Supporting Information
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Supporting Information

Total Synthesis of Cordyheptapeptide A

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General remarks

All commercially available reagents were used without further purification. Dichloromethane (DCM) was dried before use following conventional procedures. HPLC grade methanol was used in all Ugi reactions. Analytical thin layer chromatography (TLC) was performed using silica gel 60 F254 aluminum sheets and the visualization of the spots has been done under UV light (254 nm) or by developing with a solution of ninhydrin 0.2% in n–butanol and 1% acetic acid and heating. Flash column chromatography was performed using silica gel (0.040–0.063 mm). $^1$H and $^{13}$C-NMR spectra were recorded in solutions on a NMR spectrometer at 22°C at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to TMS ($^1$H NMR) and to the solvent signal ($^{13}$C-NMR spectra). HRMS (ESI+) spectra were obtained from
a Fourier transform ion cyclotron resonance (FT–ICR) mass spectrometer equipped with an Infinity™ cell, a 7.0 Tesla superconducting magnet, an RF–only hexapole ion guide and an external electrospray ion source (off axis spray). Convertible isocyanide 4-isocyanopermethylbutane-1,1,3-triol (IPB) was prepared as previously reported.¹

**General Boc removal procedure:** The peptide is dissolved in a trifluoroacetic acid (20% v/v) solution in dichloromethane, and the mixture is stirred at room temperature for 5 h. As the material dissolved, gas evolution could be detected and the pressure that built up inside the reaction flask is regularly relieved by opening the reaction flask. The end of the reaction is confirmed by ESI-MS analysis. The solvent is removed under reduced pressure in a rotavap. To the crude material is added toluene (20 mL) and the contents are concentrated under reduced pressure in a rotavap to dryness. This operation is repeated two times in order to remove remaining amounts of TFA. The resulting salt is used forward without further purification and assuming quantitative yield.

**General methyl ester removal procedure:** The peptide (1.0 equiv) is dissolved in THF/H₂O (2:1, 8 mL) and LiOH (2.5 equiv) is added at 0 °C. The mixture is stirred at 0 °C for 5 h and then acidified with aqueous 10% NaHSO₄ to pH 3.00. The resulting phases are separated and the aqueous phase is additionally extracted with EtOAc (2 × 50 mL). The combined organic phases are dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to yield the C-deprotected peptide.

**General N-alquilation procedure:** To a stirred solution of the aminoacid (1.0 equiv) and methyl iodide (7.0 equiv) in anhydrous THF (150 mL) at 0 °C is added sodium hydride (60% dispersion in mineral oil; 7.0 equiv) in equal portions each ten minutes. The mixture was stirred at room temperature for 24 h under N₂ atmosphere. The reaction was cooled

to 0 °C and carefully quenched by adding water (20 mL). The THF was evaporated under reduced pressure. To the remaining content were added water (100 mL) and ethyl acetate (200 mL). The organic layer was washed with water (1 × 50 mL) Na₂S₂O₅ aqueous solution (30% w/w, 1 × 50 mL), brine (1 × 50 mL) and was dried over Na₂SO₄. The solvent is evaporated under reduced pressure and the remaining crude residue is purified by column chromatography.

**General esterification procedure:** To a suspension of N-terminus protected aminoacid (1.0 equiv) and potassium carbonate (2.0 equiv) in DMF (30 mL) is added iodomethane (1.5 equiv), and the mixture is stirred at room temperature for 30 h. The mixture is filtered, and the filter cake was washed with ethyl acetate (50 mL), dissolved in water (100 mL), and extracted with ethyl acetate (100 mL x 2). All the ethyl acetate solutions were combined with the filtrate, and the solution was evaporated under vacuum until most of the DMF has been removed. The residue was re-dissolved in ether (250 mL), washed with water (100 mL) and brine (50 mL), dried (Na₂SO₄), and evaporated to afford desired product as a yellow oil. The resulting product is used forward without further purification.

**TFA-H-Ile-Leu-NMe-d-Phe-OMe (1):** Peptide 8 (3.44 g, 7.0 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 1 (3.76 g, quant) was used in the next step without further purification.

**TFA-H-Pro-Sar-OMe (2):** To a solution of compound 14 (4.31 g, 10.0 mmol) in toluene (200 mL) were added 10-camphorsulfonic acid (0.23 g, 1.0 mmol) and quinoline (0.2 g, 1.0 mmol). The contents were stirred for 1 min at room temperature and were then refluxed for 30 min. The contents were cooled, transferred to a separatory funnel and washed with 1M aqueous HCl (2 × 80 mL). The acidic aqueous phase was further extracted with ethyl acetate (1 × 80 mL). The organic layers were combined, washed with brine (2 × 80 mL), dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure.
pressure in a rotavap. The obtained material (2.18 g, 6.5 mmol) was dissolved in anhydrous methanol (50 mL) before sodium methoxide (0.43 g, 8.0 mmol) was added. The mixture was stirred for 16 h, quenched with acetic acid (10 mL) and evaporated. The contents were dissolved in ethyl acetate (100 mL) washed with saturated aqueous NaHCO₃ (2 × 40 mL), brine (2 × 40 mL) and dried over Na₂SO₄. The obtained material (1.87 g, overall yield 58%) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The white solid product 2 (1.94 g, quant) was used in the next step without further purification.

**Cbz-Phe-NMe-Tyr(Bzl)-OH (3):** Peptide 11 (2.7 g, 4.65 mmol) was subjected to the general saponification procedure of the C-terminus methylester. The colorless oil product 3 (2.58 g, 98%) was used in the next step without further purification. Rₛ 0.53 (ethyl acetate/methanol/acetic acid 94:4:2). [α]²⁶⁻⁻50.63 (c 1.0, MeOH). ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.17 (m, 15H), 6.96 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 5.66 (d, J = 9.1 Hz, 1H), 5.12 – 4.77 (m, 5H), 3.27 (m, 1H), 3.06 – 2.86 (m, 3H), 2.96 and 2.74 (2s, 3H), O-H signal not observed. ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 172.5, 157.6, 155.6, 136.9, 136.3, 135.9, 130.2, 129.8, 129.5, 129.0, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.4, 127.2, 126.9, 115.4, 114.9, 69.9, 66.8, 59.9, 53.4, 52.2, 38.9, 33.5. HRMS (ESI+) m/z calcd for C₃₄H₃₄N₂NaO₆, [M+Na]⁺; 589.2315 found, 589.2309.

**Boc-NMe-D-Phe-OMe (4):** The N-terminus protected aminoacid Boc-D-Phe-OH (3.7 g, 14.0 mmol) was subjected to the general alquilation procedure of the N-amide group. The obtained material (3.63 g, 13.0 mmol) was subjected to the general esterification procedure of the free C-terminus. The pale yellow oil product 4 (3.8 g, 99%) was used in the next step without further purification. ¹H NMR (400 MHz, CDCl₃) 7.27 – 7.16 (m, 5H), 5.28 (s, 1H), 3.74 (s, 3H), 3.39 (m, 1H), 3.01 (m, 1H), 2.72 (s, 3H), 1.37 and 1.33
(2s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.7, 171.2, 155.6, 154.7 137.5, 137.2, 128.9, 128.8, 128.4, 128.2, 126.5, 126.3, 80.1, 79.8, 61.5, 59.4, 52.2, 35.4, 34.9, 32.4, 31.8, 28.1.

**TFA-H-NMe-d-Phe-OMe (5):** Peptide 4 (3.8 g, 12.9 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 5 (3.9 g, quant) was used in the next step without further purification.

**Boc-Leu-NMe-d-Phe-OMe (6):** To a solution of Boc-Leu-OH (2.93 g, 12.7 mmol) in DMF (25 mL) at 0 °C were added 5 (3.9 g, 12.7 mmol), HBTU (4.81 g, 12.7 mmol) and DIPEA (4.92 g, 6.6 mL, 38.1 mmol). The reaction mixture was warmed up to room temperature and stirred for further 24 h. The mixture was poured in water (200 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO$_3$ (2 × 50 mL), brine (2 × 50 mL), dried over Na$_2$SO$_4$. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (ethyl acetate / hexane 1:4) as eluents to afford (3.93 g, 76%) of compound 6 as a colorless oil. $R_f$ 0.41 (hexane / ethyl acetate 1:1). [α]$_D^{25}$ +37.1 (c 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) 7.29 – 7.16 (m, 5H), 5.33 (dd, $J = 11.6$, 5.0 Hz, 1H), 5.16 (s, 1H), 4.49 (td, $J = 9.6$, 3.7 Hz, 1H), 3.74 (s, 3H), 3.42 and 3.38 (2d, $J = 5.0$ Hz, 1H), 3.03 (dd, $J = 14.3$, 5.0 Hz, 1H), 2.87 (s, 3H), 1.42 (s, 11H), 0.98 (m, 1H), 0.83 (d, $J = 6.5$ Hz, 3H), δ 0.74 (d, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.8, 170.8, 155.4, 136.5, 128.7, 128.4, 126.7, 79.2, 58.1, 52.2, 48.6, 42.1, 34.7, 32.3, 28.2, 24.2, 23.1, 21.6. HRMS (ESI+) $m/z$ calcd for C$_{22}$H$_{34}$N$_2$O$_5$, [M+H]$^+$ 407.2468; found, 407.2543.

**TFA-H-Leu-NMe-d-Phe-OMe (7):** Peptide 6 (3.9 g, 9.60 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 7 (4.06 g, quant) was used in the next step without further purification.
**Boc-Ile-Leu-NMe-α-Phe-OMe (8):** To dipeptide 7 (4.06 g, 9.67 mmol) in DMF (20 mL) at 0 °C were added Boc-Ile-OH (2.68 g, 11.6 mmol), HATU (4.41 g, 11.6 mmol) and DIPEA (4.5 g, 6.06 mL, 34.8 mmol). The reaction mixture were warmed up to room temperature and stirred for further 24 h. The mixture was poured in water (200 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO₃ (2 × 50 mL), brine (2 × 50 mL), dried over Na₂SO₄. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (ethyl acetate / CH₂Cl₂ 7:3) as eluents to afford (5.0 g, 98%) of compound 8 as a colorless oil. Rf 0.55 (hexane / ethyl acetate 1:1). [α]²⁶⁺D +4.45 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.14 (m, 5H), 6.60 (s, 1H), 5.38 (dd, J = 11.7, 4.8 Hz, 1H), 5.07 (d, J = 8.5 Hz, 1H), 4.84 (td, J = 9.6, 3.9 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.73 (s, 3H), 3.41 (dd, J = 14.6, 5.0 Hz, 1H), 3.01 (dd, J = 14.5, 11.9 Hz, 1H), 2.88 (s, 3H), 1.79 (s, 1H), 1.53 – 1.45 (m, 1H), 1.42 (s, 9H), 1.37 – 1.25 (m, 1H), 1.17 – 1.00 (m, 2H), 0.96 – 0.85 (m, 7H), 0.82 (d, J = 6.5 Hz, 3H), 0.72 (d, J = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.9, 171.1, 170.7, 155.4, 136.5, 128.7, 128.4, 126.7, 79.5, 59.0, 58.1, 52.2, 47.1, 42.0, 37.5, 34.6, 32.4, 28.2, 28.1, 24.6, 24.2, 23.0, 21.6, 15.3, 11.3. HRMS (ESI+) m/z calcd for C₂₈H₄₅N₃O₆, [M+Na]⁺; 542.3308 found, 542.3193.

**Boc-NMe-Tyr(Bzl)-OMe (9):** The N-terminus protected aminoacid Boc-Tyr(Bzl)-OH (5.6 g, 15.0 mmol) was subjected to the general alquilation procedure of the N-amide group. The obtained material (5.4 g, 14.0 mmol) was subjected to the general esterification procedure of the free C-terminus. The pale yellow oil product 9 (5.5 g, 99%) was used in the next step without further purification. ¹H NMR (400 MHz, CDCl₃) 7.42 – 6.88 (m, 9H), 5.02 (s, 1H), 3.73 and 3.71 (2s, 3H), 3.22 (m, 1H), 2.95 (m, 1H), 2.72 (s, 3H), 1.37 and 1.33 (2s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 171.5, 157.5,
157.4, 155.7, 136.9, 114.8, 114.7, 80.1, 79.8, 69.9, 61.7, 50.5, 53.3, 52.0, 34.5, 34.0, 32.5, 31.7, 28.1.

**TFA-H-NMe-Tyr(Bzl)-OMe (10):** Peptide 9 (2.5 g, 6.2 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 10 (2.7 g, quant) was used in the next step without further purification.

**Cbz-Phe-NMe-Tyr(Bzl)-OMe (11):** To Cbz-Phe-OH (2.4 g, 8.04 mmol), 10 (2.7 g, 6.7 mmol) and PyBrop (3.7 g, 8.04 mmol) in CH₂Cl₂ (150 mL) was added DIPEA (3.46 g, 4.66 mL, 26.8 mmol) at 0 °C under stirring. The ice bath was removed and stirring was continued for 18 h. The solvent was removed under reduced pressure in a rotavap and the residue dissolved in EtOAc (120 mL). The organic phase was washed with water (1 × 50 mL), HCl 5% v/v (2 × 50 mL), saturated NaHCO₃ (1 × 50 mL), brine (1 × 50 mL) and dried over Na₂SO₄. After filtration the solvent was evaporated under reduced pressure in a rotavap and the residue was purified by silica gel column chromatography (gradient 1:2, hexane/AcOEt) to afford compound 11 (3.7 g, 94%) as a colorless oil. Rf 0.38 (hexane / ethyl acetate 1:1). [α]_D^{26} -69.41 (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.14 (m, 15H), 7.01 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.35 (d, J = 8.9 Hz, 1H), 5.22 (dd, J = 9.8, 6.0 Hz, 1H), 5.02 (dd, J = 49.6, 12.3 Hz, 5H), 4.85 – 4.77 (m, 1H), 3.67 (s, 3H), 2.93 – 2.80 (m, 3H), 2.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 170.7, 157.6, 155.4, 136.9, 136.3, 136.0, 129.8, 129.5, 128.8, 128.4, 128.3, 128.0, 127.8, 127.4, 126.8, 114.7, 69.9, 66.7, 58.5, 52.1, 51.9, 39.1, 33.7, 32.4. HRMS (ESI+) m/z calcd for C₃₅H₃₆N₂O₆, [M+Na]^+: 603.2573 found, 603.2461.

**Cbz-Phe-NMe-Tyr(Bzl)-Ile-Leu-NMe-D-Phe-OMe (12):** To tripeptide 1 (2.02 g, 3.79 mmol) in DMF (12 mL) at 0 °C were added peptide 3 (2.58 g, 4.55 mmol), HATU (1.44 g, 3.79 mmol) and DIPEA (1.47 g, 1.98 mL, 11.37 mmol). The contents were warmed up
to room temperature and the mixture stirred for further 24 h. The mixture was poured in water (150 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO₃ (2 × 50 mL), brine (2 × 50 mL), dried over Na₂SO₄. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (ethyl acetate / CH₂Cl₂ 3:7) as eluents to afford (2.3 g, 63%) of compound 12 as an amorphous solid. Rf (AcOEt / MeOH 95:5) = 0.5. [α]D⁰ 24.27 (c 0.6, MeOH). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.3 Hz, 1H), 7.51 – 7.02 (m, 16H), 6.98 (d, J = 7.1 Hz, 2H), 6.79 (m, 4H), 6.39 (d, 9.3 Hz, 1H), 6.08 (bs, 1H), 5.34 (m, 1H), 5.20 – 5.05 (m, 1H), 5.04 – 4.90 (m, 2H), 4.87 – 4.57 (m, 4H), 4.40 – 4.18 (m, 1H), 3.71 (2s, 3H), 3.38 (dt, J = 16.8, 8.5 Hz, 1H), 3.23 (m, 2H), 3.18 – 2.66 (m, 9H), 2.40 (dd, J = 14.8, 11.0 Hz, 1H), 1.99 – 1.79 (m, 1H), 1.72 – 1.03 (m, 4H), 1.05 – 0.41 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 172.9, 172.8, 171.9, 170.9, 170.8, 170.0, 169.5, 169.2, 157.9, 157.6, 156.7, 157.7, 136.9, 136.7, 136.6, 136.5, 136.4, 135.9, 135.3, 130.3, 130.0, 129.8, 129.5, 128.9, 128.8, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.4, 127.2, 126.9, 126.8, 115.4, 114.9, 69.9, 67.3, 66.8, 63.2, 59.2, 57.8, 52.7, 52.3, 50.0, 47.2, 41.8, 41.5, 38.9, 36.3, 34.7, 33.2, 33.0, 32.5, 32.2, 29.8, 25.0, 24.6, 24.3, 23.0, 21.8, 21.7, 15.6, 11.4, 10.8. HRMS (ESI+) m/z calcd for C₄₇H₆₀N₅NaO₉ [M+Na]⁺; 990.4993 found, 990.4987.

Cbz-Phe-NMe-Tyr(Bzl)-Ile-Leu-NMe-D-Phe-OH (13): Peptide 12 (2.3 g, 2.4 mmol) was subjected to the general saponification procedure of the C-terminus methylester. The colorless oil product 13 (2.19 g, 95%) was used in the next step without further purification.

Boc-Pro-Sar-2,4,4-trimethoxybutylamide (14): To a solution of methylamine hydrochloride (2.16 g, 32.0 mmol) in methanol (320 ml) were added paraformaldehyde (0.9 g, 30.0 mmol) and triethylamine (3.2 g, 4.4 mL, 32.0 mmol). This suspension was
stirred at room temperature for 24 h before Boc-Pro-OH (4.74 g, 22.0 mmol) and IPB (3.46 g, 20.0 mmol) were added subsequently. After stirring for 72 h the solvent was removed under reduced pressure in a rotavap. The crude residue was purified by column chromatography (MeOH/ethyl acetate 1:6) to give compound 14 (7.00 g, 80%) as a colorless oil. Rf 0.43 (MeOH/ethyl acetate 1:6). $^1$H-NMR (400 MHz, CD$_3$OD): δ 4.61–4.53 (m, 2), 3.65–3.43 (m, 6H), 3.40–3.38 (m, 3H), 3.32 (s, 3H), 3.31 (s, 3H), 3.19–3.17 (2s, 3H), 2.17–1.70 (m, 8H), 1.45 (s, 9H). $^{13}$C-NMR (100 MHz, CD$_3$OD): δ 173.8, 173.3, 172.6, 168.7, 168.6, 168.1, 154.8, 154.8, 153.6, 102.0, 101.9, 101.8, 80.1, 79.9, 79.5, 57.3, 55.6, 55.5, 53.1, 53.0, 52.9, 52.7, 52.5, 52.4, 46.9, 41.9, 41.7, 36.6, 35.9, 35.7, 29.3, 28.42, 28.3, 28.2, 24.7, 24.6. HRMS (ESI+) m/z calcd for C$_{20}$H$_{37}$N$_3$O$_7$ [M+Na]$: 454.2632 found, 454.2515.

**Cbz-Phe-NMe-Tyr(Bzl)-Ile-Leu-NMe-D-Phe-Pro-Sar-OMe (15):** To dipeptide 2 (0.71 g, 2.25 mmol) in DMF (12 mL) at 0 °C were added the carboxylic acid 13 (2.19 g, 2.29 mmol), HATU (0.87 g, 2.29 mmol) and DIPEA (0.87 g; 1.2 mL, 6.75 mmol). The contents were warmed up to room temperature and the mixture stirred for further 24 h. The mixture was poured in water (200 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO$_3$ (2 × 50 mL), brine (2 × 50 mL), dried over Na$_2$SO$_4$. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (ethyl acetate) as eluents to afford (1.09 g, 43%) of 15 as a colorless oil. Rf 0.33 (hexane / ethyl acetate 1:9). [$\alpha$]$^D_{24}$ -15.25 (c 0.4, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, $J = 8.0$ Hz, 1H), 7.49 – 6.67 (m, 24H), 6.55 (d, $J = 8.7$ Hz, 1H), 6.34 (d, $J = 8.4$ Hz, 1H), 5.74 – 5.52 (m, 2H), 5.19 – 4.36 (m, 8H), 4.26 – 4.08 (m, 1H), 3.93 – 3.66 (m, 4H), 3.50 (m, 2H), 3.35 – 2.72 (m, 15H), 2.43 – 1.82 (m, 10H), 1.65 – 0.50 (m, 12H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ 172.7, 170.2, 169.0, 164.7, 157.9, 138.6,
136.7, 130.6, 130.3, 129.8, 129.7, 129.6, 128.8, 128.5, 128.3, 128.2, 128.0, 127.9, 127.5, 127.2, 126.5, 123.3, 115.5, 114.9, 71.9, 69.9, 69.4, 67.4, 67.2, 66.8, 64.1, 62.9, 60.2, 57.3, 56.2, 55.8, 55.7, 55.7, 53.2, 51.8, 49.7, 48.8, 47.1, 44.9, 36.2, 33.6, 33.4, 31.5, 30.5, 29.7, 29.1, 27.9, 27.0, 25.0, 24.9, 24.5, 24.1, 23.4, 22.2, 21.4, 19.8, 15.4, 12.6, 10.8. HRMS (ESI+) \( m/z \) calcld for C\textsubscript{65}H\textsubscript{81}N\textsubscript{7}NaO\textsubscript{11}, [M+Na]\textsuperscript{+}; 1158.5892 found, 1158.5886.

**Boc-Pro-Sar-OH (16):** To a solution of compound 14 (1.2 g, 2.78 mmol) in toluene (20 mL) were added 10-camphorsulfonic acid (0.06 g, 0.28 mmol) and quinoline (0.04 g, 0.28 mmol). The contents were stirred for 1 min at room temperature and were then refluxed for 30 min. The contents were cooled, transferred to a separatory funnel and washed with 1M aqueous HCl (2 \( \times \) 30 mL). The acidic aqueous phase was further extracted with ethyl acetate (1 \( \times \) 20 mL). The organic layers were combined, washed with brine (2 \( \times \) 20 mL), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and evaporated under reduced pressure in a rotavap. The obtained material (0.77 g, 2.3 mmol) was dissolved in a mixture of THF (8 mL) and water (8 mL) at 0°C after LiOH.H\textsubscript{2}O (0.1 g, 2.4 mmol) was added in one portion. After stirring for 10 h, the mixture was transferred to a separatory funnel and water (10 mL) was added. The solution was washed with diethyl ether (2 \( \times \) 20 mL). The aqueous layer was acidified to pH 3.0 using a saturated NaHSO\textsubscript{4} solution and brine (20 mL) was added. The contents were extracted with EtOAc (3 \( \times \) 40 mL). The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed under reduced pressure after filtration to afford (0.63 g, Overall yield: 77%) of product 16 as a colorless oil that was used in the next step without further purification. \( R_f \) 0.31 (ethyl acetate / methanol / acetic acid 94:4:2). \([\alpha]_D^{24} = -60.67 \) (c 1.0, MeOH). \(^1\)H-NMR (400 MHz, CD\textsubscript{3}OD): \( \delta \) 5.93 (bs, 1H), 4.73 – 4.57 (m, 1H), 4.39 – 4.22 (m, 1H), 4.04 – 3.91 (m, 1H), 3.50 (m, 2H), 3.16 (2s, 3H), 2.24 – 1.78 (m, 4H), 1.52 – 1.34 (m, 9H). \(^{13}\)C-NMR (100 MHz, CD\textsubscript{3}OD): \( \delta \) 173.6, 171.1, 80.3, 56.25,
50.5, 46.9, 46.5, 36.6, 30.1, 29.1, 28.4, 28.2, 24.2, 23.4. HRMS (ESI+) (ESI+) m/z: calcd for C_{13}H_{22}N_{2}O_{5}, 286.1529; found, 285.1456.

**HCl H-Phe-NMe-Tyr-OMe (17):** To a stirred solution of compound dipeptide 11 (1.0 g, 1.7 mmol) in MeOH (10 mL) were added Pd(OH)$_2$ (0.1 g, 10% w/w) and HCl 4M solution in 1,4-dioxane (0.3 mL). The reaction vessel was evacuated, purged with hydrogen and kept under H$_2$ atmosphere (1 atm.). The suspension was stirred for 2 h at room temperature. After filtration through Celite®, the solvent was removed under reduced pressure. The crude material was suspended in toluene (10 mL), evaporated under reduced pressure to dryness, suspended in diethyl ether (20 mL) and evaporated to dryness again to afford (0.82 g, quant) of product 17, as a white solid which was used in the next step without further purification.

**Boc-Pro-Sar-Phe-NMe-Tyr-OMe (18):** To dipeptide 17 (0.41 g, 1.4 mmol) in DMF (25 mL) at 0 °C were added dipeptide 16 (0.56 g, 1.96 mmol), HATU (0.75 g, 1.96 mmol) and DIPEA (0.72 g, 1.0 mL, 5.6 mmol). The contents were warmed up to room temperature and the mixture stirred for further 24 h. The mixture was poured in water (200 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO$_3$ (2 × 50 mL), brine (2 × 50 mL), dried over Na$_2$SO$_4$. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (ethyl acetate / hexane / MeOH 75:20:5) as eluents to afford (0.79 g, 82%) of compound 18 as a colorless oil. Rf 0.24 (hexane / ethyl acetate / methanol 20:75:5). $[\alpha]_D^{23}$ -81.98 (c 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (bs, 1H), 7.62 (bs, 1H), 7.37 – 7.06 (m, 5H), 6.99 – 6.76 (m, 2H), 6.75 – 6.45 (m, 2H), 5.46 (dd, $J = 30.5, 10.8$ Hz, 1H), 5.21 – 4.90 (m, 1H), 4.63 (m, 2H), 4.04 (m, 1H), 3.69 (3s, 3H), 3.50 (m, 2H), 3.28 – 2.50 (m, 9H), 2.42 – 1.69 (m, 5H), 1.60 – 1.32 (m, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.7, 170.9, 170.8, 167.5,
TFA H-Pro-Sar-Phe-NMe-Tyr-OMe (19): Peptide 18 (0.5 g, 0.8 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 19 (0.51 g, quant) was used in the next step without further purification.

Boc-Ile-Leu-NMe-D-Phe-OH (20): Peptide 8 (1.32 g, 2.5 mmol) was subjected to the general saponification procedure of the C-terminus methylester. The colorless oil product 20 (1.01 g, 92%) was used in the next step without further purification. Rf 0.52 (ethyl acetate / methanol / acetic acid 94:4:2). [α]D25 -9.31 (c 1.0, CHCl3). 1H NMR (400 MHz, CDCl3) δ 9.20 (bs, 1H), 7.56 – 6.86 (m, 5H), 5.56 – 5.13 (m, 2H), 4.78 (m, 1H), 4.00 (m, 1H), 3.58 – 3.29 (m, 1H), 3.19 – 2.97 (m, 1H), 2.94 (s, 3H), 1.90 – 1.03 (m, 15H), 1.03 – 0.46 (m, 12H). 13C NMR (100 MHz, CDCl3) δ 175.5, 173.1, 172.0, 155.9, 136.7, 129.9, 128.8, 128.6, 127.9, 126.9, 79.9, 59.0, 47.6, 41.4, 37.6, 34.7, 32.9, 28.3, 24.7, 24.3, 23.0, 21.8, 15.3, 11.2. HRMS (ESI+) m/z calcd for C27H42N3O6, [M-H]–; 504.3074 found, 504.3079.

Boc-Ile-Leu-NMe-D-Phe-Pro-Sar-Phe-NMe-Tyr-OMe (21): To tetrapeptide 19 (0.51 g, 0.8 mmol) in DMF (10 mL) at 0 ºC were added tripeptide 20 (0.4 g, 0.8 mmol), HATU (0.3 g, 0.8 mmol) and DIPEA (0.41 g; 0.56 mL, 3.2 mmol). The contents were warmed up to room temperature and the mixture stirred for further 24 h. The mixture was poured in water (100 mL) and extracted with ethyl acetate (3 × 30 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 30 mL), saturated aqueous NaHCO3 (2 × 20 mL), brine (2 × 20 mL), dried over Na2SO4. The organic phase was evaporated to
dryness and the crude material purified by silica gel column chromatography (ethyl acetate / hexane / MeOH 75:20:5) as eluents to afford (0.8 g, 99%) of 21 as a colorless oil. Rf (AcOEt / MeOH 95:5) = 0.5. [α]$_D^{24}$ +17.01 (c 1.0, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.32 – 7.04 (m, 10H), 6.98 – 6.79 (m, 2H), 6.79 – 6.51 (m, 2H), 6.30 (dd, J = 21.8, 8.1 Hz, 1H), 5.71 – 5.40 (m, 2H), 5.16 – 4.88 (m, 2H), 4.83 – 4.55 (m, 2H), 4.14 – 3.37 (m, 8H), 3.33 – 2.35 (m, 16H), 2.14 – 1.60 (m, 7H), 1.33 (m, 9H), 1.14 – 0.37 (m, 13H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.2, 171.9, 170.9, 168.3, 167.2, 155.6, 136.7, 135.9, 130.1, 129.6, 129.5, 128.8, 128.3, 128.2, 126.9, 126.6, 115.6, 79.9, 59.3, 57.3, 55.7, 52.3, 51.5, 50.0, 47.5, 47.3, 40.8, 38.6, 37.6, 36.9, 36.2, 34.6, 33.2, 31.2, 30.5, 28.3, 28.2, 25.5, 24.7, 24.4, 23.3, 21.1, 15.3, 11.1. HRMS (ESI+) m/z calcd for C$_{55}$H$_{77}$N$_7$O$_{11}$, [M+Na]$^+$; 1034.5681 found, 1034.5528.

**H-Phe-NMe-Tyr(Bzl)-Ile-Leu-NMe-D-Phe-Pro-Sar-OH (22):** Peptide 15 (1.08 g, 0.95 mmol) was subjected to the general saponification procedure of the C-terminus methylester. The obtained material (1.01 g, 95%) was subjected to the general hydrogenolysis procedure of the free N-terminus. The white solid product 22 (98 mg, quant) was used in the next step without further purification.

**H-Ile-Leu-NMe-D-Phe-Pro-Sar-Phe-NMe-Tyr-OH (23):** Peptide 21 (0.12 g, 0.11 mmol) was subjected to the general saponification procedure of the C-terminus methylester. The obtained material (0.1 g, 0.1 mmol) was subjected to the general deprotection procedure of the N-terminus by Boc removal. The crude product 23 (0.121 g, 0.12 mmol) was used in the next step without further purification.

**Cordyheptapeptide A (24). Cyclization strategy A:**

To heptapeptide 22 (60 mg, 0.07 mmol) in MeCN (120 mL) at 0 °C were added HOAt (10 mg, 0.07 mmol), HATU (26 mg, 0.07 mmol) and DIPEA (0.026 g, 35 μL, 0.2 mmol). The contents were warmed up to room temperature and the mixture stirred for further 72
h. The solvent was evaporated and the residue dissolved in ethyl acetate (100 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 20 mL), saturated aqueous NaHCO₃ (2 × 20 mL), brine (2 × 20 mL), dried over Na₂SO₄. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (CH₂Cl₂ / MeOH 9:1) as eluents to afford 1.1 mg of cordyheptapeptide A as a white solid, Yield: 4%.

**Cordyheptapeptide A. (23). Cyclization strategy B:**

To heptapeptide 23 (0.12 g, 0.12 mmol) in MeCN (120 mL) at 0 °C were added HOAt (0.015 g, 0.11 mmol), HATU (0.041 g, 0.11 mmol) and DIPEA (0.09 g, 0.12 mL, 0.7 mmol). The contents were warmed up to room temperature and the mixture stirred for further 72 h. The solvent was evaporated and the residue dissolved in ethyl acetate (150 mL). The organic layer was washed with aqueous hydrochloric acid 10% v/v (2 × 50 mL), saturated aqueous NaHCO₃ (2 × 50 mL), brine (2 × 50 mL), dried over Na₂SO₄. The organic phase was evaporated to dryness and the crude material purified by silica gel column chromatography (CH₂Cl₂ / MeOH 9:1) as eluents to afford 0.105 g of a mixture of cordyheptapeptide A (88 mg, 0.1 mmol) and its epimer (8.4 mg) as a white solid, Yield: 82%.

**Cordyheptapeptide A:**

Rₜ (CH₂Cl₂ / MeOH 9:1) = 0.54. [α]²⁴ D -49.77 (c 1.5, CHCl₃). [α]²⁶ D -68.50 (c 0.56, CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ 8.60 (d, J = 9.5 Hz, 1H), 8.20 (d, J = 9.6 Hz, 1H), 7.35 (m, 4H), 7.15 (m, 6H), 6.53 (d, J = 8.1 Hz, 2H), 6.22 (d, J = 8.1 Hz, 2H), 5.88 (d, J = 9.6 Hz, 1H), 5.56 (dd, J = 11.7, 4.5 Hz, 1H), 5.42 (m, 1H), 5.36 (m, 1H), 4.93 (bt, J = 10.8 Hz, 1H), 4.45 (dd, J = 9.6, 2.7 Hz, 1H), 4.39 (dd, J = 9.0, 2.4 Hz, 1H), 3.77 (m, 1H), 3.60 (m, 1H), 3.40 (m, 1H), 3.34 (m, 1H), 3.33 (dd, J = 12.5, 11.7 Hz, 1H), 3.14 (m, 1H), 3.05 (dd, J = 12.3, 11.7 Hz, 1H), 3.04 (s, 3H), 2.91 (s, 3H), 2.82 (dd, J = 12.3, 3.0 Hz,

S14
1H), 2.72 (m, 1H), 2.61 (s, 3H), 2.74 (m, 1H), 2.42 (m, 2H), 2.33 (m, 1H), 2.03 (m, 1H), 1.85 (m, 1H), 1.55 (m, 1H), 1.39 (br t, J = 12.0 Hz, 1H), 1.35 (m, 1H), 1.00 (m, 1H), 0.93 (t, J = 6.6 Hz, 3H), 0.91 (d, J = 6.3 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 0.84 (d, J = 6.9 Hz, 3H), 0.12 (br t, J = 12.0 Hz, 1H). 13C NMR (151 MHz, CDCl3) δ 174.2, 172.2, 170.7, 170.4, 170.2, 168.3, 167.8, 154.5, 137.4, 136.9, 130.1, 129.9, 129.7, 128.6, 128.5, 127.9, 126.7, 115.6, 69.1, 58.2, 57.7, 54.4, 50.7, 50.0, 48.4, 47.4, 40.5, 39.9, 38.2, 35.5, 35.4, 35.2, 32.3, 31.8, 31.4, 30.0, 29.7, 29.4, 29.2, 29.1, 28.8, 26.7, 26.6, 24.7, 24.2, 23.7, 22.6, 22.0, 20.8, 16.3, 12.1. HRMS (ESI+) m/z calcd for C49H65N7O8, [M+Na]+; 902.4895 found, 902.4786.

**Epi-Cordyheptapeptide A:**

Yield: 8%. Rf (CH2Cl2 / MeOH 9:1) = 0.54. [α]D24 +19.54 (c 4.1, CHCl3). 1H NMR (600 MHz, CDCl3) δ 8.61 (d, J = 9.5 Hz, 1H), 7.55 (d, J = 9.6 Hz, 1H), 7.33 (m, 4H), 7.12 (m, 6H), 6.99 (d, J = 8.1 Hz, 2H), 6.72 (d, J = 8.1 Hz, 2H), 5.56 (dd, J = 11.7, 4.5 Hz, 1H), 5.47 (d, J = 9.6 Hz, 1H), 5.42 (m, 2H), 4.78 (bt, J = 10.8 Hz, 1H), 4.48 (dd, J = 9.6, 2.7 Hz, 1H), 4.28 (dd, J = 9.0, 2.4 Hz, 1H), 3.75 (m, 1H), 3.59 (m, 1H), 3.34 (m, 3H), 3.21 (s, 3H), 3.14 (m, 1H), 3.05 (m, 2H), 3.00 (s, 3H), 2.90 (dd, J = 12.3, 3.0 Hz, 1H), 2.81 (s, 3H), 2.74 (m, 1H), 2.44 (m, 2H), 2.32 (m, 1H), 2.01 (m, 1H), 1.88 (m, 1H), 1.55 (m, 1H), 1.39 (br t, J = 12.0 Hz, 1H), 1.35 (m, 1H), 1.00 (m, 1H), 0.93 (t, J = 6.6 Hz, 3H), 0.91 (d, J = 6.3 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 0.12 (br t, J = 12.0 Hz, 1H). 13C NMR (150 MHz, CDCl3) δ 174.4, 172.1, 171.8, 171.4, 171.1, 168.3, 167.5, 155.0, 137.6, 136.8, 130.3, 129.6, 129.5, 128.5, 128.4, 127.4, 126.7, 126.5, 115.7, 61.4, 57.6, 57.5, 54.6, 50.6, 50.2, 48.4, 47.4, 39.5, 37.9, 35.5, 35.3, 35.0, 34.2, 31.9, 31.3, 30.0, 24.5, 23.7, 23.6, 21.9, 20.5, 15.6, 11.1. HRMS (ESI+) m/z calcd for C49H65N7O8, [M+Na]+; 902.4895 found, 902.4786.
Please note that spectra of $N$-alkyl–amides (peptoids) like Ugi products display double signal sets due to interconvertible isomers with $s$–$cis$ and $s$–$trans$ amide bonds. Depending on substitution pattern, solvent and temperature the equilibrium between these forms is shifted and may lead to broadened or doubled peaks of varied intensity.
Figure S1: $^1$H-NMR spectrum of compound 9
Figure S2: $^{13}$C-NMR spectrum of compound 9
Figure S3: $^1$H-NMR spectrum of cordyheptapeptide A
Figure S4: $^{13}$C-NMR / DEPT spectrum of cordyheptapeptide A
Figure S5: gDQCOSY spectrum of cordyheptapeptide A
Figure S6: zTOCSY spectrum of cordyheptapeptide A
Figure S7: ROESY spectrum of cordyheptapeptide A
Figure S8: gHSQCAD spectrum of cordyheptapeptide A
Figure S9: gHMBCAD spectrum of cordyheptapeptide A
**Figure S10:** $^1$H-NMR spectrum of epi-cordyheptapeptide A
Figure S11: $^{13}$C-NMR / DEPT spectrum of epi-cordyheptapeptide A
Figure S12: gDQCOSY spectrum of epi-cordyheptapeptide A
Figure S13: zTOCSY spectrum of epi-cordyheptapeptide A
Figure S14: ROESY spectrum of epi-cordyheptapeptide A
Figure S15: gHSQCAD spectrum of epi-cordyheptapeptide A
Figure S16: gHMBCAD spectrum of epi-cordyheptapeptide A
Figure S17: ESI-MS of cordyheptapeptide A
Figure S18: HPLC Chromatogram of crude cordyheptapeptide A.
Table 1. Comparison of the $^1$H and $^{13}$C NMR data of synthetic and natural Cordyheptapeptide A.

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