48 (s, 2H), 4.17 (t, 4H), 2.45 (dt, 4H), 2.25 (t, 2H), 2.02 (quint, 4H); \(^{13}\)C-NMR (75 MHz, CD\(_2\)OD) \(\delta\) 168.75, 152.91, 126.30, 117.60, 84.14, 70.04, 69.34, 29.42, 15.72; IR (cm\(^{-1}\)): 3267, 2938, 2875, 1673, 1505, 1217

Compound 6a

1.30 g 25 (3.94 mmol), 2.17 g pentafluorophenol (11.8 mmol, 3 equiv), 4.11 mL DIPEA (23.6 mmol, 6 equiv) and 4.48 g HBTU (11.8 mmol, 3 equiv) were dissolved in 80 mL dry THF and stirred overnight at room temperature. The mixture was concentrated \textit{in vacuo} and dry-loaded on silica and purified by column chromatography (PE/EtOAc 10:1 \(\rightarrow\) 8:1 \(\rightarrow\) 6:1) to give 6a (2.07 g, 3.13 mmol, 79%) as an off-white solid. Melting point: 113-115 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.67 (s, 2H), 4.26 (t, 4H), 2.46 (dt, 4H), 2.08 (quint, 4H), 1.98 (t, 2H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 160.92, 152.90, 143.20, 139.84, 138.34, 136.50, 122.35, 117.31, 83.21, 69.24, 68.17, 28.13, 15.08; IR (cm\(^{-1}\)): 3316, 2943, 1755, 1519, 1416, 1390, 1230, 1201
Compound 7

1.94 g 5 (1.89 mmol), 1.38 g 6a (2.08 mmol, 1.1 equiv), 2.45 g Cs$_2$CO$_3$ (7.58 mmol, 4 equiv) and 1.00 g 4 Å MS were dissolved in 750 mL dry CH$_3$CN and the mixture was stirred overnight at 60 °C under N$_2$ atmosphere. The solvent was evaporated and the residue was taken in ca. 20 mL CH$_2$Cl$_2$ and filtered through a plug of Celite, which was washed with CH$_2$Cl$_2$. The organic layer was concentrated in vacuo and dry-loaded on silica and purified by column chromatography (PE:EtOAc 4:1 → 3:1) to give 7 (1.72 g, 1.31 mmol, 69%) as a thick colorless oil. Due to the complexity of the $^1$H-NMR spectrum, please consult supplementary figure 37; IR (cm$^{-1}$): 2924, 2853, 2093, 1740, 1637, 1618, 1504, 1410, 1183, 1108; HRMS (FD) calcd for C$_{79}$H$_{96}$N$_8$O$_{10}$[M$^+$]: 1316.7249, found: 1316.7239

![Chemical structure of Compound 7](image)

Compound 8

For the CuAAC reaction the ligand TBTA was used, as first described by Sharpless et al.$^4$: 420 mg 7 (0.319 mmol) and 42 mg TBTA (0.080 mmol, 0.25 equiv) were dissolved in 65 mL dry CH$_2$Cl$_2$ and degassed with five vacuum/N$_2$ cycles, after which 25 mg Cu(CH$_3$CN)$_4$BF$_4$ (0.080 mmol, 0.25 equiv) was added and the mixture was stirred overnight at reflux under N$_2$ atmosphere. The reaction mixture was concentrated in vacuo and dry-loaded on silica and purified by column chromatography (PE:EtOAc 1:1 → 1:2 → 0:1) to give 8 (333 mg, 0.253 mmol, 79%) as an a colorless foam. Melting point: 113-119 °C; Due to the complexity of the $^1$H-NMR spectrum, please consult supplementary figure 38; IR (cm$^{-1}$): 2925, 2853, 1746, 1640, 1617, 1504, 1411, 1187, 1100; HRMS (FD) calcd for C$_{79}$H$_{96}$N$_8$O$_{10}$[M$^+$]: 1316.7249, found: 1316.7243
Compound 9

79 mg 8 (0.060 mmol) was dissolved in 60 mL dry CH₂Cl₂ and degassed with five vacuum / N₂ cycles. To the solution was added 10 mg Grubbs II catalyst (0.012 mmol, 0.2 equiv) and the mixture was stirred overnight at 40 °C. The mixture was concentrated in vacuo, dry-loaded on silica and purified by column chromatography (PE:EtOAc 1:2 → 1:3 → 1:4) to give 9 (55 mg, 0.043 mmol, 71%) as a beige solid. Due to the complexity of the ¹H-NMR spectrum, please consult supplementary figure 39; IR (cm⁻¹): 2924, 2853, 1749, 1618, 1505, 1411, 1187, 1111; HRMS (FD) calcd for C₇₇H₉₂N₈O₁₀ [M⁺]: 1288.6936, found: 1288.6911

Compound 26

55 mg 9 (0.043 mmol) was dissolved in 2 mL dry THF/CH₃OH 1:1 and 12 mg anhydrous NaOCH₃ (0.21 mmol, 5 equiv) was added and the mixture was stirred at room temperature for 1h. The reaction was quenched by addition of 0.5 mL AcOH and the reaction was diluted with 15 mL EtOAc and 10 mL saturated NaHCO₃. The water layer was extracted with 2 x 5 mL EtOAc and the combined organic layers were dried over MgSO₄ and concentrated in vacuo to give 26 (58 mg, 0.043 mmol, quant) as a slight yellow film. Due to the complexity of the ¹H-NMR spectrum, please consult supplementary figure 40; IR (cm⁻¹): 2923, 2853, 1726, 1619, 1599, 1436, 1203; HRMS (FD) calcd for C₇₉H₁₀₀N₄O₁₂ [(M+H)⁺]: 1353.7539, found: 1353.7597
Compound 2

58 mg 26 (0.043 mmol) was dissolved in 5 mL TFA/CH₂Cl₂ 9:1 and 0.136 mL Et₃SiH (0.854 mmol, 20 equiv) was added. The mixture was stirred overnight at room temperature and concentrated in vacuo. The residue was dissolved in 10 mL CH₂Cl₂ and 0.5 mL NEt₃ was added and stirred for 5 minutes. The organic layer was washed with 10 mL 1M HCl, 10 mL NaHCO₃, dried over MgSO₄ and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (CH₂Cl₂/CH₃OH 96:4 → 94:6) to give 2 (43 mg, 0.0397 mmol, 93%) as a colorless foam. ¹H-NMR (300 MHz, CDCl₃) δ 7.98 (s, 2H), 7.57 (d, 2H), 7.35 (s, 2H), 7.21 (d, 2H), 6.95 (s, 2H), 4.49 (t, 2H), 4.07 (m, 8H), 3.85 (s, 6H), 3.05 (t, 4H), 2.67 (t, 4H), 2.52 (q, 4H), 2.44 (s, 4H), 2.41 (m, 4H), 2.21 (quint, 4H), 1.43 (quint, 4H), 1.35 (quint, 4H), 1.22 (sext, 4H), 1.05 (quint, 4H), 0.92 (sext, 4H), 0.66-0.42 (m, 8H); ¹³C-NMR (75 MHz, CDCl₃) δ 167.66, 166.18, 151.40, 146.77, 146.07, 139.61, 139.17, 130.52, 128.52, 124.59, 124.38, 123.55, 120.51, 115.81, 66.89, 52.34, 50.87, 47.12, 38.70, 32.58, 31.57, 30.41, 29.65, 29.55, 29.36, 29.23, 29.10, 28.97, 28.52, 26.28, 20.96; IR (cm⁻¹): 3325, 2925, 2853, 1726, 1659, 1436, 1205; HRMS (FD) calcd for C₆₃H₆₄N₈O₈ [M⁺]: 1080.6412, found: 1080.6432

Compound 2-H₂

40 mg 2 (0.037 mmol) was dissolved in 3 mL THF/EtOH 1:1 and 20 mg Pd/C (10 % w/w) was added. Through the solution was bubbled H₂ gas (balloon) for 5 minutes and the reaction was stirred overnight under H₂ atmosphere at 50 °C. The mixture was filtered through a plug of Celite and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (CH₂Cl₂/CH₃OH 96:4 → 94:6) to give 2-H₂ (31 mg, 0.029 mmol, 77%) as a colorless solid.
A crystal was grown in the following way: The purified product was dissolved in ca. 0.5 mL EtOAc and transferred to a test tube, which was put in a closed container filled with pentane, allowing for diffusion of the solvents. After standing overnight, small crystals had formed on the walls of the test tube, which were suitable for the X-ray analysis.

Melting point: 164-166 °C; \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.98 (s, 2H), 7.59 (d, 2H), 7.36 (s, 2H), 7.23 (d, 2H), 6.96 (s, 2H), 4.50 (t, 2H), 4.09 (m, 8H), 3.86 (s, 6H), 3.06 (t, 4H), 2.68 (t, 4H), 2.53 (q, 4H), 2.44-2.38 (m, 8H), 2.22 (quint, 4H), 1.44-1.34 (m, 16H), 1.22 (quint, 4H), 1.08 (quint, 4H), 0.95 (quint, 4H), 0.67-0.48 (m, 8H); \(^1^3\)C-NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.69, 166.32, 151.50, 146.91, 146.20, 139.77, 139.30, 128.60, 124.71, 124.48, 123.67, 120.56, 115.90, 67.00, 52.47, 51.03, 47.26, 47.14, 38.78, 31.69, 30.53, 29.46, 29.44, 29.31, 29.16, 29.04, 28.93, 28.81, 28.60, 26.31, 21.06; IR (cm\(^{-1}\)): 3413, 2925, 2853, 1727, 1660, 1436, 1207; HRMS (FD) calcd for C\(_{63}\)H\(_{86}\)N\(_8\)O\(_8\)[M\(^+\)]: 1082.6569, found: 1082.6533

### Compound 10

**Method 1:** 129 mg 8 (0.0980 mmol) was dissolved in 4 mL dry THF/CH\(_3\)OH 1:1 and 105 mg NaOCH\(_3\) (1.96 mmol, 20 equiv) was added. The reaction was stirred for at room temperature for 2h and was quenched with 0.2 mL AcOH. The mixture was diluted with 15 mL EtOAc and 10 mL H\(_2\)O. The water layer was extracted with 2 x 5 mL EtOAc and the combined organic layers were washed with 10 mL saturated NaCl, dried over MgSO\(_4\) and concentrated in vacuo to give 10 (138 mg, 0.0980 mmol, quant) as a colorless film.

**Method 2:** 112 mg 5 (0.110 mmol, 1.1 equiv), 36 mg 6b (0.10 mmol) and 11 mg TBTA (0.020 mmol, 0.2 equiv) were dissolved in 100 mL dry CH\(_2\)Cl\(_2\) and the mixture was degassed with five vacuum/N\(_2\) cycles. After degassing, 6 mg Cu(CH\(_3\)CN\(_2\))BF\(_4\) (0.02 mmol, 0.2 equiv) was added and the mixture was stirred overnight at reflux under N\(_2\) atmosphere. The reaction was concentrated in vacuo and dry-loaded on silica and purified by column chromatography (PE:EtOAc 1:2 \(\rightarrow\) 1:3) to give 10 (58 mg, 0.042 mmol, 42%) as a colorless film. Due to the complexity of the \(^1\)H-NMR spectrum, please consult supplementary figure 49; IR (cm\(^{-1}\)): 2926, 2854, 1726, 1600, 1505, 1437, 1202; HRMS (FD) calcd for C\(_{81}\)H\(_{104}\)N\(_8\)O\(_{12}\)[(M+H)\(^+\)]: 1381.8, found: 1381.5
Compound 27

151 mg 10 (0.109 mmol) was dissolved in 110 mL dry CH₂Cl₂ and was degassed with five vacuum/N₂ cycles. After degassing, 18 mg Grubbs II catalyst (0.021 mmol, 0.2 equiv) was added and the mixture was stirred overnight at 35 °C. The mixture concentrated in vacuo and the crude product was dry-loaded on silica and purified by column chromatography (PE/EtOAc 1:3 → 1:5 → 1:7 → 0:1) to give 27 (62 mg, 0.046 mmol, 42%) as a slightly brown film. Due to the complexity of the ¹H-NMR spectrum, please consult supplementary figure 50; IR (cm⁻¹): 2923, 2852, 1728, 1599, 1435, 1201; HRMS (FD) calcd for C₇₉H₁₀₁N₈O₁₂ [(M+H)⁺]: 1353.7539; found: 1353.7556

Compound 1

62 mg 27 (0.046 mmol) was dissolved in 1 mL dry CH₃OH and added dropwise to a 5 mL 3M HCl in CH₃OH solution (made via addition of acetyl chloride to CH₃OH at 0 °C). The reaction was stirred overnight at 50 °C and was concentrated in vacuo. The residue was partitioned between 20 mL CH₂Cl₂ and 15 mL NaHCO₃. The water layer was extracted with 2 x 5 mL CH₂Cl₂ and the combined organic layers were dried over MgSO₄ and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (EtOAc/CH₃OH 97:3 → 96:4) to give 1 (32 mg, 0.030 mmol, 65%) as a colorless film. ¹H-NMR (300 MHz, CDCl₃) δ 7.84 (t, 2H), 7.39 (d, 2H), 7.22 (s, 2H), 7.15 (s, 2H), 6.96 (s, 2H), 6.78 (d, 2H), 5.37 (s, 2H), 4.35 (t, 4H), 3.93 (s, 6H), 3.71 (t, 4H), 3.40 (q, 4H), 2.69 (t, 4H), 2.57 (t, 4H), 2.53 (s, 4H), 2.20 (quint, 4H), 2.07-1.94 (m, 8H), 1.91-1.81 (m, 8H), 1.63 (quint, 4H), 1.48-1.25 (m, 32H); ¹³C-NMR (75 MHz, CDCl₃) δ 171.26, 166.07, 151.62, 149.46, 139.17, 136.91, 130.75, 127.91, 124.40, 124.13, 119.54, 116.26, 68.19, 52.45, 50.25, 50.10, 42.84, 39.77, 33.84, 32.29, 31.19, 29.65, 29.53, 29.43, 29.04, 28.35, 27.94, 27.27, 27.09, 26.93, 26.41, 26.24, 21.50; IR (cm⁻¹): 3256, 2925, 2853, 1727, 1637, 1436, 1206; HRMS (FD) calcd for C₆₃H₅₄N₄O₈ [M⁺]: 1080.6412; found: 1080.6391
Compound 1-H₂

19 mg 1 (0.018 mmol) was dissolved in 2 mL THF/EtOH 1:1 and 8 mg Pd/C (10% w/w) was added. H₂ gas (balloon) was bubbled through the solution for 5 minutes, and the reaction was stirred overnight at 50 °C under H₂ atmosphere. The solution was filtered through a plug of Celite (washed with EtOH) and the combined organic layers were concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (EtOAc/CH₂OH 96:4) to give 1-H₂ (13 mg, 0.012 mmol, 68%) as a colorless film. ¹H-NMR (300 MHz, CDCl₃) δ 7.79 (t, 2H), 7.39 (d, 2H), 7.22 (s, 2H), 7.15 (s, 2H), 6.96 (s, 2H), 6.77 (d, 2H), 4.35 (t, 4H), 3.70 (s, 6H), 3.39 (q, 4H), 2.68 (t, 4H), 2.57 (t, 4H), 2.53 (s, 4H), 2.26 (quint, 4H), 2.03-1.60 (m, 16H), 1.45-1.27 (m, 52H); ¹³C-NMR (125 MHz, CDCl₃) δ 171.27, 166.09, 151.64, 149.46, 146.25, 139.21, 136.94, 127.95, 124.41, 124.15, 122.46, 119.57, 116.28, 68.21, 52.49, 50.32, 50.11, 42.94, 39.91, 35.64, 35.16, 33.87, 32.07, 31.23, 29.84, 29.59, 29.21, 29.12, 29.08, 28.83, 28.58, 28.53, 28.29, 27.99, 27.10, 27.00, 26.45, 26.42, 26.26, 22.83, 21.52; IR (cm⁻¹): 3262, 2924, 2853, 1728, 1637, 1410, 1206; HRMS (FD) calcld for C₆₃H₈₆N₈O₈ [M⁺]: 1082.6569; found: 1082.6559

Compound 28

6.20 g 3,3,3-tris(4-tertbutylphenyl)propionic acid² (13.2 mmol) was dissolved in 100 mL dry THF under N₂ atmosphere and cooled to 0 °C. After cooling, 3.12 mL BH₃•SMe₂ (32.9 mmol, 2.5 equiv) was added dropwise and the icebath was removed. The reaction was stirred overnight at room temperature and was quenched carefully with 10 mL H₂O and stirred for 15 minutes. The mixture was concentrated in vacuo and the residue was partitioned between 150 mL Et₂O and 75 mL H₂O. The water layer was extracted with 30 mL Et₂O and the combined organic layers were washed with 75 mL brine and dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (CH₂Cl₂) to give 28 (5.07 g, 11.1 mmol, 84%) as a colorless foam. Melting point: 98 – 110 °C; ¹H-NMR (400 MHz, CDCl₃) δ 7.31 (d, 6H), 7.24 (d, 6H), 3.54 (t, 2H), 2.93 (t, 2H), 1.35 (s, 27H); ¹³C-NMR (100 MHz, CDCl₃) δ 148.55, 144.32, 128.65, 124.80, 60.84, 54.08, 43.13, 34.41, 31.51; IR (cm⁻¹): 3340, 2957, 2866, 1508, 1362, 1269

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Compound 29

2.73 g 28 (5.98 mmol), 1.32 g phthalimide (8.97 mmol, 1.5 equiv) and 1.80 g PPh₃ (6.88 mmol, 1.15 equiv) were dissolved in 60 mL dry THF under N₂ atmosphere and cooled to 0 °C. After cooling, 1.30 mL DIAD (6.58 mmol, 1.1 equiv) was added dropwise and the mixture was stirred at 0 °C for 2 h and overnight at room temperature. The mixture was concentrated in vacuo, dry-loaded on silica and purified by column chromatography (PE/EtOAc 8:1) to give 29 (3.24 g, 5.53 mmol, 92%) as a white powder. Melting-point: 256 – 264 °C; ¹H-NMR (400 MHz, CDCl₃) δ 7.84 (m, 2H), 7.72 (m, 2H), 7.33 (d, 6H), 7.28 (d, 6H), 3.47 (t, 2H), 2.93 (t, 2H), 1.32 (s, 27H); ¹³C-NMR (100 MHz, CDCl₃) δ 168.38, 148.60, 143.85, 133.94, 132.35, 128.78, 124.83, 123.15, 54.18, 38.88, 36.24, 34.40, 31.48; IR (cm⁻¹): 2961, 2902, 2866, 1711, 1397, 1360

Compound 30

2.32 g 29 (3.97 mmol) was dissolved in a mixture of 40 mL CH₂Cl₂/EtOH 1:1 and 1.93 mL hydrazine hydrate (39.7 mmol, 10 equiv) was added and the reaction was stirred at 50 °C for 3h. The mixture was cooled to room temperature and filtered (cake washed with 10 mL CH₂Cl₂) and the filtrate was concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (CH₂Cl₂/CH₃OH 94:6 → 90:10) to give 30 (1.58 g, 3.46 mmol, 87%) as a colorless solid. Melting-point: 151 - 158 °C; ¹H-NMR (300 MHz, CDCl₃) δ 7.28 (d, 6H), 7.19 (d, 6H), 2.78 (t, 2H), 2.55 (t, 2H), 1.31 (s, 27H); ¹³C-NMR (75 MHz, CDCl₃) δ 148.37, 144.53, 128.72, 124.66, 54.56, 44.48, 39.33, 34.38, 31.49; IR (cm⁻¹): 2958, 2901, 2866, 1507, 1362, 1269
Compound 11

455 mg 30 (1.00 mmol) and 0.166 mL NEt$_3$ (1.20 mmol, 1.2 equiv) were dissolved in 10 mL dry CH$_2$Cl$_2$ and cooled to 0 °C. After cooling, 0.097 mL acryloyl chloride (1.1 mmol, 1.1 equiv) was added dropwise and the mixture was stirred for 1h at 0 °C and overnight at room temperature. The organic layer was washed with 10 mL 1M HCl and the water layer was extracted with 5 mL CH$_2$Cl$_2$. The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography (CH$_2$Cl$_2$) to give 11 (400 mg, 0.790 mmol, 79%) as a colorless powder. Melting point: 254-256 °C; $^1$H-NMR (300 MHz, CDCl$_3$) δ 7.29 (d, 6H), 7.25 (d, 6H), 6.17 (d, 1H), 5.85 (dd, 1H), 5.53 (d, 1H), 5.22 (t, 1H), 3.20 (q, 2H), 2.82 (t, 2H), 1.32 (s, 27H); $^{13}$C-NMR (75 MHz, CDCl$_3$) δ 165.47, 148.64, 144.06, 130.98, 128.77, 125.98, 124.89, 54.65, 40.00, 37.31, 34.42, 31.49; IR (cm$^{-1}$): 3279, 2953, 2902, 2866, 1656, 1555

Compound 12

66 mg 8 (0.050 mmol) and 102 mg 11 (0.200 mmol, 4 equiv) were dissolved in 10 mL dry CH$_2$Cl$_2$ and the mixture was degassed with 5 vacuum/N$_2$ cycles. After degassing, 9 mg Grubbs II catalyst (0.01 mmol, 0.2 equiv) was added and the mixture was stirred overnight at 40 °C. The solution was concentrated in vacuo and dry-loaded on silica and purified by column chromatography (PE/EtOAc 1:1 → 1:2) to give 12 (65 mg, 0.029 mmol, 57%) as a faint yellow solid film. Melting point: 153-160 °C; Due to the complexity of the $^1$H-NMR spectrum, please consult supplementary figure 65; IR (cm$^{-1}$): 3293, 2961, 2928, 2858, 1746, 1668, 1618, 1506, 1201; HRMS (FD) calcd for C$_{147}$H$_{185}$N$_{10}$O$_{12}$ [(M+H)$^+$]: 2280.4017, found 2280.4065
Compound 31

65 mg 12 (0.029 mmol) was dissolved in 2 mL THF/CH$_3$OH 3:1 and 16 mg NaOCH$_3$ (0.29 mmol, 10 equiv) was added and the reaction was stirred at room temperature for 2h and was subsequently quenched with 0.1 mL AcOH. The reaction was diluted with 20 mL CH$_2$Cl$_2$ and 10 mL NaHCO$_3$. The water layer was extracted with 2 x 5 mL CH$_2$Cl$_2$ and the combined organic layers were dried over MgSO$_4$ and concentrated in vacuo to give 31 (66 mg, 0.028 mmol, 98%) as a faint yellow glassy solid. Melting point: 133-140 °C; Due to the complexity of the $^1$H-NMR spectrum, please consult supplementary figure 66; IR (cm$^{-1}$): 2960, 2928, 2857, 1726, 1669, 1601, 1507, 1203; HRMS (FD) calcd for C$_{149}$H$_{191}$N$_{10}$O$_{14}$ [(M+H)$^+$]: 2344.4541, found: 2344.4529

Compound 3

66 mg 31 (0.028 mmol) was dissolved in 1 mL THF and added dropwise to 4 mL 3M HCl in CH$_3$OH (made via addition of acetyl chloride to CH$_3$OH at 0 °C). The reaction was stirred overnight at 50 °C and was subsequently concentrated in vacuo. The residue was partitioned between 20 mL CH$_2$Cl$_2$ and 15 mL NaHCO$_3$ and the water layer was extracted with 2 x 5 mL CH$_2$Cl$_2$. The combined organic layers were dried over MgSO$_4$ and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (EtOAc/CH$_3$OH 99:1 → 98:2 → 97:3) to give 3 (16 mg, 0.0077 mmol, 27%, together with 34 mg mixed fractions (< 0.016 mmol, < 58%)) as a faint yellow solid.

Note: two products are formed, which do separate on TLC, but badly on column resulting in only a limited amount of pure fractions of the desired product. To obtain analytically pure material, the mixed fractions of above were subjected to supercritical preparative HPLC using liquid CO$_2$ as an eluent (see general methods for details) to give a white powder. Melting point: 106-111°C (stays thick and oily); $^1$H-NMR (400 MHz, CDCl$_3$) δ 7.92 (s, 2H), 7.61 (d, 2H), 7.37 (s, 2H), 7.30-7.21 (m, 26H), 6.94 (s, 2H), 6.78 (dt, 2H), 5.53 (d, 2H), 5.18 (t, 2H), 4.68 (t, 2H), 4.08 (m, 8H), 3.89 (s, 6H), 3.18 (q, 4H), 3.05 (t, 4H), 2.81 (t, 4H), 2.56 (q, 4H), 2.44 (m, 8H), 2.24 (quint, 4H), 2.12 (q, 4H), 1.46-1.18 (m, 68H), 1.09 (quint, 4H), 0.98 (quint, 4H), 0.70 (bs, 8H); $^{13}$C-NMR (125 MHz, CDCl$_3$) δ 168.04, 166.42, 166.06, 151.44, 148.58, 147.38, 146.16, 144.38, 144.12, 139.47, 139.19, 128.80, 128.41, 124.86, 124.58, 124.51, 123.72, 123.68, 120.64, 115.84, 67.04, 54.64, 52.55, 50.86, 47.35, 46.56, 40.11, 38.89, 37.28, 34.44, 32.05, 31.66, 31.51, 30.51, 29.50, 29.43, 29.31, 29.24, 28.60, 28.41, 26.56, 21.13; IR (cm$^{-1}$): 3294, 2957, 2926, 2856, 1726, 1665, 1630, 1507, 1206; HRMS (FD) calcd for C$_{133}$H$_{175}$N$_{10}$O$_{10}$ [(M+H)$^+$]: 2072.3493, found 2072.3424
Compound 32

58 mg 10 (0.042 mmol) and 51 mg 11 (0.10 mmol, 2.4 equiv) were dissolved in 4 mL dry CH₂Cl₂ and the mixture was degassed with five vacuum/N₂ cycles. After degassing, 7 mg Grubbs II catalyst (0.008 mmol, 0.2 equiv) was added and the mixture was stirred overnight at 35 °C. The solution was concentrated in vacuo and dry-loaded on silica and purified by column chromatography (PE/EtOAc 1:2 → 1:3) to give 32 (41 mg, 0.018 mmol, 42%) as a faint yellow solid film. Melting trajectory: 140-156 °C (stays thick and oily); Due to the complexity of the ¹H-NMR spectrum, please consult supplementary figure 69; IR (cm⁻¹): 2959, 2928, 2856, 1729, 1670, 1601, 1506; HRMS (FD) calcd for C₁₄₉H₁₉N₁₀O₁₄ [(M+H)⁺]: 2344.4541, found: 2344.4423

Compound 4

41 mg 32 (0.018 mmol) was dissolved in 1 mL THF and added dropwise to 3 mL 3M HCl in CH₃OH (made via addition of acetyl chloride to CH₃OH at 0 °C). The reaction was stirred overnight at 50 °C and was subsequently concentrated in vacuo. The residue was partitioned between 20 mL CH₂Cl₂ and 15 mL NaHCO₃ and the water layer was extracted with 2 x 5 mL CH₂Cl₂. The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The crude product was dry-loaded on silica and purified by column chromatography (PE/EtOAc/CH₃OH 1:2:0 → 1:4:0 → 1:6:0 → 0:1:0 → 0:97:3) to give 4 (24 mg, 0.012 mmol, 66%) as a faint yellow solid film. Melting trajectory: 130-138 °C (stays thick and oily); ¹H-NMR (300 MHz, CDCl₃) δ 7.71 (t, 2H), 7.37 (d, 2H), 7.29-7.22 (m, 26H), 7.15 (s, 2H), 6.97 (s, 2H), 6.80-6.73 (m, 4H), 5.51 (d, 2H), 5.17 (t, 2H), 4.33 (t, 4H), 3.91 (s, 6H), 3.70+3.60 (dt, 6H), 3.69 (q, 4H), 3.36 (q, 4H), 2.78 (t, 4H), 2.68 (t, 4H), 2.60-2.53 (m, 8H), 2.19 (quint, 4H), 2.12 (q, 4H), 1.95 (quint, 4H), 1.80-1.59 (m, 10H), 1.43-1.21 (m, 90H); ¹³C-NMR (75 MHz, CDCl₃) δ 171.20, 166.08, 151.60, 149.39, 148.55, 146.26, 144.42, 144.11, 139.18, 136.95, 127.95, 124.84, 124.39, 124.12, 123.63, 122.46, 119.63, 116.23, 68.12, 54.62, 52.47, 50.33, 50.03, 43.02, 40.07, 39.92, 37.24, 34.42, 33.77, 32.03, 31.49, 31.15, 29.83, 29.72, 29.54, 29.43, 29.19, 28.37, 28.00, 27.22, 21.49; IR (cm⁻¹): 3291, 2961, 2928, 2856, 1726, 1667, 1632, 1507, 1206; HRMS (FD) calcd C₁₃₃H₁₇₃N₁₀O₁₀ [(M+H)⁺]: 2072.3493, found: 2072.3566
Supplementary References


