Supplementary Information

Modulation of DNA-Polyamide Interaction by *β*-alanine Substitutions: A Study of Positional Effects on Binding Affinity, Kinetics and Thermodynamics

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Section 1. Biophysical results

Table S1. Binding enthalpy (Δ*H*) of KA1033, KJK6021 and KA2127 determined by ITC.

[ligand] (μM)	**1/ [ligand] (μM^{-1})**	**Binding enthalpy (Δ*H*, kcal mol^{-1})**		
		KA1033	**KJK6021**	**KA2127**
10.0	0.10	--	-0.3 ± 0.1	-2.2 ± 0.1
5.0	0.20	-0.15 ± 0.05	-6.7 ± 0.2	-8.3 ± 0.3
3.3	0.30	-4.4 ± 0.1	-11.7 ± 0.2	-11.9 ± 0.2
2.5	0.40	-8.5 ± 0.2	-14.3 ± 0.2	-13.0 ± 0.4
2.0	0.50	-11.8 ± 0.2	-13.9 ± 0.2	-12.9 ± 0.3
1.5	0.67	-11.8 ± 0.3	-14.4 ± 0.3	-13.0 ± 0.5

* Errors listed are the standard errors for the fit to the 1:1 binding model. The binding enthalpy for KA1033 with 10 μM sample could not be measured due to the compound aggregation.

Table S2. ΔT_m values of KA1033, KJK6021 and their derivatives with different counterions (KJK6053 and KJK6064, respectively) binding to their cognate and mutant DNA sequences*. PAs are classified based on their C-terminus groups and counterions.

		Dp group		Ta group	
DNA sequence	**T_m (°C) for free DNA**	**KA1033 ·CF_3COO^-**	**KJK6053 ·$HCOO^-$**	**KJK6064 ·CF_3COO^-**	**KJK6021 ·$HCOO^-$**
TGGAGA	67.7	7.8	7.8	9.1	8.8
1.TGCAGA	69.8	0.6	0.5	2.5	2.6
2.TGGCGA	75.0	3.4	3.4	5.1	5.0
3.TGGATA	64.1	6.9	6.7	8.0	7.9
4.TGGTGA	69.5	9.0	8.9	10.3	10.2
5.TGAGGA	68.1	4.3	4.5	6.4	6.3

*The error of these ΔT_m values is ± 0.2 ºC, based on experimental reproducibility.

(A)

Cognate sequence:	5′-CCT**TGGAGA**G TTTT CTCTCCAAGG
Mutant sequences: 1.	5′-CCT**TGCAGA**G TTTT CTCTGCAAGG
2.	5′-CCT**TGGCGA**G TTTT CTCGCCAAGG
3.	5′-CCT**TGGATA**G TTTT CTATCCAAGG
4.	5′-CCT**TGGTGA**G TTTT CTCACCAAGG
5.	5′-CCT**TGAGGA**G TTTT CTCCTCAAGG

(B)

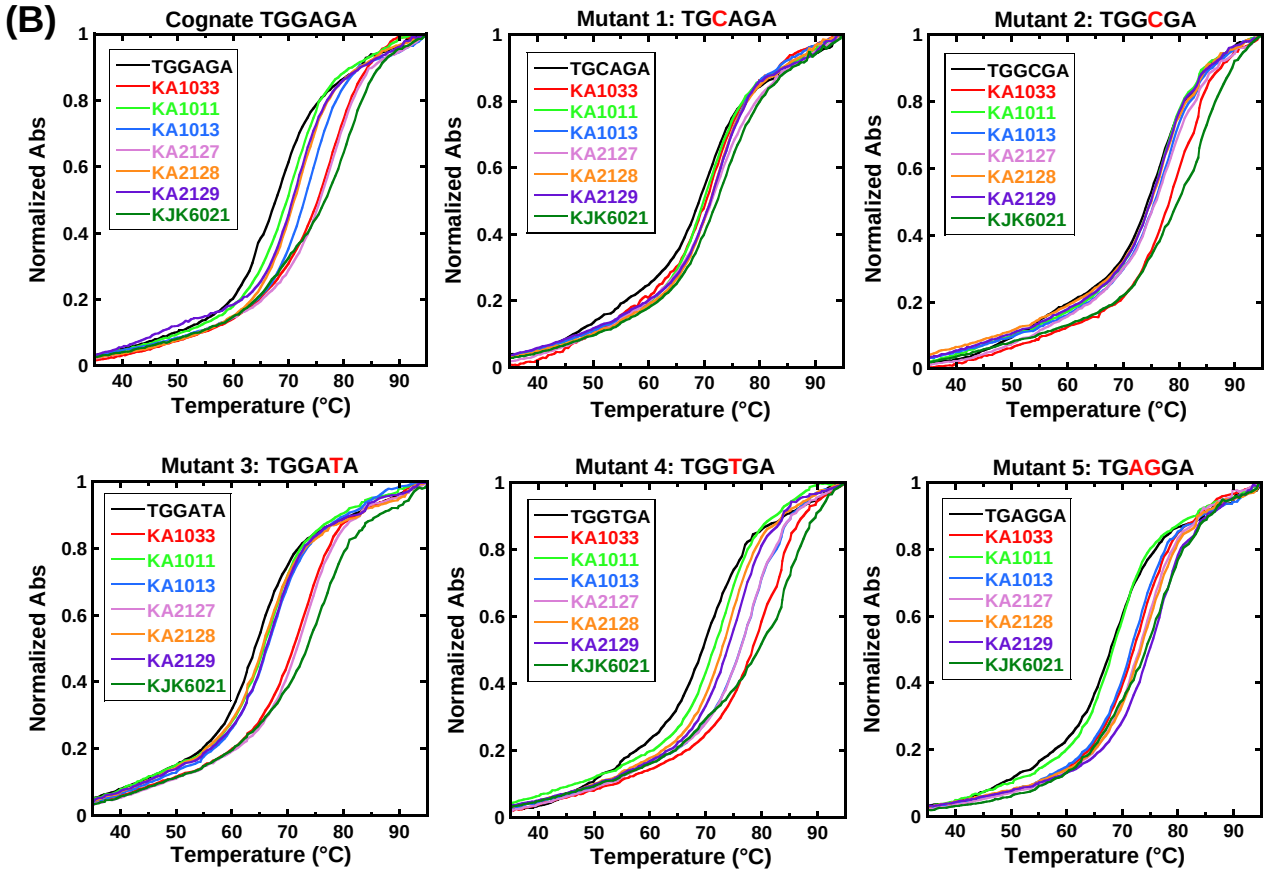


Figure S1. (A) Cognate and mutant DNA sequences. **(B)** Normalized melting curves for six PAs with cognate and mutant DNAs at 1:1 molar ratio.

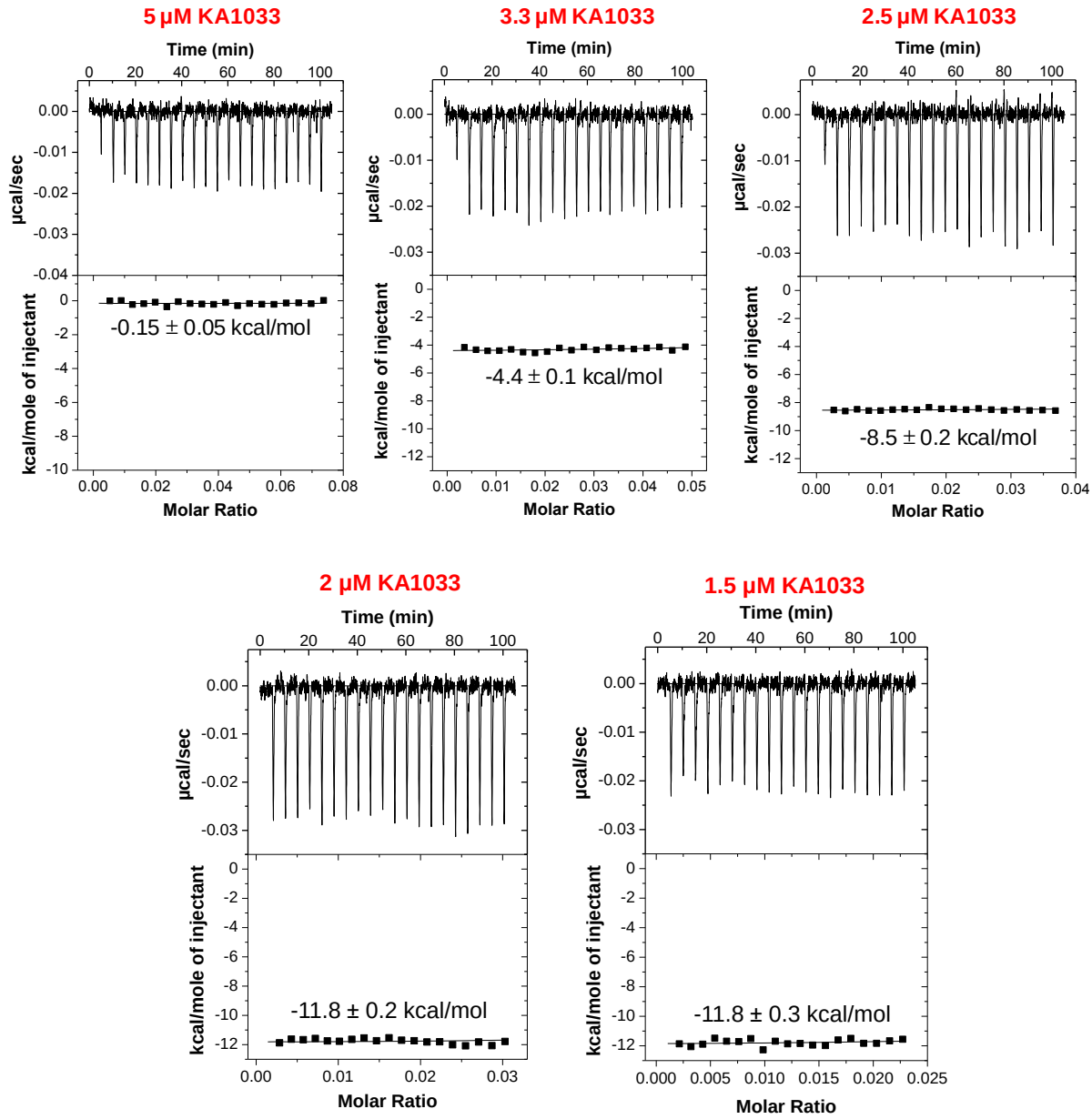


Figure S2. ITC titrations of 5, 3.3, 2.5, 2, 1.5 µM of KA1033 into 10 µM TGGAGA hairpin duplexes at 25 ºC are shown at the top of each panel. The integrated heats after subtraction of the heat of dilution are plotted versus KA1033/DNA molar ratio in the bottom of each panel. Errors listed are the standard errors for the fit to the 1:1 binding model.

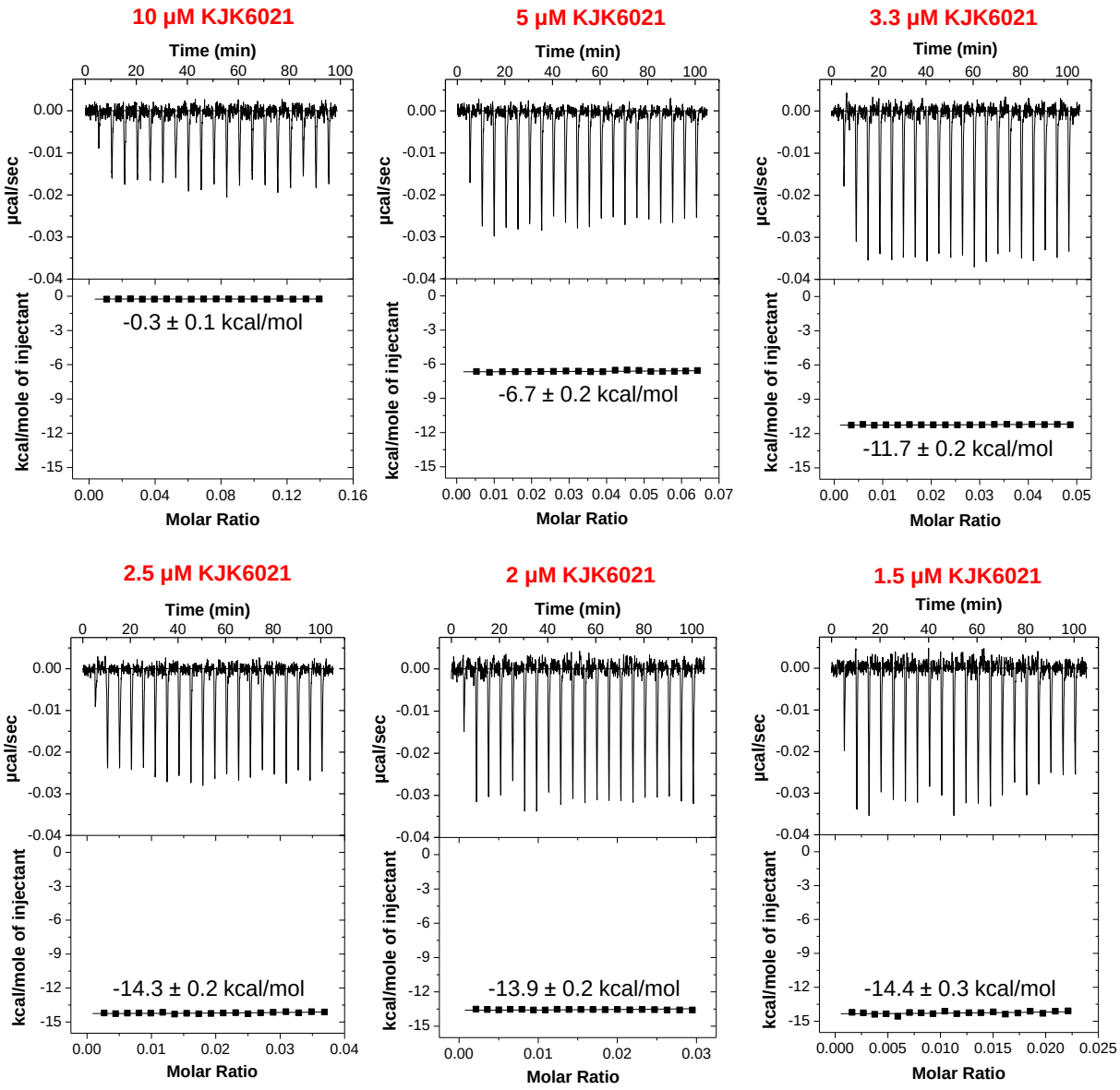


Figure S3. ITC titrations of 10, 5, 3.3, 2.5, 2, 1.5 µM of KJK6021 into 10 µM TGGAGA hairpin duplexes at 25 ºC are shown at the top of each panel. The integrated heats after subtraction of the heat of dilution are plotted versus KJK6021/DNA molar ratio in the bottom of each panel. Errors listed are the standard errors for the fit to the 1:1 binding model.

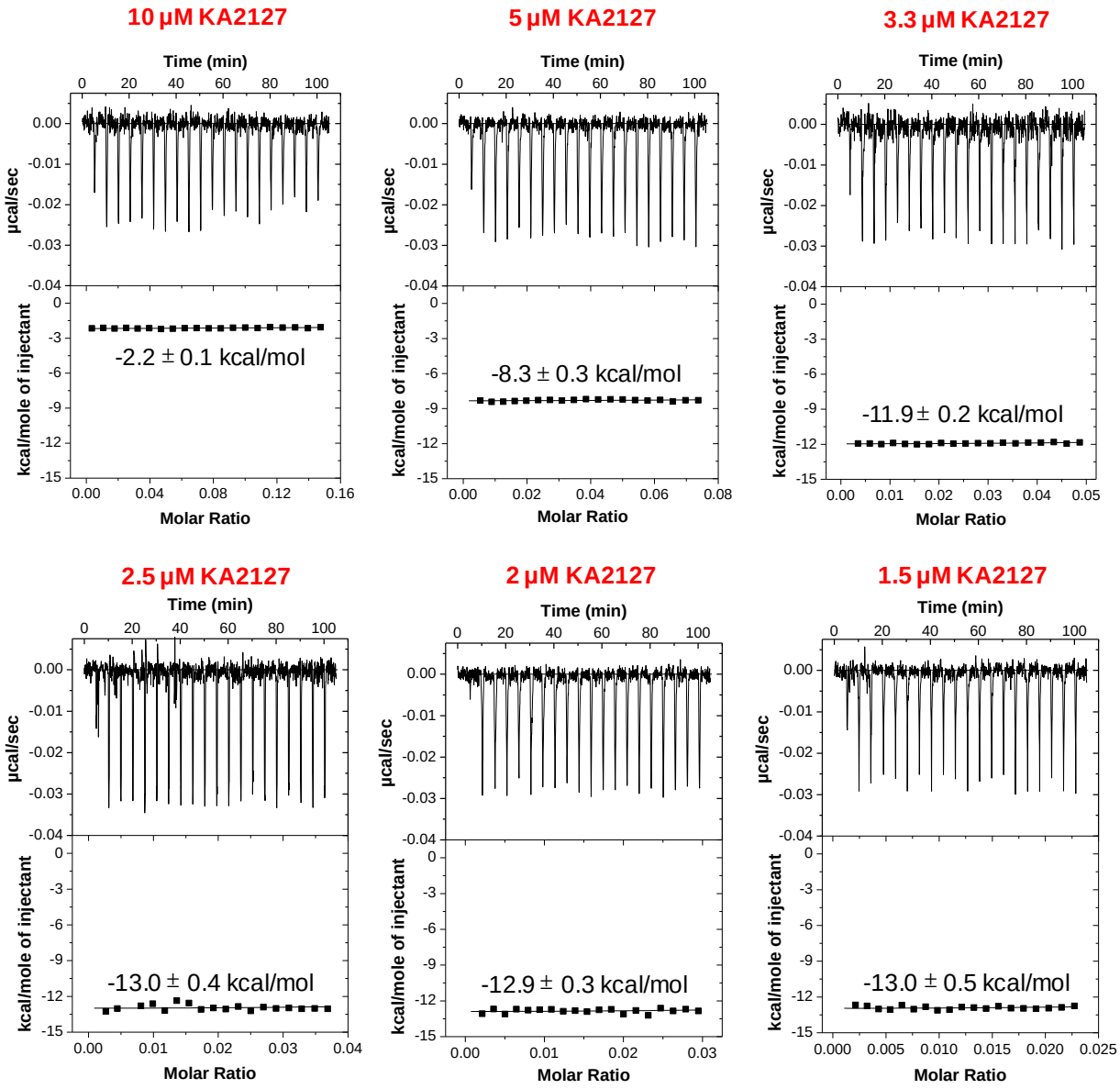


Figure S4. ITC titrations of 10, 5, 3.3, 2.5, 2, 1.5 µM of KA2127 into 10 µM TGGAGA hairpin duplexes at 25 ºC are shown at the top of each panel. The integrated heats after subtraction of the heat of dilution are plotted versus KA2127/DNA molar ratio in the bottom of each panel. Errors listed are the standard errors for the fit to the 1:1 binding model.

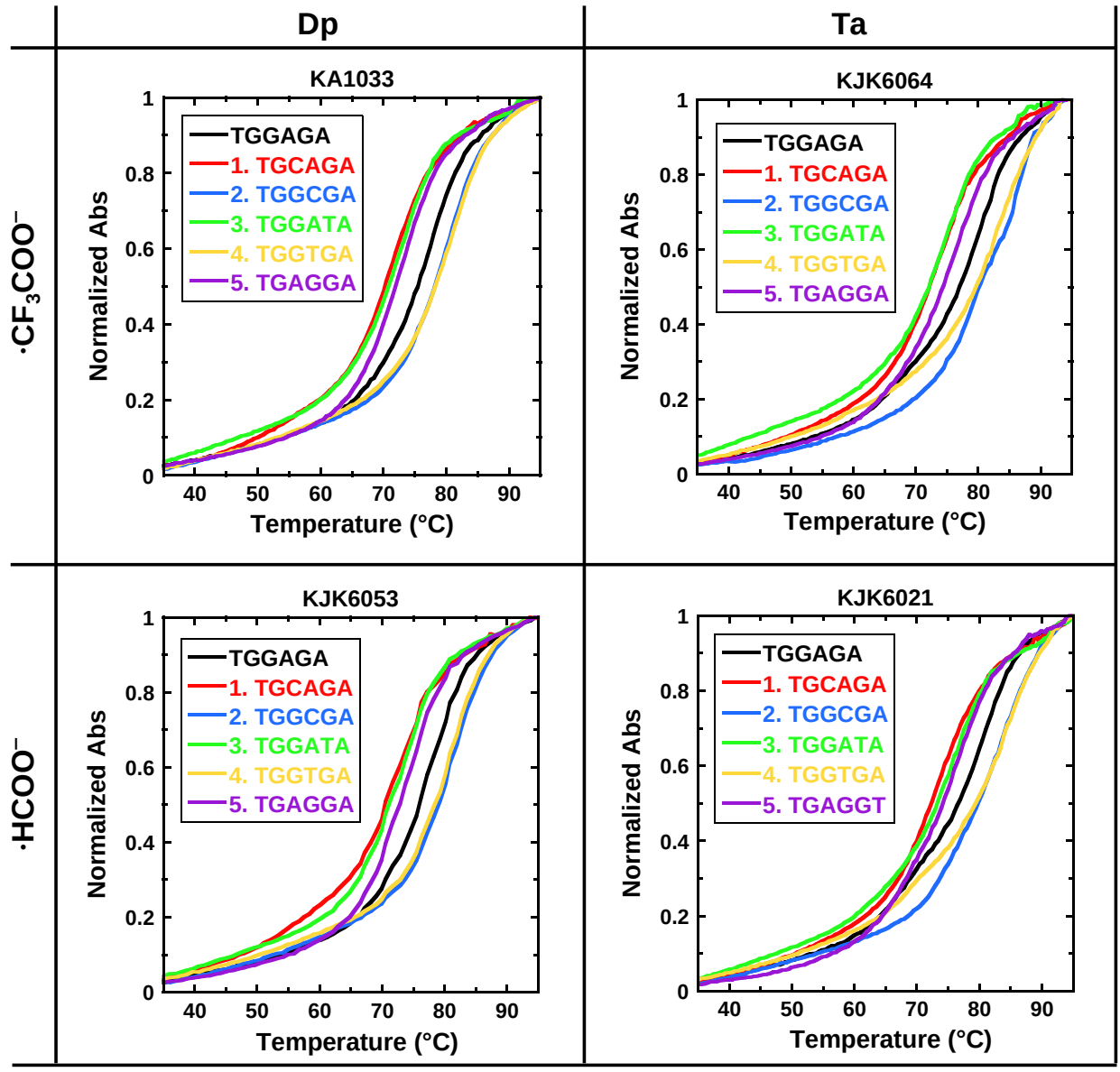


Figure S5. Normalized melting curves for KA1033, KJK6021, KJK6053 and KJK6064 with cognate and mutant DNAs at 1:1 molar ratio. PAs are classified based on their C-terminus groups and counterions.

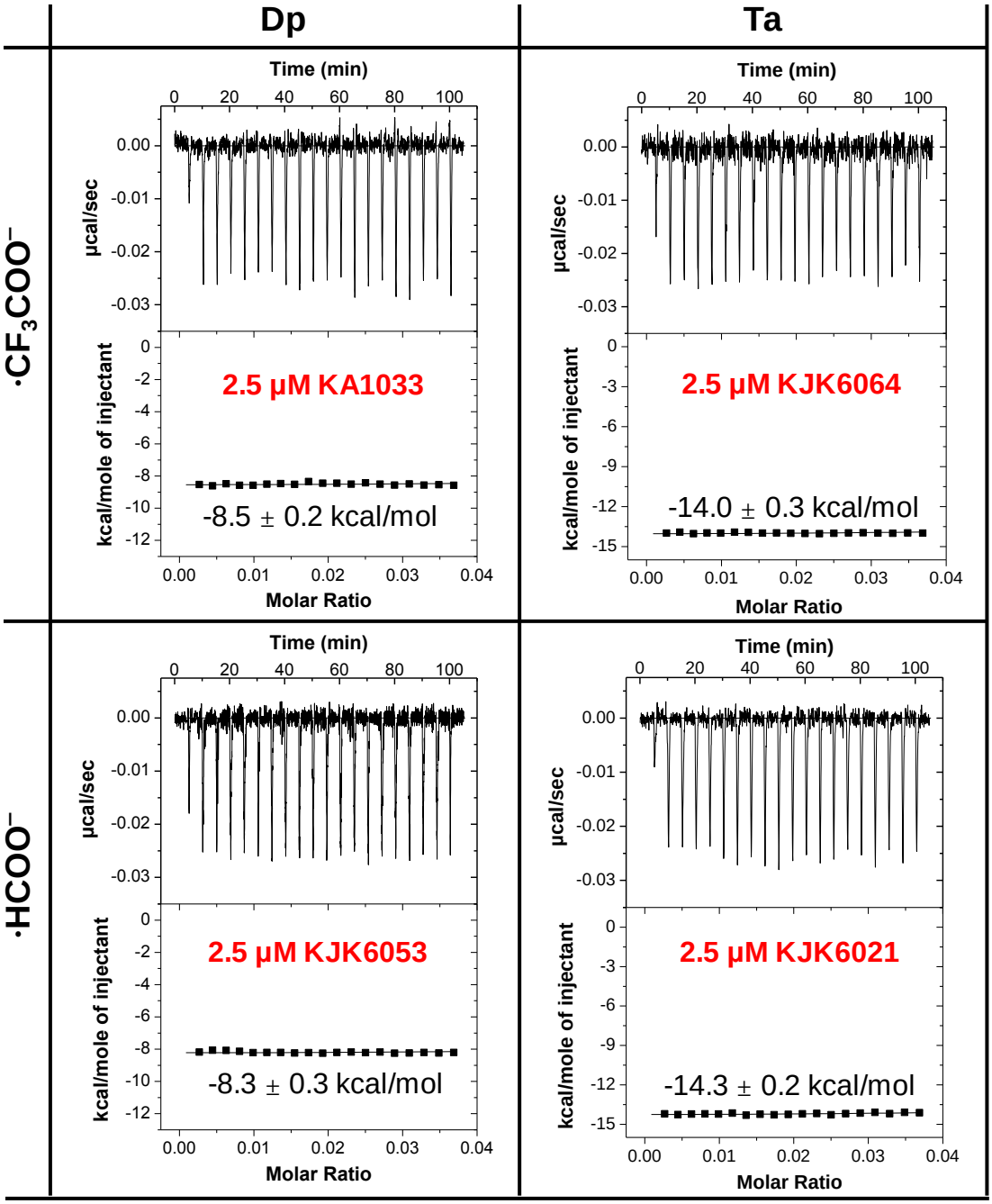


Figure S6. ITC titrations 2.5 µM of KA1033, KJK6021, KJK6053 and KJK6064 into 10 µM TGGAGA hairpin duplexes at 25 ºC are shown at the top of each panel. The integrated heats after subtraction of the heat of dilution are plotted versus PA/DNA molar ratio in the bottom of each panel. Errors listed are the standard errors for the fit to the 1:1 binding model. PAs are classified based on their C-terminus groups and counterions.

Section 2. Synthetic details

Chemical Characterization, Use of Dimers in Polyamide Syntheses, and Dimer Syntheses

KA1033 (ImImPyImγPyPyPyPyβDp TFA salt):

^{1}H NMR (500 MHz, DMSO-d_6) δ = 10.28 (s, 1 H), 10.26 (s, 1 H), 9.93 (s, 1 H), 9.91 (s, 1 H), 9.89 (s, 1 H), 9.84 (s, 1 H), 9.76 (s, 1 H), 9.23 (br. s., 1 H), 8.09 - 8.00 (m, *J* = 5.7, 10.6, 10.6 Hz, 6 H), 7.58 (s, 1 H), 7.50 (s, 1 H), 7.46 (s, 1 H), 7.39 (d, *J* = 1.6 Hz, 1 H), 7.23 (d, *J* = 1.6 Hz, 1 H), 7.22 (d, *J* = 1.6 Hz, 1 H), 7.16 (s, 3 H), 7.08 (d, *J* = 1.0 Hz, 1 H), 7.07 (s, 2 H), 6.90 - 6.87 (m, 2 H), 4.01 (s, 6 H), 3.94 (s, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.42 - 3.35 (m, 2 H), 3.33 - 3.26 (m, 2 H), 3.15 - 3.08 (m, 2 H), 3.04 - 2.97 (m, 2 H), 2.74 (d, *J* = 5.1 Hz, 6 H), 2.38 - 2.33 (m, 2 H), 2.28 (t, *J* = 7.5 Hz, 2 H), 1.85 - 1.78 (m, 2 H), 1.78 - 1.70 (m, 2 H)

EA calc'd for $C_{57}H_{70}N_{22}O_{10}$ (7 CF_3CO_2H)(6 H_2O): C, 40.04%; H, 4.21%; N, 14.47%. Found: C, 40.79%; H, 3.96%; N, 13.43%.

HRMS (ESI) calc'd for $C_{57}H_{71}N_{22}O_{10}$ $[MH]^+$, 1223.5724, found, 1223.5736.

KA2127 (ImImPyImγPyβPyPyβTa formate salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.30 (s, 1 H), 10.30 (s, 1 H), 9.94 (s, 1 H), 9.89 (s, 1 H), 9.82 (s, 1 H), 8.35 (br. s., 2 H), 8.09 (t, *J* = 5.6 Hz, 1 H), 8.06 (t, *J* = 5.9 Hz, 1 H), 8.02 (t, *J* = 5.6 Hz, 1 H), 7.95 (t, *J* = 5.6 Hz, 1 H), 7.58 (s, 1 H), 7.49 (s, 1 H), 7.46 (s, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H), 7.17 (s, 2 H), 7.15 (d, *J* = 1.8 Hz, 1 H), 7.11 (d, *J* = 1.8 Hz, 1 H), 7.08 (s, 1 H), 6.86 (s, 1 H), 6.83 (s, 1 H), 6.65 (d, *J* = 1.8 Hz, 1 H), 4.01 (s, 6 H), 3.93 (s, 3 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.42 (td, *J* = 7.0, 12.9 Hz, 2 H), 3.39 - 3.32 (m, *J* = 1.0, 1.0, 1.0 Hz, 2 H), 3.31 - 3.23 (m, *J* = 1.0, 1.0, 1.0 Hz, 2 H), 3.06 (q, *J* = 6.5 Hz, 2 H), 2.81 (t, *J* = 7.0 Hz, 2 H), 2.53 - 2.46 (m, 2 H), 2.36 - 2.29 (m, 4 H), 2.29 - 2.22 (m, 4 H), 2.09 (s, 3 H), 1.83 - 1.74 (m, 2 H), 1.70 - 1.60 (m, 2 H), 1.52 (quin, *J* = 6.9 Hz, 2 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 170.4, 169.0, 167.8, 161.2, 158.7, 158.7, 158.4, 155.8, 155.6, 137.8, 136.0, 134.7, 134.4, 134.1, 127.7, 127.1, 122.8, 122.7, 122.2, 122.1, 121.9, 121.9, 121.4, 119.5, 118.2, 117.9, 117.6, 114.3, 114.1, 105.8, 104.2, 103.9, 103.4, 54.6, 54.3, 41.3, 40.0, 38.0, 37.7, 36.6, 36.3, 36.1, 36.0, 35.8, 35.6, 35.5, 35.5, 35.2, 35.2, 34.9, 33.1, 26.7, 25.6, 24.5

EA calc'd for $C_{56}H_{74}N_{22}O_{10}$ (5 HCO_2H): C, 50.69%; H, 5.86%; N, 21.32%. Found: C, 50.93; H, 6.34%; N, 20.96%.

HRMS (ESI) calc'd for $C_{56}H_{74}N_{22}O_{10}$ $[M]^+$, 1214.5958, found, 1214.5952.

KA2128 (ImImβImγPyβPyPyβTa formate salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.38 (s, 1 H), 9.94 (s, 1 H), 9.89 (s, 1 H), 9.80 (s, 1 H), 8.35 (br. s., 2 H), 8.24 (t, *J* = 5.6 Hz, 1 H), 8.14 - 8.06 (m, 1 H), 8.06 - 8.00 (m, 1 H), 8.00 - 7.91 (m, 2 H), 7.52 (s, 1 H), 7.43 (s, 1 H), 7.41 (s, 1 H), 7.18 (s, 2 H), 7.10 (s, 1 H), 7.05 (s, 1 H), 6.86 (s, 1 H), 6.83 (s, 1 H), 6.64 (s, 1 H), 3.99 (s, 3 H), 3.96 (s, 3 H), 3.89 (s, 3 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.54 - 3.46 (m, 2 H), 3.46 - 3.39 (m, *J* = 5.9 Hz, 2 H), 3.39 - 3.32 (m, 2 H), 3.29 - 3.21 (m, 2 H), 3.06 (q, *J* = 6.5 Hz, 2 H), 2.81 (t, *J* = 6.7 Hz, 2 H), 2.59 (t, *J* = 6.7 Hz, 2 H), 2.56 - 2.47 (m, 2 H), 2.33 (t, *J* = 7.0 Hz, 4 H), 2.25 (td, *J* = 7.3, 14.2 Hz, 4 H), 2.09 (s, 3 H), 1.77 (quin, *J* = 6.9 Hz, 2 H), 1.72 - 1.61 (m, 2 H), 1.57 - 1.48 (m, 2 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 170.4, 169.0, 168.5, 167.8, 161.2, 158.7, 158.4, 158.3, 155.9, 137.8, 135.8, 134.7, 134.1, 133.9, 127.6, 127.0, 122.8, 122.7, 122.1, 121.9, 118.2, 117.9, 117.7, 113.9, 113.6, 104.2, 103.9, 103.4, 54.5, 54.3, 54.0, 41.3, 41.2, 40.0, 38.1, 37.7, 37.2, 36.6, 36.1, 36.0, 36.0, 35.8, 35.6, 35.5, 35.5, 35.1, 35.1, 34.9, 34.9, 34.9, 33.1, 26.7, 25.6, 24.6, 24.4

EA calc'd for $C_{53}H_{73}N_{21}O_{10}$ (5 HCO_2H): C, 49.96%; H, 6.00%; N, 21.09%. Found: C, 50.08; H, 6.57%; N, 21.38%.

HRMS (ESI) calc'd for $C_{53}H_{73}N_{21}O_{10}$ $[M]^+$, 1163.5849, found, 1163.5833.

KA2129 (ImImβImγPyPyβPyβTa formate salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.37 (s, 1 H), 9.87 (s, 1 H), 9.86 (s, 1 H), 9.83 (s, 1 H), 9.79 (br. s., 1 H), 8.23 (t, *J* = 6.2 Hz, 1 H), 8.15 (s, 1 H), 8.07 (t, *J* = 5.6 Hz, 1 H), 8.03 (t, *J* = 5.6 Hz, 1 H), 7.99 (t, *J* = 5.9 Hz, 2 H), 7.52 (s, 1 H), 7.43 (s, 1 H), 7.41 (s, 1 H), 7.18 (d, *J* = 1.2 Hz, 1 H), 7.14 (d, *J* = 1.2 Hz, 1 H), 7.12 (d, *J* = 1.8 Hz, 1 H), 7.05 (s, 1 H), 6.84 (d, *J* = 1.8 Hz, 1 H), 6.83 (d, *J* = 1.8 Hz, 1 H), 6.66 (d, *J* = 1.8 Hz, 1 H), 6.60 (br. s., 1 H), 3.98 (s, 3 H), 3.96 (s, 3 H), 3.90 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.53 - 3.47 (m, 2 H), 3.45 - 3.40 (m, 2 H), 3.40 - 3.32 (m, 2 H), 3.29 - 3.23 (m, 2 H), 3.12 - 3.04 (m, 2 H), 2.88 - 2.82 (m, 2 H), 2.76 - 2.67 (m, 2 H), 2.67 - 2.62 (m, 2 H), 2.60 (t, *J* = 6.7 Hz, 2 H), 2.50 - 2.47 (m, 2 H), 2.41 (br. s., 3 H), 2.32 (t, *J* = 7.0 Hz, 2 H), 2.26 (t, *J* = 7.3 Hz, 2 H), 1.83 - 1.74 (m, 4 H), 1.68 - 1.59 (m, 2 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 170.7, 169.1, 168.5, 167.8, 163.1, 161.3, 161.2, 158.7, 158.4, 158.3, 155.9, 137.8, 135.8, 134.7, 134.1, 133.9, 127.6, 127.0, 122.8, 122.8, 122.7, 122.1, 122.0, 121.9, 118.1, 118.0, 117.7, 113.9, 113.6, 104.2, 103.9, 103.5, 53.9, 53.2, 40.3, 40.0, 38.1, 37.3, 37.0, 36.1, 36.0, 35.8, 35.6, 35.5, 35.5, 35.1, 35.1, 34.9, 34.9, 34.9, 33.2, 25.6, 25.4, 23.1

EA calc'd for $C_{53}H_{73}N_{21}O_{10}$ (5 HCO_2H)(6 H_2O): C, 46.36%; H, 6.37%; N, 19.58%. Found: C, 46.47; H, 5.76%; N, 19.13%.

HRMS (ESI) calc'd for $C_{53}H_{73}N_{21}O_{10}$ $[M]^+$, 1163.5849, found, 1163.5825.

KJK6021 (ImImPyImγPyPyPyPyβTa formate salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.31 (s, 1 H), 10.29 (s, 1 H), 9.96 (s, 1 H), 9.94 (s, 1 H), 9.93 (s, 1 H), 9.91 (s, 1 H), 8.41 (s, 2 H), 8.07 (t, *J* = 6.2 Hz, 1 H), 8.04 (t, *J* = 5.6 Hz, 1 H), 7.98 (t, *J* = 5.6 Hz, 1 H), 7.57 (s, 1 H), 7.50 (s, 1 H), 7.45 (s, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H), 7.23 (s, 2 H), 7.19 (d, *J* = 1.2 Hz, 1 H), 7.17 (d, *J* = 1.2 Hz, 1 H), 7.16 (d, *J* = 1.8 Hz, 1 H), 7.07 (s, 1 H), 7.06 (d, *J* = 1.2 Hz, 1 H), 7.05 (s, 1 H), 6.89 (s, 1 H), 6.85 (d, *J* = 1.2 Hz, 1 H), 4.01 (s, 3 H), 4.01 (s, 3 H), 3.94 (s, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.81 - 3.79 (m, 3 H), 3.40 - 3.33 (m, 2 H), 3.32 - 3.26 (m, 2 H), 3.06 (q, *J* = 6.5 Hz, 2 H), 2.78 (t, *J* = 6.7 Hz, 2 H), 2.37 - 2.21 (m, 8 H), 2.08 (s, 3 H), 1.81 (td, *J* = 7.1, 14.5 Hz, 2 H), 1.66 (td, *J* = 7.1, 14.5 Hz, 2 H), 1.52 (td, *J* = 7.0, 13.6 Hz, 2 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 170.4, 169.1, 165.5, 161.2, 158.7, 158.7, 158.5, 158.5, 158.4, 155.7, 155.6, 137.8, 136.0, 134.7, 134.4, 134.1, 127.7, 127.1, 122.8, 122.7, 122.7, 122.2, 122.2, 122.2, 122.1, 122.0, 121.3, 119.5, 118.5, 118.4, 118.1, 117.9, 114.3, 114.0, 105.8, 104.7, 104.2, 104.0, 54.5, 54.4, 41.4, 40.0, 38.0, 37.7, 36.6, 36.2, 36.1, 36.1, 36.0, 35.5, 35.5, 35.2, 35.1, 34.9, 33.1, 26.7, 25.6, 24.9

EA calc'd for $C_{59}H_{75}N_{23}O_{10}$ (5 HCO_2H)(6 H_2O): C, 47.91%; H, 6.09%; N, 20.08%. Found: C, 47.46; H, 6.13%; N, 20.48%.

HRMS (ESI) calc'd for $C_{59}H_{75}N_{23}O_{10}$ $[M]^+$, 1265.6067, found, 1265.5994.

KJK6053 (ImImPyImγPyPyPyPyβDp formate salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.30 (s, 1 H), 10.28 (s, 1 H), 9.95 (s, 1 H), 9.93 (s, 1 H), 9.91 (s, 1 H), 9.88 (s, 1 H), 8.33 (s, 2 H), 8.07 (t, *J* = 5.6 Hz, 1 H), 8.01 (t, *J* = 5.0 Hz, 1 H), 7.91 (t, *J* = 5.0 Hz, 1 H), 7.58 (s, 1 H), 7.50 (s, 1 H), 7.45 (s, 1 H), 7.39 (s, 1 H), 7.24 (s, 2 H), 7.20 (s, 1 H), 7.17 (s, 1 H), 7.15 (s, 1 H), 7.07 (s, 1 H), 7.06 (s, 1 H), 7.05 (s, 1 H), 6.89 (s, 1 H), 6.83 (s, 1 H), 4.02 (s, 3 H), 4.01 (s, 3 H), 3.94 (s, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.36 (q, *J* = 6.0 Hz, 2 H), 3.29 (q, *J* = 6.5 Hz, 2 H), 3.06 (q, *J* = 6.5 Hz, 2 H), 2.83 - 2.75 (m, 2 H), 2.35 - 2.23 (m, 6 H), 2.15 (s, 3 H), 1.85 - 1.77 (m, 2 H), 1.70 - 1.62 (m, 2 H), 1.54 (td, *J* = 6.8, 13.9 Hz, 2 H), 1.23 (s, 2 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 170.4, 169.1, 161.2, 158.7, 158.7, 158.5, 158.5, 158.4, 155.7, 155.6, 137.8, 136.0, 134.7, 134.4, 134.1, 127.7, 127.1, 122.8, 122.7, 122.7, 122.2, 122.2, 122.2, 122.1, 122.0, 121.3, 119.5, 118.5, 118.4, 118.2, 117.9, 114.3, 114.1, 105.8, 104.7, 104.7, 104.1, 104.0, 56.4, 44.8, 44.7, 40.0, 38.0, 36.7, 36.2, 36.1, 36.0, 35.5, 35.5, 35.2, 35.1, 34.9, 33.1, 26.8, 25.7

EA calc'd for $C_{57}H_{70}N_{22}O_{10}$ (5 HCO_2H)(3 H_2O): C, 49.40%; H, 5.75%; N, 20.44%. Found: C, 49.47%; H, 5.82%; N, 19.63%.

KJK6064 (ImImPyImγPyPyPyPyβTa TFA salt):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 10.28 (s, 1 H), 10.26 (s, 1 H), 9.93 (s, 1 H), 9.91 (s, 1 H), 9.89 (s, 1 H), 9.85 (s, 1 H), 9.82 (s, 1 H), 9.67 (br. s., 1 H), 8.10 (t, *J* = 5.9 Hz, 1 H), 8.08 - 8.02 (m, 2 H), 7.95 (br. s., 1 H), 7.89 (br. s., 3 H), 7.58 (s, 1 H), 7.50 (s, 1 H), 7.47 (s, 1 H), 7.39 (d, *J* = 1.8 Hz, 1 H), 7.23 (d, *J* = 1.2 Hz, 1 H), 7.22 (d, *J* = 1.8 Hz, 1 H), 7.17 (d, *J* = 1.8 Hz, 1 H), 7.16 (d, *J* = 1.2 Hz, 2 H), 7.10 (s, 1 H), 7.07 (s, 2 H), 6.90 - 6.87 (m, 2 H), 4.01 (s, 6 H), 3.94 (s, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.42 - 3.35 (m, 2 H), 3.30 (q, *J* = 6.5 Hz, 2 H), 3.22 - 3.16 (m, 2 H), 3.16 - 3.10 (m, 2 H), 3.10 - 2.98 (m, 2 H), 2.91 - 2.83 (m, 2 H), 2.74 (d, *J* = 4.7 Hz, 3 H), 2.36 (t, *J* = 7.3 Hz, 2 H), 2.29 (t, *J* = 7.3 Hz, 2 H), 1.97 - 1.88 (m, 2 H), 1.86 - 1.74 (m, 4 H)

EA calc'd for $C_{59}H_{75}N_{23}O_{10}$ (6 CF_3CO_2H)(6 H_2O): C, 41.42%; H, 4.55%; N, 15.65%. Found: C, 42.22%; H, 4.20%; N, 14.82%.

KA1071D (BOCPyβCO_2H, Figure S7):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 12.17 (br. s., 1 H), 9.03 (s, 1 H), 7.97 (t, *J* = 5.3 Hz, 1 H), 6.82 (s, 1 H), 6.61 (s, 1 H), 3.75 (s, 3 H), 3.36 - 3.31 (m, 2 H), 2.45 (t, *J* = 7.3 Hz, 2 H), 1.44 (s, 9 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 173.0, 161.2, 152.8, 122.8, 122.2, 116.4, 103.3, 78.2, 35.9, 34.8, 34.0, 28.2

HRMS (FAB) calc'd for $C_{14}H_{21}N_3O_5$ $[M + Na]^+$, 334.1379, found, 334.1380.

KA1173B (BOCβPyCO_2H, Figure S8) (for large scale prep, see below and Figure S9):

^{1}H NMR (600 MHz, DMSO-d_6) δ = 12.16 (s, 1 H), 9.83 (s, 1 H), 7.28 (s, 1 H), 6.80 (s, 1 H), 6.65 (d, *J* = 1.8 Hz, 1 H), 3.79 (d, *J* = 1.0 Hz, 3 H), 3.20 - 3.14 (m, 2 H), 2.37 (t, *J* = 7.3 Hz, 2 H), 1.37 (s, 9 H)

^{13}C NMR (151 MHz, DMSO-d_6) δ = 167.6, 161.9, 155.5, 122.4, 119.9, 119.6, 107.7, 77.6, 36.7, 36.1, 36.0, 28.2

HRMS (FAB) calc'd for $C_{14}H_{21}N_3O_5$ $[M + Na]^+$, 334.1379, found, 334.1385.

Dimer syntheses and the use of dimers in polyamide synthesis (Table S3) are shown in the figures and text that follow.

Table S3. Illustration of dimer application in solid-phase syntheses.

KA1033/KJK6053	(ImIm)-(PyIm)-γ-(PyPy)-(PyPy)-β-Pam
KA1011	(ImIm-(PyIm)-γ-(PyPy)-(βPy)-β-Pam
KA1013	(ImIm)-(βIm)-γ-(PyPy)-(PyPy)-β-Pam
KA2127	(ImIm)-(PyIm)-γ-(Pyβ)-(PyPy)-β-Pam
KA2128	(ImIm)-(βIm)-γ-(Pyβ)-(PyPy)-β-Pam
KA2129	(ImIm)-(βIm)-γ-(PyPy)-(βPy)-β-Pam
KJK6021/KJK6064	(ImIm)-(PyIm)-γ-(PyPy)-(PyPy)-β-Pam

*Parentheses indicate how building blocks were employed, i.e. (PyPy) means that the pyrrole-pyrrole dimer was used.

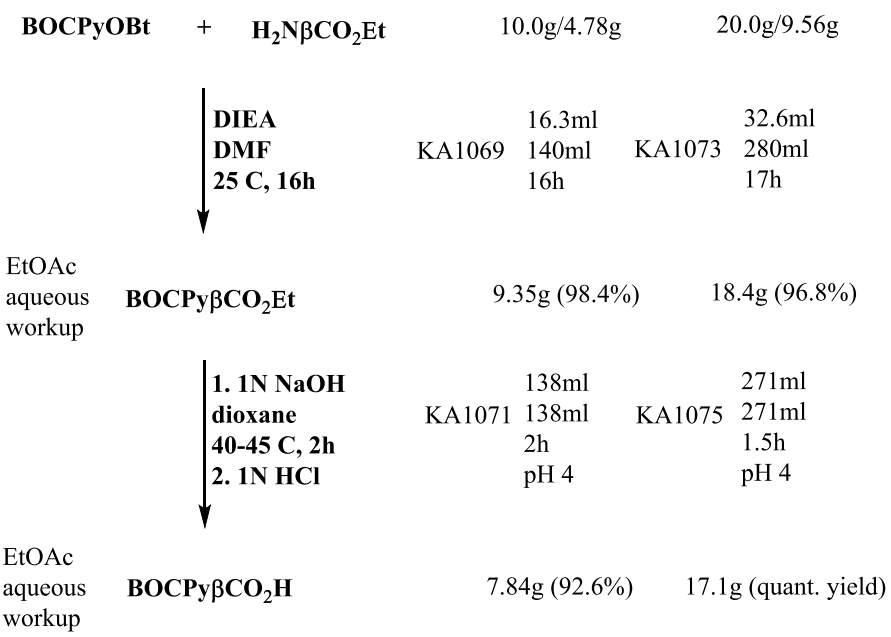


Figure S7. Synthesis of BOC-Py-β-CO_2H.

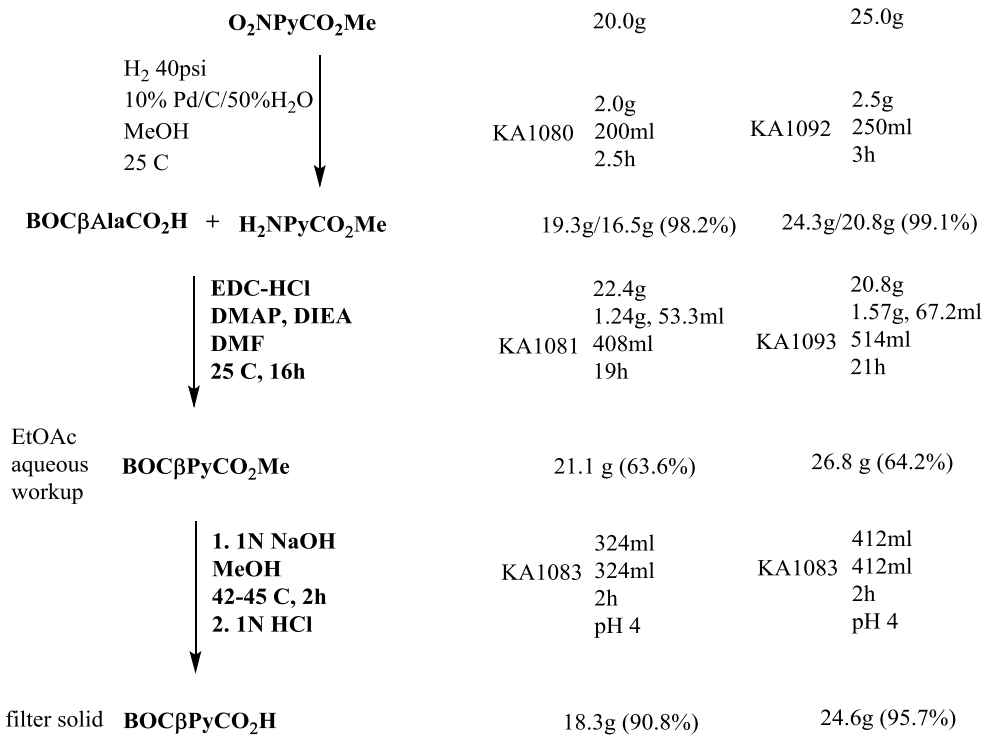


Figure S8. Synthesis of BOC-β-Py-CO_2H.

Large Scale Preparation of Boc-β-Py-COOH (Figure S9)

The nitro pyrrole (**1**), was hydrogenated using a Parr shaker apparatus with ~20 psi hydrogen and Pd on carbon catalyst for about 1 hour. The reaction mixture was vacuum filtered through Celite to remove the Pd/C and conc'd by rotavap to give the crude amino monomer (**2**). This amine was used as is, but kept under nitrogen until further use.

BOC-beta-alanine (0.95 eq) was activated with carbonyl diimidazole (CDI) in DMF solution and couple to the amino-pyrrole ester (**2**) with imidazole-HCl catalysis. When the amino-pyrrole ester (**2**) was nearly consumed, the reaction mixture was added dropwise to excess aq. HCl to precipitate the intermediate (**3**). The precipitate was cooled in ice water and vacuum filtered, washing with water and dried under vacuum. The isolated intermediate (**8**) was saponified with aq. NaOH in dioxane. The sodium salt was neutralized by addition of aq. HCl to precipitate the desire product (**4**). The precipitated product was cooled in ice water and vacuum filtered, washing with water and dried under vacuum.

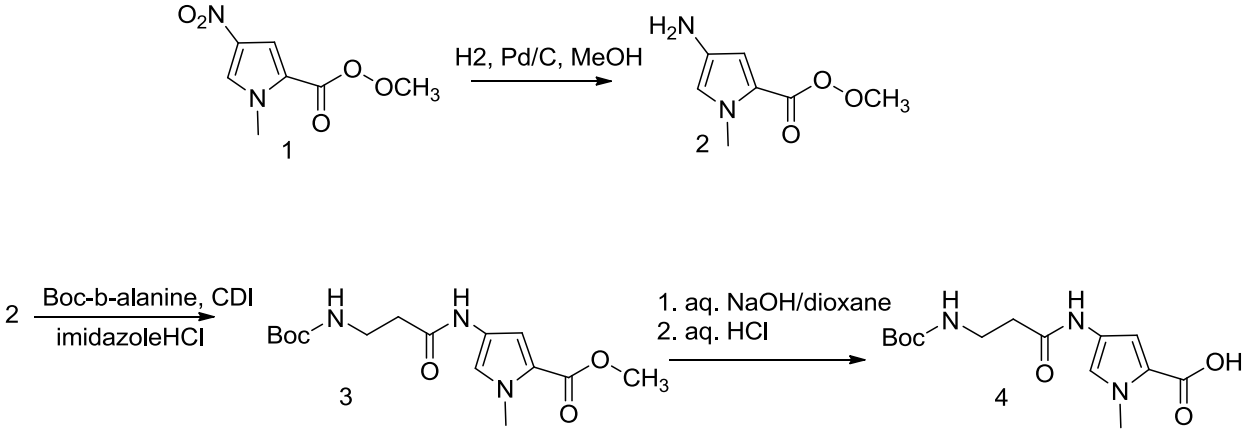


Figure S9. Large-scale Dimer Synthesis of Boc-*β*-Py-COOH with carbonyldiimidazole (CDI).

Section 3. Crystallography

X-ray Structure Determination of Compounds Boc-β-Py-COOH as its 0.5 dioxane and 1.0 MeOH solvates and Boc-Py-β-COOH as its 0.5 dioxane solvate.

Crystals of appropriate dimensions were mounted on MiTeGen cryoloops in random orientations. Preliminary examination and data collection were performed using a Bruker X8 Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo Kα radiation (λ= 0.71073 Å) from a fine focus sealed tube X-Ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ϖ and ϕ scan frames with typical scan width of 0.5° and counting time of 10-15 seconds/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages (*Bruker Analytical X-Ray, Madison, WI, 2010*) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections harvested from the complete data set. Collected data were corrected for systematic errors using SADABS (*Bruker Analytical X-Ray, Madison, WI, 2010*) based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Xray Tables 1 and 7. Structure solution and refinement were carried out using the SHELXTL- PLUS software package (*Sheldrick, G.M. (2008). Acta Cryst. A64,112-122*). The structures was solved by direct methods and refined successfully in the space groups $P\bar{1}$, $P2_1/c$ and $P2_1/n$ respectively for Compounds Boc-*β*-Py-COOH as its 0.5 dioxane and 1.0 MeOH solvates and Boc-Py-*β*-COOH as its 0.5 dioxane solvate. Full matrix least-squares refinements were carried out by minimizing $\Sigma w(F_O^2 - F_C^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The N-H and O-H hydrogens were located and refined bond distance restraints. Other hydrogen atoms were treated using appropriate riding model (AFIX m3). The final residual values and structure refinement parameters are listed in X-ray Tables 1, 7 and 13.

Complete listings of positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms are listed as supplementary material (X-ray Tables 2-6, 8-12 and 13-17). Table of calculated and observed structure factors are available in electronic format. Structure data for all the X-ray structures can be obtained from the Cambridge Crystallographic Data Center, CCDC #993654 Boc-β-Py acid 0.5 dioxane solvate, CCDC #993655 Boc-β-Py acid 1.0 methanol solvate and CCDC #993894 Boc-Py-β acid 0.5 dioxane solvate. Tables of crystal data, atomic coordinates, bond lengths and bond angles, along with thermal ellipsoid and hydrogen bonding Figures follow.

X-ray Table 1. Crystal data and structure refinement for Boc-β-Py-COOH (0.5 dioxane solvate).

Identification code	Boc-β-Py-COOH/bas1612	
Empirical formula	$C_{16}\ H_{25}\ N_3\ O_6$	
Formula weight	355.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 5.6994(4) Å	α= 73.506(3)°
	b = 12.1727(8) Å	β= 88.323(4)°
	c = 13.5102(9) Å	γ = 89.037(4)°
Volume	898.31(11) $Å^3$	
Z	2	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	380	
Crystal size	0.41 x 0.30 x 0.30 mm^3	
Theta range for data collection	1.74 to 31.18°	
Index ranges	-8≤h≤8, -17≤k≤17, -19≤l≤19	
Reflections collected	31016	
Independent reflections	5776 [R(int) = 0.0297]	
Completeness to theta = 31.18°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9708 and 0.9601	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5776 / 3 / 242	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0957	
R indices (all data)	R1 = 0.0511, wR2 = 0.1043	
Largest diff. peak and hole	0.390 and -0.228 $e.Å^{-3}$	

X-ray Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (0.5 dioxane solvate). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(8)	13346(1)	1166(1)	4632(1)	22(1)
O(9)	12956(1)	-503(1)	4252(1)	22(1)
O(5')	3438(1)	2380(1)	1472(1)	24(1)
O(1")	2867(1)	1444(1)	-1753(1)	20(1)
O(2")	3954(1)	3319(1)	-2173(1)	23(1)
N(1)	9224(1)	1991(1)	3428(1)	19(1)
N(4')	1976(2)	2571(1)	-715(1)	19(1)
N(10)	5663(1)	760(1)	1879(1)	19(1)
C(2)	10258(2)	930(1)	3582(1)	18(1)
C(3)	9039(2)	335(1)	3034(1)	17(1)
C(4)	7242(2)	1061(1)	2529(1)	17(1)
C(5)	7384(2)	2080(1)	2788(1)	19(1)
C(6)	9879(2)	2888(1)	3878(1)	29(1)
C(7)	12308(2)	558(1)	4201(1)	18(1)
C(1')	3865(2)	1417(1)	1401(1)	18(1)
C(2')	2400(2)	844(1)	770(1)	19(1)
C(3')	754(2)	1682(1)	64(1)	19(1)
C(2")	2942(2)	2363(1)	-1559(1)	17(1)
C(4")	5407(2)	3280(1)	-3074(1)	20(1)
C(5")	7425(2)	2439(1)	-2748(1)	32(1)
C(6")	3934(2)	3004(1)	-3885(1)	27(1)
C(7")	6307(2)	4496(1)	-3452(1)	34(1)
O(1S)	2127(1)	4850(1)	-508(1)	22(1)
C(1S)	2114(2)	5104(1)	464(1)	23(1)
C(2S)	100(2)	5333(1)	-1072(1)	23(1)

X-ray Table 3. Bond lengths [Å] and angles [°] for Boc-β-Py-COOH (0.5 dioxane solvate).

O(8)-C(7)	1.2315(11)
O(9)-C(7)	1.3198(12)
O(9)-H(9)	0.841(2)
O(5')-C(1')	1.2223(11)
O(1")-C(2")	1.2210(11)
O(2")-C(2")	1.3486(11)
O(2")-C(4")	1.4637(12)
N(1)-C(5)	1.3616(12)
N(1)-C(2)	1.3734(12)
N(1)-C(6)	1.4510(12)
N(4')-C(2")	1.3376(12)
N(4')-C(3')	1.4485(13)
N(4')-H(4')	0.880(2)
N(10)-C(1')	1.3510(12)
N(10)-C(4)	1.3983(11)
N(10)-H(10)	0.879(2)
C(2)-C(3)	1.3815(12)
C(2)-C(7)	1.4470(13)
C(3)-C(4)	1.4011(13)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3855(13)
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(1')-C(2')	1.5193(12)
C(2')-C(3')	1.5162(13)
C(2')-H(2'A)	0.9900
C(2')-H(2'B)	0.9900
C(3')-H(3'A)	0.9900
C(3')-H(3'B)	0.9900
C(4")-C(6")	1.5141(13)
C(4")-C(7")	1.5154(15)
C(4")-C(5")	1.5157(15)
C(5")-H(5'1)	0.9800
C(5")-H(5'2)	0.9800
C(5")-H(5'3)	0.9800
C(6")-H(6'1)	0.9800
C(6")-H(6'2)	0.9800
C(6")-H(6'3)	0.9800
C(7")-H(7'1)	0.9800
C(7")-H(7'2)	0.9800
C(7")-H(7'3)	0.9800
O(1S)-C(2S)	1.4268(12)
O(1S)-C(1S)	1.4316(12)
C(1S)-C(2S)#1	1.5043(15)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(2S)-C(1S)#1	1.5043(15)

C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900
C(7)-O(9)-H(9)	110.5(12)
C(2")-O(2")-C(4")	120.95(7)
C(5)-N(1)-C(2)	109.12(8)
C(5)-N(1)-C(6)	123.63(9)
C(2)-N(1)-C(6)	127.24(8)
C(2")-N(4')-C(3')	121.15(8)
C(2")-N(4')-H(4')	118.1(9)
C(3')-N(4')-H(4')	120.4(9)
C(1')-N(10)-C(4)	125.67(8)
C(1')-N(10)-H(10)	119.0(8)
C(4)-N(10)-H(10)	115.2(8)
N(1)-C(2)-C(3)	108.14(8)
N(1)-C(2)-C(7)	123.84(8)
C(3)-C(2)-C(7)	128.00(9)
C(2)-C(3)-C(4)	107.11(8)
C(2)-C(3)-H(3)	126.4
C(4)-C(3)-H(3)	126.4
C(5)-C(4)-N(10)	128.70(9)
C(5)-C(4)-C(3)	107.67(8)
N(10)-C(4)-C(3)	123.62(8)
N(1)-C(5)-C(4)	107.95(8)
N(1)-C(5)-H(5)	126.0
C(4)-C(5)-H(5)	126.0
N(1)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(8)-C(7)-O(9)	123.48(9)
O(8)-C(7)-C(2)	123.66(9)
O(9)-C(7)-C(2)	112.87(8)
O(5')-C(1')-N(10)	123.43(8)
O(5')-C(1')-C(2')	122.88(8)
N(10)-C(1')-C(2')	113.69(8)
C(3')-C(2')-C(1')	112.20(8)
C(3')-C(2')-H(2'A)	109.2
C(1')-C(2')-H(2'A)	109.2
C(3')-C(2')-H(2'B)	109.2
C(1')-C(2')-H(2'B)	109.2
H(2'A)-C(2')-H(2'B)	107.9
N(4')-C(3')-C(2')	113.10(8)
N(4')-C(3')-H(3'A)	109.0
C(2')-C(3')-H(3'A)	109.0
N(4')-C(3')-H(3'B)	109.0
C(2')-C(3')-H(3'B)	109.0
H(3'A)-C(3')-H(3'B)	107.8
O(1")-C(2")-N(4')	124.53(9)

O(1")-C(2")-O(2")	125.10(8)
N(4')-C(2")-O(2")	110.35(8)
O(2")-C(4")-C(6")	110.75(8)
O(2")-C(4")-C(7")	102.01(8)
C(6")-C(4")-C(7")	110.57(9)
O(2")-C(4")-C(5")	110.29(8)
C(6")-C(4")-C(5")	112.20(9)
C(7")-C(4")-C(5")	110.57(9)
C(4")-C(5")-H(5'1)	109.5
C(4")-C(5")-H(5'2)	109.5
H(5'1)-C(5")-H(5'2)	109.5
C(4")-C(5")-H(5'3)	109.5
H(5'1)-C(5")-H(5'3)	109.5
H(5'2)-C(5")-H(5'3)	109.5
C(4")-C(6")-H(6'1)	109.5
C(4")-C(6")-H(6'2)	109.5
H(6'1)-C(6")-H(6'2)	109.5
C(4")-C(6")-H(6'3)	109.5
H(6'1)-C(6")-H(6'3)	109.5
H(6'2)-C(6")-H(6'3)	109.5
C(4")-C(7")-H(7'1)	109.5
C(4")-C(7")-H(7'2)	109.5
H(7'1)-C(7")-H(7'2)	109.5
C(4")-C(7")-H(7'3)	109.5
H(7'1)-C(7")-H(7'3)	109.5
H(7'2)-C(7")-H(7'3)	109.5
C(2S)-O(1S)-C(1S)	110.26(7)
O(1S)-C(1S)-C(2S)#1	110.13(8)
O(1S)-C(1S)-H(1S1)	109.6
C(2S)#1-C(1S)-H(1S1)	109.6
O(1S)-C(1S)-H(1S2)	109.6
C(2S)#1-C(1S)-H(1S2)	109.6
H(1S1)-C(1S)-H(1S2)	108.1
O(1S)-C(2S)-C(1S)#1	111.02(8)
O(1S)-C(2S)-H(2S1)	109.4
C(1S)#1-C(2S)-H(2S1)	109.4
O(1S)-C(2S)-H(2S2)	109.4
C(1S)#1-C(2S)-H(2S2)	109.4
H(2S1)-C(2S)-H(2S2)	108.0

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z

X-ray Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (0.5 dioxane solvate). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(8)	24(1)	22(1)	22(1)	-7(1)	-4(1)	-2(1)
O(9)	23(1)	21(1)	24(1)	-8(1)	-6(1)	2(1)
O(5')	30(1)	18(1)	27(1)	-9(1)	-8(1)	5(1)
O(1")	25(1)	15(1)	22(1)	-7(1)	-1(1)	1(1)
O(2")	32(1)	15(1)	20(1)	-5(1)	3(1)	-2(1)
N(1)	22(1)	17(1)	19(1)	-7(1)	-1(1)	-1(1)
N(4')	26(1)	15(1)	17(1)	-6(1)	-1(1)	1(1)
N(10)	20(1)	15(1)	22(1)	-7(1)	-4(1)	2(1)
C(2)	19(1)	18(1)	16(1)	-5(1)	0(1)	-1(1)
C(3)	19(1)	17(1)	17(1)	-5(1)	0(1)	0(1)
C(4)	18(1)	17(1)	17(1)	-5(1)	0(1)	-1(1)
C(5)	20(1)	18(1)	20(1)	-6(1)	-1(1)	1(1)
C(6)	35(1)	21(1)	37(1)	-15(1)	-11(1)	2(1)
C(7)	19(1)	20(1)	14(1)	-4(1)	1(1)	-1(1)
C(1')	20(1)	17(1)	16(1)	-4(1)	0(1)	1(1)
C(2')	21(1)	17(1)	18(1)	-5(1)	-2(1)	1(1)
C(3')	19(1)	20(1)	18(1)	-5(1)	-1(1)	1(1)
C(2")	18(1)	15(1)	17(1)	-4(1)	-4(1)	2(1)
C(4")	21(1)	20(1)	18(1)	-4(1)	-1(1)	-2(1)
C(5")	20(1)	36(1)	33(1)	-1(1)	-1(1)	3(1)
C(6")	28(1)	34(1)	19(1)	-6(1)	-3(1)	-5(1)
C(7")	43(1)	26(1)	30(1)	-2(1)	3(1)	-12(1)
O(1S)	18(1)	22(1)	27(1)	-10(1)	0(1)	2(1)
C(1S)	19(1)	26(1)	28(1)	-13(1)	-4(1)	2(1)
C(2S)	25(1)	23(1)	22(1)	-7(1)	-2(1)	4(1)

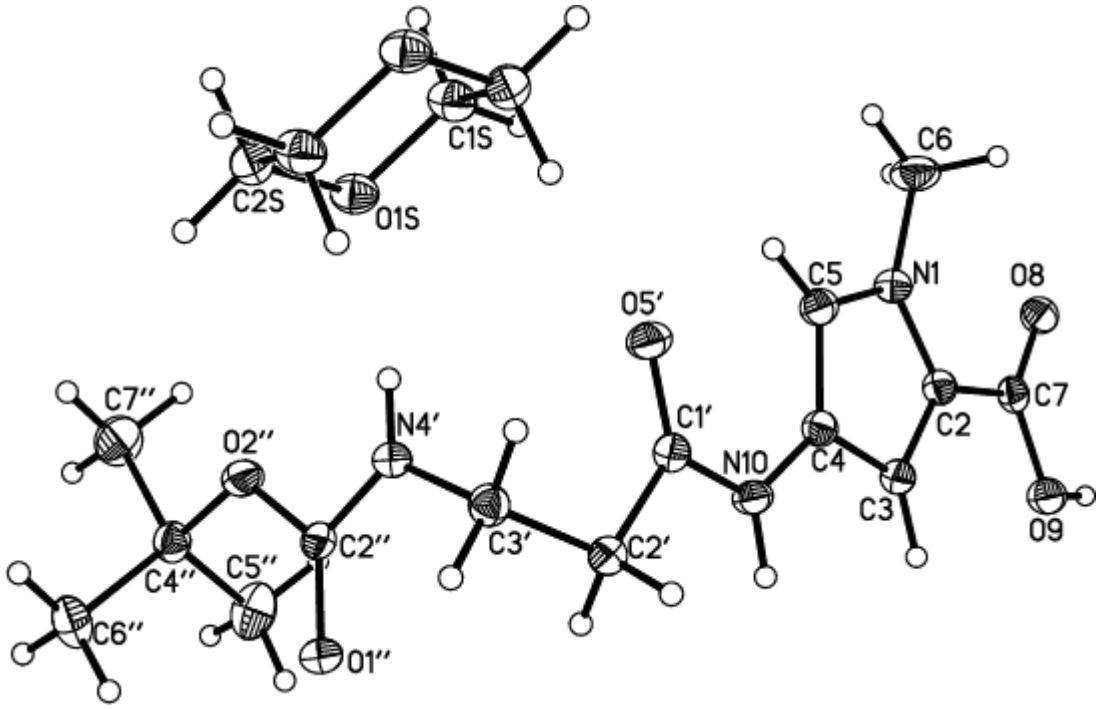
X-ray Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (0.5 dioxane solvate).

	x	y	z	U(eq)
H(3)	9359	-424	3004	21
H(5)	6375	2726	2560	23
H(6A)	11482	3136	3652	44
H(6B)	9800	2594	4633	44
H(6C)	8796	3540	3653	44
H(2'A)	3457	492	349	22
H(2'B)	1468	225	1244	22
H(3'A)	-253	1257	-282	23
H(3'B)	-280	2044	485	23
H(5'1)	8559	2536	-3326	47
H(5'2)	6824	1655	-2550	47
H(5'3)	8198	2583	-2159	47
H(6'1)	4897	3072	-4513	41
H(6'2)	2606	3542	-4045	41
H(6'3)	3346	2220	-3624	41
H(7'1)	7207	4669	-2908	51
H(7'2)	4976	5030	-3626	51
H(7'3)	7319	4576	-4067	51
H(1S1)	2217	5943	346	28
H(1S2)	3495	4740	860	28
H(2S1)	110	5134	-1733	28
H(2S2)	142	6178	-1231	28
H(9)	14175(17)	-685(14)	4599(11)	52(5)
H(10)	5860(20)	69(5)	1806(10)	25(3)
H(4')	2250(20)	3236(6)	-607(11)	32(4)

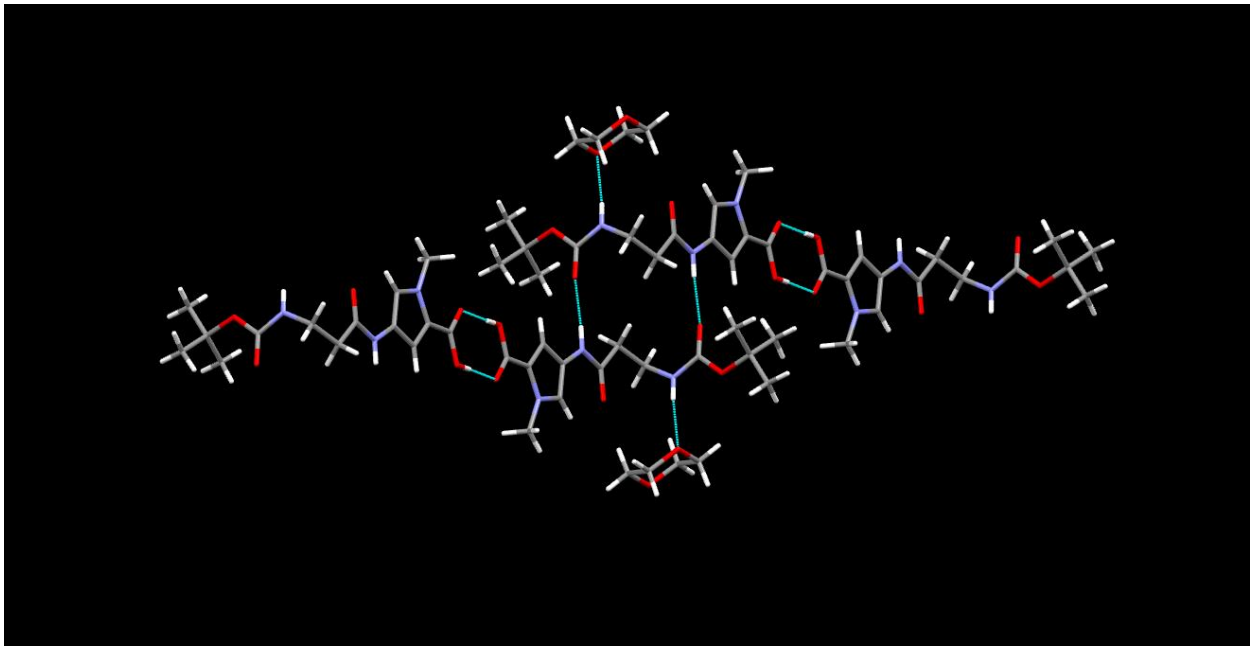
X-ray Table 6. Torsion angles [°] for Boc-β-Py-COOH (0.5 dioxane solvate).

C(5)-N(1)-C(2)-C(3)	-0.31(11)
C(6)-N(1)-C(2)-C(3)	178.10(9)
C(5)-N(1)-C(2)-C(7)	178.25(9)
C(6)-N(1)-C(2)-C(7)	-3.34(15)
N(1)-C(2)-C(3)-C(4)	0.57(10)
C(7)-C(2)-C(3)-C(4)	-177.91(9)
C(1')-N(10)-C(4)-C(5)	-2.87(16)
C(1')-N(10)-C(4)-C(3)	177.98(9)
C(2)-C(3)-C(4)-C(5)	-0.62(11)
C(2)-C(3)-C(4)-N(10)	178.68(8)
C(2)-N(1)-C(5)-C(4)	-0.08(11)
C(6)-N(1)-C(5)-C(4)	-178.56(9)
N(10)-C(4)-C(5)-N(1)	-178.82(9)
C(3)-C(4)-C(5)-N(1)	0.44(11)
N(1)-C(2)-C(7)-O(8)	-1.41(15)
C(3)-C(2)-C(7)-O(8)	176.85(9)
N(1)-C(2)-C(7)-O(9)	178.85(8)
C(3)-C(2)-C(7)-O(9)	-2.88(14)
C(4)-N(10)-C(1')-O(5')	1.36(16)
C(4)-N(10)-C(1')-C(2')	-178.12(8)
O(5')-C(1')-C(2')-C(3')	13.06(13)
N(10)-C(1')-C(2')-C(3')	-167.46(8)
C(2")-N(4')-C(3')-C(2')	78.06(10)
C(1')-C(2')-C(3')-N(4')	63.60(10)
C(3')-N(4')-C(2")-O(1")	0.92(14)
C(3')-N(4')-C(2")-O(2")	179.35(8)
C(4")-O(2")-C(2")-O(1")	-10.00(14)
C(4")-O(2")-C(2")-N(4')	171.58(8)
C(2")-O(2")-C(4")-C(6")	67.07(11)
C(2")-O(2")-C(4")-C(7")	-175.23(8)
C(2")-O(2")-C(4")-C(5")	-57.74(11)
C(2S)-O(1S)-C(1S)-C(2S)#1	57.14(11)
C(1S)-O(1S)-C(2S)-C(1S)#1	-57.67(11)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z



X-ray Figure 1. Projection view with 50% thermal ellipsoids of Boc-β-Py-COOH (0.5 dioxane solvate).



X-ray Figure 2. Hydrogen bonding between molecules in the crystal structure of Boc-β-Py-COOH (0.5 dioxane solvate).

X-ray Table 7. Crystal data and structure refinement for Boc-β-Py-COOH (methanol solvate).

Identification code	Boc-Py-β-COOH/ bas1812	
Empirical formula	C_{15} H_{25} N_3 O_6	
Formula weight	343.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.6327(4) Å	α= 90°.
	b = 8.4467(4) Å	β= 95.597(3)°.
	c = 24.0094(12) Å	γ = 90°.
Volume	1742.37(14) $Å^3$	
Z	4	
Density (calculated)	1.309 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	736	
Crystal size	0.38 x 0.34 x 0.30 mm^3	
Theta range for data collection	1.70 to 30.64°.	
Index ranges	-12≤h≤12, -12≤k≤12, -34≤l≤34	
Reflections collected	56397	
Independent reflections	5366 [R(int) = 0.0401]	
Completeness to theta = 30.64°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9704 and 0.9629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5366 / 4 / 238	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1087	
R indices (all data)	R1 = 0.0550, wR2 = 0.1168	
Largest diff. peak and hole	0.511 and -0.278 $e.Å^{-3}$	

X-ray Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (methanol solvate). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(8)	6294(1)	13588(1)	5169(1)	19(1)
O(9)	4329(1)	13573(1)	4483(1)	20(1)
O(5')	6921(1)	5908(1)	4081(1)	21(1)
O(1")	6917(1)	4074(1)	2111(1)	23(1)
O(2")	9418(1)	4161(1)	2515(1)	19(1)
N(1)	7099(1)	10440(1)	4803(1)	15(1)
N(10)	5394(1)	7890(1)	3714(1)	16(1)
N(4')	7514(1)	3922(1)	3051(1)	19(1)
C(2)	5903(1)	11367(1)	4568(1)	15(1)
C(3)	5122(1)	10530(1)	4132(1)	15(1)
C(4)	5865(1)	9061(1)	4106(1)	14(1)
C(5)	7089(1)	9036(1)	4525(1)	16(1)
C(6)	8225(1)	10848(1)	5272(1)	20(1)
C(7)	5550(1)	12929(1)	4772(1)	16(1)
C(1')	5916(1)	6388(1)	3722(1)	16(1)
C(2')	5138(1)	5362(1)	3259(1)	20(1)
C(3')	5931(1)	3778(1)	3196(1)	19(1)
C(2")	7867(1)	4050(1)	2523(1)	17(1)
C(4")	10146(1)	4274(2)	1986(1)	21(1)
C(5")	9586(2)	5736(1)	1664(1)	24(1)
C(6")	9851(2)	2756(2)	1653(1)	27(1)
C(7")	11855(2)	4440(2)	2197(1)	33(1)
C(1S)	10631(2)	4119(2)	4320(1)	38(1)
O(1S)	9121(1)	3537(1)	4186(1)	27(1)

X-ray Table 9. Bond lengths [Å] and angles [°] for Boc-β-Py-COOH (methanol solvate).

O(8)-C(7)	1.2284(13)
O(9)-C(7)	1.3209(13)
O(9)-H(9)	0.841(2)
O(5')-C(1')	1.2305(13)
O(1")-C(2")	1.2217(13)
O(2")-C(2")	1.3440(13)
O(2")-C(4")	1.4731(13)
N(1)-C(5)	1.3604(14)
N(1)-C(2)	1.3719(13)
N(1)-C(6)	1.4551(13)
N(10)-C(1')	1.3453(14)
N(10)-C(4)	1.3990(13)
N(10)-H(10)	0.880(2)
N(4')-C(2")	1.3376(14)
N(4')-C(3')	1.4472(14)
N(4')-H(4')	0.880(2)
C(2)-C(3)	1.3845(14)
C(2)-C(7)	1.4503(15)
C(3)-C(4)	1.4008(14)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3867(14)
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(1')-C(2')	1.5156(15)
C(2')-C(3')	1.5172(16)
C(2')-H(2'1)	0.9900
C(2')-H(2'2)	0.9900
C(3')-H(3'1)	0.9900
C(3')-H(3'2)	0.9900
C(4")-C(5")	1.5122(17)
C(4")-C(7")	1.5191(17)
C(4")-C(6")	1.5191(17)
C(5")-H(5'1)	0.9800
C(5")-H(5'2)	0.9800
C(5")-H(5'3)	0.9800
C(6")-H(6'1)	0.9800
C(6")-H(6'2)	0.9800
C(6")-H(6'3)	0.9800
C(7")-H(7'1)	0.9800
C(7")-H(7'2)	0.9800
C(7")-H(7'3)	0.9800
C(1S)-O(1S)	1.4014(16)

C(1S)-H(1S1)	0.9800
C(1S)-H(1S2)	0.9800
C(1S)-H(1S3)	0.9800
O(1S)-H(1S)	0.840(2)

C(7)-O(9)-H(9)	109.5(12)
C(2")-O(2")-C(4")	121.76(8)
C(5)-N(1)-C(2)	109.10(9)
C(5)-N(1)-C(6)	123.89(9)
C(2)-N(1)-C(6)	127.01(9)
C(1')-N(10)-C(4)	125.55(9)
C(1')-N(10)-H(10)	116.3(11)
C(4)-N(10)-H(10)	118.1(11)
C(2")-N(4')-C(3')	122.83(9)
C(2")-N(4')-H(4')	120.7(11)
C(3')-N(4')-H(4')	116.4(11)
N(1)-C(2)-C(3)	108.13(9)
N(1)-C(2)-C(7)	123.74(9)
C(3)-C(2)-C(7)	128.11(9)
C(2)-C(3)-C(4)	107.13(9)
C(2)-C(3)-H(3)	126.4
C(4)-C(3)-H(3)	126.4
C(5)-C(4)-N(10)	128.97(9)
C(5)-C(4)-C(3)	107.51(9)
N(10)-C(4)-C(3)	123.52(9)
N(1)-C(5)-C(4)	108.13(9)
N(1)-C(5)-H(5)	125.9
C(4)-C(5)-H(5)	125.9
N(1)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(8)-C(7)-O(9)	123.41(10)
O(8)-C(7)-C(2)	124.20(10)
O(9)-C(7)-C(2)	112.39(9)
O(5')-C(1')-N(10)	122.29(10)
O(5')-C(1')-C(2')	123.88(10)
N(10)-C(1')-C(2')	113.83(9)
C(1')-C(2')-C(3')	113.91(9)
C(1')-C(2')-H(2'1)	108.8
C(3')-C(2')-H(2'1)	108.8
C(1')-C(2')-H(2'2)	108.8
C(3')-C(2')-H(2'2)	108.8
H(2'1)-C(2')-H(2'2)	107.7

N(4')-C(3')-C(2')	113.29(9)
N(4')-C(3')-H(3'1)	108.9
C(2')-C(3')-H(3'1)	108.9
N(4')-C(3')-H(3'2)	108.9
C(2')-C(3')-H(3'2)	108.9
H(3'1)-C(3')-H(3'2)	107.7
O(1")-C(2")-N(4')	124.89(10)
O(1")-C(2")-O(2")	125.30(10)
N(4')-C(2")-O(2")	109.81(9)
O(2")-C(4")-C(5")	110.60(9)
O(2")-C(4")-C(7")	101.65(9)
C(5")-C(4")-C(7")	110.29(11)
O(2")-C(4")-C(6")	109.64(10)
C(5")-C(4")-C(6")	112.97(9)
C(7")-C(4")-C(6")	111.13(11)
C(4")-C(5")-H(5'1)	109.5
C(4")-C(5")-H(5'2)	109.5
H(5'1)-C(5")-H(5'2)	109.5
C(4")-C(5")-H(5'3)	109.5
H(5'1)-C(5")-H(5'3)	109.5
H(5'2)-C(5")-H(5'3)	109.5
C(4")-C(6")-H(6'1)	109.5
C(4")-C(6")-H(6'2)	109.5
H(6'1)-C(6")-H(6'2)	109.5
C(4")-C(6")-H(6'3)	109.5
H(6'1)-C(6")-H(6'3)	109.5
H(6'2)-C(6")-H(6'3)	109.5
C(4")-C(7")-H(7'1)	109.5
C(4")-C(7")-H(7'2)	109.5
H(7'1)-C(7")-H(7'2)	109.5
C(4")-C(7")-H(7'3)	109.5
H(7'1)-C(7")-H(7'3)	109.5
H(7'2)-C(7")-H(7'3)	109.5
O(1S)-C(1S)-H(1S1)	109.5
O(1S)-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	109.5
O(1S)-C(1S)-H(1S3)	109.5
H(1S1)-C(1S)-H(1S3)	109.5
H(1S2)-C(1S)-H(1S3)	109.5
C(1S)-O(1S)-H(1S)	103.4(14)

X-ray Table 10. Anisotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (methanol solvate). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(8)	18(1)	19(1)	20(1)	-4(1)	-1(1)	1(1)
O(9)	17(1)	18(1)	23(1)	-4(1)	-3(1)	3(1)
O(5')	19(1)	21(1)	21(1)	-2(1)	-4(1)	4(1)
O(1")	19(1)	32(1)	17(1)	-1(1)	-4(1)	-5(1)
O(2")	16(1)	30(1)	13(1)	-1(1)	0(1)	1(1)
N(1)	13(1)	18(1)	15(1)	0(1)	0(1)	1(1)
N(10)	14(1)	18(1)	15(1)	-1(1)	-2(1)	1(1)
N(4')	16(1)	26(1)	15(1)	-2(1)	0(1)	2(1)
C(2)	13(1)	16(1)	16(1)	0(1)	1(1)	0(1)
C(3)	13(1)	16(1)	16(1)	1(1)	1(1)	0(1)
C(4)	14(1)	16(1)	14(1)	0(1)	1(1)	0(1)
C(5)	14(1)	17(1)	16(1)	-1(1)	0(1)	2(1)
C(6)	17(1)	24(1)	18(1)	-3(1)	-4(1)	2(1)
C(7)	13(1)	17(1)	16(1)	1(1)	3(1)	-1(1)
C(1')	13(1)	18(1)	17(1)	-2(1)	2(1)	0(1)
C(2')	16(1)	21(1)	21(1)	-5(1)	-1(1)	0(1)
C(3')	20(1)	18(1)	21(1)	-3(1)	4(1)	-2(1)
C(2")	17(1)	16(1)	16(1)	-2(1)	0(1)	-1(1)
C(4")	19(1)	29(1)	15(1)	-1(1)	3(1)	1(1)
C(5")	26(1)	25(1)	20(1)	1(1)	1(1)	-5(1)
C(6")	37(1)	26(1)	19(1)	-2(1)	5(1)	6(1)
C(7")	18(1)	56(1)	26(1)	0(1)	3(1)	2(1)
C(1S)	24(1)	40(1)	46(1)	0(1)	-5(1)	-1(1)
O(1S)	20(1)	29(1)	31(1)	-5(1)	-1(1)	6(1)

X-ray Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Boc-β-Py-COOH (methanol solvate).

	x	y	z	U(eq)
H(3)	4248	10886	3894	18
H(5)	7796	8186	4605	19
H(6A)	8893	9931	5371	30
H(6B)	7675	11150	5594	30
H(6C)	8867	11736	5167	30
H(2'1)	5119	5945	2900	23
H(2'2)	4046	5171	3333	23
H(3'1)	5937	3185	3552	23
H(3'2)	5319	3155	2902	23
H(5'1)	8494	5596	1517	35
H(5'2)	10221	5902	1352	35
H(5'3)	9679	6657	1912	35
H(6'1)	10163	1845	1890	41
H(6'2)	10459	2770	1329	41
H(6'3)	8741	2675	1524	41
H(7'1)	11998	5375	2438	50
H(7'2)	12472	4558	1877	50
H(7'3)	12199	3494	2411	50
H(1S1)	10755	5118	4121	56
H(1S2)	11388	3345	4208	56
H(1S3)	10807	4302	4724	56
H(1S)	8553(19)	4321(15)	4238(8)	48(5)
H(10)	4672(13)	8132(19)	3442(4)	27(4)
H(9)	4130(20)	14455(10)	4624(7)	36(5)
H(4')	8251(14)	3900(20)	3331(5)	35(4)

X-ray Table 12. Torsion angles [°] for Boc-β-Py-COOH (methanol solvate).

C(5)-N(1)-C(2)-C(3)	-0.16(12)
C(6)-N(1)-C(2)-C(3)	179.66(10)
C(5)-N(1)-C(2)-C(7)	178.28(9)
C(6)-N(1)-C(2)-C(7)	-1.90(17)
N(1)-C(2)-C(3)-C(4)	0.32(12)
C(7)-C(2)-C(3)-C(4)	-178.04(10)
C(1')-N(10)-C(4)-C(5)	10.61(17)
C(1')-N(10)-C(4)-C(3)	-169.68(10)
C(2)-C(3)-C(4)-C(5)	-0.35(12)
C(2)-C(3)-C(4)-N(10)	179.89(9)
C(2)-N(1)-C(5)-C(4)	-0.07(12)
C(6)-N(1)-C(5)-C(4)	-179.89(10)
N(10)-C(4)-C(5)-N(1)	180.00(10)
C(3)-C(4)-C(5)-N(1)	0.26(12)
N(1)-C(2)-C(7)-O(8)	1.07(17)
C(3)-C(2)-C(7)-O(8)	179.19(11)
N(1)-C(2)-C(7)-O(9)	-178.88(9)
C(3)-C(2)-C(7)-O(9)	-0.76(15)
C(4)-N(10)-C(1')-O(5')	-2.01(17)
C(4)-N(10)-C(1')-C(2')	177.13(9)
O(5')-C(1')-C(2')-C(3')	-12.27(15)
N(10)-C(1')-C(2')-C(3')	168.60(9)
C(2")-N(4')-C(3')-C(2')	-86.69(13)
C(1')-C(2')-C(3')-N(4')	-62.04(13)
C(3')-N(4')-C(2")-O(1")	0.67(18)
C(3')-N(4')-C(2")-O(2")	-179.82(9)
C(4")-O(2")-C(2")-O(1")	-2.13(17)
C(4")-O(2")-C(2")-N(4')	178.37(9)
C(2")-O(2")-C(4")-C(5")	60.66(13)
C(2")-O(2")-C(4")-C(7")	177.77(10)
C(2")-O(2")-C(4")-C(6")	-64.57(13)

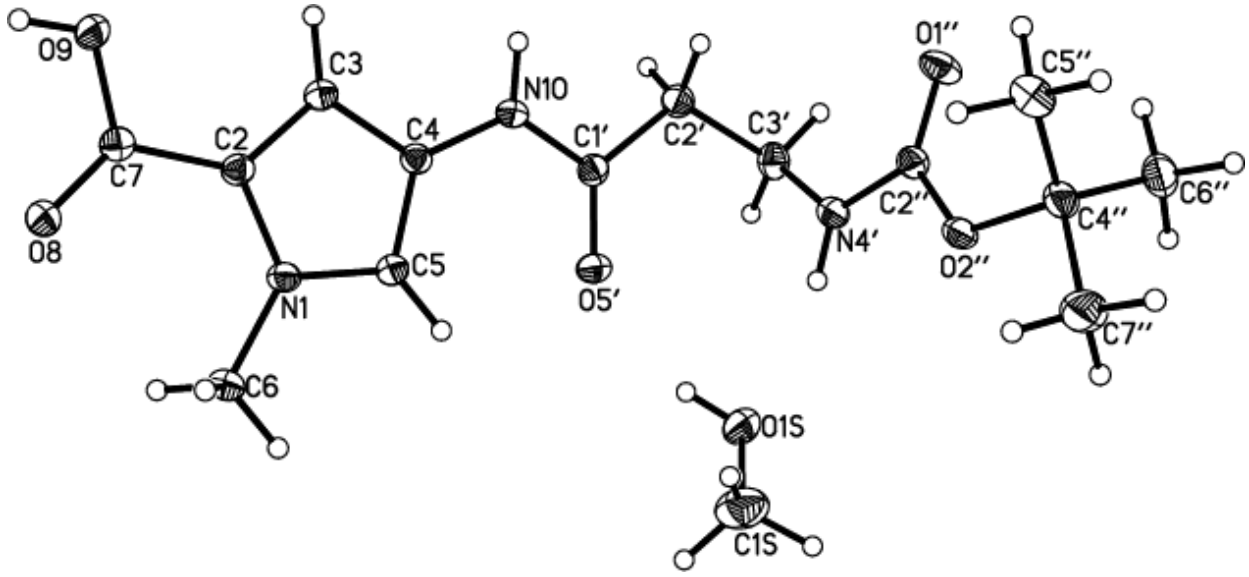


Figure X-ray 3. Projection view with 50% thermal ellipsoids for Boc-β-Py-COOH (methanol solvate).

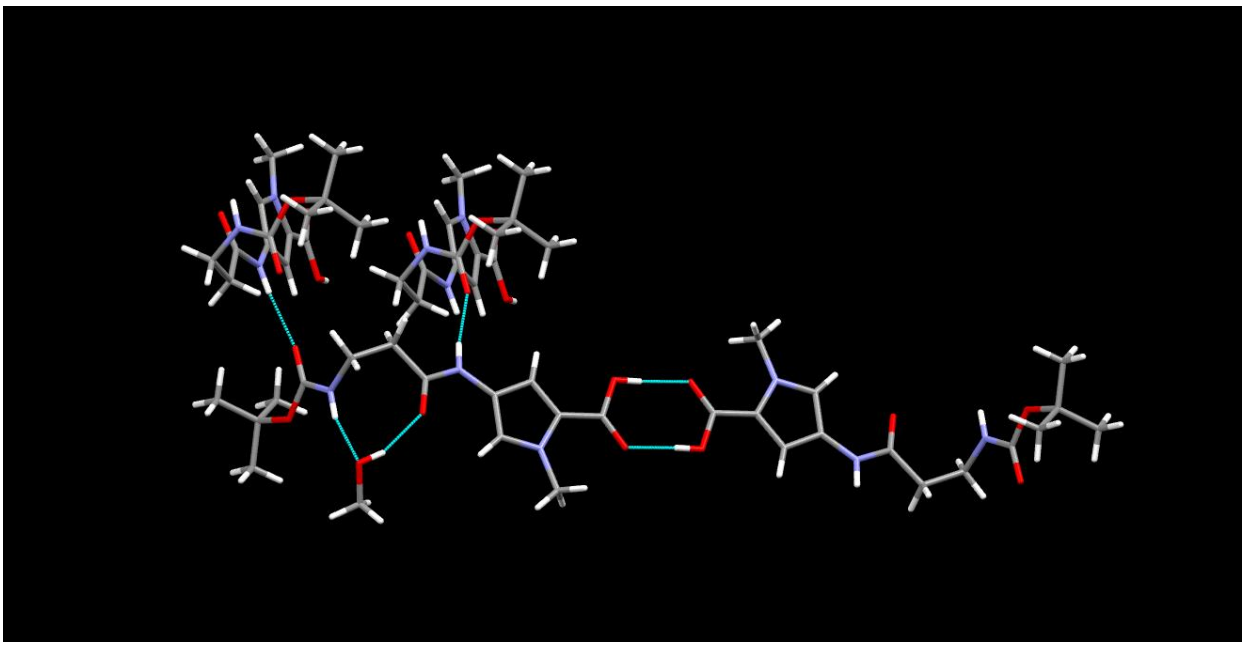


Figure X-ray 4. Intermolecular H-bonding for Boc-β-Py-COOH (methanol solvate):

X-ray Table 13. Crystal data and structure refinement for Boc-Py-beta-COOH·0.5dioxane solvate.

Identification code	bas1912/b1912	
Empirical formula	$C_{17}\ H_{27}\ N_3\ O_6$	
Formula weight	369.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.2285(9) Å	α= 90°.
	b = 8.4147(6) Å	β= 104.836(4)°
	c = 18.9773(15) Å	γ = 90°.
Volume	1887.6(2) $Å^3$	
Z	4	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	792	
Crystal size	0.37 x 0.23 x 0.08 mm^3	
Theta range for data collection	1.79 to 27.23°	
Index ranges	-15≤h≤15, -10≤k≤10, -24≤l≤24	
Reflections collected	63224	
Independent reflections	4196 [R(int) = 0.0703]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9918 and 0.9643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4196 / 0 / 240	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0888	
R indices (all data)	R1 = 0.0652, wR2 = 0.1018	
Largest diff. peak and hole	0.232 and -0.238 e.$Å^{-3}$	

X-ray Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for Boc-Py-beta-COOH·0.5dioxane solvate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1250(1)	6466(1)	2157(1)	19(1)
O(2)	768(1)	3962(1)	-1137(1)	24(1)
O(3)	3977(1)	3515(1)	6266(1)	22(1)
O(4)	2261(1)	4751(2)	5877(1)	28(1)
O(5)	-3(1)	2750(2)	-350(1)	39(1)
N(1)	1146(1)	5508(2)	3606(1)	18(1)
N(2)	2488(1)	4447(2)	2178(1)	17(1)
N(3)	3281(1)	3911(2)	5101(1)	22(1)
C(2)	1513(1)	5134(2)	4328(1)	21(1)
C(3)	2569(1)	4451(2)	4446(1)	19(1)
C(4)	2848(1)	4390(2)	3776(1)	17(1)
C(5)	1954(1)	5054(2)	3262(1)	16(1)
C(6)	7(1)	6110(2)	3286(1)	23(1)
C(7)	1859(1)	5364(2)	2490(1)	16(1)
C(8)	2560(1)	4700(2)	1429(1)	19(1)
C(9)	1671(1)	3769(2)	877(1)	18(1)
C(10)	1751(1)	4122(2)	104(1)	20(1)
C(11)	755(1)	3519(2)	-470(1)	20(1)
C(12)	3092(1)	4125(2)	5763(1)	20(1)
C(13)	4031(1)	3592(2)	7043(1)	20(1)
C(14)	5136(1)	2745(2)	7376(1)	23(1)
C(15)	4093(2)	5305(2)	7286(1)	33(1)
C(16)	3057(1)	2688(3)	7203(1)	35(1)
O(1S)	4870(1)	4508(2)	684(1)	39(1)
C(1S)	5692(2)	3808(3)	369(1)	43(1)
C(2S)	4678(2)	6114(2)	441(1)	42(1)

X-ray Table 15. Bond lengths [Å] and angles [°] for Boc-Py-beta-COOH.

O(1)-C(7)	1.2540(18)
O(2)-C(11)	1.3242(18)
O(2)-H(2A)	0.8400
O(3)-C(12)	1.3473(18)
O(3)-C(13)	1.4613(18)
O(4)-C(12)	1.2120(19)
O(5)-C(11)	1.1987(19)
N(1)-C(2)	1.3646(19)
N(1)-C(5)	1.3714(19)
N(1)-C(6)	1.4602(19)
N(2)-C(7)	1.3315(19)
N(2)-C(8)	1.4603(18)
N(2)-H(2B)	0.8800
N(3)-C(12)	1.346(2)
N(3)-C(3)	1.3983(19)
N(3)-H(3)	0.8800
C(2)-C(3)	1.378(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.399(2)
C(4)-C(5)	1.384(2)
C(4)-H(4)	0.9500
C(5)-C(7)	1.462(2)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(8)-C(9)	1.520(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.523(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.499(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(13)-C(16)	1.508(2)
C(13)-C(15)	1.509(2)
C(13)-C(14)	1.515(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
O(1S)-C(1S)	1.423(2)
O(1S)-C(2S)	1.428(2)
C(1S)-C(2S)#1	1.487(3)

C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(2S)-C(1S)#1	1.487(3)
C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900

C(11)-O(2)-H(2A)	109.5
C(12)-O(3)-C(13)	121.23(12)
C(2)-N(1)-C(5)	108.76(12)
C(2)-N(1)-C(6)	122.06(13)
C(5)-N(1)-C(6)	128.77(12)
C(7)-N(2)-C(8)	122.29(13)
C(7)-N(2)-H(2B)	118.9
C(8)-N(2)-H(2B)	118.9
C(12)-N(3)-C(3)	124.70(13)
C(12)-N(3)-H(3)	117.7
C(3)-N(3)-H(3)	117.7
N(1)-C(2)-C(3)	108.31(13)
N(1)-C(2)-H(2)	125.8
C(3)-C(2)-H(2)	125.8
C(2)-C(3)-N(3)	128.68(14)
C(2)-C(3)-C(4)	107.66(13)
N(3)-C(3)-C(4)	123.66(13)
C(5)-C(4)-C(3)	107.09(13)
C(5)-C(4)-H(4)	126.5
C(3)-C(4)-H(4)	126.5
N(1)-C(5)-C(4)	108.17(13)
N(1)-C(5)-C(7)	123.01(13)
C(4)-C(5)-C(7)	128.68(14)
N(1)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(1)-C(7)-N(2)	122.67(13)
O(1)-C(7)-C(5)	121.45(13)
N(2)-C(7)-C(5)	115.83(13)
N(2)-C(8)-C(9)	112.66(12)
N(2)-C(8)-H(8A)	109.1
C(9)-C(8)-H(8A)	109.1
N(2)-C(8)-H(8B)	109.1
C(9)-C(8)-H(8B)	109.1
H(8A)-C(8)-H(8B)	107.8
C(8)-C(9)-C(10)	110.66(12)
C(8)-C(9)-H(9A)	109.5
C(10)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
C(10)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1
C(11)-C(10)-C(9)	113.17(13)

C(11)-C(10)-H(10A)	108.9
C(9)-C(10)-H(10A)	108.9
C(11)-C(10)-H(10B)	108.9
C(9)-C(10)-H(10B)	108.9
H(10A)-C(10)-H(10B)	107.8
O(5)-C(11)-O(2)	122.15(14)
O(5)-C(11)-C(10)	124.65(14)
O(2)-C(11)-C(10)	113.17(13)
O(4)-C(12)-N(3)	125.19(14)
O(4)-C(12)-O(3)	126.69(14)
N(3)-C(12)-O(3)	108.11(13)
O(3)-C(13)-C(16)	110.29(13)
O(3)-C(13)-C(15)	109.66(13)
C(16)-C(13)-C(15)	113.64(15)
O(3)-C(13)-C(14)	101.83(12)
C(16)-C(13)-C(14)	110.15(14)
C(15)-C(13)-C(14)	110.63(14)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(1S)-O(1S)-C(2S)	109.34(14)
O(1S)-C(1S)-C(2S)#1	110.82(16)
O(1S)-C(1S)-H(1S1)	109.5
C(2S)#1-C(1S)-H(1S1)	109.5
O(1S)-C(1S)-H(1S2)	109.5
C(2S)#1-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	108.1
O(1S)-C(2S)-C(1S)#1	110.96(18)
O(1S)-C(2S)-H(2S1)	109.4
C(1S)#1-C(2S)-H(2S1)	109.4
O(1S)-C(2S)-H(2S2)	109.4
C(1S)#1-C(2S)-H(2S2)	109.4
H(2S1)-C(2S)-H(2S2)	108.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

X-ray Table 16. Anisotropic displacement parameters ($Å^2$ x 10^3) for Boc-Py-beta-COOH●0.5dioxane solvate. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	18(1)	17(1)	2(1)	0(1)	1(1)
O(2)	23(1)	33(1)	15(1)	2(1)	2(1)	-3(1)
O(3)	22(1)	31(1)	12(1)	2(1)	2(1)	8(1)
O(4)	23(1)	41(1)	20(1)	2(1)	6(1)	10(1)
O(5)	34(1)	56(1)	23(1)	7(1)	0(1)	-24(1)
N(1)	17(1)	21(1)	15(1)	0(1)	2(1)	4(1)
N(2)	17(1)	18(1)	15(1)	2(1)	2(1)	1(1)
N(3)	21(1)	30(1)	16(1)	2(1)	4(1)	10(1)
C(2)	21(1)	25(1)	16(1)	0(1)	6(1)	2(1)
C(3)	20(1)	19(1)	16(1)	0(1)	2(1)	2(1)
C(4)	17(1)	18(1)	16(1)	-1(1)	3(1)	2(1)
C(5)	16(1)	15(1)	17(1)	-2(1)	3(1)	-1(1)
C(6)	18(1)	29(1)	21(1)	1(1)	4(1)	6(1)
C(7)	14(1)	17(1)	15(1)	-1(1)	1(1)	-4(1)
C(8)	19(1)	23(1)	16(1)	1(1)	6(1)	-2(1)
C(9)	19(1)	20(1)	16(1)	1(1)	4(1)	0(1)
C(10)	19(1)	24(1)	18(1)	0(1)	5(1)	-2(1)
C(11)	21(1)	21(1)	18(1)	2(1)	5(1)	0(1)
C(12)	21(1)	23(1)	16(1)	0(1)	3(1)	2(1)
C(13)	20(1)	27(1)	12(1)	1(1)	2(1)	2(1)
C(14)	21(1)	28(1)	19(1)	2(1)	1(1)	2(1)
C(15)	41(1)	32(1)	24(1)	-4(1)	4(1)	9(1)
C(16)	23(1)	54(1)	29(1)	13(1)	5(1)	-2(1)
O(1S)	39(1)	48(1)	36(1)	19(1)	21(1)	10(1)
C(1S)	36(1)	52(1)	48(1)	25(1)	23(1)	14(1)
C(2S)	47(1)	41(1)	45(1)	13(1)	26(1)	8(1)

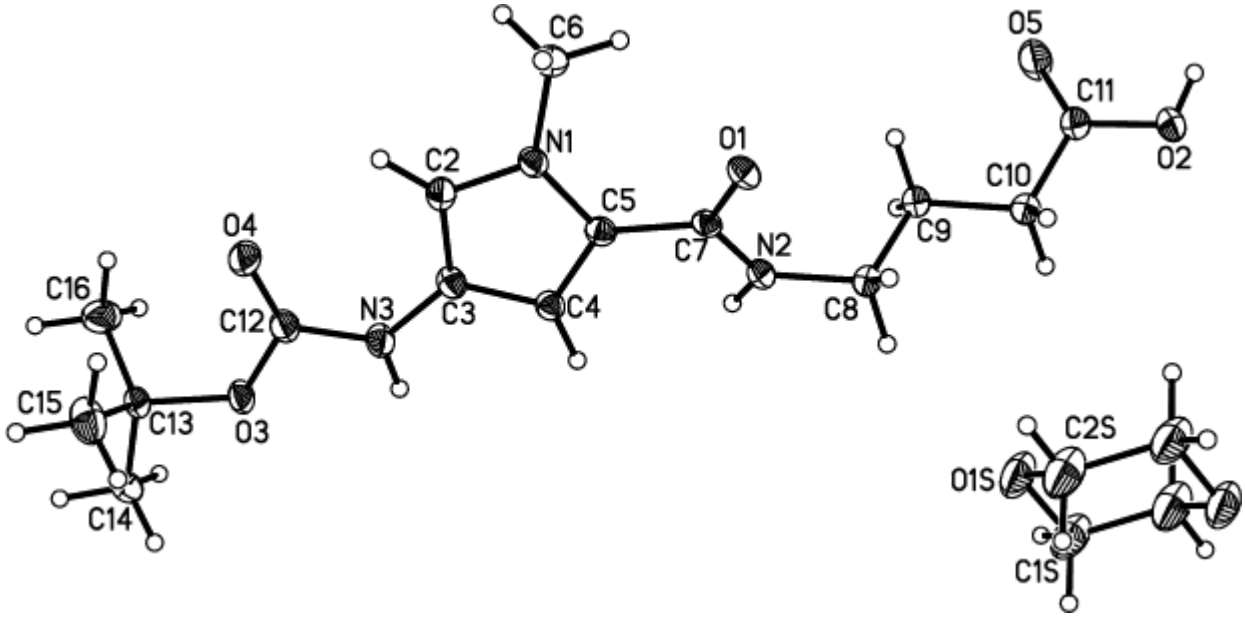
X-ray Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Boc-Py-beta-COOH·0.5dioxane solvate.

	x	y	z	U(eq)
H(2A)	160	3688	-1432	37
H(2B)	2874	3661	2430	21
H(3)	3898	3395	5079	27
H(2)	1110	5314	4687	25
H(4)	3525	3971	3691	20
H(6A)	-521	5636	3538	34
H(6B)	-225	5830	2768	34
H(6C)	2	7269	3339	34
H(8A)	3320	4379	1389	23
H(8B)	2466	5847	1313	23
H(9A)	909	4058	925	22
H(9B)	1782	2617	976	22
H(10A)	1812	5285	47	24
H(10B)	2449	3630	31	24
H(14A)	5090	1649	7196	35
H(14B)	5275	2741	7908	35
H(14C)	5755	3299	7238	35
H(15A)	4719	5836	7145	50
H(15B)	4220	5351	7817	50
H(15C)	3381	5842	7054	50
H(16A)	2349	3255	6993	53
H(16B)	3170	2598	7732	53
H(16C)	3020	1623	6989	53
H(1S1)	5810	2685	524	51
H(1S2)	6422	4374	543	51
H(2S1)	5382	6734	616	50
H(2S2)	4089	6593	648	50

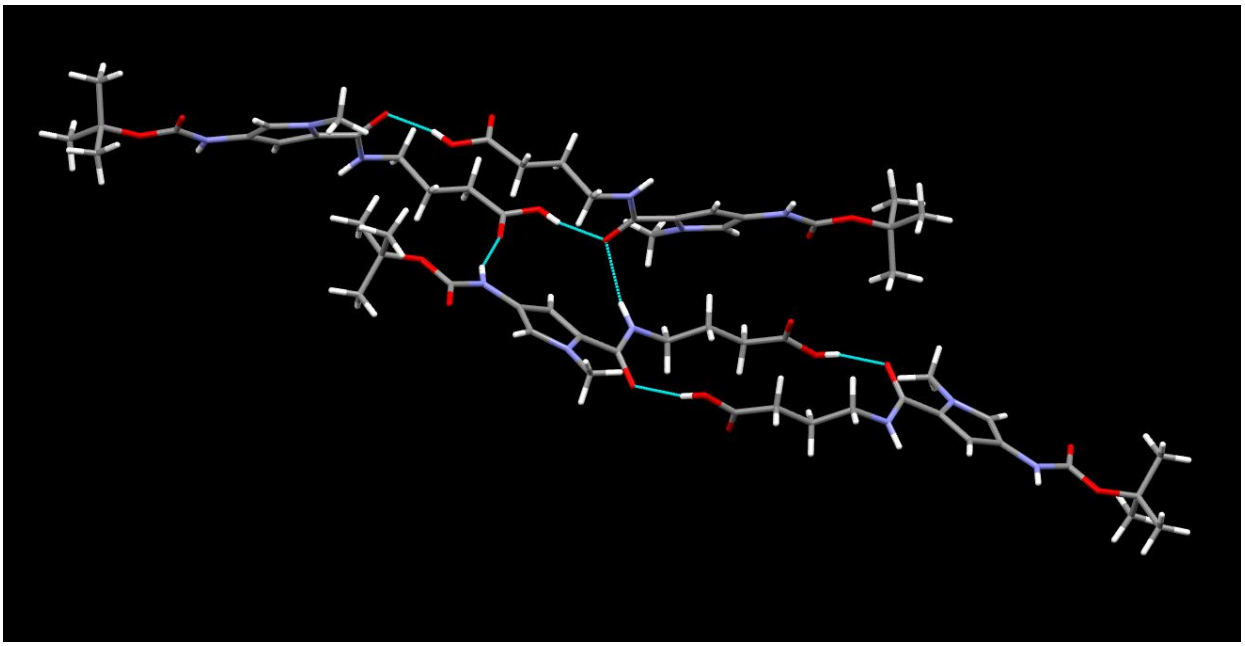
X-ray Table 18. Torsion angles [°] for Boc-Py-beta-COOH·0.5dioxane solvate.

C(5)-N(1)-C(2)-C(3)	0.62(17)
C(6)-N(1)-C(2)-C(3)	173.91(14)
N(1)-C(2)-C(3)-N(3)	178.55(15)
N(1)-C(2)-C(3)-C(4)	-0.69(18)
C(12)-N(3)-C(3)-C(2)	-7.3(3)
C(12)-N(3)-C(3)-C(4)	171.84(15)
C(2)-C(3)-C(4)-C(5)	0.49(18)
N(3)-C(3)-C(4)-C(5)	-178.79(14)
C(2)-N(1)-C(5)-C(4)	-0.31(17)
C(6)-N(1)-C(5)-C(4)	-173.01(15)
C(2)-N(1)-C(5)-C(7)	-176.39(14)
C(6)-N(1)-C(5)-C(7)	10.9(2)
C(3)-C(4)-C(5)-N(1)	-0.12(17)
C(3)-C(4)-C(5)-C(7)	175.67(14)
C(8)-N(2)-C(7)-O(1)	2.9(2)
C(8)-N(2)-C(7)-C(5)	-174.63(12)
N(1)-C(5)-C(7)-O(1)	23.2(2)
C(4)-C(5)-C(7)-O(1)	-152.00(15)
N(1)-C(5)-C(7)-N(2)	-159.19(14)
C(4)-C(5)-C(7)-N(2)	25.6(2)
C(7)-N(2)-C(8)-C(9)	-90.57(17)
N(2)-C(8)-C(9)-C(10)	177.79(12)
C(8)-C(9)-C(10)-C(11)	-167.89(13)
C(9)-C(10)-C(11)-O(5)	-4.4(2)
C(9)-C(10)-C(11)-O(2)	173.62(13)
C(3)-N(3)-C(12)-O(4)	3.2(3)
C(3)-N(3)-C(12)-O(3)	-177.18(14)
C(13)-O(3)-C(12)-O(4)	-1.6(2)
C(13)-O(3)-C(12)-N(3)	178.84(13)
C(12)-O(3)-C(13)-C(16)	61.90(18)
C(12)-O(3)-C(13)-C(15)	-63.97(18)
C(12)-O(3)-C(13)-C(14)	178.82(13)
C(2S)-O(1S)-C(1S)-C(2S)#1	-57.4(3)
C(1S)-O(1S)-C(2S)-C(1S)#1	57.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z



X-ray Figure 5. Projection view with 50% thermal ellipsoids for Boc-Py-β-COOH·0.5dioxane solvate.



X-ray Figure 6. Intermolecular hydrogen bonding in the crystal structure of Boc-Py-β-COOH·0.5dioxane solvate.