Organocatalytic Asymmetric Assembly Reactions: One Pot Synthesis of functionalized β -Amino Alcohols from Aldehydes, Ketones and Azodicarboxylates

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Supporting Information

General. Chemicals and solvents were either purchased *puriss p.A.* from commercial suppliers or purified by standard techniques. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H₂SO₄ (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating. Flash chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm), ¹H NMR and ¹³C NMR spectra were recorded on Bruker DRX-500 MHz. Chemical shifts are given in δ relative to tetramethylsilane (TMS), the coupling constants *J* are given in Hz. The spectra were recorded in CDCl₃ as solvent at room temperature, TMS served as internal standard (δ = 0 ppm) for ¹H NMR, and CDCl₃ was used as internal standard (δ = 77.0 ppm) for ¹³C NMR. *Due to the rigid nature of compounds ¹H NMR and ¹³C NMR shows poor resolution even at 60 °C.* HPLC was carried out using a Hitachi organizer consisting of a D-2500 Chromato-Integrator, a L-4000 UV-Detector, and a L-6200A Intelligent Pump. Optical rotations were recorded on a Perkin Elemer 241 Polarimeter (λ = 589 nm, 1 dm cell). High resolution mass spectra were recorded on an IonSpec FTMS mass spectrometer with a DHB-matrix.

General experimental procedure for one pot reaction (table 1): To a mixture of solvent (3 mL), dibenzyl azodicarboxylate (90%, 330 mg, 1 mmol), L-proline (23 mg, 0.2 mmol) and propionaldehyde (79 μ L, 1.1 mmol), was added acetone (2 mL) and the reaction was stirred at room temperature for 72 h. Then, half saturated NH₄Cl solution and ethyl acetate were added

with vigorous stirring, the layers were separated and the aqueous phase was extracted thoroughly with ethyl acetate. The combined organic phases were dried (Na_2SO_4), concentrated, and purified by flash column chromatography (silica gel, mixtures of hexanes/ethyl acetate) to afford the desired amino alcohol as a white solid with mixture of diastereomers.

Determination of the absolute stereochemistry of (4*R*,5*S*)-5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-hexan-2-one (3**) by X-ray analysis of acetate of **3**. (table 1, entry 1):**

To a mixture of anhydrous DMSO (3 mL), dibenzyl azodicarboxylate (90%, 330 mg, 1 mmol), L-proline (23 mg, 0.2 mmol) and propionaldehyde (79 μL , 1.1 mmol) was added acetone (2 mL) and the reaction stirred at room temperature for 72 h. Then, half saturated NH_4Cl solution and ethyl acetate were added with vigorous stirring, the layers were separated and the aqueous phase was extracted thoroughly with ethyl acetate. The combined organic phases were dried (Na_2SO_4), concentrated. Recrystallization of crude product (**2**:**3** = 13:87) from CH_2Cl_2 -hexane afforded the crystallized racemate **3** and enantioenriched mother liquor with **2** and **3**. Further recrystallization of **2** and **3** from CH_2Cl_2 -hexane afforded **3** as white solid (>99% ee). $[\alpha]_{\text{D}} = + 3.6$ (c = 1.0, CHCl_3); ^1H NMR (60 $^\circ\text{C}$): 1.20 (d, 3H, $J = 6.95$ Hz, CH_3CH), 2.06 (s, 3H, CH_3CO), 2.54, 2.74 (2 m, CH_2CH), 3.31 (brs, 1H, CHOH), 4.08 (brs, 1H, CHN), 4.16 (m, 1H, CHOH), 5.11, 5.13 (2 s, 4H, 2 X PhCH_2), 6.56 (brs, 1H, NH), 7.29 (m, 10H, Ar-**H**); ^{13}C NMR (60 $^\circ\text{C}$): 12.03, 30.40, 47.01, 67.97, 68.32, 69.55, 127.95, 128.27, 135.94, 155.79, 209.07; HRMS for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_6\text{Na}$ (MNa^+): calcd 437.1683, obsd 437.1665. Compound **3** was treated with Ac_2O in pyridine at room temperature for 2 days. The volatiles were removed under vacuum and subsequent column chromatography followed by crystallization from CH_2Cl_2 -hexane afforded the acetic acid 1-[-1-(*N,N'*-bisbenzyloxycarbonyl-hydrazino)-ethyl]-3-oxo-butyl ester as colorless, plate-like crystals. $[\alpha]_{\text{D}} = - 0.2$ (c = 1.0, CHCl_3); ^1H NMR (60 $^\circ\text{C}$): 1.18 (d, 3H, $J = 5.9$ Hz, CH_3CH), 1.98 (s, 6H, CH_3CO and CH_3COO), 2.64 (dd, 1H, $J = 5.5$ and 16.8 Hz, 2.88 (brs, 1H), 4.40 (brs, 1H), 5.10 (s, 2H), 5.12 (s, 2H), 5.16 (m, 1H, CHOAc), 6.63 (brs, 1H, NH), 7.24 (s, 10H, Ar-**H**); ^{13}C NMR (60 $^\circ\text{C}$): 11.9, 14.0, 30.6, 46.9, 57.3, 67.6, 68.0, 69.3, 127.6, 127.9, 128.2, 135.7, 155.16, 156.9, 209.0. HRMS for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_7\text{Na}$ (MNa^+): calcd 479.1789, obsd 479.1772.

General experimental procedure for tandem reactions : A mixture of anhydrous CH₃CN (3 mL), dibenzyl azodicarboxylate (1 mmol), L-proline (23 mg, 0.2 mmol) and aldehyde (1.1 mmol) were stirred at room temperature for 20- 40 min. To this acetone (2 mL) is added and stirred at room temperature for 96 h. Then, half saturated NH₄Cl solution and ethyl acetate were added with vigorous stirring, the layers were separated and the aqueous phase was extracted thoroughly with ethyl acetate. The combined organic phases were dried (Na₂SO₄), concentrated, and purified by flash column chromatography (silica gel, mixtures of hexanes/ethyl acetate) to afford the desired amino alcohol as a white solid with mixture of diastereomers.

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-hexan-2-one (table 2, entry 1):

¹H NMR (60 °C) : 1.12 (d, *J* = 6.95 Hz, *anti* - CH₃CH), 1.19 (d, *J* = 6.6 Hz, *syn* - CH₃CH), 2.06 (s, *syn* - CH₃CO), 2.13 (s, *anti* - CH₃CO), 2.54, 2.73 (2 brs, CH₂CH), 3.34 (brs, CHOH), 3.90 (brs, CHN), 4.08 (brs, CHOH), 4.16 (t), 4.21 (brs), 5.12, 5.13 (2 s, PhCH₂), 6.64, 6.65 (2 brs, NH), 7.29 (m, Ar-H); HRMS for C₂₂H₂₆N₂O₆Na (MNa⁺): calcd 437.1683, obsd 437.1665; HPLC (Daicel Chiralcel OD-R, H₂O/MeCN = 65:35, 0.1% TFA, flow rate 1.0 mL/min, λ = 254 nm): t_R = 22.29 min (*syn*, major), t_R = 24.40 min (*syn*, minor), t_R = 33.41 min (*anti*, major), t_R = 35.49 min (*anti*, minor).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-6-phenyl-hexan-2-one (table 2, entry 2):

¹H NMR (60 °C) : 2.01 (s, *syn* - CH₃CO), 2.11 (s, *anti* - CH₃CO), 2.84, (m, CH₂CH), 3.63 (m, CHOH), 4.04, 4.13 (2 m, CHN), 4.48 (m, CHOH), 4.98 - 5.24 (m, 3 X PhCH₂), 6.06, 6.25 (2 brs, NH), 7.12 - 7.30 (m, 15 H Ar-H); ¹³C NMR (60 °C): 30.43, 30.53, 31.73, 38.12, 46.91, 50.06, 67.85, 68.06, 126.55, 128.14, 128.22, 128.38, 128.44, 128.51, 128.56, 128.59, 128.76, 128.78, 135.46, 135.72, 135.79, 138.27, 156.05, 209.88; HRMS for C₂₈H₃₀N₂O₆Na (MNa⁺): calcd 513.1996, obsd 513.1997; HPLC (Daicel Chirapak AD, hexane/isopropanol = 98 : 2, flow rate 1.0 mL/min, λ = 254 nm): t_R = 28.31 min (*syn*, major), t_R = 34.54 min (*syn*, minor), t_R = 31.12 min (*anti*, minor), t_R = 47.79 min (*anti*, major).

6-Cyclohexyl-5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-6-phenyl-hexan-2-one

(table 2, entry 3): ¹H NMR (60 °C) : 0.78, 0.89, 1.11 (3 brs, 5H), 1.59 (brs, 5H), 2.08 (s,

CH₃CO), 2.54 (brs, 1H), 2.81 (m), 3.88, 3.97, 4.07, 4.15 (m), 5.09 (s, 4H, 2 X PhCH₂), 6.83 (brs, NH), 7.26 (s, 10H, Ar-H); ¹³C NMR (60 °C): 25.7, 25.8, 26.0, 26.1, 26.2, 26.3, 30.1, 30.3, 30.6, 32.1, 32.1, 32.7, 33.8, 34.0, 34.2, 37.0, 47.1, 51.9, 67.5, 67.6, 69.8, 125.4, 127.3, 127.8, 127.9, 128.0, 128.2, 128.3, 135.6, 143.0, 156.3, 176.1, 208.1, 209.4; HRMS for C₂₈H₃₆N₂O₆Na (MNa⁺): calcd 519.2465, obsd 519.2449; HPLC (Daicel Chiralcel OD-R, H₂O/MeCN = 50:50, 0.1% TFA, flow rate 0.3 mL/min, λ = 254 nm): t_R = 73.30 min (*syn*, major), t_R = 83.88 min (*syn*, minor), t_R = 99.25 min (*anti*, minor), t_R = 105.47 min (*anti*, major).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-decan-2-one (table 2, entry 4):
¹H NMR (60 °C) : 0.84 (brs, 3H, CH₃CH₂), 1.24 (brs, 2H, CH₃CH₂), 1.54 (brs, 2H, CH₃CH₂CH₂CH₂), 2.12 (s, 3H, CH₃CO), 2.57 (brs, 1H, CH₂CO), 2.92 (brs, 1H, CH₂CO), 3.39 (brs, 1H, CHOH), 4.01 (2 brs, 2H, CHOH and CHN), 5.13 (brs, 4H, 2 X PhCH₂), 6.56, 6.66 (2 brs, 1H NH), 7.29 (brs, 10H, Ar-H); ¹³C NMR (60 °C): 13.7, 22.3, 25.8, 26.0, 30.3, 31.4, 31.5, 47.0, 47.2, 67.9, 68.3, 125.5, 127.7, 127.8, 135.3, 135.5, 135.7, 135.8, 135.9, 156.4, 209.6; HRMS for C₂₆H₃₄N₂O₆Na (MNa⁺): calcd 493.2309, obsd 493.2300; HPLC (Daicel Chiralcel OD-R, H₂O/MeCN = 51:49, 0.1% TFA, flow rate 0.3 mL/min, λ = 254 nm): t_R = 80.07 min (*syn*, major), t_R = 102.60 min (*syn*, minor), t_R = 114.16 min (*anti*, minor), t_R = 118.15 min (*anti*, major).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-tridec-7-en-2-one (table 2, entry 5):
¹H NMR (60 °C) : 0.85 (t, *J* = 7.0 Hz, CH₃CH₂), 1.24 (m, 6H, -(CH₂)₃-), 1.90 (m, 2H, CH:CHCH₂CH₂), 2.13 (s, 3H, CH₃CO), 2.25 (m, 2H, CHCH₂CH:CH), 2.56 (m, 2H, CH₂CO), 3.44 (brs, 1H, CHOH), 4.00 (brs, 1H, CHN), 4.13 (brs, 1H, CHOH), 5.14 (brs, 4H, 2 X PhCH₂), 5.30 (brs, 1H, CHCH₂CH:CH), 5.49 (brs, 1H, CHCH₂CH:CH), 6.36 (brs, *syn*-NH), 6.45 (brs, *anti*-NH), 7.30 (brs, 10H, Ar-H); ¹³C NMR (60 °C): 13.7, 22.3, 28.9, 31.2, 32.2, 32.3, 32.3, 46.9, 67.7, 67.9, 68.3, 128.0, 128.2, 133.6, 134.0, 135.5, 135.7, 135.8, 135.9, 156.3, 209.8; HRMS for C₂₉H₃₈N₂O₆Na (MNa⁺): calcd 533.2622, obsd 533.2621; HPLC (Daicel Chiralcel OD-R, H₂O/MeCN = 48:52, 0.1% TFA, flow rate 0.3 mL/min, λ = 254 nm): t_R = 82.05 min (*syn*, major), t_R = 101.67 min (*syn*, minor), t_R = 115.15 min (*anti*, minor), t_R = 119.00 min (*anti*, major).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-heptan-2-one (table 2, entry 6):

^1H NMR (60 °C) : 0.94 (m, 3H, CH_3CH_2), 1.64 (m, 2H, CH_3CH_2), 2.15 (s, *syn* - CH_3CO), 2.23 (brs, *anti* - CH_3CO), 3.03, 3.45 (2 brs, 2H, CH_2CO), 3.45 (brs, 1H, CHOH), 4.07 (brs, 2H, CHN and CHOH), 5.20, 5.25 (2 brs, 4H, 2 X PhCH_2), 6.53 (brs, *syn-NH*), 6.62 (brs, *anti-NH*), 7.40 (brs, 10H, Ar-**H**); ^{13}C NMR (60 °C): 10.6, 10.8, 21.0, 30.3, 30.8, 47.1, 67.9, 68.3, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 135.4, 135.5, 135.8, 135.9, 156.5, 209.7; HRMS for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_6\text{Na}$ (MNa^+): calcd 451.1839, obsd 451.1833; HPLC (Daicel Chiralcel OD-R, $\text{H}_2\text{O}/\text{MeCN}$ = 60:40, 0.1% TFA, flow rate 0.5 mL/min, λ = 254 nm): t_R = 36.37 min (*syn*, major), t_R = 40.44 min (*syn*, minor), t_R = 56.23 min (*anti*).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-oct-7-en-2-one (table 2, entry 7):

^1H NMR (60 °C) : 2.06 (brs, *syn* - CH_3CO), 2.12 (brs, *anti* - CH_3CO), 2.34 (brs, 2H, $\text{CHCH}_2\text{CH}:\text{CH}_2$), 2.61 (brs, 2H, CH_2CO), 2.99, 3.48 (brs, 1H, CHOH), 4.01 (brs, 1H, CHN), 4.18 (brs, 1H, CHOH), 4.99 (m, 2H, $\text{CH}:\text{CH}_2$), 5.13 (brs, 4H, 2 X PhCH_2), 5.71 (brs, 1H, $\text{CH}:\text{CH}_2$), 6.45 (brs, *syn-NH*), 6.55 (brs, *anti-NH*), 7.29 (brs, 10H, Ar-**H**); ^{13}C NMR (60 °C): 30.3, 30.8, 32.8, 46.8, 68.0, 68.3, 68.7, 117.1, 128.1, 128.4, 128.5, 135.4, 135.8, 156.2, 209.7; HRMS for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_6\text{Na}$ (MNa^+): calcd 463.1839, obsd 463.1826; HPLC (Daicel Chiralcel OD-R, $\text{H}_2\text{O}/\text{MeCN}$ = 60:40, 0.1% TFA, flow rate 0.5 mL/min, λ = 254 nm): t_R = 55.20 min (*syn*, major), t_R = 60.63 min (*syn*, minor), t_R = 84.56 min (*anti*).

5-(*N,N'*-Bisbenzyloxycarbonyl-hydrazino)-4-hydroxy-6-methyl-heptan-2-one (table 2, entry 8):

^1H NMR (60 °C) : 0.88-1.03 (m, 6H, $(\text{CH}_3)_2\text{CH}$), 1.35 (m, 1H, $(\text{CH}_3)_2\text{CH}$), 2.09 (brs, 3H, CH_3CO), 2.74 (brs, 2H, CH_2CO), 3.75 (brs, 1H, CHOH), 3.96 (brs, 1H, CHN), 4.30 (brs, 1H, CHOH), 5.16 (brs, 4H, 2 X PhCH_2), 6.36 (brs, *syn-NH*), 6.55 (brs, *anti-NH*), 7.31 (brs, 10H, Ar-**H**); HRMS for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_6\text{Na}$ (MNa^+): calcd 465.1996, obsd 465.1999; HPLC (Daicel Chiralcel OD-R, $\text{H}_2\text{O}/\text{MeCN}$ = 60:40, 0.1% TFA, flow rate 0.5 mL/min, λ = 254 nm): t_R = 106.01 min (*syn*, minor), t_R = 109.21 min (*syn*, major), t_R = 120.04 min (*anti*).

Synthesis of 5-Amino-6-cyclohexyl-2-methyl-hexane-2,4-diol (scheme 3): To a 1.4 M methyl magnesium bromide (0.75 mmol, 0.535 ml) in toluene-THF (3:1) amino alcohol (0.15 mmol, 74.4 mg) was added at 0 °C with stirring. After 1 h the reaction was quenched with aqueous

NH_4Cl solution and extracted with ethyl acetate. The combined organic phases were dried (Na_2SO_4), concentrated, and purified by flash column chromatography (silica gel, mixtures of hexanes/ethyl acetate) to afford the desired *tert*-alcohol as white solid. HRMS for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{O}_6\text{Na}$ (MNa^+): calcd 535.2778, obsd 535.2773; ^1H NMR (60 $^\circ\text{C}$): 0.85 (m), 1.26 (m), 1.42 (m), 1.64 (m), 4.04 (brs, 1H), 4.20 (brs, 1H), 5.15 (brs, 4H), 7.30 (s, 10H). The *tert*-alcohol was dissolved in methanol (5 ml), AcOH (5 drops) and treated with ca. 200 mg of Raney nickel (pre washed with methanol) under 30 bar of hydrogen for 20 h. The reaction mixture was filtered over celite to obtain the corresponding aminodiol (72% overall yield). $[\alpha]_{\text{D}} = -1.2$ ($c = 0.5$, CHCl_3); HRMS for $\text{C}_{13}\text{H}_{28}\text{NO}_2$ (MH^+): calcd 230.2115, obsd 230.2114; ^1H NMR (60 $^\circ\text{C}$): 0.88 (brs), 1.25 (brs), 1.68 (brs), 2.04 (brs), 2.09 (brs), 3.24 (brs).

Experimental

A colorless, plate-like crystal (0.02x0.12x0.18 mm) was mounted along with the largest dimension and data were collected with a Bruker SMART APEX diffractometer equipped with a molybdenum sealed tube and a highly oriented graphite monochromator. The frame data are acquired with SMART software using a three axis stage. The χ -axis on this stage is fixed at 54.74° , and the CCD detector is maintained at -40°C . Cell constants are determined from 1200 30s frames. A complete hemisphere of data is scanned on ω (0.3°) with a run time of 30 s per frame at the detector resolution of 512x512 pixels. A total of 1800 frames are collected in three sets. The frames are then processed on a IBM compatible PC by using SAINT+ software to give the hkl file corrected for L_p /decay and absorption. See Table 1 for cell parameters and other relevant data.

There were no systematic absences in the data. Since $Z=1$ and there is no symmetry site possible in the structure, the space group P1 was assumed and later confirmed by successful refinement of the structure. The structure was solved by direct methods using SHELXTL-PC. All non-hydrogen atoms were refined anisotropically by the full matrix least-squares method. The function minimized was $\sum w(\|F_o\| - \|F_c\|)^2$. Hydrogen atoms were included in the ideal positions with fixed isotropic U values equal to 1.2 times that of the atom they are attached to. A weighting scheme of the form $w=1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $a=0.0419$ and $b=0.0024$ was used. (P is defined as $\text{Max}(F_o^2, 0) + 2F_c^2/3$.) There was no evidence of secondary extinction; therefore it was not applied. The refinement converged to the R indices given in the Table 1 which also includes the the largest difference peak and the hole in the last cycles of refinement. The final difference map was devoid of significant features.

All calculations were done on an IBM compatible PC using Windows-NT operating system. The programs used were SMART (data collection), SAINT+ (data reduction), SADABS (absorption correction), SHELXTL-PC (XS for solution, XL for refinement, XP for plotting and XCIF for tables). Final atomic coordinates are listed in Table 2 and selected bond lengths and bond angles in Table 3.

References

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Table 1. Crystal data and structure refinement for chowd.

Empirical formula	$C_{24}H_{28}N_2O_7$
Formula weight	456.48
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1 (No. 1, C_1^1)
Unit cell dimensions	$a = 5.7043(9)$ Å $\alpha = 96.699(3)^\circ$ $b = 7.5376(12)$ Å $\beta = 91.816(3)^\circ$ $c = 13.940(2)$ Å $\gamma = 91.662(3)^\circ$
Volume, Z	594.68(17) Å ³ , 1
Density (calculated)	1.275 Mg/m ³
Absorption coefficient	0.094 mm ⁻¹
$F(000)$	242
Crystal size	0.18 x 0.12 x 0.02 mm
θ range for data collection	2.72 to 25.00°
Limiting indices	$-6 \leq h \leq 6$, $-8 \leq k \leq 8$, $-16 \leq l \leq 16$
Reflections collected	4421
Independent reflections	3520 ($R_{int} = 0.0139$)
Completeness to $\theta = 25.00^\circ$	99.6 %
Absorption correction	Semi-empirical
Max. and min. transmission	0.9981 and 0.9832
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3520 / 3 / 301
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0388$, $wR2 = 0.0822$
R indices (all data)	$R1 = 0.0495$, $wR2 = 0.0880$
Flack's Abso. str. parameter	-0.5(9)
Largest diff. peak and hole	0.109 and -0.099 eÅ ⁻³

$$R1 = (\sum \|F_o\| - \|F_c\|) / \sum \|F_o\|, \quad wR2 = \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2, \quad S = [\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$$

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for chowd. $U(\text{eq})$ is defined as

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i a_j a_i a_j$$

	x	y	z	$U(\text{eq})$
O(1)	7074(4)	5639(3)	8924(2)	80(1)
O(2)	10049(3)	10108(2)	5780(1)	52(1)
O(3)	7350(3)	8566(2)	4774(1)	52(1)
O(4)	7388(3)	9860(2)	8996(1)	60(1)
O(5)	3660(5)	9490(4)	9411(2)	113(1)
O(6)	5710(3)	5514(2)	6127(1)	62(1)
O(7)	1941(3)	6099(2)	5768(1)	55(1)
N(1)	6611(3)	9153(3)	6341(1)	46(1)
N(2)	4431(3)	8337(3)	6117(1)	47(1)
C(1)	10943(7)	4887(5)	8561(3)	105(1)
C(2)	8824(6)	5995(4)	8524(2)	59(1)
C(3)	9016(4)	7554(4)	7953(2)	53(1)
C(4)	7021(4)	8816(3)	8063(2)	47(1)
C(5)	6991(4)	10121(3)	7311(2)	49(1)
C(6)	5224(6)	11579(4)	7492(2)	70(1)
C(7)	8150(4)	9335(3)	5632(2)	41(1)
C(8)	8933(5)	8667(4)	4001(2)	57(1)
C(9)	7771(4)	7881(3)	3063(2)	50(1)
C(10)	5612(5)	7034(4)	2980(2)	61(1)
C(11)	4705(6)	6317(4)	2077(3)	77(1)
C(12)	5940(7)	6446(4)	1270(2)	81(1)
C(13)	8101(7)	7269(5)	1348(2)	85(1)
C(14)	8997(6)	7995(4)	2227(2)	69(1)
C(15)	5568(7)	10129(5)	9578(2)	76(1)
C(16)	6341(9)	11363(6)	10455(3)	120(2)
C(17)	4194(4)	6527(3)	6012(2)	44(1)
C(18)	1314(5)	4200(3)	5595(2)	57(1)
C(19)	1497(4)	3531(3)	4549(2)	49(1)
C(20)	-263(5)	3868(4)	3898(2)	59(1)
C(21)	-160(6)	3277(4)	2938(3)	73(1)
C(22)	1699(7)	2326(5)	2593(3)	80(1)
C(23)	3483(6)	1960(4)	3228(3)	80(1)
C(24)	3374(5)	2568(4)	4205(2)	64(1)

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

O(1)-C(2)	1.198(3)	O(2)-C(7)	1.215(3)
O(3)-C(7)	1.328(3)	O(3)-C(8)	1.435(3)
O(4)-C(15)	1.344(4)	O(4)-C(4)	1.445(3)
O(5)-C(15)	1.182(4)	O(6)-C(17)	1.189(3)
O(7)-C(17)	1.339(3)	O(7)-C(18)	1.456(3)
N(1)-C(7)	1.358(3)	N(1)-N(2)	1.382(2)
N(1)-C(5)	1.467(3)	N(2)-C(17)	1.358(3)
C(1)-C(2)	1.492(4)	C(2)-C(3)	1.497(4)
C(3)-C(4)	1.505(3)	C(4)-C(5)	1.519(4)
C(5)-C(6)	1.518(4)	C(8)-C(9)	1.498(4)
C(9)-C(10)	1.366(3)	C(9)-C(14)	1.387(4)
C(10)-C(11)	1.388(4)	C(11)-C(12)	1.357(4)
C(12)-C(13)	1.359(5)	C(13)-C(14)	1.361(4)
C(15)-C(16)	1.494(5)	C(18)-C(19)	1.494(4)
C(19)-C(24)	1.378(4)	C(19)-C(20)	1.380(4)
C(20)-C(21)	1.365(4)	C(21)-C(22)	1.366(5)
C(22)-C(23)	1.382(5)	C(23)-C(24)	1.390(5)
C(7)-O(3)-C(8)	114.98(19)	C(15)-O(4)-C(4)	119.4(2)
C(17)-O(7)-C(18)	116.4(2)	C(7)-N(1)-N(2)	120.17(19)
C(7)-N(1)-C(5)	121.26(19)	N(2)-N(1)-C(5)	117.36(19)
C(17)-N(2)-N(1)	119.84(19)	O(1)-C(2)-C(1)	121.4(3)
O(1)-C(2)-C(3)	122.5(3)	C(1)-C(2)-C(3)	116.1(3)
C(2)-C(3)-C(4)	114.8(2)	O(4)-C(4)-C(3)	106.50(19)
O(4)-C(4)-C(5)	107.0(2)	C(3)-C(4)-C(5)	112.9(2)
N(1)-C(5)-C(6)	110.7(2)	N(1)-C(5)-C(4)	110.2(2)
C(6)-C(5)-C(4)	113.9(2)	O(2)-C(7)-O(3)	124.5(2)
O(2)-C(7)-N(1)	123.0(2)	O(3)-C(7)-N(1)	112.5(2)
O(3)-C(8)-C(9)	110.0(2)	C(10)-C(9)-C(14)	118.2(3)
C(10)-C(9)-C(8)	124.3(2)	C(14)-C(9)-C(8)	117.5(2)
C(9)-C(10)-C(11)	119.9(3)	C(12)-C(11)-C(10)	120.7(3)
C(11)-C(12)-C(13)	119.7(3)	C(12)-C(13)-C(14)	120.1(3)
C(13)-C(14)-C(9)	121.4(3)	O(5)-C(15)-O(4)	124.8(3)
O(5)-C(15)-C(16)	126.0(4)	O(4)-C(15)-C(16)	109.2(4)
O(6)-C(17)-O(7)	126.5(2)	O(6)-C(17)-N(2)	126.0(2)
O(7)-C(17)-N(2)	107.4(2)	O(7)-C(18)-C(19)	110.5(2)
C(24)-C(19)-C(20)	118.3(3)	C(24)-C(19)-C(18)	122.1(3)
C(20)-C(19)-C(18)	119.6(2)	C(21)-C(20)-C(19)	121.3(3)
C(20)-C(21)-C(22)	120.6(3)	C(21)-C(22)-C(23)	119.4(3)
C(22)-C(23)-C(24)	119.9(3)	C(19)-C(24)-C(23)	120.5(3)

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for chowd.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 \{ (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}) \}$$

	U11	U22	U33	U23	U13	U12
O(1)	86(2)	79(2)	78(1)	19(1)	14(1)	11(1)
O(2)	40(1)	47(1)	67(1)	6(1)	-3(1)	-8(1)
O(3)	44(1)	59(1)	51(1)	2(1)	-2(1)	-8(1)
O(4)	60(1)	66(1)	49(1)	-13(1)	-4(1)	7(1)
O(5)	68(2)	167(3)	97(2)	-17(2)	20(1)	11(2)
O(6)	45(1)	51(1)	88(1)	7(1)	-11(1)	3(1)
O(7)	42(1)	43(1)	77(1)	-3(1)	-7(1)	-5(1)
N(1)	35(1)	52(1)	50(1)	1(1)	-6(1)	-9(1)
N(2)	35(1)	44(1)	59(1)	-2(1)	-7(1)	-1(1)
C(1)	102(3)	86(3)	134(4)	33(2)	2(2)	41(2)
C(2)	63(2)	63(2)	49(2)	-3(1)	-3(1)	9(2)
C(3)	48(2)	59(2)	52(2)	0(1)	-3(1)	3(1)
C(4)	41(1)	54(2)	44(1)	-7(1)	-7(1)	3(1)
C(5)	43(2)	46(2)	55(2)	-4(1)	-6(1)	-4(1)
C(6)	81(2)	53(2)	72(2)	-4(2)	-16(2)	11(2)
C(7)	37(1)	35(1)	53(2)	10(1)	-6(1)	1(1)
C(8)	53(2)	59(2)	58(2)	6(1)	7(1)	-8(1)
C(9)	53(2)	40(2)	58(2)	5(1)	2(1)	4(1)
C(10)	57(2)	63(2)	60(2)	7(2)	-2(1)	-7(2)
C(11)	72(2)	71(2)	85(3)	4(2)	-15(2)	-10(2)
C(12)	108(3)	72(2)	61(2)	4(2)	-14(2)	-5(2)
C(13)	109(3)	89(3)	54(2)	0(2)	13(2)	-10(2)
C(14)	74(2)	63(2)	67(2)	2(2)	12(2)	-10(2)
C(15)	83(3)	91(3)	54(2)	-5(2)	4(2)	28(2)
C(16)	163(4)	120(4)	69(3)	-32(2)	4(3)	32(3)
C(17)	37(1)	49(2)	45(1)	2(1)	-2(1)	0(1)
C(18)	51(2)	43(2)	76(2)	6(1)	-1(1)	-11(1)
C(19)	41(2)	36(1)	69(2)	5(1)	4(1)	-8(1)
C(20)	51(2)	46(2)	78(2)	2(2)	-2(1)	1(1)
C(21)	75(2)	67(2)	77(2)	15(2)	-11(2)	-5(2)
C(22)	92(3)	71(2)	73(2)	-2(2)	12(2)	-18(2)
C(23)	70(2)	59(2)	107(3)	-11(2)	32(2)	-4(2)
C(24)	43(2)	53(2)	96(2)	8(2)	2(2)	-3(1)

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

	x	y	z	U(eq)
H(2A)	3226	8975	6044	56
H(1A)	10657	3954	8961	126
H(1B)	12260	5626	8827	126
H(1C)	11277	4367	7920	126
H(3A)	9111	7105	7275	64
H(3B)	10469	8218	8148	64
H(4A)	5521	8141	8038	57
H(5A)	8551	10708	7334	59
H(6A)	5321	12365	6999	84
H(6B)	5561	12246	8113	84
H(6C)	3671	11048	7478	84
H(8A)	10335	8020	4125	68
H(8B)	9396	9905	3964	68
H(10A)	4750	6938	3528	73
H(11A)	3234	5741	2024	92
H(12A)	5311	5974	668	98
H(13A)	8969	7336	798	102
H(14A)	10462	8579	2269	82
H(16A)	5217	11296	10949	144
H(16B)	6457	12565	10293	144
H(16C)	7845	11021	10687	144
H(18A)	-279	4001	5792	68
H(18B)	2353	3544	5978	68
H(20A)	-1545	4512	4119	71
H(21A)	-1367	3524	2514	88
H(22A)	1765	1929	1938	96
H(23A)	4753	1309	3001	96
H(24A)	4577	2322	4631	77

Table 6. Torsion angles [$^{\circ}$] for chowd.

C(7)-N(1)-N(2)-C(17)	82.5(3)	C(5)-N(1)-N(2)-C(17)	-109.9(2)
O(1)-C(2)-C(3)-C(4)	10.2(4)	C(1)-C(2)-C(3)-C(4)	-170.3(3)
C(15)-O(4)-C(4)-C(3)	-135.0(3)	C(15)-O(4)-C(4)-C(5)	104.1(3)
C(2)-C(3)-C(4)-O(4)	75.9(3)	C(2)-C(3)-C(4)-C(5)	-166.9(2)
C(7)-N(1)-C(5)-C(6)	109.3(3)	N(2)-N(1)-C(5)-C(6)	-58.2(3)
C(7)-N(1)-C(5)-C(4)	-123.8(2)	N(2)-N(1)-C(5)-C(4)	68.8(3)
O(4)-C(4)-C(5)-N(1)	-179.71(18)	C(3)-C(4)-C(5)-N(1)	63.4(3)
O(4)-C(4)-C(5)-C(6)	-54.7(3)	C(3)-C(4)-C(5)-C(6)	-171.5(2)
C(8)-O(3)-C(7)-O(2)	1.3(3)	C(8)-O(3)-C(7)-N(1)	-178.1(2)
N(2)-N(1)-C(7)-O(2)	176.7(2)	C(5)-N(1)-C(7)-O(2)	9.6(3)
N(2)-N(1)-C(7)-O(3)	-3.8(3)	C(5)-N(1)-C(7)-O(3)	-170.9(2)
C(7)-O(3)-C(8)-C(9)	-175.7(2)	O(3)-C(8)-C(9)-C(10)	-6.1(3)
O(3)-C(8)-C(9)-C(14)	175.2(2)	C(14)-C(9)-C(10)-C(11)	0.0(4)
C(8)-C(9)-C(10)-C(11)	-178.7(3)	C(9)-C(10)-C(11)-C(12)	0.0(5)
C(10)-C(11)-C(12)-C(13)	0.8(5)	C(11)-C(12)-C(13)-C(14)	-1.5(6)
C(12)-C(13)-C(14)-C(9)	1.5(5)	C(10)-C(9)-C(14)-C(13)	-0.8(4)
C(8)-C(9)-C(14)-C(13)	178.0(3)	C(4)-O(4)-C(15)-O(5)	4.3(5)
C(4)-O(4)-C(15)-C(16)	-175.3(3)	C(18)-O(7)-C(17)-O(6)	-2.4(4)
C(18)-O(7)-C(17)-N(2)	178.4(2)	N(1)-N(2)-C(17)-O(6)	2.8(4)
N(1)-N(2)-C(17)-O(7)	-178.09(19)	C(17)-O(7)-C(18)-C(19)	-92.0(2)
O(7)-C(18)-C(19)-C(24)	102.2(3)	O(7)-C(18)-C(19)-C(20)	-78.2(3)
C(24)-C(19)-C(20)-C(21)	-0.3(4)	C(18)-C(19)-C(20)-C(21)	-179.9(3)
C(19)-C(20)-C(21)-C(22)	0.1(4)	C(20)-C(21)-C(22)-C(23)	0.2(5)
C(21)-C(22)-C(23)-C(24)	-0.3(5)	C(20)-C(19)-C(24)-C(23)	0.2(4)
C(18)-C(19)-C(24)-C(23)	179.8(3)	C(22)-C(23)-C(24)-C(19)	0.1(4)