

Supporting Information

Synthesis of Optically Active β -Aminoacid-N-Carboxyanhydrides

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Experimental Details:

General. Tetrahydrofuran, hexane, dichloromethane, and diethyl ether were dried by passage through alumina under nitrogen prior to use.¹ Chemicals were purchased from commercial suppliers and used without purification. Infrared spectra were recorded on a Perkin Elmer RX1 FTIR Spectrophotometer calibrated using polystyrene film. ¹H NMR spectra were recorded on a Bruker AVANCE 200 MHz spectrometer. Circular Dichroism measurements were carried out on an Olis Rapid Scanning Monochromator at room temperature. The path length of the quartz cell was 1.0 mm and the concentration of polypeptide was 0.2 - 1.0 mg/mL. MALDI mass spectra were collected using a Thermo BioAnalysis DYNAMO mass spectrometer running in positive ion mode with samples prepared by mixing solutions of analyte in TFA with solutions of 6-aza-2-thiothymine in TFA and allowing the mixture to air dry. N β -BOC or N β -CBZ β -amino acids **2a-f** were synthesized according to the methods developed by Seebach.²⁻⁸ Separations of diastereomeric dipeptides⁹ were performed on a HPLC equipped with a

Phenomenex Jupiter column (5 μ m C₁₈ 300Å, 25 cm $\times$ 4.6 mm I.D.). Isocratic elution was carried out with 0.01 M ammonium acetate (pH 6.6) at ambient temperature (*ca.* 20 °C) using a flow rate of 1.0 mL/min.

General Procedures for the Synthesis of β -NCAs

An N β -CBZ β -amino acid or an N β -BOC- β -amino acid (6 mmol) in a 100 mL Schlenk flask was first dried under vacuum for 2 hours. Anhydrous dichloromethane (60 mL) was then transferred to this flask under nitrogen and PBr₃ (0.6 equiv.) was added dropwise to the resulting solution. In some cases, Et₃N (1.0 equiv.) was added dropwise to the reaction mixture immediately after addition of PBr₃. The mixture was stirred under nitrogen for 24 h and then the solvent was removed under vacuum. The residue was recrystallized from THF and hexanes in a nitrogen filled glove box.

(S)-3-Aminobutyric acid N-carboxyanhydride (β -HALa NCA) 3a: Either (S)-3-benzyloxycarbonylaminobutyric acid **2a** or (S)-3-*tert*-butoxycarbonylaminobutyric acid **2g** was used as the starting material. **3a** was isolated as colorless needles in yields of 95% from **2a** and 93 % from **2g**, respectively. FTIR (THF): 1805 cm⁻¹ (vCO, s), 1760 cm⁻¹ (vCO, s). ¹H NMR (CDCl₃): δ 7.03 (br, 1H, NHC(O)OC(O)CH₂CHCH₃), 3.77 (m, 1H, NHC(O)OC(O)CH₂CHCH₃), 2.87 (dd, 1H, NHC(O)OC(O)CH₂CHCH₃, $J_{gem} = 16.1$ Hz, $J_{vic} = 4.6$ Hz), 2.55 (dd, 1H, NHC(O)OC(O)CH₂CHCH₃, $J_{gem} = 16.1$ Hz, $J_{vic} = 9.2$ Hz), 1.32 (d, 3H, NHC(O)OC(O)CH₂CHCH₃, $J = 6.5$ Hz). ¹³C NMR (CDCl₃): δ 164.5, 150.5, 43.1, 36.6, 21.1. $[\alpha]_D^{24}$ (THF, C = 0.02) = + 20.3. mp 88-90 °C. Anal. Calcd. for C₅H₇NO₃: 46.51% C, 5.46% H, 10.85% N; found: 46.06% C, 5.41% H, 10.68% N. The x-ray crystal structure of **3a** was also determined to confirm the proposed NCA structure; the details are given at the end of the Supporting Information.

(S)-3-Amino-4-methylpentanoic acid N-carboxyanhydride (β -HVal NCA) 3b: Either (S)-3-benzyloxycarbonylamino-4-methylpentanoic acid **2b** or (S)-3-*tert*-butoxycarbonylamino-4-methylpentanoic acid **2h** was used as the starting material. **3b** was isolated as a white solid. The yield was 80 % from **2b** and 88 % from **2h**, respectively. FTIR (THF): 1802 cm^{-1} (vCO, s), 1760 cm^{-1} (vCO, s). ^1H NMR (CDCl_3): δ 7.23 (br, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$), 3.28 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$), 2.67 (dd, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{vic}} = 5.3$ Hz), 2.48 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{vic}} = 7.9$ Hz), 1.68 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$), 0.85 (d, 3H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$, $J = 6.7$ Hz), 0.84 (d, 3H, $\text{NHC(O)OC(O)CH}_2\text{CHCH(CH}_3)_2$, $J = 6.7$ Hz). ^{13}C NMR (CDCl_3): δ 165.3, 151.1, 52.5, 32.2, 31.6, 17.9. $[\alpha]_{\text{D}}^{24}$ (THF, $C = 0.02$) = -1.1. mp 55-57 $^\circ\text{C}$. This compound was found to be too thermally unstable to give satisfactory C, H, N analysis.

(S)-3-Amino-5-methylhexanoic acid N-carboxyanhydride (β -HLeu NCA) 3c: Either (S)-3-benzyloxycarbonylamino-5-methylhexanoic acid **2c** or (S)-3-*tert*-butoxycarbonylamino-5-methylhexanoic acid **2i** was used as the starting material. **3c** was isolated as colorless oil in yields of 85 % from **2c** and 74 % from **2i**, respectively. FTIR (THF): 1802 cm^{-1} (vCO, s), 1758 cm^{-1} (vCO, s). ^1H NMR (CDCl_3): δ 7.30 (br, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$), 3.68 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$), 2.86 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 4.8$ Hz), 2.54 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 8.1$ Hz), 1.73 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$), 1.50 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$), 1.37 (m, 2H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$), 0.95 (d, 3H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$, $J = 6.5$ Hz), 0.92 (d, 3H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH(CH}_3)_2$, $J = 6.5$ Hz), ^{13}C NMR (CDCl_3): δ 165.5, 150.5, 45.5,

44.2, 35.2, 24.7, 22.9, 22.5. $[\alpha]_D^{24}$ (THF, C = 0.02) = -8.1. This compound was found to be too thermally unstable to give satisfactory C, H, N analysis.

(S)-3-Amino-4-phenylbutyric acid N-carboxyanhydride (β -HPhe NCA) 3d: Either (S)-3-benzyloxycarbonylamino-4-phenylbutyric acid **2d** or (S)-3-*tert*-butoxycarbonylamino-4-phenylbutyric acid **2j** was used as the starting material. **3d** was isolated as white crystals in yields of 75 % from **2d** and 70 % from **2j**, respectively. FTIR (THF): 1805 cm^{-1} (vCO, s), 1760 cm^{-1} (vCO, s). ^1H NMR (CDCl_3): δ 7.35 (m, 5H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$), 6.7 (br, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$), 3.84 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$), 2.89 (dd, 2H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 6.7$ Hz, $J_{\text{vic}} = 2.3$ Hz), 2.83 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{vic}} = 5.0$ Hz), 2.50 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.2$ Hz, $J_{\text{vic}} = 7.8$ Hz). ^{13}C NMR (CDCl_3): δ 164.5, 150.2, 129.4, 127.9, 48.5, 41.6, 34.2. $[\alpha]_D^{24}$ (THF, C = 0.02) = -55.9. Mp: 88-90 °C. Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: 64.38% C, 5.39% H, 6.82% N; found: 64.18% C, 5.05% H, 6.85% N.

(S)-3-Amino-5-benzyloxycarbonylpentanoic acid N-carboxyanhydride (β -HGLu NCA) 3e: Either (S)-3-benzyloxycarbonylamino-5-benzyloxycarbonylpentanoic acid **2e** or (3S)-3-*tert*-butoxycarbonylamino-5-benzyloxycarbonylpentanoic acid **2k** was used as the starting material. **3e** was isolated as white crystals in yields of 54 % from **2e** and 52 % from **2k**, respectively. FTIR (THF): 1802 cm^{-1} (vCO, s), 1760 cm^{-1} (vCO, s), 1737 cm^{-1} (vCO, s). ^1H NMR (CDCl_3): δ 7.26 (m, 5H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$), 6.60 (br, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$), 5.01 (s, 2H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$), 3.51 (m, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$), 2.71 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$), 2.41 (m, 2H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 4.9$ Hz).

$\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$, 2.28 (dd, 1H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 8.0$ Hz), 1.77 (m, 2H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{C(O)OCH}_2\text{C}_6\text{H}_5$). ^{13}C NMR (CDCl_3): δ 172.6, 164.4, 150.0,
 135.5, 128.8, 128.6, 67.1, 46.6, 34.5, 30.2, 29.7. $[\alpha]_{\text{D}}^{24}$ (THF, $C = 0.02$) = -3.9. Mp 102-105
 $^{\circ}\text{C}$. Anal. Calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_5$: 60.64% C, 5.45% H, 5.05% N; found: 59.47% C, 5.99% H,
 5.03% N.

(S)-3-Amino-7-benzyloxycarbonylaminoheptanoic acid N-carboxyanhydride (β -HLys NCA) 3f: (S)-3-*tert*-Butoxycarbonylamino-7-benzyloxycarbonylaminoheptanoic acid **2f** was
 used as the starting material. **3f** was isolated as colorless oil (45% yield). FTIR (THF): 1802
 cm^{-1} (vCO, s), 1760 cm^{-1} (vCO, s), 1727 cm^{-1} (vCO, s). ^1H NMR (CDCl_3): δ 7.20 (s, 5H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 7.04 (br, 1H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 5.05 (br, 1H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 4.94 (s, 2H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 3.35 (m, 1H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 3.05 (m, 2H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, 2.63 (dd, 1H,
 $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 4.5$ Hz), 2.35
 (dd, 1H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$, $J_{\text{gem}} = 16.1$ Hz, $J_{\text{vic}} = 8.7$),
 1.41-1.03 (m, 6H, $\text{NHC(O)OC(O)CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC(O)OCH}_2\text{C}_6\text{H}_5$). ^{13}C NMR
 (CDCl_3): δ 164.8, 157.0, 150.5, 136.7, 128.7, 128.3, 66.9, 46.7, 40.3, 34.5, 34.0, 29.5, 21.7.
 $[\alpha]_{\text{D}}^{24}$ (THF, $C = 0.02$) = -1.4. Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_5$: 59.99% C, 6.29% H, 8.74% N;
 found: 59.30% C, 6.05% H, 8.66% N.

Polymerization of β -HPhe NCA with NaOtBu In the dry box, β -HPhe NCA (41 mg, 0.2 mmol) was dissolved in THF (0.5 mL) and placed in a 25 mL reaction tube which could be sealed with a Teflon stopcock. An aliquot of NaOtBu (200 μ L of a 0.019 M solution in THF) was then added *via* syringe to the flask. A stirbar was added and the flask was sealed, removed from the dry box, and stirred at 50 °C for 3 days. Polymer was precipitated from the THF solution by addition of the reaction mixture to methanol. The solid polymer was dried *in vacuo* to give poly(β -HPhe) (30 mg, 93% yield). FT-IR (THF): 1638 cm^{-1} (amide I, s br), 1552 cm^{-1} (amide II, s br). ^1H NMR (TFA- d): δ 7.35 (br m, 5H, $-(\text{NHC}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{CHCH}_2\text{C}_6\text{H}_5)_n-$), 4.3 (br s, 1H, $-(\text{NHC}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{CHCH}_2\text{C}_6\text{H}_5)_n-$), 3.15-2.96 (br m, 4H, $-(\text{NHC}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{CHCH}_2\text{C}_6\text{H}_5)_n-$). The polymer was found to be insoluble in most organic solvents but was soluble in TFA. Molecular weight analysis using MALDI(TOF)-MS: $M_n = 1370$; Range: 665 (tetramer) to 2444 (pentadecamer).

Synthesis of β -HAla-Ala dipeptide¹⁰ L-Alanine (50 mg) was dissolved in aqueous sodium borate (2 mL of a 0.4 M solution, pH 10). The solution was vigorously stirred while placed in an ice bath. β -HAla NCA (65 mg, 0.9 equiv.) was added to the solution in one portion. The solution pH value was maintained at 10 by adding drops of 1 N NaOH solution as the reaction proceeded. After two minutes, 1 N HCl was added to bring the pH to 5. The solution was freeze dried and the residue was extracted three times with methanol. The solution was then concentrated on a hot plate to the cloud point. Slow addition of diethyl ether to this methanol solution gave the dipeptide β -HAla-Ala (113 mg, 64% yield). ^1H NMR (D_2O): δ 4.23 (m, 1H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$), 3.75 (m, 1H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$), 2.76 (d, 1H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$, $J = 7.0$ Hz), 2.55 (d, 1H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$, $J = 7.0$ Hz), 1.57 (d, 3H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$, $J = 7.0$ Hz).

$\text{CH}_2\text{C}(\text{O})\text{NHCH}(\text{CH}_3)\text{COOH}$, $J = 7.0 \text{ Hz}$) 1.37 (d, 3H, $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}(\text{O})\text{NH}-$
 $\text{CH}(\text{CH}_3)\text{COOH}$, $J = 7.0 \text{ Hz}$). The isolated dipeptide possessed the same HPLC retention time
as an authentic sample prepared using standard BOC-mediated peptide synthesis.

X-ray Data Collection, Structure Solution and Refinement for 3a A colorless crystal of
approximate dimensions 0.23 x 0.28 x 39 mm was mounted on a glass fiber and transferred to a
Bruker CCD platform diffractometer. The SMART¹¹ program package was used to determine
the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction
data). The raw frame data was processed using SAINT¹² and SADABS¹³ to yield the reflection
data file. Subsequent calculations were carried out using the SHELXTL¹⁴ program. The
diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic
space groups $C2$, Cm or $C2/m$. It was later determined that the noncentrosymmetric space group
 $C2$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix
least-squares techniques. The analytical scattering factors¹⁵ for neutral atoms were used
throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and
refined (x, y, z and U_{iso}). There were two molecules of the formula unit present which formed a
hydrogen bonded dimeric structure. At convergence, $wR2 = 0.0891$ and $\text{GOF} = 1.064$ for 220
variables refined against 2772 data (As a comparison for refinement on F , $R1 = 0.0328$ for those
2642 data with $I > 2.0\sigma(I)$). The absolute structure could not be assigned by refinement of
the Flack parameter¹⁶ or by inversion of the molecule.

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Table 1. Crystal data and structure refinement for **3a**.

Identification code	3a	
Empirical formula	C ₅ H ₇ NO ₃	
Formula weight	129.12	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 18.6720(13) Å	α = 90°.
	b = 9.6069(7) Å	β = 97.5190(10)°.
	c = 6.5761(5) Å	γ = 90°.
Volume	1169.48(15) Å ³	
Z	8	
Density (calculated)	1.467 Mg/m ³	
Absorption coefficient	0.122 mm ⁻¹	
F(000)	544	
Crystal size	0.39 x 0.28 x 0.23 mm ³	
Theta range for data collection	2.20 to 28.31°.	
Index ranges	-24 ≤ h ≤ 24, -12 ≤ k ≤ 12, -8 ≤ l ≤ 8	
Reflections collected	6209	
Independent reflections	2772 [R(int) = 0.0230]	
Completeness to theta = 28.31°	96.9 %	
Absorption correction	None	
Max. and min. transmission	0.9724 and 0.9538	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2772 / 1 / 220	
Goodness-of-fit on F ²	1.064	
Final R indices [I > 2σ(I)]	R1 = 0.0328, wR2 = 0.0880	
R indices (all data)	R1 = 0.0343, wR2 = 0.0891	
Absolute structure parameter	-0.4(7)	
Extinction coefficient	0.0061(12)	
Largest diff. peak and hole	0.277 and -0.167 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10708(1)	6129(1)	8426(2)	23(1)
O(2)	11699(1)	5033(1)	9818(1)	21(1)
O(3)	12770(1)	4074(1)	10566(2)	29(1)
N(1)	10687(1)	3763(1)	8559(2)	20(1)
C(1)	10988(1)	5008(2)	8861(2)	18(1)
C(2)	12164(1)	3911(1)	9787(2)	20(1)
C(3)	11842(1)	2631(1)	8728(2)	22(1)
C(4)	11061(1)	2443(2)	9080(2)	22(1)
C(5)	10692(1)	1298(2)	7752(3)	32(1)
O(4)	9240(1)	3970(1)	6234(2)	26(1)
O(5)	8228(1)	5086(1)	5088(1)	24(1)
O(6)	7251(1)	6146(1)	3615(2)	35(1)
N(2)	9197(1)	6300(1)	6792(2)	20(1)
C(6)	8934(1)	5091(2)	6096(2)	20(1)
C(7)	7850(1)	6297(2)	4467(2)	23(1)
C(8)	8249(1)	7631(2)	4884(2)	22(1)
C(9)	8757(1)	7552(2)	6881(2)	20(1)
C(10)	9238(1)	8823(2)	7220(3)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **3a**.

O(1)-C(1)	1.2147(18)
O(2)-C(2)	1.3859(17)
O(2)-C(1)	1.3932(14)
O(3)-C(2)	1.1903(15)
N(1)-C(1)	1.3249(19)
N(1)-C(4)	1.4670(17)
N(1)-H(1)	0.85(2)
C(2)-C(3)	1.4996(19)
C(3)-C(4)	1.5168(18)
C(3)-H(3A)	0.895(17)
C(3)-H(3B)	0.934(16)
C(4)-C(5)	1.513(2)
C(4)-H(4)	0.969(16)
C(5)-H(5A)	0.93(2)
C(5)-H(5B)	0.972(19)
C(5)-H(5C)	0.986(18)
O(4)-C(6)	1.2175(18)
O(5)-C(7)	1.3937(18)
O(5)-C(6)	1.3958(15)
O(6)-C(7)	1.1931(16)
N(2)-C(6)	1.3191(19)
N(2)-C(9)	1.4615(18)
N(2)-H(2)	0.82(2)
C(7)-C(8)	1.4893(19)
C(8)-C(9)	1.5181(18)
C(8)-H(8A)	1.014(18)
C(8)-H(8B)	0.956(18)
C(9)-C(10)	1.5157(19)
C(9)-H(9)	0.928(15)
C(10)-H(10A)	1.01(2)
C(10)-H(10B)	0.97(2)
C(10)-H(10C)	0.98(2)
C(2)-O(2)-C(1)	122.83(11)

C(1)-N(1)-C(4)	124.47(11)
C(1)-N(1)-H(1)	113.5(14)
C(4)-N(1)-H(1)	121.9(14)
O(1)-C(1)-N(1)	127.17(11)
O(1)-C(1)-O(2)	116.51(12)
N(1)-C(1)-O(2)	116.31(11)
O(3)-C(2)-O(2)	117.03(12)
O(3)-C(2)-C(3)	127.48(12)
O(2)-C(2)-C(3)	115.48(10)
C(2)-C(3)-C(4)	111.22(11)
C(2)-C(3)-H(3A)	107.6(10)
C(4)-C(3)-H(3A)	108.8(10)
C(2)-C(3)-H(3B)	104.9(10)
C(4)-C(3)-H(3B)	108.5(9)
H(3A)-C(3)-H(3B)	115.8(13)
N(1)-C(4)-C(5)	109.07(11)
N(1)-C(4)-C(3)	107.40(11)
C(5)-C(4)-C(3)	111.89(12)
N(1)-C(4)-H(4)	108.5(9)
C(5)-C(4)-H(4)	111.0(9)
C(3)-C(4)-H(4)	108.9(9)
C(4)-C(5)-H(5A)	111.9(12)
C(4)-C(5)-H(5B)	106.6(12)
H(5A)-C(5)-H(5B)	107.7(16)
C(4)-C(5)-H(5C)	109.9(11)
H(5A)-C(5)-H(5C)	110.6(16)
H(5B)-C(5)-H(5C)	110.1(15)
C(7)-O(5)-C(6)	123.08(11)
C(6)-N(2)-C(9)	123.57(11)
C(6)-N(2)-H(2)	114.3(13)
C(9)-N(2)-H(2)	121.3(13)
O(4)-C(6)-N(2)	127.10(12)
O(4)-C(6)-O(5)	115.95(12)
N(2)-C(6)-O(5)	116.95(12)
O(6)-C(7)-O(5)	116.31(13)
O(6)-C(7)-C(8)	127.34(13)

O(5)-C(7)-C(8)	116.32(10)
C(7)-C(8)-C(9)	110.88(11)
C(7)-C(8)-H(8A)	109.3(10)
C(9)-C(8)-H(8A)	114.0(10)
C(7)-C(8)-H(8B)	106.1(10)
C(9)-C(8)-H(8B)	108.1(9)
H(8A)-C(8)-H(8B)	108.1(14)
N(2)-C(9)-C(10)	110.12(10)
N(2)-C(9)-C(8)	107.30(10)
C(10)-C(9)-C(8)	112.20(12)
N(2)-C(9)-H(9)	108.9(10)
C(10)-C(9)-H(9)	107.9(10)
C(8)-C(9)-H(9)	110.4(9)
C(9)-C(10)-H(10A)	108.3(12)
C(9)-C(10)-H(10B)	112.0(12)
H(10A)-C(10)-H(10B)	109.1(17)
C(9)-C(10)-H(10C)	107.5(11)
H(10A)-C(10)-H(10C)	111.4(17)
H(10B)-C(10)-H(10C)	108.5(16)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	23(1)	20(1)	25(1)	0(1)	1(1)	2(1)
O(2)	19(1)	20(1)	23(1)	-4(1)	0(1)	0(1)
O(3)	20(1)	27(1)	38(1)	1(1)	-3(1)	1(1)
N(1)	16(1)	21(1)	22(1)	1(1)	0(1)	-1(1)
C(1)	16(1)	24(1)	15(1)	-2(1)	3(1)	2(1)
C(2)	19(1)	19(1)	21(1)	3(1)	2(1)	2(1)
C(3)	21(1)	18(1)	25(1)	1(1)	1(1)	3(1)
C(4)	23(1)	19(1)	24(1)	3(1)	1(1)	-1(1)
C(5)	29(1)	21(1)	43(1)	-3(1)	-4(1)	-3(1)
O(4)	27(1)	24(1)	27(1)	-2(1)	0(1)	3(1)
O(5)	21(1)	23(1)	26(1)	-3(1)	-1(1)	-2(1)
O(6)	22(1)	37(1)	44(1)	-6(1)	-8(1)	1(1)
N(2)	16(1)	23(1)	19(1)	0(1)	-1(1)	1(1)
C(6)	19(1)	24(1)	16(1)	1(1)	3(1)	0(1)
C(7)	20(1)	28(1)	21(1)	-3(1)	1(1)	1(1)
C(8)	21(1)	22(1)	23(1)	0(1)	0(1)	3(1)
C(9)	20(1)	19(1)	20(1)	-1(1)	2(1)	-1(1)
C(10)	25(1)	23(1)	40(1)	-1(1)	-5(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3a**.

	x	y	z	U(eq)
H(1)	10257(12)	3790(20)	7930(30)	35(5)
H(3A)	12098(9)	1900(19)	9260(20)	19(4)
H(3B)	11854(8)	2796(17)	7330(20)	19(4)
H(4)	11046(8)	2253(16)	10520(20)	19(4)
H(5A)	10890(10)	420(20)	8110(30)	34(5)
H(5B)	10191(11)	1290(20)	8010(30)	34(4)
H(5C)	10720(9)	1500(20)	6290(30)	32(4)
H(2)	9612(11)	6266(19)	7360(30)	30(4)
H(8A)	7891(9)	8428(18)	4820(30)	25(4)
H(8B)	8534(9)	7750(17)	3790(30)	20(4)
H(9)	8497(8)	7478(18)	7990(20)	16(3)
H(10A)	9521(10)	8910(20)	6020(30)	45(6)
H(10B)	8962(11)	9670(20)	7330(30)	37(5)
H(10C)	9559(10)	8680(20)	8510(30)	34(5)

Table 6. Torsion angles [°] for **3a**.

C(4)-N(1)-C(1)-O(1)	178.58(13)
C(4)-N(1)-C(1)-O(2)	-2.78(18)
C(2)-O(2)-C(1)-O(1)	-157.58(12)
C(2)-O(2)-C(1)-N(1)	23.63(17)
C(1)-O(2)-C(2)-O(3)	176.24(12)
C(1)-O(2)-C(2)-C(3)	-2.64(18)
O(3)-C(2)-C(3)-C(4)	145.40(14)
O(2)-C(2)-C(3)-C(4)	-35.86(16)
C(1)-N(1)-C(4)-C(5)	-155.58(13)
C(1)-N(1)-C(4)-C(3)	-34.13(17)
C(2)-C(3)-C(4)-N(1)	51.07(14)
C(2)-C(3)-C(4)-C(5)	170.74(12)
C(9)-N(2)-C(6)-O(4)	-168.98(12)
C(9)-N(2)-C(6)-O(5)	10.96(18)
C(7)-O(5)-C(6)-O(4)	-167.85(11)
C(7)-O(5)-C(6)-N(2)	12.20(17)
C(6)-O(5)-C(7)-O(6)	179.75(12)
C(6)-O(5)-C(7)-C(8)	1.62(17)
O(6)-C(7)-C(8)-C(9)	147.39(14)
O(5)-C(7)-C(8)-C(9)	-34.72(15)
C(6)-N(2)-C(9)-C(10)	-165.31(13)
C(6)-N(2)-C(9)-C(8)	-42.93(17)
C(7)-C(8)-C(9)-N(2)	51.78(14)
C(7)-C(8)-C(9)-C(10)	172.86(12)

Table 7. Hydrogen bonds for **3a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)	0.85(2)	2.08(2)	2.9312(16)	175.3(19)
N(2)-H(2)...O(1)	0.82(2)	2.08(2)	2.8893(15)	172.5(17)

3a

