Total Synthesis of (±)-Pentacycloanammoxic Acid

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Materials and methods

Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvent. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone before use. Dichloromethane, benzene, toluene and acetonitrile were distilled from CaH₂. Methanol was distilled over magnesium methoxide. Thin-layer chromatography (TLC) was performed using E. Merck[®] silica gel 60 F₂₅₄ pre-coated plates (0.25 mm). Visualization of the developed chromatogram was performed by UV absorbance (254 or 366 nm), anisaldehyde stain or ethanolic phosphomolybdic acid stain. Column chromatography was performed using Bakerbond[®] silica gel (40 μm particle size) using the indicated solvent system as eluent. NMR spectra were recorded in deuteriochloroform on Varian[®] Inova-600 (¹H: 600 MHz), Inova-500 (¹H:

500 MHz; ^{13}C : 125 MHz) or Mercury-400 (^1H : 400 MHz; ^{13}C : 100 MHz) instruments. ^1H chemical shifts are reported in parts per million (ppm) on δ scale using residual undeuterated solvent as an internal standard (7.26 ppm). The abbreviations used for the multiplicity are: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^{13}C chemical shifts are reported in parts per million (ppm) on δ scale using the central peak of deuteriochloroform as an internal standard (77 ppm). IR spectra were recorded on an Avatar[®] 360 FT-IR spectrometer and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. High-resolution mass spectral analyses were performed at Harvard University Mass Spectrometry Center. Melting points (m.p.) are uncorrected and were recorded on a Thomas-Hoover Unimelt capillary melting point apparatus. X-ray data were collected at Harvard University using a Bruker SMART CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K.

Experimental part

Dibromide 3

Dibromide **3** was prepared in two steps starting from cyclooctatetraene according to a literature procedure¹. It was recrystallized from a mixture of hexanes/EtOAc to furnish X-ray quality white crystals (m.p. = 108-109°C; lit.¹ m.p. = 110-112°C).

Olefin 4

To **3** (47.9 g, 85.2 mmol) dissolved in a mixture of EtOH/THF (2/1 vol., 420 mL) were added NaNO₂ (176 mg, 0.03 equiv.) and PtO₂ (970 mg, 0.05 equiv.). The resulting mixture was degassed and placed under an atmosphere of H₂ (1 atm) until the ¹H NMR of an aliquot indicated the complete consumption of the starting material. N₂ was then bubbled through the solution for 20 min. Filtration and concentration furnished the corresponding dibromide which was used in the next step without further purification.

The former crude dibromide was dissolved in AcOH (170 mL) and the resulting solution was heated to 95°C (oil bath temperature). Freshly activated zinc (45 g, 8 equiv.) was added portionwise over 1 hour until complete consumption of the starting material. The resulting mixture was then cooled to room temperature and filtered over a pad of Celite[®]. The pad was thoroughly washed with MeCN and the combined organic phase was concentrated under reduced pressure. Purification by flash chromatography over silica gel (hexanes/EtOAc : 8/2) gave olefin **4** as an oil (27.5 g, 80% from **3**). *Data for the mixture of rotamers*; ¹H NMR (500 MHz, CDCl₃); δ (ppm): 7.35 (brs, 10H), 6.26 (brs, 2H), 5.40-5.00 (brm, 4H), 4.60-4.30 (brm, 2H), 3.30-3.00 (brm, 2H), 2.00-1.60 (brm, 4H). IR (film, cm⁻¹): 3035, 2944, 1731, 1698, 1499, 1457, 1393, 1335, 1304, 1279, 1254, 1235, 1167, 1054. HRMS calcd for C₂₄ H₂₅ N₂ O₄ (M+ H⁺) 405.1814, found 405.1815.

Adduct of **4** and 2-Cyclopenten-1-one

To **4** (29.8 g, 73.6 mmol) in a 1 L Pyrex[®] round bottom flask were added MeCN (12 mL) and 2-cyclopenten-1-one (3 mL, 0.5 equiv.). The resulting solution was purged with N₂ and the bottom of the flask was placed at 1 cm of the quartz cooling jacket of a 450W Hanovia[®] UV lamp (medium pressure mercury lamp). The solution was then irradiated for 12 hours at room temperature under N₂. 0.25 equiv. more of 2-cyclopenten-1-one was then added every 12 hours (for 36 hours). At this point, TLC of the crude reaction indicated ~50% conversion. The reaction mixture was concentrated and purified by flash chromatography over silica gel (hexanes/EtOAc : 7/3) to give 18 g of unreacted **4** and 5.72 g of photoadduct as a colorless foam (40% yield at 40% conversion). *Data for the mixture of rotamers*; ¹H NMR (500 MHz, CDCl₃); δ (ppm): 7.35 (brs, 10H), 5.40-5.00 (brm, 4H), 4.25 (brs, 2H), 3.18-2.96 (brm, 1H), 2.88-2.72 (brm, 1H), 2.67 (brs, 1H), 2.63-2.39 (brm, 4H), 2.38-2.26 (brm, 1H), 2.25-2.10 (m, 1H), 2.09-1.70 (brm, 5H). IR (film, cm⁻¹): 2946, 1731, 1698, 1545, 1393, 1337, 1310, 1268, 1210, 1164, 1150, 1125, 1063. HRMS calcd for C₂₉ H₃₁ N₂ O₅ (M⁺ H⁺) 487.2233, found 487.2227.

Ketone **5**

To the above photoadduct (1.38 g, 2.8 mmol) dissolved in EtOH (28 mL) was added Pd-C (10% wt., 150 mg, 0.05 equiv.). The resulting mixture was degassed and placed under an atmosphere of H₂ (1 atm) until TLC indicated the complete consumption of the starting material (1 to 2 hours). N₂ was bubbled through the reaction mixture for 20 min. and then the solution was placed under O₂ (1 atm) and vigorously stirred for 30 min. Filtration, concentration and purification by flash chromatography over silica gel (hexanes/EtOAc : 1/1 to 2/8) gave ketone **5** as a white solid (464 mg, 76%). **5** was recrystallized from EtOAc/heptane to furnish X-ray quality colorless crystals (plate shape) m.p. = 144°C. ¹H NMR (500 MHz, CDCl₃); δ (ppm): 5.25 (m, 1H), 5.22 (m, 1H), 2.93 (dd, 1H, *J* = 7.3 and 5.9 Hz), 2.73 (d, 1H, *J* = 5.9 Hz), 2.60 (m, 1H), 2.57 (m, 1H, [appears as a fine singlet]), 2.53 (m, 1H, [appears as a fine singlet]), 2.35 (ddt, 1H, *J* = 18.1, 9.3 and 2.0 Hz), 2.27 (m, 1H), 2.21 (m, 1H), 2.16 (m, 1H), 2.00 (m, 1H), 1.92-1.80 (m, 2H), 1.24-1.10 (m, 2H). ¹³C NMR (125 MHz, CDCl₃); δ (ppm): 220.3 (HMBC), 63.2, 62.8, 50.5, 41.2, 39.7, 37.2, 36.8, 36.3, 36.2, 28.3, 16.5, 16.1. IR (film, cm⁻¹): 2948, 2877, 1729, 1515, 1463, 1412, 1165. HRMS calcd for C₁₃ H₁₇ N₂ O (M+ H⁺) 217.1341, found 217.1343.

Dimethyl Ketal of **5**

To a solution of **5** (1.25 g, 5.78 mmol) in MeOH (58 mmol) was added trimethyl orthoformate (1.9 mL, 3 equiv.) [distilled before use] followed by p-toluenesulfonic acid monohydrate (22 mg, 0.02 equiv.). The resulting solution was stirred at 40°C for 1 hour then cooled to room temperature and diluted with CH₂Cl₂ (100 mL). The organic phase was

washed with a saturated aqueous solution of NaHCO_3 (20 mL) and dried over Na_2SO_4 . Concentration and purification by flash chromatography over silica gel (hexanes/EtOAc : 6/4 to 4/6) gave the dimethyl ketal of **5** as a white solid (1.39 g, 91%). m.p. = 108-109°C. ^1H NMR (600 MHz, CDCl_3); δ (ppm): 5.21 (m, 2H), 3.18 (s, 3H), 3.15 (s, 3H), 2.63 (t, 1H, $J = 6.0$ Hz), 2.57 (d, 1H, $J = 6.0$ Hz), 2.42 (d, 1H, $J = 3.6$ Hz), 2.25 (d, 1H, $J = 3.6$ Hz), 2.14-2.06 (m, 3H), 1.96-1.82 (m, 3H), 1.77 (td, 1H, $J = 13.2$ and 6.6 Hz), 1.54 (dd, 1H, $J = 12.6$ and 6.0 Hz), 1.20-1.10 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3); δ (ppm): 111.9, 63.7 (x2), 50.6, 48.4, 47.9, 42.3, 38.5, 36.7, 36.4, 33.2, 30.3, 29.5, 16.7, 16.5. IR (film, cm^{-1}): 2948, 2879, 2829, 1515, 1465, 1328, 1200, 1164, 1111, 1050. UV (λ_{max} in MeCN, nm): 204, 375, 385. HRMS calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_2$ ($\text{M} + \text{H}^+$) 263.1759, found 263.1755.

Ketone **6**

A solution of the above dimethyl ketal (100 mg, 381 μmol) in degassed MeCN (80 mL) was irradiated at 50°C under N_2 atmosphere for 3 hours using a photoreactor equipped with a 450W Hanovia[®] UV lamp (medium pressure mercury lamp) and a Pyrex[®] cooling jacket. The reaction mixture was concentrated and redissolved in a mixture of AcOH/H₂O (4/1 vol., 500 μL) and stirred at room temperature for 15 min. Concentration, codistillation twice with benzene and purification by flash chromatography over silica gel (hexanes/EtOAc : 92/08) gave **6** (4.4 mg, 6%) as an oil. ^1H NMR (600 MHz, CDCl_3), δ (ppm): 2.92 (t, 1H, $J = 6.6$ Hz), 2.87 (d, 1H, $J = 1.2$ Hz), 2.80-2.78 (m, 2H), 2.70-2.65 (m, 2H), 2.64-2.53 (m, 4H), 2.45 (m, 1H, [appears as a singlet]), 2.30 (ddt, 1H, $J = 18.0, 9.6$ and 1.5 Hz), 2.18 (m, 1H),

2.08-2.02 (m, 2H); 2.00 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3); δ (ppm): 221.6 (HMBC), 51.5, 50.7, 50.4, 46.3, 43.2, 41.4, 41.2, 40.6, 36.5, 29.1, 26.4, 26.3. IR (film, cm^{-1}): 2925, 2852, 1737, 1457, 1169. HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{NO}$ ($\text{M} + \text{NH}_4^+$) 206.1545, found 206.1554.

In addition to ketone **6** the following fragmentation product (from a more polar fraction) was also isolated:

^1H NMR (500 MHz, CDCl_3), δ (ppm): 5.60-5.47 (m, 4H), 3.34 (m, 1H), 3.27 (brt, 1H, $J = 8.0$ Hz), 2.82 (m, 1H), 2.67 (m, 1H), 2.53 (m, 1H), 2.44-2.27 (m, 3H), 2.10 (m, 1H), 2.04-1.91 (m, 3H).

α -Hydroxymethylene Derivative of **6**

To a solution of freshly distilled ethyl formate (280 μL , 20 equiv.) in benzene (2.2 mL) at 8°C was added MeONa (190 mg, 20 equiv.) [dried under reduced pressure in a desiccator] in one portion. A solution of **6** (33 mg, 175 μmol) in benzene (1 mL) was then added dropwise and the resulting suspension was stirred at room temperature for 12 hours. The reaction was quenched by dropwise addition of a saturated aqueous solution of NH_4Cl (2 mL) and the resulting solution was diluted with Et_2O (20 mL). The aqueous phase was extracted with Et_2O (5 x 10 mL), the combined organic phase was dried over Na_2SO_4 and

concentrated under reduced pressure. The crude α -hydroxymethylene ketone obtained was used in the next step without further purification.

For analytical purposes, the crude material was purified by flash chromatography over silica gel (hexanes/EtOAc : 6/4). ^1H NMR (600 MHz, CDCl_3), δ (ppm): 7.72 (s, 1H), 3.19 (d, 1H, $J = 6.0$ Hz), 2.98 (ddd, 1H, $J = 15.0, 9.0$ and 1.2 Hz), 2.92 (m, 1H, [appears as a singlet]), 2.89 (m, 1H), 2.77 (m, 1H, [appears as a singlet]), 2.71-2.63 (m, 3H), 2.60-2.52 (m, 3H), 2.44 (m, 1H, [appears as a singlet]), 2.09-2.01 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3); δ (ppm): 206.7 (HMBC), 167.5, 113.2 (HMBC), 52.9, 50.7, 50.6, 48.5, 46.2, 41.3, 41.1, 39.2, 32.0, 26.4, 26.3. MS (AP $-$) m/z (%): 215 ($\text{M} - \text{H}^+$, 90).

α -Diazoketone 7

To a solution of α -hydroxymethylene derivative of **6** in CH_2Cl_2 (8.5 mL) was added at 0°C tosyl azide (138 mg, 4 equiv.) followed by Et_3N (200 μL , 8 equiv.) and the resulting solution was stirred at room temperature for 20 hours. The solution was diluted with 10 mL of CH_2Cl_2 and 2 mL of a 7% aqueous solution of KOH were added dropwise. The organic phase was separated, washed with H_2O (3 x 2 mL) and dried over Na_2SO_4 . Concentration and purification by flash chromatography over silica gel (hexanes/EtOAc : 9/1) gave the α -diazoketone **7** (30 mg, 80%) as a yellow oil that solidifies upon standing. ^1H NMR (500 MHz, CDCl_3); δ (ppm): 3.45 (dd, 1H, $J = 14.0$ and 9.0 Hz), 3.11 (d, 1H, $J = 6.0$ Hz), 2.97 (d, 1H, $J = 13.5$ Hz), 2.91-2.85 (m, 2H), 2.78 (s, 1H), 2.73 (s, 1H), 2.68 (m, 2H), 2.61-2.54 (m, 2H),

2.53 (s, 1H), 2.11-1.98 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3); δ (ppm): 202.2 (HMBC), 59.5 (HMBC), 53.4, 50.6, 50.4, 48.5, 45.8, 41.3, 41.0, 37.4, 31.5, 26.4, 26.2.

Methyl esters

To a solution of **7** (19.5 mg, 91 μmol) in MeOH (3 mL) in a quartz test tube was added 490 μL of a 0.09 M solution of Et_3N (0.5 equiv.) in MeOH. The solution was degassed and the test tube was placed at about 10 cm of the Pyrex[®] cooling jacket of a 450W Hanovia[®] UV lamp (medium pressure mercury lamp). The solution was irradiated at room temperature under N_2 atmosphere for 3 hours and concentrated. The crude product was purified by flash chromatography over silica gel (hexanes/ EtOAc : 95/5) to give a 3:1 mixture of endo and exo esters (14.3 mg, 72%). *Data for the endo diastereomer*; ^1H NMR (600 MHz, CDCl_3), δ (ppm): 3.68 (s, 3H), 3.67 (m, 1H), 3.05(m, 1H), 2.78-2.70 (m, 3H), 2.70-2.62 (m, 4H), 2.59-2.51 (m, 3H), 2.48 (ddd, 1H, $J = 13.2, 7.8$ and 3.6 Hz), 2.08-2.00 (m, 2H).

The above 3:1 diastereomeric mixture of methyl ester (2 mg, 9 μmol) was dissolved in 2 mL of a 0.09 M solution of MeONa in MeOH and degassed before being gently refluxed for 20 hours under N_2 atmosphere. The solution was neutralized to pH 7 by dropwise addition of a solution of HCl in MeOH and concentrated. Purification by flash chromatography over silica gel (hexanes/ EtOAc : 95/5) afforded a 2:1 mixture of exo and endo esters (1.5 mg, 75%). *Data for the exo diastereomer*; ^1H NMR (600 MHz, CDCl_3), δ (ppm): 3.70 (s, 3H), 3.18 (m, 1H), 2.93 (m, 1H, [appears as a singlet]), 2.86 (dt, 1H, $J = 12.0$ and 7.5 Hz), 2.78-2.70 (m,

3H), 2.70-2.62 (m, 3H), 2.60-2.52 (m, 3H), 2.29 (ddd, 1H, $J = 11.5, 8.5$ and 1.5 Hz), 2.08-2.00 (m, 2H). HRMS calcd for $C_{14}H_{19}O_2$ ($M+H^+$) 219.1385, found 219.1380.

Aldehyde 8

To a solution of a 3:1 mixture of endo and exo diastereomeric methyl esters (10 mg, 45.8 μ mol) in toluene (2.3 mL) at -78°C was added dropwise a solution of DIBAL-H in toluene (460 μ L, 5 equiv., 0.5 M) and the resulting solution was stirred at this temperature for 30 min. 1 mL of a 1 M HCl aqueous solution was then added dropwise followed by 5 mL of a solution of hexanes/EtOAc (1/1 vol.). The mixture was then warmed to room temperature and stirred at this temperature for 30 min. The organic phase was separated, washed with water (1 mL) and brine (1 mL) and dried over Na_2SO_4 . Concentration under reduced pressure gave the corresponding crude mixture of alcohols which was used in the next step without further purification.

A solution of DMSO (20 μ L, 6 equiv.) in CH_2Cl_2 (700 μ L) was added dropwise to a solution of oxalyl chloride (12 μ L, 3 equiv.) in CH_2Cl_2 (1.7 mL) at -78°C and the resulting solution was stirred at this temperature for 30 min. The former crude mixture of alcohols (~ 45.8 μ mol) dissolved in CH_2Cl_2 (1.5 mL) was added dropwise and the mixture was then warmed to -60°C over 30 min. Et_3N (60 μ L, 9 equiv.) was added and the solution was stirred for 20 min. more at -60°C before being warmed to room temperature. 1 mL of a 1% HCl aqueous solution was added followed by 10 mL of CH_2Cl_2 . The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 x 5 mL). The combined organic phase was washed

with brine (5 mL), dried over MgSO_4 and concentrated under reduced pressure. The resulting crude material was then passed through a short plug of silica gel (hexanes/EtOAc : 85/15) to afford a mixture of endo and exo diastereomeric aldehydes (7.8 mg, 91%).

This mixture of aldehydes was dissolved in Et_3N (1.5 mL), degassed and stirred under N_2 atmosphere at room temperature in the dark for 6 days. Concentration under reduced pressure afforded a 7:1 mixture of exo and endo aldehydes (determined by ^1H NMR) which was used in the next step without further purification. *Data for the exo aldehyde (8)*; ^1H NMR (600 MHz, CDCl_3), δ (ppm): 9.77 (d, 1H, $J = 1.5$ Hz), 3.25 (m, 1H), 2.97 (m, 1H, [appears as a singlet]), 2.87 (dt, 1H, $J = 12.6$ and 6.6 Hz), 2.80-2.52 (m, 9H), 2.18 (ddd, 1H, $J = 13.2$, 9.0 and 2.4 Hz), 2.08-2.00 (m, 2H).

Δ^7 -Dehydro-($\pm$)-pentacycloanammoxic Acid

To a solution of (*i*-Pr) $_2\text{NH}$ (22 μL , 4.16 equiv.) in THF (1 mL) at -78°C was added dropwise a solution of *n*-BuLi (58 μL , 4.16 equiv., 2.67 M) in hexanes and the resulting solution was stirred at this temperature for 30 min. A fine powder of $(\text{Br, Ph}_3\text{P(CH}_2\text{)}_6\text{CO}_2\text{H})^2$ (35 mg, 2 equiv.) [dried overnight under reduced pressure in a desiccator over P_2O_5] was then added in one portion and the mixture warmed to room temperature over 2 hours (apparition of an orange coloration corresponding to the anion) before being cooled again to -78°C . The above 7:1 mixture of exo (**8**) and endo aldehydes (7 mg, 37 μmol) in THF (1.2 mL) [cooled beforehand at -78°C] was added dropwise (disappearance of the orange color within a minute after addition; only a yellowish color remains) and the reaction stirred at this temperature for

1 hour before being warmed to room temperature over 4 hours. 200 μL of a 1 M HCl aqueous solution was added dropwise followed by 10 mL of Et_2O . The organic phase was separated and the aqueous phase was extracted with Et_2O (5 x 10 mL). The combined organic phase was dried over Na_2SO_4 , concentrated and purified by flash chromatography over silica gel (hexanes/ EtOAc : 95/5 to 65/35) to afford Δ^7 -dehydro-($\pm$)-pentacycloanammoxic acid (7.5 mg, 67%). ^1H NMR (500 MHz, CDCl_3); δ (ppm): 5.64 (dd, 1H, $J = 10.3$ and 9.3 Hz), 5.23 (m, 1H), 3.19 (m, 1H), 2.74 (m, 2H), 2.70-2.64 (m, 3H), 2.64 (bs, 2H), 2.60-2.52 (m, 2H), 2.48 (bs, 1H), 2.34 (m, 1H), 2.33 (t, 2H, $J = 7.5$ Hz), 2.26 (m, 1H), 2.04 (m, 2H, [appears as a broad doublet]), 1.96 (m, 2H), 1.62 (bt, 2H, $J = 7.2$ Hz), 1.36-1.28 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3); δ (ppm): 178.5 (HMBC), 136.2, 127.3, 49.5, 49.2, 49.1, 48.6, 48.5, 41.8, 41.7, 38.5, 37.6, 34.5, 33.7, 29.3, 28.6, 27.3, 26.5, 26.4, 24.5. IR (film, cm^{-1}): 3438, 2923, 2854, 1710, 1465. MS (AP +) m/z (%): 300.5 (M^+ , 100).

($\pm$)-Pentacycloanammoxic Acid

To a solution of the above unsaturated acid (5mg, 16.6 μmol) in 95% EtOH (4 mL) was added anhydrous hydrazine (1 mL) followed by dropwise addition of an aqueous solution of CuSO_4 (100 μL , 72 mg/mL). The resulting mixture was vigorously stirred in the dark under O_2 (1 atm) for 12 hours. 100 μL more of hydrazine followed by 50 μL of the solution of aqueous CuSO_4 were then added every 12 hours (for 2 days), the solution being vigorously stirred in the dark under O_2 (1 atm). The reaction mixture was then cooled to 8°C , acidified by dropwise addition of a 2 M HCl aqueous solution and diluted with Et_2O (20 mL). The organic

phase was separated and the aqueous phase was extracted with Et₂O (5 x 15 mL). The combined organic phase was washed with 2 M HCl (10 mL), brine (10 mL) and dried over MgSO₄. Concentration and purification by flash chromatography over silica gel (hexanes/EtOAc : 7/3 to 1/1) afforded (±)-pentacycloanammoxic acid (4.4 mg, 88%). ¹H NMR (500 MHz, CDCl₃); δ (ppm): 2.73 (bd, 2H), 2.63 (bs, 2H), 2.62 (m, 1H), 2.59 (bs, 1H), 2.57 (bs, 1H), 2.58-2.52 (m, 2H), 2.35 ([appears as a broad triplet], 1H + 2H, *J* = 7.3 Hz), 2.20 (m, 1H), 2.18 (m, 1H), 2.04 (m, 2H, [appears as a broad doublet]), 2.00 (m, 1H), 1.63 (bt, 2H, *J* = 7.1 Hz), 1.50-1.38 (m, 2H), 1.32-1.26 (m, 6H), 1.22 (m, 2H). ¹³C NMR (125 MHz, CDCl₃); δ (ppm): 178.5, 49.4, 49.3, 49.2, 48.3, 47.3, 41.8 (x2), 39.9, 38.5, 37.3, 33.8, 33.3, 29.4, 29.3, 29.0, 26.5 (x2), 26.4, 24.7. IR (film, cm⁻¹): 3429, 2919, 2850, 1700, 1465. MS (AP +) *m/z* (%): 302.6 (M⁺, 100).

(±)-Pentacycloanammoxic Acid Methyl Ester 1

To a solution of (±)-pentacycloanammoxic acid (2 mg, 6.6 μmol) in Et₂O (2 mL) was added at 0°C a solution of diazomethane in Et₂O (until a yellow color remained). The resulting solution was stirred at this temperature for 2 hours then N₂ was bubbled into the solution for 15 min. Concentration and purification by flash chromatography over silica gel (hexanes/EtOAc : 95/05) afforded ester **1** (2 mg, 95%). ¹H NMR (600 MHz, CDCl₃); δ (ppm): 3.66 (s, 3H), 2.73 (bd, 2H), 2.63 (bs, 2H), 2.63 (m, 1H), 2.59 (bs, 1H), 2.57 (bs, 1H), 2.58-2.52 (m, 2H), 2.34 (bs, 1H), 2.30 (t, 2H, *J* = 7.5 Hz), 2.21 (m, 1H), 2.17 (m, 1H), 2.04 (m, 2H, [appears as a doublet]), 2.00 (m, 1H), 1.61 (bt, 2H, *J* = 7.0 Hz), 1.49-1.37 (m, 2H), 1.32-1.26

(m, 6H), 1.22 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3); δ (ppm): 174.3 (HMBC), 51.4, 49.4, 49.3, 49.2, 48.3, 47.3, 41.8 (x2), 39.9, 38.5, 37.3, 34.1, 33.3, 29.5, 29.3, 29.1, 26.5 (x2), 26.4, 25.0. IR (film, cm^{-1}): 2921, 2852, 1742, 1465, 1437, 1378, 1260, 1167. HRMS calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2$ ($\text{M} + \text{H}^+$) 317.2480, found 317.2475.

1

(CDCl₃, 600 MHz, 295 K)

1

(CDCl₃, 125 MHz, 295 K)

(quaternary carbon observed by HMBC)

1

(CDCl₃, 125 MHz, 295 K)

X-ray data for compound 3

Table 1. Crystal data and structure refinement for ejc78t.

Identification code	ejc78t	
Empirical formula	C ₂₄ H ₂₂ Br ₂ N ₂ O ₄	
Formula weight	562.26	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.590(7) Å	$\alpha = 90^\circ$.
	b = 7.564(5) Å	$\beta = 97.05(4)^\circ$.
	c = 25.78(2) Å	$\gamma = 90^\circ$.
Volume	2243(3) Å ³	
Z	4	
Density (calculated)	1.665 Mg/m ³	
Absorption coefficient	3.648 mm ⁻¹	
F(000)	1128	
Crystal size	0.12 x 0.12 x 0.12 mm ³	
Theta range for data collection	1.59 to 22.50°.	
Index ranges	-12 ≤ h ≤ 12, -8 ≤ k ≤ 7, -26 ≤ l ≤ 27	
Reflections collected	9310	
Independent reflections	2930 [R(int) = 0.0492]	
Completeness to theta = 22.50°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.6687 and 0.6687	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2930 / 138 / 283	
Goodness-of-fit on F ²	1.290	
Final R indices [I > 2σ(I)]	R1 = 0.0665, wR2 = 0.1080	
R indices (all data)	R1 = 0.0851, wR2 = 0.1129	
Largest diff. peak and hole	0.631 and -0.485 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ejc78t. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1)	-2268(1)	577(1)	1441(1)	45(1)
Br(2)	-1469(1)	-4685(1)	1968(1)	38(1)
O(1)	787(4)	1606(5)	3733(2)	28(1)
O(2)	619(4)	3251(6)	3000(2)	35(1)
O(3)	2897(4)	-670(6)	3613(2)	30(1)
O(4)	2255(4)	-3469(6)	3609(2)	30(1)
N(1)	1205(4)	396(7)	2973(2)	21(1)
N(2)	1117(4)	-1281(6)	3210(2)	20(1)
C(1)	855(5)	351(9)	2398(2)	23(2)
C(2)	-467(5)	58(8)	2349(2)	21(1)
C(3)	-1103(6)	-831(9)	1859(3)	30(2)
C(4)	-1545(6)	-2237(9)	2204(3)	27(2)
C(5)	-712(5)	-1609(8)	2676(2)	21(1)
C(6)	453(5)	-2543(8)	2840(2)	20(2)
C(7)	1155(5)	-2741(9)	2392(3)	23(2)
C(8)	1412(6)	-1231(9)	2184(3)	25(2)
C(9)	826(5)	1868(9)	3225(3)	21(2)
C(10)	495(7)	3195(9)	4006(3)	36(2)
C(11)	390(6)	2750(9)	4562(3)	30(2)
C(12)	-622(6)	3071(9)	4771(3)	33(2)
C(13)	-730(7)	2757(10)	5287(3)	41(2)
C(14)	202(7)	2060(10)	5606(3)	40(2)
C(15)	1217(7)	1709(10)	5408(3)	46(2)
C(16)	1318(7)	2069(10)	4890(3)	43(2)
C(17)	2116(6)	-1951(9)	3484(2)	23(2)
C(18)	3920(6)	-1213(10)	3951(3)	40(2)
C(19)	4553(6)	411(10)	4169(3)	31(2)
C(20)	4070(7)	2055(10)	4148(3)	36(2)
C(21)	4691(8)	3487(11)	4355(3)	47(2)
C(22)	5812(8)	3261(13)	4599(3)	50(2)
C(23)	6291(7)	1625(13)	4625(3)	51(2)
C(24)	5674(6)	184(11)	4413(3)	43(2)

Table 3. Bond lengths [Å] and angles [°] for ejc78t.

Br(1)-C(3)	1.939(6)
Br(2)-C(4)	1.954(7)
O(1)-C(9)	1.332(8)
O(1)-C(10)	1.454(8)
O(2)-C(9)	1.207(7)
O(3)-C(17)	1.340(8)
O(3)-C(18)	1.442(8)
O(4)-C(17)	1.198(8)
N(1)-C(9)	1.387(8)
N(1)-N(2)	1.417(7)
N(1)-C(1)	1.490(8)
N(2)-C(17)	1.377(8)
N(2)-C(6)	1.496(8)
C(1)-C(8)	1.497(9)
C(1)-C(2)	1.538(9)
C(1)-H(1)	0.9900
C(2)-C(3)	1.537(9)
C(2)-C(5)	1.562(9)
C(2)-H(2)	0.9900
C(3)-C(4)	1.517(10)
C(3)-H(3)	0.9900
C(4)-C(5)	1.532(9)
C(4)-H(4)	0.9900
C(5)-C(6)	1.536(8)
C(5)-H(5)	0.9900
C(6)-C(7)	1.500(9)
C(6)-H(6)	0.9900
C(7)-C(8)	1.311(9)
C(7)-H(7)	0.9400
C(8)-H(8)	0.9400
C(10)-C(11)	1.492(10)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(12)	1.370(10)
C(11)-C(16)	1.383(10)
C(12)-C(13)	1.374(10)

C(12)-H(12)	0.9400
C(13)-C(14)	1.380(11)
C(13)-H(13)	0.9400
C(14)-C(15)	1.365(11)
C(14)-H(14)	0.9400
C(15)-C(16)	1.382(11)
C(15)-H(15)	0.9400
C(16)-H(16)	0.9400
C(18)-C(19)	1.504(10)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(19)-C(20)	1.362(10)
C(19)-C(24)	1.383(10)
C(20)-C(21)	1.372(10)
C(20)-H(20)	0.9400
C(21)-C(22)	1.383(11)
C(21)-H(21)	0.9400
C(22)-C(23)	1.355(11)
C(22)-H(22)	0.9400
C(23)-C(24)	1.380(11)
C(23)-H(23)	0.9400
C(24)-H(24)	0.9400
C(9)-O(1)-C(10)	113.0(5)
C(17)-O(3)-C(18)	115.1(5)
C(9)-N(1)-N(2)	118.2(5)
C(9)-N(1)-C(1)	114.9(5)
N(2)-N(1)-C(1)	112.6(5)
C(17)-N(2)-N(1)	116.7(5)
C(17)-N(2)-C(6)	115.3(5)
N(1)-N(2)-C(6)	110.8(4)
N(1)-C(1)-C(8)	107.9(5)
N(1)-C(1)-C(2)	103.4(5)
C(8)-C(1)-C(2)	108.9(5)
N(1)-C(1)-H(1)	112.0
C(8)-C(1)-H(1)	112.0
C(2)-C(1)-H(1)	112.0
C(3)-C(2)-C(1)	120.2(6)
C(3)-C(2)-C(5)	89.4(5)

C(1)-C(2)-C(5)	108.5(5)
C(3)-C(2)-H(2)	112.1
C(1)-C(2)-H(2)	112.1
C(5)-C(2)-H(2)	112.1
C(4)-C(3)-C(2)	89.2(5)
C(4)-C(3)-Br(1)	116.7(5)
C(2)-C(3)-Br(1)	116.6(5)
C(4)-C(3)-H(3)	110.9
C(2)-C(3)-H(3)	110.9
Br(1)-C(3)-H(3)	110.9
C(3)-C(4)-C(5)	91.3(5)
C(3)-C(4)-Br(2)	116.8(5)
C(5)-C(4)-Br(2)	119.5(4)
C(3)-C(4)-H(4)	109.3
C(5)-C(4)-H(4)	109.3
Br(2)-C(4)-H(4)	109.3
C(4)-C(5)-C(6)	121.5(5)
C(4)-C(5)-C(2)	87.8(5)
C(6)-C(5)-C(2)	107.9(5)
C(4)-C(5)-H(5)	112.3
C(6)-C(5)-H(5)	112.3
C(2)-C(5)-H(5)	112.3
N(2)-C(6)-C(7)	105.7(5)
N(2)-C(6)-C(5)	104.4(5)
C(7)-C(6)-C(5)	112.1(5)
N(2)-C(6)-H(6)	111.5
C(7)-C(6)-H(6)	111.5
C(5)-C(6)-H(6)	111.5
C(8)-C(7)-C(6)	113.6(6)
C(8)-C(7)-H(7)	123.2
C(6)-C(7)-H(7)	123.2
C(7)-C(8)-C(1)	114.6(6)
C(7)-C(8)-H(8)	122.7
C(1)-C(8)-H(8)	122.7
O(2)-C(9)-O(1)	125.1(6)
O(2)-C(9)-N(1)	121.7(6)
O(1)-C(9)-N(1)	113.1(6)
O(1)-C(10)-C(11)	109.2(5)

O(1)-C(10)-H(10A)	109.8
C(11)-C(10)-H(10A)	109.8
O(1)-C(10)-H(10B)	109.8
C(11)-C(10)-H(10B)	109.8
H(10A)-C(10)-H(10B)	108.3
C(12)-C(11)-C(16)	117.7(7)
C(12)-C(11)-C(10)	120.8(7)
C(16)-C(11)-C(10)	121.4(7)
C(11)-C(12)-C(13)	122.3(7)
C(11)-C(12)-H(12)	118.9
C(13)-C(12)-H(12)	118.9
C(12)-C(13)-C(14)	119.1(8)
C(12)-C(13)-H(13)	120.5
C(14)-C(13)-H(13)	120.5
C(15)-C(14)-C(13)	119.9(8)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.2(8)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	120.8(8)
C(15)-C(16)-H(16)	119.6
C(11)-C(16)-H(16)	119.6
O(4)-C(17)-O(3)	124.1(6)
O(4)-C(17)-N(2)	124.6(6)
O(3)-C(17)-N(2)	111.2(6)
O(3)-C(18)-C(19)	108.7(6)
O(3)-C(18)-H(18A)	110.0
C(19)-C(18)-H(18A)	110.0
O(3)-C(18)-H(18B)	110.0
C(19)-C(18)-H(18B)	110.0
H(18A)-C(18)-H(18B)	108.3
C(20)-C(19)-C(24)	119.3(7)
C(20)-C(19)-C(18)	123.5(6)
C(24)-C(19)-C(18)	117.2(7)
C(19)-C(20)-C(21)	120.8(7)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-H(20)	119.6

C(20)-C(21)-C(22)	119.9(8)
C(20)-C(21)-H(21)	120.1
C(22)-C(21)-H(21)	120.1
C(23)-C(22)-C(21)	119.5(8)
C(23)-C(22)-H(22)	120.3
C(21)-C(22)-H(22)	120.3
C(22)-C(23)-C(24)	120.8(8)
C(22)-C(23)-H(23)	119.6
C(24)-C(23)-H(23)	119.6
C(23)-C(24)-C(19)	119.7(8)
C(23)-C(24)-H(24)	120.2
C(19)-C(24)-H(24)	120.2

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ejc78t. 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}
Br(1)	43(1)	43(1)	43(1)	-2(1)	-17(1)	9(1)
Br(2)	43(1)	30(1)	43(1)	-8(1)	6(1)	-12(1)
O(1)	43(3)	20(3)	19(3)	0(2)	5(2)	4(2)
O(2)	56(4)	20(3)	27(3)	2(2)	3(3)	1(3)
O(3)	25(3)	25(3)	38(3)	6(2)	-9(2)	-4(2)
O(4)	29(3)	20(3)	38(3)	3(2)	-3(2)	5(2)
N(1)	28(3)	16(3)	18(3)	-5(3)	1(2)	-2(3)
N(2)	21(3)	15(3)	22(3)	7(2)	0(3)	-2(2)
C(1)	24(4)	29(4)	17(4)	4(3)	1(3)	-4(3)
C(2)	23(3)	17(3)	22(3)	-5(2)	3(2)	3(2)
C(3)	28(4)	37(5)	24(4)	-4(3)	-6(3)	2(3)
C(4)	19(4)	29(4)	34(4)	-2(3)	4(3)	-1(3)
C(5)	23(3)	17(3)	22(3)	-5(2)	3(2)	3(2)
C(6)	24(4)	14(4)	21(4)	-1(3)	-4(3)	-3(3)
C(7)	14(4)	26(4)	28(4)	-10(3)	-2(3)	0(3)
C(8)	21(4)	33(4)	23(4)	-3(3)	7(3)	-8(3)

C(9)	11(4)	28(5)	23(5)	4(3)	2(3)	-7(3)
C(10)	52(5)	22(4)	36(5)	-2(3)	13(4)	8(4)
C(11)	40(5)	21(4)	29(5)	-4(3)	7(4)	1(3)
C(12)	32(5)	33(4)	36(5)	-6(4)	10(4)	-4(4)
C(13)	44(5)	48(5)	35(5)	-12(4)	22(4)	-17(4)
C(14)	55(6)	43(5)	24(5)	-6(4)	8(4)	-14(4)
C(15)	50(5)	53(5)	34(5)	-4(4)	5(4)	11(4)
C(16)	48(5)	45(5)	38(5)	1(4)	18(4)	11(4)
C(17)	23(4)	30(5)	14(4)	3(3)	3(3)	4(4)
C(18)	29(4)	40(5)	47(5)	3(4)	-8(4)	5(4)
C(19)	26(4)	42(5)	25(4)	1(4)	4(3)	-6(4)
C(20)	41(5)	34(5)	30(5)	1(4)	1(4)	-4(4)
C(21)	73(7)	38(5)	34(5)	-2(4)	19(5)	-2(5)
C(22)	46(6)	68(7)	35(5)	-16(5)	4(4)	-27(5)
C(23)	37(5)	81(7)	34(5)	-9(5)	-2(4)	-12(5)
C(24)	30(5)	55(5)	44(5)	-5(4)	2(4)	1(4)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ejc78t.

	x	y	z	U(eq)
H(1)	1059	1460	2226	28
H(2)	-885	1116	2454	25
H(3)	-542	-1338	1639	36
H(4)	-2354	-1955	2261	33
H(5)	-1123	-1311	2979	25
H(6)	339	-3694	3009	24
H(7)	1387	-3842	2271	28
H(8)	1907	-1149	1922	30
H(10A)	-241	3682	3838	43
H(10B)	1102	4089	3990	43
H(12)	-1264	3523	4553	40
H(13)	-1429	3014	5421	49
H(14)	139	1826	5960	48
H(15)	1849	1222	5624	55
H(16)	2026	1849	4759	51
H(18A)	4427	-1914	3753	48
H(18B)	3698	-1945	4236	48
H(20)	3302	2210	3990	43
H(21)	4355	4620	4331	57
H(22)	6237	4235	4746	60
H(23)	7054	1470	4790	61
H(24)	6013	-947	4434	52

Table 6. Torsion angles [°] for ejc78t.

C(9)-N(1)-N(2)-C(17)	-100.1(7)
C(1)-N(1)-N(2)-C(17)	122.0(6)
C(9)-N(1)-N(2)-C(6)	125.3(5)
C(1)-N(1)-N(2)-C(6)	-12.5(7)
C(9)-N(1)-C(1)-C(8)	175.4(5)
N(2)-N(1)-C(1)-C(8)	-45.3(7)
C(9)-N(1)-C(1)-C(2)	-69.2(6)
N(2)-N(1)-C(1)-C(2)	70.1(6)
N(1)-C(1)-C(2)-C(3)	-154.1(5)
C(8)-C(1)-C(2)-C(3)	-39.5(8)
N(1)-C(1)-C(2)-C(5)	-53.6(6)
C(8)-C(1)-C(2)-C(5)	61.0(6)
C(1)-C(2)-C(3)-C(4)	122.5(6)
C(5)-C(2)-C(3)-C(4)	11.3(5)
C(1)-C(2)-C(3)-Br(1)	-117.8(6)
C(5)-C(2)-C(3)-Br(1)	131.0(5)
C(2)-C(3)-C(4)-C(5)	-11.6(5)
Br(1)-C(3)-C(4)-C(5)	-131.1(5)
C(2)-C(3)-C(4)-Br(2)	-135.9(5)
Br(1)-C(3)-C(4)-Br(2)	104.5(5)
C(3)-C(4)-C(5)-C(6)	-98.3(7)
Br(2)-C(4)-C(5)-C(6)	23.8(8)
C(3)-C(4)-C(5)-C(2)	11.4(5)
Br(2)-C(4)-C(5)-C(2)	133.4(5)
C(3)-C(2)-C(5)-C(4)	-11.2(5)
C(1)-C(2)-C(5)-C(4)	-133.0(5)
C(3)-C(2)-C(5)-C(6)	111.2(5)
C(1)-C(2)-C(5)-C(6)	-10.6(7)
C(17)-N(2)-C(6)-C(7)	-72.6(6)
N(1)-N(2)-C(6)-C(7)	62.7(6)
C(17)-N(2)-C(6)-C(5)	169.0(5)
N(1)-N(2)-C(6)-C(5)	-55.7(6)
C(4)-C(5)-C(6)-N(2)	165.6(6)
C(2)-C(5)-C(6)-N(2)	67.0(6)
C(4)-C(5)-C(6)-C(7)	51.7(8)
C(2)-C(5)-C(6)-C(7)	-46.9(6)

N(2)-C(6)-C(7)-C(8)	-53.2(7)
C(5)-C(6)-C(7)-C(8)	59.9(7)
C(6)-C(7)-C(8)-C(1)	-6.0(8)
N(1)-C(1)-C(8)-C(7)	57.3(7)
C(2)-C(1)-C(8)-C(7)	-54.3(7)
C(10)-O(1)-C(9)-O(2)	-1.6(9)
C(10)-O(1)-C(9)-N(1)	174.6(5)
N(2)-N(1)-C(9)-O(2)	-162.5(6)
C(1)-N(1)-C(9)-O(2)	-25.6(9)
N(2)-N(1)-C(9)-O(1)	21.1(7)
C(1)-N(1)-C(9)-O(1)	158.0(5)
C(9)-O(1)-C(10)-C(11)	176.0(5)
O(1)-C(10)-C(11)-C(12)	-122.0(7)
O(1)-C(10)-C(11)-C(16)	60.7(9)
C(16)-C(11)-C(12)-C(13)	0.7(11)
C(10)-C(11)-C(12)-C(13)	-176.8(7)
C(11)-C(12)-C(13)-C(14)	-1.4(11)
C(12)-C(13)-C(14)-C(15)	0.7(11)
C(13)-C(14)-C(15)-C(16)	0.7(12)
C(14)-C(15)-C(16)-C(11)	-1.4(12)
C(12)-C(11)-C(16)-C(15)	0.8(11)
C(10)-C(11)-C(16)-C(15)	178.2(7)
C(18)-O(3)-C(17)-O(4)	-3.8(9)
C(18)-O(3)-C(17)-N(2)	173.4(6)
N(1)-N(2)-C(17)-O(4)	-163.2(6)
C(6)-N(2)-C(17)-O(4)	-30.7(9)
N(1)-N(2)-C(17)-O(3)	19.6(8)
C(6)-N(2)-C(17)-O(3)	152.2(5)
C(17)-O(3)-C(18)-C(19)	-165.7(6)
O(3)-C(18)-C(19)-C(20)	14.6(10)
O(3)-C(18)-C(19)-C(24)	-166.9(6)
C(24)-C(19)-C(20)-C(21)	1.5(11)
C(18)-C(19)-C(20)-C(21)	179.9(7)
C(19)-C(20)-C(21)-C(22)	-1.5(12)
C(20)-C(21)-C(22)-C(23)	0.9(12)
C(21)-C(22)-C(23)-C(24)	-0.2(13)
C(22)-C(23)-C(24)-C(19)	0.2(12)
C(20)-C(19)-C(24)-C(23)	-0.8(11)

C(18)-C(19)-C(24)-C(23)	-179.4(7)
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Symmetry transformations used to generate equivalent atoms:

X-ray data for compound 5

Table 1. Crystal data and structure refinement for ejc70t.

Identification code	ejc70t	
Empirical formula	C ₁₃ H ₁₆ N ₂ O	
Formula weight	216.28	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.316(9) Å	α = 90°.
	b = 6.229(5) Å	β = 97.375(14)°.
	c = 15.518(13) Å	γ = 90°.
Volume	1084.8(15) Å ³	
Z	4	
Density (calculated)	1.324 Mg/m ³	
Absorption coefficient	0.085 mm ⁻¹	
F(000)	464	

Crystal size	0.12 x 0.08 x 0.04 mm ³
Theta range for data collection	2.10 to 27.92°.
Index ranges	-11<=h<=14, -8<=k<=6, -19<=l<=20
Reflections collected	6788
Independent reflections	2557 [R(int) = 0.0410]
Completeness to theta = 27.92°	98.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2557 / 0 / 209
Goodness-of-fit on F ²	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1203
R indices (all data)	R1 = 0.0554, wR2 = 0.1265
Largest diff. peak and hole	0.296 and -0.162 e.Å ⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for ejc70t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-593(1)	1596(2)	3889(1)	56(1)
N(1)	5108(1)	4016(2)	6413(1)	41(1)
N(2)	4366(1)	5479(2)	6472(1)	42(1)
C(1)	425(1)	1053(3)	3839(1)	40(1)
C(2)	1508(1)	2494(2)	4019(1)	36(1)
C(3)	1966(1)	2438(2)	4999(1)	31(1)
C(4)	2961(1)	4084(2)	5291(1)	33(1)
C(5)	3095(1)	4821(2)	6241(1)	36(1)
C(6)	2883(1)	3012(3)	6866(1)	38(1)
C(7)	3743(2)	1193(2)	6742(1)	38(1)
C(8)	4580(1)	1926(2)	6103(1)	34(1)
C(9)	3925(1)	2372(2)	5193(1)	30(1)
C(10)	2954(1)	785(2)	4819(1)	27(1)
C(11)	2578(1)	1086(2)	3828(1)	33(1)
C(12)	2039(1)	-887(3)	3336(1)	41(1)
C(13)	818(1)	-1181(3)	3637(1)	45(1)

Table 3. Bond lengths [Å] and angles [°] for ejc70t.

O(1)-C(1)	1.212(2)
N(1)-N(2)	1.251(2)
N(1)-C(8)	1.487(2)
N(2)-C(5)	1.494(2)
C(1)-C(13)	1.507(3)
C(1)-C(2)	1.517(2)
C(2)-C(3)	1.542(2)
C(2)-C(11)	1.554(2)
C(2)-H(1)	0.967(19)
C(3)-C(4)	1.547(2)
C(3)-C(10)	1.571(2)
C(3)-H(2)	0.978(17)
C(4)-C(5)	1.534(2)
C(4)-C(9)	1.546(2)
C(4)-H(3)	0.998(18)
C(5)-C(6)	1.526(2)
C(5)-H(4)	0.942(17)
C(6)-C(7)	1.522(2)
C(6)-H(6)	0.973(18)
C(6)-H(5)	0.990(18)
C(7)-C(8)	1.526(2)
C(7)-H(8)	0.97(2)
C(7)-H(7)	0.96(2)
C(8)-C(9)	1.533(2)
C(8)-H(9)	0.962(17)
C(9)-C(10)	1.536(2)
C(9)-H(10)	0.995(16)
C(10)-C(11)	1.554(2)
C(10)-H(11)	0.979(17)
C(11)-C(12)	1.531(2)
C(11)-H(12)	0.956(18)
C(12)-C(13)	1.525(3)
C(12)-H(13)	0.961(18)
C(12)-H(14)	0.978(19)
C(13)-H(16)	1.01(2)
C(13)-H(15)	0.98(2)

N(2)-N(1)-C(8)	114.55(13)
N(1)-N(2)-C(5)	114.66(13)
O(1)-C(1)-C(13)	125.45(16)
O(1)-C(1)-C(2)	125.12(16)
C(13)-C(1)-C(2)	109.35(13)
C(1)-C(2)-C(3)	109.22(12)
C(1)-C(2)-C(11)	105.17(13)
C(3)-C(2)-C(11)	90.29(10)
C(1)-C(2)-H(1)	112.8(11)
C(3)-C(2)-H(1)	116.9(11)
C(11)-C(2)-H(1)	120.0(11)
C(2)-C(3)-C(4)	114.38(11)
C(2)-C(3)-C(10)	89.78(10)
C(4)-C(3)-C(10)	88.76(11)
C(2)-C(3)-H(2)	116.2(9)
C(4)-C(3)-H(2)	117.3(10)
C(10)-C(3)-H(2)	125.3(10)
C(5)-C(4)-C(9)	108.45(11)
C(5)-C(4)-C(3)	117.26(12)
C(9)-C(4)-C(3)	90.62(12)
C(5)-C(4)-H(3)	109.0(10)
C(9)-C(4)-H(3)	115.1(10)
C(3)-C(4)-H(3)	115.3(10)
N(2)-C(5)-C(6)	105.97(12)
N(2)-C(5)-C(4)	106.64(12)
C(6)-C(5)-C(4)	112.71(13)
N(2)-C(5)-H(4)	107.2(10)
C(6)-C(5)-H(4)	112.3(10)
C(4)-C(5)-H(4)	111.6(10)
C(7)-C(6)-C(5)	108.29(12)
C(7)-C(6)-H(6)	109.5(10)
C(5)-C(6)-H(6)	108.6(11)
C(7)-C(6)-H(5)	113.4(10)
C(5)-C(6)-H(5)	109.9(10)
H(6)-C(6)-H(5)	107.0(14)
C(6)-C(7)-C(8)	108.64(12)
C(6)-C(7)-H(8)	110.9(11)

C(8)-C(7)-H(8)	108.0(11)
C(6)-C(7)-H(7)	110.0(12)
C(8)-C(7)-H(7)	109.9(12)
H(8)-C(7)-H(7)	109.5(16)
N(1)-C(8)-C(7)	108.02(12)
N(1)-C(8)-C(9)	105.40(12)
C(7)-C(8)-C(9)	112.70(13)
N(1)-C(8)-H(9)	107.7(10)
C(7)-C(8)-H(9)	111.3(10)
C(9)-C(8)-H(9)	111.4(10)
C(8)-C(9)-C(10)	117.97(11)
C(8)-C(9)-C(4)	107.37(11)
C(10)-C(9)-C(4)	90.06(11)
C(8)-C(9)-H(10)	109.8(9)
C(10)-C(9)-H(10)	113.5(9)
C(4)-C(9)-H(10)	117.0(9)
C(9)-C(10)-C(11)	112.83(11)
C(9)-C(10)-C(3)	90.11(11)
C(11)-C(10)-C(3)	89.21(10)
C(9)-C(10)-H(11)	118.9(9)
C(11)-C(10)-H(11)	116.4(9)
C(3)-C(10)-H(11)	123.6(9)
C(12)-C(11)-C(2)	106.18(13)
C(12)-C(11)-C(10)	115.90(12)
C(2)-C(11)-C(10)	89.96(10)
C(12)-C(11)-H(12)	113.7(10)
C(2)-C(11)-H(12)	115.4(10)
C(10)-C(11)-H(12)	113.4(10)
C(13)-C(12)-C(11)	105.22(13)
C(13)-C(12)-H(13)	114.5(10)
C(11)-C(12)-H(13)	114.3(10)
C(13)-C(12)-H(14)	109.9(11)
C(11)-C(12)-H(14)	108.7(11)
H(13)-C(12)-H(14)	104.2(15)
C(1)-C(13)-C(12)	104.86(14)
C(1)-C(13)-H(16)	108.5(11)
C(12)-C(13)-H(16)	110.4(11)
C(1)-C(13)-H(15)	109.3(12)

C(12)-C(13)-H(15)	113.7(12)
H(16)-C(13)-H(15)	109.9(16)

Symmetry transformations used to generate equivalent atoms.

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ejc70t. 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)	35(1)	72(1)	57(1)	-5(1)	-5(1)	11(1)
N(1)	36(1)	49(1)	39(1)	-7(1)	6(1)	-9(1)
N(2)	48(1)	36(1)	40(1)	-4(1)	2(1)	-9(1)
C(1)	36(1)	50(1)	33(1)	-1(1)	-5(1)	6(1)
C(2)	39(1)	32(1)	36(1)	3(1)	-3(1)	7(1)
C(3)	29(1)	31(1)	32(1)	-1(1)	3(1)	4(1)
C(4)	38(1)	25(1)	34(1)	3(1)	3(1)	2(1)
C(5)	38(1)	30(1)	40(1)	-7(1)	3(1)	5(1)
C(6)	35(1)	49(1)	31(1)	-5(1)	9(1)	-3(1)
C(7)	52(1)	32(1)	30(1)	2(1)	5(1)	-1(1)
C(8)	28(1)	37(1)	35(1)	-5(1)	2(1)	5(1)
C(9)	29(1)	33(1)	29(1)	0(1)	7(1)	-3(1)
C(10)	29(1)	26(1)	28(1)	1(1)	3(1)	2(1)
C(11)	35(1)	36(1)	28(1)	2(1)	4(1)	2(1)
C(12)	42(1)	43(1)	35(1)	-7(1)	-2(1)	5(1)
C(13)	39(1)	45(1)	50(1)	-6(1)	-5(1)	-2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ejc70t.

	x	y	z	U(eq)
H(1)	1386(16)	3890(30)	3754(12)	48(5)
H(2)	1364(15)	2200(30)	5389(11)	37(4)
H(3)	2981(15)	5370(30)	4908(11)	43(4)
H(4)	2622(15)	6040(30)	6314(11)	41(4)
H(6)	3042(15)	3550(30)	7458(12)	44(4)
H(5)	2036(16)	2570(30)	6773(11)	47(5)
H(8)	4226(17)	840(30)	7288(13)	54(5)
H(7)	3309(18)	-50(30)	6520(12)	55(5)
H(9)	5222(15)	920(30)	6082(10)	40(4)
H(10)	4512(14)	2710(20)	4787(10)	33(4)
H(11)	2986(13)	-690(30)	5034(10)	33(4)
H(12)	3165(15)	1810(30)	3542(11)	40(4)
H(13)	2538(15)	-2140(30)	3399(11)	40(4)
H(14)	1947(16)	-580(30)	2713(13)	51(5)
H(16)	888(16)	-2070(30)	4190(13)	53(5)
H(15)	228(18)	-1820(30)	3198(13)	59(5)

Table 6. Torsion angles [$^\circ$] for ejc70t.

C(8)-N(1)-N(2)-C(5)	1.38(17)
O(1)-C(1)-C(2)-C(3)	86.68(18)
C(13)-C(1)-C(2)-C(3)	-90.29(15)
O(1)-C(1)-C(2)-C(11)	-177.58(14)
C(13)-C(1)-C(2)-C(11)	5.45(16)
C(1)-C(2)-C(3)-C(4)	-171.86(11)
C(11)-C(2)-C(3)-C(4)	81.94(14)
C(1)-C(2)-C(3)-C(10)	99.60(13)
C(11)-C(2)-C(3)-C(10)	-6.59(10)
C(2)-C(3)-C(4)-C(5)	154.60(12)

C(10)-C(3)-C(4)-C(5)	-116.20(12)
C(2)-C(3)-C(4)-C(9)	-94.19(12)
C(10)-C(3)-C(4)-C(9)	-5.00(9)
N(1)-N(2)-C(5)-C(6)	59.50(16)
N(1)-N(2)-C(5)-C(4)	-60.81(15)
C(9)-C(4)-C(5)-N(2)	52.98(15)
C(3)-C(4)-C(5)-N(2)	153.63(11)
C(9)-C(4)-C(5)-C(6)	-62.89(16)
C(3)-C(4)-C(5)-C(6)	37.76(17)
N(2)-C(5)-C(6)-C(7)	-59.53(15)
C(4)-C(5)-C(6)-C(7)	56.75(16)
C(5)-C(6)-C(7)-C(8)	5.33(16)
N(2)-N(1)-C(8)-C(7)	-59.61(16)
N(2)-N(1)-C(8)-C(9)	61.10(15)
C(6)-C(7)-C(8)-N(1)	52.01(16)
C(6)-C(7)-C(8)-C(9)	-64.02(16)
N(1)-C(8)-C(9)-C(10)	-160.00(11)
C(7)-C(8)-C(9)-C(10)	-42.41(16)
N(1)-C(8)-C(9)-C(4)	-60.36(14)
C(7)-C(8)-C(9)-C(4)	57.22(15)
C(5)-C(4)-C(9)-C(8)	4.76(14)
C(3)-C(4)-C(9)-C(8)	-114.35(11)
C(5)-C(4)-C(9)-C(10)	124.22(11)
C(3)-C(4)-C(9)-C(10)	5.11(10)
C(8)-C(9)-C(10)-C(11)	-166.05(11)
C(4)-C(9)-C(10)-C(11)	84.16(12)
C(8)-C(9)-C(10)-C(3)	104.76(13)
C(4)-C(9)-C(10)-C(3)	-5.03(9)
C(2)-C(3)-C(10)-C(9)	119.43(10)
C(4)-C(3)-C(10)-C(9)	5.03(9)
C(2)-C(3)-C(10)-C(11)	6.59(10)
C(4)-C(3)-C(10)-C(11)	-107.80(10)
C(1)-C(2)-C(11)-C(12)	13.68(14)
C(3)-C(2)-C(11)-C(12)	123.71(12)
C(1)-C(2)-C(11)-C(10)	-103.37(11)
C(3)-C(2)-C(11)-C(10)	6.66(10)
C(9)-C(10)-C(11)-C(12)	155.64(12)
C(3)-C(10)-C(11)-C(12)	-114.57(14)

C(9)-C(10)-C(11)-C(2)	-96.33(13)
C(3)-C(10)-C(11)-C(2)	-6.54(10)
C(2)-C(11)-C(12)-C(13)	-27.47(15)
C(10)-C(11)-C(12)-C(13)	70.59(16)
O(1)-C(1)-C(13)-C(12)	160.58(15)
C(2)-C(1)-C(13)-C(12)	-22.46(17)
C(11)-C(12)-C(13)-C(1)	30.54(16)

Symmetry transformations used to generate equivalent atoms:

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1. Askani, R. *Chem. Ber.* **1969**, *102*, 3304-3309.
 2. Kato, K.; Ohkawa, S.; Terao, S.; Terashita, Z.; Nishikawa, K. *J. Med. Chem.* **1985**, *28*, 287-294.