Supplementary information:

Bend-ribbon forming γ-peptides

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1. General experimental procedures.

1.1 Solvents and Reagents

THF was distilled under an atmosphere of dry nitrogen from lithium aluminium hydride and calcium hydride in the presence of triphenylmethane; DCM was distilled from calcium hydride; triethylamine was distilled from calcium hydride and stored over potassium hydroxide. Reactions performed under an atmosphere of hydrogen gas were maintained by an inflated balloon. pH 7 Buffer was prepared by dissolving KH_2PO_4 (85 g) and NaOH (14.5 g) in distilled water (950 mL). All other reagents and solvents were used as supplied, without prior purification.

1.2 Chromatography

Thin layer chromatography (TLC) was performed on glass plates coated with Merck 60 F_{254} silica and visualization was achieved by UV light or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was carried out using Merck Kieselgel (230-400 mesh).

1.3 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker Avance 700 (^{1}H: 700 MHz and ^{13}C: 175 MHz), Bruker Avance 400 (^{1}H: 400 MHz and ^{13}C: 100 MHz), or Bruker Avance Cryo 500 (^{1}H: 500 MHz and ^{13}C: 125 MHz). Chemical shifts are quoted in ppm and are referenced to the residual non-deuterated solvent peak, and are reported (based on appearance rather than interpretation) as follows: chemical shift δ/ppm (number of protons, multiplicity, coupling constant J/Hz, assignment) [br, broad; s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet]. ^{1}H and ^{13}C NMR assignments are based upon the numbering scheme outlined on the structures in red; this is distinct from the numbering scheme used in the systematic naming of these compounds.

1.4 Infrared Spectroscopy

Infrared spectra were recorded neat on a Perkin-Elmer Spectrum One spectrometer fitted with an attenuated total reflectance attachment with internal referencing.

1.5 Mass Spectrometry

Accurate mass measurements were performed on a Finnigan MAT 900 XLT (ES+) at the EPSRC National Mass Spectrometry Service Centre at Swansea.

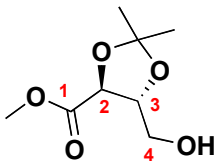
1.6 Polarimetry

Optical rotations were recorded on a Perkin-Elmer 241 polarimeter with a path length of 1 dm.

2. 1 Experimental procedures and data for monomer units

Both D- and L-tartrate derived monomer units have been prepared, and the data for the D-series is presented here. Where a reference to a specific enantiomeric series is intended (for example in the preparation of heterochiral oligomers), the prefix D- or L- will be used before the number of the compound.

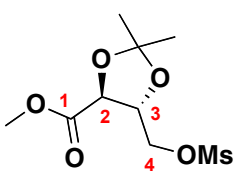
(4*S*,5*R*)-methyl 5-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [8]



This compound was prepared by a modification of a literature procedure.[i] Sodium borohydride (104 mg, 2.75 mmol) was added portion-wise over 1 h to a stirred solution of dimethyl-2,3-*O*-isopropylidene-D-tartrate (1 g, 4.59 mmol) in methanol (4.5 mL) at -10°C. After 65 minutes, TLC (EtOAc/petrol, 1:1) indicated conversion of starting material (R_f 0.72) to the desired alcohol (R_f 0.35) and diol (R_f ~0). The reaction mixture was brought to room temperature and quenched with saturated ammonium chloride (1 mL). The reaction mixture was diluted with DCM (30 mL) and washed with water (20 mL). The aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The compounds were separated and purified by flash column chromatography (EtOAc/petrol, 1:2 – 1:1) to yield the desired alcohol D-**8** (280 mg, 32%) and starting material (450 mg, 45%).

R_f 0.35 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +8.3 (c 0.53, $CHCl_3$); ν_{max}/cm^{-1} (film): 3485 (OH), 2991 and 2940 (CH), 1737 (C=O, ester), 1206 and 1100 (C-O); δ_H (400 MHz, $CDCl_3$) 4.47 (1H, d, J 7.7, H2), 4.24 (1H, td, J 6.9, 3.4, 3.4, H3), 3.95 (1H, dd, J 12.2, 3.1, H4), 3.80 (3H, s, CO_2CH_3), 3.75 (1H, dd, J 12.2, 3.8, H4'), 1.89 (1H, brs, OH), 1.49 and 1.45 (2 x 3H, 2 x s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 171.6 (C=O), 111.8 (qC), 79.6 (CH), 75.3 (CH), 62.2 (CH_2), 52.9 (CO_2CH_3), 27.2 (CH_3), 26.0 (CH_3); *m/z* HRMS (ES+) found 191.0913; $C_8H_{14}O_5$ $[M+H]^+$ requires 191.0913.

(4*S*,5*R*)-methyl 2,2-dimethyl-5-((methylsulfonyloxy)methyl)-1,3-dioxolane-4-carboxylate [9]

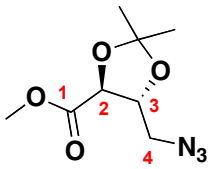


Methanesulfonyl chloride (1.18 mL, 15.15 mmol) and triethylamine (2.64 mL, 18.94 mmol) were added to a stirred solution of alcohol D-**8** (2.4 g, 12.63 mmol) in DCM (25 mL) at 0°C. After 10 minutes, TLC

(EtOAc/petrol, 1:1) indicated complete conversion of starting material (R_f 0.39) to a single product (R_f 0.46). The reaction mixture was diluted with DCM (50 mL), washed with saturated ammonium chloride (30 mL) and water (30 mL). The aqueous washes were extracted with DCM (2 x 50 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo* to yield the product D-**9** (3.5 g) as light yellow colour oil. A small quantity was purified by flash column chromatography (EtOAc/petrol, 1:2 – 1:1) for analytical purposes.

R_f 0.46 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +20.4 (c 0.41, $CHCl_3$); ν_{max}/cm^{-1} (film): 2992 and 2942 (CH), 1759 and 1733 (C=O, ester), 1296 and 1168 (C-O); δ_H (400 MHz, $CDCl_3$) 4.54 (1H, d, J 10.2, H2), 4.45-4.40 (1H, m, H3), 4.38 (1H, dd, J 3.8, 1.7, H4), 4.36 (1H, dd, J 2.9, 1.8, H4'), 3.82 (3H, s, CO_2CH_3), 3.08 (3H, s, SO_2CH_3), 1.49 and 1.45 (2 x 3H, 2 x s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 170.2 (C=O), 112.3 (qC), 76.5 (CH), 75.0 (CH), 68.1 (CH_2), 52.7 (CO_2CH_3), 37.8 (SO_2CH_3), 26.7 (CH_3), 25.7 (CH_3); *m/z* HRMS (ES+) found 286.0955; $C_9H_{16}O_7S$ $[M+NH_4]^+$ requires 286.0955.

(4*S*,5*R*)-methyl 5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [10]

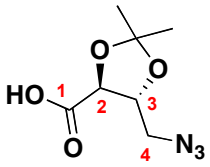


Sodium azide (800 mg, 12.31 mmol) was added to a stirred solution of D-**9** (3.5 g) in DMF (25 mL). The reaction mixture was heated at 95°C. After 3 h, TLC (EtOAc/petrol, 1:1) indicated complete conversion of starting material (R_f 0.50) to a single product (R_f 0.82). The reaction mixture was diluted with ethyl acetate (50 mL) and washed with 10% magnesium sulfate solution (50 mL). The aqueous layer was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/petrol, 1:2 – 1:1) to yield D-**10** (2.35 g, 87%) over two steps as a light yellow coloured oil.

R_f 0.82 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +84.9 (c 0.69, $CHCl_3$); ν_{max}/cm^{-1} (film): 2991 and 2956 (CH), 2100 (N_3), 1762 and 1733 (C=O, ester),* 1205 and 1097 (C-O); δ_H (400 MHz, $CDCl_3$) 4.43 (1H, d, J 7.5, H2), 4.32 (1H, ddd, J 7.5, 4.5, 3.1, H3), 3.79 (3H, s, CO_2CH_3), 3.70 (1H, dd, J 13.3, 3.1, H4), 3.36 (1H, dd, J 13.3, 4.5, H4'), 1.52 and 1.44 (2 x 3H, 2 x s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 170.6 (C=O), 111.9 (qC), 77.9 (CH), 75.6 (CH), 52.5 (CO_2CH_3), 51.6 (CH_2), 26.6 (CH_3), 25.7 (CH_3); *m/z* HRMS (ES+) found 233.1244; $C_8H_{13}N_3O_4$ $[M+NH_4]^+$ requires 233.1244.

* We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

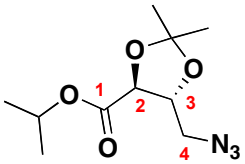
(4*S*,5*R*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid [11]



1 M Aqueous NaOH (21 mL, 20.91 mmol) was added to a stirred solution of azido ester D-**10** (1.5 g, 6.97 mmol) in ethanol (35 mL) at room temperature. After 15 minutes, TLC (EtOAc/petrol, 1:1) indicated complete conversion of starting material (R_f 0.82) to a single product (R_f 0.1). The solvent was removed under reduced pressure and the resulting residue was dissolved in water (25 mL) and acidified to pH 2-3 with 3M aqueous HCl. The resulting mixture was extracted with DCM (3 x 50 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give the azido acid D-**11** (1.34 g, 96%) as a yellow coloured solid.

R_f 0.1 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +77.4 (c 0.795, $CHCl_3$); ν_{max}/cm^{-1} (film): 3112 (OH), 2991 and 2937 (CH), 1733 (C=O, ester), 1210 and 1095 (C-O); δ_H (400 MHz, $CDCl_3$) 5.76 (1H, brs, CO_2H), 4.48 (1H, d, J 7.7, H2), 4.36 (1H, ddd, J 7.5, 4.4, 2.9, H3), 3.74 (1H, dd, J 4.9, 2.1, H4), 3.40 (1H, dd, J 13.4, 4.4, H4'), 1.54 and 1.47 (2 x 3H, 2 x s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 173.4 (C=O), 112.3 (qC), 78.0 (CH), 75.1 (CH), 51.4 (CH_2), 26.7 (CH_3), 25.7 (CH_3); *m/z* (ES+) $[M+H]^+$ 201.1.

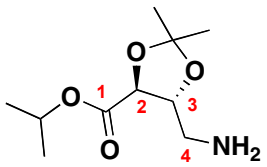
(4*S*,5*R*)-isopropyl 5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [2]



Potassium carbonate (1.42 g, 10.23 mmol) was added to a stirred solution of methyl ester D-**10** (2.0 g, 9.30 mmol) in isopropanol (83 mL). The reaction mixture was heated at 90°C. After 3 h, TLC (EtOAc/petrol, 1:1) indicated complete conversion of starting material (R_f 0.82) to a single product (R_f 0.86). The reaction mixture was filtered, diluted with chloroform (100 mL) and washed with pH 7 buffer (2 x 30 mL). The aqueous washes were extracted with chloroform (2 x 50 mL) and the combined organic layer was dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (EtOAc/petrol, 1:1) to give isopropyl ester D-**2** as a colourless liquid (1.73 g, 77%).

R_f 0.86 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +72.6 (c 0.43, $CHCl_3$); ν_{max}/cm^{-1} (film): 2986 and 2938 (CH), 2099 (N_3), 1754 and 1724 (C=O, ester),* 1201 and 1092 (C-O); δ_H (400 MHz, $CDCl_3$) 5.12 (1H, sept, J 6.3, *i*Pr CH), 4.38 (1H, d, J 7.4, H2), 4.30 (1H, ddd, J 7.5, 4.6, 3.2, H3), 3.69 (1H, dd, J 13.3, 3.1, H4), 3.36 (1H, dd, J 13.3, 4.6, H4'), 1.53 and 1.45 (2 x 3H, 2 x s, 2CH_3), 1.29 (3H, d, J 2.3, CH(CH_3)), 1.27 (3H, d, J 2.3, *i*Pr CH_3); δ_C (100 MHz, $CDCl_3$) 170.6 (C=O), 112.2 (qC), 78.4 (CH), 76.3 (CH), 69.8 (*i*Pr CH), 52.2 (CH_2), 27.1 (CH_3), 26.1 (CH_3), 22.1 and 22.0 (*i*Pr CH_3); *m/z* HRMS (ES+) found 261.1557; $C_{10}H_{17}N_3O_4$ $[M+NH_4]^+$ requires 261.1557.

(4*S*,5*R*)-isopropyl 5-(aminomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [12]

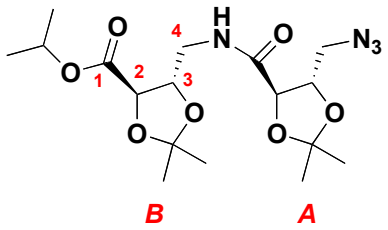


Palladium on activated carbon, 10 wt % (35 mg) was added to isopropanol and stirred under a hydrogen atmosphere for 30 minutes. The isopropyl ester D-**2** (350 mg, 1.44 mmol) was dissolved in isopropanol and added slowly to the reaction mixture (still under a hydrogen atmosphere) *via* syringe. After 1 h, TLC indicated complete conversion of the starting material to a major product D-**12**, which was filtered through Celite™ (eluent: isopropanol), concentrated and used without further purification.

* We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

2. 2 Experimental procedures and data for homochiral oligomers

(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [13]



TBTU (115 mg, 0.36 mmol) and diisopropylethylamine (83 µL, 0.48 mmol) were added to a stirred solution of azido acid L-**11** (52 mg, 0.24 mmol) and crude amino ester L-**12** (50 mg, 0.25 mmol) in DMF, (2.5 mL). After 48 h at ambient temperature, TLC (diethyl ether/petroleum ether 40-60, 2:1) indicated conversion of the starting materials (R_f 0-0.1) to a major product (R_f 0.36) and a minor product (R_f 0.55). The reaction mixture was concentrated *in vacuo* and dissolved in DCM (30 mL). The solution was washed with 1M HCl (5 mL) and pH 7 buffer (5 mL). The aqueous layers were extracted with DCM (20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (diethyl ether/ petroleum ether 40-60, 2:1) to yield the desired dimer **13** (70 mg, 73 % from L-**12**) as the major product.

R_f 0.36 (diethyl ether/petroleum ether 40-60, 2:1); $[\alpha]_D^{25}$ = +53.0 (c 0.5, $CHCl_3$); ν_{max}/cm^{-1} (film): 2986 (C-H), 2102 (N_3), 1752 and 1727 (C=O ester),* 1676 (C=O, amide), 1209 and 1095 (C-O); *m/z* HRMS (ESI) found 423.1869; $C_{17}H_{28}N_4O_7Na$ $[M^+Na]^+$ requires 423.1850.

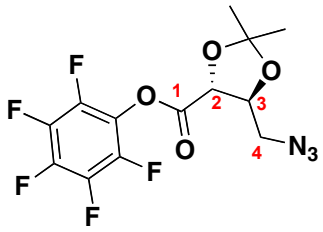
^1H (500 MHz, 5.6 mM in $CHCl_3$ @ 7.27 ppm) and ^{13}C (125 MHz, $CHCl_3$).

Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.4
	C-2		4.28	d	8.0	77.89
	C-3		4.18	ddd	2.5, 4.7, 7.9	79.42
	C-4	4	3.18	dd	4.6, 13.4	52.39
		4’	3.45	dd	2.6, 13.3	
B	C-1		-	-	-	170.4
	C-2		4.28	d	7.1	76.87
	C-3		4.34	dt	5.0, 6.9	78.49
	C-4	4	3.47	dt	5.8, 13.6	41.36
		4’	3.67	ddd	4.6, 6.0, 13.9	
	NH		6.84	t	5.6	-
***i*Pr**	CH		5.04	sept	6.2	69.40
	Me		1.11	d	6.3	21.93

* We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

Residue	Position	δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
	Me	1.08	d	6.3	21.88
A - B	q*C*$(CH_3)_2$	-	-	-	111.87
		-	-	-	111.51
A	Isopropylidene CH_3 groups	1.45, 1.45	s	-	27.52, 26.2
B		1.41, 1.27	s	-	27.15, 26.2

(4*R*,5*S*)-perfluorophenyl 5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [14]

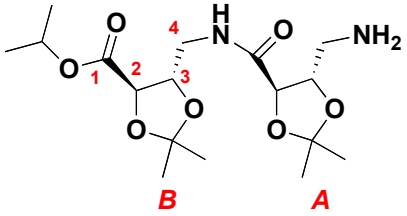


A solution of pentafluorophenol (412 mg, 2.24 mmol) in DCM (1 mL) was added dropwise to a stirred solution of azido acid L-**11** (300 mg, 1.49 mmol) and EDCI (429 mg, 2.24 mmol) in DCM (2 mL). The reaction mixture was sonicated for 30 mins when TLC (EtOAc/petroleum ether 40-60, 1:16) indicated conversion of starting material (R_f 0-0.1) to a single product (R_f 0.3). The reaction mixture was concentrated and the residue was subjected to flash column chromatography (EtOAc/petroleum ether 40-60, 1:16) to yield the ester L-**14** (329 mg, 60%) as a colourless liquid.

R_f 0.34 (EtOAc/petroleum ether 40-60, 1:16); $[\alpha]_D^{25} = -69.0$ (c 0.52, $CHCl_3$); ν_{max} /cm^{-1}(film): 2995, 2941, 2105 (N_3), 1806, 1777, 1518 (C=O), 1384, 1214, 1144, 1077, 995; δ_H (400 MHz, $CDCl_3$) 4.81 (1H, d, J 7.1 , H2), 4.55 (1H, ddd, J 3.3, 4.0, 7.2, H3), 3.81 (1H, dd, J 3.2,13.5 , H4), 3.44 (1H, dd, J 4.0, 13.5, H4'), 1.59 and 1.49 (2 x 3H, 2 x s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 167.1 (C=O), 113.1 (qC), 78.2 (C-2), 75.1 (C-3), 51.2 (C-4), 25.6, 25.2 ($2CH_3$), 124.3 (at, *J* 14.7, C), 140.9 (dm, *J* 252.30, CF), 139.9 (dm, *J* 250.9, CF), 137.90 (dm, *J* 250.2, CF).[§]

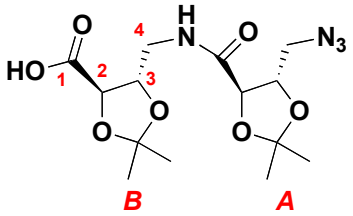
(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(aminomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [15]

[§] The ^{13}C signals for the pentafluorophenol are complex (and unresolved at this field strength), but we have quoted the chemical shifts as the centre of the multiplet patterns, described some of these patterns as 'dm' (doublets of multiplets) and quoted the larger $^1J_{C,F}$ coupling constant for information.



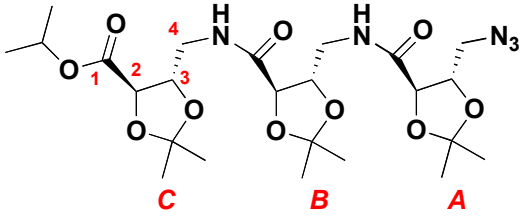
Palladium on activated carbon, 10 wt % (10 % w/w, 20 mg) was added to isopropanol (3 mL) and stirred under a hydrogen atmosphere for 15 minutes. A solution of dimer **13** (200 mg, 0.5 mmol) was in isopropanol (2 mL) and added slowly to the stirred reaction mixture (under a hydrogen atmosphere) *via* syringe. After 2 h, TLC (diethyl ether/petroleum ether 40-60, 2:1) indicated complete conversion of the starting material (R_f 0.36) to a single product (R_f 0-0.1). The mixture was filtered through Celite™ (eluting with isopropanol) and concentrated *in vacuo* to afford amine **15** (186 mg, quantitative crude yield) that was used without further purification.

(4*R*,5*S*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid [16]



0.5 M NaOH (1.0 mL, 0.5 mmol) was added to a stirred solution of dimer **13** (200 mg, 0.5 mmol) in 1,4-dioxane (5 mL). The reaction was stirred at ambient temperature for 2 h when TLC (diethyl ether/ petroleum ether 40-60, 2:1) indicated complete conversion of starting material (R_f 0.36) to a single product (R_f 0-0.1). Amberlite IR-120 (H^+) resin (4 g) was added to the solution, which was stirred for 5 minutes. The resin was removed by filtration, washed with 1,4-dioxane and the filtrate concentrated *in vacuo* to yield the crude dimer acid **16** (179 mg, quantitative crude yield) that was used without further purification.

(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [17]



A solution of dimeric amino ester **15** (127 mg, 0.34 mmol) in DCM (0.5 mL) was added dropwise to a stirring suspension of pentafluorophenol ester **14** (125 mg, 0.34 mmol) and Hunig's base (122 μL, 0.68 mmol) in DCM (1 mL). After 1h, TLC (EtOAc/petroleum ether 40-60, 5:5) indicated the complete conversion of starting materials into a major product (Rf 0.35). The mixture was concentrated *in vacuo* and the residue was subjected to flash column chromatography (EtOAc/petroleum ether 40-60, 5:5) to yield the trimeric azido ester **17** (170 mg, 90%) as a colourless liquid.

R_f 0.40 (EtOAc/petroleum ether 40-60, 1:1); $[\alpha]_D^{25} = -36.7$ (c 0.43, $CHCl_3$); ν_{max}/cm^{-1} (film): 2987 (C-H), 2102 (N_3), 1753 and 1727 (C=O ester),** 1671 (C=O, amide), 1210 and 1091 (C-O); *m/z* HRMS (ES+) found 558.2778; $C_{24}H_{39}N_5O_{10}$ $[M+H]^+$ requires 558.2770.

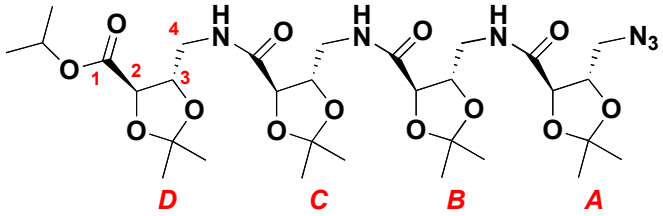
^1H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6).

Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.07
	C-2		4.27	d	8.1	76.72
	C-3		4.22	ddt	3.9, 5.8, 8.0	79.17
	C-4	4	3.13	dd	13.4, 4.7	52.02
		4’	3.38	dd	13.4, 2.6	
B	C-1		-	-	-	170.37
	C-2		4.05	d	7.6	79.17
	C-3		4.01	dt	4.4, 7.2, 7.4	77.90
	C-4	4	3.47	ddd	4.8, 6.9, 13.5	41.65
		4’	3.80	ddd	4.4, 6.7, 13.5	
	NH		7.30	dd	5.0, 6.2	-
C	C-1		-	-	-	170.02
	C-2		4.17	d	7.0	77.42
	C-3		4.22	ddt	3.9, 5.8, 8.0	78.03
	C-4	4	3.35	dt	5.8, 13.9	41.02
		4’	3.54	ddd	4.6, 5.9, 13.9	
	NH		6.75	t	5.8	-
Others	$\underline{CH}(CH_3)_2$		4.95	sept	6.3	69.04
	*i*Pr Me		0.98	d	6.3	21.57
	*i*Pr Me		1.02	d	6.3	21.51

** We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

Residue	Position	δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
	Isopropylidene qC(CH_3)$_2$	-	-	-	111.49 111.21 110.66
	Isopropylidene CH_3 groups	1.39 1.35 (2CH_3) 1.33 1.24 1.15	s	-	27.12 26.94 26.90 25.97 25.77 25.68

(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [4]



TBTU (320 mg, 1.0 mmol) and diisopropylethylamine (0.13 mL, 0.75 mmol) were added to a stirred solution of the dimeric acid **16** (179 mg, 0.5 mmol) and dimeric amine **15** (187 mg, 0.5 mmol) in DCM/DMF, 1:1 (1.5 mL). After 24 h at room temperature, TLC (ethyl acetate/petroleum ether 40-60, 1:1) indicated almost complete conversion of starting materials (R_f 0-0.1) to a major product (R_f 0.12). The reaction mixture was concentrated *in vacuo* and dissolved in chloroform (100 mL). The solution was washed with pH 2 buffer (30 mL) and pH 7 buffer (30 mL). The aqueous layers were extracted with chloroform (50 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether 40-60, 1:1 - 2:1) to yield the desired tetramer **4** (235 mg, 66%) as the major product.

R_f 0.12 (ethyl acetate/petroleum ether 40-60, 1:1); $[\alpha]_D^{25}$ = +23.3 (c 0.275, $CHCl_3$); ν_{max}/cm^{-1} (film): 2987 and 2937 (C-H), 2100 (N_3), 1752 and 1740 (C=O ester),* 1673 (C=O amide), 1214 and 1094 (C-O); *m/z* HRMS (ESI) found 737.3338; $C_{31}H_{51}N_6O_{13}$ $[M^+Na]^+$ requires 715.3509.

^1H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

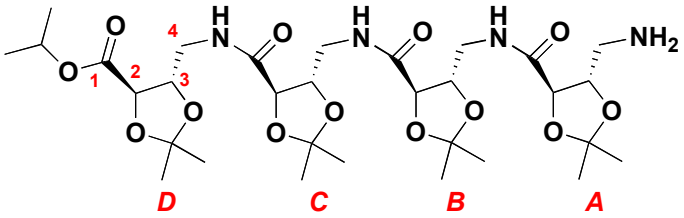
Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.12
	C-2		4.29	d	8.1	76.78
	C-3		4.21-4.24	m	-	79.18
	C-4	4	3.14	dd	4.7, 13.4	52.07
		4’	3.40	dd	2.6, 13.4	
B	C-1		-	-	-	170.57
	C-2		4.25	a-tt	5.2, 7.6	79.61
	C-3		4.25	a-tt	5.2, 7.6	77.90
	C-4	4	3.48-3.50	m	-	41.78
		4’	3.89-3.93	m	-	
	NH		7.49	a-dd	4.7, 6.2	-
C	C-1		-	-	-	170.47
	C-2		4.04	d	7.6	79.18
	C-3		3.99	dt	4.4, 7.4	77.74
	C-4	4	3.42-3.55	m	-	41.82

* We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
		4’	3.78	ddd	4.4, 6.7, 13.5	
	NH		7.40	a-dd	5.1, 5.9	-
D	C-1		-	-	-	170.06
	C-2		4.17	d	7.0	77.39
	C-3		4.21-4.24	m	-	78.01
	C-4	4	3.35-3.38	m	-	41.02
		4'	3.51-3.55	m	-	
	NH		6.76	t	6.0	-
Others	^{i}Pr		4.96	septet	6.3	69.07
			1.03	d	6.3	21.58
			1.00	d	6.3	21.53
	Isopropylidene qC$(CH_3)_2$		-	-	-	111.51 111.27 110.78 110.70
	Isopropylidene CH_3 groups		1.40 1.38 1.36 1.35 1.34 1.32 1.24 1.16	s	-	27.13 27.07 26.96 26.99 25.98 25.83 25.77 25.65

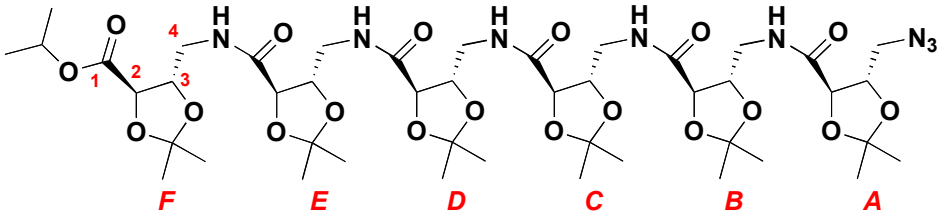
Residue	Position	NOEs to:
A	H-2	3A, 4A, 4’A, C$(CH_3)_2$
	H-3	2A, 4A, 4’A, C$(CH_3)_2$
	H-4	4’A, 3A, 2A
	H-4’	4A, 3A, 2A,
B	H-2	3B, 4B, 4’B, C$(CH_3)_2$
	H-3	2B, 4B, 4’B, C$(CH_3)_2$
	H-4	4’B, 3B, 2B
	H-4’	4B, 3B, 2B
	NH^B	$H_2{}^B$, $H_3{}^B$, $H_4{}^B$, $H_4{}^B$ C$(CH_3)_2$
C	H-2	3C, 4C, 4’C, C$(CH_3)_2$
	H-3	2C, 4C, 4’C, C$(CH_3)_2$
	H-4	4’C, 3C, 2C
	H-4’	4C, 3C, 2C
	NH^C	$H_2{}^B$, $H_3{}^B$, $H_2{}^C$, $H_3{}^C$ $H_4{}^C$, $H_4{}^C$, C$(CH_3)_2$
D	H-2	3D, 4D, 4’D, C$(CH_3)_2$
	H-3	2D, 4D, 4’D, C$(CH_3)_2$
	H-4	2D, 4’D, 3D
	H-4’	4D, 3D, 2D
	NH^D	$H_3{}^D$, $H_2{}^D$, $H_2{}^C$, $H_4{}^D$, C$(CH_3)_2$

(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(aminomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [18]



Palladium on activated carbon, 10 wt % (10 % w/w, 10 mg) was added to isopropanol (2 mL) and stirred under a hydrogen atmosphere for 15 minutes. A solution of tetramer **4** (100 mg, 0.14 mmol) in isopropanol (2 mL) was added slowly to the stirred reaction mixture (under a hydrogen atmosphere) *via* syringe. After 2 hours, TLC (ethyl acetate/petroleum ether 40-60, 2:1) indicated complete consumption of the starting material (R_f 0.26). The mixture was filtered through Celite™ (eluting with isopropanol) and concentrated *in vacuo* to afford amine **18** (96 mg, quantitative crude yield) that was used without further purification.

(4*R*,5*S*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [5]



TBTU (90 mg, 0.28 mmol) and diisopropylethylamine (37 µl, 0.21 mmol) were added to a stirred solution of the acid **16** (50 mg, 0.14 mmol) and amine **18** (96 mg, 0.14 mmol) in DCM/DMF, 1:1 (1 mL). After 24 h at ambient temperature, TLC (ethyl acetate/ petroleum ether 40-60, 19:1) indicated almost complete conversion of the starting materials (R_f 0-0.1) to a major product (R_f 0.17). The reaction mixture was concentrated *in vacuo* and dissolved in chloroform (75 mL). The solution was washed with pH 2 buffer (20 mL) and pH 7 buffer (20 mL). The aqueous layers were extracted with chloroform (50 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The

residue was purified by flash column chromatography (ethyl acetate / petroleum ether 40-60, 25:1) to yield the desired hexamer **5** (96 mg, 67% from the dimer **13**) as the major product.

R_f 0.17 (ethyl acetate/petroleum ether 40-60, 19:1); $[\alpha]_D^{25}$ = +14.0 (c 0.5, $CHCl_3$); ν_{max}/cm^{-1} (film): 2987 and 2938 (C-H), 2104 (N_3), 1751 and 1740 (C=O ester),* 1666 (C=O amide), 1213 and 1092 (C-O).

^1H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.13
	C-2		4.32	d	8.1	76.81
	C-3		4.23-4.26	m	-	77.41*
	C-4	4	3.17	dd	13.4, 4.7	52.10
		4’	3.38-3.48	m	-	
B	C-1		-	-	-	170.60
	C-2		4.10-4.18	m	-	79.57*
	C-3		4.10-4.18	m	-	79.18*
	C-4	4	3.50-3.56	m	-	42.00*
		4’	3.85-3.95	m	-	
	NH		7.44	dd	4.6, 6.4	-
C	C-1		-	-	-	170.64
	C-2		4.10-4.18	m	-	79.10*
	C-3		4.10-4.18	m	-	79.10*
	C-4	4	3.38-3.48	m	-	41.91*
		4’	3.85-3.95	m	-	
	NH		7.57	dd	7.9, 12.1	-
D	C-1		-	-	-	170.64
	C-2		4.10-4.18	m	-	79.76*
	C-3		4.10-4.18	m	-	79.72*
	C-4	4	3.38-3.48	m	-	41.89*
		4’	3.85-3.95	m	-	
	NH		7.44	dd	4.6, 6.4	-
E	C-1		-	-	-	170.48
	C-2		4.06	d	7.6	78.01*
	C-3		4.02	dt	4.3, 7.3, 7.4	77.87*
	C-4	4	3.38-3.48	m	-	41.79*
		4’	3.81	ddd	13.4, 6.7, 4.3	
	NH		7.58	a-t	-	-
F	C-1		-	-	-	170.09
	C-2		4.20	d	7.0	77.77*
	C-3		4.23-4.26	m	-	77.27*
	C-4	4	3.38-3.48	m	-	41.03*
		4’	3.50-3.56	m	-	
	NH		6.82	t	5.9	-
Others	$\underline{CH}(CH_3)_2$		4.97	septet	6.3	69.0
	i-Pr Me		1.00	d	6.3	21.59
	i-Pr Me		1.04	d	6.3	21.54

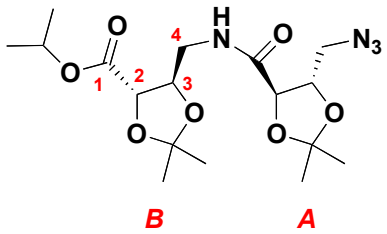
* We attribute this band to Fermi Resonance - an overtone from the stretch at around 860cm^{-1}.

Residue	Position	δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
	Isopropylidene qC(CH_3)$_2$	-	-	-	111.53 111.30 110.86 110.84 110.81 110.73
	Isopropylidene CH_3 groups	1.41 1.39 ($2CH_3$) 1.37 1.36 1.35 1.34 1.33 1.33 ($2CH_3$) 1.26 1.18	s	-	27.14 27.09 27.06 27.04 26.98 26.89 26.99 25.83 25.77 25.65

Due to resonance overlap some ^{13}C peaks cannot be unambiguously correlated with their respective proton signals (and hence to their respective residues); these are indicated with '*' and hence the exact assignments given should be treated as somewhat tentative.

2. 3 Experimental procedures and data for heterochiral oligomers.

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [19]



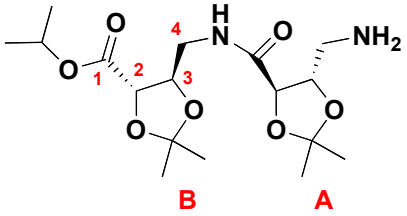
Diisopropylethylamine (0.16 mL, 0.92 mmol) and TBTU (224 mg, 0.692 mmol) were added to a stirred solution of crude amino ester D-**12** and crude azido acid L-**11** in DCM (1 mL). After 10 minutes, TLC (diethylether/petrol, 2:1) showed complete conversion to a single product (R_f 0.50). The reaction mixture was diluted with DCM (20 mL) and washed with water (2 x 15 mL). The aqueous washes were extracted with DCM (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/petrol, 1:1) to yield the desired dimer **19** (152 mg, 83% from D-**2**).

R_f 0.35 (diethylether/petrol, 2:1); $[\alpha]_D^{25}$ = -35.2 (c 0.165, $CHCl_3$); ν_{max}/cm^{-1} (film): 3424 (NH), 2987 and 2938 (CH), 2101 (N_3), 1752 and 1726 (C=O, ester), 1676 (Amide I), 1526 (Amide II), 1209 and 1094 (C-O); *m/z* HRMS (ES+) found 401.2030; $C_{17}H_{28}N_4O_7$ $[M+H]^+$ requires 401.2031.

^{1}H (500 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

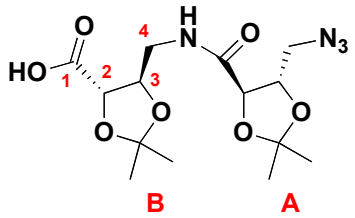
Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	169.9
	C-2		4.19	d	8.22	76.3
	C-3		4.02	ddd	2.6, 4.4, 8.2	79.2
	C-4	4	3.30	dd	2.6, 13.5	51.8
		4’	3.08	dd	4.4, 13.5	
B	C-1		-	-	-	170.1
	C-2		4.15	d	7.2	77.1
	C-3		4.25	ddd	4.1, 5.1, 7.1	78.1
	C-4	4	3.53	ddd	5.1, 6.9, 14.0	40.5
		4’	3.41	ddd	4.2, 5.0, 13.8	
	NH		6.65	s	-	-
Others	C*H*$(CH_3)_2$		4.95	sept	6.3	69.0
	i-Pr Me		1.00 (3H)	d	6.3	21.5
	i-Pr Me		0.99 (3H)	d	6.3	21.5
	Isopropylidene q*C*$(CH_3)_2$		-	-	-	111.4, 111.0
	Isopropylidene CH_3 groups		1.35, 1.35 1.30, 1.18	s	-	27.0, 26.7, 26.0, 25.6

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(aminomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [20]



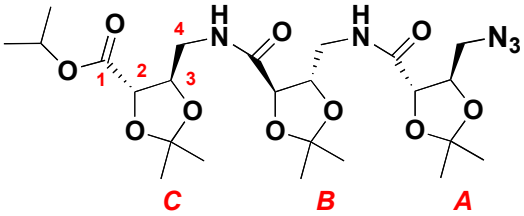
Palladium on activated carbon, 10 wt % (10 % w/w, 20 mg) was added to isopropanol and stirred under a hydrogen atmosphere for 30 minutes. The isopropyl ester **19** (200 mg, 0.5 mmol) was dissolved in isopropanol and added to the reaction mixture (still under a hydrogen atmosphere) *via* syringe. After 1 hour, TLC indicated complete conversion of the starting material to a major product **20** (99% crude yield), which was filtered through Celite™ (eluent: isopropanol), concentrated and used without further purification.

(4*S*,5*R*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylic acid [21]



1 M Aqueous NaOH (1.5 mL, 1.5 mmol) was added to a stirred solution of azido ester **19** (200 mg, 0.5 mmol) in ethanol (2.5 mL) at room temperature. After 15 minutes, TLC (EtOAc/petrol, 1:1) indicated complete conversion of starting material to a single product (R_f 0.1). The solvent was removed under reduced pressure and the resulting residue was dissolved in water (30 mL) and acidified to pH 2-3 with 3M aqueous HCl. The resulting mixture was extracted with DCM (2 x 50 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo* to give the crude azido acid **21** which was used without further purification.

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [22]



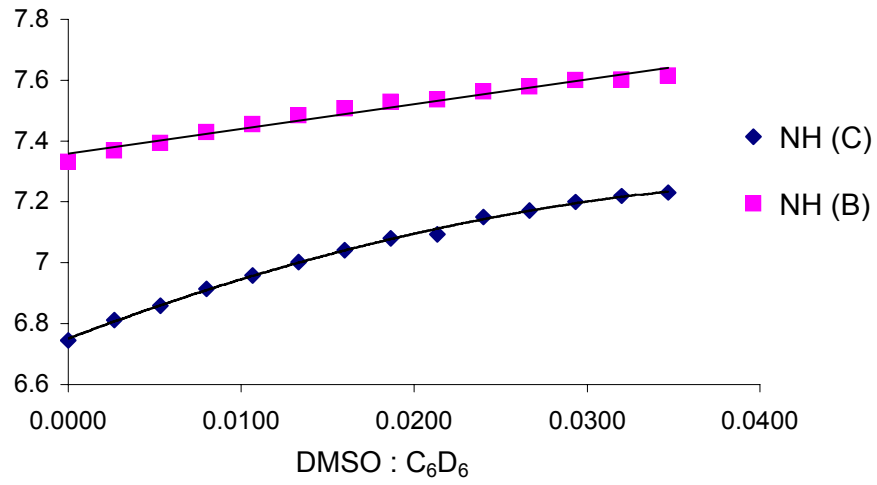
Diisopropylethylamine (90 µL, 0.53 mmol) and TBTU (129 mg, 0.40 mmol) were added to a stirred solution of crude amino ester **20** (100 mg) and crude azido acid D-**11** (53 mg) in DCM (0.5 mL). After 10 minutes, the TLC (EtOAc/petrol, 1:1) showed conversion to a major product (R_f 0.15). The reaction mixture was diluted with DCM (20 mL) and washed with water (2 x 15 mL). The aqueous washes were extracted with DCM (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc) to yield the desired trimer **22** (105 mg, 70 % from **19**).

R_f 0.15 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = +37.4 (c 0.265, $CHCl_3$); ν_{max}/cm^{-1} (film): 3425 (NH), 2987 and 2938 (CH), 2102 (N_3), 1752 and 1726 (C=O, ester), 1670 (Amide I), 1526 (Amide II), 1210 and 1087 (C-O); *m/z* HRMS (ES+) found 558.2771; $C_{24}H_{40}N_5O_{10}$ $[M+H]^+$ requires 558.2770.

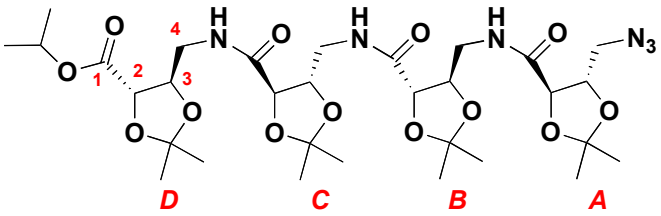
^1H (500 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

Residue	Position		δ_H (ppm)	Multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.0
	C-2		4.29	d	8.2	76.7
	C-3		4.13-4.16	m	-	79.3
	C-4	4	3.37	dd	2.6, 13.4	52.0
		4’	3.12	dd	4.7, 13.4	
B	C-1		-	-	-	170.3
	C-2		3.93	d	7.7	79.0
	C-3		3.97-4.00	m	-	77.9
	C-4	4	4.01-4.05	m	-	41.4
		4’	3.18-3.23	m	-	
	NH		7.33	dd	6.1, 9.9	-
C	C-1		-	-	-	170.1
	C-2		4.12	d	7.1	77.1
	C-3		4.23-4.26	m	-	77.9
	C-4	4	3.52	ddd	5.1, 6.9, 14.0	40.6
		4’	3.40	td	5.1, 8.3	
	NH		6.74	t	5.8, 5.8	-
Others	C*H*(CH_3)$_2$		4.96	sept	6.3	69.0
	i-Pr Me		1.02 (3H)	d	6.3	21.6
	i-Pr Me		0.99 (3H)	d	6.3	21.5
	Isopropylidene q*C*(CH_3)$_2$		-	-	-	111.4, 111.1, 110.5
	Isopropylidene CH_3 groups		1.39, 1.37, 1.35, 1.34, 1.21, 1.17	s	-	27.0, 26.9, 26.8, 26.1, 25.8, 25.5

DMSO titration for **[22]** (addition of 2µL aliquots of DMSO-d_6 to a 5.6 mM solution of trimer **22** in benzene-d_6, 400 MHz, referenced to TMS @ 0 ppm)



(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [6]



Diisopropylethylamine (85 µL, 0.5 mmol) and TBTU (120.4 mg, 0.374 mmol) were added to a stirred solution of crude amino ester **20** (94 mg) and crude azido acid **21** (90 mg) in DCM (0.5 mL). After 10 minutes, the TLC (EtOAc/petrol, 1:1) showed conversion to a major product (R_f 0.1). The reaction mixture was diluted with DCM (20 mL) and washed with water (2 x 15 mL). The aqueous washes were extracted with DCM (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc) to yield the desired tetramer **6** (105 mg, 59% from **19**).

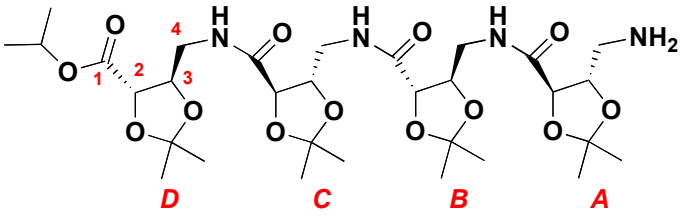
R_f 0.1 (EtOAc/petrol, 1:1); $[\alpha]_D^{25}$ = -19.0 (c 0.105, $CHCl_3$); ν_{max}/cm^{-1} (film): 3426 (NH), 2987 and 2937 (CH), 2102 (N_3), 1751 and 1726 (C=O, ester), 1667 (Amide I), 1525 (Amide II), 1210 and 1087 (C-O); *m/z* HRMS (ES+) found 715.3506; $C_{31}H_{50}N_6O_{13}$ $[M+H]^+$ requires 715.3509.

^1H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

Residue	Position		δ_H (ppm)	multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.1
	C-2		4.30	d	8.2	76.8
	C-3		4.18-4.20	m	-	79.3
	C-4	4	3.41	dd	2.6, 13.4	52.1
		4’	3.15	dd	4.8, 13.4	
B	C-1		-	-	-	170.4
	C-2		4.03	d	7.9	79.6
	C-3		4.08-4.11	m	-	77.9
	C-4	4	4.13-4.16	m	-	41.6
		4’	3.22	ddd	3.6, 7.1, 13.4	
	NH		7.55	dd	3.0, 7.3	-
C	C-1		-	-	-	170.3
	C-2		3.90	dd	7.5, 14.7	79.1
	C-3		3.96-3.99	m	-	77.7
	C-4	4	4.00-4.04	m	-	41.5
		4’	3.17-3.19	m	-	
	NH		7.45	dd	3.2, 7.2	-
D	C-1		-	-	-	170.1
	C-2		4.12	d	7.1	77.1
	C-3		4.25	ddd	4.3, 5.0, 7.1	77.9
	C-4	4	3.53	ddd	5.1, 6.9, 7.1	40.7
		4’	3.38	dd	4.6, 9.4	
	NH		6.74	t	6.0, 6.0	-
Others	C*H*$(CH_3)_2$		4.97	sept	6.3	69.1
	i-Pr Me		1.03 (3H)	d	6.3	21.6
	i-Pr Me		1.00 (3H)	d	6.3	21.5
	Isopropylidene q*C*$(CH_3)_2$		-	-	-	111.5, 111.3, 110.7, 110.6
	Isopropylidene CH_3 groups		1.42, 1.40, 1.36, 1.35, 1.34, 1.30, 1.23, 1.18	s	-	27.1, 27.0, 27.0, 26.8, 26.1, 25.9, 25.8, 25.5

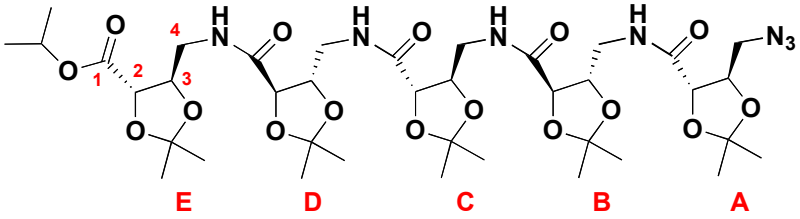
Residue	Position	NOEs to
A	H-2	3A, 4A, 4’A, $C(CH_3)_2$
	H-3	2A, 4A, 4’A, $C(CH_3)_2$
	H-4	2A, 3A, 4’A
	H-4’	2A, 3A, 4A
B	H-2	3B, 4B, 4’B, $C(CH_3)_2$
	H-3	2B, 4B, 4’B, $C(CH_3)_2$
	H-4	2B, 3B, 4’B
	H-4’	2B, 3B, 4B
	NH^B	$H_2{}^B$, $H_3{}^B$, $H_4{}^B$, $H_4{}^{,B}$
C	H-2	3C, 4C, 4’C, $C(CH_3)_2$
	H-3	2C, 4C, 4’C, $C(CH_3)_2$
	H-4	2C, 3C, 4’C
	H-4’	2C, 3C, 4C
	NH^C	$H_2{}^C$, $H_3{}^C$, $H_4{}^C$, $H_4{}^{,C}$
D	H-2	3D, 4D, 4’D, $C(CH_3)_2$
	H-3	2D, 4D, 4’D, $C(CH_3)_2$
	H-4	2D, 3D, 4’D
	H-4’	2D, 3D, 4D
	NH^D	$H_2{}^C$ (w), $H_2{}^D$, $H_3{}^D$, $H_4{}^D$, $H_4{}^{,D}$

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(((4*R*,5*S*)-5-(aminomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [23]



Palladium on activated carbon, 10 wt % (10 % w/w, 20 mg) was added to isopropanol and stirred under a hydrogen atmosphere for 30 minutes. The isopropyl ester **6** (200 mg, 0.28 mmol) was dissolved in isopropanol and added to the reaction mixture (still under a hydrogen atmosphere) *via* syringe. After 1 hour, TLC indicated complete conversion of the starting material to a major product **23**, which was filtered through Celite™ (eluent: isopropanol), concentrated and used without further purification (quantitative crude yield).

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [24]



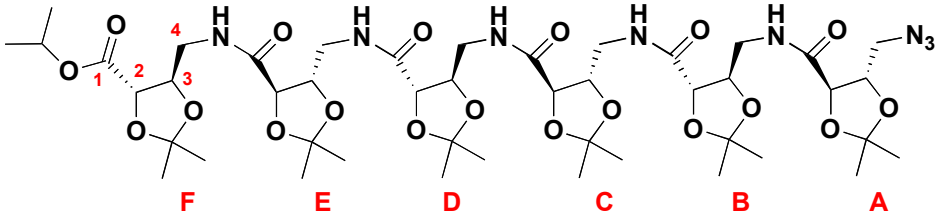
Diisopropylethylamine (50 µL, 0.29 mmol) and TBTU (70 mg, 0.218 mmol) were added to a stirred solution of crude amino ester **23** (100 mg) and crude azido acid D-**11** (30 mg) in DCM (0.5 mL). After 10 minutes, the TLC (EtOAc/petrol, 2:1) showed conversion to a major product (R_f 0.3). The reaction mixture was diluted with DCM (20 mL) and washed with water (2 x 15 mL). The aqueous washes were extracted with DCM (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc) to yield the desired pentamer **24** (77 mg, 63% from **6**).

R_f 0.3 (EtOAc/petrol, 2:1); $[\alpha]_D^{25}$ = -4.6 (c 0.22, $CHCl_3$); ν_{max}/cm^{-1} (film): 3424 (NH), 2987 and 2937 (CH), 2103 (N_3), 1747 (C=O, ester), 1664 (Amide I), 1529 (Amide II), 1211 and 1087 (C-O); *m/z* HRMS (ES+) found 872.4246; $C_{38}H_{62}N_7O_{16}$ $[M+H]^+$ requires 872.4248.

^{1}H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

Residue	Position		δ_H (ppm)	multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	168.5
	C-2		4.31	d	8.2	76.8
	C-3		4.21	ddd	2.6, 4.9, 8.1	79.2
	C-4	4	3.44	dd	2.6, 13.4	52.2
		4’	3.17	dd	2.7, 6.0	
B	C-1		-	-	-	170.5
	C-2		4.06	d	7.9	79.7
	C-3		4.11	ddd	4.6, 7.2, 15.0	77.8
	C-4	4	4.16	dd	1.8, 3.8	41.6
		4’	3.22	ddd	3.5, 7.1, 13.4	
	NH		7.62	dd	3.1, 7.5	-
C	C-1		-	-	-	170.5
	C-2		4.01	d	1.9	79.7
	C-3		4.04	dd	3.9, 7.6	77.8
	C-4	4	4.14	dd	3.7, 5.9	41.6
		4’	3.15	dd	3.5, 7.4	
	NH		7.68	dd	3.2, 7.9	-
D	C-1		-	-	-	170.4
	C-2		3.93	d	7.7	78.9
	C-3		4.00	ddd	2.9, 6.2, 7.7	77.7
	C-4	4	4.04	dd	3.9, 7.6	41.4
		4’	3.18	dd	4.4, 9.0	
	NH		7.45	dd	3.5, 7.4	-
E	C-1		-	-	-	170.2
	C-2		4.15	d	7.0	77.2
	C-3		4.28	ddd	2.1, 3.5, 5.1	77.8
	C-4	4	3.57	ddd	5.2, 6.9, 13.9	40.8
		4’	3.44	dd	2.6, 13.4	
	NH		6.80	t	5.9, 5.9	-
Others	C*H*$(CH_3)_2$		4.97	sept	6.3	69.1
	i-Pr Me		1.04 (3H)	d	6.3	21.6
	i-Pr Me		1.01 (3H)	d	6.3	21.5
	Isopropylidene q*C*$(CH_3)_2$		-	-	-	111.5, 111.3, 110.8, 110.7, 110.6
	Isopropylidene CH_3 groups		1.45, 1.44, 1.36, 1.35, 1.32, 1.29, 1.24, 1.20, 1.20, 1.16	s	-	27.0, 26.9, 26.8, 26.1, 25.9, 25.9, 25.7, 25.5

(4*S*,5*R*)-isopropyl 5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(((4*R*,5*S*)-5-(((4*S*,5*R*)-5-(((4*R*,5*S*)-5-(azidomethyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxamido)methyl)-2,2-dimethyl-1,3-dioxolane-4-carboxylate [7]



Diisopropylethylamine (40 μL, 0.232 mmol) and TBTU (56 mg, 0.174 mmol) were added to a stirred solution of crude amino ester **23** (80 mg) and crude azido acid **21** (40.5 mg) in DCM (0.25 mL). After 10 minutes, the TLC (EtOAc/petrol, 2:1) showed conversion to a major product (R_f 0.2). The reaction mixture was diluted with DCM (20 mL) and washed with water (2 x 15 mL). The aqueous washes were extracted with DCM (2 x 20 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc) to yield the desired hexamer **7** (85 mg, 59% from **6**).

R_f 0.2 (EtOAc/petrol, 2:1); $[\alpha]_D^{25}$ = -12.6 (c 0.475, $CHCl_3$); ν_{max}/cm^{-1} (film): 3471 (NH), 2987 and 2935 (CH), 2103 (N_3), 1747 (C=O, ester), 1656 (Amide I), 1530 (Amide II), 1212 and 1085 (C-O); *m/z* HRMS (ES+) found 1046.5250; $C_{45}H_{76}N_9O_{19}$ $[M+NH_4]^+$ requires 1046.5252.

^{1}H (700 MHz, 5.6 mM in benzene-d_6 @ 7.15 ppm) and ^{13}C (125 MHz, benzene-d_6)

Residue	Position		δ_H (ppm)	multiplicity	J (Hz)	δ_C (ppm)
A	C-1		-	-	-	170.1
	C-2		4.30	d	8.2	76.8
	C-3		4.22	dd	2.6, 4.8	79.2
	C-4	4	3.46	dd	2.6, 13.5	52.2
		4’	3.19	dd	4.8, 13.5	
C	C-1		-	-	-	170.5
	C-2		4.04	d	8.3	79.7
	C-3		4.06-4.09	m	-	77.8
	C-4	4	4.16-4.19	m	-	41.6
		4’	3.15-3.18	m	-	
	NH		7.74	dd	3.6	-
B*	C-1		-	-	-	170.5
	C-2		4.01-4.03	m	-	79.7
	C-3		4.27-4.29	m	-	77.8
	C-4	4	4.13-4.15	m	-	41.6
		4’	3.13-3.16	m	-	
	NH		7.64	m	-	-
D*	C-1		-	-	-	170.4
	C-2		4.02-4.04	m	-	78.9
	C-3		4.06-4.08	m	-	77.7
	C-4	4	4.11-4.14	m	-	41.4
		4’	3.23-3.26	m	-	
	NH		7.64	m	-	-
E	C-1		-	-	-	170.4
	C-2		3.99	d	7.8	79.7
	C-3		4.02-4.04	m	-	77.8
	C-4	4	4.06-4.08	m	-	41.5
		4’	3.23-3.26	m	-	
	NH		7.51	dd	3.3, 7.6	-
F	C-1		-	-	-	170.1
	C-2		4.15	d	7.0	77.2
	C-3		4.27-4.29	m	-	77.8
	C-4	4	3.56-3.60	m	-	41.4
		4’	3.41-3.44	m	-	
	NH		6.82	t	6.0, 6.0	-
Others	C*H*$(CH_3)_2$		4.97	sept	6.3	69.1
	i-Pr Me		1.04 (3H)	d	6.3	21.6
	i-Pr Me		1.01 (3H)	d	6.3	21.5
	Isopropylidene q*C*$(CH_3)_2$		-	-	-	111.5, 111.3, 110.9, 110.8, 110.8, 110.6
	Isopropylidene CH_3 groups		1.47, 1.44, 1.43, 1.42, 1.37, 1.37, 1.35, 1.33, 1.31, 1.31, 1.25, 1.21	s	-	27.1, 27.0, 27.0, 26.9, 26.8, 26.1, 26.0, 26.0, 25.9, 25.8, 25.8, 25.6

*Due to resonance overlap, unambiguous sequence-specific assignments were not possible (though each individual spin system can be identified) and so these are tentative assignments based on the available data. Consequently, the sequence of these residues may be reversed.

[i] A. S. Batsanov, M. J. Begley, R. J. Fletcher and J. A. Murphy, *J. Chem. Soc., Perkin Trans. 1*, **1995**, 1281.