Supporting Information

A Facile Method to Construct 2,4,9-Triazaadamantane Skeleton and Synthesis of Nitramine Derivatives

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1. General Information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification. Ozone was produced from a Sankang Ozone Generator. Because of the strong oxidizing properties, ozone can affect especially the eyes and respiratory systems, even at low concentrations. Thus manipulation of ozone must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times. Petroleum ether refers to the fraction boiling in the 60-90°C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on aluminium oxide gel (spherical, neutral, 200-300 mesh) or silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were obtained at 500 and 125 MHz, respectively, and CDCl₃, DMSO-d₆, acetone-d₆, CD₃OD-d₄ were used as the solvent with TMS as the internal standard. All FTIR spectra were obtained using a Nicolet FTIR IS10 Spectrometer. TGA and DSC were measured with TGA/SDTA851e and DSC823e, respectively, at a heating rate of 5°Cmin⁻¹. Elemental analysis of all new compounds was performed by using a Vario EL III CHN elemental analyzer. MS/MS (ESI) mass spectra were recorder on a Finnigan TSQ Quantum ultra-AM mass spectrometer (Thermo Fisher Scientific, Waltham, MA USA). X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-K α radiation (λ =0.71073 Å). The known compounds were identified by comparison of their physical and spectral data with those reported in the literature. Yields refers to isolated yield of analytically pure material unless otherwise noted. Dimethyl-1,3-acetonedicarboxylate 5, Dimethyl-3-cyanomethyleneglutarate 6, Methanetriacetic acid 7, trimethyl methanetriacetate 8¹ and 1,3,5-Triacetyl-1,3,5-triazacyclohexane² were prepared according to reported procedures. The spectroscopic data of 2,4,9-Trioxaazadamantane-7-ol are consistent with reported in literature.³

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2. H. Stetter, M. Dohr, Chem. Ber., 1953, 86, 589.

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2. Experimental Procedures and Spectroscopic Data of the Synthesized Compounds

Synthesis of Compound 5

$$\begin{array}{ccc} \text{COOH} & \text{H}_2\text{SO}_4 \\ \text{HOOC} & \begin{array}{c} \text{OH} & \text{H}_2\text{SO}_4 \\ \text{OH} & \text{CH}_3\text{OH}, 65^\circ\text{C} \\ \textbf{4} & 68\% & \textbf{5} \end{array} \end{array} \begin{array}{c} \text{OOMe} \\ \text{COOMe} \\$$

To a concentrate sulfuric acid (24 mL, 0.45 mol) was added citric acid **4** (19.25 g, 0.1 mol) at 65°C. After 10 min, oleum was added dropwise. After 3 h, the mixture was left to cool to room temperature. CH₃OH (70 mL) was slowly added to the mixture. After being stirred for 3 h at room temperature, the mixture was quenched with water and extracted with CH₂Cl₂ (3×80 mL). The combined organic extracts washed with saturated NaHCO₃ solution (150 mL), brine (100 mL), dried over anhydrous Na₂SO₄ and filtered. The solvent was removed in vacuum, and the residue was purified by flash silica gel column chromatography (1:5 ethyl acetate/petroleum ether) to afford the ester **5** (11.7 g, 68% yield) as a pale yellow oil. Compound **5** ¹H NMR (500 MHz, CDCl₃), δ (ppm): 3.79 (s, 6H), 3.67 (s, 4H); ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 195.4, 167.4, 52.8, 49.0.

Synthesis of Compound 6



A mixture of ester **5** (3.48 g, 20 mmol), cyanoacetic acid (3.19 g, 30 mmol), ammonium acetate (1.03 g, 10 mmol), toluene 50 mL and acetic acid (1 mL) was refluxed under stirring for 24 h using a Dean-Stark to remove the water formed azeotropically. The reaction mixture was cooled and washed with water (2×40 mL) and then with a saturated NaHCO₃ solution (2×50 mL). The aqueous washings were extracted with CH₂Cl₂ (3×80 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered, concentrated and purified by silica gel flash-chromatography, yielding ester **6** (2.39 g, 56% yield) as an thin yellow oil. Compound **6** ¹H NMR (500 MHz, CDCl₃), δ (ppm): 5.56 (s, 1H), 3.77 (d, J=10 Hz, 6H), 3.67 (s, 2H), 3.44 (s, 2H); ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 169.4, 167.2, 152.1, 115.7, 103.3, 52.7, 41.3, 39.5.

Synthesis of Compound 7



A mixture of the ester **6** (5 g, 30 mmol) and Pd(OAc)₂ (100 mg) in MeOH (40 mL) was placed under H₂ atmosphere. The reaction mixture was vigorously stirred until TLC showed complete conversion to the ester **6**. The mixture was filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was used without further purification. A NaOH solution (35 mL, 5M) was added to the residue oil leaded a two-phase system. The mixture was heated and vigorously stirred for 2 h. After cooling, the clear solution was acidified with 5M sulfuric acid and then evaporated to dryness. The solid was extracted several times with diethyl ether and the combined extracts were dried with anhydrous Na₂SO₄. After filtration, the evaporation of the solvent to afford the acid **7** as a white solid (2.51 g, 81% yield). Compound **7** ¹H NMR (500 MHz, CD₃OD), δ (ppm): 2.68 (m, 1H), 2.48 (d, J=10 Hz, 6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 173.8, 37.7, 28.7.

Synthesis of Compound 8



To a mixture of acid **7** (1.81 g, 10 mmol) and CH₃OH (30 mL) was added dropwise concentrated sulfuric acid (1 mL). The reaction mixture was stirred for 3 h. The reaction mixture was diluted with dichloromethane (50 mL) and washed with saturated aqueous NaHCO₃ (2×80 mL), brine (100 mL), dried over anhydrous Na₂SO₄. The solvent was removed in vacuum, and the residue oil was purified by flash silica gel column chromatography (1:5 ethyl acetate/petroleum ether) to afford the ester **8** (2.14 g, 97% yield) as a colorless oil. Compound **8** ¹H NMR (500 MHz, CDCl₃), δ (ppm): 3.65 (s, 9H), 2.75 (m, 1H), 2.45 (d, J=5 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 171.8, 51.1, 37.0, 28.2.

Synthesis of Compound 3



Sodium borohydride (2 g, 50 mmol) was suspended in 60 mL absolute THF under dry nitrogen. A solution of ester **8** (1 g, 7.5 mmol) in 100 mL absolute THF was added dropwise to keep the solution refluxing. The reaction mixture was heated for another hour and hydrolysed after cooling with a minimum amount of water. This suspension was filtered and washed with hot ethanol (3×20 mL). The solvent was evaporated to yield the product **3** (0.6 g, 64% yield) as colorless oil. Compound **3** ¹H NMR (500 MHz, DMSO), δ (ppm): 4.33 (br, 3H), 3.40 (t, J=7 Hz, 6H), 2.45 (d, J=5 Hz, 6H), 1.57 (m, 1H), 1.38 (q, J=6.8 Hz, 6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 58.8, 36.9, 28.1.

Synthesis of Compound 10



To a solution of allylmagnesium bromide in ether (1M, 500mL) was added dropwise a solution of ethyl chloroformate **9** (13.2 mL, 0.139 mol) in Et₂O at 0°C under N₂ atmosphere. The reaction mixture was allowed to stir at 0°C for 2 h and then quenched via addition of saturated NH₄Cl (200 mL). The mixture was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (3×400 mL), and the combined organic extracts were washed with brine (400 mL), dried with anhydrous Na₂SO₄, and concentrated in vacuum. The product was purified by flash chromatography (1:30 ethyl acetate/petroleum ether) to afford the alcohol **10** (15 g, 71% yield) as a clear oil. Compound **10** ¹H NMR (500 MHz, DMSO), δ (ppm): 5.84 (m, 3H), 5.02 (m, 6H), 2.10 (d, J=7.2 Hz, 6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 134.7, 117.2, 72.1, 43.5.

Synthesis of Compound 11



 O_3 was passed through alcohol **10** (0.51 g, 3.38 mmol) in CH₂Cl₂ at -30°C for 8 h. The reaction mixture was warmed to ambient temperature and dimethyl sulfide (0.82 mL, 11.18mmol) was added. The reaction was allowed to stir for 2 h. The mixture was concentrated in vacuum. The product was purified by flash chromatography (1:2 ethyl acetate/petroleum ether) to afford alcohol **11** (0.16 g, 32% yield) as pale yellow solid. Compound **11** ¹H NMR (500 MHz, DMSO), δ (ppm): 5.37 (s, 3H), 5.28 (s, 1H), 1.91 (s, 6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 94.4, 61.8, 42.8.

Synthesis of 1,3,5-Triacetyl-1,3,5-triazacyclohexane (TRAT)



Acetonitrile (4.5 mL, 86.7 mmol) and 0.1 mL (1.8 mmol) H_2SO_4 were mixed in a 25 mL flask at 80 °C. 1,3,5-trioxane (1.3 g) was added, and the reaction was refluxed for 3 h. The mixture was concentrated in vacuum and the residue was recrystallized from H_2O to afford a white solid (2.1g, 70% yield). **TRAT** ¹H NMR (500 MHz, CD₃OD), δ (ppm): 5.33 (s, 3H), 2.22 (s, 3H).

	Effect of Temperature on the Yield of TRA	AT ^a
Entry	<i>T</i> (°C)	yield $(\%)^b$
1	70	63
2	80	68
3	90	59
4	100	56

^{*a*}1,3,5-trioxane (1.3 g, 14.4 mmol), H₂SO₄ (0.1 mL, 1.8 mmol); reaction time was 3 h; molar ratio of 1,3,5-trioxane to acetonitrile was 1:6. ^{*b*}The yield was calculated by the equation: yield% = n(TRAT)/n(1,3,5-trioxane).

Entry	<i>t</i> (h)	yield $(\%)^b$
1	2	58
2	3	62
3	4	59
4	5	55

^{*a*}1,3,5-trioxane (1.3 g, 14.4 mmol), H₂SO₄ (0.1 mL, 1.8 mmol); reaction temperature was 80 °C; molar ratio of 1,3,5-trioxane to acetonitrile was 1:6. ^{*b*}The yield was calculated by the equation: yield% = n(TRAT)/n(1,3,5-trioxane).

Effect of Molar Ratio of 1,5,5-1110xane to Acctomutine on the Field of TRAT"					
Entry	molar ratio	yield $(\%)^b$			
1	1:1	59			
2	1:2	68			
3	1:3	60			
4	1:4	56			
$a_{1,3,5}$ triovana (1.3 g. 14)	4 mmol H-SO, $(0.1 mJ - 1.8 mm)$	ol): reaction temperature			

Effect of Molar Ratio of 1,3,5-Trioxane to Acetonitrile on the Yield of TRAT^a

^{*a*}1,3,5-trioxane (1.3 g, 14.4 mmol), H₂SO₄ (0.1 mL, 1.8 mmol); reaction temperature was 80 °C and reaction time was 3 h. ^{*b*}The yield was calculated by the equation: yield% = n(TRAT)/n(1,3,5-trioxane).

Factor-level Table						
Level	А	В	С			
	molar ratio	<i>T</i> (°C)	time (h)			
1	1:1	70	2			
2	1:2	80	3			
3	1:3	90	4			

L9 (3³) Orthogonal Factor-Level Table^a

		-		
	Α	В	С	-11(0/)h
entry	molar ratio	<i>T</i> (°C)	<i>t</i> (h)	yield (%) ⁵
1	1:1	70	2	55
2	1:1	80	3	62
3	1:1	90	4	56
4	1:2	70	3	68
5	1:2	80	4	64
6	1:2	90	2	63
7	1:3	70	4	52
8	1:3	80	2	58
9	1:3	90	3	55
K_{I}	173	175	176	
K_2	195	184	185	
K_{I}	173	175	176	
k_{I}	57.7	58.3	58.7	
k_2	65	61.3	61.7	
k_3	55	58	57.3	
R	10	0.3	4.3	
Optimum	A_2B	${}_{2}C_{2}$		

^a1,3,5-trioxane (1.3 g, 14.4 mmol), H₂SO₄ (0.1 mL, 1.8 mmol); reaction temperature was 80 °C; molar ratio of molar ratio of 1,3,5-trioxane to acetonitrile was 1:3. ^bThe yield was calculated by the equation: yield% = n(TRAT)/n(1,3,5-trioxane).

Synthesis of Compound 1c



O3 was passed through the solution of 10 (0.2 g, 1.32 mmol) in ethanol (55 mL) at -78°C for 6 h, then warmed to ambient temperature and charged with Pd/BaSO₄ under 1 atm of H₂ (balloon). The mixture was filtered through a pad of Celite and then BnNH₂ (0.52 mL, 4.75 mmol, 3.6 equiv) was added. The mixture was allowed to stir at ambient temperature for 1 h and then concentrated in vacuum. The product was purified by flash chromatography (1:5 to 1:3 to 1:2 to 1:1 ethyl acetate/petroleum ether) to afford 1c (0.24 g, 42% yield) as a yellow solid. Compound 1c IR (thin film, v cm⁻¹): 3539, 3425, 2928, 1487, 1308, 738, 693; ¹H NMR (500 MHz, DMSO), δ (ppm): 7.26-7.16 (m, 15H), 4.75 (s, 1H), 3.95 (s, 6H), 3.69 (s, 3H), 1.78 (s,

6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 140.3, 128.1, 126.5, 71.7, 64.7, 55.9; ESI-MS: m/z [(M+H)⁺]: 426.20; C₂₈H₃₁N₃O (425.58): calcd. C 79.02, H 7.34, N 9.87; found C 79.13, H 7.39, N 9.79.

Synthesis of Compound 1b



To a 250 mL pressure vessel was charged with **1c** (0.21 g, 0.51 mmol) Pd(OH)₂/C (0.22 g, 10% Pd), acetic anhydride (30 mL) with an atmosphere of H₂ under the pressure of 0.8 MPa. The reaction mixture was warmed to 45°C and stirred for 7 h. The reaction mixrute was cooled to ambient temperature and filtered through a pad of Celite. The mixture was concentrated in vacuum. The resulting red solid was washed with acetone to afford acetamide **1b** (0.12 g, 81% yield) as a white solid. Compound **1b** IR (thin film, v cm⁻¹): 3444, 1629, 1137, 1000, 757; ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.68 (s, 3H), 2.27 (s, 9H), 2.10 (q, *J*=8.1 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 168.9, 65.9, 60.8, 42.2, 21.4; ESI-MS: m/z [(M+Na)⁺]: 282.05; C₁₃H₁₉N₃O₄ (281.31): calcd. C 55.51, H 6.81, N 14.94; found C 55.60, H 6.86, N 14.81.

Synthesis of Compound 13 and 14



To a mixture of fuming nitric acid (1.86 mL, 60 equiv) and H_2SO_4 (0.47 mL, 12 equiv) at 0°C was added alcohol **1b** (0.20 g, 0.71 mmol). The reaction mixture was heated to 83°C. After stirred for 3 h, the reaction mixture was cooled to ambient temperature and poured into ice-water (30 mL) with agitation. The white participate was filtered, washed with water and dried in vacuum. The product was purified by flash chromatography (1:10 to 1:5 to 1:2 ethyl acetate/petroleum ether) to afford **13** (0.15 g, 61% yield) as a white solid. IR (thin film, v cm⁻¹): 3055, 2917, 1653, 1552, 1233, 853, 715; ¹H NMR (500 MHz, DMSO), δ (ppm): 7.42 (s, 3H), 2.27 (s, 6H); ¹³C NMR (126 MHz, DMSO), δ (ppm): 81.7, 69.0, 34.6; ESI-MS: m/z [(M+Cl)⁻]: 369.91; C₇H₉N₇O₉ (335.19): calcd. C 25.08, H 2.71, N 29.25; found C 25.19, H 2.77, N 29.18.

Continued elution gave **14** (0.064 g, 31% yield) as a white solid. IR (thin film, υ cm⁻¹): 3493, 3047, 2923, 1541, 1268, 901, 772; ¹H NMR (500 MHz, (CD₃)₂CO), δ (ppm): 7.38 (s, 3H), 5.00 (s, 1H), 2.42 (s, 6H); ¹³C NMR (126 MHz, (CD₃)₂CO), δ (ppm): 69.2, 66.0, 38.6; ESI-MS: m/z [(M-H)⁻]: 289.04; C₇H₁₀N₆O₇ (290.19): calcd. C 28.97, H 3.47, N 28.96; found C 29.11, H 3.51, N 28.87.

3. ¹H-NMR, ¹³C-NMR, FT-IR and ESI-MS Spectra of Compounds



¹H NMR spectrum of compound 5 (CDCl₃, 500 MHz)

¹³C NMR spectrum of compound 5 (CDCl₃, 126 MHz)





¹H NMR spectrum of compound 7 (CD₃OD, 500 MHz)



¹³C NMR spectrum of compound 7 (DMSO-*d*₆, 126 MHz)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

¹H NMR spectrum of compound 8 (CDCl₃, 500 MHz)



¹³C NMR spectrum of compound 8 (CDCl₃, 126 MHz)





13





¹H NMR spectrum of compound 11 (DMSO-*d*₆, 500 MHz)



¹³C NMR spectrum of compound 11 (DMSO-*d*₆, 126 MHz)



¹H NMR spectrum of compound 1b (DMSO-*d*₆, 500 MHz)



¹³C NMR spectrum of compound 1b (DMSO-*d*₆, 126 MHz)







Electrospray Ionization (ESI) Mass Spectrometry of compound 1b

(m/z of 426.2)





IR spectrum of compound 1c



Electrospray Ionization (ESI) Mass Spectrometry of compound 1c

(m/z of 282.05)





¹³C NMR spectrum of compound 13 (DMSO-*d*₆, 126 MHz)



IR spectrum of compound 13



Electrospray Ionization (ESI) Mass Spectrometry of compound 13 (m/z of 369.91)





¹³C NMR spectrum of compound 14 (acetone-*d*₆, 126 MHz)



¹H NMR spectrum of compound 14 (acetone-*d*₆, 500 MHz)

IR spectrum of compound 14



Electrospray Ionization (ESI) Mass Spectrometry of compound 14 (m/z of 289.04)



4. X-ray Crystal Structures and Data of Compound 13

X-ray structure of compound 13



Figure S1. ORTEP diagram of 13 Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).



Figure S2. Crystal packing of 13 Color code: Carbon (grey), Oxygen (red), Nitrogen (blue).

Compound	13
Empirical formula	C ₇ H ₉ N ₇ O ₉
Formula weight	335.21
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, Cc
Space group	P2(1)/n
Unit cell dimensions	<i>a</i> =7.6272 (7) A alpha=90 deg.
	<i>b</i> =13.3952 (13) A beta=90.870 (3) deg
	<i>c</i> =11.8460 (12) A gamma=90 deg
Volume	1210.1(2) A^3
Z, Calculated density	4, 1.840 Mg/m^3
Absorption coefficient	0.170 mm^-1
<i>F</i> (000)	688
Crystal size	0.280×0.250×0.220 mm
Theta range for data collection	3.495 to 28.469 deg.
Limiting indices	-7<=h<=10, -17<=k<=17, -15<=l<=15
Reflections collected / unique	5528 / 2653 [R(int) = 0.0214]
Completeness to theta $= 25.242$	98.30%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2653 / 2 / 208
Goodness-of-fit on F ²	1.058
<pre>Final R indices [I>2sigma(I)]</pre>	<i>R</i> 1=0.0256, <i>wR</i> 2=0.0682
R indices (all data)	<i>R</i> 1=0.0262, <i>wR</i> 2=0.0686
Absolute structure parameter	0.2(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.265 and -0.174 e. A^-3
CCDC	1537833

Table 1. Crystal data and structure refinement for 13

Table 2. Atomic coordinates ($x \ 10^{4}$) and equivalent isotropic displacement parameters (A² x 10³) for **13**.

U(eq) is defined as one third of the trace of the orthogonalized															
Uted) is defined as one third of the trace of the orthogonalized	1	I(aa)	:	defined	00	0100	thind	of	tha	traga	of	the	antha	~~~~~	lined
		Uteq	15	uenneu	as	one	uma	OI.	une	uace	01	une	ortino	gona	inzea

		e-j		
	Х	у	Z	U(eq)
O(1)	3670(2)	6374(1)	7666(1)	24(1)
O(2)	6182(2)	7122(1)	7843(1)	24(1)
O(9)	6822(2)	5214(1)	3135(1)	20(1)
O(6)	7674(2)	8900(1)	6096(1)	28(1)
O(5)	5866(2)	9461(1)	4803(2)	27(1)
O(4)	1030(2)	7154(1)	5917(1)	27(1)
O(8)	8975(2)	4623(1)	2158(1)	32(1)
N(2)	5064(2)	6671(1)	7304(1)	17(1)
O(7)	8919(2)	6226(1)	2451(1)	31(1)

O(3)	2165(2)	8522(1)	5256(2)	33(1)
N(1)	5466(2)	6412(1)	6189(1)	15(1)
N(3)	3358(2)	7043(1)	4808(1)	16(1)
N(6)	6575(2)	8788(1)	5346(1)	18(1)
N(5)	6126(2)	7834(1)	5065(1)	19(1)
N(7)	8386(2)	5383(1)	2537(1)	22(1)
N(4)	2117(2)	7616(1)	5381(2)	21(1)
C(4)	7689(2)	6282(1)	4765(2)	15(1)
C(7)	4007(2)	6150(1)	5412(2)	14(1)
C(2)	4764(2)	5453(1)	4521(2)	15(1)
C(3)	5498(3)	6918(1)	3327(2)	17(1)
C(1)	6244(2)	5995(1)	3918(2)	14(1)
C(5)	6885(2)	6969(1)	5654(2)	14(1)
C(6)	4742(2)	7606(1)	4239(2)	17(1)

Table 3. Bond lengths [A] and angles [deg] for **13**.

	-			
O(1)-N(2)	1.220(2)	C(6)-N(5)-C(5)	115.45(13)	
O(2)-N(2)	1.218(2)	O(8)-N(7)-O(7)	129.35(18)	
O(9)-N(7)	1.415(2)	O(8)-N(7)-O(9)	111.97(16)	
O(9)-C(1)	1.470(2)	O(7)-N(7)-O(9)	118.66(16)	
O(6)-N(6)	1.221(2)	O(4)-N(4)-O(3)	126.04(18)	
O(5)-N(6)	1.229(2)	O(4)-N(4)-N(3)	116.25(15)	
O(4)-N(4)	1.221(2)	O(3)-N(4)-N(3)	117.60(18)	
O(8)-N(7)	1.202(2)	C(1)-C(4)-C(5)	108.09(14)	
N(2)-N(1)	1.403(2)	C(1)-C(4)-H(4A)	110.1	
O(7)-N(7)	1.206(2)	C(5)-C(4)-H(4A)	110.1	
O(3)-N(4)	1.223(2)	C(1)-C(4)-H(4B)	110.1	
N(1)-C(5)	1.466(2)	C(5)-C(4)-H(4B)	110.1	
N(1)-C(7)	1.476(2)	H(4A)-C(4)-H(4B)	108.4	
N(3)-N(4)	1.402(2)	N(3)-C(7)-N(1)	110.75(13)	
N(3)-C(6)	1.470(2)	N(3)-C(7)-C(2)	106.70(14)	
N(3)-C(7)	1.475(2)	N(1)-C(7)-C(2)	106.69(14)	
N(6)-N(5)	1.363(2)	N(3)-C(7)-H(7)	110.8	
N(5)-C(6)	1.461(2)	N(1)-C(7)-H(7)	110.8	
N(5)-C(5)	1.468(2)	C(2)-C(7)-H(7)	110.8	
C(4)-C(1)	1.528(2)	C(1)-C(2)-C(7)	108.76(13)	
C(4)-C(5)	1.534(2)	C(1)-C(2)-H(2A)	109.9	
C(4)-H(4A)	0.9700	C(7)-C(2)-H(2A)	109.9	
C(4)-H(4B)	0.9700	C(1)-C(2)-H(2B)	109.9	

C(7)-C(2)	1.530(2)	C(7)-C(2)-H(2B)	109.9
C(7)-H(7)	0.9800	H(2A)-C(2)-H(2B)	108.3
C(2)-C(1)	1.528(2)	C(1)-C(3)-C(6)	107.72(14)
C(2)-H(2A)	0.9700	C(1)-C(3)-H(3A)	110.2
C(2)-H(2B)	0.9700	C(6)-C(3)-H(3A)	110.2
C(3)-C(1)	1.527(2)	C(1)-C(3)-H(3B)	110.2
C(3)-C(6)	1.539(3)	C(6)-C(3)-H(3B)	110.2
C(3)-H(3A)	0.9700	H(3A)-C(3)-H(3B)	108.5
C(3)-H(3B)	0.9700	O(9)-C(1)-C(3)	113.61(15)
C(5)-H(5A)	0.9800	O(9)-C(1)-C(4)	111.91(14)
C(6)-H(6)	0.9800	C(3)-C(1)-C(4)	110.89(14)
N(7)-O(9)-C(1)	117.74(13)	O(9)-C(1)-C(2)	100.81(12)
O(1)-N(2)-O(2)	125.79(17)	C(3)-C(1)-C(2)	109.03(15)
O(1)-N(2)-N(1)	117.06(16)	C(4)-C(1)-C(2)	110.10(15)
O(2)-N(2)-N(1)	117.01(16)	N(1)-C(5)-N(5)	108.58(15)
N(2)-N(1)-C(5)	117.03(14)	N(1)-C(5)-C(4)	107.31(13)
N(2)-N(1)-C(7)	118.18(15)	N(5)-C(5)-C(4)	107.78(14)
C(5)-N(1)-C(7)	113.95(14)	N(1)-C(5)-H(5A)	111.0
N(4)-N(3)-C(6)	115.81(14)	N(5)-C(5)-H(5A)	111.0
N(4)-N(3)-C(7)	115.67(15)	C(4)-C(5)-H(5A)	111.0
C(6)-N(3)-C(7)	113.63(14)	N(5)-C(6)-N(3)	108.44(15)
O(6)-N(6)-O(5)	125.62(16)	N(5)-C(6)-C(3)	108.73(15)
O(6)-N(6)-N(5)	117.42(16)	N(3)-C(6)-C(3)	107.07(15)
O(5)-N(6)-N(5)	116.93(17)	N(5)-C(6)-H(6)	110.8
N(6)-N(5)-C(6)	122.42(15)	N(3)-C(6)-H(6)	110.8
N(6)-N(5)-C(5)	121.87(16)	C(3)-C(6)-H(6)	110.8

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Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for **13**.

The anisotropic displacement factor exponent takes the form:

	-2 pi^2 [h^2 a*^2 U11 + + 2 h k a* b* U12]					
	U11	U22	U33	U23	U13	U12
O(1)	24(1)	28(1)	19(1)	3(1)	7(1)	4(1)
O(2)	28(1)	27(1)	17(1)	-5(1)	-6(1)	4(1)
O(9)	20(1)	20(1)	21(1)	-8(1)	8(1)	-5(1)
O(6)	29(1)	20(1)	36(1)	-4(1)	-10(1)	-8(1)
O(5)	27(1)	13(1)	41(1)	5(1)	-2(1)	0(1)

O(4) $14(1)$ $38(1)$ $27(1)$ $-8(1)$ $0(1)$ $O(8)$ $28(1)$ $35(1)$ $33(1)$ $-17(1)$ $11(1)$ $N(2)$ $22(1)$ $17(1)$ $14(1)$ $1(1)$ $-2(1)$ $O(7)$ $31(1)$ $32(1)$ $30(1)$ $-6(1)$ $12(1)$ $O(3)$ $37(1)$ $22(1)$ $40(1)$ $-6(1)$ $-5(1)$ $N(1)$ $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ $N(3)$ $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ $N(6)$ $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$ $N(5)$ $24(1)$ $10(1)$ $24(1)$ $1(1)$ $11(1)$	
O(8) $28(1)$ $35(1)$ $33(1)$ $-17(1)$ $11(1)$ $N(2)$ $22(1)$ $17(1)$ $14(1)$ $1(1)$ $-2(1)$ $O(7)$ $31(1)$ $32(1)$ $30(1)$ $-6(1)$ $12(1)$ $O(3)$ $37(1)$ $22(1)$ $40(1)$ $-6(1)$ $-5(1)$ $N(1)$ $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ $N(3)$ $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ $N(6)$ $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$	5(1)
N(2) $22(1)$ $17(1)$ $14(1)$ $1(1)$ $-2(1)$ O(7) $31(1)$ $32(1)$ $30(1)$ $-6(1)$ $12(1)$ O(3) $37(1)$ $22(1)$ $40(1)$ $-6(1)$ $-5(1)$ N(1) $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ N(3) $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ N(6) $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$ N(5) $24(1)$ $10(1)$ $24(1)$ $1(1)$ $11(1)$	-2(1)
O(7) $31(1)$ $32(1)$ $30(1)$ $-6(1)$ $12(1)$ $O(3)$ $37(1)$ $22(1)$ $40(1)$ $-6(1)$ $-5(1)$ $N(1)$ $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ $N(3)$ $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ $N(6)$ $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$ $N(5)$ $24(1)$ $10(1)$ $24(1)$ $1(1)$ $11(1)$	7(1)
O(3) $37(1)$ $22(1)$ $40(1)$ $-6(1)$ $-5(1)$ $N(1)$ $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ $N(3)$ $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ $N(6)$ $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$ $N(5)$ $24(1)$ $10(1)$ $24(1)$ $1(1)$ $11(1)$	-12(1)
N(1) $15(1)$ $16(1)$ $13(1)$ $-1(1)$ $-1(1)$ N(3) $14(1)$ $16(1)$ $18(1)$ $-2(1)$ $-2(1)$ N(6) $17(1)$ $12(1)$ $24(1)$ $-1(1)$ $3(1)$ N(5) $24(1)$ $10(1)$ $24(1)$ $1(1)$ $11(1)$	13(1)
N(3)14(1)16(1)18(1) $-2(1)$ $-2(1)$ N(6)17(1)12(1)24(1) $-1(1)$ 3(1)N(5)24(1)10(1)24(1)1(1)11(1)	1(1)
N(6) 17(1) 12(1) 24(1) -1(1) 3(1) N(5) 24(1) 10(1) 24(1) 1(1) 11(1)	3(1)
N(5) = 24(1) = 10(1) = 24(1) = 1(1) = 11(1)	-4(1)
N(3) = 24(1) = 10(1) = 24(1) = -11(1) = -11(1)	-1(1)
N(7) 20(1) 30(1) 17(1) -8(1) 4(1)	-6(1)
N(4) 17(1) 24(1) 21(1) -8(1) -9(1)	8(1)
C(4) 13(1) 16(1) 16(1) -2(1) 1(1)	0(1)
C(7) 14(1) 13(1) 16(1) 0(1) -1(1)	-1(1)
C(2) 16(1) 12(1) 18(1) -2(1) 4(1)	-3(1)
C(3) 20(1) 17(1) 14(1) 2(1) -3(1)	-4(1)
C(1) 15(1) 14(1) 13(1) -2(1) 3(1)	-2(1)
C(5) 14(1) 13(1) 15(1) 0(1) -2(1)	1(1)
C(6) 18(1) 14(1) 18(1) 2(1) -6(1)	-1(1)

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Table 5. Hydrogen coordinates ($x \ 10^{4}$) and isotropic

	х	У	Z	U(eq)
H(4A)	8629	6625	4382	18
H(4B)	8168	5689	5122	18
H(7)	3057	5823	5819	17
H(2A)	5211	4851	4877	18
H(2B)	3854	5265	3980	18
H(3A)	4584	6726	2791	21
H(3B)	6414	7261	2921	21
H(5A)	7770	7178	6214	17
H(6)	4270	8220	3901	20

displacement parameters ($A^2 \times 10^3$) for 13

Table 6. Torsion angles [deg] for 13.

O(1)-N(2)-N(1)-C(5)	164.57(15)	C(6)-C(3)-C(1)-C(4)	-59.90(19)	
O(2)-N(2)-N(1)-C(5)	-19.5(2)	C(6)-C(3)-C(1)-C(2)	61.49(18)	
O(1)-N(2)-N(1)-C(7)	22.4(2)	C(5)-C(4)-C(1)-O(9)	-171.07(13)	
O(2)-N(2)-N(1)-C(7)	-161.71(15)	C(5)-C(4)-C(1)-C(3)	60.95(18)	
O(6)-N(6)-N(5)-C(6)	175.65(18)	C(5)-C(4)-C(1)-C(2)	-59.81(18)	

O(5)-N(6)-N(5)-C(6)	-6.0(3)	C(7)-C(2)-C(1)-O(9)	178.53(14)
O(6)-N(6)-N(5)-C(5)	1.7(3)	C(7)-C(2)-C(1)-C(3)	-61.66(18)
O(5)-N(6)-N(5)-C(5)	-179.93(17)	C(7)-C(2)-C(1)-C(4)	60.21(19)
C(1)-O(9)-N(7)-O(8)	162.15(17)	N(2)-N(1)-C(5)-N(5)	-91.21(18)
C(1)-O(9)-N(7)-O(7)	-19.4(3)	C(7)-N(1)-C(5)-N(5)	52.56(17)
C(6)-N(3)-N(4)-O(4)	-175.40(16)	N(2)-N(1)-C(5)-C(4)	152.54(14)
C(7)-N(3)-N(4)-O(4)	-38.8(2)	C(7)-N(1)-C(5)-C(4)	-63.69(18)
C(6)-N(3)-N(4)-O(3)	8.1(2)	N(6)-N(5)-C(5)-N(1)	118.77(18)
C(7)-N(3)-N(4)-O(3)	144.67(18)	C(6)-N(5)-C(5)-N(1)	-55.6(2)
N(4)-N(3)-C(7)-N(1)	-84.71(19)	N(6)-N(5)-C(5)-C(4)	-125.28(18)
C(6)-N(3)-C(7)-N(1)	52.81(19)	C(6)-N(5)-C(5)-C(4)	60.4(2)
N(4)-N(3)-C(7)-C(2)	159.55(15)	C(1)-C(4)-C(5)-N(1)	59.04(17)
C(6)-N(3)-C(7)-C(2)	-62.93(18)	C(1)-C(4)-C(5)-N(5)	-57.73(18)
N(2)-N(1)-C(7)-N(3)	90.90(18)	N(6)-N(5)-C(6)-N(3)	-118.29(18)
C(5)-N(1)-C(7)-N(3)	-52.43(18)	C(5)-N(5)-C(6)-N(3)	56.0(2)
N(2)-N(1)-C(7)-C(2)	-153.35(14)	N(6)-N(5)-C(6)-C(3)	125.62(18)
C(5)-N(1)-C(7)-C(2)	63.32(17)	C(5)-N(5)-C(6)-C(3)	-60.1(2)
N(3)-C(7)-C(2)-C(1)	59.58(18)	N(4)-N(3)-C(6)-N(5)	83.91(18)
N(1)-C(7)-C(2)-C(1)	-58.84(18)	C(7)-N(3)-C(6)-N(5)	-53.55(19)
N(7)-O(9)-C(1)-C(3)	73.2(2)	N(4)-N(3)-C(6)-C(3)	-158.93(15)
N(7)-O(9)-C(1)-C(4)	-53.3(2)	C(7)-N(3)-C(6)-C(3)	63.61(18)
N(7)-O(9)-C(1)-C(2)	-170.31(15)	C(1)-C(3)-C(6)-N(5)	56.62(19)
C(6)-C(3)-C(1)-O(9)	173.04(14)	C(1)-C(3)-C(6)-N(3)	-60.34(18)

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Symmetry transformations used to generate equivalent atoms.