Supporting information

Z-Formamidoximes in molecular folding and macrocycles.

Weiwen Zhao, Ruiyao Wang and Anne Petitjean*

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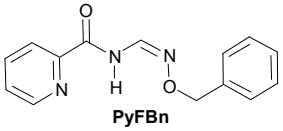
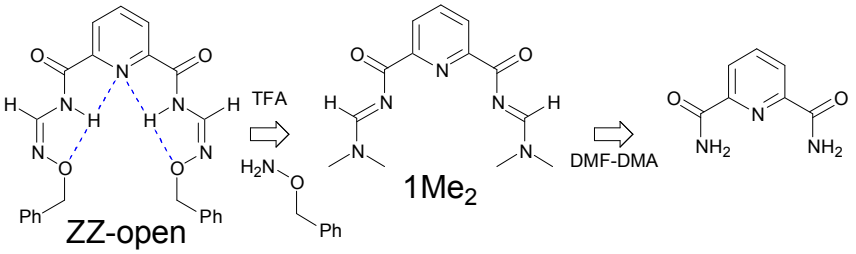


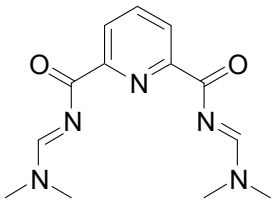
A. Synthesis

Materials and Methods: Commercially available compounds were used as received. Anhydrous dichloromethane and toluene were dried by passing through an activated alumina column. All reactions were performed under Argon (Ar) unless stated otherwise. Deuterated solvents were used as received, except for $CDCl_3$ which was sometimes neutralized by passing through a short column of basic alumina (such treated $CDCl_3$ will be signaled below by an asterisk, i. e. '$CDCl_3$*'). ^{1}H NMR and ^{13}C NMR were performed using 300 MHz, 400 MHz and 500 MHz Bruker instruments. Peak listings for all NMR spectra are given in ppm and referenced against the solvent residual signal. Thin layer chromatography (TLC) analysis was performed on silica gel with a pore diameter of 60 Å or activated basic Aluminum oxide with a pore diameter of 58 Å. Column chromatography was performed on silica gel with a particle size of 40-63 µm and a pore diameter of 60 Å.

A.1. Retrosynthesis of ZZ-open

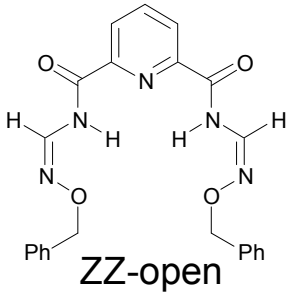


Bis(N',N'-dimethylformamidyl-N-acyl)-2,6-pyridine (1Me$_2$): Pyridyl-2,6-dicarboxamide



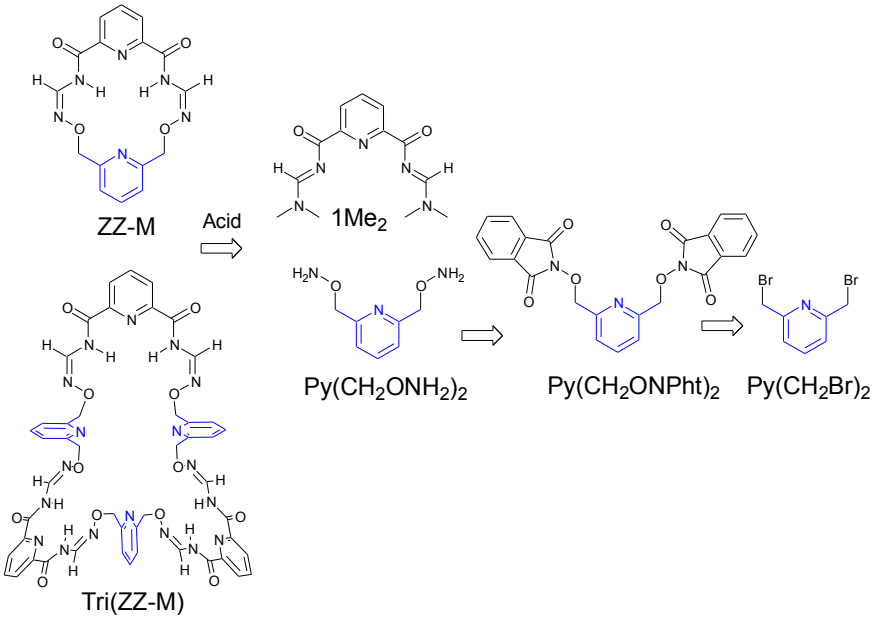
(11 mmol, 1.0 eq) was mixed with N,N-dimethylformamide dimethyl-acetal (DMF-DMA, 35 mmol, 3.2 eq) in dimethyl sulfoxide (20 mL). The reaction was heated at 85 °C for 3.5 hours while the methanol by-product distilled off. After cooling to room temperature, the white precipitate was filtered and washed with diethyl ether. The resulting N,N-dimethylformamidine product (74 %) was then used without further purification. δ ^{1}**H** NMR ($CDCl_3$*, 500 MHz, 25 °C) 8.59 (s, 2 H), 8.31 (d, ^3J = 7.5 Hz, 2 H), 7.82 (t, ^3J = 7.5 Hz, 1 H), 3.16 (br s, 6 H), 3.11 (br s, 6 H). δ ^{13}**C** NMR ($CDCl_3$*, 125 MHz, 25 °C) 176.0, 161.3, 153.5, 137.0, 126.5, 41.3, 35.4. EI$^+$-HRMS: calc. for $C_{13}H_{17}N_5O_2$: 275.1382; found: 275.1382 $[M]^+$, 232.0981 $[M\text{-}Me_2N\text{-}H]^+$, 220.0929 $[M\text{-}Me_2N\text{-}H\text{-}C]^+$, 205.0839 $[M\text{-}Me_2N\text{-}H\text{-}C\text{-}NH]^+$. EA calc. for $C_{13}H_{17}N_5O_2$: %C 56.71, %H 6.22, %N 25.44; found %C 56.38, %H 6.20, %N 25.22. Mp 204 °C (dec.).

ZZ-open: Bis-reactive formamidine **1Me$_2$** (131 mg, 0.48 mmol, 1.0 eq) was mixed with O-benzylhydroxylamine (117 mg, 0.95 mmol, 2.0 eq) and trifluoroacetic acid (147 µL, 1.9 mmol, 4.0 eq) in anhydrous dichloromethane (2 mL), and the resulting solution stirred overnight at room temperature. The organic solution was washed with saturated aqueous potassium carbonate (2 mL) and the aqueous layer was extracted with dichloromethane. The combined organic

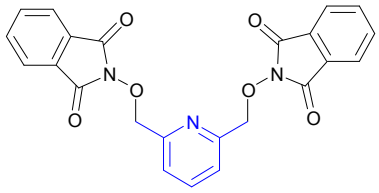


layers were dried over sodium sulphate and concentrated in vacuo. Recrystallization of the crude from 95% ethanol gave a white solid (150 mg, 72 %).δ ^{1}**H** NMR ($CDCl_3$*, 500 MHz, 25 °C) 10.23 (d, ^3J = 10 Hz, 2 H), 8.48 (d, ^3J = 8.0 Hz, 2 H), 8.16 (t, ^3J = 8.0 Hz, 1 H), 7.84 (d, ^3J = 10 Hz, 2 H), 7.25-7.35 (m, 10 H), 5.04 (s, 4 H). δ ^{13}**C** NMR ($CDCl_3$*, 125 MHz, 25 °C) 160.4, 147.8, 139.7, 137.5, 133.8, 128.5, 128.0, 127.5, 127.2, 76.1. EI$^+$-HRMS: calc. for $C_{23}H_{21}N_5O_4$: 431.1594; found: 431.1603 $[M]^+$, 324.1182 $[M\text{-}BnO]^+$, 218.0715 $[M\text{-}2BnO\text{+}H]^+$, 148.0552 $[M\text{-}2BnO\text{-}CONHCHN]^+$. Mp 162-163 °C. EA: $C_{23}H_{21}N_5O_4$, calc.: % C 64.03, % H 4.91, % N 16.23; found: % C 64.16, % H 4.88, % N 16.25.

A.2. Retrosynthesis of ZZ-M and Tri(ZZ-M)

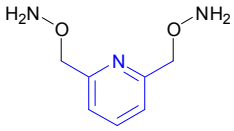


Py(CH$_2$ONPht)$_2$: Sodium hydride suspension in mineral oil (60%, 1.24 g, 31 mmol, 2.8 eq) was washed with hexanes under argon, and suspended in dry DMF under argon. N-hydroxyphthalimide (4.24 g, 26 mmol, 2.4 eq) was then added portionwise as a solid, as the mixture was stirred in an ice/water bath. 2,6-Dibromomethylpyridine (3.0 g, 11 mmol, 1.0 eq) was then added at once and the mixture was stirred at 60 ºC for 21 hours under argon. Water was then added at room temperature, the precipitate filtered and washed with copious amounts of water. The solid



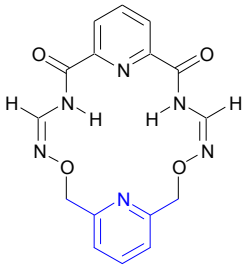
was then dissolved in dichloromethane and washed with water The organic layer was isolated, dried on sodium sulphate and concentrated in vacuo to give a white solid (3.83, 81 %). δ ^{1}**H** (300 MHz; $CDCl_3$; 25 ºC): 7.7-7.9 (m, 11 H), 5.26 (s, 4H).

Py(CH$_2$ONH$_2$)$_2$: Py(CH$_2$ONPht)$_2$ (3.83 g, 8.9 mmol, 1.0 eq) was suspended in 95% ethanol (150 mL). Most of the reagent was dissolved by heating gently, and hydrazine hydrate (1.1 mL, 22 mmol, 2.5 eq) was added. The mixture was then heated at 80 ºC for 4 hours. Back to room temperature, the suspension was concentrated in vacuo to give a white solid which was taken up in diethyl ether (80 mL). The precipitate was filtered and washed with more diethyl ether (6 × 50 mL). The combined filtrates were concentrated in vacuo to give 1.53 g of a crude oil which was purified by column chromatography (silica gel, 100:1:5 Et_2O/Et_3N/CH_3OH) to give of a colourless oil (1.12 g, 6.63 mmol, 73 %). δ ^{1}**H** (300 MHz; $CDCl_3$*; 25 ºC): 7.72 (t, ^3J = 7.8 Hz, 1 H), 7.32 (d, ^3J = 7.8 Hz, 2 H), 5.61 (s, 4 H), 4.83 (s, 4 H). δ ^{13}**C** NMR ($CDCl_3$*, 125 MHz,



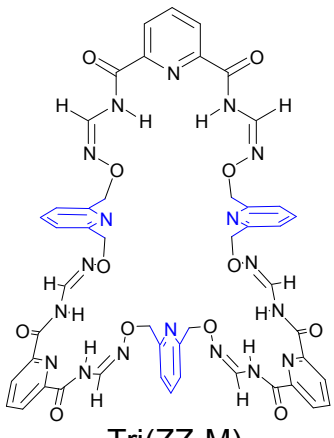
25 °C) 157.6, 137.2, 120.7, 78.4. R_f (SiO_2, 100:1:15 $Et_2O/Et_3N/CH_3OH$) = 0.25; $C_7H_{11}N_3O_2 \cdot 0.45\ H_2O$: calc. %C 47.42, %H 6.77, %N 23.70; found %C 47.66, %H 6.83, %N 23.31.

ZZ-M and Tri(ZZ-M) : Bis-reactive **$Py(CH_2ONH_2)_2$** nucleophile (18.4 mg, 0.108 mmol, 1.0 eq) and bis-reactive electrophile **$1Me_2$** (29.9 mg, 0.108 mmol, 1.0 eq) were mixed in 2 mL of anhydrous dichloromethane in the presence of acetic acid (24.7 µL, 0.43 mmol, 4.0 eq). The solution was stirred at room temperature for 3 days, and washed with saturated aqueous potassium bicarbonate (2 mL). The aqueous layer was extracted with dichloromethane and the combined organic layers were dried over sodium sulphate, concentrated in vacuo and purified by preparative TLC with 2:100 MeOH/ CH_2Cl_2 as an eluent to give pure ZZ-M (10 mg, 26%) and Tri(ZZ-M) (3 mg, ~ 8%) as a more polar fraction (mixed with minor impurities).



ZZ-M

δ ^{1}**H** NMR ($CDCl_3$*, 500 MHz, 25 °C) 10.63 (d, ^3J = 10 Hz, 2 H), 8.48 (d, ^3J = 7.5 Hz, 2 H), 8.11 (t, ^3J = 7.5 Hz, 1 H), 7.86 (d, ^3J = 10 Hz, 2 H), 7.75 (t, ^3J = 7.5 Hz, 1 H), 7.31 (d, ^3J = 7.5 Hz, 2 H), 5.29 (s, 4 H). δ ^{1}**H** NMR (CD_3OD, 300 MHz, 25°C, low solubility) 8.65 (dd, ^3J = 7.8 Hz, ^3J = 8 Hz, 2 H), 8.27 (dd, ^3J = 7.4 Hz, ^3J = 8.2 Hz, 1 H), 7.93 (t, ^3J = 7.7 Hz, 1 H), 7.89 (s, 1 H), 7.48 (d, ^3J = 7.6 Hz, 2 H), 5.31 (s, 4 H). δ ^{13}**C** NMR ($CDCl_3$* 100 MHz, 25 °C) 162.0, 161.6, 155.7, 148.1, 137.9, 134.3, 127.6, 122.6, 76.7. Mp: 200 °C (dec.). See details of crystal structures further in supporting information.



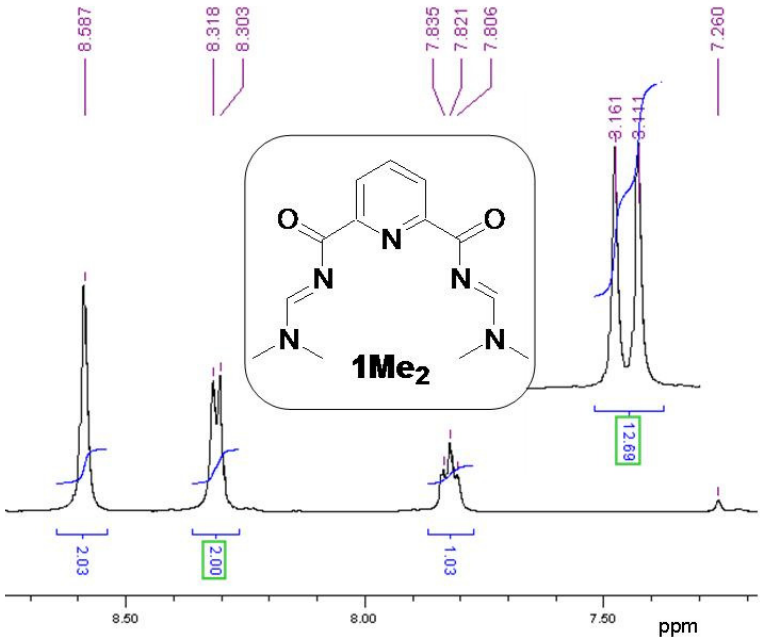
Tri(ZZ-M)

δ ^{1}**H** NMR ($CDCl_3$*, 500 MHz, 25°C): 10.39 (d, ^3J = 10 Hz, 6 H), 8.50 (d, ^3J = 7.9 Hz, 6 H), 8.17 (t, ^3J = 7.9 Hz, 3 H), 7.82 (d, ^3J = 10 Hz, 6 H), 7.60 (t, ^3J = 7.6 Hz, 3 H), 7.22 (d, ^3J = 7.9 Hz, 6 H), 5.09 (s, 12 H). ESI$^+$-MS: calc. for $C_{48}H_{42}N_{18}O_{12}$: 1063.32 [MH^+], 1085.31 [MNa^+]; found: 1063.2 [MH^+], 1085.2 [MNa^+].

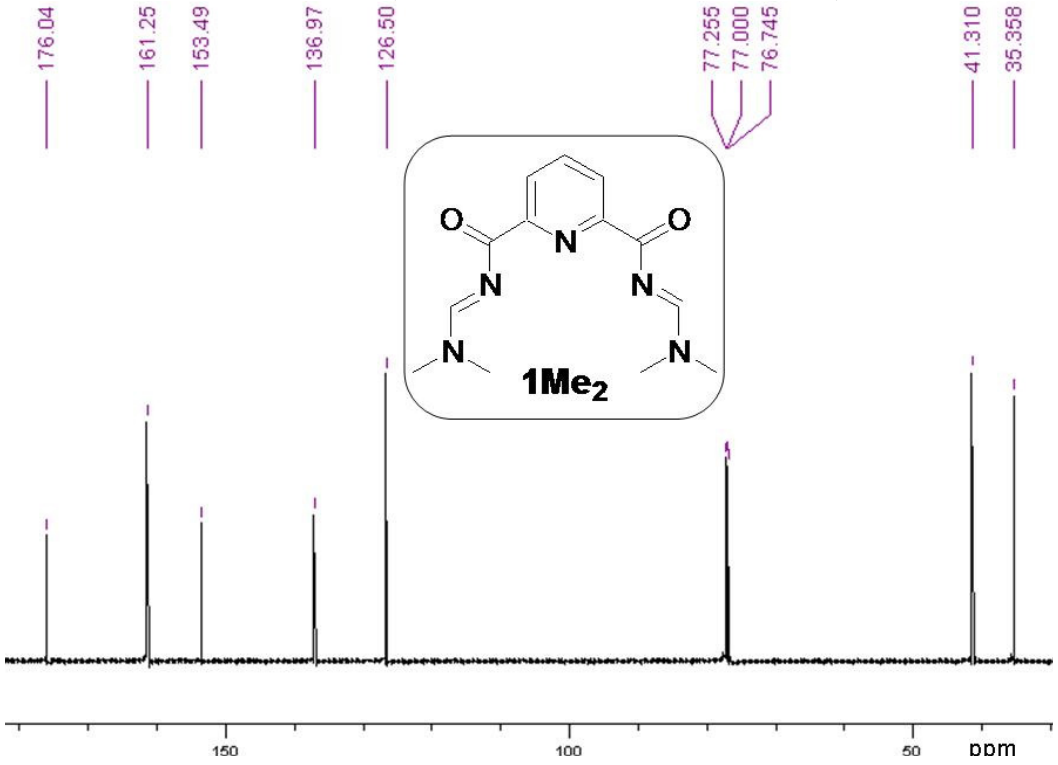
See details of crystal structures further in supporting information.

B. Copy of ^{1}H and ^{13}C NMR spectra

Dimethylformamidine precursor **1Me$_2$**: ^{1}H NMR ($CDCl_3$*, 500 MHz, 25 °C)



^{13}C NMR ($CDCl_3$*, 125 MHz, 25 °C)



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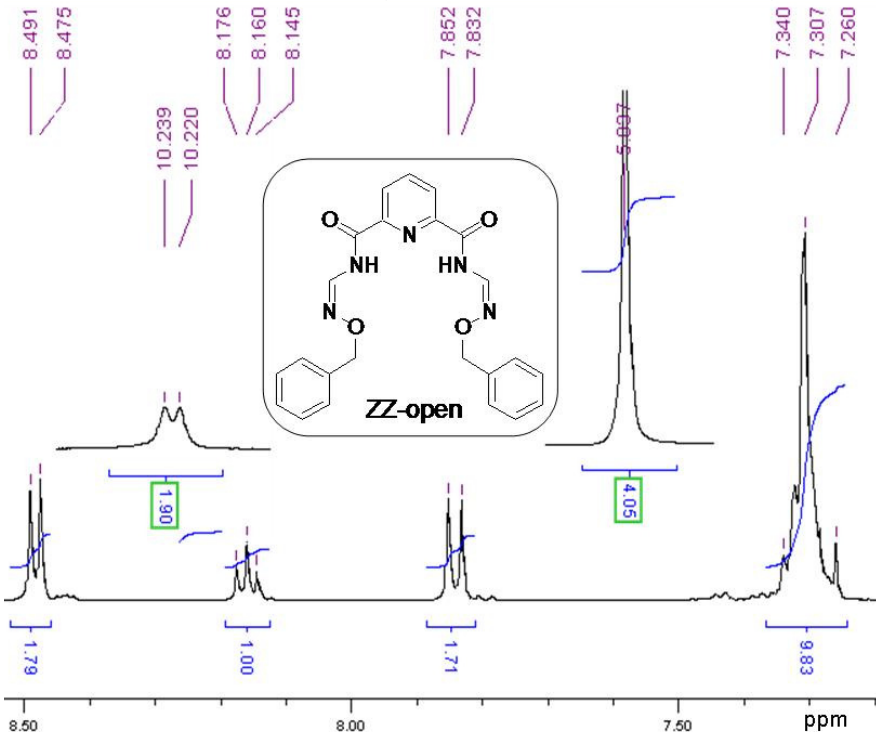
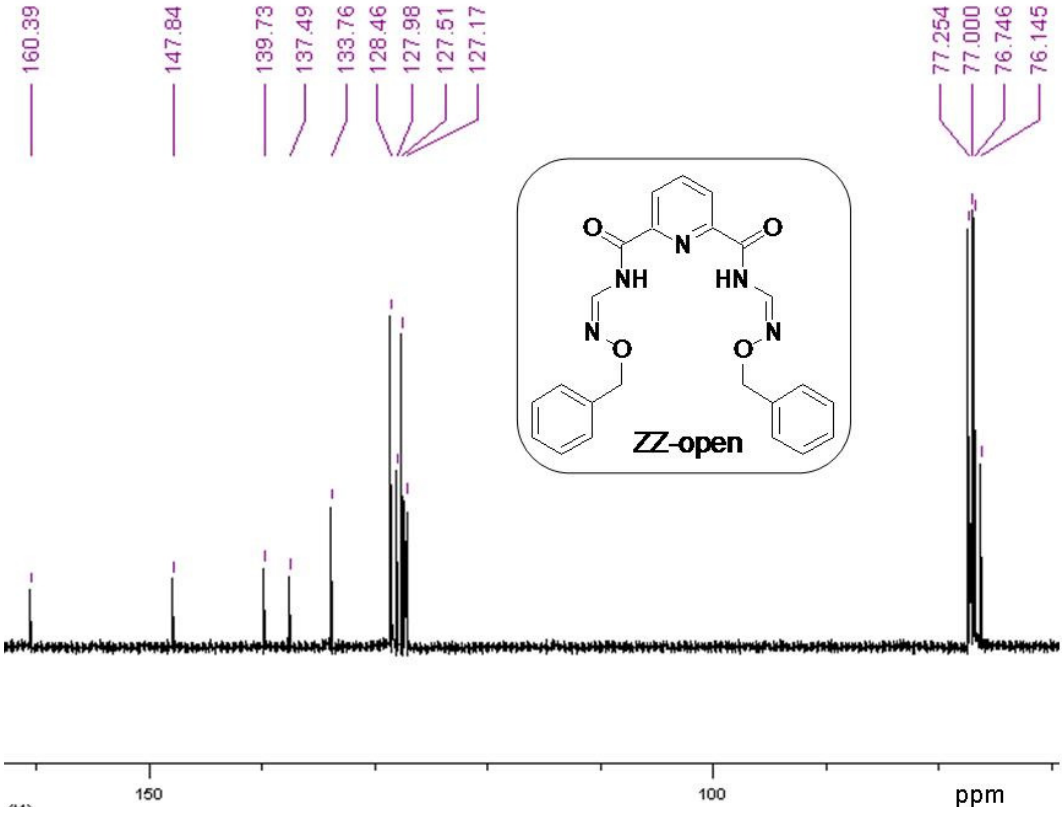
ZZ-open

^{1}H NMR ($CDCl_3$*, 500 MHz, 25 °C)



^{13}C NMR ($CDCl_3$*, 125 MHz, 25 °C)



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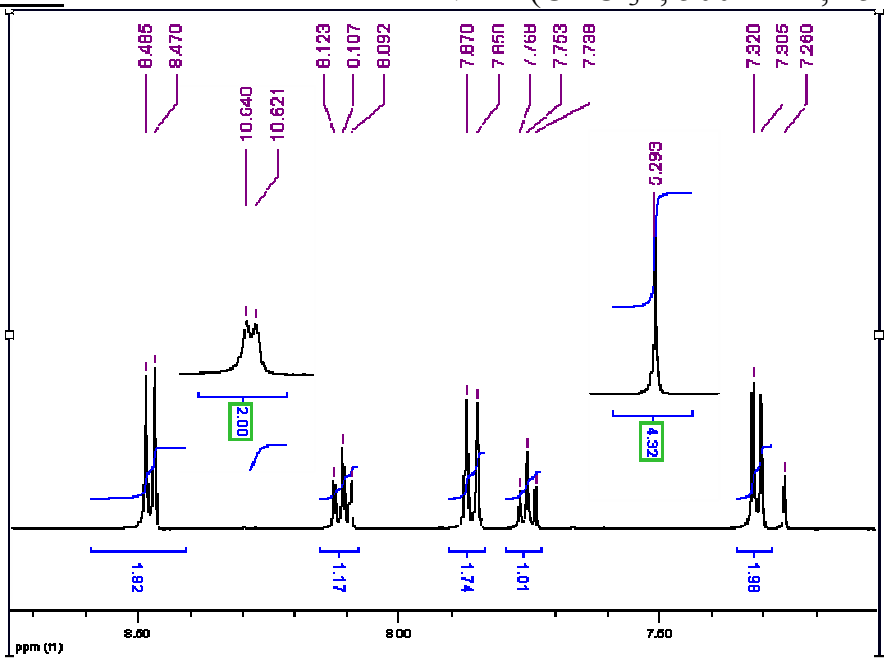
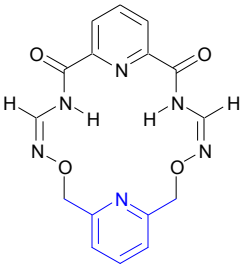
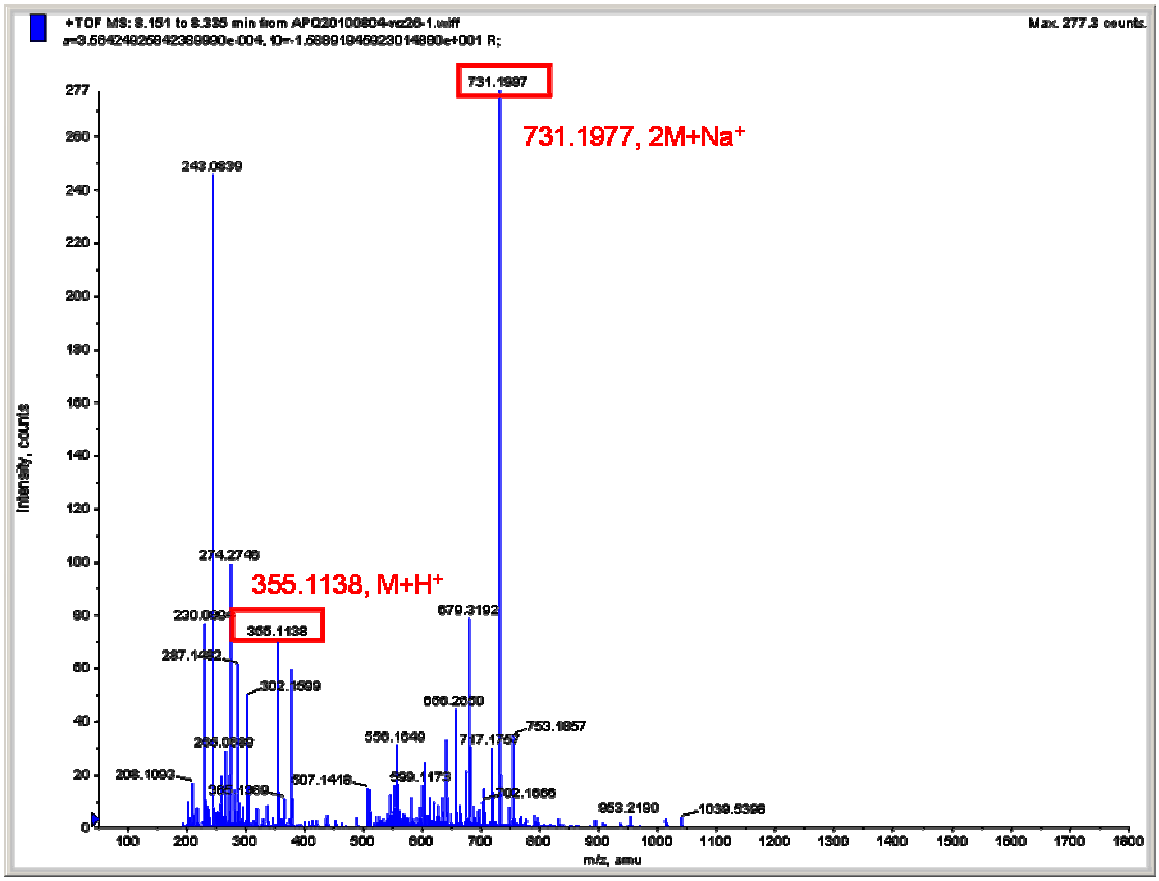
ZZ-M ^{1}H NMR ($CDCl_3$*, 500 MHz, 25 °C)





ZZ-M

ESI$^+$-MS



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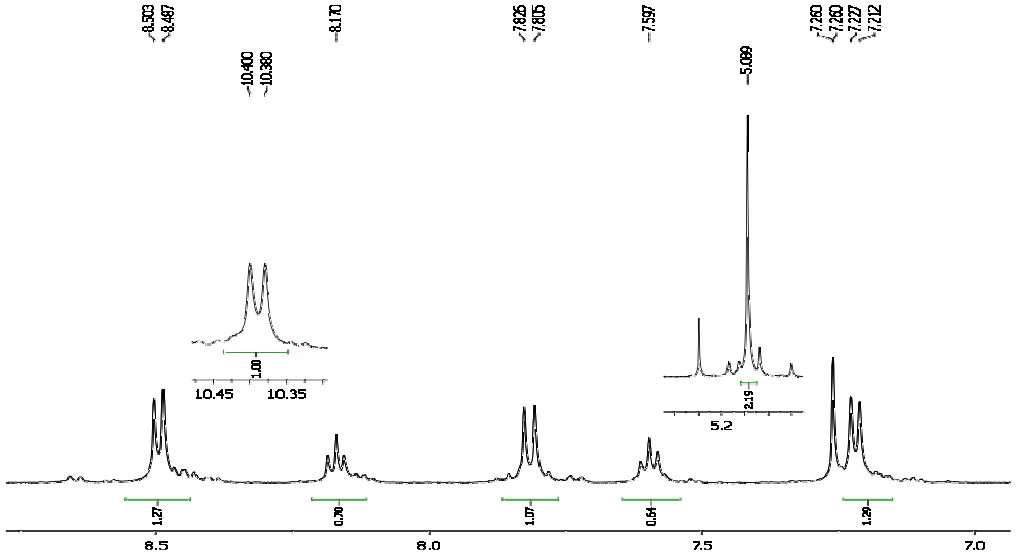
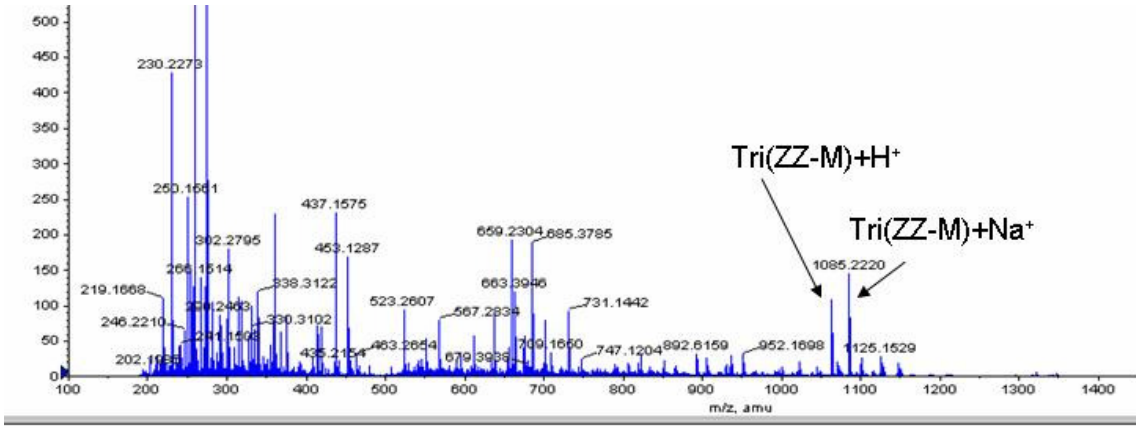
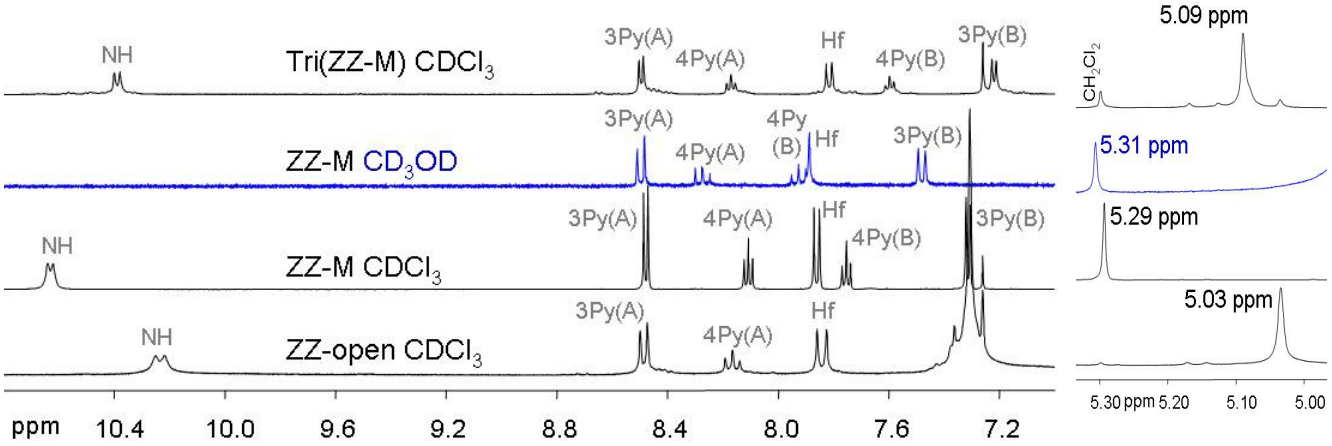
Tri(ZZ-**M**) ^{1}H NMR (500 MHz; $CDCl_3$; 25 ºC)



ESI$^+$-MS



C. Complete stacked plot ^{1}H NMR ZZ-open, ZZ-M, Tri(ZZ-M)



D. Crystallographic data

D.1: ZZ-M

ZZ-**M** was crystallized by slow diffusion of diethyl ether into a solution of ZZ-M in dichloromethane, in the presence of N,N-dimethylammonium triflate (by-products of the condensation reaction), resulting in their incorporation inside the crystal lattice.

A crystal of the compound (colorless, block-shaped, size 0.32 × 0.28 × 0.25 mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 3.02 ~ 52.00º. No significant decay was observed during the data collection. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package:[1] Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT (Bruker, 2005); structure solution: XPREP (Bruker, 2005) and SHELXTL (Bruker, 2000); structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[2] The crystal is triclinic space group *P*-1, based on the systematic absences, *E* statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w\ (F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. The H atoms of water were located from difference Fourier maps. All of the other H atoms were placed in geometrically calculated positions, with C-H = 0.95 (aromatic), 0.99(CH_2), and 0.88(N-H) Å, and refined as riding atoms, with Uiso(H) = 1.2 Ueq(C or N). The two triflates are disordered. SHELX command, EADP, was used to resolve the disorder. Convergence to final R_1 = 0.0569 and wR_2 = 0.1408 for 8004 (I>2σ(I)) independent reflections, and R_1 = 0.0663 and wR_2 = 0.1494 for all 9507 (R(int) = 0.0185) independent reflections, with 703 parameters and 0 restraints, were achieved.[3] The largest residual peak and hole to be 0.692 and – 0.706 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles and H-bonding information are given in Tables S1 to S7. The molecular structure and the cell packing are shown in Figure S1.

[1] Bruker AXS Crystal Structure Analysis Package: Bruker (2000). SHELXTL. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA; Bruker (2005). XPREP. Version 2005/2. Bruker AXS Inc., Madison, Wisconsin, USA; Bruker (2005). SAINT. Version 7.23A. Bruker AXS Inc., Madison,Wisconsin, USA; Bruker (2006). APEX2. Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

[3] $R_1 = \sum | |Fo| - |Fc| | / \sum |Fo|$

$wR_2 = \{\sum [w (Fo^2 - Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/2}$

($w = 1 / [\sigma^2(Fo^2) + (0.0625P)^2 + 3.25P]$, where $P = [\text{Max}\ (Fo^2, 0) + 2Fc^2] / 3$)

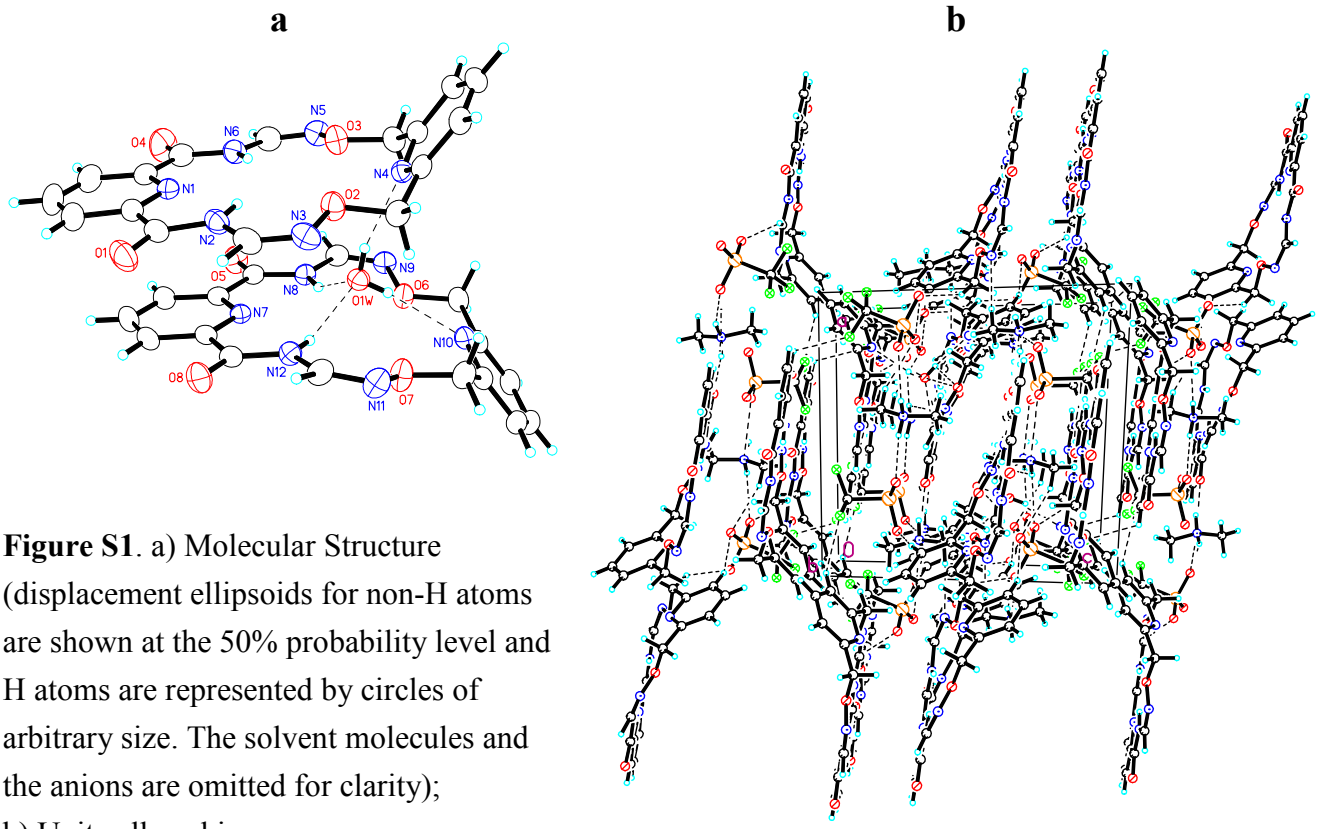


Figure S1. a) Molecular Structure (displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are represented by circles of arbitrary size. The solvent molecules and the anions are omitted for clarity);
b) Unit cell packing.

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Table S1. Crystal data and structure refinement for ap16

Identification code	ap16	
Empirical formula	C19 H23 F3 N7 O7.50 S	
Formula weight	558.50	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.4432(8) Å	α= 64.0350(10)°.
	b = 14.6020(8) Å	β= 76.9770(10)°.
	c = 14.6895(8) Å	γ = 61.12°.
Volume	2438.6(2) $Å^3$	
Z	4	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	1156	
Crystal size	0.32 x 0.28 x 0.25 mm^3	
Theta range for data collection	1.54 to 26.00°.	
Index ranges	-17<=h<=17, -18<=k<=18, -18<=l<=18	
Reflections collected	24537	
Independent reflections	9507 [R(int) = 0.0185]	
Completeness to theta = 26.00°	99.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9486 and 0.9349	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9507 / 0 / 703	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1408	
R indices (all data)	R1 = 0.0663, wR2 = 0.1494	
Largest diff. peak and hole	0.692 and -0.706 $e.Å^{-3}$	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for ap16. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5464(2)	3398(2)	8915(2)	33(1)
N(2)	3585(2)	5323(2)	8679(2)	32(1)
N(3)	1725(2)	6347(2)	8429(2)	35(1)
N(4)	1720(2)	3509(2)	8383(2)	27(1)
N(5)	4579(2)	615(2)	8675(2)	38(1)
N(6)	5472(2)	1518(2)	8875(2)	36(1)
N(7)	4895(2)	4470(2)	6277(1)	26(1)
N(8)	4806(2)	2684(2)	6175(2)	28(1)
N(9)	3938(2)	1873(2)	5785(2)	33(1)
N(10)	1308(2)	4980(2)	5027(2)	28(1)
N(11)	1224(2)	7545(2)	5661(2)	36(1)
N(12)	3046(2)	6394(2)	6059(2)	29(1)
O(1)	4485(2)	6243(2)	8670(2)	47(1)
O(2)	1836(1)	5287(1)	8542(1)	36(1)
O(3)	3681(1)	1597(2)	8728(2)	38(1)
O(4)	7246(2)	601(2)	9075(2)	64(1)
O(5)	6572(1)	1658(2)	6434(2)	44(1)
O(6)	3190(1)	3016(1)	5370(1)	34(1)
O(7)	1405(1)	6717(2)	5303(2)	38(1)
O(8)	3932(2)	7211(2)	6274(2)	40(1)
O(1W)	2799(1)	4361(2)	6532(2)	30(1)
C(1)	6390(2)	2469(2)	9038(2)	38(1)
C(2)	7346(2)	2418(3)	9160(2)	51(1)
C(3)	7354(3)	3364(3)	9144(2)	56(1)
C(4)	6419(2)	4331(3)	9002(2)	48(1)
C(5)	5495(2)	4309(2)	8899(2)	36(1)
C(6)	4487(2)	5377(2)	8741(2)	35(1)
C(7)	2618(2)	6273(2)	8521(2)	35(1)
C(8)	882(2)	5452(2)	8215(2)	33(1)
C(9)	895(2)	4304(2)	8664(2)	27(1)
C(10)	127(2)	4074(2)	9349(2)	32(1)
C(11)	220(2)	2981(2)	9771(2)	34(1)
C(12)	1087(2)	2149(2)	9510(2)	32(1)

C(13)	1816(2)	2448(2)	8810(2)	28(1)
C(14)	2774(2)	1589(2)	8496(2)	35(1)
C(15)	5415(2)	648(2)	8771(2)	39(1)
C(16)	6414(2)	1442(2)	9007(2)	42(1)
C(17)	4948(2)	5340(2)	6318(2)	28(1)
C(18)	5884(2)	5315(2)	6454(2)	34(1)
C(19)	6807(2)	4336(3)	6561(2)	40(1)
C(20)	6772(2)	3426(2)	6523(2)	36(1)
C(21)	5801(2)	3529(2)	6382(2)	28(1)
C(22)	5763(2)	2538(2)	6340(2)	30(1)
C(23)	4711(2)	1799(2)	6140(2)	32(1)
C(24)	2295(2)	3065(2)	5063(2)	35(1)
C(25)	1567(2)	4300(2)	4531(2)	28(1)
C(26)	1195(2)	4695(2)	3576(2)	33(1)
C(27)	524(2)	5828(2)	3119(2)	34(1)
C(28)	258(2)	6542(2)	3613(2)	31(1)
C(29)	668(2)	6085(2)	4565(2)	27(1)
C(30)	417(2)	6831(2)	5127(2)	33(1)
C(31)	2079(2)	7324(2)	5994(2)	33(1)
C(32)	3934(2)	6398(2)	6220(2)	29(1)
S(1)	1173(1)	2(1)	7167(1)	47(1)
C(33)	643(3)	34(3)	8398(3)	56(1)
O(11A)	174(3)	483(3)	6681(3)	52(1)
O(12A)	1894(4)	-1068(3)	7301(3)	52(1)
O(13A)	1588(5)	859(5)	6796(4)	52(1)
F(11A)	-38(3)	1046(3)	8428(3)	66(1)
F(12A)	223(4)	-645(4)	8973(3)	66(1)
F(13A)	1509(3)	-263(4)	8947(3)	66(1)
O(11B)	508(5)	-182(7)	6703(5)	52(1)
O(12B)	2150(5)	-1247(6)	7640(6)	52(1)
O(13B)	1493(8)	799(9)	6637(8)	52(1)
F(11B)	-390(6)	946(6)	8087(6)	74(2)
F(12B)	514(7)	-954(7)	8902(7)	74(2)
F(13B)	1084(7)	213(7)	8856(6)	74(2)
S(2)	2951(1)	2313(1)	2449(1)	35(1)
C(34)	2924(2)	2942(3)	1081(2)	51(1)

O(21)	1846(2)	2725(2)	2728(2)	51(1)
O(22)	3514(2)	2771(2)	2682(2)	51(1)
O(23)	3496(2)	1123(2)	2681(2)	56(1)
F(21A)	3941(5)	2440(7)	690(5)	55(1)
F(22A)	2217(7)	2889(8)	708(4)	55(1)
F(23A)	2397(5)	4173(6)	894(6)	55(1)
F(21B)	3835(5)	2827(7)	648(4)	62(1)
F(22B)	2527(7)	2458(8)	739(4)	62(1)
F(23B)	2534(5)	3983(6)	632(5)	62(1)
N(13A)	1418(3)	85(3)	3413(3)	60(1)
C(35A)	1352(3)	346(3)	4251(3)	62(1)
C(36A)	1160(20)	960(20)	2430(20)	101(3)
N(13B)	980(7)	1091(9)	3234(9)	60(1)
C(35B)	1352(3)	346(3)	4251(3)	62(1)
C(36B)	1300(60)	850(60)	2440(60)	101(3)
N(14)	4233(2)	8503(2)	7115(2)	38(1)
C(37)	4234(3)	9305(3)	6067(2)	54(1)
C(38)	3996(2)	9000(3)	7874(3)	50(1)

Table S3. Bond lengths [Å] and angles [°] for ap16.

N(1)-C(5)	1.341(3)	C(4)-H(4A)	0.9500	S(1)-O(13A)	1.484(5)
N(1)-C(1)	1.343(3)	C(5)-C(6)	1.499(4)	S(1)-O(12B)	1.627(7)
N(2)-C(6)	1.368(3)	C(7)-H(7A)	0.9500	S(1)-C(33)	1.810(4)
N(2)-C(7)	1.386(3)	C(8)-C(9)	1.501(3)	C(33)-F(13B)	1.199(9)
N(2)-H(2B)	0.8800	C(8)-H(8A)	0.9900	C(33)-F(12A)	1.296(6)
N(3)-C(7)	1.274(3)	C(8)-H(8B)	0.9900	C(33)-F(11A)	1.337(5)
N(3)-O(2)	1.413(3)	C(9)-C(10)	1.385(3)	C(33)-F(12B)	1.386(9)
N(4)-C(13)	1.338(3)	C(10)-C(11)	1.384(4)	C(33)-F(13A)	1.424(6)
N(4)-C(9)	1.342(3)	C(10)-H(10A)	0.9500	C(33)-F(11B)	1.436(9)
N(5)-C(15)	1.272(4)	C(11)-C(12)	1.383(4)	S(2)-O(23)	1.427(2)
N(5)-O(3)	1.414(3)	C(11)-H(11A)	0.9500	S(2)-O(21)	1.439(2)
N(6)-C(16)	1.363(4)	C(12)-C(13)	1.386(3)	S(2)-O(22)	1.442(2)
N(6)-C(15)	1.385(4)	C(12)-H(12A)	0.9500	S(2)-C(34)	1.808(3)
N(6)-H(6A)	0.8800	C(13)-C(14)	1.499(3)	C(34)-F(23B)	1.235(7)
N(7)-C(17)	1.337(3)	C(14)-H(14A)	0.9900	C(34)-F(21B)	1.291(7)
N(7)-C(21)	1.339(3)	C(14)-H(14B)	0.9900	C(34)-F(22A)	1.309(7)

N(8)-C(22)	1.356(3)	C(15)-H(15A)	0.9500	C(34)-F(22B)	1.383(7)
N(8)-C(23)	1.388(3)	C(17)-C(18)	1.393(3)	C(34)-F(21A)	1.405(8)
N(8)-H(8C)	0.8800	C(17)-C(32)	1.506(3)	C(34)-F(23A)	1.491(8)
N(9)-C(23)	1.274(3)	C(18)-C(19)	1.379(4)	N(13A)-C(35A)	1.410(5)
N(9)-O(6)	1.411(3)	C(18)-H(18A)	0.9500	N(13A)-C(36A)	1.43(3)
N(10)-C(29)	1.342(3)	C(19)-C(20)	1.380(4)	N(13A)-H(13A)	0.9200
N(10)-C(25)	1.346(3)	C(19)-H(19A)	0.9500	N(13A)-H(13B)	0.9200
N(11)-C(31)	1.272(3)	C(20)-C(21)	1.390(3)	C(35A)-H(35A)	0.9800
N(11)-O(7)	1.413(2)	C(20)-H(20A)	0.9500	C(35A)-H(35B)	0.9800
N(12)-C(32)	1.359(3)	C(21)-C(22)	1.502(3)	C(35A)-H(35C)	0.9800
N(12)-C(31)	1.385(3)	C(23)-H(23A)	0.9500	C(36A)-H(36A)	0.9800
N(12)-H(12B)	0.8800	C(24)-C(25)	1.507(3)	C(36A)-H(36B)	0.9800
O(1)-C(6)	1.221(3)	C(24)-H(24A)	0.9900	C(36A)-H(36C)	0.9800
O(2)-C(8)	1.436(3)	C(24)-H(24B)	0.9900	N(13B)-C(36B)	1.29(8)
O(3)-C(14)	1.434(3)	C(25)-C(26)	1.386(4)	N(13B)-H(13C)	0.9200
O(4)-C(16)	1.217(3)	C(26)-C(27)	1.378(4)	N(13B)-H(13D)	0.9200
O(5)-C(22)	1.226(3)	C(26)-H(26A)	0.9500	C(36B)-H(36D)	0.9800
O(6)-C(24)	1.422(3)	C(27)-C(28)	1.383(4)	C(36B)-H(36E)	0.9800
O(7)-C(30)	1.424(3)	C(27)-H(27A)	0.9500	C(36B)-H(36F)	0.9800
O(8)-C(32)	1.223(3)	C(28)-C(29)	1.387(3)	N(14)-C(37)	1.471(4)
O(1W)-H(1WB)	0.80(4)	C(28)-H(28A)	0.9500	N(14)-C(38)	1.476(3)
O(1W)-H(1WA)	0.79(4)	C(29)-C(30)	1.509(3)	N(14)-H(14C)	0.9200
C(1)-C(2)	1.394(4)	C(30)-H(30A)	0.9900	N(14)-H(14D)	0.9200
C(1)-C(16)	1.504(4)	C(30)-H(30B)	0.9900	C(37)-H(37A)	0.9800
C(2)-C(3)	1.377(5)	C(31)-H(31A)	0.9500	C(37)-H(37B)	0.9800
C(2)-H(2A)	0.9500	S(1)-O(13B)	1.318(11)	C(37)-H(37C)	0.9800
C(3)-C(4)	1.375(5)	S(1)-O(12A)	1.347(4)	C(38)-H(38A)	0.9800
C(3)-H(3A)	0.9500	S(1)-O(11A)	1.459(4)	C(38)-H(38B)	0.9800
C(4)-C(5)	1.394(4)	S(1)-O(11B)	1.470(7)	C(38)-H(38C)	0.9800

C(5)-N(1)-C(1)	116.6(2)	C(29)-C(30)-H(30A)	110.5
C(6)-N(2)-C(7)	120.5(2)	O(7)-C(30)-H(30B)	110.5
C(6)-N(2)-H(2B)	119.8	C(29)-C(30)-H(30B)	110.5
C(7)-N(2)-H(2B)	119.8	H(30A)-C(30)-H(30B)	108.7
C(7)-N(3)-O(2)	110.2(2)	N(11)-C(31)-N(12)	126.9(2)
C(13)-N(4)-C(9)	118.3(2)	N(11)-C(31)-H(31A)	116.6

C(15)-N(5)-O(3)	109.8(2)	N(12)-C(31)-H(31A)	116.6
C(16)-N(6)-C(15)	121.3(2)	O(8)-C(32)-N(12)	123.0(2)
C(16)-N(6)-H(6A)	119.3	O(8)-C(32)-C(17)	120.6(2)
C(15)-N(6)-H(6A)	119.3	N(12)-C(32)-C(17)	116.4(2)
C(17)-N(7)-C(21)	117.0(2)	O(13B)-S(1)-O(12A)	116.1(5)
C(22)-N(8)-C(23)	119.7(2)	O(13B)-S(1)-O(11A)	101.1(4)
C(22)-N(8)-H(8C)	120.1	O(12A)-S(1)-O(11A)	119.9(2)
C(23)-N(8)-H(8C)	120.1	O(13B)-S(1)-O(11B)	120.5(5)
C(23)-N(9)-O(6)	110.17(19)	O(12A)-S(1)-O(11B)	86.7(3)
C(29)-N(10)-C(25)	117.9(2)	O(11A)-S(1)-O(11B)	33.3(3)
C(31)-N(11)-O(7)	109.8(2)	O(13B)-S(1)-O(13A)	12.8(5)
C(32)-N(12)-C(31)	119.6(2)	O(12A)-S(1)-O(13A)	116.2(3)
C(32)-N(12)-H(12B)	120.2	O(11A)-S(1)-O(13A)	110.0(3)
C(31)-N(12)-H(12B)	120.2	O(11B)-S(1)-O(13A)	132.7(3)
N(3)-O(2)-C(8)	108.65(18)	O(13B)-S(1)-O(12B)	112.6(5)
N(5)-O(3)-C(14)	107.75(18)	O(12A)-S(1)-O(12B)	19.5(3)
N(9)-O(6)-C(24)	108.94(17)	O(11A)-S(1)-O(12B)	136.9(3)
N(11)-O(7)-C(30)	109.32(17)	O(11B)-S(1)-O(12B)	104.1(4)
H(1WB)-O(1W)-H(1WA)	105(3)	O(13A)-S(1)-O(12B)	108.2(4)
N(1)-C(1)-C(2)	123.2(3)	O(13B)-S(1)-C(33)	112.1(5)
N(1)-C(1)-C(16)	119.0(2)	O(12A)-S(1)-C(33)	108.1(2)
C(2)-C(1)-C(16)	117.8(3)	O(11A)-S(1)-C(33)	98.0(2)
C(3)-C(2)-C(1)	119.1(3)	O(11B)-S(1)-C(33)	110.5(3)
C(3)-C(2)-H(2A)	120.5	O(13A)-S(1)-C(33)	101.1(3)
C(1)-C(2)-H(2A)	120.5	O(12B)-S(1)-C(33)	93.4(3)
C(4)-C(3)-C(2)	118.8(3)	F(13B)-C(33)-F(12A)	113.8(5)
C(4)-C(3)-H(3A)	120.6	F(13B)-C(33)-F(11A)	74.8(4)
C(2)-C(3)-H(3A)	120.6	F(12A)-C(33)-F(11A)	105.4(3)
C(3)-C(4)-C(5)	118.6(3)	F(13B)-C(33)-F(12B)	115.9(6)
C(3)-C(4)-H(4A)	120.7	F(12A)-C(33)-F(12B)	20.2(3)
C(5)-C(4)-H(4A)	120.7	F(11A)-C(33)-F(12B)	125.6(4)
N(1)-C(5)-C(4)	123.8(3)	F(13B)-C(33)-F(13A)	26.9(4)
N(1)-C(5)-C(6)	118.7(2)	F(12A)-C(33)-F(13A)	105.8(4)
C(4)-C(5)-C(6)	117.5(3)	F(11A)-C(33)-F(13A)	101.7(4)
O(1)-C(6)-N(2)	122.5(3)	F(12B)-C(33)-F(13A)	99.3(5)
O(1)-C(6)-C(5)	121.0(2)	F(13B)-C(33)-F(11B)	111.8(5)

N(2)-C(6)-C(5)	116.4(2)	F(12A)-C(33)-F(11B)	90.3(4)
N(3)-C(7)-N(2)	127.0(2)	F(11A)-C(33)-F(11B)	37.0(3)
N(3)-C(7)-H(7A)	116.5	F(12B)-C(33)-F(11B)	106.7(5)
N(2)-C(7)-H(7A)	116.5	F(13A)-C(33)-F(11B)	138.7(4)
O(2)-C(8)-C(9)	105.78(19)	F(13B)-C(33)-S(1)	118.1(4)
O(2)-C(8)-H(8A)	110.6	F(12A)-C(33)-S(1)	119.0(3)
C(9)-C(8)-H(8A)	110.6	F(11A)-C(33)-S(1)	116.9(3)
O(2)-C(8)-H(8B)	110.6	F(12B)-C(33)-S(1)	104.1(4)
C(9)-C(8)-H(8B)	110.6	F(13A)-C(33)-S(1)	106.1(3)
H(8A)-C(8)-H(8B)	108.7	F(11B)-C(33)-S(1)	98.1(4)
N(4)-C(9)-C(10)	122.4(2)	O(23)-S(2)-O(21)	115.00(14)
N(4)-C(9)-C(8)	115.5(2)	O(23)-S(2)-O(22)	115.03(14)
C(10)-C(9)-C(8)	122.1(2)	O(21)-S(2)-O(22)	114.85(12)
C(11)-C(10)-C(9)	118.9(2)	O(23)-S(2)-C(34)	104.01(16)
C(11)-C(10)-H(10A)	120.5	O(21)-S(2)-C(34)	102.72(15)
C(9)-C(10)-H(10A)	120.5	O(22)-S(2)-C(34)	102.81(14)
C(12)-C(11)-C(10)	118.9(2)	F(23B)-C(34)-F(21B)	92.0(6)
C(12)-C(11)-H(11A)	120.5	F(23B)-C(34)-F(22A)	91.1(4)
C(10)-C(11)-H(11A)	120.5	F(21B)-C(34)-F(22A)	122.3(5)
C(11)-C(12)-C(13)	118.8(2)	F(23B)-C(34)-F(22B)	111.7(4)
C(11)-C(12)-H(12A)	120.6	F(21B)-C(34)-F(22B)	108.0(4)
C(13)-C(12)-H(12A)	120.6	F(22A)-C(34)-F(22B)	23.7(3)
N(4)-C(13)-C(12)	122.6(2)	F(23B)-C(34)-F(21A)	110.3(6)
N(4)-C(13)-C(14)	115.9(2)	F(21B)-C(34)-F(21A)	20.2(3)
C(12)-C(13)-C(14)	121.5(2)	F(22A)-C(34)-F(21A)	111.5(4)
O(3)-C(14)-C(13)	107.15(19)	F(22B)-C(34)-F(21A)	92.5(4)
O(3)-C(14)-H(14A)	110.3	F(23B)-C(34)-F(23A)	19.2(3)
C(13)-C(14)-H(14A)	110.3	F(21B)-C(34)-F(23A)	101.3(6)
O(3)-C(14)-H(14B)	110.3	F(22A)-C(34)-F(23A)	99.8(5)
C(13)-C(14)-H(14B)	110.3	F(22B)-C(34)-F(23A)	123.0(4)
H(14A)-C(14)-H(14B)	108.5	F(21A)-C(34)-F(23A)	121.3(6)
N(5)-C(15)-N(6)	126.6(2)	F(23B)-C(34)-S(2)	120.2(5)
N(5)-C(15)-H(15A)	116.7	F(21B)-C(34)-S(2)	114.3(3)
N(6)-C(15)-H(15A)	116.7	F(22A)-C(34)-S(2)	113.2(3)
O(4)-C(16)-N(6)	122.6(3)	F(22B)-C(34)-S(2)	109.2(3)
O(4)-C(16)-C(1)	120.7(3)	F(21A)-C(34)-S(2)	109.4(3)

N(6)-C(16)-C(1)	116.7(2)	F(23A)-C(34)-S(2)	101.1(4)
N(7)-C(17)-C(18)	123.6(2)	C(35A)-N(13A)-C(36A)	120.2(12)
N(7)-C(17)-C(32)	117.8(2)	C(35A)-N(13A)-H(13A)	107.3
C(18)-C(17)-C(32)	118.6(2)	C(36A)-N(13A)-H(13A)	107.3
C(19)-C(18)-C(17)	118.3(2)	C(35A)-N(13A)-H(13B)	107.3
C(19)-C(18)-H(18A)	120.9	C(36A)-N(13A)-H(13B)	107.3
C(17)-C(18)-H(18A)	120.9	H(13A)-N(13A)-H(13B)	106.9
C(18)-C(19)-C(20)	119.2(2)	N(13A)-C(35A)-H(35A)	109.5
C(18)-C(19)-H(19A)	120.4	N(13A)-C(35A)-H(35B)	109.5
C(20)-C(19)-H(19A)	120.4	H(35A)-C(35A)-H(35B)	109.5
C(19)-C(20)-C(21)	118.6(2)	N(13A)-C(35A)-H(35C)	109.5
C(19)-C(20)-H(20A)	120.7	H(35A)-C(35A)-H(35C)	109.5
C(21)-C(20)-H(20A)	120.7	H(35B)-C(35A)-H(35C)	109.5
N(7)-C(21)-C(20)	123.4(2)	N(13A)-C(36A)-H(36A)	109.5
N(7)-C(21)-C(22)	118.1(2)	N(13A)-C(36A)-H(36B)	109.5
C(20)-C(21)-C(22)	118.5(2)	H(36A)-C(36A)-H(36B)	109.5
O(5)-C(22)-N(8)	122.8(2)	N(13A)-C(36A)-H(36C)	109.5
O(5)-C(22)-C(21)	120.5(2)	H(36A)-C(36A)-H(36C)	109.5
N(8)-C(22)-C(21)	116.6(2)	H(36B)-C(36A)-H(36C)	109.5
N(9)-C(23)-N(8)	126.5(2)	C(36B)-N(13B)-H(13C)	105.7
N(9)-C(23)-H(23A)	116.8	C(36B)-N(13B)-H(13D)	105.7
N(8)-C(23)-H(23A)	116.8	H(13C)-N(13B)-H(13D)	106.2
O(6)-C(24)-C(25)	107.18(19)	N(13B)-C(36B)-H(36D)	109.5
O(6)-C(24)-H(24A)	110.3	N(13B)-C(36B)-H(36E)	109.5
C(25)-C(24)-H(24A)	110.3	H(36D)-C(36B)-H(36E)	109.5
O(6)-C(24)-H(24B)	110.3	N(13B)-C(36B)-H(36F)	109.5
C(25)-C(24)-H(24B)	110.3	H(36D)-C(36B)-H(36F)	109.5
H(24A)-C(24)-H(24B)	108.5	H(36E)-C(36B)-H(36F)	109.5
N(10)-C(25)-C(26)	122.6(2)	C(37)-N(14)-C(38)	113.3(2)
N(10)-C(25)-C(24)	116.8(2)	C(37)-N(14)-H(14C)	108.9
C(26)-C(25)-C(24)	120.6(2)	C(38)-N(14)-H(14C)	108.9
C(27)-C(26)-C(25)	118.9(2)	C(37)-N(14)-H(14D)	108.9
C(27)-C(26)-H(26A)	120.6	C(38)-N(14)-H(14D)	108.9
C(25)-C(26)-H(26A)	120.6	H(14C)-N(14)-H(14D)	107.7
C(26)-C(27)-C(28)	119.3(2)	N(14)-C(37)-H(37A)	109.5
C(26)-C(27)-H(27A)	120.4	N(14)-C(37)-H(37B)	109.5

C(28)-C(27)-H(27A)	120.4	H(37A)-C(37)-H(37B)	109.5
C(27)-C(28)-C(29)	118.5(2)	N(14)-C(37)-H(37C)	109.5
C(27)-C(28)-H(28A)	120.7	H(37A)-C(37)-H(37C)	109.5
C(29)-C(28)-H(28A)	120.7	H(37B)-C(37)-H(37C)	109.5
N(10)-C(29)-C(28)	122.9(2)	N(14)-C(38)-H(38A)	109.5
N(10)-C(29)-C(30)	116.6(2)	N(14)-C(38)-H(38B)	109.5
C(28)-C(29)-C(30)	120.6(2)	H(38A)-C(38)-H(38B)	109.5
O(7)-C(30)-C(29)	106.28(19)	N(14)-C(38)-H(38C)	109.5
O(7)-C(30)-H(30A)	110.5	H(38A)-C(38)-H(38C)	109.5
		H(38B)-C(38)-H(38C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ap16. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	32(1)	42(1)	24(1)	-8(1)	0(1)	-21(1)
N(2)	38(1)	32(1)	34(1)	-13(1)	2(1)	-21(1)
N(3)	42(1)	27(1)	39(1)	-16(1)	4(1)	-17(1)
N(4)	27(1)	30(1)	27(1)	-12(1)	0(1)	-13(1)
N(5)	33(1)	29(1)	46(1)	-18(1)	4(1)	-6(1)
N(6)	26(1)	33(1)	39(1)	-12(1)	1(1)	-9(1)
N(7)	28(1)	29(1)	22(1)	-9(1)	1(1)	-14(1)
N(8)	26(1)	21(1)	33(1)	-11(1)	-2(1)	-6(1)
N(9)	34(1)	20(1)	41(1)	-12(1)	-4(1)	-8(1)
N(10)	26(1)	28(1)	32(1)	-13(1)	0(1)	-13(1)
N(11)	40(1)	25(1)	46(1)	-20(1)	-9(1)	-7(1)
N(12)	34(1)	24(1)	32(1)	-13(1)	-3(1)	-13(1)
O(1)	59(1)	53(1)	51(1)	-24(1)	7(1)	-40(1)
O(2)	34(1)	26(1)	49(1)	-14(1)	-6(1)	-13(1)
O(3)	28(1)	32(1)	56(1)	-26(1)	3(1)	-9(1)
O(4)	32(1)	46(1)	92(2)	-18(1)	-14(1)	-4(1)
O(5)	28(1)	32(1)	62(1)	-20(1)	-4(1)	-4(1)
O(6)	31(1)	21(1)	51(1)	-13(1)	-10(1)	-8(1)
O(7)	31(1)	33(1)	58(1)	-29(1)	-8(1)	-7(1)
O(8)	48(1)	37(1)	51(1)	-24(1)	0(1)	-24(1)
O(1W)	31(1)	31(1)	28(1)	-12(1)	2(1)	-15(1)
C(1)	31(1)	47(2)	29(1)	-6(1)	-3(1)	-17(1)

C(2)	32(2)	66(2)	47(2)	-14(2)	-7(1)	-20(1)
C(3)	41(2)	89(3)	51(2)	-26(2)	-3(1)	-38(2)
C(4)	49(2)	73(2)	38(2)	-22(2)	3(1)	-40(2)
C(5)	38(1)	52(2)	24(1)	-12(1)	3(1)	-28(1)
C(6)	45(2)	47(2)	25(1)	-14(1)	6(1)	-31(1)
C(7)	43(2)	32(1)	37(1)	-17(1)	7(1)	-21(1)
C(8)	30(1)	30(1)	37(1)	-12(1)	-4(1)	-11(1)
C(9)	25(1)	29(1)	29(1)	-12(1)	-5(1)	-10(1)
C(10)	25(1)	37(1)	36(1)	-20(1)	0(1)	-10(1)
C(11)	30(1)	46(2)	33(1)	-18(1)	6(1)	-22(1)
C(12)	34(1)	32(1)	34(1)	-12(1)	-1(1)	-18(1)
C(13)	29(1)	30(1)	29(1)	-14(1)	-2(1)	-14(1)
C(14)	34(1)	35(1)	42(1)	-20(1)	3(1)	-17(1)
C(15)	31(1)	30(1)	44(2)	-14(1)	1(1)	-6(1)
C(16)	30(1)	39(2)	39(2)	-5(1)	-5(1)	-10(1)
C(17)	34(1)	31(1)	21(1)	-9(1)	3(1)	-18(1)
C(18)	40(1)	42(1)	31(1)	-15(1)	7(1)	-28(1)
C(19)	31(1)	56(2)	40(2)	-18(1)	6(1)	-28(1)
C(20)	26(1)	43(2)	35(1)	-14(1)	4(1)	-16(1)
C(21)	29(1)	31(1)	22(1)	-8(1)	2(1)	-14(1)
C(22)	27(1)	28(1)	27(1)	-9(1)	0(1)	-10(1)
C(23)	33(1)	22(1)	36(1)	-12(1)	-2(1)	-7(1)
C(24)	34(1)	28(1)	49(2)	-16(1)	-4(1)	-15(1)
C(25)	24(1)	29(1)	37(1)	-15(1)	2(1)	-14(1)
C(26)	31(1)	39(1)	40(1)	-23(1)	1(1)	-18(1)
C(27)	33(1)	41(1)	33(1)	-15(1)	-5(1)	-17(1)
C(28)	27(1)	30(1)	35(1)	-11(1)	-4(1)	-11(1)
C(29)	22(1)	28(1)	32(1)	-13(1)	0(1)	-11(1)
C(30)	29(1)	31(1)	39(1)	-18(1)	-5(1)	-8(1)
C(31)	41(1)	23(1)	37(1)	-14(1)	-8(1)	-10(1)
C(32)	38(1)	31(1)	24(1)	-11(1)	1(1)	-19(1)
S(1)	45(1)	56(1)	44(1)	-14(1)	-3(1)	-28(1)
C(33)	63(2)	48(2)	57(2)	-14(2)	8(2)	-33(2)
O(11A)	63(2)	33(1)	55(1)	-5(1)	-13(1)	-22(1)
O(12A)	63(2)	33(1)	55(1)	-5(1)	-13(1)	-22(1)
O(13A)	63(2)	33(1)	55(1)	-5(1)	-13(1)	-22(1)

F(11A)	74(2)	68(2)	56(1)	-27(1)	10(1)	-34(1)
F(12A)	74(2)	68(2)	56(1)	-27(1)	10(1)	-34(1)
F(13A)	74(2)	68(2)	56(1)	-27(1)	10(1)	-34(1)
O(11B)	28(2)	52(3)	67(3)	-21(2)	1(2)	-14(2)
O(12B)	28(2)	52(3)	67(3)	-21(2)	1(2)	-14(2)
O(13B)	28(2)	52(3)	67(3)	-21(2)	1(2)	-14(2)
F(11B)	84(3)	79(3)	91(3)	-57(3)	38(2)	-54(3)
F(12B)	84(3)	79(3)	91(3)	-57(3)	38(2)	-54(3)
F(13B)	84(3)	79(3)	91(3)	-57(3)	38(2)	-54(3)
S(2)	33(1)	35(1)	40(1)	-20(1)	3(1)	-14(1)
C(34)	44(2)	62(2)	45(2)	-10(2)	-6(1)	-29(2)
O(21)	38(1)	58(1)	74(2)	-44(1)	16(1)	-25(1)
O(22)	43(1)	65(1)	63(1)	-37(1)	1(1)	-26(1)
O(23)	58(1)	34(1)	63(1)	-17(1)	1(1)	-13(1)
F(21A)	55(2)	57(2)	52(2)	-22(2)	-5(1)	-22(2)
F(22A)	55(2)	57(2)	52(2)	-22(2)	-5(1)	-22(2)
F(23A)	55(2)	57(2)	52(2)	-22(2)	-5(1)	-22(2)
F(21B)	68(2)	63(3)	47(2)	-19(2)	2(1)	-26(2)
F(22B)	68(2)	63(3)	47(2)	-19(2)	2(1)	-26(2)
F(23B)	68(2)	63(3)	47(2)	-19(2)	2(1)	-26(2)
N(13A)	33(2)	51(2)	90(3)	-41(2)	-10(2)	1(2)
C(35A)	61(2)	59(2)	53(2)	-19(2)	3(2)	-20(2)
C(36A)	167(9)	143(8)	57(3)	-20(5)	-3(5)	-131(7)
N(13B)	33(2)	51(2)	90(3)	-41(2)	-10(2)	1(2)
C(35B)	61(2)	59(2)	53(2)	-19(2)	3(2)	-20(2)
C(36B)	167(9)	143(8)	57(3)	-20(5)	-3(5)	-131(7)
N(14)	42(1)	33(1)	48(1)	-21(1)	2(1)	-19(1)
C(37)	75(2)	42(2)	51(2)	-17(1)	6(2)	-34(2)
C(38)	40(2)	60(2)	63(2)	-42(2)	0(1)	-15(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^2$) for ap16.

	x	y	z	U(eq)
H(2B)	3618	4681	8741	39
H(6A)	4887	2131	8856	43
H(8C)	4247	3337	6091	34
H(12B)	3084	5804	5996	34

H(1WB)	2590(30)	4100(30)	7090(30)	46(9)
H(1WA)	2390(30)	4490(30)	6170(30)	48(10)
H(2A)	7982	1740	9254	61
H(3A)	7995	3348	9229	67
H(4A)	6403	5001	8974	57
H(7A)	2621	6941	8476	42
H(8A)	867	5757	7467	40
H(8B)	254	5989	8460	40
H(10A)	-455	4657	9526	38
H(11A)	-303	2804	10234	41
H(12A)	1180	1388	9805	39
H(14A)	2794	827	8868	42
H(14B)	2760	1786	7761	42
H(15A)	6066	12	8772	47
H(18A)	5887	5956	6474	41
H(19A)	7459	4289	6660	48
H(20A)	7398	2744	6592	43
H(23A)	5278	1065	6406	39
H(24A)	1931	2703	5660	42
H(24B)	2517	2663	4600	42
H(26A)	1398	4194	3243	39
H(27A)	246	6115	2471	41
H(28A)	-194	7328	3307	37
H(30A)	-41	7630	4718	39
H(30B)	48	6586	5778	39
H(31A)	2052	7854	6222	40
H(13A)	987	-264	3555	72
H(13B)	2100	-444	3378	72
H(35A)	1520	-343	4869	93
H(35B)	633	911	4310	93
H(35C)	1856	651	4155	93
H(36A)	1240	637	1938	152
H(36B)	1634	1324	2232	152
H(36C)	426	1529	2429	152
H(13C)	260	1329	3272	72
H(13D)	1078	1720	3086	72

H(35D)	1084	784	4680	93
H(35E)	2127	-15	4244	93
H(35F)	1098	-239	4519	93
H(36D)	975	1528	1838	152
H(36E)	1104	266	2504	152
H(36F)	2073	557	2374	152
H(14C)	4884	7885	7246	46
H(14D)	3738	8251	7181	46
H(37A)	4394	8928	5601	81
H(37B)	4772	9562	5986	81
H(37C)	3537	9958	5915	81
H(38A)	4015	8425	8554	75
H(38B)	3291	9642	7755	75
H(38C)	4524	9262	7815	75

Table S6. Torsion angles [°] for ap16.

C(7)-N(3)-O(2)-C(8)	-167.3(2)	C(25)-C(26)-C(27)-C(28)	1.3(4)
C(15)-N(5)-O(3)-C(14)	173.2(2)	C(26)-C(27)-C(28)-C(29)	-1.0(4)
C(23)-N(9)-O(6)-C(24)	-174.8(2)	C(25)-N(10)-C(29)-C(28)	0.8(3)
C(31)-N(11)-O(7)-C(30)	168.2(2)	C(25)-N(10)-C(29)-C(30)	-178.3(2)
C(5)-N(1)-C(1)-C(2)	1.0(4)	C(27)-C(28)-C(29)-N(10)	-0.1(4)
C(5)-N(1)-C(1)-C(16)	-176.8(2)	C(27)-C(28)-C(29)-C(30)	179.0(2)
N(1)-C(1)-C(2)-C(3)	-0.9(4)	N(11)-O(7)-C(30)-C(29)	169.4(2)
C(16)-C(1)-C(2)-C(3)	177.0(3)	N(10)-C(29)-C(30)-O(7)	58.5(3)
C(1)-C(2)-C(3)-C(4)	-0.3(5)	C(28)-C(29)-C(30)-O(7)	-120.6(2)
C(2)-C(3)-C(4)-C(5)	1.2(4)	O(7)-N(11)-C(31)-N(12)	-3.2(4)
C(1)-N(1)-C(5)-C(4)	-0.1(4)	C(32)-N(12)-C(31)-N(11)	165.6(3)
C(1)-N(1)-C(5)-C(6)	178.6(2)	C(31)-N(12)-C(32)-O(8)	-2.9(4)
C(3)-C(4)-C(5)-N(1)	-1.0(4)	C(31)-N(12)-C(32)-C(17)	177.9(2)
C(3)-C(4)-C(5)-C(6)	-179.8(3)	N(7)-C(17)-C(32)-O(8)	178.4(2)
C(7)-N(2)-C(6)-O(1)	0.6(4)	C(18)-C(17)-C(32)-O(8)	-1.0(3)
C(7)-N(2)-C(6)-C(5)	-179.2(2)	N(7)-C(17)-C(32)-N(12)	-2.4(3)
N(1)-C(5)-C(6)-O(1)	-176.3(2)	C(18)-C(17)-C(32)-N(12)	178.2(2)
C(4)-C(5)-C(6)-O(1)	2.5(4)	O(13B)-S(1)-C(33)-F(13B)	-40.3(7)
N(1)-C(5)-C(6)-N(2)	3.5(3)	O(12A)-S(1)-C(33)-F(13B)	89.0(6)
C(4)-C(5)-C(6)-N(2)	-177.7(2)	O(11A)-S(1)-C(33)-F(13B)	-145.8(5)

O(2)-N(3)-C(7)-N(2)	1.7(4)	O(11B)-S(1)-C(33)-F(13B)	-177.7(6)
C(6)-N(2)-C(7)-N(3)	178.5(2)	O(13A)-S(1)-C(33)-F(13B)	-33.4(6)
N(3)-O(2)-C(8)-C(9)	-161.58(19)	O(12B)-S(1)-C(33)-F(13B)	75.8(6)
C(13)-N(4)-C(9)-C(10)	-2.4(3)	O(13B)-S(1)-C(33)-F(12A)	174.8(5)
C(13)-N(4)-C(9)-C(8)	175.5(2)	O(12A)-S(1)-C(33)-F(12A)	-56.0(4)
O(2)-C(8)-C(9)-N(4)	-60.0(3)	O(11A)-S(1)-C(33)-F(12A)	69.2(4)
O(2)-C(8)-C(9)-C(10)	117.8(2)	O(11B)-S(1)-C(33)-F(12A)	37.3(5)
N(4)-C(9)-C(10)-C(11)	1.0(4)	O(13A)-S(1)-C(33)-F(12A)	-178.4(4)
C(8)-C(9)-C(10)-C(11)	-176.7(2)	O(12B)-S(1)-C(33)-F(12A)	-69.1(4)
C(9)-C(10)-C(11)-C(12)	1.2(4)	O(13B)-S(1)-C(33)-F(11A)	46.2(6)
C(10)-C(11)-C(12)-C(13)	-1.9(4)	O(12A)-S(1)-C(33)-F(11A)	175.5(3)
C(9)-N(4)-C(13)-C(12)	1.6(3)	O(11A)-S(1)-C(33)-F(11A)	-59.3(4)
C(9)-N(4)-C(13)-C(14)	-177.7(2)	O(11B)-S(1)-C(33)-F(11A)	-91.2(4)
C(11)-C(12)-C(13)-N(4)	0.6(4)	O(13A)-S(1)-C(33)-F(11A)	53.1(4)
C(11)-C(12)-C(13)-C(14)	179.8(2)	O(12B)-S(1)-C(33)-F(11A)	162.3(4)
N(5)-O(3)-C(14)-C(13)	165.7(2)	O(13B)-S(1)-C(33)-F(12B)	-170.5(7)
N(4)-C(13)-C(14)-O(3)	57.7(3)	O(12A)-S(1)-C(33)-F(12B)	-41.2(5)
C(12)-C(13)-C(14)-O(3)	-121.6(2)	O(11A)-S(1)-C(33)-F(12B)	84.0(5)
O(3)-N(5)-C(15)-N(6)	-2.3(4)	O(11B)-S(1)-C(33)-F(12B)	52.1(6)
C(16)-N(6)-C(15)-N(5)	177.8(3)	O(13A)-S(1)-C(33)-F(12B)	-163.7(5)
C(15)-N(6)-C(16)-O(4)	-2.6(4)	O(12B)-S(1)-C(33)-F(12B)	-54.4(6)
C(15)-N(6)-C(16)-C(1)	175.8(2)	O(13B)-S(1)-C(33)-F(13A)	-66.3(5)
N(1)-C(1)-C(16)-O(4)	177.1(3)	O(12A)-S(1)-C(33)-F(13A)	63.0(3)
C(2)-C(1)-C(16)-O(4)	-0.9(4)	O(11A)-S(1)-C(33)-F(13A)	-171.8(3)
N(1)-C(1)-C(16)-N(6)	-1.3(4)	O(11B)-S(1)-C(33)-F(13A)	156.2(4)
C(2)-C(1)-C(16)-N(6)	-179.3(3)	O(13A)-S(1)-C(33)-F(13A)	-59.5(4)
C(21)-N(7)-C(17)-C(18)	0.5(3)	O(12B)-S(1)-C(33)-F(13A)	49.8(4)
C(21)-N(7)-C(17)-C(32)	-178.94(19)	O(13B)-S(1)-C(33)-F(11B)	79.9(6)
N(7)-C(17)-C(18)-C(19)	-0.5(4)	O(12A)-S(1)-C(33)-F(11B)	-150.8(3)
C(32)-C(17)-C(18)-C(19)	178.9(2)	O(11A)-S(1)-C(33)-F(11B)	-25.6(3)
C(17)-C(18)-C(19)-C(20)	0.4(4)	O(11B)-S(1)-C(33)-F(11B)	-57.5(4)
C(18)-C(19)-C(20)-C(21)	-0.3(4)	O(13A)-S(1)-C(33)-F(11B)	86.7(4)
C(17)-N(7)-C(21)-C(20)	-0.3(3)	O(12B)-S(1)-C(33)-F(11B)	-164.0(4)
C(17)-N(7)-C(21)-C(22)	179.9(2)	O(23)-S(2)-C(34)-F(23B)	-177.2(4)
C(19)-C(20)-C(21)-N(7)	0.2(4)	O(21)-S(2)-C(34)-F(23B)	62.6(4)
C(19)-C(20)-C(21)-C(22)	180.0(2)	O(22)-S(2)-C(34)-F(23B)	-57.0(4)

C(23)-N(8)-C(22)-O(5)	2.1(4)	O(23)-S(2)-C(34)-F(21B)	-69.3(5)
C(23)-N(8)-C(22)-C(21)	-179.2(2)	O(21)-S(2)-C(34)-F(21B)	170.5(5)
N(7)-C(21)-C(22)-O(5)	-179.9(2)	O(22)-S(2)-C(34)-F(21B)	50.9(5)
C(20)-C(21)-C(22)-O(5)	0.4(4)	O(23)-S(2)-C(34)-F(22A)	76.9(6)
N(7)-C(21)-C(22)-N(8)	1.4(3)	O(21)-S(2)-C(34)-F(22A)	-43.3(6)
C(20)-C(21)-C(22)-N(8)	-178.3(2)	O(22)-S(2)-C(34)-F(22A)	-162.9(5)
O(6)-N(9)-C(23)-N(8)	3.2(4)	O(23)-S(2)-C(34)-F(22B)	51.8(5)
C(22)-N(8)-C(23)-N(9)	-164.0(2)	O(21)-S(2)-C(34)-F(22B)	-68.4(5)
N(9)-O(6)-C(24)-C(25)	-174.44(19)	O(22)-S(2)-C(34)-F(22B)	172.0(5)
C(29)-N(10)-C(25)-C(26)	-0.4(3)	O(23)-S(2)-C(34)-F(21A)	-48.2(4)
C(29)-N(10)-C(25)-C(24)	179.5(2)	O(21)-S(2)-C(34)-F(21A)	-168.4(4)
O(6)-C(24)-C(25)-N(10)	-51.9(3)	O(22)-S(2)-C(34)-F(21A)	72.1(4)
O(6)-C(24)-C(25)-C(26)	128.0(2)	O(23)-S(2)-C(34)-F(23A)	-177.3(3)
N(10)-C(25)-C(26)-C(27)	-0.6(4)	O(21)-S(2)-C(34)-F(23A)	62.5(3)
C(24)-C(25)-C(26)-C(27)	179.5(2)	O(22)-S(2)-C(34)-F(23A)	-57.0(3)

Table S7. Hydrogen bonds for ap16 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8C)...O(1W)	0.88	2.06	2.873(3)	153.1
N(12)-H(12B)...O(1W)	0.88	2.11	2.920(3)	151.9
O(1W)-H(1WB)...N(4)	0.80(4)	2.11(4)	2.893(3)	166(3)
O(1W)-H(1WA)...N(10)	0.79(4)	2.19(4)	2.976(3)	174(3)
N(13A)-H(13B)...O(5)#1	0.92	1.85	2.759(4)	169.0
N(13A)-H(13A)...O(11A)#2	0.92	1.98	2.844(5)	156.0
N(13B)-H(13C)...O(11B)#2	0.92	2.40	2.991(13)	122.1
N(13B)-H(13C)...N(11)#3	0.92	2.66	3.334(10)	130.3
N(13B)-H(13D)...O(21)	0.92	2.07	2.953(12)	159.7
N(14)-H(14C)...O(22)#4	0.92	2.04	2.871(3)	149.6
N(14)-H(14D)...O(12B)#5	0.92	2.09	2.813(7)	134.7
N(14)-H(14D)...O(8)	0.92	2.31	2.889(3)	120.3
N(14)-H(14D)...O(12A)#5	0.92	2.35	3.093(5)	138.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x,-y,-z+1 #3 -x,-y+1,-z+1

#4 -x+1,-y+1,-z+1 #5 x,y+1,z

D.2: Tri(ZZ-**M)**

A crystal of the compound (colorless, block-shaped, size 0.10 × 0.15 × 0.20 mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 3.24 ~ 52.00º. No significant decay was observed during the data collection. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package:[1] Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT (Bruker, 2005); structure solution: XPREP (Bruker, 2005) and SHELXTL (Bruker, 2000); structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[2] The crystal is monoclinic space group *C*c, based on the systematic absences, *E* statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w (F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. All H atoms were placed in geometrically calculated positions, with C-H = 0.95 (aromatic), 0.99(CH_2), 0.88(N-H) Å, and refined as riding atoms, with Uiso(H) = 1.5UeqC(CH_3) or 1.2 UeqC(N or other C). Convergence to final R_1 = 0.0443 and wR_2 = 0.0898 for 7115 (I>2σ(I)) independent reflections, and R_1 = 0.0742 and wR_2 = 0.1869 for all 9760 (R(int) = 0.0581) independent reflections, with 718 parameters and 4 restraints, were achieved.[3] The largest residual peak and hole to be 0.234 and – 0.165 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles and hydrogen bonding information are given in Table S8 to 14. The molecular structure and the cell packing are shown in Figure S2.

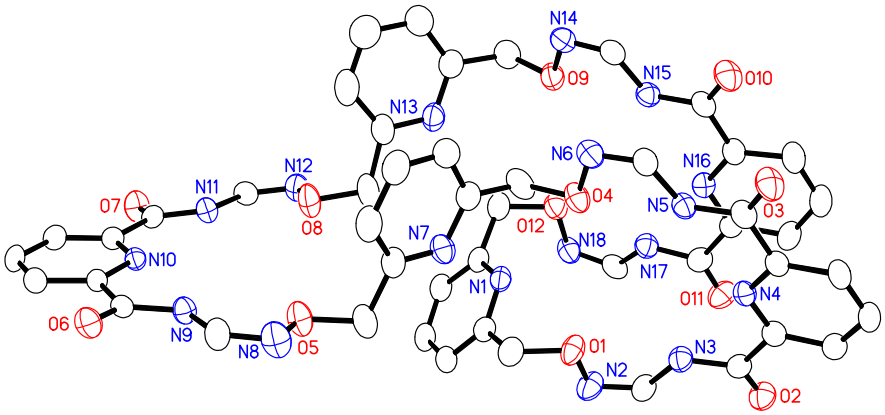
[1] Bruker AXS Crystal Structure Analysis Package: Bruker (2000). SHELXTL. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA. Bruker (2005). XPREP. Version 2005/2. Bruker AXS Inc., Madison, Wisconsin, USA. Bruker (2005). SAINT. Version 7.23A. Bruker AXS Inc., Madison,Wisconsin, USA. Bruker (2006). APEX2. Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA. [2] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

[3] $R_1 = \sum | |Fo| - |Fc| | / \sum |Fo|$ $\quad wR_2 = \{\sum [w (Fo^2 - Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/2}$

$(w = 1 / [\sigma^2(Fo^2) + (0.0459P)^2 + 0.4069P]$, where $P = [\text{Max}(Fo^2, 0) + 2Fc^2] / 3)$

Figure S2. a) Molecular Structure (displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are omitted for clarity); b) Unit cell packing.

a)



b)

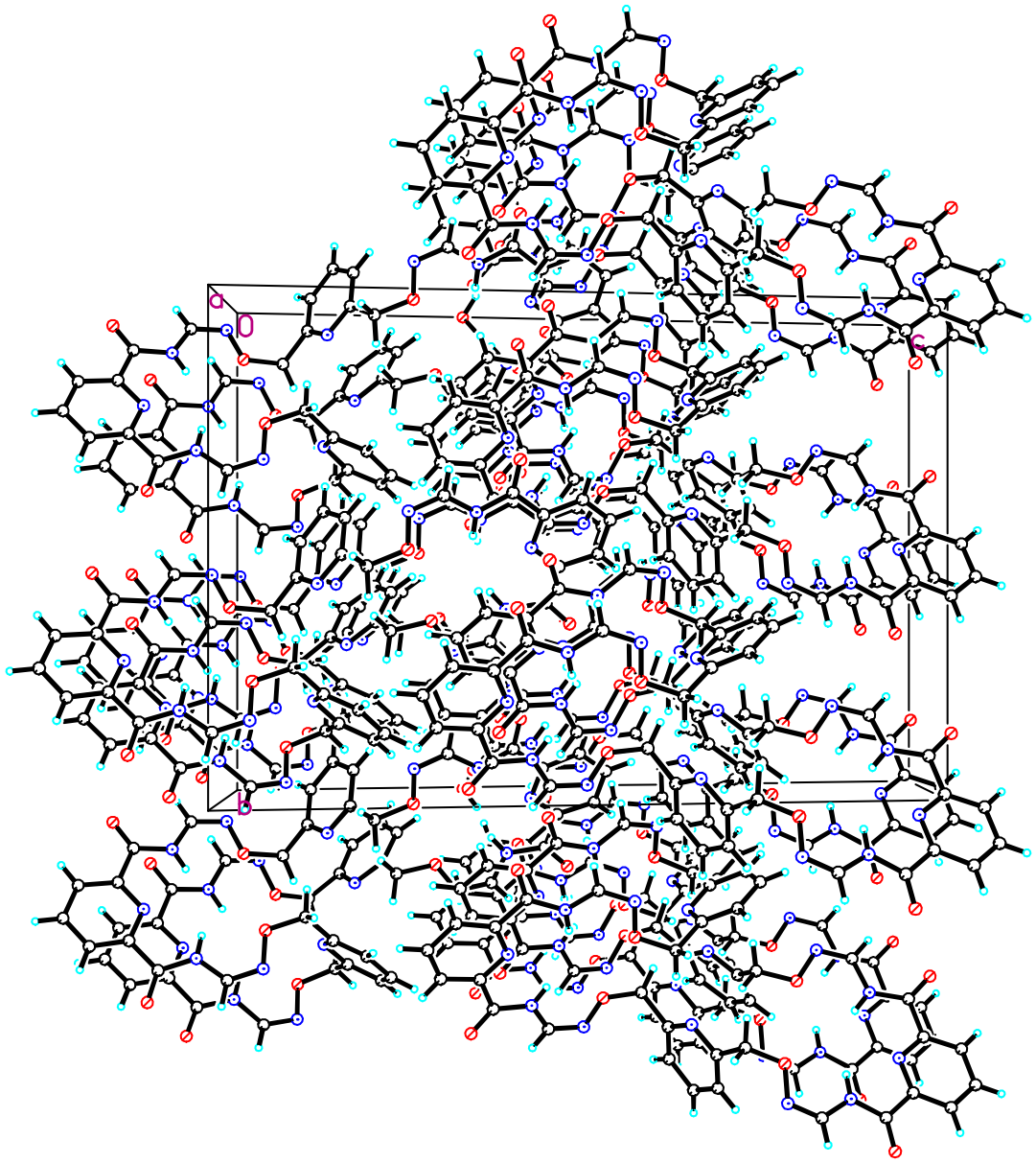


Table S8. Crystal data and structure refinement for ap17

Identification code	ap17	
Empirical formula	C48 H44 N18 O13	
Formula weight	1081.01	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 11.3994(2) Å	α= 90°.
	b = 17.3955(4) Å	β= 102.6120(10)°.
	c = 25.7476(5) Å	γ = 90°.
Volume	4982.51(17) $Å^3$	
Z	4	
Density (calculated)	1.441 Mg/m^3	
Absorption coefficient	0.109 mm^{-1}	
F(000)	2248	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.62 to 26.00°.	
Index ranges	-14<=h<=14, -21<=k<=21, -31<=l<=31	
Reflections collected	35628	
Independent reflections	9760 [R(int) = 0.0581]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9892 and 0.9786	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9760 / 4 / 718	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0898	
R indices (all data)	R1 = 0.0742, wR2 = 0.1042	
Absolute structure parameter	N/A	
Largest diff. peak and hole	0.234 and -0.165 $e.Å^{-3}$	

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for ap17. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	11600(2)	2480(1)	5627(1)	40(1)
O(2)	11839(2)	1137(1)	4065(1)	43(1)
O(3)	8459(2)	4518(1)	3432(1)	45(1)
O(4)	8798(2)	3861(1)	5232(1)	41(1)
O(5)	12116(2)	4959(1)	7636(1)	46(1)
O(6)	13011(2)	6641(1)	9101(1)	38(1)
O(7)	9705(2)	3533(1)	9767(1)	43(1)
O(8)	9252(2)	3592(1)	7905(1)	47(1)
O(9)	5834(2)	2844(1)	5575(1)	41(1)
O(10)	5913(2)	3540(1)	3818(1)	44(1)
O(11)	9504(2)	256(1)	4477(1)	48(1)
O(12)	8110(2)	1132(1)	5956(1)	41(1)
N(1)	10135(2)	2073(1)	6375(1)	35(1)
N(2)	12174(2)	1764(2)	5614(1)	45(1)
N(3)	11421(2)	1943(1)	4695(1)	36(1)
N(4)	10146(2)	2858(1)	3931(1)	29(1)
N(5)	8826(2)	3971(1)	4256(1)	31(1)
N(6)	8111(2)	4481(1)	4971(1)	39(1)
N(7)	10247(2)	4316(1)	6420(1)	38(1)
N(8)	12727(3)	5668(2)	7655(1)	50(1)
N(9)	12360(2)	5664(1)	8526(1)	32(1)
N(10)	11262(2)	5004(1)	9248(1)	27(1)
N(11)	9735(2)	3821(1)	8908(1)	30(1)
N(12)	8800(2)	3018(1)	8201(1)	40(1)
N(13)	7024(2)	3120(2)	6727(1)	42(1)
N(14)	5335(2)	3529(2)	5320(1)	41(1)
N(15)	6174(2)	2997(1)	4641(1)	34(1)
N(16)	7622(2)	1898(1)	4344(1)	32(1)
N(17)	8751(2)	908(2)	5098(1)	38(1)
N(18)	8881(2)	482(2)	5972(1)	42(1)
C(1)	9626(3)	1624(2)	6688(1)	35(1)
C(2)	10267(3)	1327(2)	7165(1)	40(1)
C(3)	11463(3)	1477(2)	7323(1)	43(1)

C(4)	11997(3)	1943(2)	7000(1)	42(1)
C(5)	11306(3)	2228(2)	6530(1)	33(1)
C(6)	11833(3)	2741(2)	6172(1)	43(1)
C(7)	12036(3)	1542(2)	5132(1)	41(1)
C(8)	11385(3)	1725(2)	4184(1)	34(1)
C(9)	10760(3)	2281(2)	3768(1)	32(1)
C(10)	10871(3)	2191(2)	3248(1)	38(1)
C(11)	10342(3)	2725(2)	2871(1)	41(1)
C(12)	9720(3)	3332(2)	3036(1)	37(1)
C(13)	9630(2)	3372(2)	3561(1)	30(1)
C(14)	8913(3)	4010(2)	3735(1)	34(1)
C(15)	8195(3)	4494(2)	4486(1)	34(1)
C(16)	8585(3)	3790(2)	5764(1)	46(1)
C(17)	9150(3)	4442(2)	6122(1)	40(1)
C(18)	8557(3)	5130(2)	6148(1)	57(1)
C(19)	9135(4)	5713(2)	6474(1)	64(1)
C(20)	10250(4)	5575(2)	6781(1)	57(1)
C(21)	10769(3)	4873(2)	6752(1)	38(1)
C(22)	11953(3)	4644(2)	7104(1)	49(1)
C(23)	12811(3)	5965(2)	8112(1)	40(1)
C(24)	12495(2)	6033(2)	9004(1)	28(1)
C(25)	11940(2)	5629(2)	9406(1)	26(1)
C(26)	12143(3)	5918(2)	9922(1)	34(1)
C(27)	11645(3)	5541(2)	10293(1)	34(1)
C(28)	10952(3)	4891(2)	10138(1)	33(1)
C(29)	10779(2)	4647(2)	9616(1)	30(1)
C(30)	10026(3)	3947(2)	9446(1)	31(1)
C(31)	9085(3)	3186(2)	8694(1)	33(1)
C(32)	8863(3)	3400(3)	7353(1)	58(1)
C(33)	7551(3)	3567(2)	7134(1)	43(1)
C(34)	6926(4)	4149(2)	7326(1)	55(1)
C(35)	5743(4)	4275(2)	7086(2)	65(1)
C(36)	5213(4)	3824(2)	6653(1)	55(1)
C(37)	5873(3)	3260(2)	6489(1)	41(1)
C(38)	5339(3)	2723(2)	6034(1)	47(1)
C(39)	5559(3)	3553(2)	4856(1)	38(1)

C(40)	6321(3)	3022(2)	4130(1)	34(1)
C(41)	7025(3)	2375(2)	3969(1)	32(1)
C(42)	7030(3)	2293(2)	3434(1)	40(1)
C(43)	7698(3)	1710(2)	3281(1)	43(1)
C(44)	8345(3)	1228(2)	3657(1)	38(1)
C(45)	8263(3)	1337(2)	4185(1)	33(1)
C(46)	8914(3)	784(2)	4596(1)	38(1)
C(47)	9143(3)	413(2)	5518(1)	41(1)
C(48)	8317(3)	1449(2)	6483(1)	45(1)
O(1W)	5444(2)	5022(2)	3259(1)	63(1)

Table S10. Bond lengths [Å] and angles [°] for ap17.

O(1)-N(2)	1.409(3)	N(11)-H(11B)	0.8800	C(18)-H(18A)	0.9500
O(1)-C(6)	1.444(4)	N(12)-C(31)	1.275(3)	C(19)-C(20)	1.362(5)
O(2)-C(8)	1.216(3)	N(13)-C(33)	1.337(4)	C(19)-H(19A)	0.9500
O(3)-C(14)	1.217(3)	N(13)-C(37)	1.344(4)	C(20)-C(21)	1.367(4)
O(4)-N(6)	1.414(3)	N(14)-C(39)	1.276(4)	C(20)-H(20A)	0.9500
O(4)-C(16)	1.450(4)	N(15)-C(40)	1.363(4)	C(21)-C(22)	1.506(4)
O(5)-N(8)	1.413(3)	N(15)-C(39)	1.378(4)	C(22)-H(22A)	0.9900
O(5)-C(22)	1.449(4)	N(15)-H(15B)	0.8800	C(22)-H(22B)	0.9900
O(6)-C(24)	1.209(3)	N(16)-C(45)	1.335(4)	C(23)-H(23A)	0.9500
O(7)-C(30)	1.212(3)	N(16)-C(41)	1.339(4)	C(24)-C(25)	1.501(4)
O(8)-N(12)	1.418(3)	N(17)-C(46)	1.363(4)	C(25)-C(26)	1.390(4)
O(8)-C(32)	1.432(3)	N(17)-C(47)	1.380(4)	C(26)-C(27)	1.378(4)
O(9)-N(14)	1.419(3)	N(17)-H(17A)	0.8800	C(26)-H(26A)	0.9500
O(9)-C(38)	1.431(4)	N(18)-C(47)	1.272(4)	C(27)-C(28)	1.387(4)
O(10)-C(40)	1.229(3)	C(1)-C(2)	1.386(4)	C(27)-H(27A)	0.9500
O(11)-C(46)	1.216(3)	C(1)-C(48)	1.502(4)	C(28)-C(29)	1.383(4)
O(12)-N(18)	1.428(3)	C(2)-C(3)	1.359(4)	C(28)-H(28A)	0.9500
O(12)-C(48)	1.436(3)	C(2)-H(2A)	0.9500	C(29)-C(30)	1.499(4)
N(1)-C(5)	1.335(4)	C(3)-C(4)	1.392(5)	C(31)-H(31A)	0.9500
N(1)-C(1)	1.342(4)	C(3)-H(3A)	0.9500	C(32)-C(33)	1.508(5)
N(2)-C(7)	1.279(4)	C(4)-C(5)	1.384(4)	C(32)-H(32A)	0.9900
N(3)-C(8)	1.361(4)	C(4)-H(4A)	0.9500	C(32)-H(32B)	0.9900
N(3)-C(7)	1.378(4)	C(6)-H(6B)	0.9900	C(35)-C(36)	1.389(5)
N(3)-H(3B)	0.8800	C(7)-H(7A)	0.9500	C(36)-C(37)	1.360(5)

'Z-Formamidoximes in molecular folding and macrocycles'
Weiwen Zhao, Ruiyao Wang, Anne Petitjean*

N(4)-C(9)	1.342(4)	C(8)-C(9)	1.503(4)	C(36)-H(36A)	0.9500
N(4)-C(13)	1.345(4)	C(9)-C(10)	1.381(4)	C(37)-C(38)	1.517(4)
N(5)-C(14)	1.369(4)	C(10)-C(11)	1.383(4)	C(38)-H(38A)	0.9900
N(5)-C(15)	1.371(4)	C(10)-H(10A)	0.9500	C(38)-H(38B)	0.9900
N(5)-H(5A)	0.8800	C(11)-C(12)	1.388(4)	C(39)-H(39A)	0.9500
N(6)-C(15)	1.274(4)	C(11)-H(11A)	0.9500	C(40)-C(41)	1.494(4)
N(7)-C(17)	1.335(4)	C(12)-C(13)	1.382(4)	C(41)-C(42)	1.387(4)
N(7)-C(21)	1.342(4)	C(12)-H(12A)	0.9500	C(42)-C(43)	1.377(5)
N(8)-C(23)	1.270(4)	C(13)-C(14)	1.503(4)	C(42)-H(42A)	0.9500
N(9)-C(24)	1.366(3)	C(15)-H(15A)	0.9500	C(43)-C(44)	1.367(4)
N(9)-C(23)	1.384(4)	C(16)-C(17)	1.513(4)	C(43)-H(43A)	0.9500
N(9)-H(9A)	0.8800	C(16)-H(16A)	0.9900	C(44)-C(45)	1.397(4)
N(10)-C(25)	1.345(3)	C(16)-H(16B)	0.9900	C(44)-H(44A)	0.9500
N(10)-C(29)	1.348(4)	C(17)-C(18)	1.384(5)	C(45)-C(46)	1.501(4)
N(11)-C(30)	1.370(3)	C(18)-C(19)	1.388(5)	C(47)-H(47A)	0.9500
N(11)-C(31)	1.376(4)	C(33)-C(34)	1.390(5)	C(48)-H(48A)	0.9900
C(5)-C(6)	1.500(4)	C(34)-C(35)	1.373(5)	C(48)-H(48B)	0.9900
C(6)-H(6A)	0.9900	C(34)-H(34A)	0.9500	O(1W)-H(1WB)	0.95(2)
		C(35)-H(35A)	0.9500	O(1W)-H(1WA)	0.97(3)

N(2)-O(1)-C(6)	108.2(2)	C(19)-C(20)-H(20A)	120.5
N(6)-O(4)-C(16)	108.9(2)	C(21)-C(20)-H(20A)	120.5
N(8)-O(5)-C(22)	108.8(2)	N(7)-C(21)-C(20)	122.9(3)
N(12)-O(8)-C(32)	107.3(2)	N(7)-C(21)-C(22)	114.0(3)
N(14)-O(9)-C(38)	108.4(2)	C(20)-C(21)-C(22)	123.1(3)
N(18)-O(12)-C(48)	107.7(2)	O(5)-C(22)-C(21)	112.5(3)
C(5)-N(1)-C(1)	118.2(2)	O(5)-C(22)-H(22A)	109.1
C(7)-N(2)-O(1)	109.2(2)	C(21)-C(22)-H(22A)	109.1
C(8)-N(3)-C(7)	123.3(3)	O(5)-C(22)-H(22B)	109.1
C(8)-N(3)-H(3B)	118.3	C(21)-C(22)-H(22B)	109.1
C(7)-N(3)-H(3B)	118.3	H(22A)-C(22)-H(22B)	107.8
C(9)-N(4)-C(13)	117.0(2)	N(8)-C(23)-N(9)	126.5(3)
C(14)-N(5)-C(15)	123.1(3)	N(8)-C(23)-H(23A)	116.7
C(14)-N(5)-H(5A)	118.4	N(9)-C(23)-H(23A)	116.7
C(15)-N(5)-H(5A)	118.4	O(6)-C(24)-N(9)	123.4(3)
C(15)-N(6)-O(4)	109.0(2)	O(6)-C(24)-C(25)	121.7(2)

C(17)-N(7)-C(21)	118.5(3)	N(9)-C(24)-C(25)	114.9(2)
C(23)-N(8)-O(5)	108.8(3)	N(10)-C(25)-C(26)	123.1(3)
C(24)-N(9)-C(23)	121.9(2)	N(10)-C(25)-C(24)	118.0(2)
C(24)-N(9)-H(9A)	119.1	C(26)-C(25)-C(24)	118.9(2)
C(23)-N(9)-H(9A)	119.1	C(27)-C(26)-C(25)	118.9(3)
C(25)-N(10)-C(29)	117.1(2)	C(27)-C(26)-H(26A)	120.6
C(30)-N(11)-C(31)	121.5(2)	C(25)-C(26)-H(26A)	120.6
C(30)-N(11)-H(11B)	119.2	C(26)-C(27)-C(28)	118.9(3)
C(31)-N(11)-H(11B)	119.2	C(26)-C(27)-H(27A)	120.5
C(31)-N(12)-O(8)	109.3(2)	C(28)-C(27)-H(27A)	120.5
C(33)-N(13)-C(37)	118.6(3)	C(29)-C(28)-C(27)	118.7(3)
C(39)-N(14)-O(9)	108.6(2)	C(29)-C(28)-H(28A)	120.6
C(40)-N(15)-C(39)	123.0(3)	C(27)-C(28)-H(28A)	120.6
C(40)-N(15)-H(15B)	118.5	N(10)-C(29)-C(28)	123.3(3)
C(39)-N(15)-H(15B)	118.5	N(10)-C(29)-C(30)	117.7(2)
C(45)-N(16)-C(41)	117.3(2)	C(28)-C(29)-C(30)	119.0(3)
C(46)-N(17)-C(47)	123.9(3)	O(7)-C(30)-N(11)	123.6(3)
C(46)-N(17)-H(17A)	118.1	O(7)-C(30)-C(29)	121.5(3)
C(47)-N(17)-H(17A)	118.1	N(11)-C(30)-C(29)	115.0(2)
C(47)-N(18)-O(12)	108.4(2)	N(12)-C(31)-N(11)	125.5(3)
N(1)-C(1)-C(2)	122.4(3)	N(12)-C(31)-H(31A)	117.3
N(1)-C(1)-C(48)	115.8(3)	N(11)-C(31)-H(31A)	117.3
C(2)-C(1)-C(48)	121.8(3)	O(8)-C(32)-C(33)	113.2(3)
C(3)-C(2)-C(1)	119.6(3)	O(8)-C(32)-H(32A)	108.9
C(3)-C(2)-H(2A)	120.2	C(33)-C(32)-H(32A)	108.9
C(1)-C(2)-H(2A)	120.2	O(8)-C(32)-H(32B)	108.9
C(2)-C(3)-C(4)	118.4(3)	C(33)-C(32)-H(32B)	108.9
C(2)-C(3)-H(3A)	120.8	H(32A)-C(32)-H(32B)	107.7
C(4)-C(3)-H(3A)	120.8	N(13)-C(33)-C(34)	121.7(3)
C(5)-C(4)-C(3)	119.3(3)	N(13)-C(33)-C(32)	114.9(3)
C(5)-C(4)-H(4A)	120.3	C(34)-C(33)-C(32)	123.4(3)
C(3)-C(4)-H(4A)	120.3	C(35)-C(34)-C(33)	119.1(3)
N(1)-C(5)-C(4)	122.1(3)	C(35)-C(34)-H(34A)	120.5
N(1)-C(5)-C(6)	116.3(3)	C(33)-C(34)-H(34A)	120.5
C(4)-C(5)-C(6)	121.6(3)	C(34)-C(35)-C(36)	118.9(3)
O(1)-C(6)-C(5)	113.4(2)	C(34)-C(35)-H(35A)	120.5

O(1)-C(6)-H(6A)	108.9	C(36)-C(35)-H(35A)	120.5
C(5)-C(6)-H(6A)	108.9	C(37)-C(36)-C(35)	119.0(4)
O(1)-C(6)-H(6B)	108.9	C(37)-C(36)-H(36A)	120.5
C(5)-C(6)-H(6B)	108.9	C(35)-C(36)-H(36A)	120.5
H(6A)-C(6)-H(6B)	107.7	N(13)-C(37)-C(36)	122.7(3)
N(2)-C(7)-N(3)	124.9(3)	N(13)-C(37)-C(38)	115.4(3)
N(2)-C(7)-H(7A)	117.5	C(36)-C(37)-C(38)	121.9(3)
N(3)-C(7)-H(7A)	117.5	O(9)-C(38)-C(37)	112.5(3)
O(2)-C(8)-N(3)	123.7(3)	O(9)-C(38)-H(38A)	109.1
O(2)-C(8)-C(9)	121.5(3)	C(37)-C(38)-H(38A)	109.1
N(3)-C(8)-C(9)	114.8(3)	O(9)-C(38)-H(38B)	109.1
N(4)-C(9)-C(10)	123.5(3)	C(37)-C(38)-H(38B)	109.1
N(4)-C(9)-C(8)	117.2(2)	H(38A)-C(38)-H(38B)	107.8
C(10)-C(9)-C(8)	119.3(3)	N(14)-C(39)-N(15)	125.2(3)
C(9)-C(10)-C(11)	119.1(3)	N(14)-C(39)-H(39A)	117.4
C(9)-C(10)-H(10A)	120.5	N(15)-C(39)-H(39A)	117.4
C(11)-C(10)-H(10A)	120.5	O(10)-C(40)-N(15)	123.2(3)
C(10)-C(11)-C(12)	118.1(3)	O(10)-C(40)-C(41)	121.3(3)
C(10)-C(11)-H(11A)	121.0	N(15)-C(40)-C(41)	115.5(3)
C(12)-C(11)-H(11A)	121.0	N(16)-C(41)-C(42)	122.7(3)
C(13)-C(12)-C(11)	119.3(3)	N(16)-C(41)-C(40)	119.1(2)
C(13)-C(12)-H(12A)	120.4	C(42)-C(41)-C(40)	118.2(3)
C(11)-C(12)-H(12A)	120.4	C(43)-C(42)-C(41)	118.8(3)
N(4)-C(13)-C(12)	123.1(3)	C(43)-C(42)-H(42A)	120.6
N(4)-C(13)-C(14)	117.6(2)	C(41)-C(42)-H(42A)	120.6
C(12)-C(13)-C(14)	119.3(3)	C(44)-C(43)-C(42)	119.7(3)
O(3)-C(14)-N(5)	123.5(3)	C(44)-C(43)-H(43A)	120.2
O(3)-C(14)-C(13)	121.9(3)	C(42)-C(43)-H(43A)	120.2
N(5)-C(14)-C(13)	114.6(3)	C(43)-C(44)-C(45)	117.8(3)
N(6)-C(15)-N(5)	124.8(3)	C(43)-C(44)-H(44A)	121.1
N(6)-C(15)-H(15A)	117.6	C(45)-C(44)-H(44A)	121.1
N(5)-C(15)-H(15A)	117.6	N(16)-C(45)-C(44)	123.7(3)
O(4)-C(16)-C(17)	112.1(2)	N(16)-C(45)-C(46)	118.3(3)
O(4)-C(16)-H(16A)	109.2	C(44)-C(45)-C(46)	118.0(3)
C(17)-C(16)-H(16A)	109.2	O(11)-C(46)-N(17)	123.7(3)
O(4)-C(16)-H(16B)	109.2	O(11)-C(46)-C(45)	121.6(3)

C(17)-C(16)-H(16B)	109.2	N(17)-C(46)-C(45)	114.6(3)
H(16A)-C(16)-H(16B)	107.9	N(18)-C(47)-N(17)	124.1(3)
N(7)-C(17)-C(18)	121.3(3)	N(18)-C(47)-H(47A)	118.0
N(7)-C(17)-C(16)	116.6(3)	N(17)-C(47)-H(47A)	118.0
C(18)-C(17)-C(16)	122.0(3)	O(12)-C(48)-C(1)	110.8(2)
C(17)-C(18)-C(19)	119.3(3)	O(12)-C(48)-H(48A)	109.5
C(17)-C(18)-H(18A)	120.4	C(1)-C(48)-H(48A)	109.5
C(19)-C(18)-H(18A)	120.4	O(12)-C(48)-H(48B)	109.5
C(20)-C(19)-C(18)	118.8(3)	C(1)-C(48)-H(48B)	109.5
C(20)-C(19)-H(19A)	120.6	H(48A)-C(48)-H(48B)	108.1
C(18)-C(19)-H(19A)	120.6	H(1WB)-O(1W)-H(1WA)	113(3)
C(19)-C(20)-C(21)	119.1(3)		

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ap17. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	58(1)	35(1)	32(1)	6(1)	17(1)	11(1)
O(2)	50(1)	37(1)	43(1)	-1(1)	12(1)	9(1)
O(3)	58(2)	35(1)	37(1)	4(1)	2(1)	10(1)
O(4)	47(1)	39(1)	31(1)	5(1)	-1(1)	2(1)
O(5)	59(2)	44(1)	31(1)	1(1)	4(1)	-9(1)
O(6)	42(1)	33(1)	39(1)	0(1)	7(1)	-9(1)
O(7)	59(2)	38(1)	32(1)	8(1)	11(1)	-10(1)
O(8)	58(2)	56(2)	28(1)	-4(1)	10(1)	-24(1)
O(9)	46(1)	44(1)	32(1)	0(1)	5(1)	3(1)
O(10)	54(2)	38(1)	38(1)	10(1)	3(1)	6(1)
O(11)	54(1)	40(1)	55(2)	-1(1)	20(1)	8(1)
O(12)	44(1)	43(1)	34(1)	1(1)	3(1)	5(1)
N(1)	42(2)	36(1)	27(1)	-1(1)	8(1)	5(1)
N(2)	56(2)	42(2)	40(2)	7(1)	17(1)	19(1)
N(3)	40(2)	34(1)	33(1)	0(1)	8(1)	6(1)
N(4)	31(1)	27(1)	29(1)	-4(1)	4(1)	-5(1)
N(5)	34(1)	29(1)	29(1)	-2(1)	2(1)	2(1)
N(6)	40(2)	36(2)	37(2)	0(1)	2(1)	1(1)
N(7)	44(2)	38(2)	29(1)	5(1)	3(1)	0(1)
N(8)	59(2)	48(2)	43(2)	1(1)	11(1)	-18(1)

N(9)	36(1)	31(1)	28(1)	0(1)	6(1)	-5(1)
N(10)	29(1)	26(1)	25(1)	-1(1)	3(1)	2(1)
N(11)	35(1)	29(1)	26(1)	2(1)	6(1)	-7(1)
N(12)	44(2)	39(2)	37(2)	-4(1)	12(1)	-10(1)
N(13)	45(2)	51(2)	31(1)	-6(1)	12(1)	-7(1)
N(14)	37(2)	45(2)	38(2)	-3(1)	1(1)	6(1)
N(15)	35(1)	32(1)	32(1)	2(1)	4(1)	3(1)
N(16)	36(1)	30(1)	31(1)	1(1)	8(1)	-4(1)
N(17)	41(2)	36(2)	34(2)	2(1)	6(1)	5(1)
N(18)	47(2)	38(2)	35(2)	-1(1)	0(1)	3(1)
C(1)	42(2)	35(2)	28(2)	-1(1)	11(1)	2(1)
C(2)	53(2)	38(2)	30(2)	1(1)	11(2)	3(2)
C(3)	54(2)	47(2)	26(2)	0(1)	6(2)	9(2)
C(4)	45(2)	45(2)	33(2)	-11(2)	3(1)	7(2)
C(5)	39(2)	29(2)	31(2)	-2(1)	9(1)	5(1)
C(6)	50(2)	39(2)	42(2)	-6(2)	14(2)	-2(2)
C(7)	49(2)	40(2)	34(2)	5(2)	12(2)	17(2)
C(8)	31(2)	35(2)	36(2)	-1(1)	10(1)	-4(1)
C(9)	34(2)	27(2)	34(2)	-2(1)	6(1)	-3(1)
C(10)	36(2)	40(2)	36(2)	-10(1)	7(1)	-1(2)
C(11)	43(2)	53(2)	26(2)	-6(2)	7(1)	-7(2)
C(12)	41(2)	42(2)	25(2)	0(1)	2(1)	-3(2)
C(13)	30(2)	31(2)	29(2)	-2(1)	3(1)	-6(1)
C(14)	38(2)	28(2)	34(2)	-3(1)	1(1)	-4(1)
C(15)	38(2)	29(2)	33(2)	-4(1)	2(1)	0(1)
C(16)	46(2)	55(2)	34(2)	13(2)	-2(2)	-9(2)
C(17)	46(2)	48(2)	26(2)	7(1)	11(1)	5(2)
C(18)	53(2)	79(3)	35(2)	-4(2)	2(2)	24(2)
C(19)	79(3)	65(3)	42(2)	-9(2)	2(2)	40(2)
C(20)	74(3)	52(2)	40(2)	-10(2)	2(2)	20(2)
C(21)	51(2)	34(2)	30(2)	0(1)	7(1)	4(2)
C(22)	59(2)	43(2)	38(2)	-10(2)	-5(2)	6(2)
C(23)	49(2)	44(2)	30(2)	-1(2)	10(1)	-10(2)
C(24)	26(2)	30(2)	26(2)	0(1)	1(1)	4(1)
C(25)	28(2)	26(2)	23(1)	0(1)	2(1)	4(1)
C(26)	34(2)	32(2)	35(2)	-4(1)	3(1)	2(1)

C(27)	43(2)	38(2)	22(2)	-5(1)	8(1)	4(2)
C(28)	38(2)	34(2)	28(2)	2(1)	10(1)	3(1)
C(29)	32(2)	29(2)	29(2)	1(1)	4(1)	5(1)
C(30)	34(2)	28(2)	31(2)	0(1)	8(1)	4(1)
C(31)	33(2)	33(2)	35(2)	5(1)	8(1)	-5(1)
C(32)	60(2)	88(3)	26(2)	-8(2)	10(2)	-18(2)
C(33)	53(2)	47(2)	28(2)	3(2)	9(2)	-6(2)
C(34)	80(3)	43(2)	39(2)	-7(2)	7(2)	-1(2)
C(35)	80(3)	47(2)	64(3)	-5(2)	8(2)	19(2)
C(36)	64(2)	50(2)	47(2)	1(2)	3(2)	13(2)
C(37)	47(2)	45(2)	32(2)	6(2)	15(2)	-2(2)
C(38)	44(2)	55(2)	44(2)	-1(2)	10(2)	-10(2)
C(39)	35(2)	39(2)	36(2)	-2(1)	-1(1)	4(1)
C(40)	32(2)	36(2)	32(2)	-2(1)	0(1)	-7(1)
C(41)	36(2)	28(2)	31(2)	-2(1)	6(1)	-9(1)
C(42)	51(2)	38(2)	30(2)	2(1)	7(2)	-10(2)
C(43)	55(2)	46(2)	30(2)	-4(2)	12(2)	-13(2)
C(44)	48(2)	32(2)	39(2)	-9(1)	17(2)	-12(2)
C(45)	34(2)	29(2)	36(2)	-3(1)	10(1)	-7(1)
C(46)	37(2)	35(2)	42(2)	0(1)	12(1)	-4(2)
C(47)	38(2)	35(2)	44(2)	-1(2)	-3(2)	1(2)
C(48)	50(2)	54(2)	33(2)	-3(2)	14(2)	-4(2)
O(1W)	74(2)	58(2)	53(2)	4(1)	2(1)	-4(1)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for ap17.

	x	y	z	U(eq)
H(3B)	11031	2362	4749	43
H(5A)	9194	3592	4454	38
H(9A)	11974	5222	8480	38
H(11B)	9970	4154	8694	36
H(15B)	6487	2609	4844	40
H(17A)	8372	1329	5157	45
H(2A)	9874	1022	7382	48
H(3A)	11922	1268	7644	51
H(4A)	12829	2064	7102	50
H(6A)	11497	3264	6181	52

H(6B)	12713	2774	6310	52
H(7A)	12385	1064	5069	49
H(10A)	11304	1768	3151	45
H(11A)	10404	2679	2511	49
H(12A)	9361	3716	2789	44
H(15A)	7791	4894	4267	41
H(16A)	8919	3295	5920	56
H(16B)	7708	3785	5745	56
H(18A)	7763	5203	5945	68
H(19A)	8761	6199	6484	76
H(20A)	10661	5963	7011	68
H(22A)	11998	4076	7127	59
H(22B)	12615	4824	6942	59
H(23A)	13226	6441	8176	49
H(26A)	12616	6366	10017	41
H(27A)	11775	5724	10649	41
H(28A)	10602	4619	10387	40
H(31A)	8827	2845	8934	40
H(32A)	9012	2846	7306	70
H(32B)	9349	3693	7147	70
H(34A)	7312	4456	7619	66
H(35A)	5295	4665	7214	78
H(36A)	4401	3908	6475	66
H(38A)	5488	2185	6155	57
H(38B)	4458	2802	5935	57
H(39A)	5279	3987	4641	46
H(42A)	6579	2633	3177	48
H(43A)	7710	1642	2916	52
H(44A)	8833	833	3562	46
H(47A)	9641	-6	5466	49
H(48A)	8047	1078	6724	54
H(48B)	7841	1926	6478	54
H(1WB)	5360(30)	4567(17)	3448(14)	76
H(1WA)	5990(30)	5390(20)	3468(14)	76

Table S13. Torsion angles [°] for ap17.

C(6)-O(1)-N(2)-C(7)	-176.4(3)	C(29)-N(10)-C(25)-C(24)	179.5(2)
C(16)-O(4)-N(6)-C(15)	-173.1(2)	O(6)-C(24)-C(25)-N(10)	172.3(3)
C(22)-O(5)-N(8)-C(23)	176.4(3)	N(9)-C(24)-C(25)-N(10)	-7.2(3)
C(32)-O(8)-N(12)-C(31)	-177.3(3)	O(6)-C(24)-C(25)-C(26)	-7.5(4)
C(38)-O(9)-N(14)-C(39)	-166.0(2)	N(9)-C(24)-C(25)-C(26)	173.1(2)
C(48)-O(12)-N(18)-C(47)	-150.3(3)	N(10)-C(25)-C(26)-C(27)	1.1(4)
C(5)-N(1)-C(1)-C(2)	0.8(4)	C(24)-C(25)-C(26)-C(27)	-179.2(3)
C(5)-N(1)-C(1)-C(48)	-178.1(3)	C(25)-C(26)-C(27)-C(28)	-0.5(4)
N(1)-C(1)-C(2)-C(3)	-1.5(5)	C(26)-C(27)-C(28)-C(29)	-0.4(4)
C(48)-C(1)-C(2)-C(3)	177.2(3)	C(25)-N(10)-C(29)-C(28)	-0.2(4)
C(1)-C(2)-C(3)-C(4)	1.6(5)	C(25)-N(10)-C(29)-C(30)	-179.7(2)
C(2)-C(3)-C(4)-C(5)	-0.9(4)	C(27)-C(28)-C(29)-N(10)	0.7(4)
C(1)-N(1)-C(5)-C(4)	-0.1(4)	C(27)-C(28)-C(29)-C(30)	-179.7(3)
C(1)-N(1)-C(5)-C(6)	-179.2(2)	C(31)-N(11)-C(30)-O(7)	-2.6(4)
C(3)-C(4)-C(5)-N(1)	0.2(4)	C(31)-N(11)-C(30)-C(29)	177.7(2)
C(3)-C(4)-C(5)-C(6)	179.2(3)	N(10)-C(29)-C(30)-O(7)	169.3(3)
N(2)-O(1)-C(6)-C(5)	-63.7(3)	C(28)-C(29)-C(30)-O(7)	-10.3(4)
N(1)-C(5)-C(6)-O(1)	-53.3(4)	N(10)-C(29)-C(30)-N(11)	-11.0(4)
C(4)-C(5)-C(6)-O(1)	127.6(3)	C(28)-C(29)-C(30)-N(11)	169.5(3)
O(1)-N(2)-C(7)-N(3)	-0.1(4)	O(8)-N(12)-C(31)-N(11)	-0.4(4)
C(8)-N(3)-C(7)-N(2)	173.8(3)	C(30)-N(11)-C(31)-N(12)	-178.4(3)
C(7)-N(3)-C(8)-O(2)	3.9(5)	N(12)-O(8)-C(32)-C(33)	75.0(4)
C(7)-N(3)-C(8)-C(9)	-174.6(3)	C(37)-N(13)-C(33)-C(34)	2.4(5)
C(13)-N(4)-C(9)-C(10)	-0.7(4)	C(37)-N(13)-C(33)-C(32)	-176.4(3)
C(13)-N(4)-C(9)-C(8)	177.3(2)	O(8)-C(32)-C(33)-N(13)	-151.9(3)
O(2)-C(8)-C(9)-N(4)	171.1(3)	O(8)-C(32)-C(33)-C(34)	29.3(5)
N(3)-C(8)-C(9)-N(4)	-10.4(4)	N(13)-C(33)-C(34)-C(35)	-1.1(5)
O(2)-C(8)-C(9)-C(10)	-10.8(4)	C(32)-C(33)-C(34)-C(35)	177.6(3)
N(3)-C(8)-C(9)-C(10)	167.7(3)	C(33)-C(34)-C(35)-C(36)	-0.9(5)
N(4)-C(9)-C(10)-C(11)	1.1(4)	C(34)-C(35)-C(36)-C(37)	1.5(6)
C(8)-C(9)-C(10)-C(11)	-176.9(3)	C(33)-N(13)-C(37)-C(36)	-1.8(5)
C(9)-C(10)-C(11)-C(12)	0.0(4)	C(33)-N(13)-C(37)-C(38)	-179.5(3)
C(10)-C(11)-C(12)-C(13)	-1.3(4)	C(35)-C(36)-C(37)-N(13)	-0.1(5)
C(9)-N(4)-C(13)-C(12)	-0.8(4)	C(35)-C(36)-C(37)-C(38)	177.4(3)
C(9)-N(4)-C(13)-C(14)	178.5(2)	N(14)-O(9)-C(38)-C(37)	-74.9(3)

C(11)-C(12)-C(13)-N(4)	1.8(4)	N(13)-C(37)-C(38)-O(9)	-70.2(4)
C(11)-C(12)-C(13)-C(14)	-177.5(3)	C(36)-C(37)-C(38)-O(9)	112.0(4)
C(15)-N(5)-C(14)-O(3)	1.5(4)	O(9)-N(14)-C(39)-N(15)	0.6(4)
C(15)-N(5)-C(14)-C(13)	-179.0(2)	C(40)-N(15)-C(39)-N(14)	175.4(3)
N(4)-C(13)-C(14)-O(3)	176.8(3)	C(39)-N(15)-C(40)-O(10)	-0.3(4)
C(12)-C(13)-C(14)-O(3)	-3.9(4)	C(39)-N(15)-C(40)-C(41)	179.3(2)
N(4)-C(13)-C(14)-N(5)	-2.7(4)	C(45)-N(16)-C(41)-C(42)	1.6(4)
C(12)-C(13)-C(14)-N(5)	176.6(2)	C(45)-N(16)-C(41)-C(40)	-178.5(2)
O(4)-N(6)-C(15)-N(5)	1.7(4)	O(10)-C(40)-C(41)-N(16)	168.7(3)
C(14)-N(5)-C(15)-N(6)	-178.9(3)	N(15)-C(40)-C(41)-N(16)	-10.9(4)
N(6)-O(4)-C(16)-C(17)	-70.9(3)	O(10)-C(40)-C(41)-C(42)	-11.4(4)
C(21)-N(7)-C(17)-C(18)	0.4(4)	N(15)-C(40)-C(41)-C(42)	169.0(3)
C(21)-N(7)-C(17)-C(16)	-178.5(3)	N(16)-C(41)-C(42)-C(43)	-1.6(4)
O(4)-C(16)-C(17)-N(7)	-94.2(3)	C(40)-C(41)-C(42)-C(43)	178.5(3)
O(4)-C(16)-C(17)-C(18)	86.9(4)	C(41)-C(42)-C(43)-C(44)	-0.3(5)
N(7)-C(17)-C(18)-C(19)	2.8(5)	C(42)-C(43)-C(44)-C(45)	2.1(5)
C(16)-C(17)-C(18)-C(19)	-178.4(3)	C(41)-N(16)-C(45)-C(44)	0.4(4)
C(17)-C(18)-C(19)-C(20)	-3.3(6)	C(41)-N(16)-C(45)-C(46)	-178.4(2)
C(18)-C(19)-C(20)-C(21)	0.8(6)	C(43)-C(44)-C(45)-N(16)	-2.2(4)
C(17)-N(7)-C(21)-C(20)	-3.0(5)	C(43)-C(44)-C(45)-C(46)	176.6(3)
C(17)-N(7)-C(21)-C(22)	174.8(3)	C(47)-N(17)-C(46)-O(11)	-6.1(5)
C(19)-C(20)-C(21)-N(7)	2.4(5)	C(47)-N(17)-C(46)-C(45)	171.7(3)
C(19)-C(20)-C(21)-C(22)	-175.2(3)	N(16)-C(45)-C(46)-O(11)	179.4(3)
N(8)-O(5)-C(22)-C(21)	-92.4(3)	C(44)-C(45)-C(46)-O(11)	0.5(4)
N(7)-C(21)-C(22)-O(5)	-142.2(3)	N(16)-C(45)-C(46)-N(17)	1.5(4)
C(20)-C(21)-C(22)-O(5)	35.6(5)	C(44)-C(45)-C(46)-N(17)	-177.4(3)
O(5)-N(8)-C(23)-N(9)	-1.6(5)	O(12)-N(18)-C(47)-N(17)	1.4(4)
C(24)-N(9)-C(23)-N(8)	-179.7(3)	C(46)-N(17)-C(47)-N(18)	-172.0(3)
C(23)-N(9)-C(24)-O(6)	0.0(4)	N(18)-O(12)-C(48)-C(1)	54.7(3)
C(23)-N(9)-C(24)-C(25)	179.4(2)	N(1)-C(1)-C(48)-O(12)	53.9(3)
C(29)-N(10)-C(25)-C(26)	-0.7(4)	C(2)-C(1)-C(48)-O(12)	-124.9(3)

Table S14. Hydrogen bonds for ap17 [Å and °].

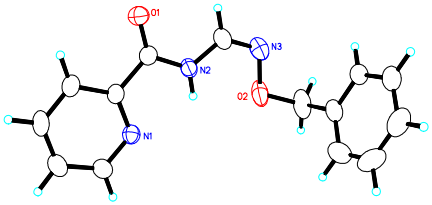
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WB)...O(10)	0.95(2)	2.06(3)	2.943(3)	155(3)
O(1W)-H(1WA)...O(2)#1	0.97(3)	2.09(3)	3.026(4)	163(3)

Symmetry transformations used to generate equivalent atoms: #1 x-1/2,y+1/2,z

D.3 PyFBn:

A crystal of the compound (colorless, plate-shaped, size 0.30 × 0.20 × 0.04 mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 4.22 ~ 52.00º. No significant decay was observed during the data collection. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package:[1] Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT (Bruker, 2005); structure solution: XPREP (Bruker, 2005) and SHELXTL (Bruker, 2000); structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[2] The crystal is monoclinic space group $P2_1/c$, based on the systematic absences, *E* statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w (F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. All of the H atoms were placed in geometrically calculated positions, with C-H = 0.95 (aromatic), 0.99(CH_2), and 0.88(N-H) Å, and refined as riding atoms, with Uiso(H) = 1.2 Ueq(C or N). Convergence to final R_1 = 0.0441 and wR_2 = 0.1017 for 1731 (I>2σ(I)) independent reflections, and R_1 = 0.0717 and wR_2 = 0.1172 for all 2469 (R(int) = 0.0217) independent reflections, with 162 parameters and 0 restraints, were achieved.[3] The largest residual peak and hole to be 0.280 and – 0.292 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles are given in Tables S15 to S20. The molecular structure and the cell packing are shown in Figure S3.

a



b

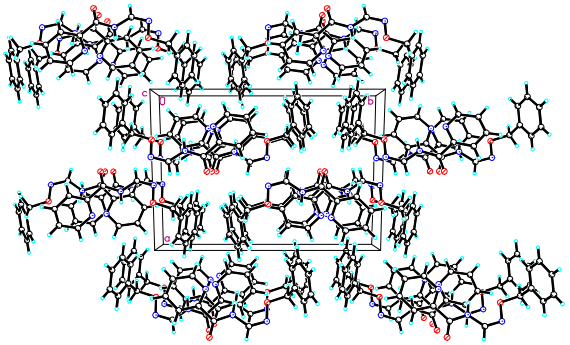


Figure S3 a) Molecular structure (displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are represented by circles of arbitrary size); b) Unit cell packing.

Table S15. Crystal data and structure refinement for ap21

Identification code	ap21	
Empirical formula	C14 H13 N3 O2	
Formula weight	255.27	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.7004(12) Å	α= 90°.
	b = 15.9776(13) Å	β= 107.250(5)°.
	c = 7.1602(6) Å	γ = 90°.
Volume	1278.3(2) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	536	
Crystal size	0.30 x 0.20 x 0.04 mm^3	
Theta range for data collection	2.22 to 26.00°.	
Index ranges	-14<=h<=14, -17<=k<=19, -7<=l<=8	
Reflections collected	5323	
Independent reflections	2469 [R(int) = 0.0217]	
Completeness to theta = 26.00°	98.1 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9963 and 0.9730	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2469 / 0 / 162	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1017	
R indices (all data)	R1 = 0.0717, wR2 = 0.1172	
Extinction coefficient	0.0067(16)	
Largest diff. peak and hole	0.280 and -0.292 $e.Å^{-3}$	

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for ap21. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2236(1)	2666(1)	-395(2)	31(1)
N(2)	3740(1)	1484(1)	1424(2)	32(1)
O(1)	4991(1)	2446(1)	3320(2)	40(1)
C(1)	1466(2)	3248(1)	-1339(3)	37(1)
C(2)	1629(2)	4095(1)	-961(3)	41(1)
C(3)	2634(2)	4360(1)	443(3)	40(1)
C(4)	3459(2)	3772(1)	1441(3)	34(1)
C(5)	3216(2)	2937(1)	973(2)	28(1)
C(6)	4077(2)	2281(1)	2021(3)	30(1)
C(7)	4395(2)	790(1)	2236(3)	39(1)
N(3)	4120(2)	33(1)	1742(3)	44(1)
O(2)	3045(1)	12(1)	183(2)	51(1)
C(8)	2657(2)	-851(1)	-134(3)	57(1)
C(9)	2071(1)	-1148(1)	1379(2)	38(1)
C(10)	2770(1)	-1522(1)	3069(2)	35(1)
C(11)	2259(1)	-1785(1)	4474(2)	43(1)
C(12)	1050(1)	-1674(1)	4190(2)	56(1)
C(13)	352(1)	-1300(1)	2499(3)	64(1)
C(14)	863(1)	-1037(1)	1094(2)	56(1)

Table S17. Bond lengths [Å] and angles [°] for ap21.

N(1)-C(1)	1.331(2)	C(3)-H(3A)	0.9500	C(9)-C(14)	1.3792
N(1)-C(5)	1.340(2)	C(4)-C(5)	1.385(2)	C(9)-C(10)	1.3793
N(2)-C(6)	1.364(2)	C(4)-H(4A)	0.9500	C(10)-C(11)	1.3792
N(2)-C(7)	1.374(2)	C(5)-C(6)	1.493(2)	C(10)-H(10A)	0.9500
N(2)-H(2B)	0.8800	C(7)-N(3)	1.275(2)	C(11)-C(12)	1.3793
O(1)-C(6)	1.220(2)	C(7)-H(7A)	0.9500	C(11)-H(11A)	0.9500
C(1)-C(2)	1.381(3)	N(3)-O(2)	1.412(2)	C(12)-C(13)	1.3793
C(1)-H(1A)	0.9500	O(2)-C(8)	1.448(2)	C(12)-H(12A)	0.9500
C(2)-C(3)	1.368(3)	C(8)-C(9)	1.519(3)	C(13)-C(14)	1.3792
C(2)-H(2A)	0.9500	C(8)-H(8A)	0.9900	C(13)-H(13A)	0.9500

C(3)-C(4)	1.384(3)	C(8)-H(8B)	0.9900	C(14)-H(14A)	0.9500

C(1)-N(1)-C(5)	116.69(16)	N(1)-C(5)-C(6)	116.37(15)	C(14)-C(9)-C(8)	120.92(13)
C(6)-N(2)-C(7)	123.14(16)	C(4)-C(5)-C(6)	119.72(16)	C(10)-C(9)-C(8)	119.07(13)
C(6)-N(2)-H(2B)	118.4	O(1)-C(6)-N(2)	123.25(17)	C(11)-C(10)-C(9)	120.0
C(7)-N(2)-H(2B)	118.4	O(1)-C(6)-C(5)	122.61(16)	C(11)-C(10)-H(10A)	120.0
N(1)-C(1)-C(2)	123.46(18)	N(2)-C(6)-C(5)	114.13(15)	C(9)-C(10)-H(10A)	120.0
N(1)-C(1)-H(1A)	118.3	N(3)-C(7)-N(2)	125.74(19)	C(10)-C(11)-C(12)	120.0
C(2)-C(1)-H(1A)	118.3	N(3)-C(7)-H(7A)	117.1	C(10)-C(11)-H(11A)	120.0
C(3)-C(2)-C(1)	119.10(18)	N(2)-C(7)-H(7A)	117.1	C(12)-C(11)-H(11A)	120.0
C(3)-C(2)-H(2A)	120.5	C(7)-N(3)-O(2)	109.59(16)	C(11)-C(12)-C(13)	120.0
C(1)-C(2)-H(2A)	120.5	N(3)-O(2)-C(8)	108.16(15)	C(11)-C(12)-H(12A)	120.0
C(2)-C(3)-C(4)	118.96(18)	O(2)-C(8)-C(9)	111.89(16)	C(13)-C(12)-H(12A)	120.0
C(2)-C(3)-H(3A)	120.5	O(2)-C(8)-H(8A)	109.2	C(14)-C(13)-C(12)	120.0
C(4)-C(3)-H(3A)	120.5	C(9)-C(8)-H(8A)	109.2	C(14)-C(13)-H(13A)	120.0
C(3)-C(4)-C(5)	117.88(18)	O(2)-C(8)-H(8B)	109.2	C(12)-C(13)-H(13A)	120.0
C(3)-C(4)-H(4A)	121.1	C(9)-C(8)-H(8B)	109.2	C(13)-C(14)-C(9)	120.0
C(5)-C(4)-H(4A)	121.1	H(8A)-C(8)-H(8B)	107.9	C(13)-C(14)-H(14A)	120.0
N(1)-C(5)-C(4)	123.91(17)	C(14)-C(9)-C(10)	120.0	C(9)-C(14)-H(14A)	120.0

Table S18. Anisotropic displacement parameters ($Å^2 \times 10^3$) for ap21. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	33(1)	29(1)	31(1)	1(1)	10(1)	-1(1)
N(2)	37(1)	27(1)	32(1)	3(1)	8(1)	2(1)
O(1)	34(1)	43(1)	40(1)	4(1)	4(1)	-3(1)
C(1)	38(1)	36(1)	35(1)	2(1)	7(1)	3(1)
C(2)	47(1)	35(1)	40(1)	8(1)	11(1)	8(1)
C(3)	57(1)	24(1)	44(1)	1(1)	20(1)	-1(1)
C(4)	42(1)	30(1)	33(1)	-1(1)	12(1)	-5(1)
C(5)	33(1)	28(1)	25(1)	2(1)	12(1)	-2(1)
C(6)	32(1)	32(1)	28(1)	2(1)	12(1)	-2(1)
C(7)	42(1)	32(1)	44(1)	6(1)	15(1)	7(1)
N(3)	54(1)	35(1)	45(1)	6(1)	15(1)	7(1)
O(2)	83(1)	29(1)	36(1)	5(1)	9(1)	-5(1)

C(8)	104(2)	31(1)	34(1)	-4(1)	16(1)	-8(1)
C(9)	56(1)	19(1)	35(1)	-7(1)	4(1)	0(1)
C(10)	40(1)	26(1)	39(1)	-2(1)	9(1)	1(1)
C(11)	54(1)	31(1)	45(1)	1(1)	15(1)	-3(1)
C(12)	57(1)	45(1)	74(2)	-11(1)	30(1)	-12(1)
C(13)	36(1)	50(2)	102(2)	-24(2)	13(1)	-5(1)
C(14)	57(1)	32(1)	59(2)	-11(1)	-15(1)	5(1)

Table S19. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for ap21.

	x	y	z	U(eq)
H(2B)	3071	1410	472	39
H(1A)	768	3072	-2324	45
H(2A)	1051	4487	-1666	50
H(3A)	2764	4940	728	49
H(4A)	4169	3937	2416	41
H(7A)	5117	884	3255	46
H(8A)	3355	-1211	-76	69
H(8B)	2080	-907	-1455	69
H(10A)	3602	-1598	3265	42
H(11A)	2740	-2042	5639	52
H(12A)	699	-1855	5158	68
H(13A)	-480	-1224	2303	77
H(14A)	382	-780	-70	68

Table S20. Torsion angles [°] for ap21.

C(5)-N(1)-C(1)-C(2)	-0.6(3)	C(6)-N(2)-C(7)-N(3)	179.61(18)
N(1)-C(1)-C(2)-C(3)	0.5(3)	N(2)-C(7)-N(3)-O(2)	1.6(3)
C(1)-C(2)-C(3)-C(4)	0.1(3)	C(7)-N(3)-O(2)-C(8)	-171.00(17)
C(2)-C(3)-C(4)-C(5)	-0.5(3)	N(3)-O(2)-C(8)-C(9)	77.7(2)
C(1)-N(1)-C(5)-C(4)	0.1(2)	O(2)-C(8)-C(9)-C(14)	87.83(19)
C(1)-N(1)-C(5)-C(6)	-179.85(15)	O(2)-C(8)-C(9)-C(10)	-91.17(19)
C(3)-C(4)-C(5)-N(1)	0.5(3)	C(14)-C(9)-C(10)-C(11)	0.0
C(3)-C(4)-C(5)-C(6)	-179.60(15)	C(8)-C(9)-C(10)-C(11)	179.01(13)
C(7)-N(2)-C(6)-O(1)	0.4(3)	C(9)-C(10)-C(11)-C(12)	0.0

C(7)-N(2)-C(6)-C(5)	-178.47(15)	C(10)-C(11)-C(12)-C(13)	0.0
N(1)-C(5)-C(6)-O(1)	-178.68(15)	C(11)-C(12)-C(13)-C(14)	0.0
C(4)-C(5)-C(6)-O(1)	1.4(2)	C(12)-C(13)-C(14)-C(9)	0.0
N(1)-C(5)-C(6)-N(2)	0.2(2)	C(10)-C(9)-C(14)-C(13)	0.0
C(4)-C(5)-C(6)-N(2)	-179.72(15)	C(8)-C(9)-C(14)-C(13)	-178.99(14)