Electronic Supplementary Information

Construction of a series of insensitive energetic materials starting from the addition reaction of 3-amino-4-cyanofurazan

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1. Single-crystal X-ray diffraction analysis of **2**

Table S1. Crystal data, data collection, and refinement for **2**

$C_6H_4N_6O$	$Z = 2$
$M_r = 176.15$	$F(000) = 180$
Triclinic, $P\bar{1}$	$D_x = 1.528$ Mg m^{-3}
$a = 3.7290$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.4768$ (8) Å	Cell parameters from 1090 reflections
$c = 14.4819$ (16) Å	$\theta = 2.9–26.0°$
$\alpha = 100.016$ (3)°	$\mu = 0.12$ mm^{-1}
$\beta = 93.884$ (4)°	$T = 170$ K
$\gamma = 104.266$ (4)°	Block, clear light colourless
$V = 382.76$ (7) Å^3	0.15 × 0.08 × 0.03 mm
Bruker D8 Venture diffractometer	1563 independent reflections
Radiation source: sealed X-ray tube	1013 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.047$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 26.4°$, $\theta_{min} = 2.9°$
phi and ω scans	$h = -4 \rightarrow 4$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0784 before and 0.0527 after correction. The Ratio of minimum to maximum transmission is 0.8990. The λ/2 correction factor is Not present.	$k = -9 \rightarrow 8$
$T_{min} = 0.670$, $T_{max} = 0.745$	$l = -17 \rightarrow 18$
4289 measured reflections	
Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.052$	All H-atom parameters refined
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.3744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1563 reflections	$\Delta\rangle_{max} = 0.26$ e Å^{-3}
135 parameters	$\Delta\rangle_{min} = -0.30$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: dual	Extinction coefficient: 0.054 (8)

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **2**

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2880 (5)	0.1637 (3)	0.03575 (13)	0.0326 (5)
N2	0.7877 (7)	0.5281 (3)	0.31339 (19)	0.0281 (6)
N6	0.2491 (7)	0.6106 (3)	0.14667 (18)	0.0271 (6)
N4	0.4197 (7)	0.1570 (3)	0.12508 (16)	0.0296 (6)
N5	0.2149 (6)	0.3374 (3)	0.03239 (16)	0.0294 (6)
N3	-0.0673 (7)	-0.0839 (3)	0.26993 (17)	0.0327 (6)
N1	0.7050 (8)	0.3002 (4)	0.50735 (19)	0.0417 (7)
C5	0.4302 (7)	0.3203 (4)	0.17704 (19)	0.0235 (6)
C3	0.4239 (8)	0.2290 (4)	0.33398 (19)	0.0249 (7)
C4	0.5530 (7)	0.3607 (4)	0.27906 (19)	0.0237 (6)
C2	0.1547 (8)	0.0555 (4)	0.29701 (19)	0.0248 (6)
C1	0.5705 (8)	0.2639 (4)	0.4302 (2)	0.0275 (7)
C6	0.3061 (7)	0.4346 (4)	0.11886 (19)	0.0241 (6)
H6A	0.439 (8)	0.693 (4)	0.1857 (19)	0.018 (7)*
H2A	0.879 (8)	0.565 (4)	0.376 (2)	0.040 (9)*
H6B	0.152 (8)	0.651 (4)	0.100 (2)	0.036 (9)*
H2B	0.889 (9)	0.613 (5)	0.271 (2)	0.057 (10)*

Table S3. Atomic displacement parameters (Å^2) for **2**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0390 (13)	0.0281 (11)	0.0258 (12)	0.0029 (9)	-0.0004 (9)	0.0022 (9)
N2	0.0321 (15)	0.0218 (13)	0.0251 (15)	-0.0018 (10)	-0.0031 (12)	0.0059 (11)
N6	0.0322 (15)	0.0254 (13)	0.0224 (14)	0.0059 (11)	-0.0027 (11)	0.0062 (11)
N4	0.0374 (15)	0.0267 (13)	0.0224 (13)	0.0050 (11)	0.0008 (11)	0.0044 (11)
N5	0.0338 (14)	0.0247 (13)	0.0262 (14)	0.0018 (10)	0.0035 (11)	0.0040 (11)
N3	0.0326 (14)	0.0276 (13)	0.0360 (15)	0.0043 (11)	0.0021 (11)	0.0073 (11)
N1	0.0463 (17)	0.0403 (16)	0.0324 (17)	0.0000 (12)	-0.0021 (13)	0.0102 (13)
C5	0.0233 (15)	0.0215 (14)	0.0234 (15)	0.0011 (11)	0.0022 (12)	0.0057 (12)
C3	0.0280 (16)	0.0228 (14)	0.0235 (16)	0.0048 (12)	0.0023 (12)	0.0065 (12)
C4	0.0223 (15)	0.0259 (15)	0.0241 (15)	0.0083 (11)	0.0025 (12)	0.0056 (12)
C2	0.0272 (16)	0.0247 (15)	0.0251 (16)	0.0078 (12)	0.0044 (12)	0.0094 (12)
C1	0.0254 (16)	0.0237 (15)	0.0320 (18)	0.0017 (12)	0.0019 (13)	0.0094 (13)
C6	0.0213 (15)	0.0249 (14)	0.0221 (15)	-0.0013 (11)	0.0031 (12)	0.0040 (12)

Table S4. Geometric parameters (Å, º) for **2**

O1—N4	1.366 (3)	N5—C6	1.310 (3)
O1—N5	1.399 (3)	N3—C2	1.146 (3)
N2—C4	1.328 (3)	N1—C1	1.152 (4)
N2—H2A	0.92 (3)	C5—C4	1.473 (4)
N2—H2B	0.98 (4)	C5—C6	1.431 (4)
N6—C6	1.379 (3)	C3—C4	1.387 (3)
N6—H6A	0.90 (3)	C3—C2	1.422 (4)
N6—H6B	0.88 (3)	C3—C1	1.417 (4)
N4—C5	1.309 (3)		
N4—O1—N5	111.17 (19)	C4—C3—C2	122.6 (2)
C4—N2—H2A	121.8 (19)	C4—C3—C1	119.6 (2)
C4—N2—H2B	120.9 (19)	C1—C3—C2	117.8 (2)
H2A—N2—H2B	117 (3)	N2—C4—C5	116.0 (2)
C6—N6—H6A	114.2 (17)	N2—C4—C3	123.5 (3)
C6—N6—H6B	112.6 (19)	C3—C4—C5	120.6 (2)
H6A—N6—H6B	117 (2)	N3—C2—C3	177.8 (3)
C5—N4—O1	105.8 (2)	N1—C1—C3	176.2 (3)
C6—N5—O1	105.1 (2)	N6—C6—C5	127.9 (2)
N4—C5—C4	120.5 (2)	N5—C6—N6	123.1 (3)
N4—C5—C6	109.2 (2)	N5—C6—C5	108.7 (2)
C6—C5—C4	130.3 (2)		
O1—N4—C5—C4	178.7 (2)	N5—O1—N4—C5	0.1 (3)
O1—N4—C5—C6	-0.7 (3)	C4—C5—C6—N6	-4.5 (4)
O1—N5—C6—N6	-175.1 (2)	C4—C5—C6—N5	-178.2 (3)
O1—N5—C6—C5	-1.1 (3)	C2—C3—C4—N2	175.9 (3)
N4—O1—N5—C6	0.7 (3)	C2—C3—C4—C5	-3.7 (4)
N4—C5—C4—N2	135.5 (3)	C1—C3—C4—N2	-5.9 (4)
N4—C5—C4—C3	-44.9 (4)	C1—C3—C4—C5	174.5 (3)
N4—C5—C6—N6	174.9 (3)	C6—C5—C4—N2	-45.2 (4)
N4—C5—C6—N5	1.2 (3)	C6—C5—C4—C3	134.4 (3)

Table S5. Hydrogen bonds (Å, º) for **2**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*A*···N3^{i}	0.90 (3)	2.27 (3)	3.162 (4)	174 (2)
N2—H2*A*···N1^{ii}	0.92 (3)	2.14 (3)	2.991 (4)	155 (3)

N6—H6*B*···N5^{iii}	0.88 (3)	2.30 (3)	3.154 (4)	162 (3)
N2—H2*B*···N6^{iv}	0.98 (4)	2.32 (4)	3.119 (3)	138 (3)
N2—H2*B*···N3^{i}	0.98 (4)	2.24 (3)	3.003 (3)	134 (3)

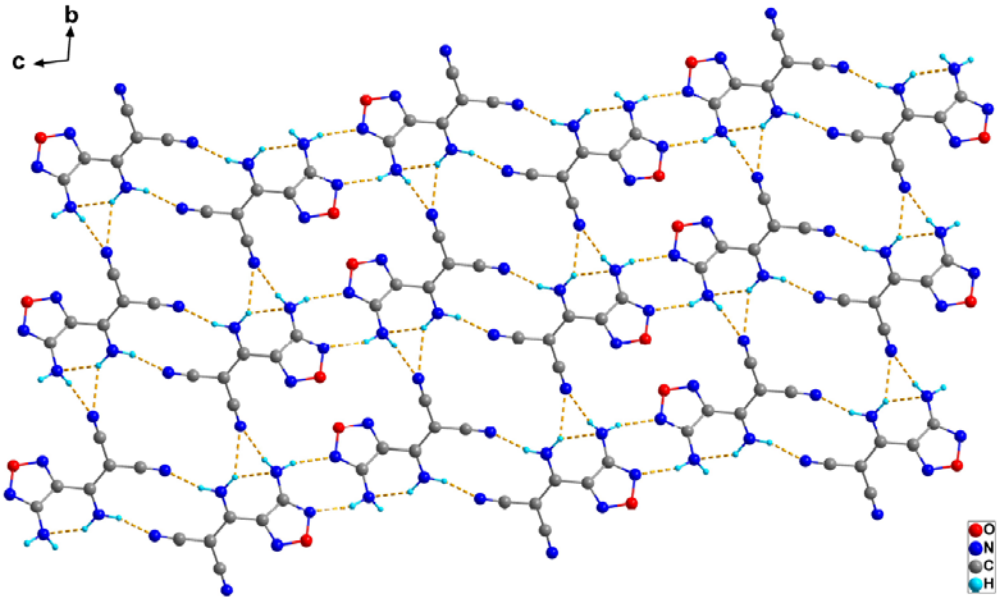


Fig. S1 Stacking diagram of **2** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

2. Single-crystal X-ray diffraction analysis of **3**

Table S6. Crystal data, data collection, and refinement for **3**

$C_5H_6N_8O$	$F(000)$ = 400
M_r = 194.18	D_x = 1.708 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 3.6810 (3) Å	Cell parameters from 1795 reflections
b = 15.3434 (13) Å	θ = 2.7–25.9°
c = 13.3774 (10) Å	μ = 0.13 mm^{-1}
β = 91.609 (2)°	T = 170 K
V = 755.24 (11) Å^3	Block, colourless
Z = 4	0.15 × 0.08 × 0.05 mm
Bruker APEX-II CCD diffractometer	1040 reflections with $I > 2\sigma(I)$
ϕ and ω scans	R_{int} = 0.069
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1098 before and 0.0637 after correction. The Ratio of minimum to maximum transmission is 0.9064.	θ_{max} = 26.4°, θ_{min} = 2.0°

The λ/2 correction factor is Not present.	
T_{min} = 0.676, T_{max} = 0.745	h = -4→4
8379 measured reflections	k = -19→19
1550 independent reflections	l = -16→16
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.047	All H-atom parameters refined
$wR(F^2)$ = 0.116	$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.394P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
1550 reflections	$\Delta\rangle_{max}$ = 0.25 e Å^{-3}
151 parameters	$\Delta\rangle_{min}$ = -0.31 e Å^{-3}
6 restraints	

Table S7. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **3**

	x	y	z	U_{iso}*/U_{eq}
O1	0.4697 (5)	0.19823 (10)	0.51762 (13)	0.0276 (5)
N4	0.7356 (5)	0.43828 (12)	0.40050 (14)	0.0199 (5)
N6	0.6624 (5)	0.52585 (12)	0.25308 (15)	0.0210 (5)
N5	0.4421 (5)	0.37914 (12)	0.25423 (14)	0.0210 (5)
N8	0.9530 (6)	0.57829 (14)	0.39407 (17)	0.0229 (5)
N2	0.5876 (6)	0.28055 (13)	0.49499 (16)	0.0255 (5)
N3	0.1785 (6)	0.20355 (14)	0.26881 (17)	0.0268 (5)
N7	0.3878 (6)	0.46492 (14)	0.11392 (16)	0.0257 (5)
N1	0.2976 (6)	0.15868 (13)	0.43384 (16)	0.0264 (5)
C3	0.5631 (6)	0.37597 (15)	0.34910 (17)	0.0185 (5)
C4	0.4908 (6)	0.29349 (15)	0.40134 (18)	0.0200 (5)
C1	0.5001 (6)	0.45734 (15)	0.20942 (18)	0.0196 (5)
C2	0.7815 (6)	0.51346 (15)	0.34762 (18)	0.0193 (6)
C5	0.3102 (6)	0.21720 (15)	0.36289 (18)	0.0216 (6)
H8A	1.006 (7)	0.6238 (13)	0.3584 (17)	0.025 (7)*
H3A	0.159 (8)	0.2513 (14)	0.2318 (19)	0.037 (8)*
H7A	0.363 (8)	0.5165 (13)	0.088 (2)	0.036 (8)*
H7B	0.263 (8)	0.4217 (16)	0.086 (2)	0.047 (9)*
H8B	1.046 (8)	0.5727 (19)	0.4570 (15)	0.045 (9)*
H3B	0.044 (8)	0.1564 (15)	0.261 (2)	0.052 (10)*

Table S8. Atomic displacement parameters (Å^2) for **3**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0380 (11)	0.0192 (9)	0.0254 (10)	-0.0033 (8)	-0.0028 (8)	0.0043 (7)
N4	0.0214 (11)	0.0166 (10)	0.0215 (11)	-0.0019 (8)	0.0004 (9)	-0.0008 (9)
N6	0.0235 (11)	0.0194 (11)	0.0200 (11)	-0.0006 (9)	-0.0004 (9)	-0.0008 (9)
N5	0.0229 (11)	0.0190 (11)	0.0210 (11)	0.0011 (9)	-0.0019 (9)	-0.0001 (8)
N8	0.0294 (12)	0.0175 (12)	0.0217 (12)	-0.0057 (9)	-0.0021 (10)	0.0019 (10)
N2	0.0327 (13)	0.0175 (11)	0.0262 (12)	-0.0004 (9)	0.0000 (10)	0.0037 (9)
N3	0.0359 (14)	0.0167 (12)	0.0274 (13)	-0.0044 (10)	-0.0048 (11)	0.0002 (10)
N7	0.0377 (14)	0.0173 (12)	0.0218 (12)	-0.0011 (11)	-0.0056 (10)	0.0018 (10)
N1	0.0325 (13)	0.0217 (11)	0.0249 (12)	-0.0042 (10)	-0.0020 (10)	-0.0016 (9)
C3	0.0191 (13)	0.0172 (12)	0.0193 (13)	0.0030 (10)	0.0015 (10)	-0.0022 (10)
C4	0.0202 (13)	0.0170 (12)	0.0227 (13)	0.0025 (10)	-0.0001 (11)	-0.0006 (10)
C1	0.0203 (13)	0.0166 (13)	0.0220 (13)	0.0018 (10)	0.0005 (10)	-0.0008 (10)
C2	0.0178 (12)	0.0189 (13)	0.0213 (14)	0.0031 (10)	0.0006 (11)	-0.0017 (10)
C5	0.0213 (13)	0.0197 (13)	0.0239 (14)	0.0000 (10)	0.0013 (11)	-0.0006 (11)

Table S9. Geometric parameters (Å, º) for **3**

O1—N2	1.372 (3)	N2—C4	1.308 (3)
O1—N1	1.409 (3)	N3—C5	1.352 (3)
N4—C3	1.329 (3)	N3—H3A	0.886 (17)
N4—C2	1.366 (3)	N3—H3B	0.881 (18)
N6—C1	1.335 (3)	N7—C1	1.337 (3)
N6—C2	1.340 (3)	N7—H7A	0.867 (17)
N5—C3	1.334 (3)	N7—H7B	0.882 (18)
N5—C1	1.361 (3)	N1—C5	1.308 (3)
N8—C2	1.324 (3)	C3—C4	1.473 (3)
N8—H8A	0.870 (17)	C4—C5	1.434 (3)
N8—H8B	0.904 (18)		
N2—O1—N1	111.03 (17)	N4—C3—N5	127.4 (2)
C3—N4—C2	113.8 (2)	N4—C3—C4	117.6 (2)
C1—N6—C2	115.6 (2)	N5—C3—C4	115.0 (2)
C3—N5—C1	113.5 (2)	N2—C4—C3	122.5 (2)
C2—N8—H8A	117.2 (16)	N2—C4—C5	109.3 (2)
C2—N8—H8B	121.9 (19)	C5—C4—C3	128.2 (2)
H8A—N8—H8B	120 (3)	N6—C1—N5	125.1 (2)
C4—N2—O1	105.76 (19)	N6—C1—N7	118.2 (2)

C5—N3—H3A	114.4 (19)	N7—C1—N5	116.7 (2)
C5—N3—H3B	115 (2)	N6—C2—N4	124.5 (2)
H3A—N3—H3B	125 (3)	N8—C2—N4	117.1 (2)
C1—N7—H7A	119.1 (19)	N8—C2—N6	118.4 (2)
C1—N7—H7B	119 (2)	N3—C5—C4	127.6 (2)
H7A—N7—H7B	118 (3)	N1—C5—N3	123.4 (2)
C5—N1—O1	104.91 (18)	N1—C5—C4	109.0 (2)
O1—N2—C4—C3	178.8 (2)	C3—N4—C2—N8	-179.7 (2)
O1—N2—C4—C5	-0.7 (3)	C3—N5—C1—N6	0.3 (3)
O1—N1—C5—N3	178.6 (2)	C3—N5—C1—N7	179.5 (2)
O1—N1—C5—C4	0.2 (3)	C3—C4—C5—N3	2.6 (4)
N4—C3—C4—N2	0.4 (3)	C3—C4—C5—N1	-179.1 (2)
N4—C3—C4—C5	179.8 (2)	C1—N6—C2—N4	-2.3 (3)
N5—C3—C4—N2	-179.0 (2)	C1—N6—C2—N8	178.3 (2)
N5—C3—C4—C5	0.3 (4)	C1—N5—C3—N4	-1.9 (4)
N2—O1—N1—C5	-0.6 (3)	C1—N5—C3—C4	177.5 (2)
N2—C4—C5—N3	-178.0 (2)	C2—N4—C3—N5	1.4 (4)
N2—C4—C5—N1	0.3 (3)	C2—N4—C3—C4	-178.0 (2)
N1—O1—N2—C4	0.8 (3)	C2—N6—C1—N5	1.7 (3)
C3—N4—C2—N6	0.9 (3)	C2—N6—C1—N7	-177.6 (2)

Table S10. Hydrogen bonds (Å, º) for **3**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3B···N6	0.88(3)	2.15(2)	3.012(3)	166(3)
N3—H3A···N5	0.89(2)	2.24(2)	2.872(3)	128(2)
N7—H7A···N1	0.87(2)	2.28(2)	3.113(3)	162(3)
N7—H7B···O1	0.88(3)	2.31(3)	3.191(3)	176(2)
N8—H8A···N3	0.87(2)	2.42(2)	3.232(3)	156(2)
N8—H8B···N4	0.90(2)	2.06(2)	2.959(3)	179(4)

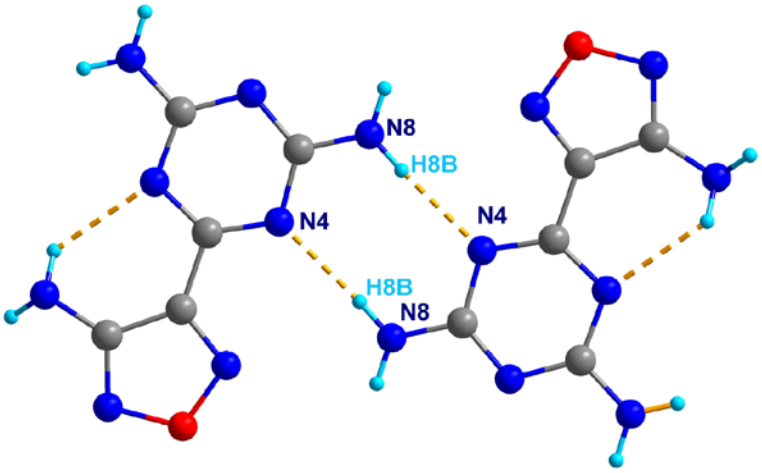


Fig. S2 The dimer of **3** formed through a pair of hydrogen bonds.

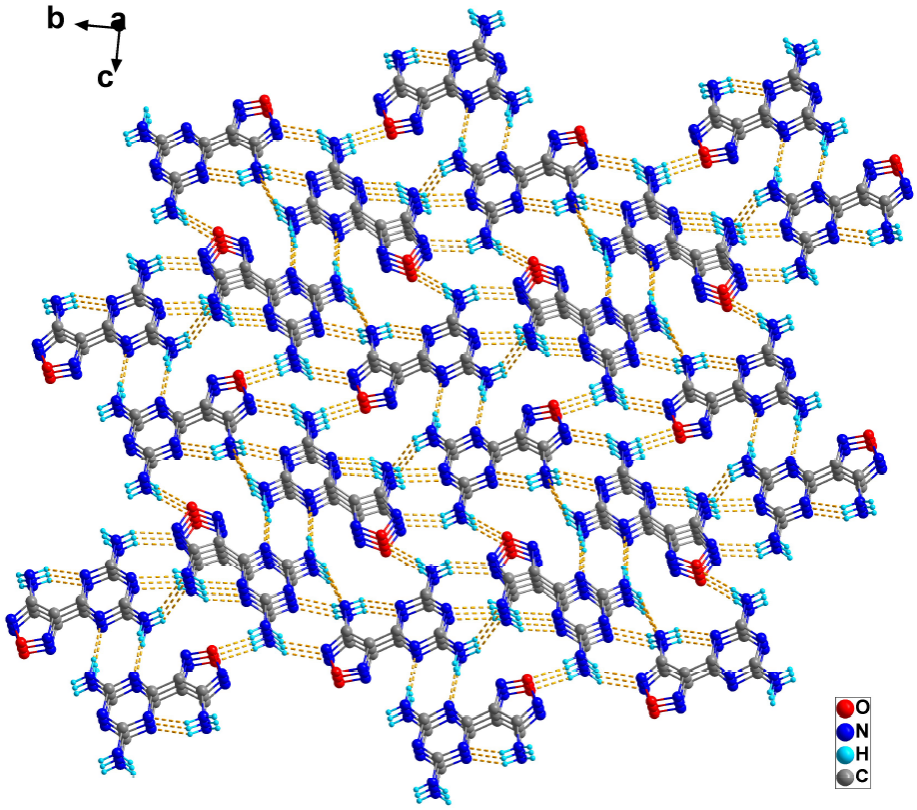


Fig. S3 Stacking diagram of **3** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

3. Single-crystal X-ray diffraction analysis of **4**

Table S11. Crystal data, data collection, and refinement for **4**

$C_6H_4N_8O_2$	$F(000)$ = 448
M_r = 220.17	D_x = 1.783 Mg m^{-3}

Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 9.522 (3) Å	Cell parameters from 1543 reflections
b = 4.7197 (17) Å	θ = 2.3–25.7°
c = 18.552 (6) Å	μ = 0.14 mm^{-1}
β = 100.397 (11)°	T = 170 K
V = 820.0 (5) Å^3	Needle, colourless
Z = 4	0.05 × 0.02 × 0.01 mm
Bruker D8 VENTURE diffractometer	1045 reflections with $I > 2\sigma(I)$
ϕ and ω scans	R_{int} = 0.071
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1689 before and 0.0631 after correction. The Ratio of minimum to maximum transmission is 0.8861. The $\lambda/2$ correction factor is Not present.	θ_{max} = 26.4°, θ_{min} = 2.2°
T_{min} = 0.661, T_{max} = 0.745	h = -11→11
5777 measured reflections	k = -5→5
1648 independent reflections	l = -21→23
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.050	All H-atom parameters refined
$wR(F^2)$ = 0.112	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.7014P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
1648 reflections	$\Delta\rangle_{max}$ = 0.30 e Å^{-3}
161 parameters	$\Delta\rangle_{min}$ = -0.28 e Å^{-3}
4 restraints	

Table S12. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **4**

	x	y	z	U_{iso}*/U_{eq}
O1	0.2682 (2)	0.1584 (4)	0.34493 (11)	0.0298 (5)
O2	0.3273 (2)	0.8715 (4)	0.73081 (11)	0.0319 (6)
N4	0.1544 (2)	0.7296 (5)	0.51553 (12)	0.0208 (6)
N3	0.3472 (2)	0.3779 (5)	0.52699 (12)	0.0241 (6)
N5	0.0041 (3)	0.8298 (5)	0.40639 (14)	0.0251 (6)
N1	0.1657 (3)	0.3691 (5)	0.34258 (13)	0.0266 (6)
N2	0.3521 (3)	0.1307 (5)	0.41486 (13)	0.0274 (6)
N7	0.4385 (3)	0.6737 (5)	0.74362 (13)	0.0274 (6)

N6	0.2554 (3)	0.8540 (5)	0.65989 (13)	0.0294 (6)
N8	0.5232 (3)	0.3282 (6)	0.67150 (15)	0.0303 (6)
C2	0.1864 (3)	0.4688 (6)	0.40965 (16)	0.0216 (7)
C1	0.1114 (3)	0.6847 (6)	0.44380 (15)	0.0202 (6)
C6	0.4322 (3)	0.5357 (6)	0.68196 (16)	0.0227 (7)
C4	0.2699 (3)	0.5794 (6)	0.55127 (15)	0.0229 (7)
C3	0.3001 (3)	0.3236 (6)	0.45416 (16)	0.0229 (7)
C5	0.3168 (3)	0.6525 (6)	0.62895 (15)	0.0231 (7)
H5A	-0.042 (3)	0.955 (6)	0.4300 (15)	0.038 (10)*
H5B	-0.016 (3)	0.803 (7)	0.3601 (10)	0.042 (10)*
H8A	0.506 (4)	0.244 (7)	0.6274 (12)	0.054 (12)*
H8B	0.580 (3)	0.245 (7)	0.7098 (15)	0.064 (13)*

Table S13. Atomic displacement parameters (Å^2) for **4**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0340 (12)	0.0305 (11)	0.0247 (12)	0.0034 (10)	0.0050 (10)	-0.0077 (10)
O2	0.0363 (12)	0.0382 (12)	0.0188 (11)	0.0074 (11)	-0.0016 (9)	-0.0047 (10)
N4	0.0208 (12)	0.0223 (12)	0.0174 (13)	0.0013 (10)	-0.0015 (10)	0.0008 (10)
N3	0.0252 (14)	0.0281 (14)	0.0190 (13)	0.0017 (11)	0.0035 (11)	-0.0002 (12)
N5	0.0284 (14)	0.0285 (14)	0.0167 (14)	0.0050 (12)	-0.0007 (12)	-0.0012 (12)
N1	0.0281 (14)	0.0252 (13)	0.0263 (14)	0.0045 (11)	0.0047 (11)	-0.0024 (12)
N2	0.0307 (14)	0.0315 (14)	0.0190 (13)	0.0025 (12)	0.0019 (11)	-0.0013 (12)
N7	0.0270 (14)	0.0312 (14)	0.0221 (14)	0.0049 (12)	-0.0006 (11)	0.0008 (12)
N6	0.0331 (15)	0.0376 (15)	0.0158 (13)	0.0040 (12)	-0.0002 (11)	-0.0008 (12)
N8	0.0299 (15)	0.0344 (15)	0.0245 (16)	0.0085 (13)	-0.0006 (13)	-0.0009 (14)
C2	0.0229 (15)	0.0195 (14)	0.0219 (17)	-0.0017 (12)	0.0032 (13)	0.0001 (13)
C1	0.0208 (15)	0.0223 (14)	0.0175 (15)	-0.0043 (12)	0.0034 (12)	0.0013 (12)
C6	0.0220 (15)	0.0238 (15)	0.0222 (16)	-0.0024 (13)	0.0038 (12)	0.0025 (13)
C4	0.0236 (15)	0.0248 (15)	0.0206 (16)	-0.0019 (13)	0.0051 (13)	0.0040 (13)
C3	0.0233 (16)	0.0230 (15)	0.0239 (17)	-0.0028 (13)	0.0081 (13)	-0.0011 (14)
C5	0.0248 (16)	0.0252 (15)	0.0190 (15)	0.0008 (14)	0.0036 (13)	0.0005 (13)

Table S14. Geometric parameters (Å, º) for **4**

O1—N1	1.388 (3)	N1—C2	1.311 (4)
O1—N2	1.401 (3)	N2—C3	1.317 (4)
O2—N7	1.399 (3)	N7—C6	1.308 (4)
O2—N6	1.372 (3)	N6—C5	1.303 (4)
N4—C1	1.337 (3)	N8—C6	1.345 (4)

N4—C4	1.374 (3)	N8—H8A	0.898 (18)
N3—C4	1.330 (4)	N8—H8B	0.902 (18)
N3—C3	1.369 (4)	C2—C1	1.454 (4)
N5—C1	1.319 (4)	C2—C3	1.415 (4)
N5—H5A	0.896 (18)	C6—C5	1.445 (4)
N5—H5B	0.855 (18)	C4—C5	1.471 (4)
N1—O1—N2	112.07 (19)	C3—C2—C1	118.0 (2)
N6—O2—N7	110.8 (2)	N4—C1—C2	117.3 (2)
C1—N4—C4	118.2 (2)	N5—C1—N4	120.7 (3)
C4—N3—C3	111.5 (2)	N5—C1—C2	122.0 (3)
C1—N5—H5A	119 (2)	N7—C6—N8	124.0 (3)
C1—N5—H5B	117 (2)	N7—C6—C5	108.3 (3)
H5A—N5—H5B	123 (3)	N8—C6—C5	127.6 (3)
C2—N1—O1	104.1 (2)	N4—C4—C5	115.3 (3)
C3—N2—O1	103.9 (2)	N3—C4—N4	130.5 (3)
C6—N7—O2	105.6 (2)	N3—C4—C5	114.3 (2)
C5—N6—O2	106.3 (2)	N3—C3—C2	124.4 (3)
C6—N8—H8A	116 (2)	N2—C3—N3	126.0 (3)
C6—N8—H8B	121 (2)	N2—C3—C2	109.6 (3)
H8A—N8—H8B	120 (3)	N6—C5—C6	109.0 (3)
N1—C2—C1	131.6 (3)	N6—C5—C4	121.5 (3)
N1—C2—C3	110.4 (3)	C6—C5—C4	129.5 (3)
O1—N1—C2—C1	-177.5 (3)	N7—O2—N6—C5	0.6 (3)
O1—N1—C2—C3	-0.1 (3)	N7—C6—C5—N6	-0.9 (3)
O1—N2—C3—N3	179.8 (3)	N7—C6—C5—C4	177.3 (3)
O1—N2—C3—C2	-0.1 (3)	N6—O2—N7—C6	-1.1 (3)
O2—N7—C6—N8	179.1 (3)	N8—C6—C5—N6	-178.7 (3)
O2—N7—C6—C5	1.2 (3)	N8—C6—C5—C4	-0.5 (5)
O2—N6—C5—C6	0.2 (3)	C1—N4—C4—N3	-3.5 (4)
O2—N6—C5—C4	-178.2 (2)	C1—N4—C4—C5	176.3 (3)
N4—C4—C5—N6	-2.6 (4)	C1—C2—C3—N3	-1.9 (4)
N4—C4—C5—C6	179.4 (3)	C1—C2—C3—N2	177.9 (2)
N3—C4—C5—N6	177.2 (3)	C4—N4—C1—N5	-177.8 (3)
N3—C4—C5—C6	-0.8 (4)	C4—N4—C1—C2	3.0 (4)
N1—O1—N2—C3	0.0 (3)	C4—N3—C3—N2	-178.1 (3)
N1—C2—C1—N4	176.6 (3)	C4—N3—C3—C2	1.7 (4)
N1—C2—C1—N5	-2.7 (5)	C3—N3—C4—N4	1.0 (4)

N1—C2—C3—N3	-179.7 (3)	C3—N3—C4—C5	-178.8 (2)
N1—C2—C3—N2	0.1 (3)	C3—C2—C1—N4	-0.6 (4)
N2—O1—N1—C2	0.1 (3)	C3—C2—C1—N5	-179.9 (3)

Table S15. Hydrogen bonds (Å, º) for **4**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5A···N4	0.90(3)	2.19(3)	3.081(4)	178(2)
N5—H5A···N6	0.90(3)	2.55(3)	2.958(4)	108(2)
N5—H5B···N7	0.855(19)	2.129(18)	2.971(4)	169(3)
N8—H8A···N3	0.90(2)	2.27(3)	2.903(4)	128(3)
N8—H8A···N2	0.90(2)	2.44(3)	3.059(4)	126(3)
N8—H8B···N1	0.90(3)	2.51(3)	3.351(4)	155(2)

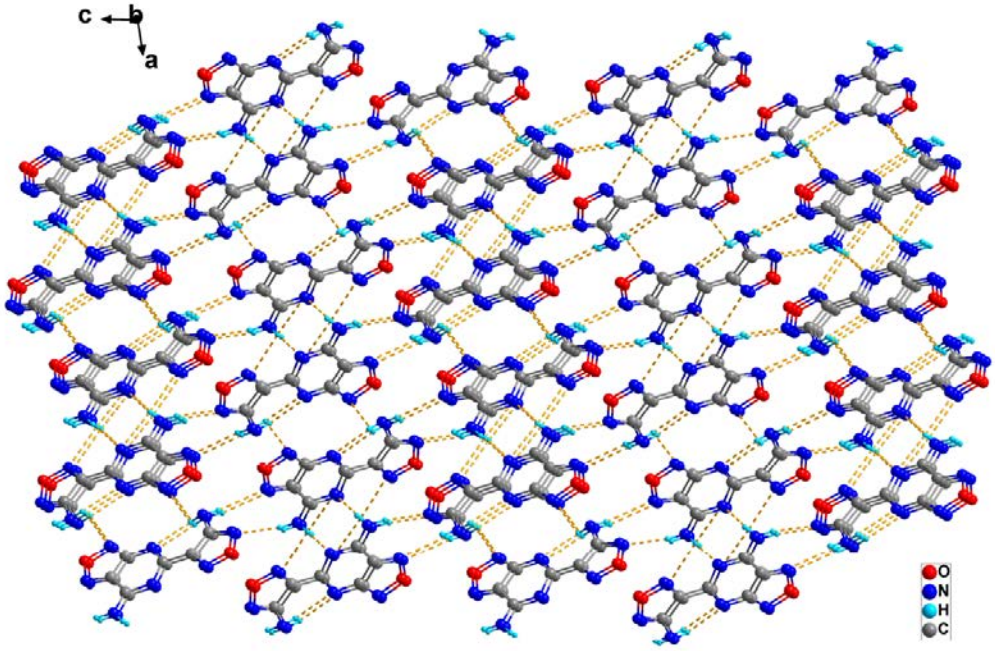


Fig. S4 Stacking diagram of **4** viewed down the *b* axis, yellow dotted lines indicate hydrogen bonding.

4. Single-crystal X-ray diffraction analysis of **5**·Diox

Table S16. Crystal data, data collection, and refinement for **5**·Diox

$C_6H_5N_9O·C_4H_8O_2$	Z = 2
M_r = 307.29	F(000) = 320
Triclinic, $P\bar{1}$	D_x = 1.445 Mg m^{-3}
a = 7.1990 (4) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 9.2561 (5) Å	Cell parameters from 5755 reflections

c = 11.4281 (5) Å	θ = 2.3–27.4°
α = 97.933 (2)°	μ = 0.11 mm^{-1}
β = 98.920 (1)°	T = 296 K
γ = 106.848 (2)°	Needle, yellow
V = 706.40 (6) Å^3	0.22 × 0.06 × 0.04 mm
Bruker D8 QUEST PHOTON 100 diffractometer	2516 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.036
ϕ and ω scans	θ_{max} = 27.6°, θ_{min} = 2.3°
Absorption correction: multi-scan *SADABS*	h = -9→9
T_{min} = 0.701, T_{max} = 0.746	k = -12→11
11062 measured reflections	l = -14→14
3241 independent reflections	
Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.0993P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.105	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rangle_{max}$ = 0.23 e Å^{-3}
3241 reflections	$\Delta\rangle_{min}$ = -0.15 e Å^{-3}
200 parameters	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.066 (14)

Table S17. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **5**·Diox

	x	y	z	U_{iso}*/U_{eq}
C1	0.6260 (3)	0.5375 (2)	0.11223 (14)	0.0641 (4)
H1A	0.600924	0.438294	0.136419	0.077*
H1B	0.726854	0.613286	0.175222	0.077*
C2	0.6986 (2)	0.5302 (2)	-0.00374 (16)	0.0676 (5)
H2A	0.731547	0.631012	-0.025243	0.081*
H2B	0.817761	0.500326	0.006544	0.081*
C3	0.3242 (2)	0.88612 (19)	0.94937 (15)	0.0632 (4)
H3A	0.309872	0.822637	1.010302	0.076*
H3B	0.208540	0.841942	0.884208	0.076*
C4	0.3332 (2)	1.0447 (2)	1.00296 (15)	0.0650 (4)

H4A	0.335523	1.106051	0.940559	0.078*
H4B	0.215654	1.040521	1.035728	0.078*
C5	1.0341 (2)	0.07061 (16)	0.67851 (12)	0.0455 (3)
C6	0.88024 (18)	0.14088 (15)	0.67465 (11)	0.0380 (3)
C7	0.64898 (17)	0.22199 (14)	0.61126 (10)	0.0347 (3)
C8	0.46523 (17)	0.24213 (13)	0.43309 (11)	0.0346 (3)
C9	0.30853 (17)	0.30166 (14)	0.38031 (11)	0.0363 (3)
C10	0.19694 (17)	0.38070 (14)	0.44275 (12)	0.0382 (3)
N1	0.84347 (17)	0.20404 (14)	0.77559 (10)	0.0488 (3)
N2	0.69367 (17)	0.25434 (14)	0.73238 (10)	0.0464 (3)
H2	0.634347	0.301116	0.776652	0.056*
N3	0.76654 (15)	0.14800 (12)	0.57098 (9)	0.0380 (3)
N4	0.50401 (14)	0.26789 (12)	0.55091 (9)	0.0372 (3)
N5	0.54806 (15)	0.17115 (13)	0.35779 (9)	0.0425 (3)
H5A	0.639936	0.135327	0.385628	0.051*
H5B	0.509914	0.160936	0.281121	0.051*
N6	0.21598 (17)	0.41700 (14)	0.56264 (10)	0.0520 (3)
H6A	0.143720	0.466131	0.592057	0.062*
H6B	0.300463	0.391156	0.610149	0.062*
N7	1.1577 (2)	0.01708 (18)	0.68442 (12)	0.0673 (4)
N8	0.25257 (17)	0.28997 (15)	0.26538 (11)	0.0516 (3)
N9	0.07348 (17)	0.41458 (14)	0.36326 (10)	0.0490 (3)
O1	0.55102 (17)	0.42229 (13)	-0.09759 (10)	0.0620 (3)
O2	0.49591 (17)	0.88517 (13)	0.90441 (9)	0.0620 (3)
O3	0.10776 (15)	0.35835 (13)	0.25082 (9)	0.0584 (3)

Table S18. Atomic displacement parameters (Å^2) for **5**·Diox

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0727 (10)	0.0709 (11)	0.0479 (9)	0.0284 (9)	0.0117 (7)	-0.0025 (8)
C2	0.0613 (9)	0.0767 (11)	0.0658 (11)	0.0265 (9)	0.0246 (8)	-0.0061 (9)
C3	0.0647 (10)	0.0656 (11)	0.0494 (9)	0.0149 (8)	0.0037 (7)	-0.0001 (8)
C4	0.0676 (10)	0.0818 (12)	0.0483 (9)	0.0374 (9)	0.0054 (8)	-0.0005 (8)
C5	0.0494 (7)	0.0564 (8)	0.0377 (7)	0.0277 (7)	0.0101 (6)	0.0070 (6)
C6	0.0406 (6)	0.0432 (7)	0.0349 (7)	0.0208 (5)	0.0093 (5)	0.0054 (5)
C7	0.0388 (6)	0.0380 (6)	0.0310 (6)	0.0171 (5)	0.0117 (5)	0.0031 (5)
C8	0.0341 (6)	0.0359 (6)	0.0355 (7)	0.0136 (5)	0.0100 (5)	0.0038 (5)
C9	0.0342 (6)	0.0386 (7)	0.0363 (7)	0.0139 (5)	0.0074 (5)	0.0033 (5)
C10	0.0330 (6)	0.0394 (7)	0.0440 (7)	0.0145 (5)	0.0095 (5)	0.0061 (5)
N1	0.0548 (7)	0.0653 (8)	0.0354 (6)	0.0352 (6)	0.0090 (5)	0.0054 (5)

N2	0.0546 (6)	0.0628 (7)	0.0331 (6)	0.0368 (6)	0.0127 (5)	0.0027 (5)
N3	0.0416 (5)	0.0453 (6)	0.0334 (6)	0.0232 (5)	0.0112 (4)	0.0038 (5)
N4	0.0397 (5)	0.0447 (6)	0.0336 (6)	0.0223 (5)	0.0108 (4)	0.0053 (4)
N5	0.0476 (6)	0.0554 (7)	0.0319 (6)	0.0298 (5)	0.0092 (4)	0.0029 (5)
N6	0.0569 (7)	0.0717 (8)	0.0426 (7)	0.0421 (6)	0.0155 (5)	0.0080 (6)
N7	0.0704 (8)	0.0941 (11)	0.0579 (8)	0.0562 (8)	0.0151 (7)	0.0151 (7)
N8	0.0509 (7)	0.0682 (8)	0.0421 (7)	0.0342 (6)	0.0046 (5)	0.0044 (6)
N9	0.0453 (6)	0.0606 (7)	0.0473 (7)	0.0288 (5)	0.0082 (5)	0.0065 (6)
O1	0.0757 (7)	0.0645 (7)	0.0515 (6)	0.0327 (6)	0.0270 (5)	-0.0083 (5)
O2	0.0764 (7)	0.0712 (7)	0.0365 (5)	0.0315 (6)	0.0070 (5)	-0.0079 (5)
O3	0.0579 (6)	0.0810 (8)	0.0442 (6)	0.0413 (6)	0.0020 (5)	0.0060 (5)

Table S19. Geometric parameters (Å, º) for **5**·Diox

C1—O1^{i}	1.4204 (19)	C7—N3	1.3292 (15)
C1—C2	1.498 (2)	C7—N2	1.3420 (16)
C1—H1A	0.9700	C7—N4	1.3638 (15)
C1—H1B	0.9700	C8—N4	1.3054 (16)
C2—O1	1.419 (2)	C8—N5	1.3258 (15)
C2—H2A	0.9700	C8—C9	1.4769 (16)
C2—H2B	0.9700	C9—N8	1.2925 (17)
C3—O2	1.412 (2)	C9—C10	1.4367 (16)
C3—C4	1.490 (2)	C10—N9	1.3051 (17)
C3—H3A	0.9700	C10—N6	1.3406 (17)
C3—H3B	0.9700	N1—N2	1.3464 (14)
C4—O2^{ii}	1.4138 (19)	N2—H2	0.8600
C4—H4A	0.9700	N5—H5A	0.8600
C4—H4B	0.9700	N5—H5B	0.8600
C5—N7	1.1349 (17)	N6—H6A	0.8600
C5—C6	1.4360 (17)	N6—H6B	0.8600
C6—N1	1.3193 (16)	N8—O3	1.3685 (14)
C6—N3	1.3528 (16)	N9—O3	1.4040 (15)
O1^{i}—C1—C2	110.13 (14)	N3—C7—N4	131.05 (11)
O1^{i}—C1—H1A	109.6	N2—C7—N4	119.69 (10)
C2—C1—H1A	109.6	N4—C8—N5	128.35 (11)
O1^{i}—C1—H1B	109.6	N4—C8—C9	113.97 (10)
C2—C1—H1B	109.6	N5—C8—C9	117.68 (11)
H1A—C1—H1B	108.1	N8—C9—C10	109.12 (11)
O1—C2—C1	110.37 (14)	N8—C9—C8	122.99 (11)

O1—C2—H2A	109.6	C10—C9—C8	127.88 (11)
C1—C2—H2A	109.6	N9—C10—N6	124.70 (11)
O1—C2—H2B	109.6	N9—C10—C9	108.75 (11)
C1—C2—H2B	109.6	N6—C10—C9	126.54 (11)
H2A—C2—H2B	108.1	C6—N1—N2	101.19 (10)
O2—C3—C4	111.78 (14)	C7—N2—N1	111.20 (10)
O2—C3—H3A	109.3	C7—N2—H2	124.4
C4—C3—H3A	109.3	N1—N2—H2	124.4
O2—C3—H3B	109.3	C7—N3—C6	102.26 (10)
C4—C3—H3B	109.3	C8—N4—C7	119.97 (10)
H3A—C3—H3B	107.9	C8—N5—H5A	120.0
O2^{ii}—C4—C3	110.82 (13)	C8—N5—H5B	120.0
O2^{ii}—C4—H4A	109.5	H5A—N5—H5B	120.0
C3—C4—H4A	109.5	C10—N6—H6A	120.0
O2^{ii}—C4—H4B	109.5	C10—N6—H6B	120.0
C3—C4—H4B	109.5	H6A—N6—H6B	120.0
H4A—C4—H4B	108.1	C9—N8—O3	106.44 (10)
N7—C5—C6	178.28 (15)	C10—N9—O3	105.06 (10)
N1—C6—N3	116.09 (11)	C2—O1—C1^{i}	110.33 (11)
N1—C6—C5	120.32 (11)	C3—O2—C4^{ii}	110.05 (12)
N3—C6—C5	123.59 (11)	N8—O3—N9	110.62 (9)
N3—C7—N2	109.25 (10)		
O1^{i}—C1—C2—O1	-57.93 (19)	N4—C7—N3—C6	178.36 (13)
O2—C3—C4—O2^{ii}	-56.85 (19)	N1—C6—N3—C7	-0.03 (15)
N4—C8—C9—N8	178.55 (12)	C5—C6—N3—C7	-179.67 (12)
N5—C8—C9—N8	-1.34 (18)	N5—C8—N4—C7	1.4 (2)
N4—C8—C9—C10	-0.67 (18)	C9—C8—N4—C7	-178.49 (10)
N5—C8—C9—C10	179.45 (12)	N3—C7—N4—C8	-1.3 (2)
N8—C9—C10—N9	0.43 (15)	N2—C7—N4—C8	177.29 (12)
C8—C9—C10—N9	179.73 (12)	C10—C9—N8—O3	-0.18 (15)
N8—C9—C10—N6	-178.61 (13)	C8—C9—N8—O3	-179.53 (11)
C8—C9—C10—N6	0.7 (2)	N6—C10—N9—O3	178.60 (12)
N3—C6—N1—N2	0.39 (16)	C9—C10—N9—O3	-0.46 (14)
C5—C6—N1—N2	-179.95 (12)	C1—C2—O1—C1^{i}	58.1 (2)
N3—C7—N2—N1	0.64 (15)	C4—C3—O2—C4^{ii}	56.42 (19)
N4—C7—N2—N1	-178.25 (11)	C9—N8—O3—N9	-0.11 (15)
C6—N1—N2—C7	-0.61 (15)	C10—N9—O3—N8	0.37 (14)
N2—C7—N3—C6	-0.36 (14)		

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*; (ii) -*x*+1, -*y*+2, -*z*+2.

Table S20. Hydrogen bonds (Å, º) for **5**·Diox

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*B*···N4	0.86	2.23	2.8136 (14)	125
N6—H6*A*···N9^{iii}	0.86	2.24	3.0912 (15)	170
N5—H5*B*···O2^{iv}	0.86	2.10	2.9206 (14)	161
N5—H5*A*···N7^{v}	0.86	2.45	3.1590 (16)	140
N5—H5*A*···N3	0.86	2.15	2.7580 (15)	128
N2—H2···O1^{vi}	0.86	1.97	2.8210 (14)	168
C3—H3*B*···O3^{iii}	0.97	2.58	3.5084 (19)	159

Symmetry codes: (iii) -*x*, -*y*+1, -*z*+1; (iv) -*x*+1, -*y*+1, -*z*+1; (v) -*x*+2, -*y*, -*z*+1; (vi) *x*, *y*, *z*+1.

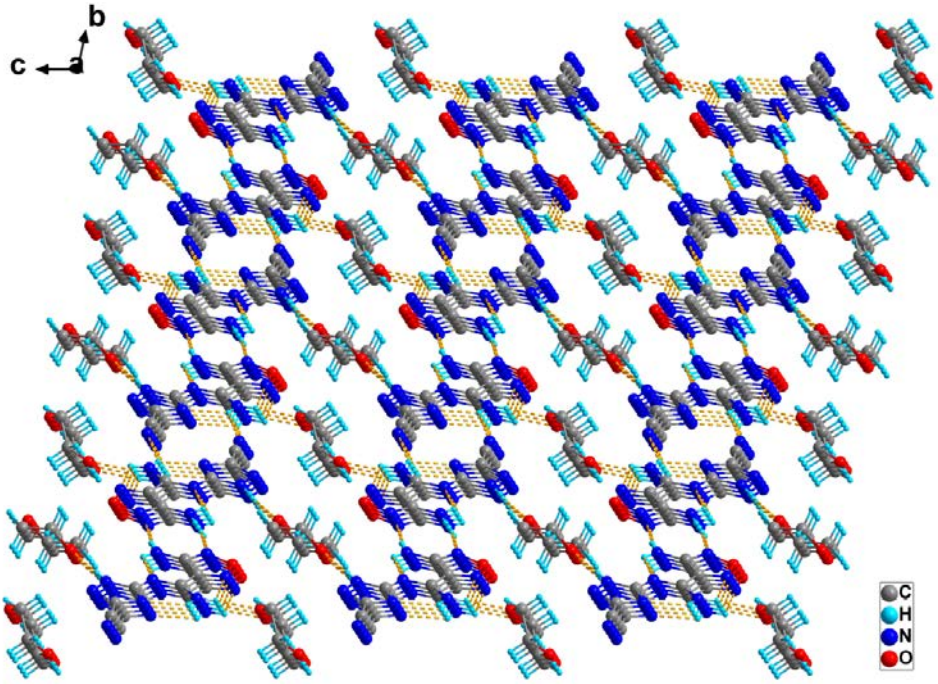


Fig. S5 Stacking diagram of **5**·Diox viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

5. Single-crystal X-ray diffraction analysis of **6**

Table S21. Crystal data, data collection, and refinement for **6**

$C_6H_5N_9O$	$F(000)$ = 448
M_r = 219.19	D_x = 1.643 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å

a = 6.8621 (15) Å	Cell parameters from 3574 reflections
b = 20.664 (4) Å	θ = 3.3–27.4°
c = 6.9785 (15) Å	μ = 0.13 mm^{-1}
β = 116.407 (6)°	T = 296 K
V = 886.3 (3) $Å^3$	Block, yellow
Bruker D8 QUEST PHOTON 100 diffractometer	1391 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.049
ϕ and ω scans	θ_{max} = 27.6°, θ_{min} = 2.0°
Absorption correction: multi-scan *SADABS*	h = -7→8
T_{min} = 0.568, T_{max} = 0.746	k = -26→26
7858 measured reflections	l = -9→7
2023 independent reflections	
Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.057	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.165	$w = 1/[\sigma^2(F_o^2) + (0.0958P)^2 + 0.1234P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max} < 0.001$
2023 reflections	$\Delta\rangle_{max}$ = 0.34 e $Å^{-3}$
151 parameters	$\Delta\rangle_{min}$ = -0.37 e $Å^{-3}$

Table S22. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for **6**

	x	y	z	U_{iso}*/U_{eq}
C1	0.2633 (3)	0.49209 (10)	0.5228 (3)	0.0284 (5)
C2	0.2285 (3)	0.55966 (10)	0.4636 (3)	0.0283 (5)
C3	0.1195 (4)	0.57301 (10)	0.2411 (4)	0.0345 (5)
C4	0.2999 (3)	0.60858 (10)	0.6151 (3)	0.0290 (5)
C5	0.2646 (3)	0.67726 (10)	0.5489 (3)	0.0294 (5)
C6	0.4150 (3)	0.73036 (10)	0.6274 (4)	0.0320 (5)
N1	0.3632 (3)	0.46783 (9)	0.7183 (3)	0.0363 (5)
N2	0.3598 (3)	0.40241 (9)	0.6935 (3)	0.0407 (5)
N3	0.2644 (3)	0.38705 (9)	0.4948 (3)	0.0392 (5)
N4	0.2024 (3)	0.44273 (8)	0.3844 (3)	0.0334 (5)
H4	0.134713	0.446069	0.247428	0.040*
N5	0.0302 (4)	0.57770 (10)	0.0606 (3)	0.0525 (6)

N6	0.4074 (3)	0.59810 (9)	0.8235 (3)	0.0407 (5)
H6A	0.436467	0.559172	0.871462	0.049*
H6B	0.448143	0.630229	0.910977	0.049*
N7	0.3143 (3)	0.78262 (9)	0.5291 (3)	0.0405 (5)
N8	0.0790 (3)	0.69810 (9)	0.4067 (3)	0.0384 (5)
N9	0.6225 (3)	0.72976 (11)	0.7811 (4)	0.0452 (6)
H9A	0.708 (4)	0.7688 (13)	0.807 (4)	0.054*
H9B	0.696 (4)	0.6938 (14)	0.803 (4)	0.054*
O1	0.1036 (3)	0.76330 (7)	0.3909 (3)	0.0444 (5)

Table S23. Atomic displacement parameters (Å^2) for **6**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0324 (11)	0.0223 (10)	0.0305 (11)	-0.0022 (8)	0.0139 (9)	-0.0024 (8)
C2	0.0347 (11)	0.0205 (10)	0.0278 (11)	-0.0003 (8)	0.0122 (9)	0.0011 (8)
C3	0.0452 (13)	0.0204 (11)	0.0351 (13)	-0.0046 (9)	0.0152 (11)	-0.0032 (9)
C4	0.0320 (11)	0.0225 (11)	0.0309 (11)	-0.0011 (8)	0.0127 (9)	0.0001 (8)
C5	0.0364 (12)	0.0213 (10)	0.0298 (11)	-0.0018 (8)	0.0141 (10)	-0.0012 (8)
C6	0.0371 (12)	0.0229 (11)	0.0396 (12)	-0.0029 (8)	0.0203 (11)	-0.0021 (9)
N1	0.0497 (12)	0.0223 (10)	0.0327 (10)	-0.0001 (8)	0.0145 (9)	0.0007 (7)
N2	0.0561 (13)	0.0206 (10)	0.0405 (11)	0.0012 (8)	0.0170 (10)	0.0017 (8)
N3	0.0533 (12)	0.0196 (9)	0.0411 (11)	0.0001 (8)	0.0177 (9)	0.0001 (8)
N4	0.0455 (11)	0.0219 (9)	0.0283 (9)	-0.0009 (8)	0.0124 (8)	-0.0005 (7)
N5	0.0769 (16)	0.0356 (12)	0.0305 (13)	-0.0062 (10)	0.0107 (11)	-0.0011 (9)
N6	0.0641 (13)	0.0204 (9)	0.0274 (10)	-0.0008 (9)	0.0111 (9)	-0.0021 (7)
N7	0.0439 (12)	0.0221 (10)	0.0557 (13)	-0.0020 (8)	0.0224 (10)	0.0031 (8)
N8	0.0402 (11)	0.0236 (10)	0.0459 (12)	-0.0023 (8)	0.0142 (9)	0.0047 (8)
N9	0.0374 (12)	0.0313 (12)	0.0597 (14)	-0.0037 (8)	0.0151 (11)	-0.0050 (9)
O1	0.0449 (10)	0.0238 (9)	0.0572 (11)	0.0028 (7)	0.0160 (9)	0.0107 (7)

Table S24. Geometric parameters (Å, º) for **6**

C1—N1	1.323 (3)	C6—N9	1.349 (3)
C1—N4	1.337 (3)	N1—N2	1.362 (3)
C1—C2	1.445 (3)	N2—N3	1.283 (3)
C2—C4	1.385 (3)	N3—N4	1.344 (3)
C2—C3	1.419 (3)	N4—H4	0.8600
C3—N5	1.133 (3)	N6—H6A	0.8600
C4—N6	1.324 (3)	N6—H6B	0.8600
C4—C5	1.479 (3)	N7—O1	1.393 (3)

C5—N8	1.292 (3)	N8—O1	1.368 (2)
C5—C6	1.438 (3)	N9—H9A	0.97 (3)
C6—N7	1.301 (3)	N9—H9B	0.87 (3)
N1—C1—N4	107.91 (19)	C1—N1—N2	105.89 (17)
N1—C1—C2	127.20 (19)	N3—N2—N1	110.75 (17)
N4—C1—C2	124.87 (19)	N2—N3—N4	106.68 (17)
C4—C2—C3	121.91 (19)	C1—N4—N3	108.77 (18)
C4—C2—C1	121.99 (19)	C1—N4—H4	125.6
C3—C2—C1	116.10 (18)	N3—N4—H4	125.6
N5—C3—C2	173.7 (2)	C4—N6—H6A	120.0
N6—C4—C2	123.65 (19)	C4—N6—H6B	120.0
N6—C4—C5	115.72 (18)	H6A—N6—H6B	120.0
C2—C4—C5	120.60 (19)	C6—N7—O1	105.77 (17)
N8—C5—C6	109.50 (19)	C5—N8—O1	105.99 (16)
N8—C5—C4	121.91 (19)	C6—N9—H9A	118.7 (16)
C6—C5—C4	128.57 (19)	C6—N9—H9B	117.9 (18)
N7—C6—N9	123.5 (2)	H9A—N9—H9B	115 (3)
N7—C6—C5	108.0 (2)	N8—O1—N7	110.70 (15)
N9—C6—C5	128.4 (2)		
N1—C1—C2—C4	-0.3 (3)	C4—C5—C6—N9	-0.7 (4)
N4—C1—C2—C4	-178.60 (19)	N4—C1—N1—N2	-0.3 (2)
N1—C1—C2—C3	178.9 (2)	C2—C1—N1—N2	-178.79 (19)
N4—C1—C2—C3	0.6 (3)	C1—N1—N2—N3	0.3 (2)
C3—C2—C4—N6	-178.1 (2)	N1—N2—N3—N4	-0.2 (2)
C1—C2—C4—N6	1.1 (3)	N1—C1—N4—N3	0.2 (2)
C3—C2—C4—C5	-0.1 (3)	C2—C1—N4—N3	178.75 (18)
C1—C2—C4—C5	179.06 (18)	N2—N3—N4—C1	0.0 (2)
N6—C4—C5—N8	-135.6 (2)	N9—C6—N7—O1	-177.6 (2)
C2—C4—C5—N8	46.2 (3)	C5—C6—N7—O1	0.1 (2)
N6—C4—C5—C6	42.5 (3)	C6—C5—N8—O1	-0.3 (2)
C2—C4—C5—C6	-135.6 (2)	C4—C5—N8—O1	178.15 (18)
N8—C5—C6—N7	0.1 (3)	C5—N8—O1—N7	0.4 (2)
C4—C5—C6—N7	-178.2 (2)	C6—N7—O1—N8	-0.4 (2)
N8—C5—C6—N9	177.7 (2)		

Table S25. Hydrogen bonds (Å, º) for **6**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N5^{i}	0.86	1.99	2.822 (3)	161
N6—H6*A*···N1	0.86	2.12	2.771 (3)	133
N6—H6*A*···N1^{ii}	0.86	2.63	3.175 (3)	123
N6—H6*B*···N2^{ii}	0.86	2.56	3.020 (3)	114
N6—H6*B*···N7^{iii}	0.86	2.33	3.059 (3)	142
N9—H9*A*···N8^{iv}	0.97 (3)	2.42 (3)	3.219 (3)	140 (2)

Symmetry codes: (i) -*x*, -*y*+1, -*z*; (ii) -*x*+1, -*y*+1, -*z*+2; (iii) *x*, -*y*+3/2, *z*+1/2; (iv) *x*+1, -*y*+3/2, *z*+1/2.

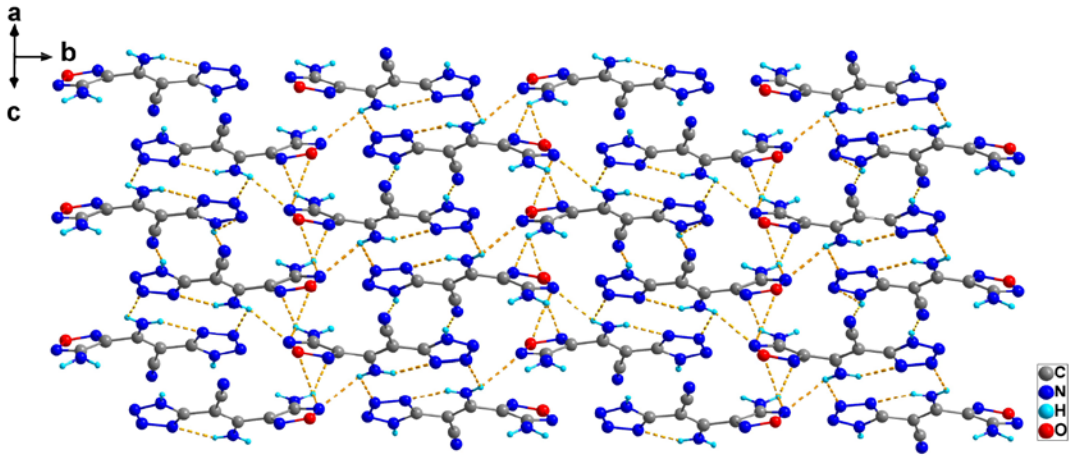


Fig. S6 Stacking diagram of **6**, yellow dotted lines indicate hydrogen bonding.

6. Single-crystal X-ray diffraction analysis of **9**

Table S26. Crystal data, data collection, and refinement for **9**

$C_6H_2N_{10}O_2$	$F(000)$ = 496
M_r = 246.18	D_x = 1.852 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 6.8409 (5) Å	Cell parameters from 3058 reflections
b = 6.1690 (5) Å	θ = 3.0–27.1°
c = 20.9286 (18) Å	μ = 0.15 mm^{-1}
β = 91.363 (3)°	T = 296 K
V = 882.97 (12) Å^3	Block, yellow
Z = 4	0.15 × 0.12 × 0.05 mm
Bruker D8 QUEST PHOTON 100 diffractometer	1398 reflections with $I > 2\sigma(I)$

Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.043
ϕ and ω scans	θ_{max} = 27.4°, θ_{min} = 3.0°
Absorption correction: multi-scan *SADABS*	h = -8→6
T_{min} = 0.586, T_{max} = 0.746	k = -7→7
7586 measured reflections	l = -20→27
1985 independent reflections	
Refinement on F^2	1 restraint
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.048	H-atom parameters constrained
$wR(F^2)$ = 0.134	$w = 1/[\sigma^2(F_o^2) + (0.0816P)^2 + 0.0196P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
1985 reflections	$\Delta\rangle_{max}$ = 0.25 e $Å^{-3}$
163 parameters	$\Delta\rangle_{min}$ = -0.28 e $Å^{-3}$

Table S27. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for **9**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3904 (3)	-0.1003 (3)	0.43901 (8)	0.0274 (4)
C2	0.5283 (2)	-0.0032 (3)	0.39846 (8)	0.0271 (4)
C3	0.4796 (2)	0.1993 (3)	0.36818 (8)	0.0243 (4)
C4	0.2938 (2)	0.2808 (3)	0.38101 (8)	0.0241 (4)
C5	0.1675 (3)	0.1705 (3)	0.42750 (8)	0.0269 (4)
C6	0.2501 (2)	0.4711 (3)	0.34702 (8)	0.0243 (4)
N1	0.4605 (3)	-0.2847 (3)	0.46051 (8)	0.0371 (4)
N2	0.6835 (2)	-0.1256 (3)	0.39470 (8)	0.0363 (4)
N3	0.2142 (2)	-0.0173 (2)	0.45418 (7)	0.0305 (4)
N4	0.0019 (2)	0.2616 (3)	0.44472 (7)	0.0381 (4)
H4A	-0.070340	0.198695	0.472213	0.046*
H4B	-0.033534	0.383846	0.428425	0.046*
N5	0.6108 (2)	0.2920 (2)	0.33033 (7)	0.0285 (4)
N6	0.5515 (2)	0.4738 (2)	0.30228 (7)	0.0278 (4)
N7	0.3746 (2)	0.5673 (2)	0.30799 (7)	0.0285 (4)
N8	0.0690 (2)	0.5681 (2)	0.35351 (7)	0.0315 (4)
N9	0.0436 (2)	0.7363 (3)	0.31913 (8)	0.0331 (4)
N10	-0.0017 (3)	0.8841 (3)	0.29282 (9)	0.0512 (5)
O1	0.6438 (2)	-0.3017 (2)	0.43288 (6)	0.0404 (4)

O2	0.66682 (18)	0.5697 (2)	0.26744 (6)	0.0403 (4)

Table S28. Atomic displacement parameters (Å^2) for **9**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0341 (10)	0.0222 (10)	0.0260 (9)	-0.0014 (8)	0.0001 (7)	-0.0008 (8)
C2	0.0277 (10)	0.0256 (10)	0.0281 (9)	0.0014 (8)	-0.0001 (7)	-0.0049 (8)
C3	0.0245 (9)	0.0255 (10)	0.0230 (9)	-0.0015 (7)	0.0011 (7)	-0.0027 (7)
C4	0.0222 (9)	0.0242 (10)	0.0261 (9)	-0.0030 (7)	0.0024 (7)	-0.0011 (7)
C5	0.0253 (10)	0.0280 (10)	0.0274 (9)	-0.0029 (8)	0.0024 (7)	0.0019 (8)
C6	0.0213 (9)	0.0254 (10)	0.0264 (9)	-0.0024 (7)	0.0012 (7)	-0.0008 (7)
N1	0.0421 (10)	0.0286 (10)	0.0408 (9)	0.0036 (8)	0.0023 (7)	0.0023 (7)
N2	0.0372 (10)	0.0322 (10)	0.0394 (9)	0.0068 (8)	0.0005 (7)	-0.0001 (7)
N3	0.0299 (9)	0.0274 (9)	0.0344 (9)	-0.0017 (7)	0.0059 (7)	0.0053 (7)
N4	0.0290 (9)	0.0393 (10)	0.0466 (10)	0.0059 (8)	0.0164 (7)	0.0163 (8)
N5	0.0244 (8)	0.0323 (9)	0.0290 (8)	0.0011 (7)	0.0030 (6)	0.0022 (7)
N6	0.0225 (8)	0.0334 (9)	0.0277 (8)	-0.0015 (7)	0.0034 (6)	0.0023 (7)
N7	0.0221 (8)	0.0322 (9)	0.0312 (8)	0.0009 (7)	0.0037 (6)	0.0040 (7)
N8	0.0245 (8)	0.0316 (9)	0.0384 (9)	0.0035 (7)	0.0062 (7)	0.0117 (7)
N9	0.0209 (8)	0.0357 (10)	0.0429 (9)	0.0007 (7)	0.0070 (6)	0.0081 (8)
N10	0.0331 (10)	0.0514 (12)	0.0697 (13)	0.0090 (9)	0.0124 (8)	0.0284 (11)
O1	0.0441 (9)	0.0314 (8)	0.0457 (8)	0.0117 (6)	0.0012 (6)	0.0022 (6)
O2	0.0273 (7)	0.0510 (9)	0.0431 (8)	-0.0044 (7)	0.0128 (6)	0.0154 (7)

Table S29. Geometric parameters (Å, º) for **9**

C1—N1	1.310 (2)	C6—N7	1.333 (2)
C1—N3	1.355 (2)	C6—N8	1.385 (2)
C1—C2	1.417 (2)	N1—O1	1.397 (2)
C2—N2	1.307 (2)	N2—O1	1.379 (2)
C2—C3	1.436 (2)	N4—H4A	0.8600
C3—N5	1.340 (2)	N4—H4B	0.8600
C3—C4	1.399 (2)	N5—N6	1.3252 (19)
C4—C6	1.402 (2)	N6—O2	1.2376 (18)
C4—C5	1.482 (2)	N6—N7	1.3483 (19)
C5—N3	1.321 (2)	N8—N9	1.272 (2)
C5—N4	1.323 (2)	N9—N10	1.105 (2)
N1—C1—N3	124.65 (17)	N7—C6—C4	123.50 (16)
N1—C1—C2	109.22 (17)	N8—C6—C4	119.52 (15)

N3—C1—C2	126.13 (16)	C1—N1—O1	104.36 (14)
N2—C2—C1	110.19 (17)	C2—N2—O1	104.43 (15)
N2—C2—C3	131.04 (17)	C5—N3—C1	116.08 (15)
C1—C2—C3	118.76 (16)	C5—N4—H4A	120.0
N5—C3—C4	125.82 (17)	C5—N4—H4B	120.0
N5—C3—C2	118.70 (15)	H4A—N4—H4B	120.0
C4—C3—C2	115.48 (15)	N6—N5—C3	114.86 (14)
C3—C4—C6	112.80 (15)	O2—N6—N5	118.20 (14)
C3—C4—C5	120.51 (16)	O2—N6—N7	115.72 (14)
C6—C4—C5	126.68 (15)	N5—N6—N7	126.08 (14)
N3—C5—N4	117.22 (16)	C6—N7—N6	116.87 (15)
N3—C5—C4	122.77 (16)	N9—N8—C6	114.03 (14)
N4—C5—C4	120.01 (16)	N10—N9—N8	170.80 (18)
N7—C6—N8	116.98 (15)	N2—O1—N1	111.81 (13)
N1—C1—C2—N2	-0.1 (2)	N3—C1—N1—O1	-179.50 (15)
N3—C1—C2—N2	179.35 (15)	C2—C1—N1—O1	-0.03 (19)
N1—C1—C2—C3	178.56 (15)	C1—C2—N2—O1	0.19 (19)
N3—C1—C2—C3	-2.0 (3)	C3—C2—N2—O1	-178.26 (17)
N2—C2—C3—N5	-2.3 (3)	N4—C5—N3—C1	-175.77 (15)
C1—C2—C3—N5	179.36 (15)	C4—C5—N3—C1	3.1 (3)
N2—C2—C3—C4	177.00 (17)	N1—C1—N3—C5	-179.58 (17)
C1—C2—C3—C4	-1.3 (2)	C2—C1—N3—C5	1.1 (3)
N5—C3—C4—C6	3.0 (3)	C4—C3—N5—N6	-1.8 (3)
C2—C3—C4—C6	-176.21 (14)	C2—C3—N5—N6	177.44 (14)
N5—C3—C4—C5	-175.59 (15)	C3—N5—N6—O2	178.88 (15)
C2—C3—C4—C5	5.2 (2)	C3—N5—N6—N7	-1.0 (2)
C3—C4—C5—N3	-6.5 (3)	N8—C6—N7—N6	179.31 (13)
C6—C4—C5—N3	175.09 (16)	C4—C6—N7—N6	-0.6 (3)
C3—C4—C5—N4	172.35 (15)	O2—N6—N7—C6	-177.74 (14)
C6—C4—C5—N4	-6.1 (3)	N5—N6—N7—C6	2.2 (2)
C3—C4—C6—N7	-1.7 (2)	N7—C6—N8—N9	1.9 (2)
C5—C4—C6—N7	176.80 (16)	C4—C6—N8—N9	-178.15 (15)
C3—C4—C6—N8	178.37 (14)	C2—N2—O1—N1	-0.22 (18)
C5—C4—C6—N8	-3.1 (3)	C1—N1—O1—N2	0.16 (18)

Table S30. Hydrogen bonds (Å, º) for **9**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4B···N8	0.86	2.07	2.733 (2)	133

N4—H4A···N3^{i}	0.86	2.16	3.014 (2)	172

Symmetry code: (i) -*x*, -*y*, -*z*+1.

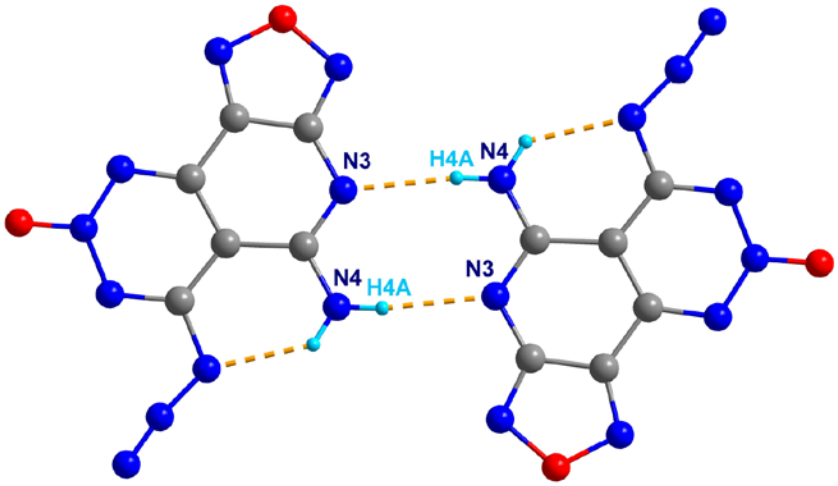


Fig. S7 The dimer of **9** formed through a pair of hydrogen bonds.

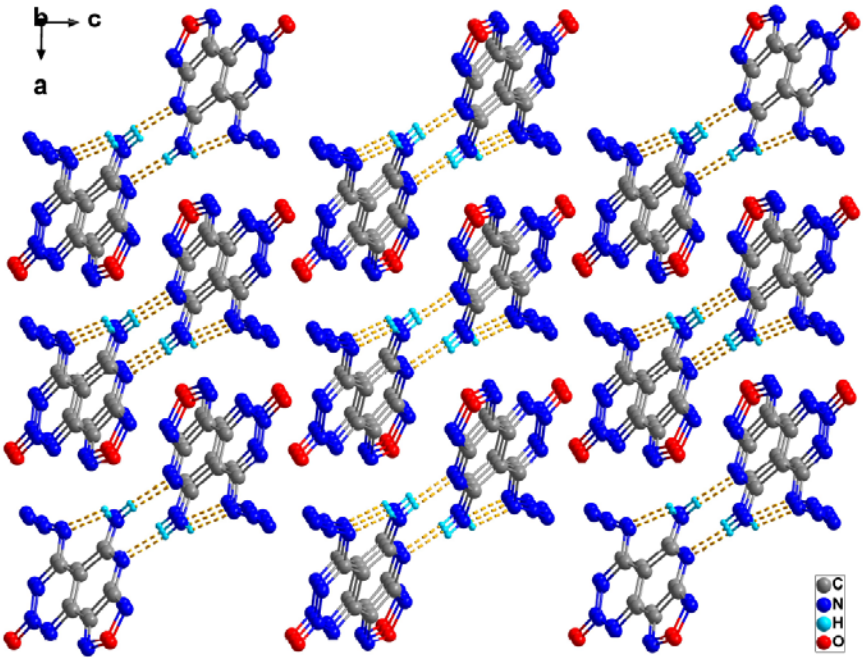


Fig. S8 Stacking diagram of **9** viewed down the *b* axis, yellow dotted lines indicate hydrogen bonding.

7. Single-crystal X-ray diffraction analysis of **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$

Table S31. Crystal data, data collection, and refinement for **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$

$C_5H_6N_9O_3 \cdot 2(NO_3) \cdot HNO_3 \cdot H_5O_2$	$Z = 2$
$M_r = 464.27$	$F(000) = 476$
Triclinic, $P\bar{1}$	$D_x = 1.788$ Mg m^{-3}
$a = 8.3729$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.7694$ (6) Å	Cell parameters from 4856 reflections
$c = 10.9412$ (7) Å	$\theta = 2.7–26.3°$
$\alpha = 75.967$ (3)°	$\mu = 0.18$ mm^{-1}
$\beta = 70.563$ (2)°	$T = 170$ K
$\gamma = 69.452$ (2)°	Block, colourless
$V = 862.29$ (9) Å^3	0.15 × 0.08 × 0.05 mm
Bruker APEX-II CCD diffractometer	3513 independent reflections
Radiation source: sealed X-ray tube	2831 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.031$
Detector resolution: 7.9 pixels mm^{-1}	$\theta_{max} = 26.4°$, $\theta_{min} = 2.0°$
phi and ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1081 before and 0.0454 after correction. The Ratio of minimum to maximum transmission is 0.9351. The λ/2 correction factor is Not present.	$k = -13 \rightarrow 13$
$T_{min} = 0.697$, $T_{max} = 0.745$	$l = -13 \rightarrow 13$
10033 measured reflections	
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.091$	All H-atom parameters refined
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.2702P]$ where $P = (F_o^2 + 2F_c^2)/3$
3513 reflections	$(\Delta/\sigma)_{max} < 0.001$
377 parameters	$\Delta\rangle_{max} = 0.29$ e Å^{-3}
9 restraints	$\Delta\rangle_{min} = -0.22$ e Å^{-3}

Table S32. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.01474 (19)	0.22916 (14)	0.87537 (14)	0.0185 (3)	
C2	0.22162 (18)	0.09793 (14)	0.99523 (14)	0.0190 (3)	
C3	0.30872 (19)	0.19969 (14)	0.78914 (14)	0.0186 (3)	
C4	0.45219 (19)	0.23093 (15)	0.67694 (14)	0.0216 (3)	
C5	0.4441 (2)	0.31415 (16)	0.55369 (14)	0.0236 (3)	
N1	0.25175 (19)	0.02070 (14)	1.10287 (13)	0.0241 (3)	
H1A	0.360 (3)	-0.0170 (18)	1.1049 (17)	0.029 (5)*	
H1B	0.164 (3)	0.005 (2)	1.169 (2)	0.044 (6)*	
N2	0.05058 (16)	0.15452 (12)	0.98811 (12)	0.0192 (3)	
H2	-0.035 (3)	0.141 (2)	1.055 (2)	0.041 (5)*	
N3	-0.14836 (17)	0.27644 (14)	0.86712 (14)	0.0246 (3)	
H3A	-0.237 (3)	0.2673 (19)	0.931 (2)	0.037 (5)*	
H3B	-0.167 (3)	0.328 (2)	0.796 (2)	0.037 (5)*	
N4	0.14766 (15)	0.25308 (12)	0.77107 (11)	0.0192 (3)	
N5	0.35683 (16)	0.12174 (12)	0.89384 (12)	0.0202 (3)	
N6	0.61732 (18)	0.18249 (15)	0.67889 (13)	0.0332 (4)	
N7	0.60376 (18)	0.31429 (16)	0.48261 (14)	0.0374 (4)	
N8	0.29046 (18)	0.38251 (14)	0.51664 (13)	0.0259 (3)	
H8	0.198 (3)	0.381 (2)	0.568 (2)	0.046 (6)*	
N9	0.28636 (19)	0.46784 (15)	0.40253 (13)	0.0335 (3)	
O7	0.71257 (15)	0.23162 (14)	0.56142 (12)	0.0437 (4)	
O10	0.14114 (16)	0.53024 (14)	0.38626 (12)	0.0442 (3)	
H4	0.312 (4)	0.518 (3)	0.893 (3)	0.106 (10)*	
O8	0.4240 (12)	0.4904 (19)	0.3330 (15)	0.048 (2)	0.66 (7)
O9	0.424 (2)	0.441 (7)	0.3138 (17)	0.062 (9)	0.34 (7)
N11	0.15289 (17)	0.62268 (13)	0.78988 (12)	0.0250 (3)	
N12	0.40732 (18)	0.33006 (15)	1.03563 (13)	0.0308 (3)	
O1	0.2506 (11)	0.346 (2)	1.0942 (17)	0.042 (2)	0.50 (8)
O3	0.452 (3)	0.386 (2)	0.9184 (11)	0.033 (2)	0.50 (8)
O2	0.52910 (14)	0.23485 (12)	1.07266 (11)	0.0334 (3)	
O4	0.22699 (18)	0.61756 (13)	0.88263 (12)	0.0401 (3)	
O5	0.06578 (15)	0.73454 (11)	0.75371 (11)	0.0301 (3)	
O6	0.17658 (17)	0.52071 (12)	0.75080 (13)	0.0391 (3)	
O1A	0.260 (2)	0.365 (3)	1.113 (3)	0.051 (4)	0.50 (8)
O3A	0.451 (3)	0.409 (3)	0.932 (2)	0.039 (4)	0.50 (8)

N10	0.81764 (16)	0.01036 (13)	0.31704 (12)	0.0238 (3)	
O11	0.80405 (14)	0.05600 (11)	0.20325 (10)	0.0264 (3)	
O12	0.68062 (14)	0.00541 (13)	0.40904 (11)	0.0347 (3)	
O13	0.96534 (14)	-0.03294 (12)	0.33997 (11)	0.0331 (3)	
O16	0.1111 (2)	0.2145 (3)	0.43303 (16)	0.0323 (6)	0.968 (8)
O15	0.4125 (3)	0.1097 (6)	0.3032 (3)	0.0290 (11)	0.663 (17)
O14	0.4183 (6)	0.1747 (16)	0.3248 (6)	0.040 (3)	0.337 (17)
H16A	0.077 (3)	0.154 (2)	0.500 (2)	0.056 (7)*	
H15A	0.501 (4)	0.090 (3)	0.346 (3)	0.074 (8)*	
H16B	0.049 (3)	0.237 (2)	0.385 (2)	0.054 (7)*	
H15B	0.455 (4)	0.174 (3)	0.220 (3)	0.087 (9)*	
O16A	0.128 (6)	0.152 (8)	0.407 (5)	0.036 (7)	0.032 (8)
H16C	0.283 (4)	0.160 (3)	0.368 (3)	0.089 (9)*	

Table S33. Atomic displacement parameters (Å^2) for **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0187 (7)	0.0181 (7)	0.0174 (7)	-0.0048 (6)	-0.0045 (5)	-0.0017 (6)
C2	0.0172 (7)	0.0186 (7)	0.0191 (7)	-0.0041 (6)	-0.0038 (6)	-0.0021 (6)
C3	0.0181 (7)	0.0192 (7)	0.0171 (7)	-0.0060 (6)	-0.0040 (5)	-0.0007 (6)
C4	0.0176 (7)	0.0242 (8)	0.0199 (7)	-0.0063 (6)	-0.0047 (6)	0.0017 (6)
C5	0.0205 (7)	0.0285 (8)	0.0181 (7)	-0.0082 (7)	-0.0031 (6)	0.0019 (6)
N1	0.0164 (7)	0.0289 (7)	0.0198 (7)	-0.0040 (6)	-0.0048 (5)	0.0055 (5)
N2	0.0142 (6)	0.0232 (7)	0.0154 (6)	-0.0046 (5)	-0.0019 (5)	0.0012 (5)
N3	0.0155 (6)	0.0321 (8)	0.0201 (7)	-0.0050 (6)	-0.0040 (5)	0.0028 (6)
N4	0.0171 (6)	0.0200 (6)	0.0173 (6)	-0.0055 (5)	-0.0038 (5)	0.0018 (5)
N5	0.0165 (6)	0.0228 (7)	0.0179 (6)	-0.0059 (5)	-0.0039 (5)	0.0024 (5)
N6	0.0194 (7)	0.0443 (9)	0.0257 (7)	-0.0106 (6)	-0.0030 (5)	0.0106 (6)
N7	0.0211 (7)	0.0504 (10)	0.0274 (8)	-0.0085 (7)	-0.0049 (6)	0.0129 (7)
N8	0.0206 (7)	0.0336 (8)	0.0175 (7)	-0.0088 (6)	-0.0041 (5)	0.0069 (6)
N9	0.0293 (8)	0.0411 (9)	0.0212 (7)	-0.0093 (7)	-0.0063 (6)	0.0087 (6)
O7	0.0175 (6)	0.0638 (9)	0.0318 (7)	-0.0122 (6)	-0.0025 (5)	0.0197 (6)
O10	0.0285 (7)	0.0519 (8)	0.0353 (7)	-0.0030 (6)	-0.0121 (5)	0.0154 (6)
O8	0.0320 (16)	0.060 (5)	0.035 (3)	-0.016 (2)	-0.0039 (15)	0.023 (3)
O9	0.034 (3)	0.090 (17)	0.026 (4)	-0.006 (6)	0.004 (2)	0.020 (6)
N11	0.0231 (7)	0.0260 (8)	0.0230 (7)	-0.0065 (6)	-0.0047 (5)	-0.0016 (6)
N12	0.0209 (7)	0.0370 (8)	0.0262 (7)	-0.0068 (6)	-0.0041 (6)	0.0041 (6)
O1	0.017 (2)	0.057 (4)	0.043 (4)	-0.012 (2)	0.0005 (19)	-0.001 (3)
O3	0.034 (3)	0.028 (4)	0.024 (2)	-0.001 (3)	-0.006 (2)	0.007 (3)
O2	0.0223 (6)	0.0389 (7)	0.0271 (6)	-0.0032 (5)	-0.0067 (5)	0.0076 (5)

O4	0.0473 (8)	0.0350 (7)	0.0384 (7)	0.0052 (6)	-0.0270 (6)	-0.0102 (6)
O5	0.0285 (6)	0.0268 (6)	0.0309 (6)	-0.0023 (5)	-0.0121 (5)	-0.0001 (5)
O6	0.0448 (8)	0.0279 (7)	0.0481 (8)	-0.0105 (6)	-0.0113 (6)	-0.0137 (6)
O1A	0.020 (3)	0.063 (6)	0.042 (5)	0.000 (3)	0.003 (3)	0.008 (4)
O3A	0.027 (3)	0.037 (5)	0.029 (3)	0.002 (3)	0.002 (2)	0.007 (4)
N10	0.0211 (7)	0.0249 (7)	0.0212 (7)	-0.0058 (6)	-0.0036 (5)	-0.0004 (5)
O11	0.0287 (6)	0.0330 (6)	0.0177 (5)	-0.0146 (5)	-0.0052 (4)	0.0027 (4)
O12	0.0184 (6)	0.0505 (8)	0.0209 (6)	-0.0054 (5)	0.0008 (4)	0.0046 (5)
O13	0.0186 (6)	0.0432 (7)	0.0307 (6)	-0.0072 (5)	-0.0083 (5)	0.0059 (5)
O16	0.0240 (7)	0.0400 (13)	0.0270 (7)	-0.0058 (7)	-0.0096 (6)	0.0040 (7)
O15	0.0242 (10)	0.034 (2)	0.0230 (11)	-0.0076 (10)	-0.0068 (8)	0.0044 (11)
O14	0.024 (2)	0.056 (7)	0.023 (2)	-0.003 (2)	-0.0048 (16)	0.008 (3)
O16A	0.029 (9)	0.039 (10)	0.027 (10)	-0.002 (10)	-0.010 (9)	0.009 (10)

Table S34. Geometric parameters (Å, º) for **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$

C1—N2	1.3616 (18)	N11—O4	1.3363 (17)
C1—N3	1.3053 (19)	N11—O5	1.2182 (17)
C1—N4	1.3493 (18)	N11—O6	1.2027 (17)
C2—N1	1.3106 (19)	N12—O1	1.223 (6)
C2—N2	1.3664 (18)	N12—O3	1.268 (6)
C2—N5	1.3446 (18)	N12—O2	1.2629 (17)
C3—C4	1.4715 (19)	N12—O1A	1.227 (7)
C3—N4	1.3290 (18)	N12—O3A	1.268 (6)
C3—N5	1.3351 (19)	O4—H4	1.06 (3)
C4—C5	1.435 (2)	N10—O11	1.2501 (16)
C4—N6	1.301 (2)	N10—O12	1.2572 (16)
C5—N7	1.304 (2)	N10—O13	1.2469 (16)
C5—N8	1.378 (2)	O16—H16A	0.90 (3)
N1—H1A	0.86 (2)	O16—H16B	0.80 (2)
N1—H1B	0.87 (2)	O16—H16C	1.36 (3)
N2—H2	0.86 (2)	O15—H15A	0.94 (3)
N3—H3A	0.85 (2)	O15—H15B	1.04 (3)
N3—H3B	0.87 (2)	O15—H16C	1.11 (3)
N6—O7	1.3610 (17)	O14—H15A	0.96 (3)
N7—O7	1.3954 (18)	O14—H15B	1.08 (3)
N8—H8	0.79 (2)	O14—H16C	1.12 (3)
N8—N9	1.3617 (18)	O16A—H16A	0.97 (6)
N9—O10	1.2141 (18)	O16A—H16B	0.96 (6)
N9—O8	1.220 (7)	O16A—H16C	1.26 (6)

N9—O9	1.229 (15)		
N3—C1—N2	120.10 (14)	O10—N9—O8	124.0 (4)
N3—C1—N4	119.66 (13)	O10—N9—O9	124.7 (8)
N4—C1—N2	120.24 (13)	O8—N9—N8	118.4 (3)
N1—C2—N2	118.92 (13)	O9—N9—N8	114.1 (13)
N1—C2—N5	120.50 (13)	N6—O7—N7	111.81 (11)
N5—C2—N2	120.58 (13)	O5—N11—O4	114.32 (13)
N4—C3—C4	114.66 (12)	O6—N11—O4	119.00 (13)
N4—C3—N5	128.90 (13)	O6—N11—O5	126.68 (14)
N5—C3—C4	116.43 (13)	O1—N12—O3	120.2 (10)
C5—C4—C3	130.01 (13)	O1—N12—O2	122.3 (10)
N6—C4—C3	121.61 (13)	O2—N12—O3	115.1 (10)
N6—C4—C5	108.38 (13)	O2—N12—O3A	117.9 (9)
N7—C5—C4	109.61 (13)	O1A—N12—O2	120.0 (10)
N7—C5—N8	125.55 (14)	O1A—N12—O3A	119.7 (11)
N8—C5—C4	124.84 (14)	N11—O4—H4	105.2 (16)
C2—N1—H1A	118.1 (12)	N12—O3A—H4	117.3 (17)
C2—N1—H1B	120.9 (13)	O11—N10—O12	119.39 (12)
H1A—N1—H1B	121.0 (18)	O13—N10—O11	120.95 (12)
C1—N2—C2	120.55 (12)	O13—N10—O12	119.64 (12)
C1—N2—H2	120.1 (13)	H16A—O16—H16B	111 (2)
C2—N2—H2	119.4 (13)	H16A—O16—H16C	109.0 (19)
C1—N3—H3A	123.4 (13)	H16B—O16—H16C	110 (2)
C1—N3—H3B	117.7 (13)	H15A—O15—H15B	101 (2)
H3A—N3—H3B	118.5 (18)	H15A—O15—H16C	109 (2)
C3—N4—C1	114.97 (12)	H15B—O15—H16C	112 (2)
C3—N5—C2	114.60 (12)	H15A—O14—H15B	98 (2)
C4—N6—O7	106.06 (12)	H15A—O14—H16C	106 (2)
C5—N7—O7	104.15 (12)	H15B—O14—H16C	108 (2)
C5—N8—H8	118.8 (15)	H16A—O16A—H16B	93 (7)
N9—N8—C5	123.26 (13)	H16A—O16A—H16C	113 (7)
N9—N8—H8	117.3 (16)	H16B—O16A—H16C	108 (6)
O10—N9—N8	116.80 (13)		
C3—C4—C5—N7	179.70 (15)	N2—C2—N5—C3	-1.8 (2)
C3—C4—C5—N8	-0.6 (3)	N3—C1—N2—C2	176.10 (14)
C3—C4—N6—O7	-179.69 (14)	N3—C1—N4—C3	-179.46 (14)
C4—C3—N4—C1	-177.54 (12)	N4—C1—N2—C2	-3.0 (2)

C4—C3—N5—C2	178.62 (12)	N4—C3—C4—C5	2.8 (2)
C4—C5—N7—O7	-0.30 (19)	N4—C3—C4—N6	-177.98 (15)
C4—C5—N8—N9	175.39 (15)	N4—C3—N5—C2	-1.9 (2)
C4—N6—O7—N7	0.2 (2)	N5—C2—N2—C1	4.1 (2)
C5—C4—N6—O7	-0.33 (19)	N5—C3—C4—C5	-177.67 (15)
C5—N7—O7—N6	0.1 (2)	N5—C3—C4—N6	1.5 (2)
C5—N8—N9—O10	-174.12 (16)	N5—C3—N4—C1	3.0 (2)
C5—N8—N9—O8	-4.1 (14)	N6—C4—C5—N7	0.4 (2)
C5—N8—N9—O9	28 (4)	N6—C4—C5—N8	-179.92 (16)
N1—C2—N2—C1	-176.30 (14)	N7—C5—N8—N9	-5.0 (3)
N1—C2—N5—C3	178.68 (14)	N8—C5—N7—O7	-179.95 (16)
N2—C1—N4—C3	-0.4 (2)		

Table S35. Hydrogen bonds (Å, º) for **10**$H^{+}\cdot H_3O^{+}\cdot 2(NO_3^{-})\cdot HNO_3\cdot H_2O$

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O11^{i}	0.86 (2)	1.99 (2)	2.8319 (16)	163.4 (19)
N8—H8···N4	0.79 (2)	2.30 (2)	2.8628 (18)	128.1 (19)
O4—H4···O3	1.06 (3)	1.53 (4)	2.58 (2)	170 (3)
O4—H4···O3*A*	1.06 (3)	1.43 (4)	2.451 (18)	158 (3)
O16—H16*A*···O13^{ii}	0.90 (3)	1.92 (3)	2.805 (2)	168 (2)
O16*A*—H16*A*···O13^{ii}	0.97 (6)	1.92 (3)	2.73 (4)	139 (6)
O15—H15*A*···O12	0.94 (3)	1.73 (3)	2.640 (3)	162 (3)
O14—H15*A*···O12	0.96 (3)	1.73 (3)	2.592 (5)	148 (3)
O16—H16*B*···O5^{iii}	0.80 (2)	1.96 (3)	2.751 (2)	168 (2)
O16*A*—H16*B*···O5^{iii}	0.96 (6)	1.96 (3)	2.58 (5)	121 (6)
O15—H15*B*···O2^{iv}	1.04 (3)	1.59 (3)	2.602 (3)	162 (3)
O14—H15*B*···O2^{iv}	1.08 (3)	1.59 (3)	2.596 (5)	153 (3)
O15—H16*C*···O16	1.11 (3)	1.36 (3)	2.461 (4)	169 (3)
O14—H16*C*···O16*A*	1.12 (3)	1.26 (6)	2.38 (5)	175 (3)

Symmetry codes: (i) *x*-1, *y*, *z*+1; (ii) -*x*+1, -*y*, -*z*+1; (iii) -*x*, -*y*+1, -*z*+1; (iv) *x*, *y*, *z*-1.

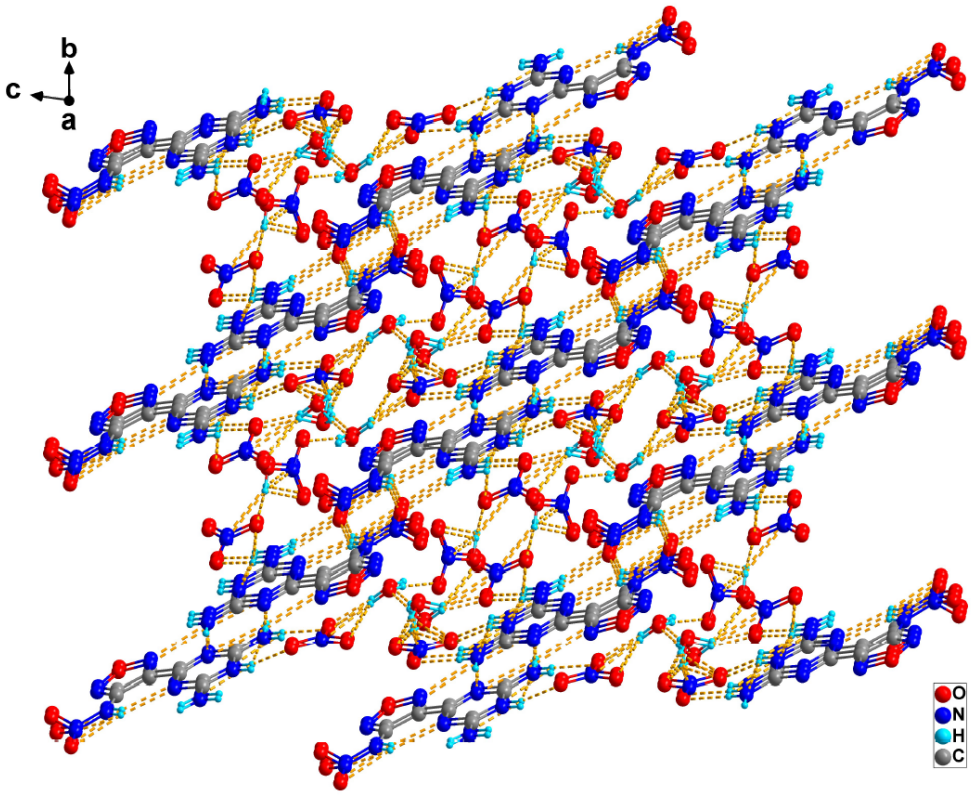


Fig. S9 Stacking diagram of **10**$H^+ \cdot H_3O^+ \cdot 2(NO_3^-) \cdot HNO_3 \cdot H_2O$ viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

8. Single-crystal X-ray diffraction analysis of **11**

Table S36. Crystal data, data collection, and refinement for **11**

$C_5H_4N_8O_3$	$F(000)$ = 456
M_r = 224.16	D_x = 1.674 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 9.437 (2) Å	Cell parameters from 4628 reflections
b = 7.6269 (18) Å	θ = 2.2–27.5°
c = 12.404 (3) Å	μ = 0.14 mm^{-1}
β = 95.116 (8)°	T = 296 K
V = 889.2 (4) Å^3	Block, yellow
Bruker D8 QUEST PHOTON 100 diffractometer	1569 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.027
ϕ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.2°
Absorption correction: multi-scan *SADABS*	h = -12→12
T_{min} = 0.687, T_{max} = 0.746	k = -8→9

8562 measured reflections	l = -15→16
2024 independent reflections	
Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.104	$(\Delta/\sigma)_{max} < 0.001$
S = 1.03	$\Delta\rangle_{max}$ = 0.18 e Å^{-3}
2024 reflections	$\Delta\rangle_{min}$ = -0.16 e Å^{-3}
146 parameters	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.057 (11)

Table S37. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **11**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.06838 (14)	0.25884 (17)	0.44150 (11)	0.0333 (3)
C2	0.20214 (16)	0.29784 (18)	0.60050 (11)	0.0355 (3)
C3	0.19646 (13)	0.50226 (17)	0.47143 (10)	0.0298 (3)
C4	0.24609 (14)	0.67518 (17)	0.43645 (11)	0.0330 (3)
C5	0.34782 (15)	0.78864 (19)	0.49126 (11)	0.0369 (3)
N1	0.11278 (13)	0.19488 (14)	0.53946 (9)	0.0375 (3)
N2	0.10908 (12)	0.41485 (14)	0.40147 (9)	0.0339 (3)
N3	0.24645 (12)	0.45788 (14)	0.57042 (9)	0.0351 (3)
N4	-0.02341 (14)	0.16294 (16)	0.37921 (11)	0.0487 (4)
H4A	-0.052151	0.063854	0.402171	0.058*
H4B	-0.054132	0.199921	0.315904	0.058*
N5	0.25270 (18)	0.24139 (18)	0.69722 (11)	0.0620 (5)
H5A	0.227957	0.140205	0.719729	0.074*
H5B	0.310298	0.305877	0.737590	0.074*
N6	0.19897 (14)	0.75247 (17)	0.34734 (11)	0.0472 (4)
N7	0.36215 (16)	0.93027 (18)	0.43712 (12)	0.0551 (4)
N8	0.43263 (14)	0.76453 (17)	0.59409 (11)	0.0427 (3)
O1	0.27008 (14)	0.90993 (16)	0.34585 (10)	0.0617 (4)
O2	0.53361 (13)	0.66791 (18)	0.59445 (12)	0.0680 (4)
O3	0.39682 (16)	0.84525 (18)	0.67078 (10)	0.0678 (4)

Table S38. Atomic displacement parameters (Å^2) for **11**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0341 (7)	0.0290 (7)	0.0360 (7)	-0.0010 (6)	-0.0014 (6)	-0.0032 (5)
C2	0.0474 (8)	0.0302 (7)	0.0284 (7)	-0.0021 (6)	0.0000 (6)	-0.0007 (5)
C3	0.0309 (7)	0.0286 (6)	0.0301 (7)	-0.0013 (5)	0.0034 (5)	-0.0019 (5)
C4	0.0345 (7)	0.0337 (7)	0.0309 (7)	-0.0039 (6)	0.0032 (5)	-0.0002 (5)
C5	0.0373 (7)	0.0344 (7)	0.0387 (8)	-0.0073 (6)	0.0023 (6)	0.0003 (6)
N1	0.0469 (7)	0.0288 (6)	0.0355 (7)	-0.0056 (5)	-0.0026 (5)	0.0001 (5)
N2	0.0369 (6)	0.0315 (6)	0.0323 (6)	-0.0042 (5)	-0.0029 (5)	-0.0005 (5)
N3	0.0426 (7)	0.0315 (6)	0.0304 (6)	-0.0063 (5)	-0.0011 (5)	-0.0020 (5)
N4	0.0570 (8)	0.0372 (7)	0.0479 (8)	-0.0159 (6)	-0.0178 (6)	0.0050 (6)
N5	0.1015 (12)	0.0415 (7)	0.0383 (8)	-0.0203 (8)	-0.0204 (8)	0.0071 (6)
N6	0.0539 (8)	0.0426 (7)	0.0436 (8)	-0.0133 (6)	-0.0042 (6)	0.0090 (6)
N7	0.0627 (9)	0.0449 (8)	0.0558 (9)	-0.0202 (7)	-0.0053 (7)	0.0086 (6)
N8	0.0417 (7)	0.0418 (7)	0.0436 (8)	-0.0138 (6)	-0.0018 (6)	-0.0043 (6)
O1	0.0756 (9)	0.0486 (7)	0.0578 (8)	-0.0231 (6)	-0.0109 (6)	0.0213 (5)
O2	0.0481 (7)	0.0765 (9)	0.0763 (9)	0.0115 (7)	-0.0117 (6)	-0.0055 (7)
O3	0.0869 (10)	0.0707 (9)	0.0454 (7)	-0.0028 (7)	0.0039 (6)	-0.0156 (6)

Table S39. Geometric parameters (Å, º) for **11**

C1—N4	1.3278 (18)	C5—N7	1.285 (2)
C1—N1	1.3413 (18)	C5—N8	1.456 (2)
C1—N2	1.3579 (17)	N4—H4A	0.8600
C2—N5	1.3230 (19)	N4—H4B	0.8600
C2—N1	1.3369 (18)	N5—H5A	0.8600
C2—N3	1.3535 (17)	N5—H5B	0.8600
C3—N3	1.3196 (17)	N6—O1	1.3766 (17)
C3—N2	1.3229 (17)	N7—O1	1.3730 (19)
C3—C4	1.4776 (18)	N8—O2	1.2043 (18)
C4—N6	1.2959 (19)	N8—O3	1.2065 (17)
C4—C5	1.420 (2)		
N4—C1—N1	117.50 (12)	C2—N1—C1	115.45 (12)
N4—C1—N2	117.45 (12)	C3—N2—C1	112.45 (11)
N1—C1—N2	125.05 (12)	C3—N3—C2	113.22 (11)
N5—C2—N1	118.73 (13)	C1—N4—H4A	120.0
N5—C2—N3	116.63 (13)	C1—N4—H4B	120.0
N1—C2—N3	124.64 (12)	H4A—N4—H4B	120.0

N3—C3—N2	129.15 (12)	C2—N5—H5A	120.0
N3—C3—C4	113.94 (11)	C2—N5—H5B	120.0
N2—C3—C4	116.91 (11)	H5A—N5—H5B	120.0
N6—C4—C5	107.28 (12)	C4—N6—O1	106.12 (12)
N6—C4—C3	124.25 (12)	C5—N7—O1	104.33 (12)
C5—C4—C3	128.45 (12)	O2—N8—O3	125.91 (15)
N7—C5—C4	111.11 (13)	O2—N8—C5	116.97 (13)
N7—C5—N8	119.26 (13)	O3—N8—C5	117.11 (14)
C4—C5—N8	129.64 (12)	N7—O1—N6	111.16 (11)
N3—C3—C4—N6	-172.46 (13)	N1—C1—N2—C3	-1.64 (19)
N2—C3—C4—N6	7.1 (2)	N2—C3—N3—C2	1.7 (2)
N3—C3—C4—C5	6.0 (2)	C4—C3—N3—C2	-178.85 (11)
N2—C3—C4—C5	-174.46 (13)	N5—C2—N3—C3	177.33 (14)
N6—C4—C5—N7	-0.07 (18)	N1—C2—N3—C3	-2.3 (2)
C3—C4—C5—N7	-178.73 (14)	C5—C4—N6—O1	0.42 (16)
N6—C4—C5—N8	-179.61 (14)	C3—C4—N6—O1	179.16 (12)
C3—C4—C5—N8	1.7 (2)	C4—C5—N7—O1	-0.32 (17)
N5—C2—N1—C1	-178.55 (14)	N8—C5—N7—O1	179.28 (13)
N3—C2—N1—C1	1.1 (2)	N7—C5—N8—O2	-102.96 (18)
N4—C1—N1—C2	-178.29 (13)	C4—C5—N8—O2	76.6 (2)
N2—C1—N1—C2	1.1 (2)	N7—C5—N8—O3	75.88 (19)
N3—C3—N2—C1	0.15 (19)	C4—C5—N8—O3	-104.61 (18)
C4—C3—N2—C1	-179.32 (11)	C5—N7—O1—N6	0.59 (18)
N4—C1—N2—C3	177.73 (12)	C4—N6—O1—N7	-0.65 (17)

Table S40. Hydrogen bonds (Å, º) for **11**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*B*···O2^{i}	0.86	2.66	3.183 (2)	121
N5—H5*B*···O1^{ii}	0.86	2.60	3.2317 (19)	132
N5—H5*A*···N2^{iii}	0.86	2.64	3.2075 (19)	125
N4—H4*B*···N6^{iv}	0.86	2.37	3.2059 (19)	163
N4—H4*A*···N1^{v}	0.86	2.20	3.0543 (18)	177

Symmetry codes: (i) -*x*+1, *y*-1/2, -*z*+3/2; (ii) *x*, -*y*+3/2, *z*+1/2; (iii) *x*, -*y*+1/2, *z*+1/2; (iv) -*x*, *y*-1/2, -*z*+1/2; (v) -*x*, -*y*, -*z*+1.

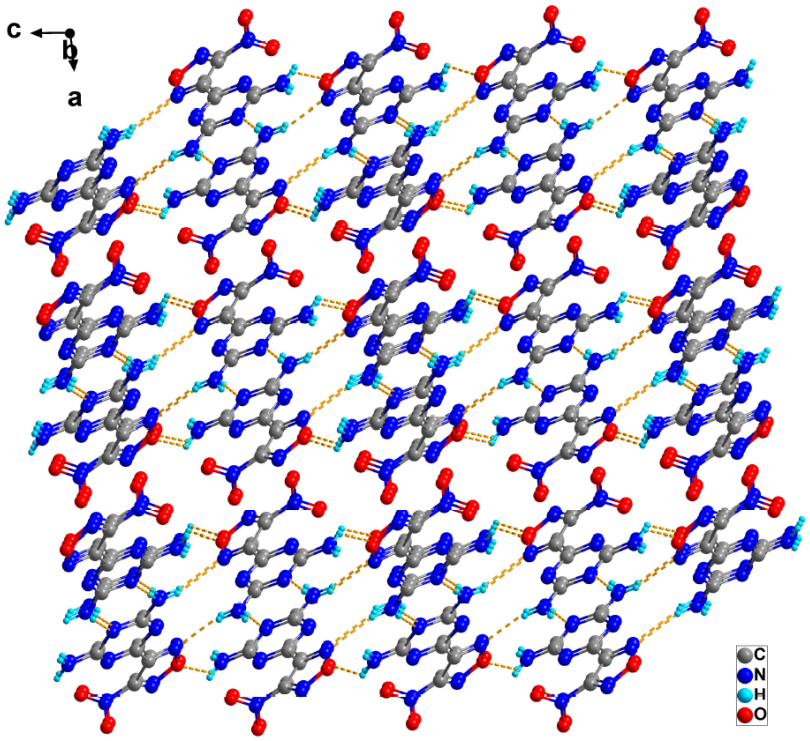


Fig. S10 Stacking diagram of **11** viewed down the *b* axis, yellow dotted lines indicate hydrogen bonding.

9. Single-crystal X-ray diffraction analysis of **12**

Table S41. Crystal data, data collection, and refinement for **12**

$C_5H_4N_8O_4$	D_x = 1.665 Mg m^{-3}
M_r = 240.16	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 5960 reflections
a = 7.6738 (4) Å	θ = 2.7–27.4°
b = 9.0828 (6) Å	μ = 0.14 mm^{-1}
c = 13.7480 (9) Å	T = 296 K
V = 958.23 (10) Å^3	Block, yellow
Z = 4	0.22 × 0.20 × 0.18 mm
F(000) = 488	
Bruker D8 QUEST PHOTON 100 diffractometer	1869 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.033
ϕ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.7°
Absorption correction: multi-scan *SADABS*	h = -9→9
T_{min} = 0.652, T_{max} = 0.746	k = -8→11

9472 measured reflections	l = -17→17
2165 independent reflections	
Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.0798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.093$	$\Delta\rangle_{max} = 0.21$ e Å^{-3}
$S = 1.03$	$\Delta\rangle_{min} = -0.20$ e Å^{-3}
2165 reflections	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
155 parameters	Extinction coefficient: 0.051 (13)
0 restraints	Absolute structure: Flack x determined using 677 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: -0.1 (6)

Table S42. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **12**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2931 (3)	-0.1427 (2)	0.44632 (15)	0.0322 (5)
C2	0.3897 (3)	0.0184 (2)	0.32326 (16)	0.0347 (5)
C3	0.1367 (3)	0.0554 (2)	0.40252 (16)	0.0346 (5)
C4	-0.0245 (3)	0.1420 (3)	0.40928 (17)	0.0388 (5)
C5	-0.0660 (3)	0.2757 (3)	0.36158 (19)	0.0451 (6)
N1	0.4126 (2)	-0.10561 (19)	0.37708 (13)	0.0329 (4)
N2	0.2476 (2)	0.1034 (2)	0.33620 (14)	0.0390 (5)
N3	0.1495 (2)	-0.0607 (2)	0.45973 (13)	0.0356 (4)
N4	0.5074 (3)	0.0516 (2)	0.25809 (16)	0.0452 (5)
H4A	0.494829	0.128861	0.222573	0.054*
H4B	0.597306	-0.003735	0.250740	0.054*
N5	0.3200 (3)	-0.2611 (2)	0.49800 (16)	0.0433 (5)
H5A	0.245269	-0.287387	0.541277	0.052*
H5B	0.412386	-0.312793	0.488777	0.052*
N6	-0.1605 (3)	0.1030 (3)	0.45841 (19)	0.0582 (6)
N7	-0.2237 (3)	0.3165 (3)	0.38044 (19)	0.0622 (7)
N8	0.0409 (4)	0.3635 (4)	0.2977 (2)	0.0736 (8)
O1	0.5519 (2)	-0.19122 (18)	0.36092 (12)	0.0414 (4)
O2	-0.2843 (3)	0.2093 (2)	0.44116 (17)	0.0688 (6)

O3	0.0367 (4)	0.3341 (4)	0.2126 (2)	0.1231 (13)
O4	0.1272 (5)	0.4564 (4)	0.3338 (3)	0.1266 (13)

Table S43. Atomic displacement parameters (Å^2) for **12**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0299 (10)	0.0325 (10)	0.0342 (10)	-0.0029 (9)	-0.0027 (9)	0.0001 (9)
C2	0.0321 (11)	0.0357 (11)	0.0362 (11)	-0.0001 (9)	0.0003 (10)	0.0014 (9)
C3	0.0329 (11)	0.0321 (10)	0.0388 (11)	0.0006 (9)	-0.0002 (9)	-0.0022 (9)
C4	0.0378 (11)	0.0369 (11)	0.0417 (12)	0.0035 (9)	0.0026 (10)	-0.0037 (9)
C5	0.0417 (13)	0.0469 (13)	0.0468 (13)	0.0091 (11)	-0.0025 (11)	0.0019 (11)
N1	0.0304 (9)	0.0336 (9)	0.0346 (9)	0.0031 (8)	0.0014 (8)	0.0012 (7)
N2	0.0346 (11)	0.0364 (10)	0.0460 (10)	0.0045 (8)	0.0034 (8)	0.0068 (8)
N3	0.0331 (9)	0.0350 (9)	0.0386 (10)	-0.0001 (8)	0.0037 (8)	0.0023 (8)
N4	0.0385 (10)	0.0449 (10)	0.0523 (12)	0.0064 (9)	0.0111 (9)	0.0133 (9)
N5	0.0357 (10)	0.0451 (11)	0.0490 (11)	0.0061 (9)	0.0072 (9)	0.0142 (9)
N6	0.0459 (12)	0.0522 (13)	0.0764 (15)	0.0082 (11)	0.0189 (12)	0.0015 (12)
N7	0.0534 (13)	0.0616 (15)	0.0715 (15)	0.0220 (12)	0.0054 (12)	0.0013 (12)
N8	0.0598 (16)	0.0752 (18)	0.086 (2)	0.0231 (15)	0.0037 (16)	0.0382 (16)
O1	0.0354 (8)	0.0422 (9)	0.0466 (9)	0.0094 (7)	0.0010 (7)	0.0009 (7)
O2	0.0471 (10)	0.0660 (13)	0.0933 (16)	0.0184 (10)	0.0233 (11)	-0.0003 (12)
O3	0.112 (2)	0.189 (3)	0.0683 (18)	0.050 (2)	0.0139 (16)	0.059 (2)
O4	0.113 (3)	0.0866 (19)	0.180 (4)	-0.0331 (19)	0.015 (2)	0.025 (2)

Table S44. Geometric parameters (Å, º) for **12**

C1—N5	1.305 (3)	C5—N7	1.291 (3)
C1—N3	1.343 (3)	C5—N8	1.442 (4)
C1—N1	1.364 (3)	N1—O1	1.341 (2)
C2—N4	1.307 (3)	N4—H4A	0.8600
C2—N2	1.348 (3)	N4—H4B	0.8600
C2—N1	1.359 (3)	N5—H5A	0.8600
C3—N3	1.319 (3)	N5—H5B	0.8600
C3—N2	1.321 (3)	N6—O2	1.375 (3)
C3—C4	1.469 (3)	N7—O2	1.364 (3)
C4—N6	1.293 (3)	N8—O4	1.182 (5)
C4—C5	1.416 (3)	N8—O3	1.200 (4)
N5—C1—N3	120.8 (2)	O1—N1—C1	120.56 (17)
N5—C1—N1	118.50 (19)	C2—N1—C1	119.86 (17)

N3—C1—N1	120.67 (18)	C3—N2—C2	115.03 (18)
N4—C2—N2	121.2 (2)	C3—N3—C1	115.01 (18)
N4—C2—N1	118.36 (19)	C2—N4—H4A	120.0
N2—C2—N1	120.48 (19)	C2—N4—H4B	120.0
N3—C3—N2	128.87 (19)	H4A—N4—H4B	120.0
N3—C3—C4	116.95 (19)	C1—N5—H5A	120.0
N2—C3—C4	114.14 (18)	C1—N5—H5B	120.0
N6—C4—C5	107.2 (2)	H5A—N5—H5B	120.0
N6—C4—C3	124.5 (2)	C4—N6—O2	105.9 (2)
C5—C4—C3	128.3 (2)	C5—N7—O2	103.7 (2)
N7—C5—C4	111.4 (3)	O4—N8—O3	125.7 (4)
N7—C5—N8	119.8 (2)	O4—N8—C5	117.3 (3)
C4—C5—N8	128.9 (2)	O3—N8—C5	117.1 (4)
O1—N1—C2	119.57 (17)	N7—O2—N6	111.79 (19)
N3—C3—C4—N6	-8.4 (4)	C4—C3—N2—C2	-174.76 (19)
N2—C3—C4—N6	169.4 (2)	N4—C2—N2—C3	178.3 (2)
N3—C3—C4—C5	175.2 (2)	N1—C2—N2—C3	-0.8 (3)
N2—C3—C4—C5	-7.0 (3)	N2—C3—N3—C1	-2.0 (3)
N6—C4—C5—N7	-0.5 (3)	C4—C3—N3—C1	175.41 (18)
C3—C4—C5—N7	176.4 (2)	N5—C1—N3—C3	-179.5 (2)
N6—C4—C5—N8	-179.6 (3)	N1—C1—N3—C3	-0.7 (3)
C3—C4—C5—N8	-2.8 (5)	C5—C4—N6—O2	0.4 (3)
N4—C2—N1—O1	-1.2 (3)	C3—C4—N6—O2	-176.6 (2)
N2—C2—N1—O1	177.84 (18)	C4—C5—N7—O2	0.4 (3)
N4—C2—N1—C1	179.4 (2)	N8—C5—N7—O2	179.6 (3)
N2—C2—N1—C1	-1.6 (3)	N7—C5—N8—O4	90.6 (4)
N5—C1—N1—O1	1.7 (3)	C4—C5—N8—O4	-90.3 (4)
N3—C1—N1—O1	-177.07 (18)	N7—C5—N8—O3	-90.6 (4)
N5—C1—N1—C2	-178.9 (2)	C4—C5—N8—O3	88.4 (4)
N3—C1—N1—C2	2.3 (3)	C5—N7—O2—N6	-0.1 (3)
N3—C3—N2—C2	2.7 (3)	C4—N6—O2—N7	-0.2 (3)

Table S45. Hydrogen bonds (Å, º) for **12**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*B*···N3^{i}	0.86	2.27	3.058 (3)	153
N5—H5*A*···O1^{ii}	0.86	2.01	2.860 (2)	169
N4—H4*B*···O4^{iii}	0.86	2.44	3.195 (4)	147
N4—H4*A*···O1^{iv}	0.86	2.03	2.888 (3)	176

Symmetry codes: (i) *x*+1/2, -*y*-1/2, -*z*+1; (ii) *x*-1/2, -*y*-1/2, -*z*+1; (iii) -*x*+1, *y*-1/2, -*z*+1/2; (iv) -*x*+1, *y*+1/2, -*z*+1/2.

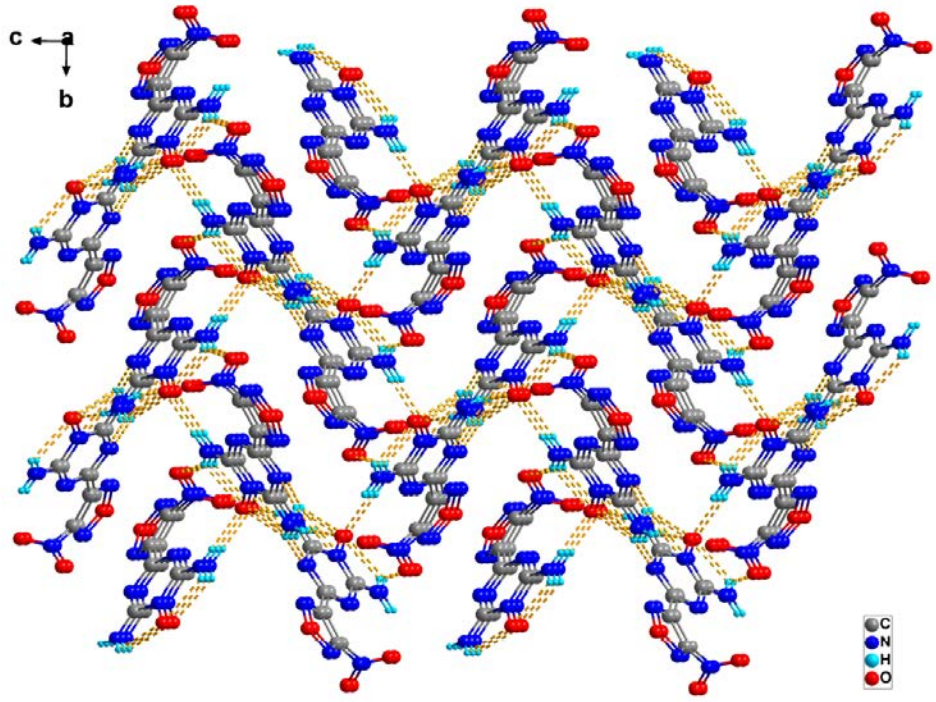


Fig. S11 Stacking diagram of **12** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

10. Single-crystal X-ray diffraction analysis of **13**·0.5H_2O

Table S46. Crystal data, data collection, and refinement for **13**·0.5H_2O

2($C_5H_5N_{10}O$)·O_4S·H_2O	D_x = 1.738 Mg m^{-3}
M_r = 556.46	Mo *K*α radiation, λ = 0.71073 Å
Orthorhombic, *Cmc*2_1	Cell parameters from 4921 reflections
a = 30.8441 (18) Å	θ = 2.6–26.9°
b = 7.2786 (4) Å	μ = 0.24 mm^{-1}
c = 9.4707 (4) Å	*T* = 296 K
V = 2126.19 (19) Å^3	Plate, red
Z = 4	0.12 × 0.10 × 0.03 mm
Bruker D8 QUEST PHOTON 100 diffractometer	1946 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.034
ϕ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.6°
Absorption correction: multi-scan *SADABS*	*h* = -38→40

T_{min} = 0.655, T_{max} = 0.746	k = -9→9
9423 measured reflections	l = -9→12
2310 independent reflections	
Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 1.5268P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.093$	$\Delta\rangle_{max}$ = 0.31 e Å^{-3}
S = 1.05	$\Delta\rangle_{min}$ = -0.28 e Å^{-3}
2310 reflections	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
185 parameters	Extinction coefficient: 0.0047 (10)
1 restraint	Absolute structure: Flack x determined using 721 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: mixed	Absolute structure parameter: 0.03 (3)

Table S47. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **13**·0.5H_2O

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.62738 (11)	0.7136 (5)	0.4746 (4)	0.0337 (7)	
C2	0.57941 (11)	0.7092 (5)	0.6527 (4)	0.0398 (9)	
C3	0.60172 (10)	0.9852 (5)	0.5475 (4)	0.0389 (8)	
C4	0.65572 (12)	0.6099 (5)	0.3771 (4)	0.0417 (9)	
C5	0.68317 (13)	0.6726 (7)	0.2642 (4)	0.0544 (11)	
N1	0.60434 (10)	0.6114 (4)	0.5644 (3)	0.0372 (7)	
N2	0.57862 (10)	0.8936 (5)	0.6460 (4)	0.0434 (8)	
H2	0.5604 (13)	0.937 (6)	0.685 (5)	0.052*	
N3	0.62818 (9)	0.8929 (4)	0.4592 (3)	0.0400 (7)	
N4	0.55624 (12)	0.6277 (6)	0.7495 (3)	0.0620 (11)	
H4A	0.556852	0.509945	0.757113	0.074*	
H4B	0.540358	0.691609	0.805686	0.074*	
N5	0.59814 (13)	1.1634 (5)	0.5386 (5)	0.0659 (12)	
H5A	0.612715	1.222755	0.476107	0.079*	
H5B	0.581196	1.221443	0.595266	0.079*	
N6	0.65889 (13)	0.4321 (5)	0.3834 (4)	0.0645 (11)	
N7	0.70210 (13)	0.5314 (8)	0.2075 (4)	0.0806 (15)	

N8	0.68861 (13)	0.8527 (6)	0.2193 (4)	0.0674 (11)	
N9	0.71012 (12)	0.8637 (7)	0.1070 (4)	0.0793 (14)	
N10	0.72823 (17)	0.8969 (9)	0.0089 (5)	0.117 (2)	
O1	0.68739 (15)	0.3800 (6)	0.2808 (4)	0.0899 (13)	
S1	0.500000	0.16999 (14)	0.83479 (11)	0.0267 (3)	
O2	0.53789 (11)	0.2382 (6)	0.7618 (4)	0.0867 (13)	
O3	0.500000	-0.0279 (5)	0.8221 (5)	0.0854 (16)	
O4	0.500000	0.2305 (5)	0.9799 (4)	0.0478 (10)	
O5	0.500000	0.6100 (6)	-0.0119 (4)	0.0648 (13)	
H5C	0.490603	0.662172	0.062319	0.097*	0.5
H5D	0.500082	0.495574	0.001644	0.097*	

Table S48. Atomic displacement parameters ($Å^2$) for **13**·0.5H_2O

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0344 (16)	0.0358 (19)	0.0310 (17)	0.0041 (14)	0.0030 (14)	-0.0024 (14)
C2	0.0371 (18)	0.052 (2)	0.0301 (17)	-0.0152 (16)	0.0018 (15)	-0.0091 (15)
C3	0.0319 (16)	0.0342 (19)	0.051 (2)	0.0012 (16)	-0.0063 (15)	-0.0119 (19)
C4	0.048 (2)	0.045 (2)	0.0320 (19)	0.0123 (17)	0.0007 (14)	-0.0025 (15)
C5	0.0373 (19)	0.093 (4)	0.033 (2)	0.014 (2)	0.0039 (17)	0.001 (2)
N1	0.0482 (16)	0.0314 (15)	0.0320 (14)	-0.0065 (13)	0.0065 (13)	-0.0014 (12)
N2	0.0338 (17)	0.051 (2)	0.0458 (19)	0.0017 (15)	0.0071 (14)	-0.0227 (16)
N3	0.0372 (15)	0.0329 (17)	0.0500 (19)	-0.0029 (13)	0.0078 (13)	0.0040 (14)
N4	0.055 (2)	0.096 (3)	0.0352 (19)	-0.033 (2)	0.0099 (15)	-0.0041 (19)
N5	0.071 (2)	0.032 (2)	0.095 (3)	0.0092 (16)	-0.020 (2)	-0.012 (2)
N6	0.096 (3)	0.060 (3)	0.0378 (19)	0.037 (2)	0.0057 (18)	-0.0083 (16)
N7	0.070 (3)	0.127 (4)	0.045 (2)	0.049 (3)	0.006 (2)	-0.012 (3)
N8	0.059 (2)	0.097 (3)	0.047 (2)	-0.018 (2)	0.0136 (18)	0.008 (2)
N9	0.050 (2)	0.142 (4)	0.046 (2)	-0.037 (2)	-0.0004 (18)	0.007 (2)
N10	0.088 (3)	0.210 (7)	0.054 (3)	-0.076 (4)	0.011 (3)	0.004 (3)
O1	0.122 (3)	0.095 (3)	0.053 (2)	0.068 (2)	0.007 (2)	-0.017 (2)
S1	0.0328 (5)	0.0226 (5)	0.0246 (5)	0.000	0.000	-0.0003 (5)
O2	0.074 (2)	0.119 (3)	0.066 (2)	-0.051 (2)	0.0332 (18)	-0.026 (2)
O3	0.184 (5)	0.022 (2)	0.050 (3)	0.000	0.000	0.001 (2)
O4	0.075 (3)	0.041 (2)	0.0274 (18)	0.000	0.000	-0.0033 (16)
O5	0.125 (4)	0.038 (2)	0.031 (2)	0.000	0.000	-0.0030 (18)

Table S49. Geometric parameters (Å, º) for **13**·0.5H_2O

C1—N3	1.314 (4)	N4—H4B	0.8600
C1—N1	1.334 (4)	N5—H5A	0.8600
C1—C4	1.478 (5)	N5—H5B	0.8600
C2—N4	1.305 (5)	N6—O1	1.364 (5)
C2—N1	1.341 (5)	N7—O1	1.379 (6)
C2—N2	1.344 (5)	N8—N9	1.256 (5)
C3—N5	1.304 (5)	N9—N10	1.111 (5)
C3—N3	1.348 (5)	S1—O4	1.443 (4)
C3—N2	1.350 (5)	S1—O3	1.446 (4)
C4—N6	1.299 (5)	S1—O2	1.446 (3)
C4—C5	1.438 (5)	S1—O2^{i}	1.446 (3)
C5—N7	1.298 (6)	O5—H5C	0.8500
C5—N8	1.388 (6)	O5—H5D	0.8428
N2—H2	0.74 (4)	O5—H5C^{i}	0.85 (7)
N4—H4A	0.8600		
N3—C1—N1	129.4 (3)	C2—N4—H4A	120.0
N3—C1—C4	115.3 (3)	C2—N4—H4B	120.0
N1—C1—C4	115.4 (3)	H4A—N4—H4B	120.0
N4—C2—N1	120.7 (4)	C3—N5—H5A	120.0
N4—C2—N2	118.5 (4)	C3—N5—H5B	120.0
N1—C2—N2	120.7 (3)	H5A—N5—H5B	120.0
N5—C3—N3	120.4 (4)	C4—N6—O1	107.0 (4)
N5—C3—N2	119.4 (4)	C5—N7—O1	106.0 (4)
N3—C3—N2	120.2 (3)	N9—N8—C5	112.6 (4)
N6—C4—C5	107.8 (3)	N10—N9—N8	171.0 (7)
N6—C4—C1	121.6 (4)	N6—O1—N7	110.4 (3)
C5—C4—C1	130.6 (4)	O4—S1—O3	112.6 (3)
N7—C5—N8	124.5 (4)	O4—S1—O2	110.52 (17)
N7—C5—C4	108.8 (5)	O3—S1—O2	107.6 (2)
N8—C5—C4	126.8 (4)	O4—S1—O2^{i}	110.52 (17)
C1—N1—C2	114.0 (3)	O3—S1—O2^{i}	107.6 (2)
C2—N2—C3	121.1 (3)	O2—S1—O2^{i}	107.9 (4)
C2—N2—H2	114 (3)	H5C—O5—H5D	108.4
C3—N2—H2	122 (4)	H5C—O5—H5C^{i}	39.9
C1—N3—C3	114.5 (3)	H5D—O5—H5C^{i}	108.3

N3—C1—C4—N6	178.2 (4)	N5—C3—N2—C2	175.9 (3)
N1—C1—C4—N6	-2.6 (5)	N3—C3—N2—C2	-4.1 (5)
N3—C1—C4—C5	-2.3 (6)	N1—C1—N3—C3	0.0 (5)
N1—C1—C4—C5	176.9 (4)	C4—C1—N3—C3	179.1 (3)
N6—C4—C5—N7	-0.5 (5)	N5—C3—N3—C1	-177.0 (3)
C1—C4—C5—N7	179.9 (4)	N2—C3—N3—C1	2.9 (5)
N6—C4—C5—N8	178.4 (4)	C5—C4—N6—O1	0.6 (5)
C1—C4—C5—N8	-1.1 (7)	C1—C4—N6—O1	-179.8 (3)
N3—C1—N1—C2	-1.7 (5)	N8—C5—N7—O1	-178.8 (4)
C4—C1—N1—C2	179.1 (3)	C4—C5—N7—O1	0.2 (5)
N4—C2—N1—C1	-177.6 (3)	N7—C5—N8—N9	7.6 (6)
N2—C2—N1—C1	0.6 (5)	C4—C5—N8—N9	-171.2 (4)
N4—C2—N2—C3	-179.6 (3)	C4—N6—O1—N7	-0.5 (5)
N1—C2—N2—C3	2.1 (5)	C5—N7—O1—N6	0.2 (5)

Symmetry code: (i) -*x*+1, *y*, *z*.

Table S50. Hydrogen bonds (Å, º) for **13**·0.5H_2O

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4A···O2	0.86	2.06	2.893 (6)	162
N4—H4B···O3^{ii}	0.86	2.40	3.125 (5)	143
N4—H4B···O5^{iii}	0.86	2.21	2.851 (5)	131
N5—H5A···N6^{ii}	0.86	2.26	3.082 (6)	159
N5—H5B···O2^{ii}	0.86	2.07	2.867 (6)	154
N2—H2···S1^{ii}	0.74 (4)	2.89 (4)	3.623 (3)	168 (4)
N2—H2···O2^{ii}	0.74 (4)	2.42 (4)	3.012 (5)	139 (4)
N2—H2···O3^{ii}	0.74 (4)	2.29 (4)	2.998 (4)	162 (4)

Symmetry codes: (ii) *x*, *y*+1, *z*; (iii) *x*, *y*, *z*+1.

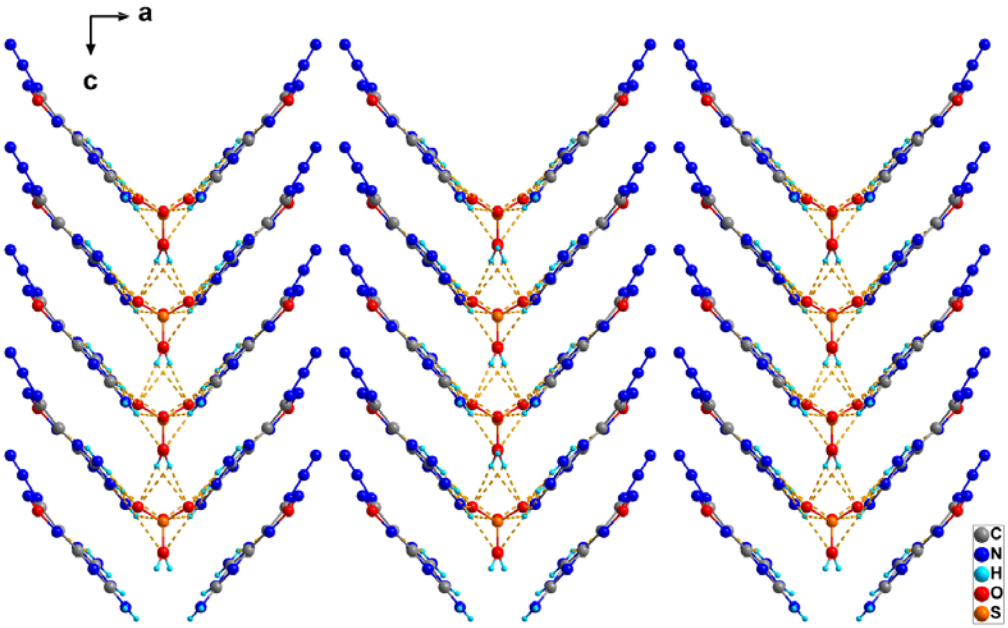


Fig. S12 Stacking diagram of **13**·0.5H_2O viewed down the *b* axis, yellow dotted lines indicate hydrogen bonding.

11. Single-crystal X-ray diffraction analysis of **14**

Table S51. Crystal data, data collection, and refinement for **14**

$C_5H_7N_8O·ClO_4$	Z = 2
M_r = 294.64	F(000) = 300
Triclinic, $P\bar{1}$	D_x = 1.855 Mg m^{-3}
a = 7.4349 (6) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 8.3262 (8) Å	Cell parameters from 4628 reflections
c = 9.1790 (8) Å	θ = 2.2–27.5°
α = 68.801 (3)°	μ = 0.40 mm^{-1}
β = 84.893 (3)°	T = 296 K
γ = 87.370 (3)°	Plate, yellow
V = 527.61 (8) Å^3	0.22 × 0.20 × 0.03 mm
Bruker D8 QUEST PHOTON 100 diffractometer	2077 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.027
ϕ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.4°
Absorption correction: multi-scan *SADABS*	h = -9→9
T_{min} = 0.687, T_{max} = 0.746	k = -10→10
8048 measured reflections	l = -11→11

2398 independent reflections	
Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 0.2956P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.07$	$\Delta\rangle_{max} = 0.58$ e Å^{-3}
2398 reflections	$\Delta\rangle_{min} = -0.37$ e Å^{-3}
177 parameters	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.051 (9)

Table S52. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **14**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5372 (2)	0.7457 (2)	0.81441 (19)	0.0237 (3)
C2	0.8124 (2)	0.8872 (2)	0.70500 (19)	0.0259 (4)
C3	0.6277 (2)	0.8140 (2)	0.55825 (18)	0.0221 (3)
C4	0.5824 (2)	0.8165 (2)	0.40430 (18)	0.0231 (3)
C5	0.4365 (2)	0.7340 (2)	0.3676 (2)	0.0272 (4)
N1	0.6910 (2)	0.8171 (2)	0.83091 (16)	0.0259 (3)
H1	0.720 (3)	0.813 (3)	0.921 (3)	0.038 (6)*
N2	0.7789 (2)	0.8909 (2)	0.56239 (16)	0.0269 (3)
N3	0.50583 (19)	0.73890 (19)	0.67468 (16)	0.0253 (3)
N4	0.4178 (2)	0.6857 (2)	0.93289 (17)	0.0305 (4)
H4A	0.319687	0.642252	0.921485	0.037*
H4B	0.437076	0.689683	1.022540	0.037*
N5	0.9591 (2)	0.9540 (3)	0.72383 (19)	0.0413 (5)
H5A	1.035171	1.000720	0.644879	0.050*
H5B	0.980194	0.951484	0.815256	0.050*
N6	0.3140 (2)	0.6296 (3)	0.46798 (19)	0.0444 (5)
H6A	0.232260	0.585789	0.433656	0.053*
H6B	0.316845	0.606043	0.567029	0.053*
N7	0.4437 (2)	0.7779 (2)	0.21454 (18)	0.0336 (4)
N8	0.6738 (2)	0.9082 (2)	0.27568 (16)	0.0271 (3)
O1	0.59276 (18)	0.88767 (17)	0.15674 (13)	0.0318 (3)
Cl1	0.97328 (6)	0.61402 (6)	0.18040 (5)	0.03111 (17)
O2	0.8046 (2)	0.5478 (3)	0.1645 (2)	0.0621 (5)

O3	1.1212 (2)	0.5086 (2)	0.1615 (2)	0.0621 (5)
O4	0.9936 (3)	0.7829 (2)	0.06244 (19)	0.0602 (5)
O5	0.9667 (2)	0.6278 (2)	0.33086 (16)	0.0438 (4)

Table S53. Atomic displacement parameters (Å^2) for **14**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0273 (8)	0.0255 (8)	0.0184 (7)	-0.0018 (6)	-0.0019 (6)	-0.0078 (6)
C2	0.0265 (9)	0.0318 (9)	0.0193 (8)	-0.0049 (7)	-0.0030 (6)	-0.0083 (7)
C3	0.0226 (8)	0.0270 (8)	0.0176 (7)	-0.0011 (6)	-0.0027 (6)	-0.0090 (6)
C4	0.0234 (8)	0.0298 (9)	0.0176 (7)	-0.0012 (6)	-0.0023 (6)	-0.0100 (6)
C5	0.0260 (9)	0.0370 (10)	0.0215 (8)	-0.0032 (7)	-0.0038 (6)	-0.0131 (7)
N1	0.0274 (8)	0.0364 (8)	0.0158 (7)	-0.0055 (6)	-0.0033 (6)	-0.0105 (6)
N2	0.0266 (7)	0.0368 (8)	0.0179 (7)	-0.0080 (6)	-0.0018 (5)	-0.0094 (6)
N3	0.0261 (7)	0.0337 (8)	0.0182 (7)	-0.0068 (6)	-0.0006 (5)	-0.0112 (6)
N4	0.0342 (8)	0.0410 (9)	0.0180 (7)	-0.0128 (7)	0.0021 (6)	-0.0121 (6)
N5	0.0362 (9)	0.0670 (12)	0.0227 (8)	-0.0239 (8)	-0.0011 (6)	-0.0160 (8)
N6	0.0387 (10)	0.0698 (13)	0.0251 (8)	-0.0285 (9)	-0.0006 (7)	-0.0147 (8)
N7	0.0341 (8)	0.0477 (10)	0.0227 (7)	-0.0102 (7)	-0.0026 (6)	-0.0159 (7)
N8	0.0297 (8)	0.0352 (8)	0.0183 (7)	-0.0046 (6)	-0.0029 (6)	-0.0114 (6)
O1	0.0358 (7)	0.0445 (8)	0.0168 (6)	-0.0079 (6)	-0.0022 (5)	-0.0120 (5)
Cl1	0.0277 (3)	0.0428 (3)	0.0226 (2)	-0.00581 (18)	-0.00065 (16)	-0.01107 (18)
O2	0.0445 (10)	0.0987 (15)	0.0586 (11)	-0.0271 (9)	-0.0015 (8)	-0.0443 (11)
O3	0.0535 (10)	0.0582 (11)	0.0689 (12)	0.0105 (8)	0.0130 (9)	-0.0213 (9)
O4	0.0713 (12)	0.0589 (11)	0.0321 (8)	-0.0020 (9)	-0.0006 (8)	0.0048 (7)
O5	0.0433 (8)	0.0647 (10)	0.0251 (7)	-0.0080 (7)	-0.0038 (6)	-0.0172 (7)

Table S54. Geometric parameters (Å, º) for **14**

C1—N4	1.302 (2)	N1—H1	0.86 (2)
C1—N3	1.345 (2)	N4—H4A	0.8600
C1—N1	1.357 (2)	N4—H4B	0.8600
C2—N5	1.299 (2)	N5—H5A	0.8600
C2—N2	1.344 (2)	N5—H5B	0.8600
C2—N1	1.366 (2)	N6—H6A	0.8600
C3—N3	1.323 (2)	N6—H6B	0.8600
C3—N2	1.329 (2)	N7—O1	1.408 (2)
C3—C4	1.474 (2)	N8—O1	1.3585 (18)
C4—N8	1.300 (2)	Cl1—O3	1.4133 (17)
C4—C5	1.436 (2)	Cl1—O5	1.4232 (14)

C5—N7	1.315 (2)	Cl1—O2	1.4329 (16)
C5—N6	1.333 (2)	Cl1—O4	1.4357 (17)
N4—C1—N3	119.55 (16)	C3—N3—C1	115.48 (14)
N4—C1—N1	120.31 (15)	C1—N4—H4A	120.0
N3—C1—N1	120.14 (15)	C1—N4—H4B	120.0
N5—C2—N2	120.21 (16)	H4A—N4—H4B	120.0
N5—C2—N1	119.27 (15)	C2—N5—H5A	120.0
N2—C2—N1	120.50 (15)	C2—N5—H5B	120.0
N3—C3—N2	128.49 (15)	H5A—N5—H5B	120.0
N3—C3—C4	114.22 (14)	C5—N6—H6A	120.0
N2—C3—C4	117.24 (14)	C5—N6—H6B	120.0
N8—C4—C5	109.70 (14)	H6A—N6—H6B	120.0
N8—C4—C3	121.28 (15)	C5—N7—O1	105.17 (13)
C5—C4—C3	128.94 (15)	C4—N8—O1	106.16 (14)
N7—C5—N6	124.66 (16)	N8—O1—N7	111.01 (12)
N7—C5—C4	107.96 (15)	O3—Cl1—O5	110.26 (11)
N6—C5—C4	127.37 (16)	O3—Cl1—O2	112.07 (12)
C1—N1—C2	120.38 (14)	O5—Cl1—O2	108.42 (10)
C1—N1—H1	121.9 (15)	O3—Cl1—O4	109.23 (11)
C2—N1—H1	117.5 (15)	O5—Cl1—O4	108.93 (11)
C3—N2—C2	114.85 (14)	O2—Cl1—O4	107.85 (12)
N3—C3—C4—N8	169.24 (16)	C4—C3—N2—C2	179.00 (15)
N2—C3—C4—N8	-8.5 (2)	N5—C2—N2—C3	177.99 (18)
N3—C3—C4—C5	-7.2 (3)	N1—C2—N2—C3	-3.6 (2)
N2—C3—C4—C5	175.08 (17)	N2—C3—N3—C1	2.0 (3)
N8—C4—C5—N7	0.4 (2)	C4—C3—N3—C1	-175.43 (14)
C3—C4—C5—N7	177.17 (17)	N4—C1—N3—C3	175.19 (16)
N8—C4—C5—N6	179.80 (19)	N1—C1—N3—C3	-3.7 (2)
C3—C4—C5—N6	-3.4 (3)	N6—C5—N7—O1	-179.75 (19)
N4—C1—N1—C2	-176.95 (17)	C4—C5—N7—O1	-0.3 (2)
N3—C1—N1—C2	1.9 (3)	C5—C4—N8—O1	-0.27 (19)
N5—C2—N1—C1	-179.60 (17)	C3—C4—N8—O1	-177.34 (15)
N2—C2—N1—C1	1.9 (3)	C4—N8—O1—N7	0.07 (19)
N3—C3—N2—C2	1.7 (3)	C5—N7—O1—N8	0.16 (19)

Table S55. Hydrogen bonds (Å, º) for **14**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*B*···O2^{i}	0.86	2.44	3.214 (3)	150
N6—H6*B*···N3	0.86	2.31	2.883 (2)	124
N6—H6*A*···O5^{i}	0.86	2.63	3.037 (2)	110
N6—H6*A*···O5^{ii}	0.86	2.22	2.975 (2)	146
N5—H5*B*···O4^{iii}	0.86	2.20	2.943 (2)	144
N5—H5*A*···N8^{iv}	0.86	2.57	3.010 (2)	113
N5—H5*A*···N2^{iv}	0.86	2.18	3.038 (2)	176
N4—H4*B*···N7^{iii}	0.86	2.15	2.974 (2)	162
N4—H4*A*···O3^{v}	0.86	2.46	2.946 (2)	116
N4—H4*A*···O2^{i}	0.86	2.27	3.021 (2)	146
N1—H1···O4^{iii}	0.86 (2)	2.46 (2)	3.165 (2)	138.8 (19)
N1—H1···O1^{iii}	0.86 (2)	2.55 (2)	3.2659 (18)	140.7 (19)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) *x*-1, *y*, *z*; (iii) *x*, *y*, *z*+1; (iv) -*x*+2, -*y*+2, -*z*+1; (v) *x*-1, *y*, *z*+1.

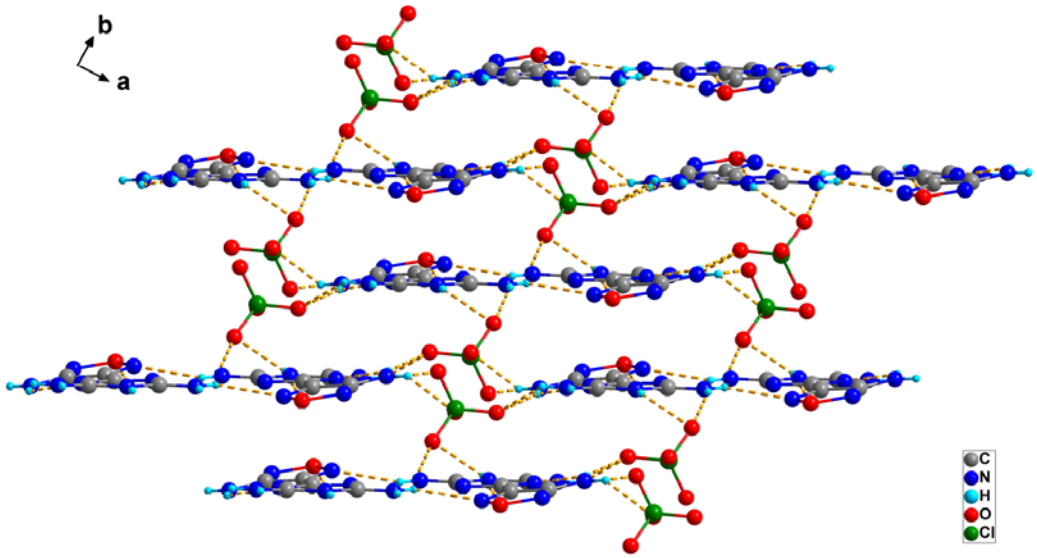


Fig. S13 Stacking diagram of **14** viewed down the *c* axis, yellow dotted lines indicate hydrogen bonding.

12. Single-crystal X-ray diffraction analysis of **14a**

Table S56. Crystal data, data collection, and refinement for **14a**

$C_5H_8N_8O \cdot 2(ClO_4) \cdot H_2O$	$F(000) = 840$
$M_r = 413.11$	$D_x = 1.879$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.3759$ (13) Å	Cell parameters from 6582 reflections
$b = 11.1406$ (13) Å	$\theta = 2.3–27.4°$
$c = 14.6936$ (19) Å	$\mu = 0.52$ mm^{-1}
$\beta = 107.926$ (4)°	$T = 273$ K
$V = 1460.3$ (3) Å^3	Block, colourless
$Z = 4$	0.22 × 0.20 × 0.08 mm
Bruker D8 QUEST PHOTON 100 diffractometer	2569 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	$R_{int} = 0.032$
ϕ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan *SADABS*	$h = -12 \rightarrow 11$
$T_{min} = 0.624$, $T_{max} = 0.746$	$k = -14 \rightarrow 14$
12616 measured reflections	$l = -19 \rightarrow 17$
3330 independent reflections	
Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 1.2194P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rangle_{max} = 0.49$ e Å^{-3}
3330 reflections	$\Delta\rangle_{min} = -0.51$ e Å^{-3}
233 parameters	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
3 restraints	Extinction coefficient: 0.0087 (16)

Table S57. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **14a**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7110 (2)	0.2665 (2)	0.39911 (16)	0.0244 (5)
C2	0.5567 (2)	0.29444 (19)	0.49607 (15)	0.0231 (5)
C3	0.4903 (2)	0.3806 (2)	0.34997 (16)	0.0264 (5)

C4	0.5299 (2)	0.2719 (2)	0.58644 (16)	0.0272 (5)
C5	0.4077 (3)	0.3137 (2)	0.61799 (18)	0.0314 (5)
N1	0.6160 (2)	0.33718 (17)	0.33457 (13)	0.0266 (4)
H1	0.634991	0.355309	0.282584	0.032*
N2	0.6780 (2)	0.24218 (17)	0.47998 (13)	0.0264 (4)
H2	0.733485	0.193662	0.521513	0.032*
N3	0.4630 (2)	0.36252 (17)	0.43449 (13)	0.0266 (4)
N4	0.3948 (2)	0.4420 (2)	0.28417 (15)	0.0375 (5)
H4A	0.411031	0.455333	0.230554	0.045*
H4B	0.315137	0.469433	0.294020	0.045*
N5	0.8308 (2)	0.22272 (19)	0.38396 (15)	0.0339 (5)
H5A	0.849954	0.239092	0.331718	0.041*
H5B	0.890598	0.177477	0.426220	0.041*
N6	0.4267 (3)	0.2698 (2)	0.70330 (17)	0.0431 (6)
N7	0.6179 (2)	0.2047 (2)	0.65216 (15)	0.0375 (5)
N8	0.2981 (2)	0.3889 (2)	0.57167 (18)	0.0439 (6)
H8A	0.232856	0.412157	0.598186	0.053*
H8B	0.292931	0.414083	0.515409	0.053*
O1	0.5584 (2)	0.20107 (19)	0.72471 (13)	0.0461 (5)
Cl1	0.03909 (7)	0.58106 (6)	0.33797 (5)	0.0400 (2)
O2	0.1903 (2)	0.5455 (2)	0.37681 (18)	0.0624 (7)
O3	-0.0024 (5)	0.5817 (3)	0.23742 (19)	0.1118 (13)
O4	0.0171 (3)	0.6966 (2)	0.37331 (19)	0.0708 (7)
O5	-0.0531 (3)	0.4950 (3)	0.3641 (3)	0.1002 (11)
Cl2	0.78359 (7)	0.93818 (5)	0.53970 (4)	0.03320 (18)
O6	0.6530 (2)	0.9644 (2)	0.46239 (17)	0.0643 (7)
O7	0.85507 (19)	1.05095 (15)	0.57755 (13)	0.0376 (4)
O8	0.8842 (2)	0.8709 (2)	0.50312 (15)	0.0564 (6)
O9	0.7515 (4)	0.8753 (2)	0.6133 (2)	0.0910 (10)
O10	0.6783 (2)	0.4395 (2)	0.19377 (14)	0.0456 (5)
H10A	0.764 (2)	0.465 (3)	0.207 (2)	0.068*
H10B	0.648 (3)	0.407 (3)	0.1406 (17)	0.068*

Table S58. Atomic displacement parameters (Å^2) for **14a**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0270 (11)	0.0264 (11)	0.0219 (11)	-0.0008 (9)	0.0106 (9)	-0.0030 (9)
C2	0.0223 (10)	0.0253 (11)	0.0229 (11)	-0.0020 (8)	0.0087 (9)	-0.0035 (9)
C3	0.0261 (11)	0.0275 (11)	0.0249 (11)	0.0004 (9)	0.0067 (9)	-0.0014 (10)
C4	0.0278 (11)	0.0293 (12)	0.0269 (12)	-0.0021 (9)	0.0122 (10)	-0.0013 (10)

C5	0.0335 (12)	0.0326 (13)	0.0347 (13)	-0.0063 (10)	0.0202 (11)	-0.0062 (11)
N1	0.0307 (10)	0.0314 (10)	0.0199 (9)	0.0029 (8)	0.0109 (8)	0.0028 (8)
N2	0.0266 (10)	0.0319 (10)	0.0232 (10)	0.0068 (8)	0.0112 (8)	0.0050 (8)
N3	0.0239 (9)	0.0314 (10)	0.0256 (10)	0.0013 (8)	0.0092 (8)	0.0004 (8)
N4	0.0340 (11)	0.0476 (13)	0.0282 (11)	0.0108 (10)	0.0059 (9)	0.0067 (10)
N5	0.0344 (11)	0.0425 (12)	0.0303 (11)	0.0099 (9)	0.0182 (9)	0.0057 (9)
N6	0.0510 (14)	0.0485 (14)	0.0416 (13)	-0.0005 (11)	0.0315 (11)	0.0006 (11)
N7	0.0434 (12)	0.0454 (13)	0.0291 (11)	0.0053 (10)	0.0193 (10)	0.0057 (10)
N8	0.0368 (12)	0.0540 (14)	0.0500 (14)	0.0098 (10)	0.0270 (11)	0.0009 (12)
O1	0.0576 (12)	0.0566 (12)	0.0331 (10)	0.0075 (10)	0.0272 (9)	0.0119 (9)
Cl1	0.0265 (3)	0.0457 (4)	0.0457 (4)	0.0084 (2)	0.0078 (3)	-0.0090 (3)
O2	0.0298 (10)	0.0614 (14)	0.0890 (18)	0.0103 (9)	0.0082 (11)	-0.0120 (12)
O3	0.175 (4)	0.097 (2)	0.0442 (15)	0.055 (2)	0.0060 (18)	-0.0026 (15)
O4	0.0582 (14)	0.0598 (14)	0.0868 (18)	0.0210 (11)	0.0112 (13)	-0.0277 (13)
O5	0.0684 (17)	0.089 (2)	0.168 (3)	-0.0314 (15)	0.074 (2)	-0.041 (2)
Cl2	0.0333 (3)	0.0336 (3)	0.0333 (3)	-0.0014 (2)	0.0111 (2)	-0.0057 (2)
O6	0.0324 (11)	0.0737 (15)	0.0693 (15)	0.0068 (10)	-0.0099 (10)	-0.0276 (12)
O7	0.0347 (9)	0.0344 (10)	0.0381 (10)	-0.0017 (7)	0.0031 (8)	-0.0029 (8)
O8	0.0512 (12)	0.0622 (14)	0.0522 (13)	0.0245 (10)	0.0104 (10)	-0.0137 (11)
O9	0.150 (3)	0.0644 (16)	0.0797 (19)	-0.0322 (17)	0.066 (2)	0.0043 (14)
O10	0.0405 (11)	0.0648 (14)	0.0324 (10)	-0.0118 (10)	0.0123 (9)	0.0057 (9)

Table S59. Geometric parameters (Å, º) for **14a**

C1—N5	1.305 (3)	N5—H5A	0.8600
C1—N1	1.339 (3)	N5—H5B	0.8600
C1—N2	1.344 (3)	N6—O1	1.403 (3)
C2—N3	1.295 (3)	N7—O1	1.347 (3)
C2—N2	1.362 (3)	N8—H8A	0.8600
C2—C4	1.447 (3)	N8—H8B	0.8600
C3—N4	1.293 (3)	Cl1—O3	1.407 (3)
C3—N1	1.356 (3)	Cl1—O2	1.412 (2)
C3—N3	1.358 (3)	Cl1—O5	1.420 (3)
C4—N7	1.297 (3)	Cl1—O4	1.427 (2)
C4—C5	1.439 (3)	Cl2—O9	1.397 (2)
C5—N6	1.306 (3)	Cl2—O6	1.421 (2)
C5—N8	1.339 (3)	Cl2—O8	1.4324 (19)
N1—H1	0.8600	Cl2—O7	1.4517 (18)
N2—H2	0.8600	O10—H10A	0.817 (17)
N4—H4A	0.8600	O10—H10B	0.830 (17)

N4—H4B	0.8600		
N5—C1—N1	121.3 (2)	H4A—N4—H4B	120.0
N5—C1—N2	121.3 (2)	C1—N5—H5A	120.0
N1—C1—N2	117.44 (19)	C1—N5—H5B	120.0
N3—C2—N2	123.5 (2)	H5A—N5—H5B	120.0
N3—C2—C4	118.10 (19)	C5—N6—O1	105.68 (18)
N2—C2—C4	118.4 (2)	C4—N7—O1	106.44 (19)
N4—C3—N1	120.1 (2)	C5—N8—H8A	120.0
N4—C3—N3	118.7 (2)	C5—N8—H8B	120.0
N1—C3—N3	121.2 (2)	H8A—N8—H8B	120.0
N7—C4—C5	109.5 (2)	N7—O1—N6	110.87 (18)
N7—C4—C2	122.2 (2)	O3—Cl1—O2	110.14 (19)
C5—C4—C2	128.3 (2)	O3—Cl1—O5	107.0 (2)
N6—C5—N8	125.4 (2)	O2—Cl1—O5	108.66 (18)
N6—C5—C4	107.5 (2)	O3—Cl1—O4	110.69 (17)
N8—C5—C4	127.0 (2)	O2—Cl1—O4	110.23 (14)
C1—N1—C3	120.96 (19)	O5—Cl1—O4	110.02 (16)
C1—N1—H1	119.5	O9—Cl2—O6	112.60 (19)
C3—N1—H1	119.5	O9—Cl2—O8	110.60 (17)
C1—N2—C2	119.93 (19)	O6—Cl2—O8	108.21 (13)
C1—N2—H2	120.0	O9—Cl2—O7	108.75 (15)
C2—N2—H2	120.0	O6—Cl2—O7	108.12 (13)
C2—N3—C3	116.60 (18)	O8—Cl2—O7	108.47 (13)
C3—N4—H4A	120.0	H10A—O10—H10B	114 (3)
C3—N4—H4B	120.0		
N3—C2—C4—N7	179.9 (2)	N1—C1—N2—C2	-3.8 (3)
N2—C2—C4—N7	0.5 (3)	N3—C2—N2—C1	4.3 (3)
N3—C2—C4—C5	1.5 (4)	C4—C2—N2—C1	-176.3 (2)
N2—C2—C4—C5	-177.8 (2)	N2—C2—N3—C3	0.2 (3)
N7—C4—C5—N6	0.2 (3)	C4—C2—N3—C3	-179.14 (19)
C2—C4—C5—N6	178.7 (2)	N4—C3—N3—C2	175.9 (2)
N7—C4—C5—N8	176.9 (2)	N1—C3—N3—C2	-5.2 (3)
C2—C4—C5—N8	-4.6 (4)	N8—C5—N6—O1	-177.0 (2)
N5—C1—N1—C3	178.8 (2)	C4—C5—N6—O1	-0.3 (3)
N2—C1—N1—C3	-1.1 (3)	C5—C4—N7—O1	0.0 (3)
N4—C3—N1—C1	-175.4 (2)	C2—C4—N7—O1	-178.6 (2)
N3—C3—N1—C1	5.7 (3)	C4—N7—O1—N6	-0.2 (3)

N5—C1—N2—C2	176.4 (2)	C5—N6—O1—N7	0.3 (3)

Table S60. Hydrogen bonds (Å, º) for **14a**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl2^{i}	0.86	2.88	3.562 (2)	137
N2—H2···O7^{i}	0.86	1.98	2.808 (3)	161
N4—H4*B*···O2	0.86	2.11	2.910 (3)	155
N4—H4*A*···Cl2^{ii}	0.86	2.94	3.670 (2)	144
N4—H4*A*···O7^{ii}	0.86	2.15	2.944 (3)	154
N5—H5*A*···N6^{iii}	0.86	2.22	3.055 (3)	164
N5—H5*B*···O8^{iv}	0.86	2.12	2.873 (3)	147
N8—H8*A*···Cl1^{v}	0.86	2.98	3.802 (2)	162
N8—H8*A*···O5^{v}	0.86	2.19	3.028 (3)	165
N8—H8*B*···N3	0.86	2.34	2.909 (3)	124
N8—H8*B*···O2	0.86	2.45	3.237 (4)	152

Symmetry codes: (i) *x*, *y*-1, *z*; (ii) *x*-1/2, -*y*+3/2, *z*-1/2; (iii) *x*+1/2, -*y*+1/2, *z*-1/2; (iv) -*x*+2, -*y*+1, -*z*+1; (v) -*x*, -*y*+1, -*z*+1.

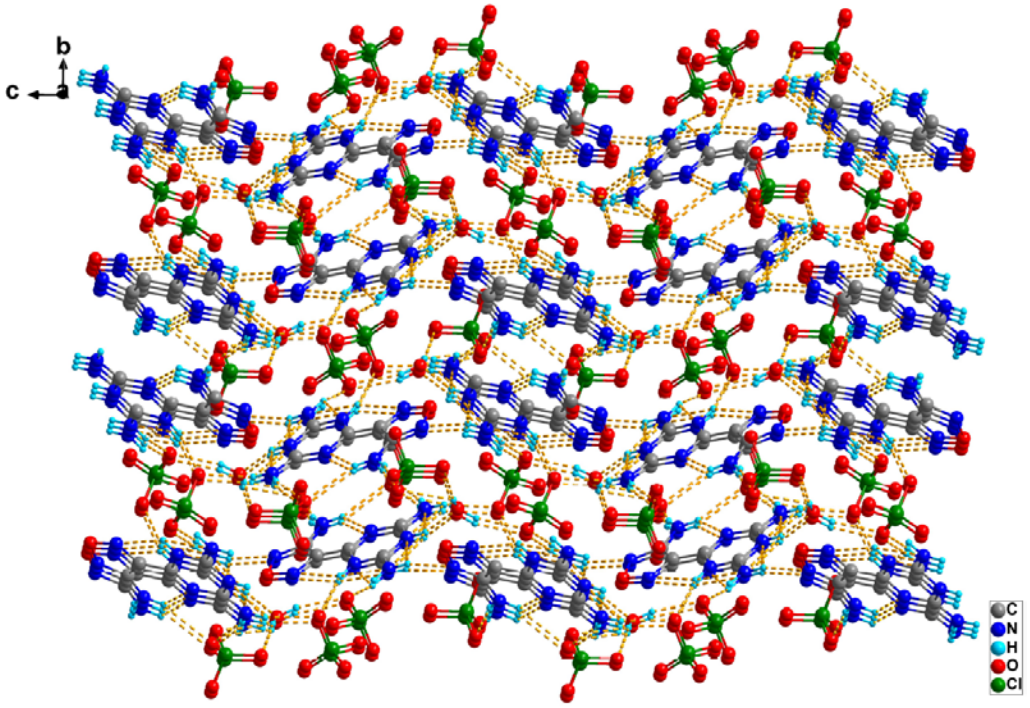


Fig. S14 Stacking diagram of **14a** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

13. Single-crystal X-ray diffraction analysis of **16**

Table S61. Crystal data, data collection, and refinement for **16**

$C_6H_3N_9O_4$	$F(000) = 536$
$M_r = 265.17$	$D_x = 1.813$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.4102$ (3) Å	Cell parameters from 1857 reflections
$b = 10.9235$ (5) Å	$\theta = 2.2–25.7°$
$c = 16.6422$ (9) Å	$\mu = 0.16$ mm^{-1}
$\beta = 98.878$ (2)°	$T = 170$ K
$V = 971.74$ (9) Å^3	Needle, colourless
$Z = 4$	0.08 × 0.05 × 0.03 mm
D8 VENTURE diffractometer	1223 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.077$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0954 before and 0.0647 after correction. The Ratio of minimum to maximum transmission is 0.8744. The $\lambda/2$ correction factor is Not present.	$\theta_{max} = 25.7°$, $\theta_{min} = 2.5°$
$T_{min} = 0.652$, $T_{max} = 0.745$	$h = -6 \rightarrow 6$
10308 measured reflections	$k = -13 \rightarrow 13$
1846 independent reflections	$l = -20 \rightarrow 20$
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	All H-atom parameters refined
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.4892P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
1846 reflections	$\Delta\rangle_{max} = 0.33$ e Å^{-3}
184 parameters	$\Delta\rangle_{min} = -0.23$ e Å^{-3}
7 restraints	

Table S62. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **16**

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.0910 (3)	0.25382 (19)	0.38326 (11)	0.0368 (5)
O2	1.2738 (4)	0.30136 (18)	0.71753 (12)	0.0383 (5)
O3	0.8457 (4)	0.58765 (18)	0.77890 (12)	0.0426 (6)

O4	0.4932 (4)	0.62106 (19)	0.69888 (13)	0.0437 (6)
N5	0.8205 (4)	0.1432 (2)	0.52317 (13)	0.0290 (6)
N9	0.7160 (5)	0.0055 (2)	0.41863 (16)	0.0331 (6)
N6	0.5642 (4)	0.3213 (2)	0.54310 (13)	0.0312 (6)
N4	1.1612 (4)	0.2374 (2)	0.65123 (13)	0.0347 (6)
N3	1.1227 (4)	0.3957 (2)	0.73852 (14)	0.0353 (6)
N8	0.1841 (4)	0.3311 (2)	0.44736 (14)	0.0361 (6)
N2	0.7109 (5)	0.4593 (2)	0.67779 (16)	0.0374 (6)
N1	0.6834 (5)	0.5623 (2)	0.72215 (15)	0.0363 (6)
N7	0.2489 (4)	0.1565 (2)	0.37525 (14)	0.0350 (6)
C6	0.6655 (5)	0.1043 (2)	0.45759 (16)	0.0273 (6)
C5	0.4382 (5)	0.1745 (2)	0.43307 (16)	0.0295 (7)
C1	0.9213 (5)	0.3875 (3)	0.68452 (17)	0.0300 (7)
C4	0.3994 (5)	0.2800 (3)	0.47763 (16)	0.0304 (7)
C3	0.7605 (5)	0.2484 (3)	0.56017 (16)	0.0291 (7)
C2	0.9433 (5)	0.2890 (3)	0.62992 (16)	0.0294 (7)
H2	0.588 (6)	0.453 (3)	0.6346 (19)	0.049 (10)*
H9A	0.852 (6)	-0.037 (3)	0.4345 (19)	0.047 (10)*
H9B	0.625 (6)	-0.013 (3)	0.3774 (19)	0.039 (9)*

Table S63. Atomic displacement parameters (Å^2) for **16**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0354 (11)	0.0450 (13)	0.0273 (11)	0.0011 (10)	-0.0040 (9)	0.0002 (10)
O2	0.0359 (11)	0.0462 (13)	0.0306 (12)	-0.0027 (10)	-0.0021 (9)	-0.0067 (10)
O3	0.0532 (13)	0.0372 (12)	0.0328 (12)	-0.0021 (10)	-0.0085 (11)	-0.0030 (10)
O4	0.0445 (13)	0.0418 (12)	0.0439 (13)	0.0064 (11)	0.0038 (10)	-0.0004 (10)
N5	0.0339 (13)	0.0310 (13)	0.0209 (12)	-0.0021 (10)	0.0007 (10)	-0.0006 (10)
N9	0.0364 (15)	0.0348 (15)	0.0245 (14)	-0.0003 (12)	-0.0064 (12)	-0.0037 (12)
N6	0.0319 (13)	0.0364 (14)	0.0243 (13)	0.0000 (11)	0.0012 (10)	-0.0013 (11)
N4	0.0354 (13)	0.0422 (15)	0.0247 (13)	-0.0045 (12)	-0.0016 (11)	-0.0061 (11)
N3	0.0395 (14)	0.0348 (14)	0.0303 (14)	-0.0031 (12)	0.0014 (11)	-0.0047 (11)
N8	0.0380 (14)	0.0422 (15)	0.0265 (14)	0.0007 (12)	0.0000 (11)	0.0004 (12)
N2	0.0458 (15)	0.0317 (13)	0.0322 (15)	0.0017 (12)	-0.0015 (12)	-0.0085 (12)
N1	0.0439 (15)	0.0324 (13)	0.0324 (14)	-0.0012 (12)	0.0054 (12)	0.0014 (11)
N7	0.0353 (14)	0.0404 (15)	0.0275 (14)	0.0016 (12)	-0.0005 (11)	0.0015 (11)
C6	0.0325 (15)	0.0308 (16)	0.0183 (14)	-0.0038 (13)	0.0027 (12)	0.0046 (13)
C5	0.0320 (16)	0.0336 (16)	0.0221 (15)	-0.0048 (13)	0.0020 (12)	0.0040 (13)
C1	0.0327 (16)	0.0312 (16)	0.0253 (16)	-0.0050 (13)	0.0024 (12)	0.0029 (13)
C4	0.0320 (16)	0.0355 (16)	0.0234 (15)	-0.0022 (13)	0.0033 (12)	0.0040 (14)

C3	0.0322 (15)	0.0338 (16)	0.0216 (15)	-0.0047 (13)	0.0049 (12)	0.0019 (13)
C2	0.0316 (16)	0.0317 (16)	0.0242 (15)	-0.0026 (13)	0.0027 (12)	0.0008 (13)

Table S64. Geometric parameters (Å, º) for **16**

O1—N8	1.393 (3)	N6—C3	1.323 (3)
O1—N7	1.383 (3)	N4—C2	1.305 (3)
O2—N4	1.367 (3)	N3—C1	1.304 (3)
O2—N3	1.393 (3)	N8—C4	1.320 (3)
O3—N1	1.218 (3)	N2—N1	1.366 (3)
O4—N1	1.224 (3)	N2—C1	1.373 (4)
N5—C6	1.339 (3)	N2—H2	0.90 (3)
N5—C3	1.366 (3)	N7—C5	1.308 (3)
N9—C6	1.309 (4)	C6—C5	1.453 (4)
N9—H9A	0.87 (3)	C5—C4	1.404 (4)
N9—H9B	0.81 (3)	C1—C2	1.425 (4)
N6—C4	1.373 (3)	C3—C2	1.472 (4)
N7—O1—N8	112.58 (19)	N9—C6—N5	120.9 (3)
N4—O2—N3	112.01 (19)	N9—C6—C5	121.9 (2)
C6—N5—C3	118.2 (2)	N7—C5—C6	131.3 (3)
C6—N9—H9A	121 (2)	N7—C5—C4	110.4 (2)
C6—N9—H9B	119 (2)	C4—C5—C6	118.3 (2)
H9A—N9—H9B	120 (3)	N3—C1—N2	127.6 (3)
C3—N6—C4	112.0 (2)	N3—C1—C2	110.4 (2)
C2—N4—O2	105.7 (2)	N2—C1—C2	122.0 (2)
C1—N3—O2	103.7 (2)	N6—C4—C5	123.9 (3)
C4—N8—O1	103.3 (2)	N8—C4—N6	126.2 (3)
N1—N2—C1	125.8 (3)	N8—C4—C5	109.9 (2)
N1—N2—H2	112 (2)	N5—C3—C2	115.5 (2)
C1—N2—H2	121 (2)	N6—C3—N5	130.4 (2)
O3—N1—O4	126.6 (2)	N6—C3—C2	114.0 (2)
O3—N1—N2	118.7 (2)	N4—C2—C1	108.3 (2)
O4—N1—N2	114.7 (2)	N4—C2—C3	123.6 (3)
C5—N7—O1	103.8 (2)	C1—C2—C3	128.2 (2)
N5—C6—C5	117.2 (2)		

Table S65. Hydrogen bonds (Å, º) for **16**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N6	0.90(3)	2.08(3)	2.716(3)	126(3)
N9—H9A···N4	0.88(3)	2.61(3)	3.012(3)	109(2)
N9—H9A···N5	0.88(3)	2.14(3)	3.019(3)	178(4)
N9—H9B···O3	0.81(3)	2.21(3)	3.003(3)	170(3)

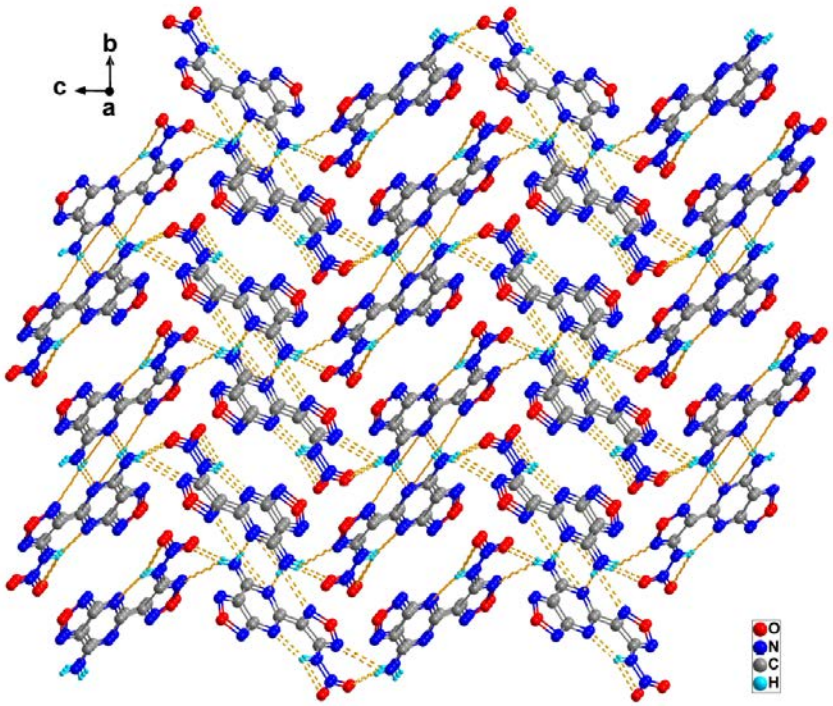


Fig. S15 Stacking diagram of **16** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

14. Single-crystal X-ray diffraction analysis of **17**

Table S66. Crystal data, data collection, and refinement for **17**

$C_6H_6N_{10}O_5$	D_x = 1.806 Mg m^{-3}
M_r = 298.21	Mo *K*α radiation, λ = 0.71073 Å
Orthorhombic, *Pnma*	Cell parameters from 710 reflections
a = 14.851 (2) Å	θ = 3.4–24.0°
b = 6.1775 (8) Å	μ = 0.16 mm^{-1}
c = 11.9579 (16) Å	*T* = 170 K
V = 1097.0 (3) Å^3	Needle, colourless
Z = 4	0.15 × 0.05 × 0.02 mm
F(000) = 608	

D8 VENTURE diffractometer	707 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.076$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0857 before and 0.0635 after correction. The Ratio of minimum to maximum transmission is 0.6896. The $\lambda/2$ correction factor is Not present.	$\theta_{max} = 26.5°$, $\theta_{min} = 2.2°$
$T_{min} = 0.514$, $T_{max} = 0.745$	$h = -18 \rightarrow 16$
3710 measured reflections	$k = -7 \rightarrow 7$
1219 independent reflections	$l = -11 \rightarrow 15$
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.081$	Only H-atom coordinates refined
$wR(F^2) = 0.182$	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 1.4263P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} < 0.001$
1219 reflections	$\Delta\rangle_{max} = 0.38$ e Å^{-3}
144 parameters	$\Delta\rangle_{min} = -0.43$ e Å^{-3}
6 restraints	

Table S67. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **17**

	x	*y*	*z*	U_{iso}*/U_{eq}
O5	0.5123 (3)	0.250000	0.7444 (4)	0.0295 (11)
H5	0.467 (3)	0.250000	0.697 (5)	0.044*
O3	0.4766 (3)	0.250000	0.1531 (4)	0.0327 (12)
O1	0.3703 (3)	0.250000	0.5893 (4)	0.0303 (11)
O2	0.3141 (3)	0.250000	0.4223 (4)	0.0315 (12)
O4	0.8696 (3)	0.250000	0.5747 (4)	0.0353 (12)
N7	0.4650 (3)	0.250000	0.4484 (4)	0.0231 (13)
N2	0.5841 (3)	0.250000	0.6678 (4)	0.0250 (13)
N5	0.7270 (4)	0.250000	0.2858 (5)	0.0290 (15)
N8	0.3819 (3)	0.250000	0.4837 (4)	0.0232 (13)
N6	0.6548 (4)	0.250000	0.4578 (5)	0.0256 (14)
N9	0.4210 (3)	0.250000	0.2486 (5)	0.0281 (13)
N4	0.8137 (3)	0.250000	0.4815 (5)	0.0294 (14)
N1	0.6739 (4)	0.250000	0.8313 (5)	0.0308 (15)
N10	0.5656 (3)	0.250000	0.1817 (5)	0.0310 (14)

C4	0.6548 (4)	0.250000	0.3469 (5)	0.0216 (15)
N3	0.8210 (3)	0.250000	0.6727 (5)	0.0345 (15)
C2	0.7363 (4)	0.250000	0.6424 (5)	0.0224 (15)
C5	0.5671 (4)	0.250000	0.2898 (6)	0.0231 (15)
C6	0.4771 (4)	0.250000	0.3329 (5)	0.0212 (15)
C3	0.7324 (4)	0.250000	0.5232 (5)	0.0236 (15)
C1	0.6602 (4)	0.250000	0.7199 (6)	0.0251 (16)
H1A	0.628 (2)	0.250000	0.876 (4)	0.003 (14)*
H1B	0.729 (2)	0.250000	0.853 (6)	0.05 (3)*
H5A	0.780 (2)	0.250000	0.316 (6)	0.04 (2)*
H5B	0.719 (5)	0.250000	0.213 (2)	0.05 (3)*
H6	0.608 (3)	0.250000	0.502 (4)	0.031 (19)*

Table S68. Atomic displacement parameters (Å^2) for **17**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O5	0.018 (3)	0.039 (3)	0.032 (3)	0.000	0.004 (2)	0.000
O3	0.015 (2)	0.053 (3)	0.030 (3)	0.000	-0.004 (2)	0.000
O1	0.024 (3)	0.046 (3)	0.021 (2)	0.000	0.006 (2)	0.000
O2	0.015 (2)	0.052 (3)	0.027 (3)	0.000	-0.006 (2)	0.000
O4	0.015 (2)	0.064 (3)	0.026 (3)	0.000	0.000 (2)	0.000
N7	0.011 (3)	0.034 (3)	0.024 (3)	0.000	-0.001 (2)	0.000
N2	0.013 (3)	0.028 (3)	0.034 (3)	0.000	0.005 (3)	0.000
N5	0.007 (3)	0.043 (4)	0.036 (4)	0.000	0.002 (3)	0.000
N8	0.015 (3)	0.026 (3)	0.028 (3)	0.000	0.002 (3)	0.000
N6	0.014 (3)	0.034 (3)	0.029 (3)	0.000	0.006 (2)	0.000
N9	0.015 (3)	0.037 (3)	0.033 (3)	0.000	0.006 (3)	0.000
N4	0.016 (3)	0.046 (4)	0.026 (3)	0.000	-0.008 (3)	0.000
N1	0.019 (3)	0.053 (4)	0.021 (3)	0.000	-0.001 (3)	0.000
N10	0.018 (3)	0.038 (4)	0.037 (4)	0.000	-0.006 (3)	0.000
C4	0.022 (4)	0.019 (3)	0.025 (4)	0.000	-0.001 (3)	0.000
N3	0.016 (3)	0.053 (4)	0.034 (4)	0.000	-0.004 (3)	0.000
C2	0.017 (3)	0.022 (3)	0.028 (4)	0.000	-0.003 (3)	0.000
C5	0.015 (3)	0.025 (4)	0.029 (4)	0.000	-0.001 (3)	0.000
C6	0.016 (3)	0.021 (3)	0.026 (4)	0.000	-0.007 (3)	0.000
C3	0.010 (3)	0.033 (4)	0.027 (4)	0.000	0.000 (3)	0.000
C1	0.018 (4)	0.022 (4)	0.035 (4)	0.000	0.001 (3)	0.000

Table S69. Geometric parameters (Å, º) for **17**

O5—H5	0.88 (2)	N6—C4	1.326 (8)
O5—N2	1.406 (6)	N6—C3	1.393 (8)
O3—N9	1.409 (6)	N6—H6	0.87 (2)
O3—N10	1.364 (6)	N9—C6	1.308 (7)
O1—N8	1.275 (7)	N4—C3	1.306 (8)
O2—N8	1.245 (6)	N1—C1	1.347 (9)
O4—N4	1.389 (7)	N1—H1A	0.87 (2)
O4—N3	1.376 (7)	N1—H1B	0.86 (2)
N7—N8	1.305 (7)	N10—C5	1.293 (8)
N7—C6	1.392 (8)	C4—C5	1.471 (8)
N2—C1	1.291 (8)	N3—C2	1.308 (7)
N5—C4	1.297 (8)	C2—C3	1.427 (8)
N5—H5A	0.87 (2)	C2—C1	1.461 (9)
N5—H5B	0.88 (2)	C5—C6	1.432 (8)
N2—O5—H5	99 (5)	N5—C4—N6	124.2 (6)
N10—O3—N9	111.3 (4)	N5—C4—C5	118.0 (6)
N3—O4—N4	111.7 (4)	N6—C4—C5	117.7 (6)
N8—N7—C6	116.3 (5)	C2—N3—O4	105.6 (5)
C1—N2—O5	110.5 (5)	N3—C2—C3	108.4 (6)
C4—N5—H5A	121 (5)	N3—C2—C1	124.6 (6)
C4—N5—H5B	116 (5)	C3—C2—C1	127.0 (6)
H5A—N5—H5B	123 (7)	N10—C5—C4	118.7 (6)
O1—N8—N7	116.6 (5)	N10—C5—C6	110.1 (5)
O2—N8—O1	118.3 (5)	C6—C5—C4	131.2 (6)
O2—N8—N7	125.0 (5)	N7—C6—C5	118.6 (5)
C4—N6—C3	124.2 (5)	N9—C6—N7	133.0 (6)
C4—N6—H6	128 (4)	N9—C6—C5	108.4 (5)
C3—N6—H6	108 (4)	N6—C3—C2	126.5 (6)
C6—N9—O3	104.6 (5)	N4—C3—N6	123.4 (6)
C3—N4—O4	104.3 (5)	N4—C3—C2	110.1 (5)
C1—N1—H1A	119 (3)	N2—C1—N1	127.5 (6)
C1—N1—H1B	116 (5)	N2—C1—C2	111.8 (6)
H1A—N1—H1B	125 (6)	N1—C1—C2	120.7 (6)
C5—N10—O3	105.5 (5)		
O5—N2—C1—N1	0.000 (1)	N10—C5—C6—N7	180.000 (1)

O5—N2—C1—C2	180.000 (1)	N10—C5—C6—N9	0.000 (1)
O3—N9—C6—N7	180.000 (1)	C4—N6—C3—N4	0.000 (1)
O3—N9—C6—C5	0.000 (1)	C4—N6—C3—C2	180.000 (1)
O3—N10—C5—C4	180.000 (1)	C4—C5—C6—N7	0.000 (1)
O3—N10—C5—C6	0.000 (1)	C4—C5—C6—N9	180.000 (1)
O4—N4—C3—N6	180.000 (1)	N3—O4—N4—C3	0.000 (1)
O4—N4—C3—C2	0.000 (1)	N3—C2—C3—N6	180.000 (1)
O4—N3—C2—C3	0.000 (1)	N3—C2—C3—N4	0.000 (1)
O4—N3—C2—C1	180.000 (1)	N3—C2—C1—N2	180.000 (1)
N5—C4—C5—N10	0.000 (1)	N3—C2—C1—N1	0.000 (2)
N5—C4—C5—C6	180.000 (1)	C6—N7—N8—O1	180.000 (1)
N8—N7—C6—N9	0.000 (1)	C6—N7—N8—O2	0.000 (1)
N8—N7—C6—C5	180.000 (1)	C3—N6—C4—N5	0.000 (1)
N6—C4—C5—N10	180.000 (1)	C3—N6—C4—C5	180.000 (1)
N6—C4—C5—C6	0.000 (1)	C3—C2—C1—N2	0.000 (1)
N9—O3—N10—C5	0.000 (1)	C3—C2—C1—N1	180.000 (1)
N4—O4—N3—C2	0.000 (1)	C1—C2—C3—N6	0.000 (1)
N10—O3—N9—C6	0.000 (1)	C1—C2—C3—N4	180.000 (1)

Table S70. Hydrogen bonds (Å, º) for **17**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1B···N3	0.86(4)	2.55(6)	2.893(8)	105(5)
N1—H1B···O1	0.86(4)	2.21(4)	3.067(7)	179(6)
O5—H5···O1	0.88(5)	1.93(5)	2.808(7)	178(5)
N5—H5A···N4	0.87(4)	2.04(7)	2.671(8)	129(5)
N5—H5A···N9	0.87(4)	2.23(4)	2.910(7)	135(6)
N5—H5B···N10	0.88(3)	2.31(7)	2.701(8)	107(5)
N5—H5B···O2	0.88(3)	2.15(5)	2.805(8)	131(6)
N6—H6···N2	0.87(5)	2.01(5)	2.722(8)	137(4)
N6—H6···N7	0.87(5)	2.22(5)	2.821(7)	126(4)

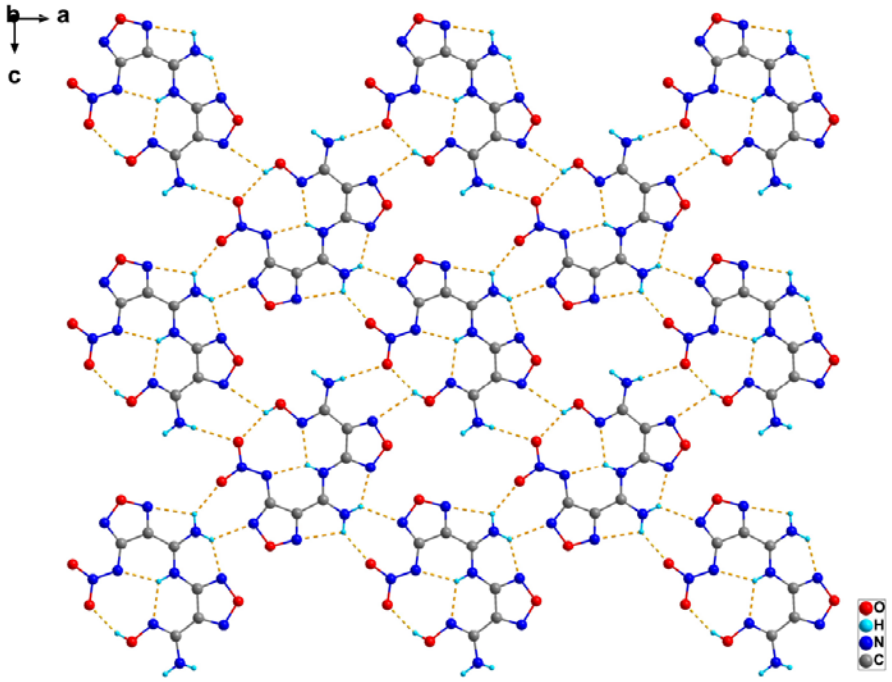


Fig. S16 Hydrogen bonds (green dotted lines) in the 2D layer of **17**.

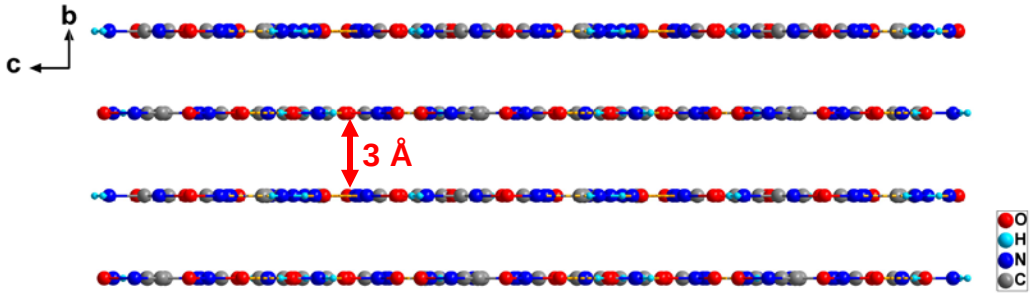


Fig. S17 Stacking diagram of **17** viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

15. Single-crystal X-ray diffraction analysis of **18**·1.5Diox

Table S71. Crystal data, data collection, and refinement for **18**·1.5Diox

$C_6H_2N_8O_4 \cdot 3(C_2H_4O)$	$Z = 2$
$M_r = 382.31$	$F(000) = 396$
Triclinic, $P\bar{1}$	$D_x = 1.506$ Mg m^{-3}
$a = 7.0395$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.1075$ (8) Å	Cell parameters from 5405 reflections
$c = 11.9166$ (9) Å	$\theta = 2.2$–$27.3°$
$\alpha = 110.120$ (3)°	$\mu = 0.13$ mm^{-1}
$\beta = 99.467$ (2)°	$T = 193$ K

γ = 98.084 (2)°	Block, colourless
V = 843.21 (10) Å^3	0.12 × 0.11 × 0.1 mm
Bruker D8 VENTURE dual wavelength Mo/Cu diffractometer	3796 independent reflections
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs DIAMOND	2998 reflections with $I > 2\sigma(I)$
Helios Multi-layer Optic monochromator	R_{int} = 0.070
Detector resolution: 7.41 pixels mm^{-1}	θ_{max} = 27.5°, θ_{min} = 3.0°
ω and ϕ scans	h = -7→9
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1231 before and 0.0663 after correction. The Ratio of minimum to maximum transmission is 0.9573. The λ/2 correction factor is Not present.	k = -14→14
T_{min} = 0.714, T_{max} = 0.746	l = -15→15
23612 measured reflections	
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.043	H-atom parameters constrained
$wR(F^2)$ = 0.113	$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.1858P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max} < 0.001$
3796 reflections	$\Delta\rangle_{max}$ = 0.34 e Å^{-3}
244 parameters	$\Delta\rangle_{min}$ = -0.20 e Å^{-3}
0 restraints	

Table S72. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **18**·1.5Diox

	x	y	z	U_{iso}*/U_{eq}
O1	0.36102 (15)	0.40637 (11)	0.16795 (9)	0.0358 (3)
O6	0.05230 (17)	0.09505 (10)	0.44964 (10)	0.0400 (3)
O7	-0.01136 (17)	0.46594 (11)	0.87383 (9)	0.0402 (3)
O4	0.46512 (17)	0.25447 (12)	0.76652 (10)	0.0429 (3)
N5	0.21161 (16)	0.40315 (11)	0.48806 (10)	0.0251 (2)
N8	0.03214 (18)	0.44408 (12)	0.63759 (10)	0.0307 (3)
H8A	-0.042136	0.481612	0.598871	0.037*
H8B	0.010299	0.438674	0.706496	0.037*
O5	0.1105 (2)	0.12575 (12)	0.07760 (12)	0.0549 (4)
N2	0.29260 (17)	0.42116 (12)	0.27273 (11)	0.0310 (3)

O2	0.5529 (2)	0.08936 (12)	0.23167 (13)	0.0597 (4)
N4	0.47570 (17)	0.28289 (12)	0.48620 (10)	0.0293 (3)
N1	0.49437 (18)	0.32567 (13)	0.15488 (11)	0.0360 (3)
N6	0.5497 (2)	0.23097 (14)	0.66597 (12)	0.0392 (3)
N3	0.63087 (19)	0.20388 (14)	0.26353 (12)	0.0384 (3)
N7	0.31204 (19)	0.31873 (13)	0.75837 (11)	0.0357 (3)
C6	0.17504 (19)	0.39630 (12)	0.59270 (12)	0.0251 (3)
O3	0.80398 (19)	0.25128 (16)	0.30672 (17)	0.0723 (5)
C2	0.37971 (19)	0.35123 (13)	0.32440 (12)	0.0260 (3)
C4	0.4486 (2)	0.28100 (13)	0.59643 (13)	0.0286 (3)
C3	0.35375 (18)	0.34400 (12)	0.44267 (12)	0.0248 (3)
C1	0.5044 (2)	0.29273 (14)	0.24900 (12)	0.0292 (3)
C5	0.3028 (2)	0.33458 (13)	0.65431 (12)	0.0273 (3)
C9	0.1258 (3)	-0.02291 (16)	0.41986 (16)	0.0430 (4)
H9A	0.258711	-0.006047	0.403913	0.052*
H9B	0.038120	-0.090867	0.344307	0.052*
C10	-0.1366 (2)	0.07188 (16)	0.47655 (17)	0.0427 (4)
H10A	-0.230856	0.006180	0.402449	0.051*
H10B	-0.185694	0.154315	0.499371	0.051*
C12	-0.0240 (3)	0.36800 (17)	0.92573 (14)	0.0404 (4)
H12A	0.108767	0.351277	0.948191	0.049*
H12B	-0.109598	0.285124	0.864531	0.049*
C11	0.1072 (3)	0.58769 (18)	0.96205 (16)	0.0442 (4)
H11A	0.111872	0.655204	0.925237	0.053*
H11B	0.243426	0.576921	0.985613	0.053*
C8	0.0356 (3)	0.03285 (19)	0.12581 (17)	0.0515 (4)
H8C	0.006955	0.079457	0.206309	0.062*
H8D	0.135868	-0.018269	0.138465	0.062*
C7	0.1485 (3)	0.05809 (19)	-0.03943 (17)	0.0524 (5)
H7A	0.250785	0.007393	-0.029841	0.063*
H7B	0.198708	0.122475	-0.073674	0.063*

Table S73. Atomic displacement parameters (Å^2) for **18**·1.5Diox

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0363 (6)	0.0496 (6)	0.0302 (5)	0.0155 (5)	0.0133 (4)	0.0207 (5)
O6	0.0437 (6)	0.0336 (6)	0.0465 (6)	0.0110 (5)	0.0111 (5)	0.0181 (5)
O7	0.0511 (7)	0.0554 (7)	0.0252 (5)	0.0234 (5)	0.0149 (5)	0.0212 (5)
O4	0.0470 (6)	0.0623 (7)	0.0353 (6)	0.0294 (6)	0.0129 (5)	0.0292 (5)
N5	0.0268 (5)	0.0274 (5)	0.0228 (5)	0.0095 (4)	0.0074 (4)	0.0095 (4)

N8	0.0365 (6)	0.0417 (7)	0.0241 (6)	0.0205 (5)	0.0135 (5)	0.0169 (5)
O5	0.0596 (8)	0.0427 (7)	0.0479 (7)	-0.0006 (6)	0.0147 (6)	0.0027 (6)
N2	0.0322 (6)	0.0400 (7)	0.0251 (6)	0.0112 (5)	0.0108 (5)	0.0140 (5)
O2	0.0659 (9)	0.0426 (7)	0.0626 (9)	0.0206 (6)	0.0033 (7)	0.0119 (6)
N4	0.0282 (6)	0.0355 (6)	0.0275 (6)	0.0128 (5)	0.0087 (5)	0.0125 (5)
N1	0.0314 (6)	0.0482 (7)	0.0319 (7)	0.0125 (5)	0.0127 (5)	0.0152 (6)
N6	0.0397 (7)	0.0530 (8)	0.0347 (7)	0.0228 (6)	0.0116 (5)	0.0221 (6)
N3	0.0374 (7)	0.0461 (8)	0.0366 (7)	0.0195 (6)	0.0146 (6)	0.0144 (6)
N7	0.0393 (7)	0.0463 (7)	0.0304 (6)	0.0192 (6)	0.0097 (5)	0.0205 (6)
C6	0.0275 (6)	0.0259 (6)	0.0217 (6)	0.0072 (5)	0.0057 (5)	0.0079 (5)
O3	0.0308 (7)	0.0825 (10)	0.1181 (14)	0.0205 (7)	0.0135 (7)	0.0539 (10)
C2	0.0232 (6)	0.0290 (6)	0.0243 (6)	0.0065 (5)	0.0055 (5)	0.0078 (5)
C4	0.0280 (7)	0.0323 (7)	0.0269 (7)	0.0101 (5)	0.0058 (5)	0.0115 (5)
C3	0.0235 (6)	0.0261 (6)	0.0233 (6)	0.0054 (5)	0.0056 (5)	0.0073 (5)
C1	0.0251 (6)	0.0355 (7)	0.0256 (7)	0.0068 (5)	0.0074 (5)	0.0089 (6)
C5	0.0286 (7)	0.0298 (7)	0.0233 (6)	0.0080 (5)	0.0051 (5)	0.0094 (5)
C9	0.0470 (9)	0.0360 (8)	0.0488 (10)	0.0133 (7)	0.0168 (7)	0.0149 (7)
C10	0.0412 (9)	0.0379 (8)	0.0540 (10)	0.0155 (7)	0.0114 (7)	0.0203 (7)
C12	0.0480 (9)	0.0489 (9)	0.0304 (8)	0.0181 (7)	0.0113 (7)	0.0181 (7)
C11	0.0478 (9)	0.0568 (10)	0.0412 (9)	0.0156 (8)	0.0211 (7)	0.0278 (8)
C8	0.0550 (11)	0.0561 (11)	0.0395 (9)	0.0115 (8)	0.0141 (8)	0.0119 (8)
C7	0.0528 (11)	0.0516 (10)	0.0494 (10)	0.0055 (8)	0.0202 (8)	0.0131 (8)

Table S74. Geometric parameters (Å, º) for **18**·1.5Diox

O1—N2	1.3773 (15)	N3—C1	1.4528 (19)
O1—N1	1.3775 (16)	N7—C5	1.3038 (18)
O6—C9	1.4289 (19)	C6—C5	1.4560 (18)
O6—C10	1.428 (2)	C2—C3	1.4781 (19)
O7—C12	1.4240 (19)	C2—C1	1.4205 (18)
O7—C11	1.430 (2)	C4—C5	1.4162 (19)
O4—N6	1.3861 (17)	C9—H9A	0.9900
O4—N7	1.3819 (16)	C9—H9B	0.9900
N5—C6	1.3388 (17)	C9—C10^{i}	1.506 (2)
N5—C3	1.3579 (17)	C10—H10A	0.9900
N8—H8A	0.8800	C10—H10B	0.9900
N8—H8B	0.8800	C12—H12A	0.9900
N8—C6	1.3082 (17)	C12—H12B	0.9900
O5—C8	1.424 (2)	C12—C11^{ii}	1.503 (2)
O5—C7	1.428 (2)	C11—H11A	0.9900

N2—C2	1.3027 (18)	C11—H11B	0.9900
O2—N3	1.2109 (18)	C8—H8C	0.9900
N4—C4	1.3648 (18)	C8—H8D	0.9900
N4—C3	1.3139 (17)	C8—C7^{iii}	1.496 (3)
N1—C1	1.2886 (19)	C7—H7A	0.9900
N6—C4	1.3177 (18)	C7—H7B	0.9900
N3—O3	1.2058 (19)		
N2—O1—N1	111.25 (10)	O6—C9—H9B	109.5
C10—O6—C9	109.56 (12)	O6—C9—C10^{i}	110.60 (13)
C12—O7—C11	110.53 (12)	H9A—C9—H9B	108.1
N7—O4—N6	112.34 (10)	C10^{i}—C9—H9A	109.5
C6—N5—C3	118.07 (11)	C10^{i}—C9—H9B	109.5
H8A—N8—H8B	120.0	O6—C10—C9^{i}	111.01 (13)
C6—N8—H8A	120.0	O6—C10—H10A	109.4
C6—N8—H8B	120.0	O6—C10—H10B	109.4
C8—O5—C7	109.43 (13)	C9^{i}—C10—H10A	109.4
C2—N2—O1	106.20 (11)	C9^{i}—C10—H10B	109.4
C3—N4—C4	111.50 (11)	H10A—C10—H10B	108.0
C1—N1—O1	104.07 (11)	O7—C12—H12A	109.6
C4—N6—O4	104.16 (11)	O7—C12—H12B	109.6
O2—N3—C1	117.14 (13)	O7—C12—C11^{ii}	110.09 (13)
O3—N3—O2	126.02 (15)	H12A—C12—H12B	108.2
O3—N3—C1	116.84 (14)	C11^{ii}—C12—H12A	109.6
C5—N7—O4	104.11 (11)	C11^{ii}—C12—H12B	109.6
N5—C6—C5	116.87 (12)	O7—C11—C12^{ii}	110.54 (13)
N8—C6—N5	121.28 (12)	O7—C11—H11A	109.5
N8—C6—C5	121.85 (12)	O7—C11—H11B	109.5
N2—C2—C3	123.94 (12)	C12^{ii}—C11—H11A	109.5
N2—C2—C1	107.00 (12)	C12^{ii}—C11—H11B	109.5
C1—C2—C3	129.00 (12)	H11A—C11—H11B	108.1
N4—C4—C5	124.04 (12)	O5—C8—H8C	109.6
N6—C4—N4	126.94 (13)	O5—C8—H8D	109.6
N6—C4—C5	109.02 (13)	O5—C8—C7^{iii}	110.29 (16)
N5—C3—C2	114.82 (11)	H8C—C8—H8D	108.1
N4—C3—N5	131.45 (13)	C7^{iii}—C8—H8C	109.6
N4—C3—C2	113.72 (12)	C7^{iii}—C8—H8D	109.6
N1—C1—N3	119.08 (13)	O5—C7—C8^{iii}	110.46 (15)
N1—C1—C2	111.48 (13)	O5—C7—H7A	109.6

C2—C1—N3	129.43 (13)	O5—C7—H7B	109.6
N7—C5—C6	131.75 (13)	C8^{iii}—C7—H7A	109.6
N7—C5—C4	110.36 (12)	C8^{iii}—C7—H7B	109.6
C4—C5—C6	117.89 (12)	H7A—C7—H7B	108.1
O6—C9—H9A	109.5		
O1—N2—C2—C3	177.44 (11)	N6—C4—C5—N7	0.07 (17)
O1—N2—C2—C1	0.09 (14)	N6—C4—C5—C6	179.45 (12)
O1—N1—C1—N3	178.68 (12)	N7—O4—N6—C4	0.09 (16)
O1—N1—C1—C2	-0.24 (15)	C6—N5—C3—N4	-3.7 (2)
O4—N6—C4—N4	179.83 (13)	C6—N5—C3—C2	177.61 (11)
O4—N6—C4—C5	-0.09 (16)	O3—N3—C1—N1	81.35 (19)
O4—N7—C5—C6	-179.28 (14)	O3—N3—C1—C2	-99.94 (19)
O4—N7—C5—C4	-0.01 (16)	C4—N4—C3—N5	0.1 (2)
N5—C6—C5—N7	176.16 (14)	C4—N4—C3—C2	178.82 (11)
N5—C6—C5—C4	-3.06 (18)	C3—N5—C6—N8	-175.77 (12)
N8—C6—C5—N7	-3.2 (2)	C3—N5—C6—C5	4.83 (17)
N8—C6—C5—C4	177.54 (13)	C3—N4—C4—N6	-178.00 (14)
N2—O1—N1—C1	0.31 (15)	C3—N4—C4—C5	1.91 (19)
N2—C2—C3—N5	7.94 (19)	C3—C2—C1—N1	-177.07 (13)
N2—C2—C3—N4	-170.97 (13)	C3—C2—C1—N3	4.1 (2)
N2—C2—C1—N1	0.10 (16)	C1—C2—C3—N5	-175.32 (13)
N2—C2—C1—N3	-178.68 (14)	C1—C2—C3—N4	5.8 (2)
O2—N3—C1—N1	-98.91 (17)	C9—O6—C10—C9^{i}	57.56 (19)
O2—N3—C1—C2	79.8 (2)	C10—O6—C9—C10^{i}	-57.32 (19)
N4—C4—C5—N7	-179.86 (13)	C12—O7—C11—C12^{i}	-57.87 (18)
N4—C4—C5—C6	-0.5 (2)	C11—O7—C12—C11^{i}	57.60 (19)
N1—O1—N2—C2	-0.25 (14)	C8—O5—C7—C8^{iii}	58.4 (2)
N6—O4—N7—C5	-0.05 (16)	C7—O5—C8—C7^{iii}	-58.3 (2)

Symmetry codes: (i) -*x*, -*y*, -*z*+1; (ii) -*x*, -*y*+1, -*z*+2; (iii) -*x*, -*y*, -*z*.

Table S75. Hydrogen bonds (Å, º) for **18**·1.5Diox

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8A···N5	0.88	2.25	3.1285(18)	174
N4—H8B···O7	0.88	1.95	2.8129(15)	168

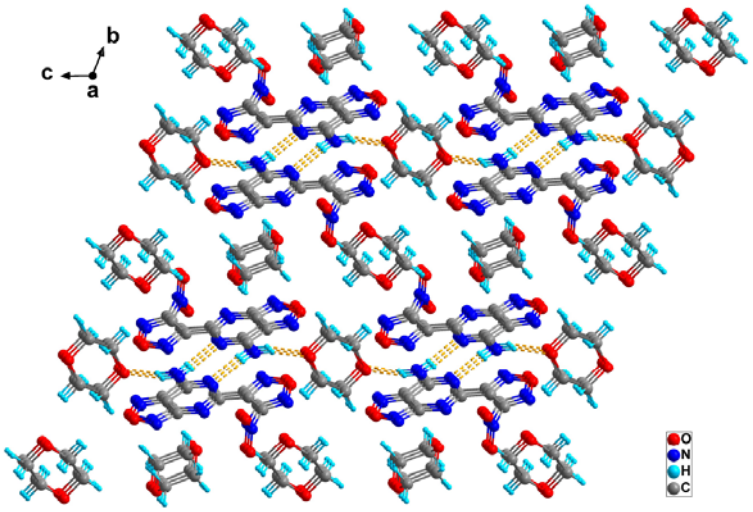


Fig. S18 Stacking diagram of **18**·1.5Diox viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

16. Single-crystal X-ray diffraction analysis of **19**·H_2O

Table S76. Crystal data, data collection, and refinement for **19**·H_2O

$C_6H_2N_{10}O_2 \cdot H_2O$	D_x = 1.678 Mg m^{-3}
M_r = 264.19	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 6455 reflections
a = 7.5756 (4) Å	θ = 2.5–27.5°
b = 11.2579 (7) Å	μ = 0.14 mm^{-1}
c = 12.2596 (8) Å	T = 296 K
V = 1045.56 (11) Å^3	Block, yellow
Z = 4	0.20 × 0.12 × 0.11 mm
F(000) = 536	
Bruker D8 QUEST PHOTON 100 diffractometer	1998 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.029
ϕ and ω scans	θ_{max} = 27.5°, θ_{min} = 2.5°
Absorption correction: multi-scan *SADABS*	h = -9→7
T_{min} = 0.682, T_{max} = 0.746	k = -13→14
11695 measured reflections	l = -15→15
2401 independent reflections	
Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 0.0832P]$ where $P = (F_o^2 + 2F_c^2)/3$

$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.075$	$\Delta\rangle_{max} = 0.17$ e Å^{-3}
$S = 1.04$	$\Delta\rangle_{min} = -0.13$ e Å^{-3}
2401 reflections	Extinction correction: *SHELXL2019*/2 (Sheldrick 2019), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
179 parameters	Extinction coefficient: 0.042 (6)
0 restraints	Absolute structure: Flack x determined using 710 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: mixed	Absolute structure parameter: -0.3 (5)

Table S77. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **19**·H_2O

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5025 (3)	0.43380 (19)	0.53125 (17)	0.0435 (5)
C2	0.3720 (3)	0.50604 (19)	0.48129 (17)	0.0405 (5)
C3	0.3915 (3)	0.61918 (18)	0.42148 (16)	0.0359 (4)
C4	0.2437 (3)	0.76939 (18)	0.33016 (15)	0.0365 (5)
C5	0.4160 (2)	0.82277 (18)	0.31527 (15)	0.0355 (5)
C6	0.5634 (2)	0.76312 (17)	0.35918 (16)	0.0351 (4)
N1	0.4288 (3)	0.34261 (18)	0.57803 (17)	0.0585 (5)
N2	0.2182 (3)	0.45760 (18)	0.49830 (17)	0.0553 (5)
N3	0.6839 (3)	0.45461 (18)	0.53057 (18)	0.0537 (5)
N4	0.7717 (3)	0.37887 (18)	0.58241 (16)	0.0520 (5)
N5	0.8677 (3)	0.3207 (2)	0.62500 (19)	0.0702 (7)
N6	0.5546 (2)	0.65847 (15)	0.41510 (14)	0.0391 (4)
N7	0.2378 (2)	0.66617 (15)	0.38326 (14)	0.0392 (4)
N8	0.7069 (2)	0.82226 (17)	0.33463 (16)	0.0448 (5)
N9	0.4662 (2)	0.91845 (17)	0.26387 (16)	0.0476 (5)
N10	0.1007 (2)	0.82061 (18)	0.29276 (14)	0.0471 (5)
H10A	-0.000554	0.787617	0.302224	0.057*
H10B	0.108045	0.887243	0.258752	0.057*
O1	0.2501 (3)	0.35660 (16)	0.55803 (15)	0.0661 (5)
O2	0.6472 (2)	0.91860 (15)	0.27558 (14)	0.0513 (4)
O3	0.1009 (2)	0.04568 (17)	0.18282 (15)	0.0584 (5)
H3A	0.179 (5)	0.044 (3)	0.133 (3)	0.088*
H3B	0.010 (5)	0.068 (3)	0.142 (3)	0.088*

Table S78. Atomic displacement parameters (Å^2) for **19**·H_2O

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0522 (13)	0.0385 (12)	0.0398 (11)	-0.0038 (10)	0.0015 (9)	0.0015 (10)
C2	0.0417 (12)	0.0395 (11)	0.0403 (11)	-0.0035 (9)	0.0040 (9)	-0.0028 (9)
C3	0.0355 (10)	0.0358 (11)	0.0363 (10)	-0.0004 (9)	0.0014 (9)	-0.0053 (8)
C4	0.0289 (9)	0.0435 (12)	0.0371 (10)	-0.0003 (9)	-0.0003 (8)	-0.0064 (9)
C5	0.0318 (10)	0.0381 (11)	0.0365 (10)	0.0004 (9)	0.0016 (8)	-0.0024 (9)
C6	0.0290 (9)	0.0390 (11)	0.0373 (10)	-0.0002 (9)	-0.0007 (8)	-0.0034 (8)
N1	0.0615 (14)	0.0519 (12)	0.0622 (12)	-0.0068 (11)	0.0022 (11)	0.0113 (10)
N2	0.0500 (12)	0.0480 (12)	0.0680 (13)	-0.0074 (9)	0.0049 (10)	0.0069 (10)
N3	0.0475 (11)	0.0496 (12)	0.0641 (12)	0.0032 (9)	-0.0041 (9)	0.0171 (11)
N4	0.0547 (12)	0.0498 (12)	0.0515 (11)	0.0039 (11)	-0.0008 (10)	0.0062 (10)
N5	0.0679 (15)	0.0728 (15)	0.0698 (14)	0.0163 (13)	-0.0026 (12)	0.0191 (13)
N6	0.0332 (8)	0.0393 (10)	0.0449 (9)	0.0000 (8)	-0.0031 (8)	0.0002 (8)
N7	0.0309 (8)	0.0409 (10)	0.0457 (9)	-0.0033 (8)	0.0000 (7)	-0.0007 (8)
N8	0.0337 (9)	0.0463 (11)	0.0545 (10)	-0.0020 (8)	-0.0014 (8)	0.0069 (9)
N9	0.0363 (9)	0.0489 (11)	0.0576 (11)	-0.0004 (9)	0.0017 (8)	0.0085 (9)
N10	0.0291 (9)	0.0550 (11)	0.0572 (11)	0.0007 (9)	-0.0062 (8)	0.0041 (10)
O1	0.0601 (11)	0.0561 (11)	0.0821 (12)	-0.0142 (10)	0.0100 (10)	0.0160 (9)
O2	0.0370 (8)	0.0509 (10)	0.0660 (10)	-0.0048 (7)	0.0022 (7)	0.0139 (8)
O3	0.0406 (9)	0.0685 (12)	0.0662 (11)	0.0074 (9)	0.0003 (8)	0.0062 (9)

Table S79. Geometric parameters (Å, º) for **19**·H_2O

C1—N1	1.302 (3)	C6—N8	1.310 (2)
C1—N3	1.394 (3)	C6—N6	1.365 (3)
C1—C2	1.419 (3)	N1—O1	1.384 (3)
C2—N2	1.303 (3)	N2—O1	1.374 (3)
C2—C3	1.477 (3)	N3—N4	1.254 (3)
C3—N6	1.314 (2)	N4—N5	1.109 (3)
C3—N7	1.362 (3)	N8—O2	1.380 (2)
C4—N10	1.310 (3)	N9—O2	1.379 (2)
C4—N7	1.333 (3)	N10—H10A	0.8600
C4—C5	1.449 (3)	N10—H10B	0.8600
C5—N9	1.305 (3)	O3—H3A	0.85 (3)
C5—C6	1.410 (3)	O3—H3B	0.89 (4)
N1—C1—N3	123.9 (2)	N8—C6—C5	109.12 (17)
N1—C1—C2	110.0 (2)	N6—C6—C5	124.35 (17)

N3—C1—C2	126.0 (2)	C1—N1—O1	104.60 (19)
N2—C2—C1	108.31 (19)	C2—N2—O1	105.92 (19)
N2—C2—C3	122.0 (2)	N4—N3—C1	113.9 (2)
C1—C2—C3	129.67 (19)	N5—N4—N3	170.9 (3)
N6—C3—N7	130.72 (19)	C3—N6—C6	111.49 (16)
N6—C3—C2	114.45 (17)	C4—N7—C3	118.55 (18)
N7—C3—C2	114.83 (17)	C6—N8—O2	104.35 (15)
N10—C4—N7	121.81 (19)	C5—N9—O2	103.91 (17)
N10—C4—C5	121.22 (19)	C4—N10—H10A	120.0
N7—C4—C5	116.97 (17)	C4—N10—H10B	120.0
N9—C5—C6	110.30 (17)	H10A—N10—H10B	120.0
N9—C5—C4	131.76 (18)	N2—O1—N1	111.14 (16)
C6—C5—C4	117.90 (18)	N9—O2—N8	112.32 (16)
N8—C6—N6	126.50 (17)	H3A—O3—H3B	98 (3)
N1—C1—C2—N2	0.0 (3)	C3—C2—N2—O1	-178.43 (18)
N3—C1—C2—N2	179.3 (2)	N1—C1—N3—N4	-2.1 (4)
N1—C1—C2—C3	178.4 (2)	C2—C1—N3—N4	178.7 (2)
N3—C1—C2—C3	-2.3 (4)	N7—C3—N6—C6	-0.8 (3)
N2—C2—C3—N6	177.4 (2)	C2—C3—N6—C6	-179.88 (17)
C1—C2—C3—N6	-0.8 (3)	N8—C6—N6—C3	-176.8 (2)
N2—C2—C3—N7	-1.9 (3)	C5—C6—N6—C3	1.0 (3)
C1—C2—C3—N7	180.0 (2)	N10—C4—N7—C3	-178.87 (18)
N10—C4—C5—N9	-3.3 (3)	C5—C4—N7—C3	1.2 (3)
N7—C4—C5—N9	176.6 (2)	N6—C3—N7—C4	-0.4 (3)
N10—C4—C5—C6	179.12 (19)	C2—C3—N7—C4	178.75 (16)
N7—C4—C5—C6	-1.0 (3)	N6—C6—N8—O2	178.14 (18)
N9—C5—C6—N8	-0.1 (2)	C5—C6—N8—O2	0.1 (2)
C4—C5—C6—N8	177.93 (17)	C6—C5—N9—O2	0.1 (2)
N9—C5—C6—N6	-178.23 (17)	C4—C5—N9—O2	-177.6 (2)
C4—C5—C6—N6	-0.2 (3)	C2—N2—O1—N1	-0.1 (3)
N3—C1—N1—O1	-179.4 (2)	C1—N1—O1—N2	0.1 (2)
C2—C1—N1—O1	-0.1 (2)	C5—N9—O2—N8	-0.1 (2)
C1—C2—N2—O1	0.1 (2)	C6—N8—O2—N9	0.0 (2)

Table S80. Hydrogen bonds (Å, º) for **19**·H_2O

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3B···N7^{i}	0.89 (4)	2.20 (4)	3.013 (3)	152 (3)
O3—H3A···N6^{ii}	0.85 (3)	2.47 (4)	3.141 (3)	136 (3)

O3—H3A···N3^{ii}	0.85 (3)	2.47 (3)	3.248 (3)	152 (3)
N10—H10B···O3^{iii}	0.86	2.01	2.870 (3)	175
N10—H10A···N8^{iv}	0.86	2.29	3.027 (2)	145

Symmetry codes: (i) -*x*, *y*-1/2, -*z*+1/2; (ii) -*x*+1, *y*-1/2, -*z*+1/2; (iii) *x*, *y*+1, *z*; (iv) *x*-1, *y*, *z*.

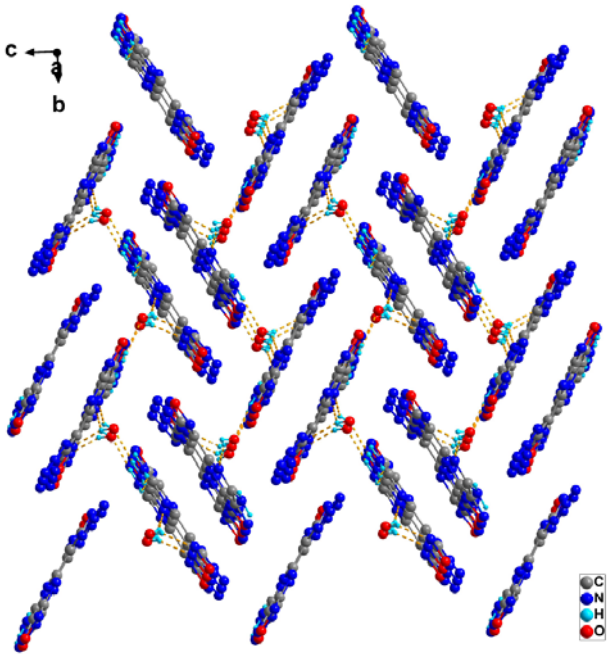


Fig. S19 Stacking diagram of **19**·H_2O viewed down the *a* axis, yellow dotted lines indicate hydrogen bonding.

17.The noncovalent interactions study

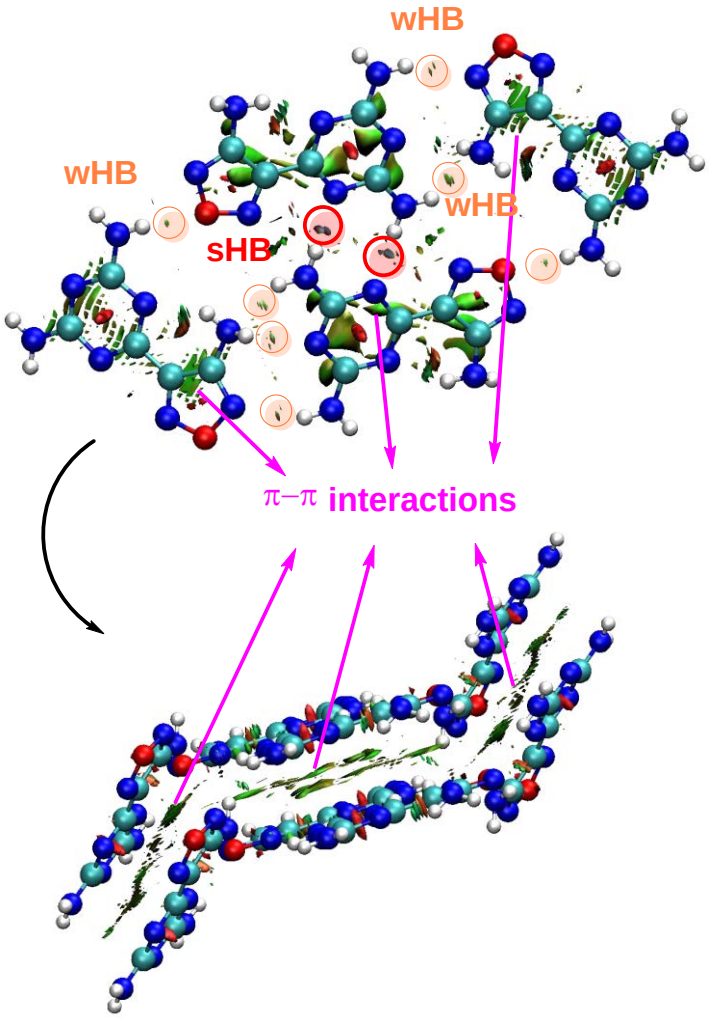


Fig. S20 Noncovalent interactions analyses, including hydrogen bonds (sHB: strong hydrogen bond; wHB: weak hydrogen bond) and π-π interactions for **3** (blue: strong attraction; green: weak interaction; red: strong repulsion).

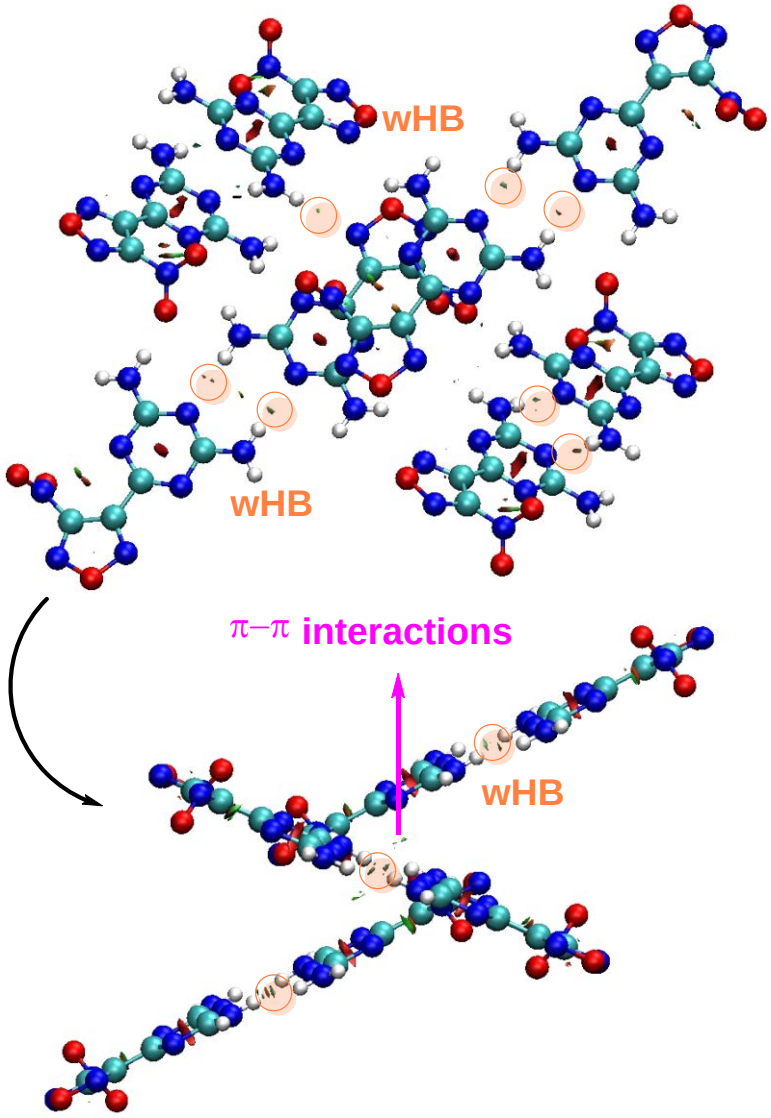


Fig. S21 Noncovalent interactions analyses, including hydrogen bonds (sHB: strong hydrogen bond; wHB: weak hydrogen bond) and π-π interactions for **11** (blue: strong attraction; green: weak interaction; red: strong repulsion).

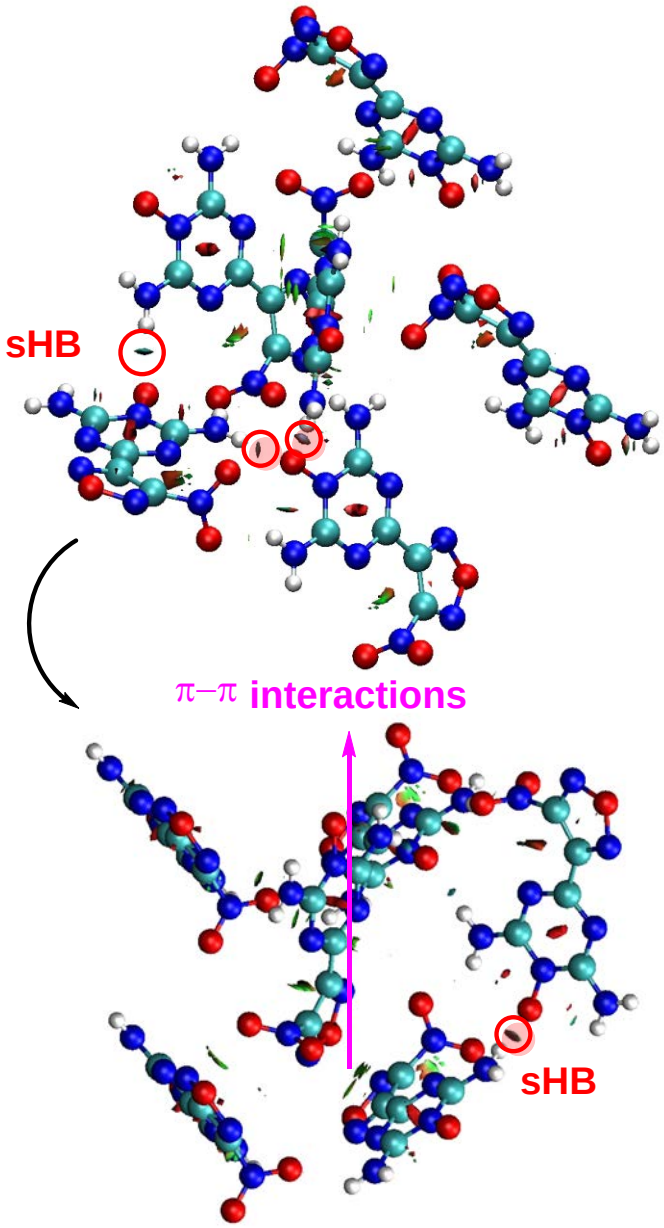


Fig. S22 Noncovalent interactions analyses, including hydrogen bonds (sHB: strong hydrogen bond; wHB: weak hydrogen bond) and π-π interactions for **12** (blue: strong attraction; green: weak interaction; red: strong repulsion).

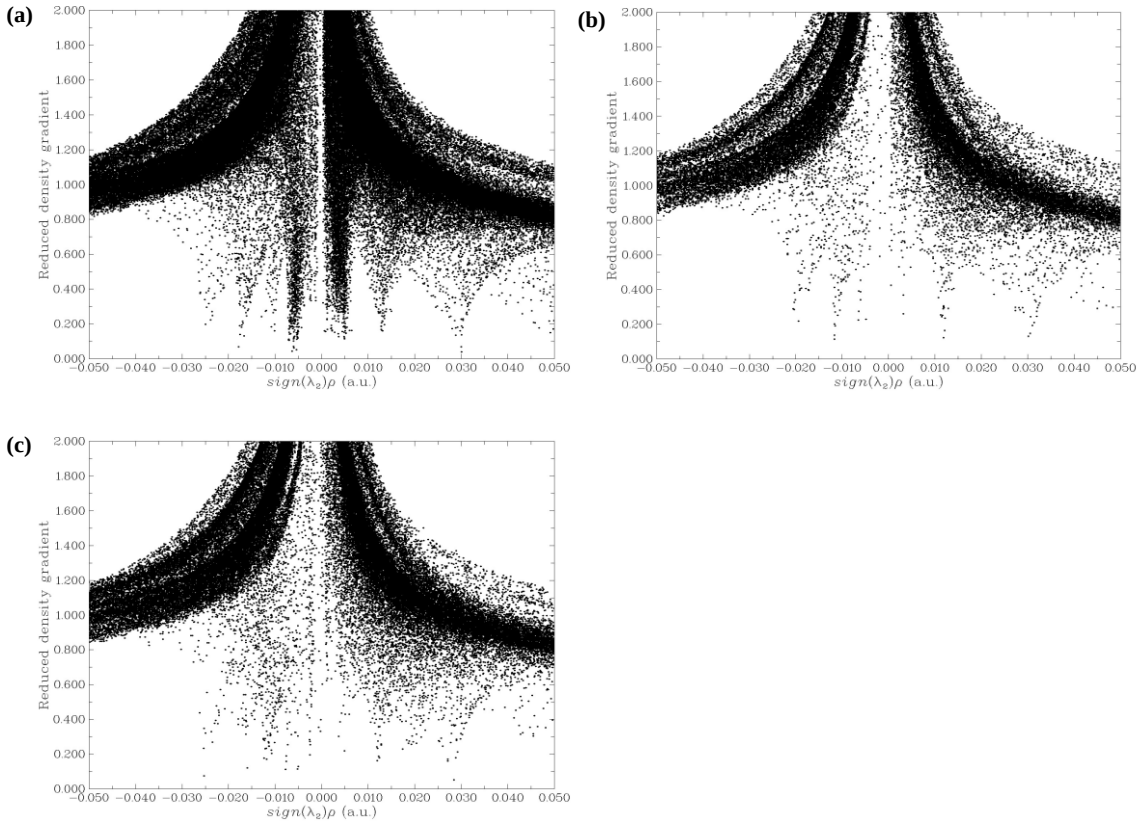


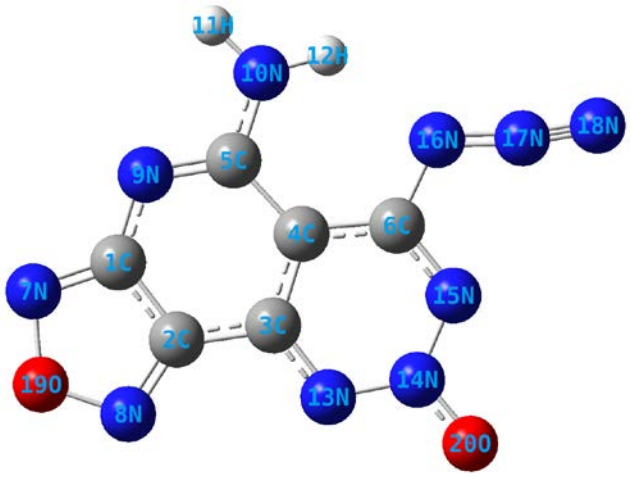
Fig. S23 (a-c) Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for **3**, **11**, **12**.

18.LBO calculation

Table S81. The Laplacian bond order (LBO) of **9**

No.	Bond	Bond order (≥0.05)
1	1(C)—2(C)	1.299694
2	1(C)—7(N)	1.493369
3	1(C)—9(N)	1.164186
4	2(C)—3(C)	1.317245
5	2(C)—8(N)	1.491517
6	3(C)—4(C)	1.387288
7	3(C)—13(N)	1.292872
8	4(C)—5(C)	1.141364
9	4(C)—6(C)	1.408987
10	5(C)—9(N)	1.393345
11	5(C)—10(N)	1.216075
12	6(C)—15(N)	1.354663

13	6(C)—16(N)	0.971561
14	7(N)—19(O)	0.309843
15	8(N)—19(O)	0.363987
16	10(N)—11(H)	0.822030
17	10(N)—12(H)	0.818638
18	13(N)—14(N)	0.897105
19	14(N)—15(N)	0.827309
20	14(N)—20(O)	0.902082
21	16(N)—17(N)	1.133646
22	17(N)—18(N)	2.355040



19.Photoluminescence

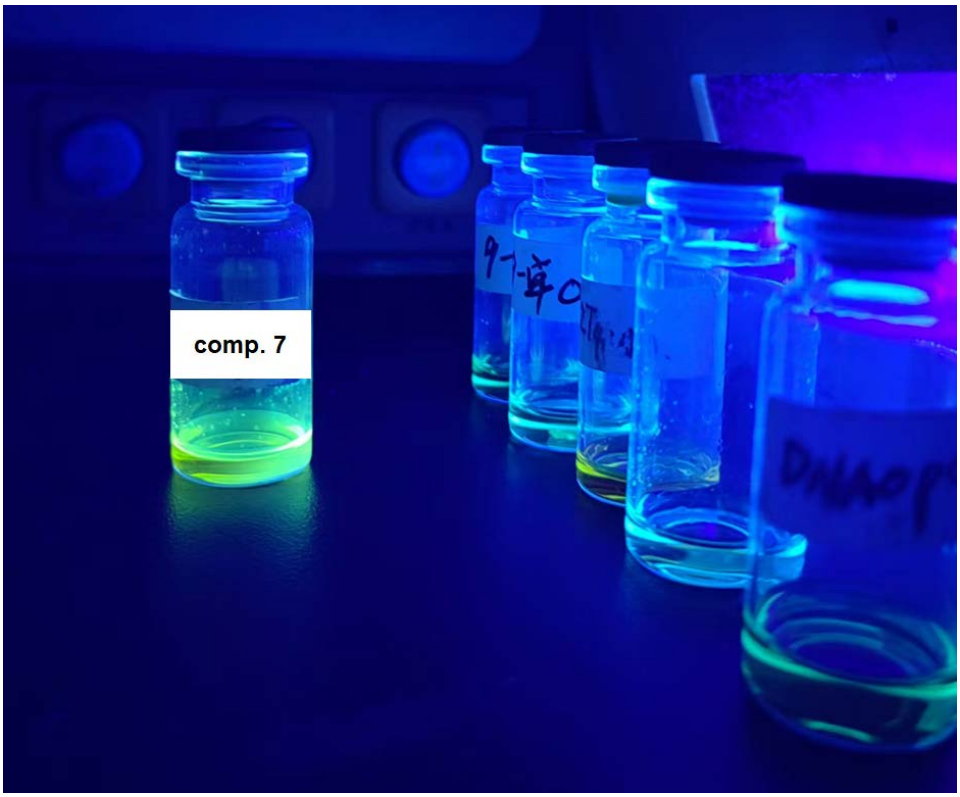


Fig. S24 Comparison of compound **7** in DMSO solution under UV with 5-amino-6-oxo-4,6-dihydro-[1,2,5]oxadiazolo[3',4':5,6]pyrido[4,3-*d*][1,2,3]triazine 8-oxide, **4**, 5,7-diaminofurazano[3,4-*b*] pyridine-6-carbonitrile, **8**, and **9** (front to back).

20.The ICSS_ZZ map for compound **9**

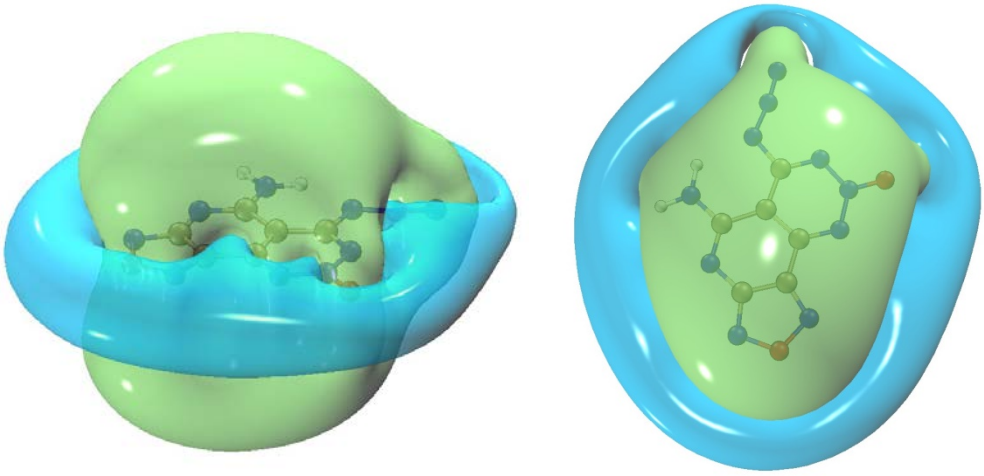


Fig. S25 The ICSS_ZZ maps for compound **9**.

21. Calculation of heats of formation

The geometric optimization and frequency analyses of neutral molecules were based on available single-crystal structures by Gaussian 09 suite of programs [1] and using the B3LYP functional with the 6-31+G(d,p) basis set. The geometrical configurations were optimized with no constraints imposed under default convergence criteria. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Thermal corrections to enthalpy were computed at the same DFT level of theory [2]. Single-point electronic energies were calculated at the MP2/6-311++G(d,p) [3]. The gas phase enthalpy (*H*) is calculated by adding the single-point electronic energy and the thermal correction to enthalpy.

For compound $C_aH_bO_cN_d$, the reaction equation can be written as:

a C(s) + b/2 H_2(g) + c/2 O_2(g) + d/2 N_2(g) $\xrightarrow{aH_{sub,C}}$ a C(g) + b/2 H_2(g) + c/2 O_2(g) + d/2 N_2(g) → $C_aH_bO_cN_d$(g)

According to the definition of heat of formation [4], its heat of formation can be calculated according to the following formula:

$$\Delta H(\text{gas}) = H_{(C_aH_bO_cN_d,g)} - a\,H_{(C,g)} - \frac{b}{2}H_{(H_2,g)} - \frac{c}{2}H_{(O_2,g)} - \frac{d}{2}H_{(N_2,g)} + a\,H_{sub,C}$$

Here, $H_{sub,C}$ represents the enthalpy of sublimation of graphite (715 kJ mol^{-1}).

According to Hess' law of constant heat summation condensed-phase heats of formation can be determined [5].

$$\Delta H(\text{solid}) = \Delta H(\text{gas}) - \Delta H(\text{sublimation}) \quad (2)$$

The enthalpy of sublimation can be represented as eq (3) and on the basis of the predicted electrostatic potential of a molecule [6, 7].

$$\Delta H(\text{sublimation}) = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + c \quad (3)$$

Here *SA* is the surface area of the 0.001 electrons $bohr^{-3}$ isosurface of the electronic density of the HEDMs, $\upsilon\sigma_{tot}^2$ is derived from the molecular electrostatic potential calculation, and a, b, c are fitting parameters reported by Politzer et al [6].

For energetic salts, the solid-phase heats of formation are calculated on the basis of a Born-Haber energy cycle (Scheme S1).

Based on a Born-Haber energy cycle, the heat of formation of a salt can be simplified by the formula given in Equation (1):

ΔH_f^o (salt, 298 K) = ΔH_f^o (cation, 298K) + ΔH_f^o (anion, 298K) – ΔH_L (1)

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [8] [Eq. (2)]

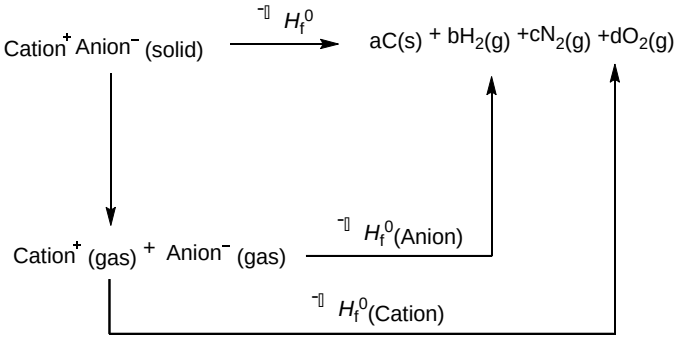
$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

where n_M and n_X depend on the nature of the ions, M_p^+ and X_q^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)

Where ρ_m/g cm^{-3} is the density, M_m is the chemical formula mass of the ionic material, and values for the coefficients γ/ kJ mol^{-1} cm and δ/kJ mol^{-1} are taken from the literature [9].



Scheme S1. Born-Haber cycle for the formation of energetic salts

22. ^{1}H and ^{13}C NMR spectra

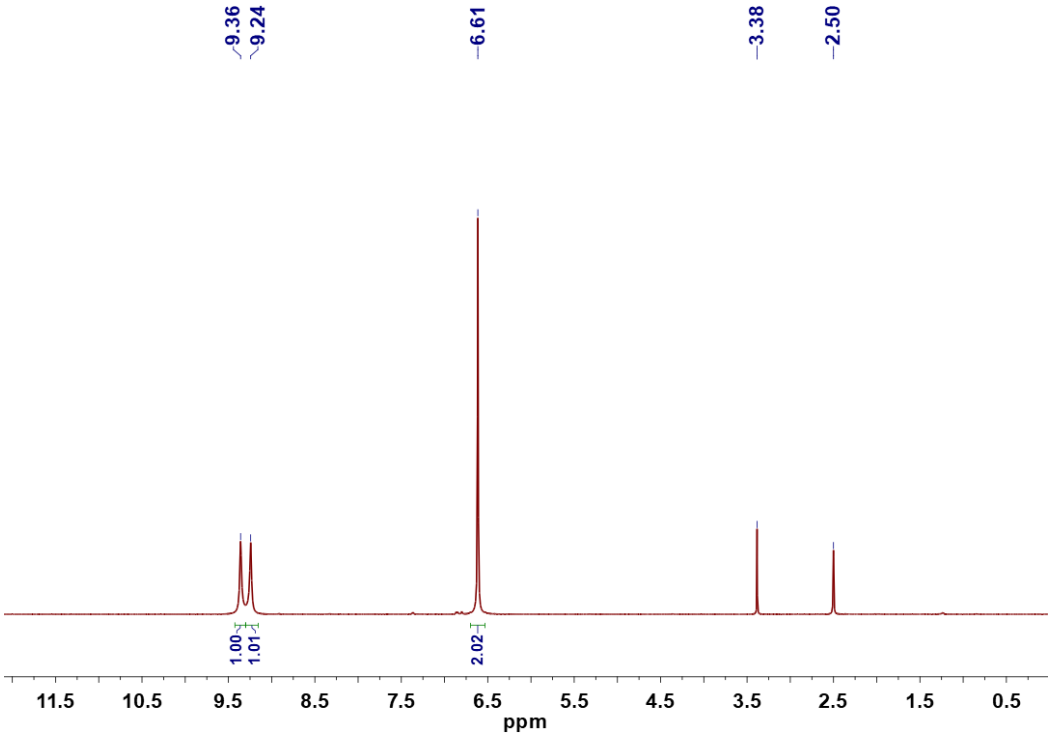


Fig. S26 ^{1}H NMR spectrum of **2** in d_6-DMSO.

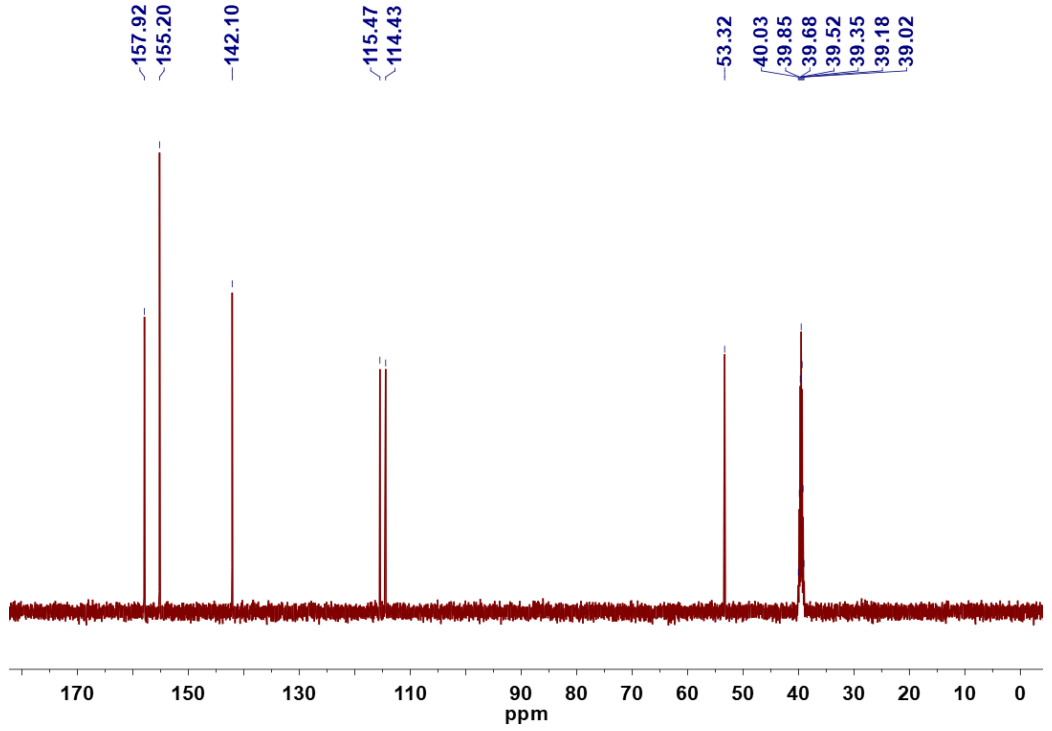


Fig. S27 ^{13}C NMR spectrum of **2** in d_6-DMSO.

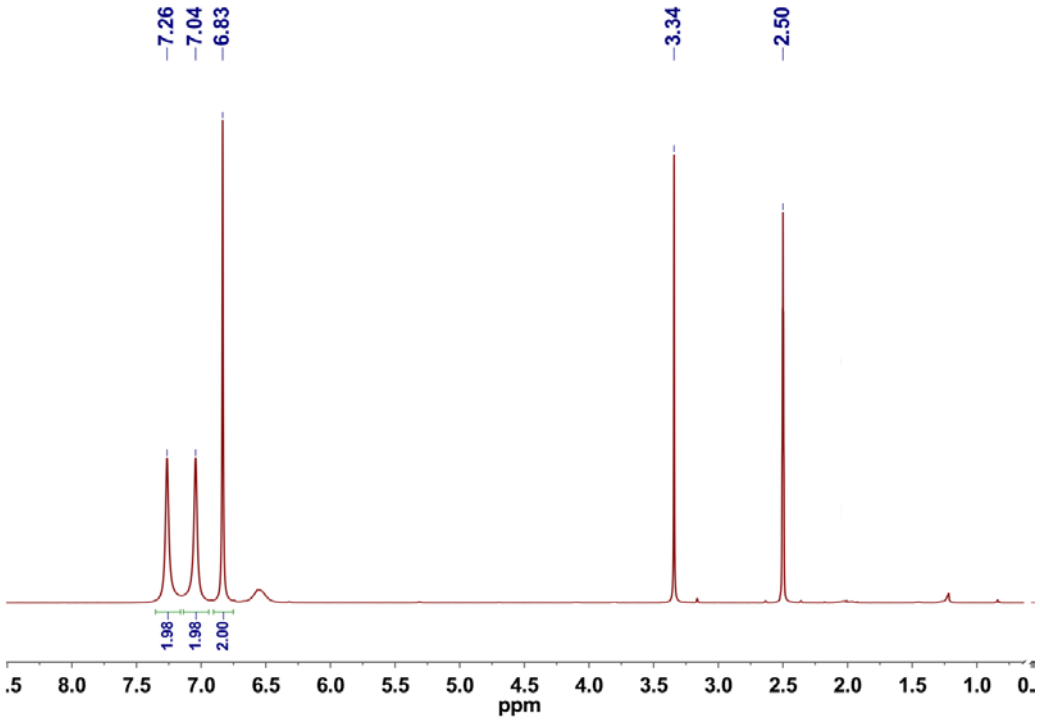


Fig. S28 ^{1}H NMR spectrum of **3** in d_6-DMSO.

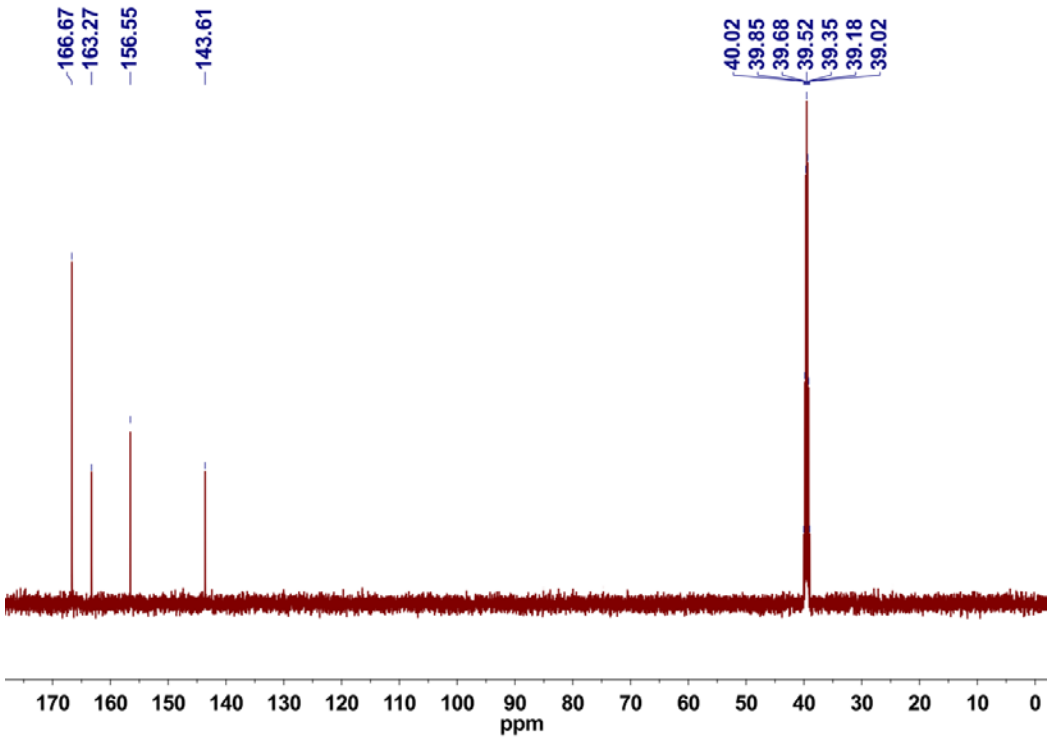


Fig. S29 ^{13}C NMR spectrum of **3** in d_6-DMSO.

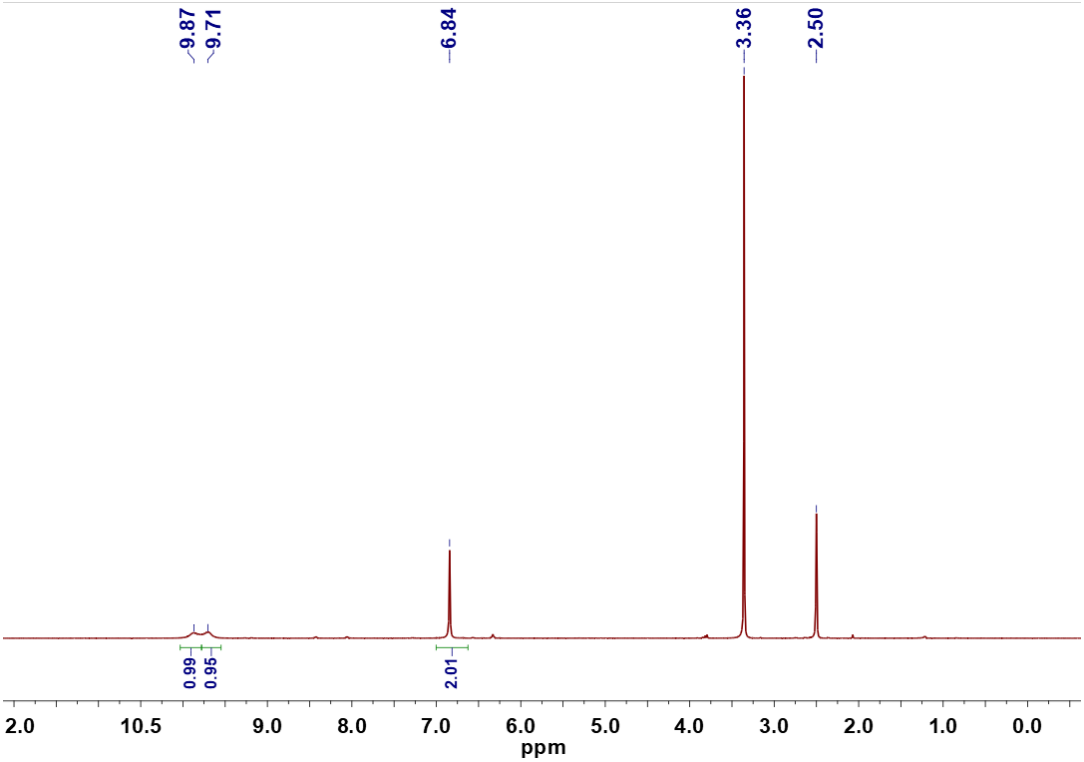


Fig. S30 ^{1}H NMR spectrum of **4** in d_6-DMSO.

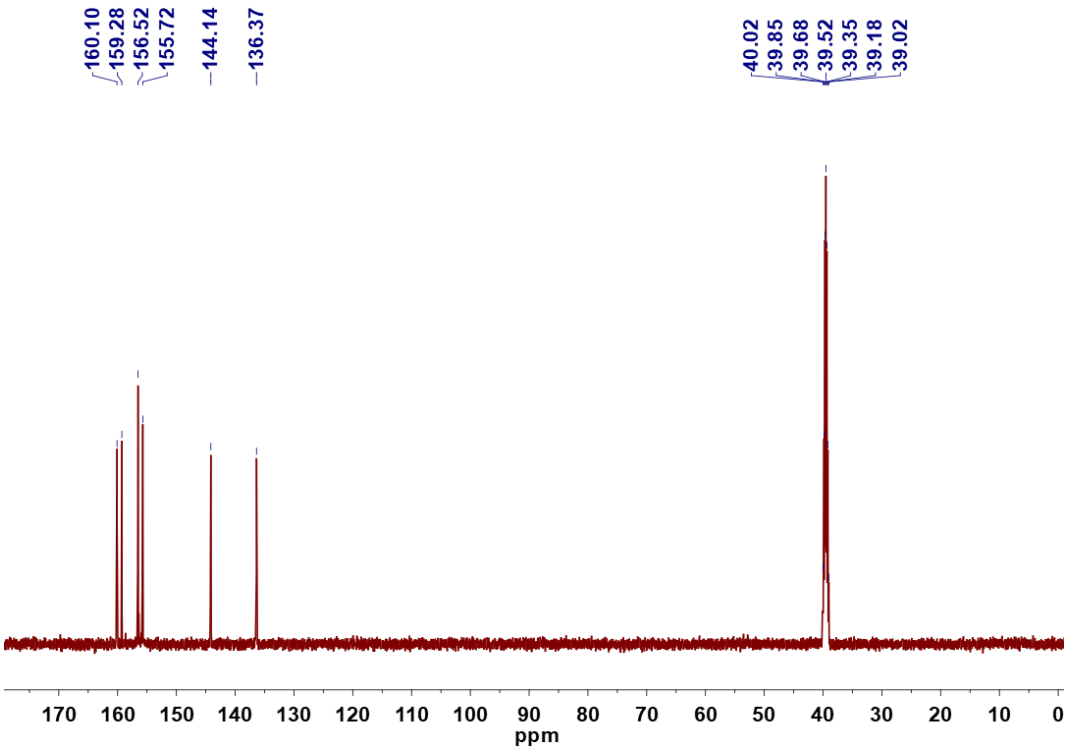


Fig. S31 ^{13}C NMR spectrum of **4** in d_6-DMSO.

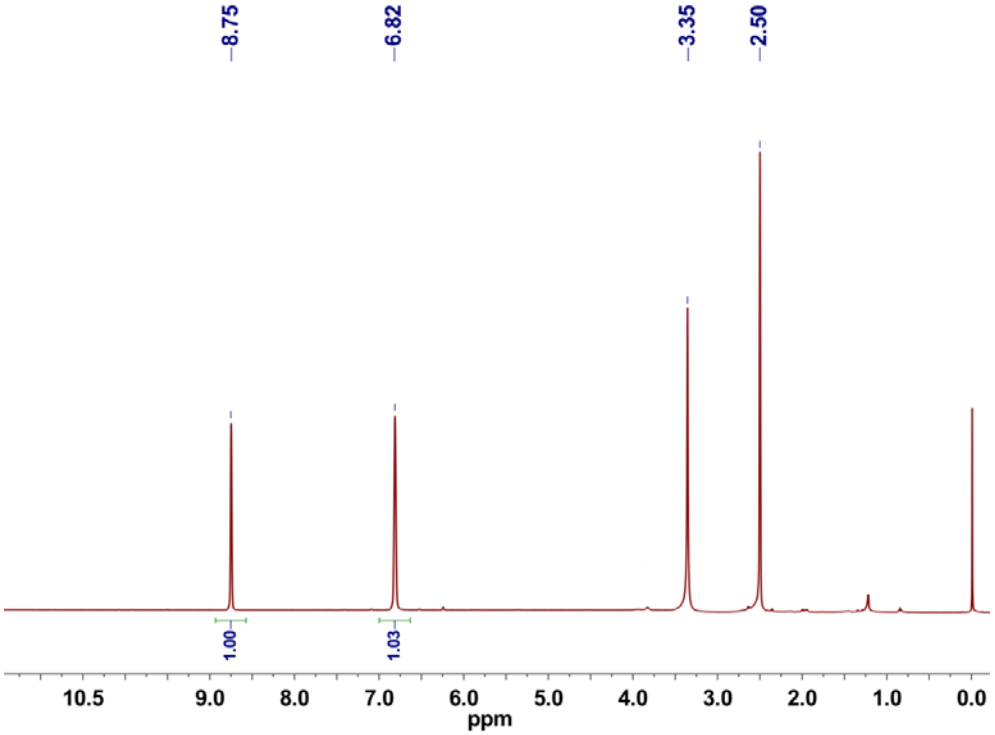


Fig. S32 ^{1}H NMR spectrum of **5** in d_6-DMSO.

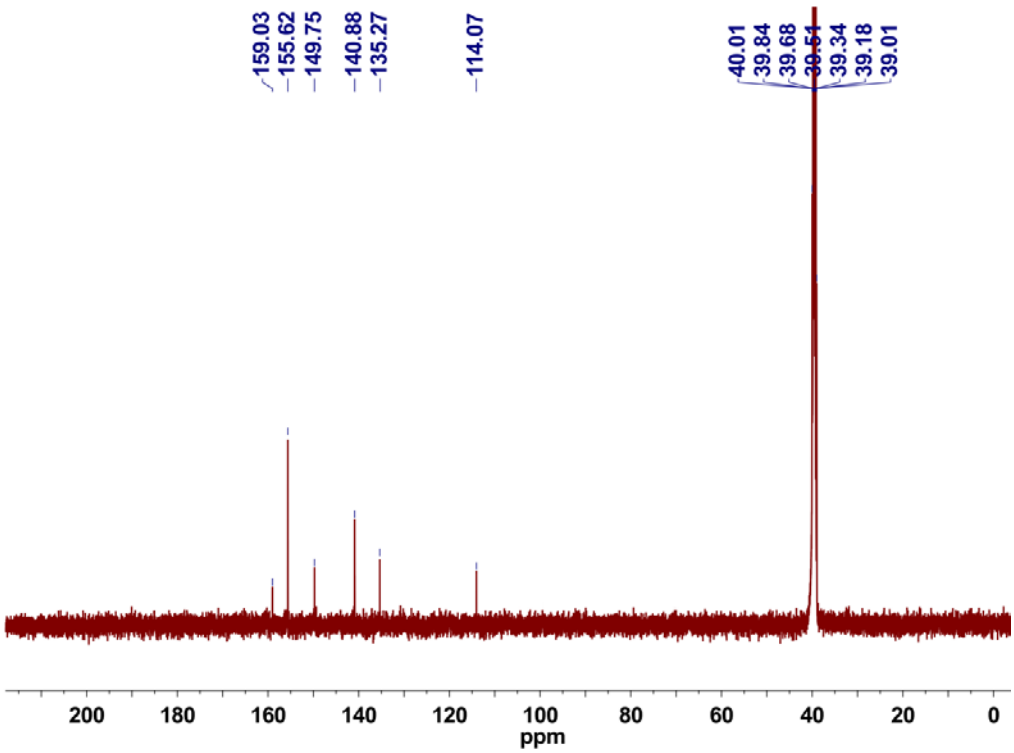


Fig. S33 ^{13}C NMR spectrum of **5** in d_6-DMSO.

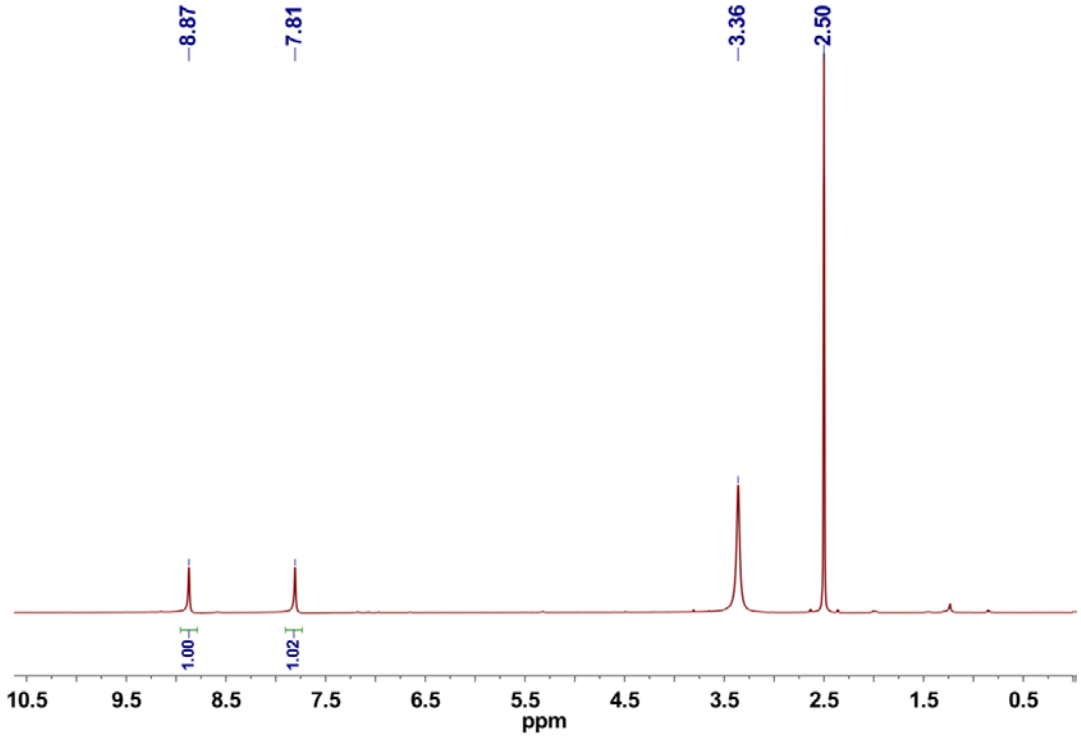


Fig. S34 ^{1}H NMR spectrum of **6** in d_6-DMSO.

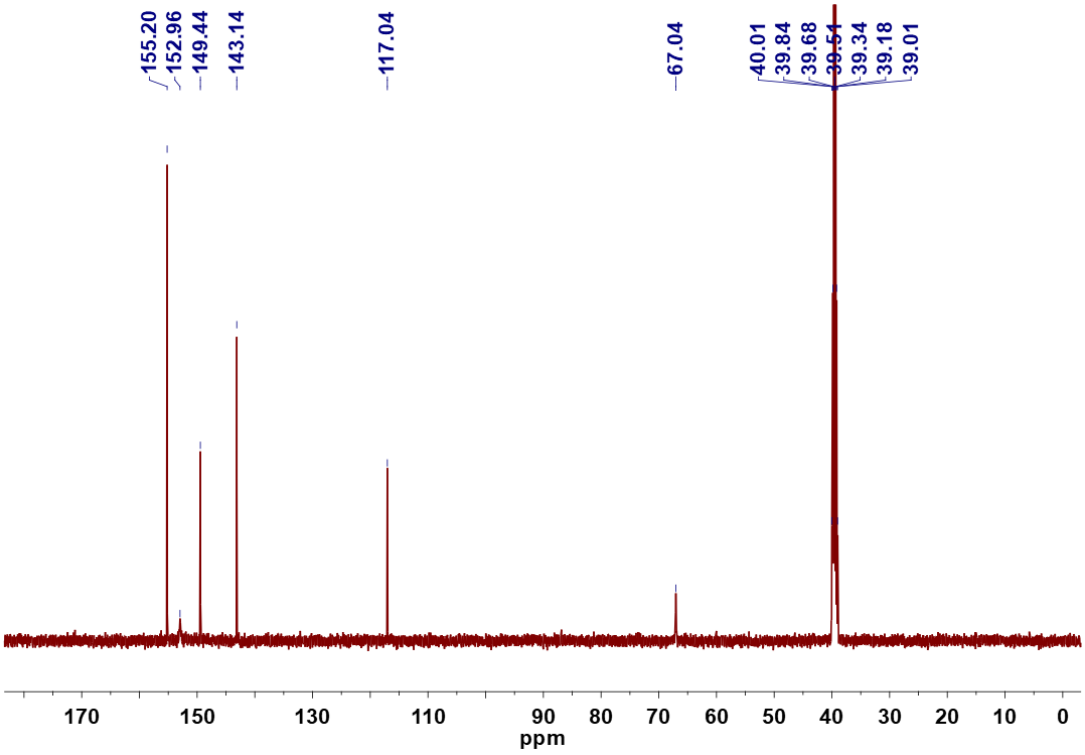


Fig. S35 ^{13}C NMR spectrum of **6** in d_6-DMSO.

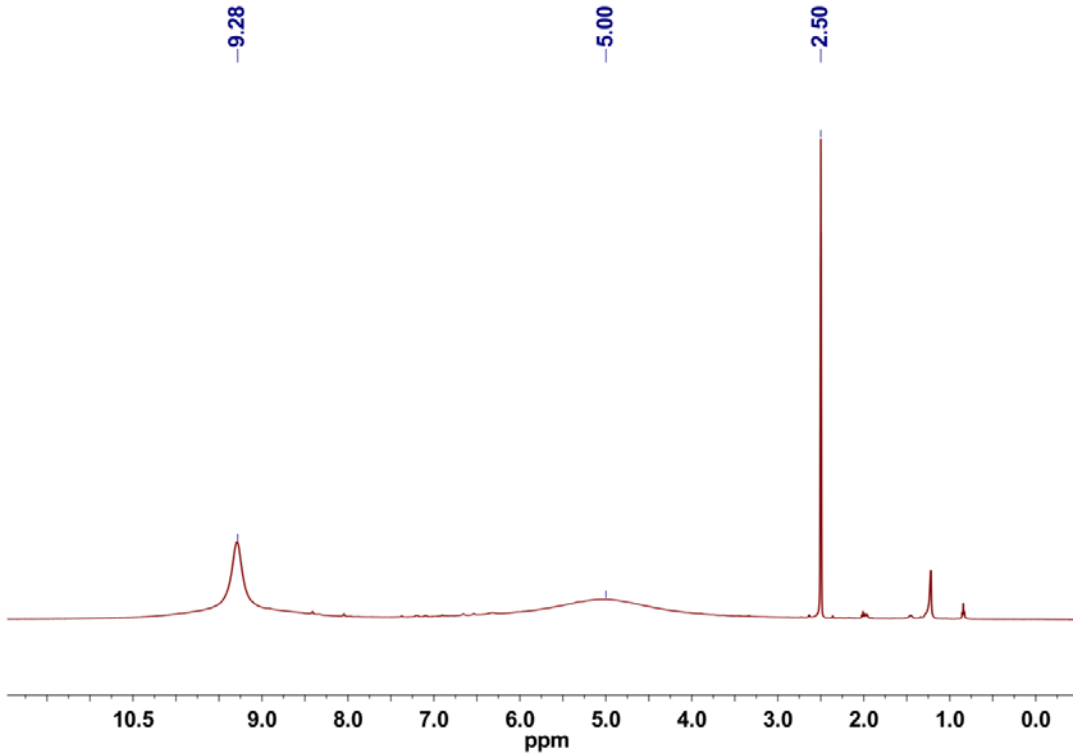


Fig. S36 ^{1}H NMR spectrum of **7** in d_6-DMSO.

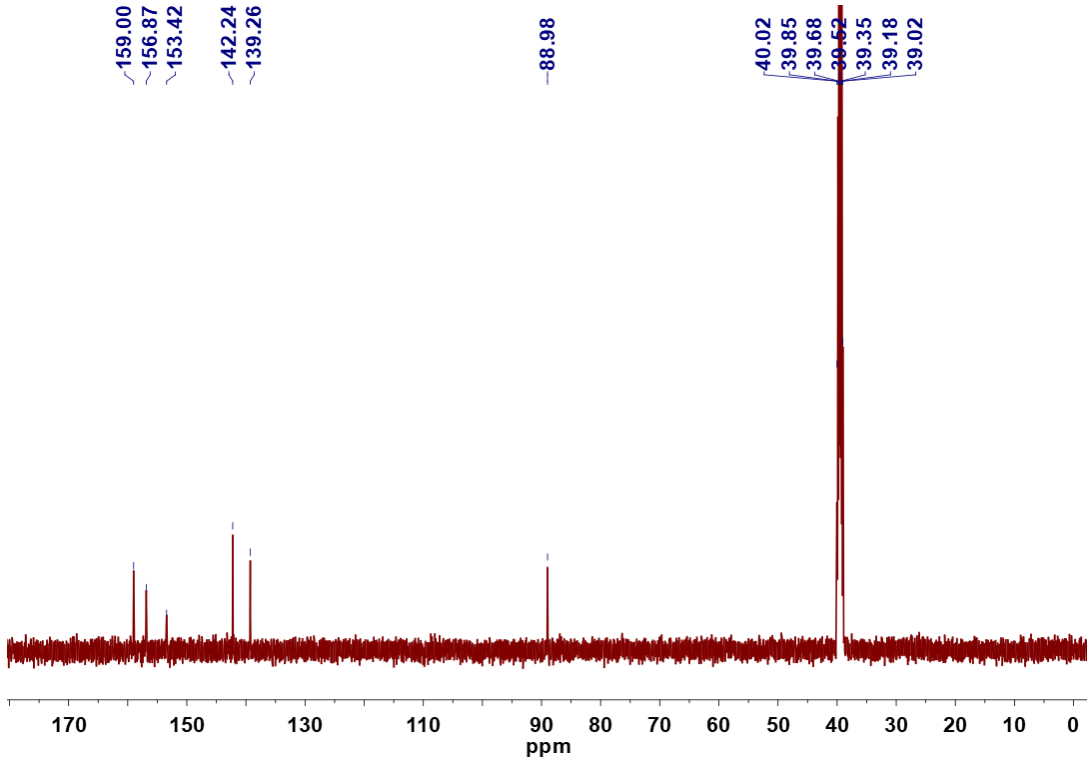


Fig. S37 ^{13}C NMR spectrum of **7** in d_6-DMSO.

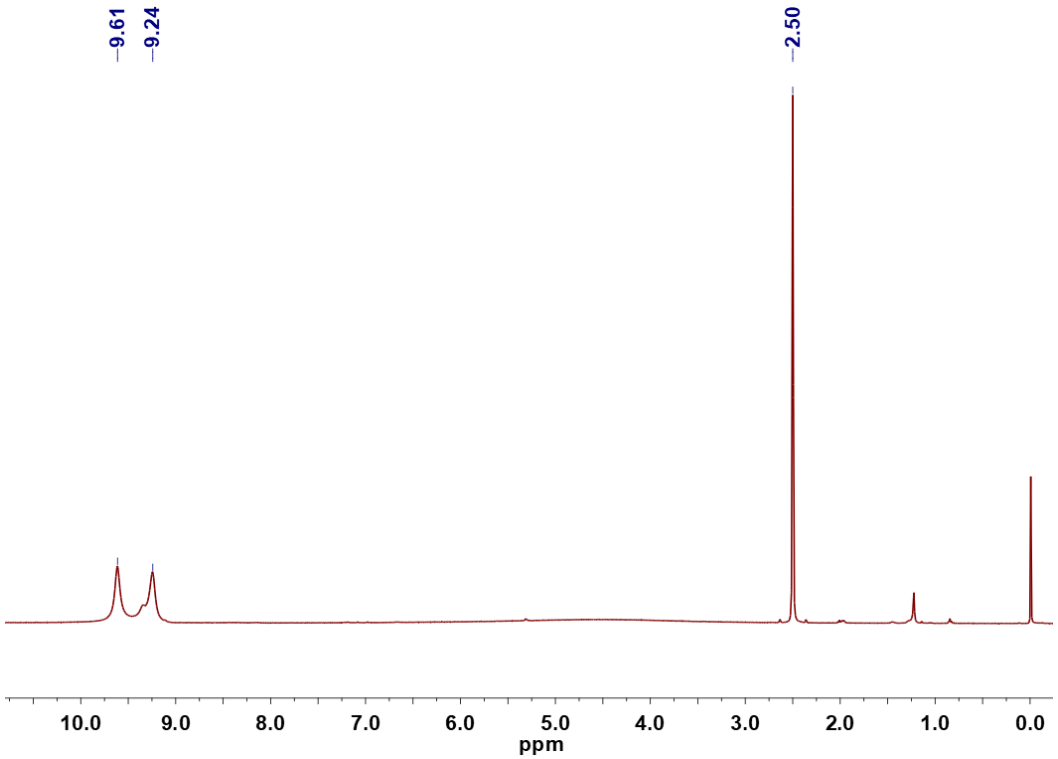


Fig. S38 ^{1}H NMR spectrum of **8** in d_6-DMSO.

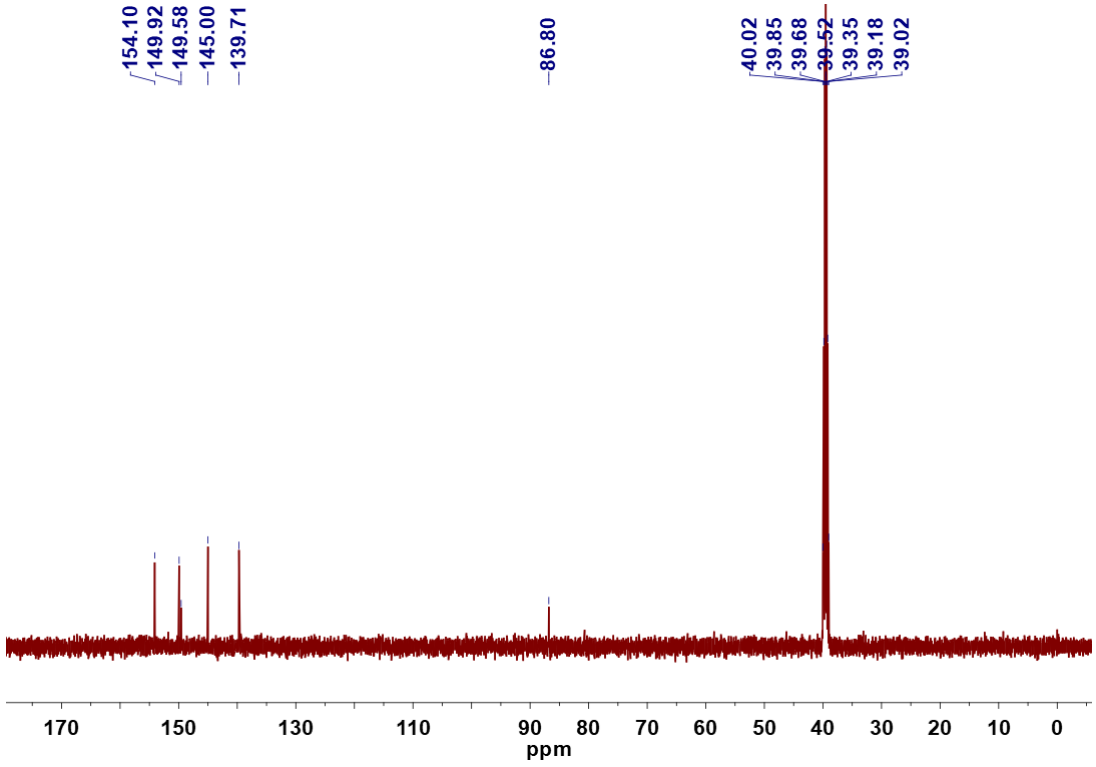


Fig. S39 ^{13}C NMR spectrum of **8** in d_6-DMSO.

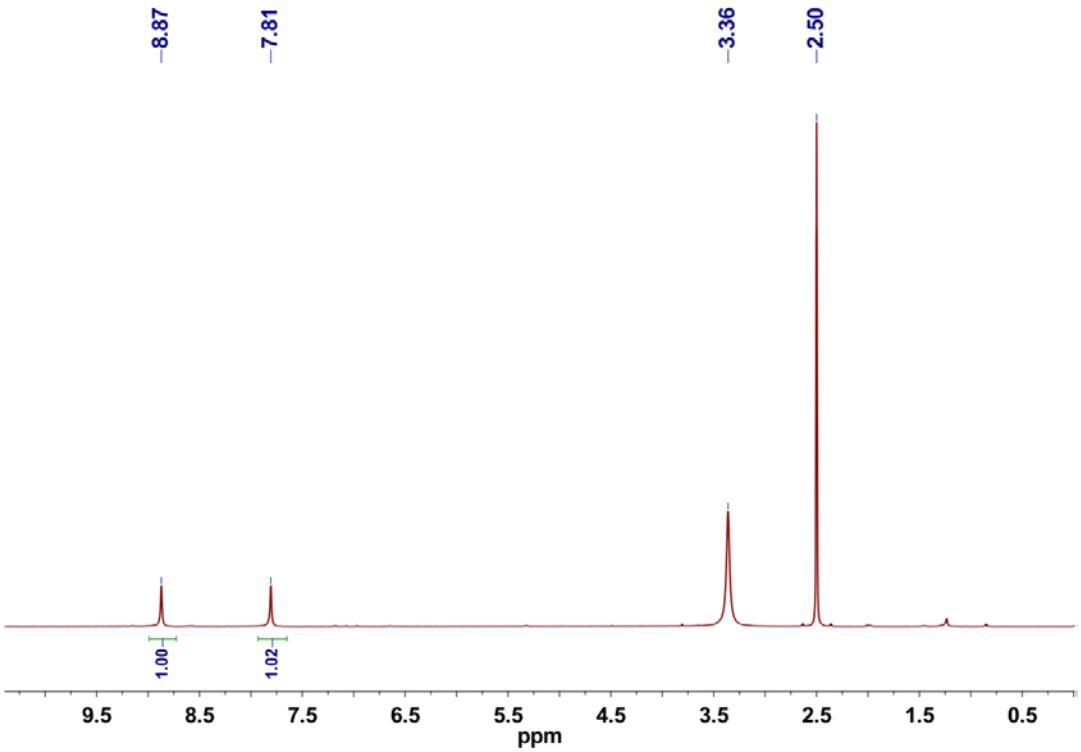


Fig. S40 ^{1}H NMR spectrum of **9** in d_6-DMSO.

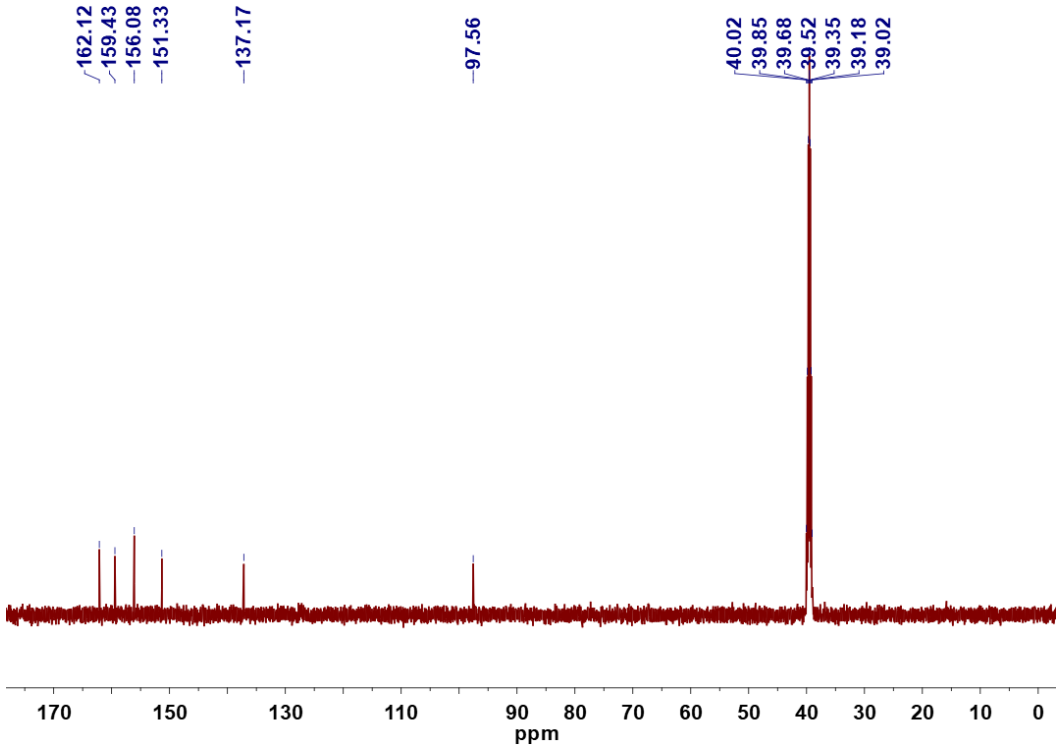


Fig. S41 ^{13}C NMR spectrum of **9** in d_6-DMSO.

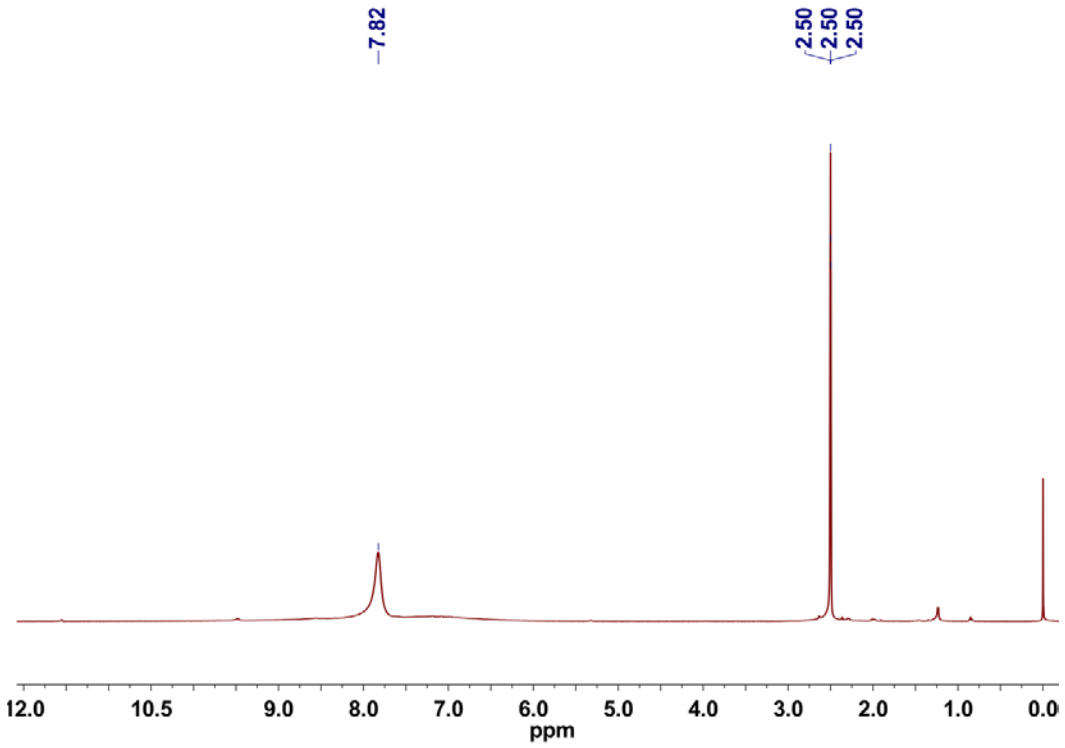


Fig. S42 ^{1}H NMR spectrum of **10** in d_6-DMSO.

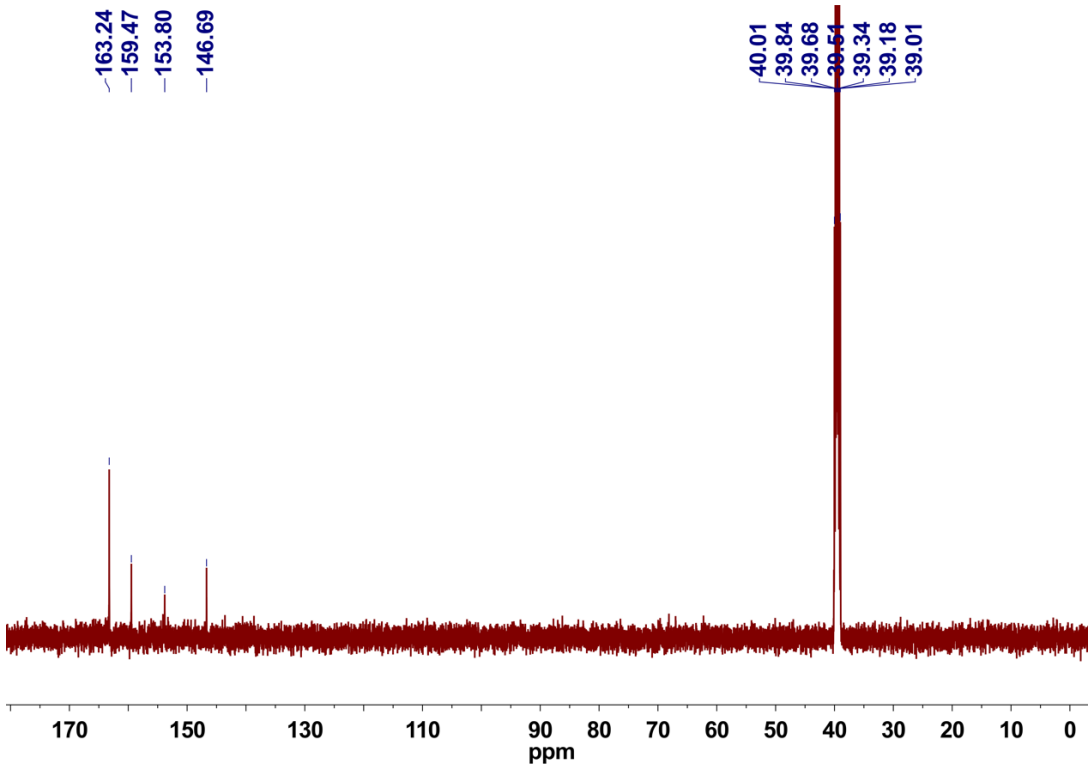


Fig. S43 ^{13}C NMR spectrum of **10** in d_6-DMSO.

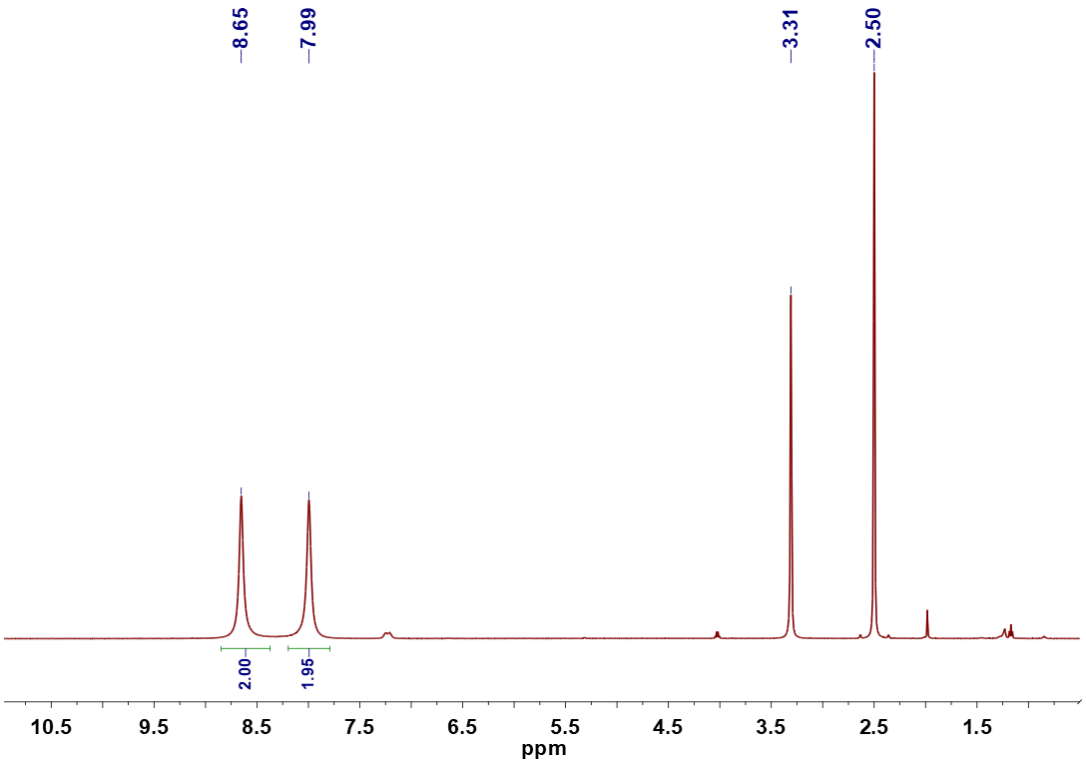


Fig. S44 ^{1}H NMR spectrum of **11** in d_6-DMSO.

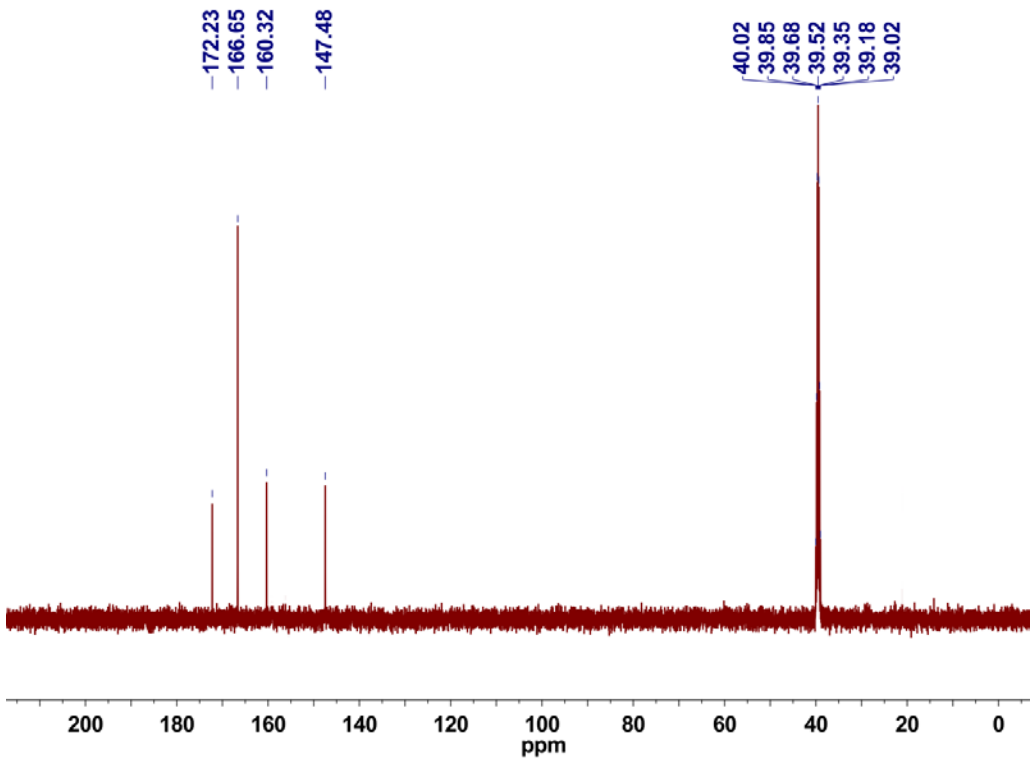


Fig. S45 ^{13}C NMR spectrum of **11** in d_6-DMSO.

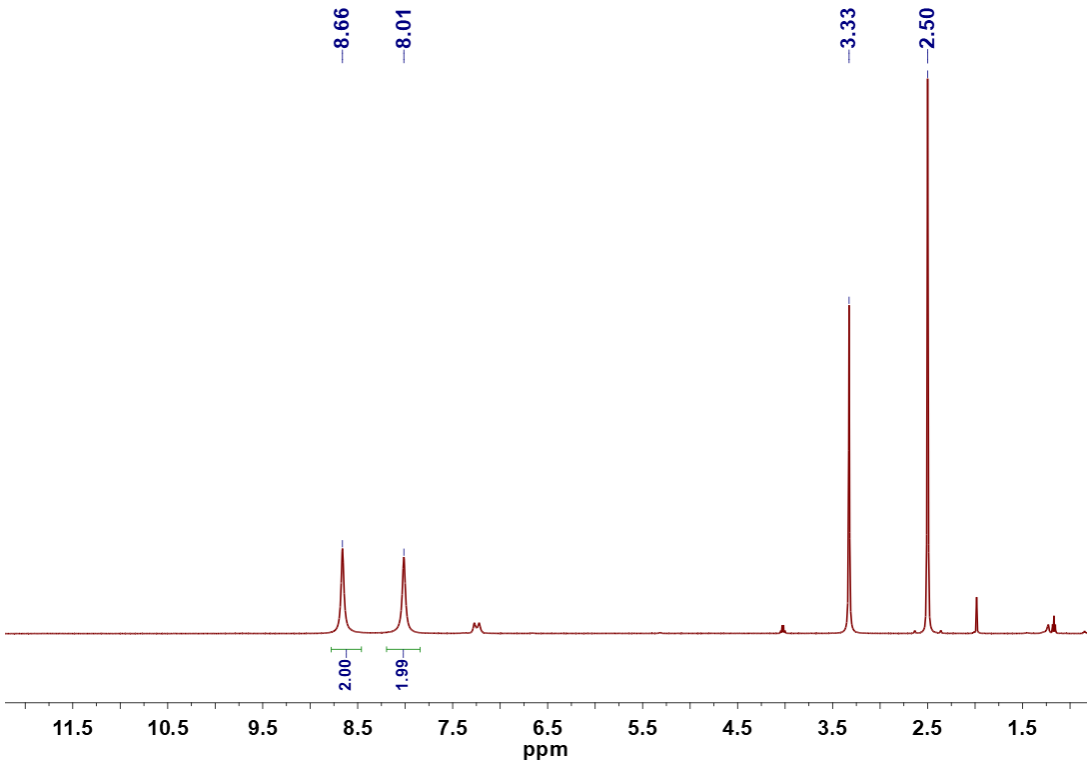


Fig. S46 ^{1}H NMR spectrum of **12** in d_6-DMSO.

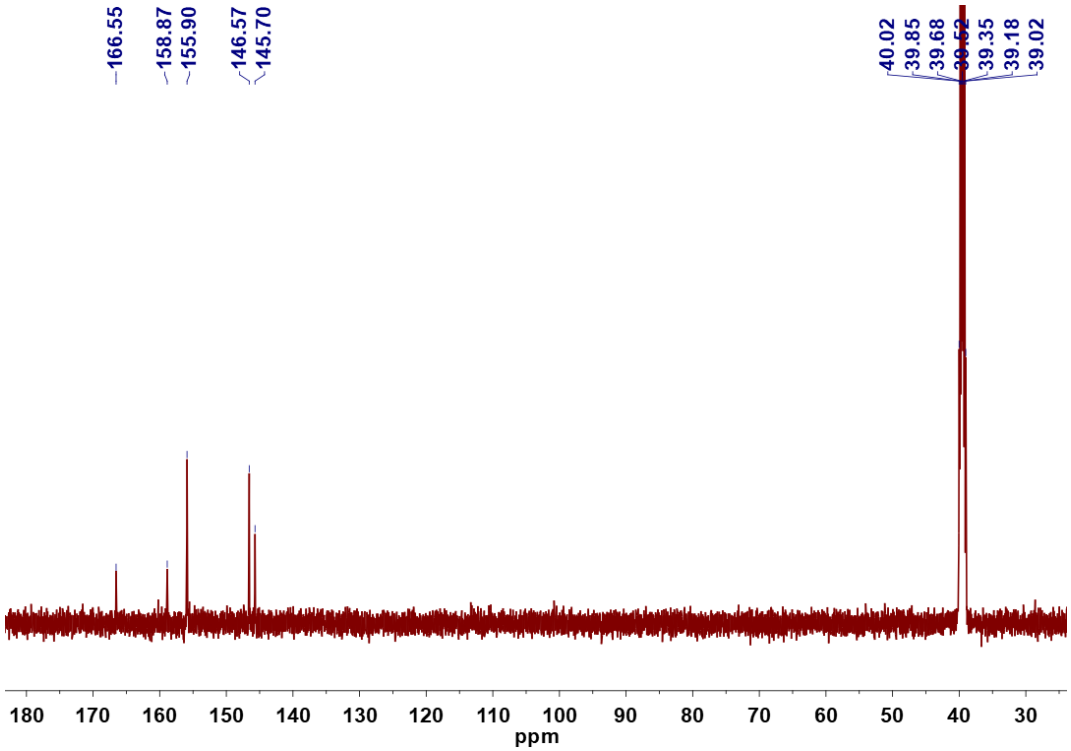


Fig. S47 ^{13}C NMR spectrum of **12** in d_6-DMSO.

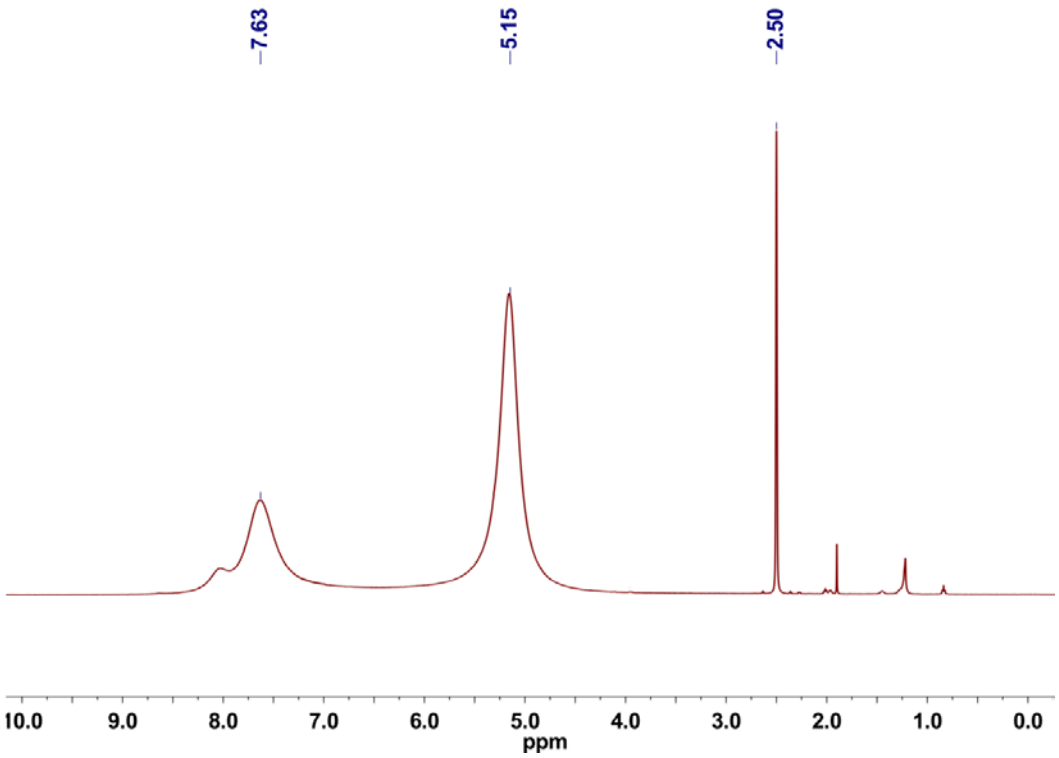


Fig. S48 ^{1}H NMR spectrum of **13** in d_6-DMSO.

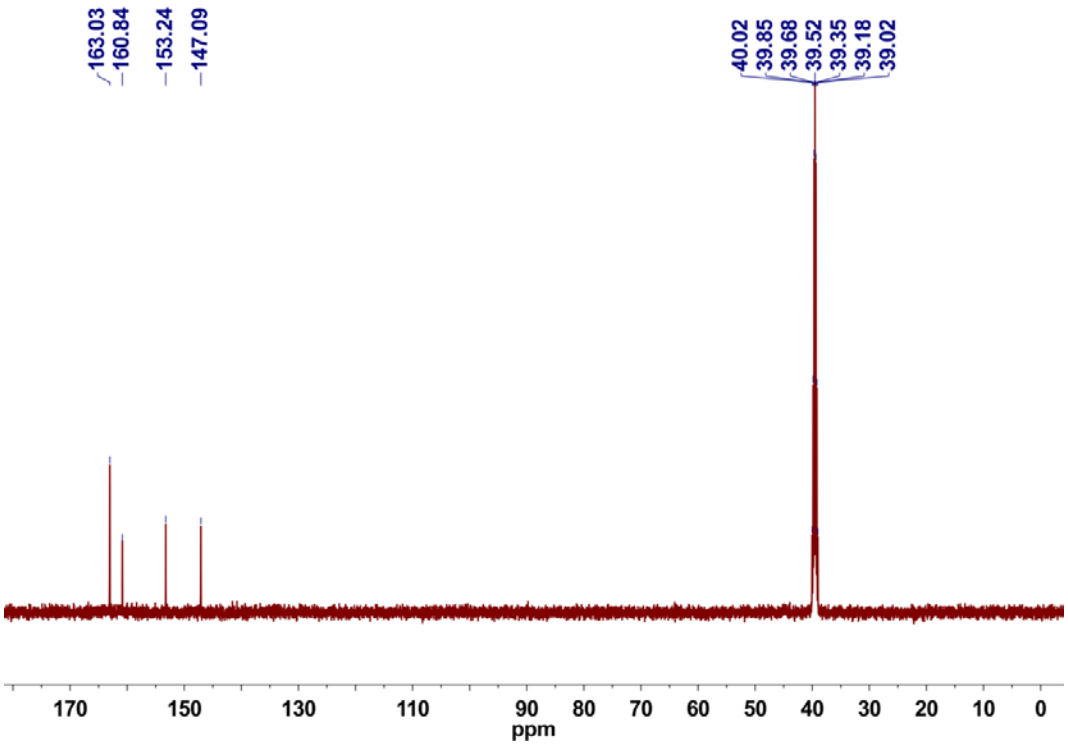


Fig. S49 ^{13}C NMR spectrum of **13** in d_6-DMSO.

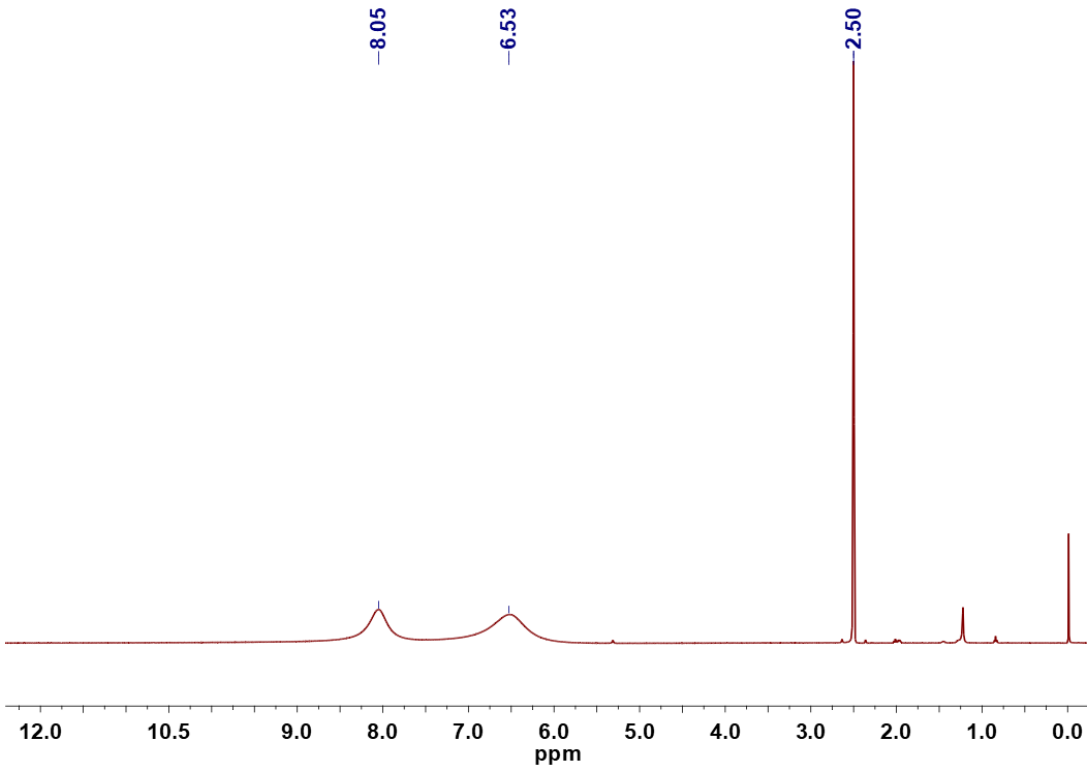


Fig. S50 ^{1}H NMR spectrum of **14** in d_6-DMSO.

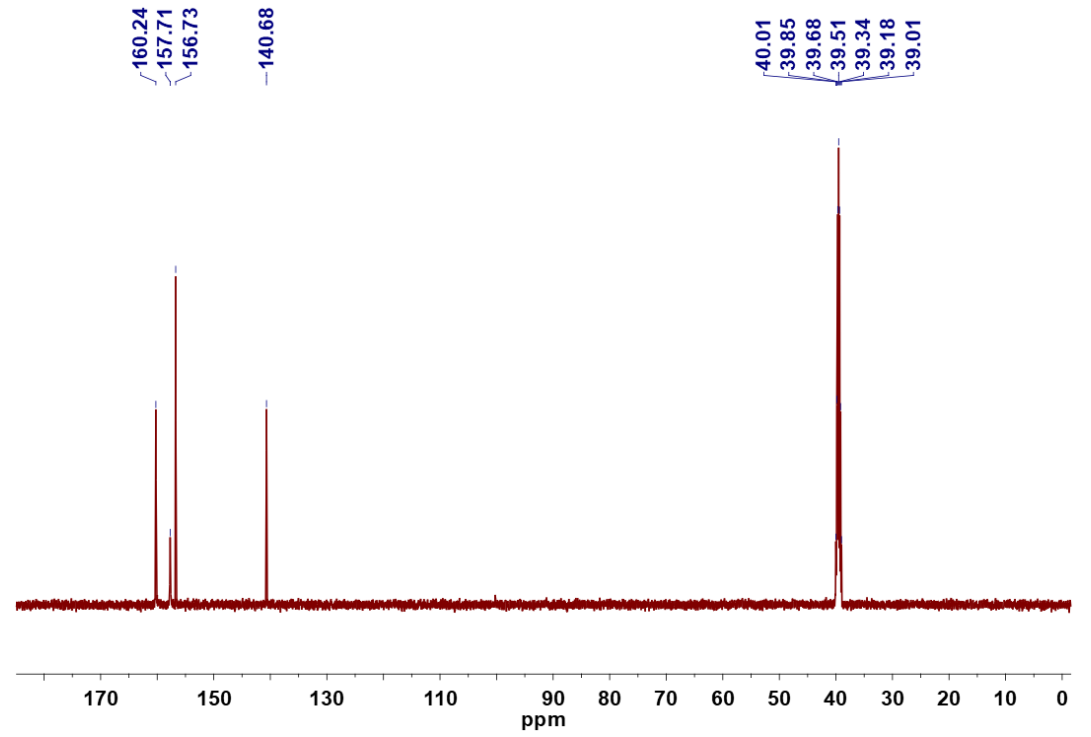


Fig. S51 ^{13}C NMR spectrum of **14** in d_6-DMSO.

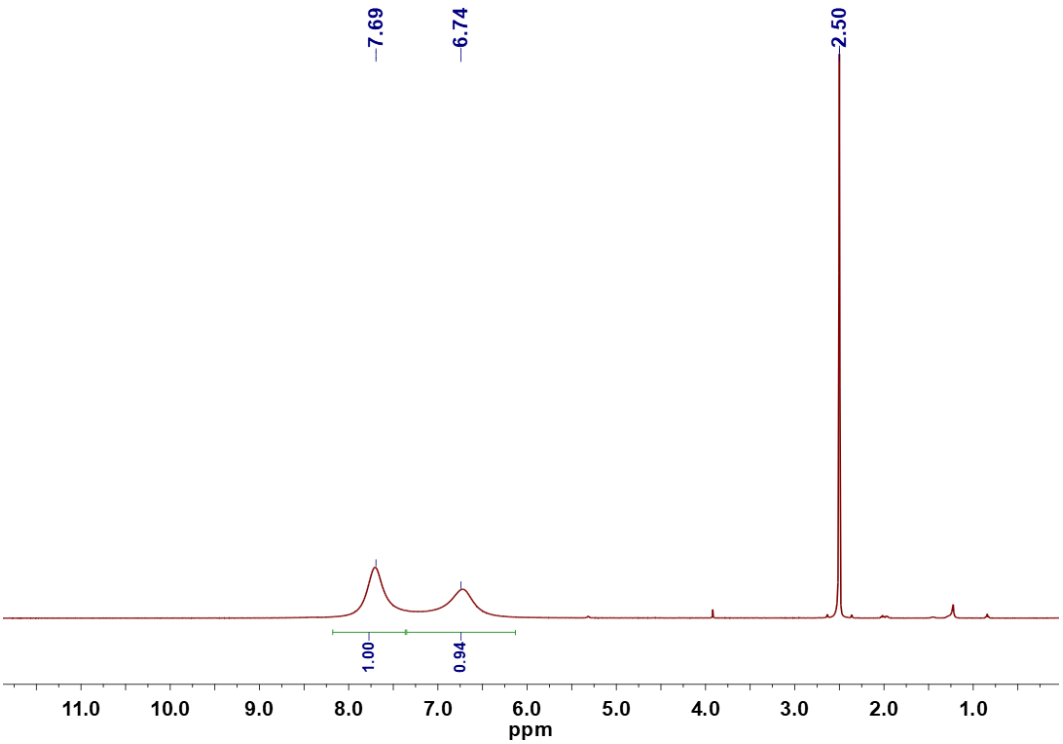


Fig. S52 ^{1}H NMR spectrum of **15** in d_6-DMSO.

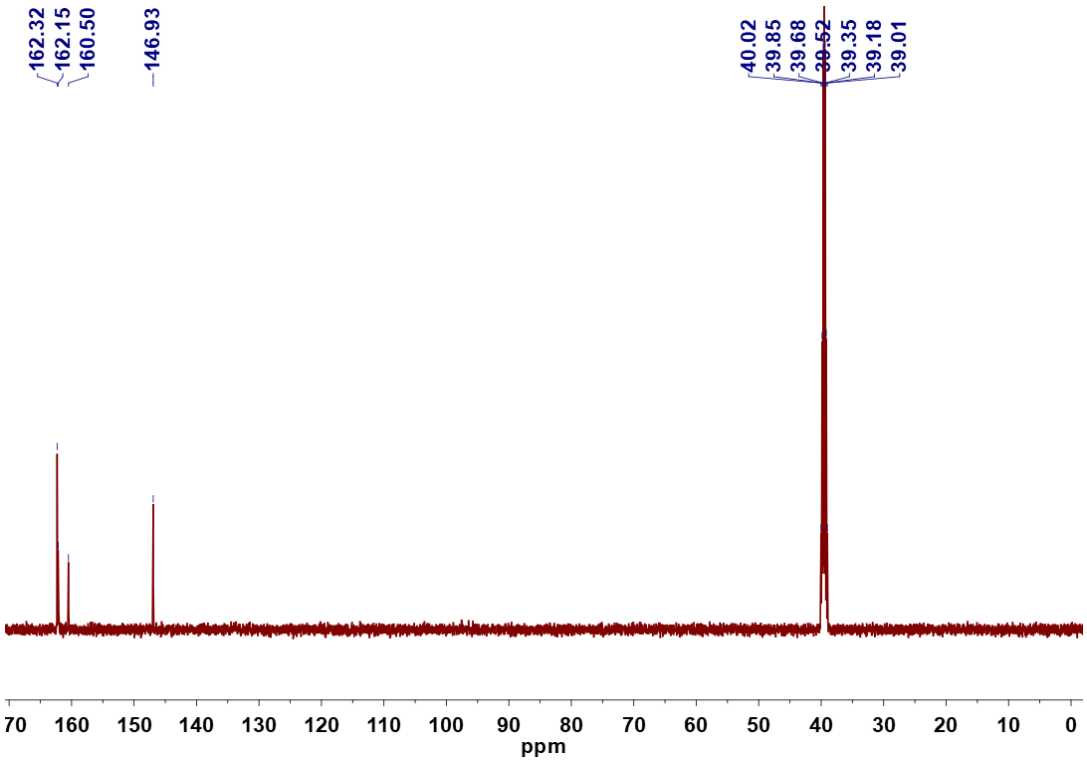


Fig. S53 ^{13}C NMR spectrum of **15** in d_6-DMSO.

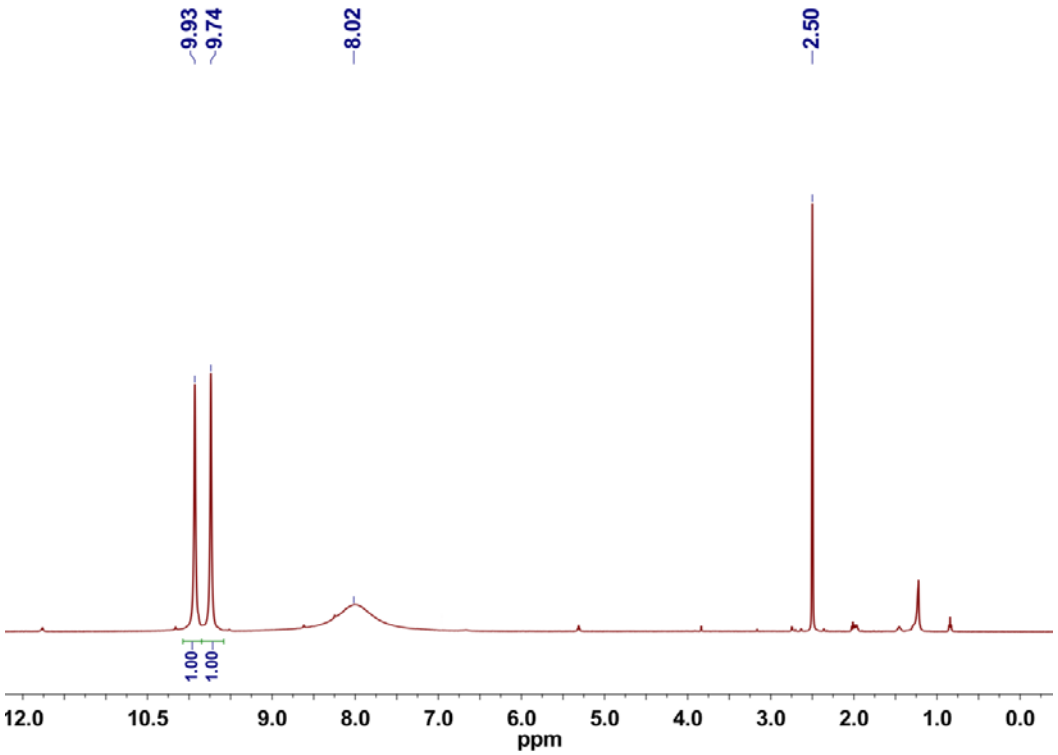


Fig. S54 ^{1}H NMR spectrum of **16** in d_6-DMSO.

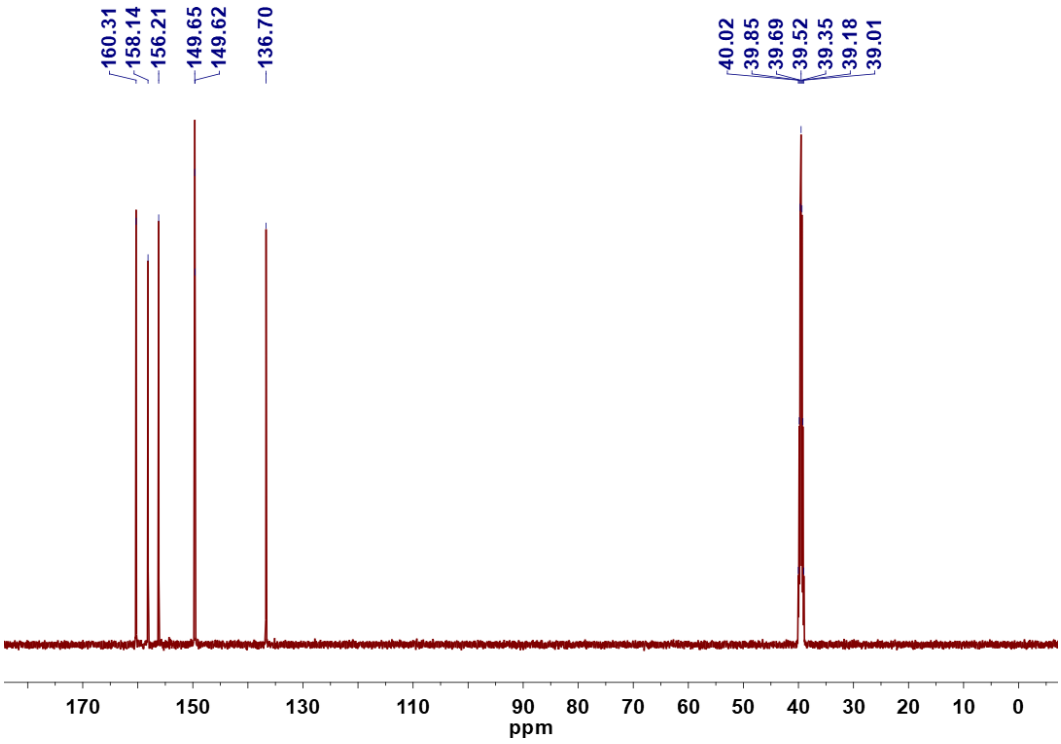


Fig. S55 ^{13}C NMR spectrum of **16** in d_6-DMSO.

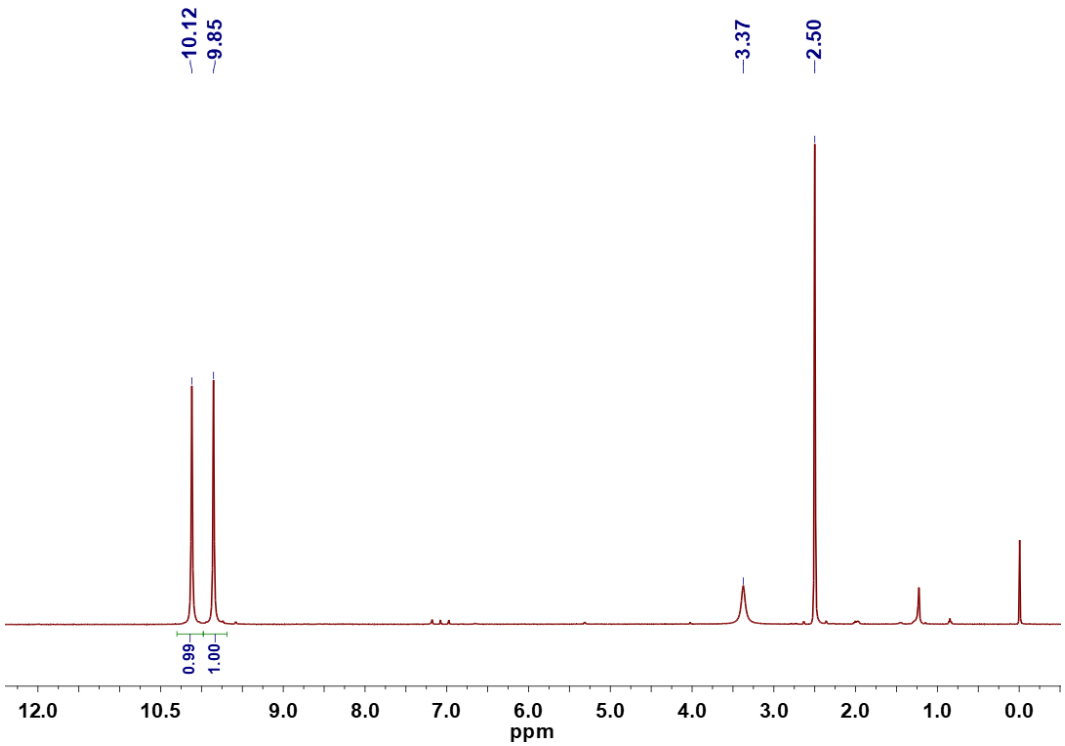


Fig. S56 ^{1}H NMR spectrum of **18** in d_6-DMSO.

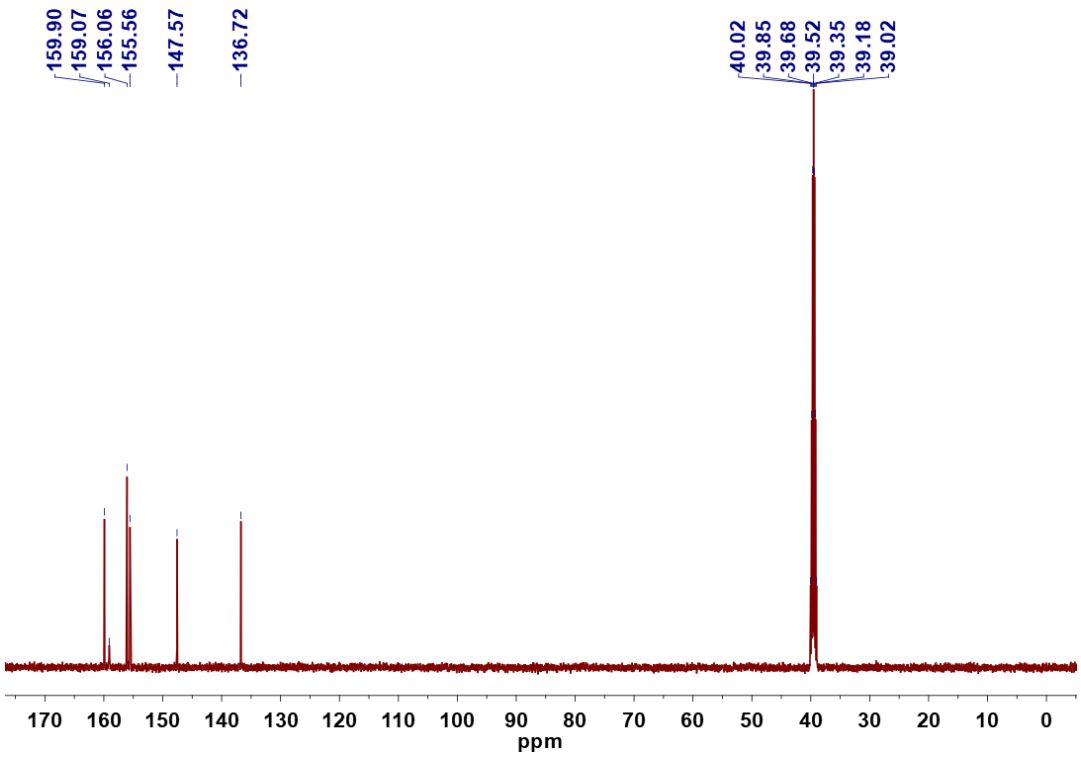


Fig. S57 ^{13}C NMR spectrum of **18** in d_6-DMSO.

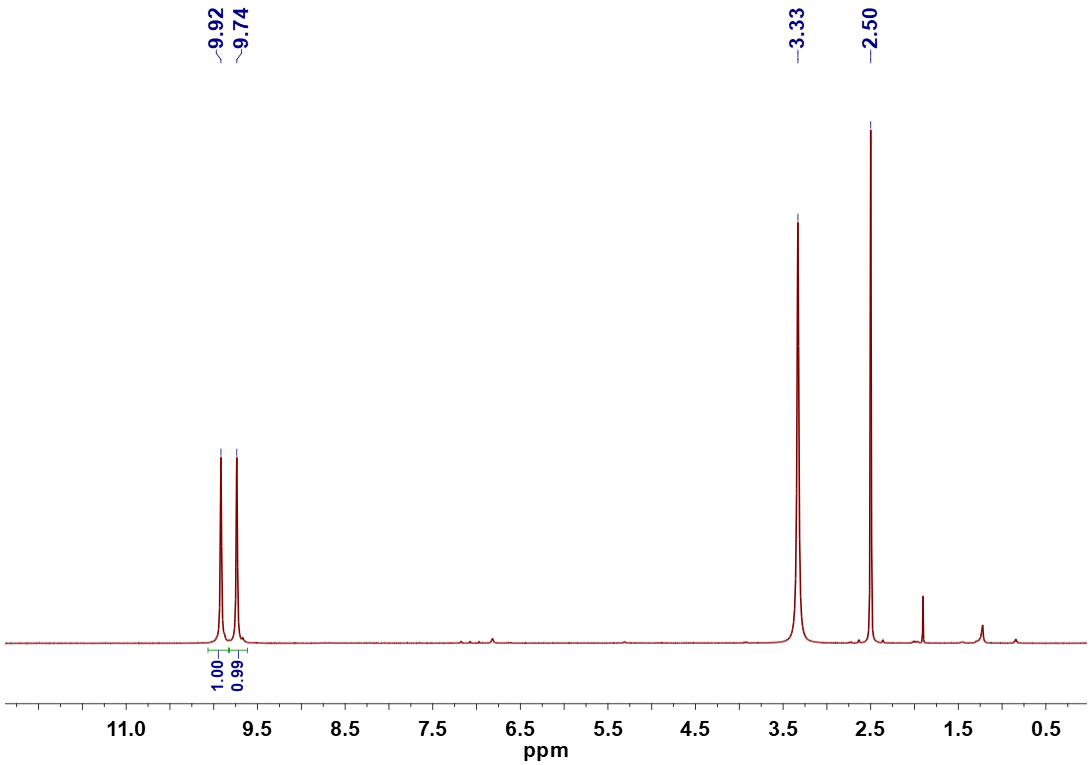


Fig. S58 ^{1}H NMR spectrum of **19** in d_6-DMSO.

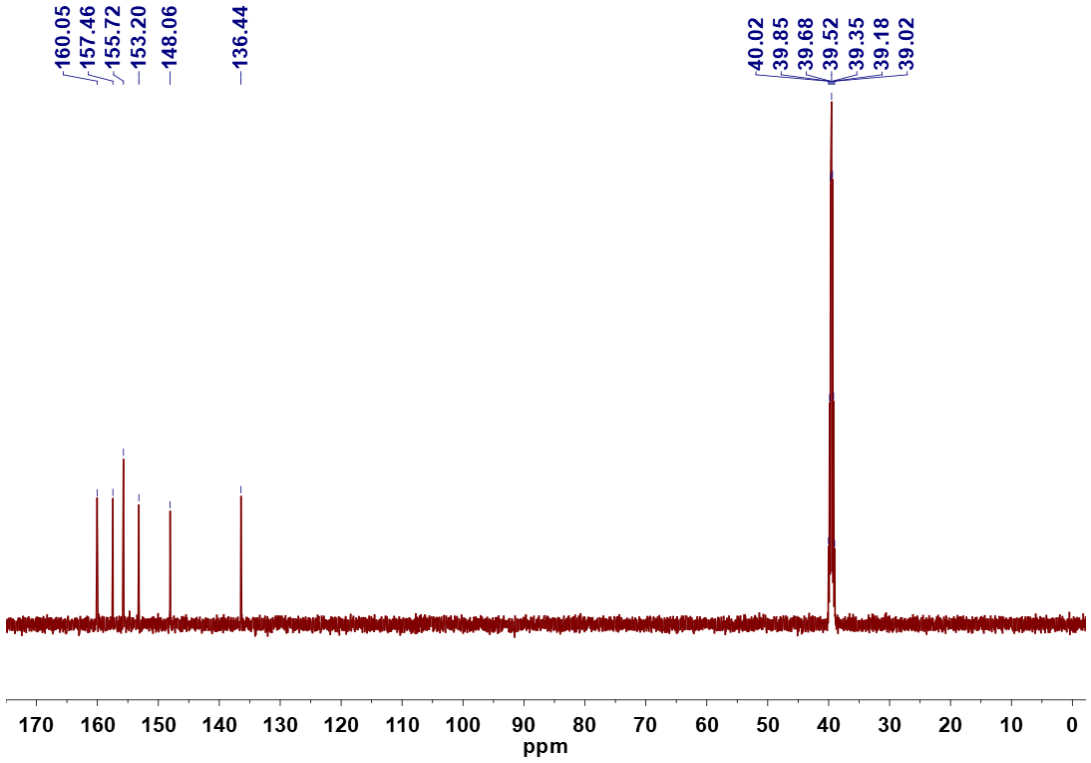


Fig. S59 ^{13}C NMR spectrum of **19** in d_6-DMSO.

23.TG and DSC curves

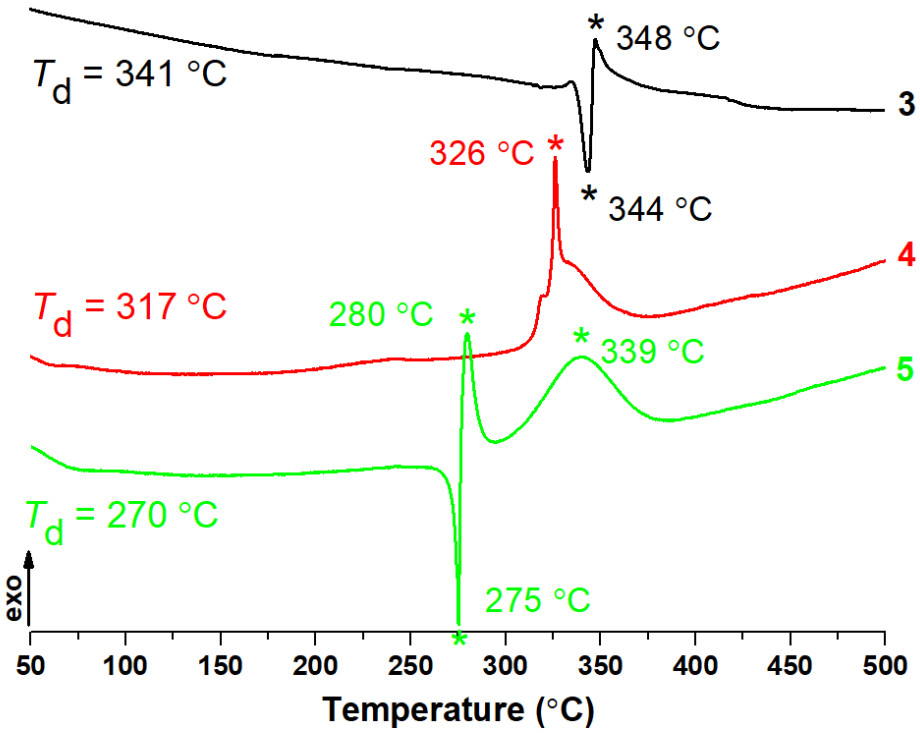


Fig. S60 DSC curves of **3**-**5** under nitrogen with a heating rate of 5 °C min^{-1}.

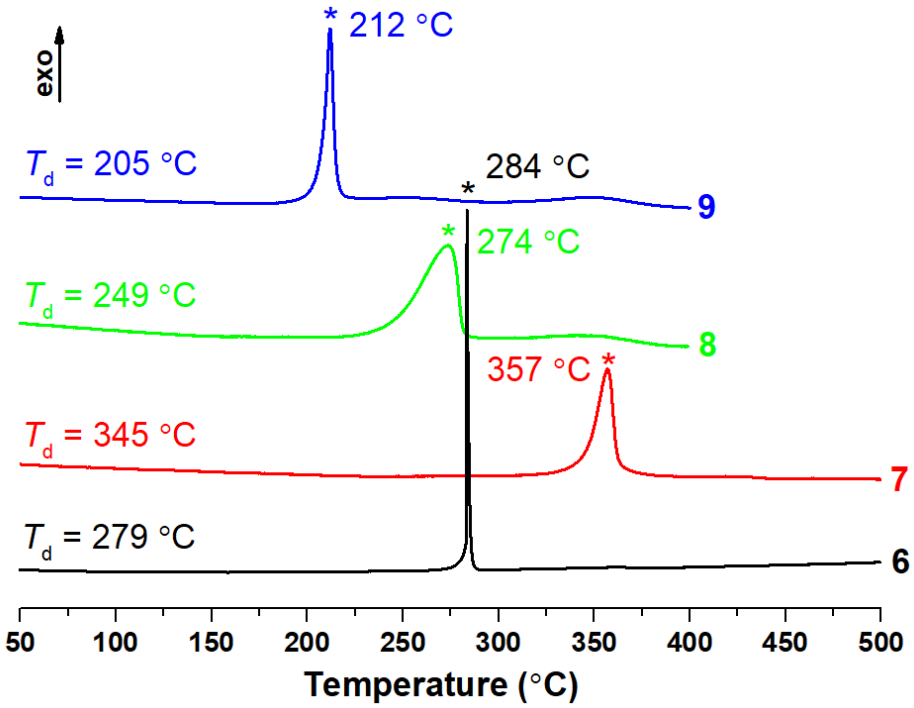


Fig. S61 DSC curves of **6**-**9** under nitrogen with a heating rate of 5 °C min^{-1}.

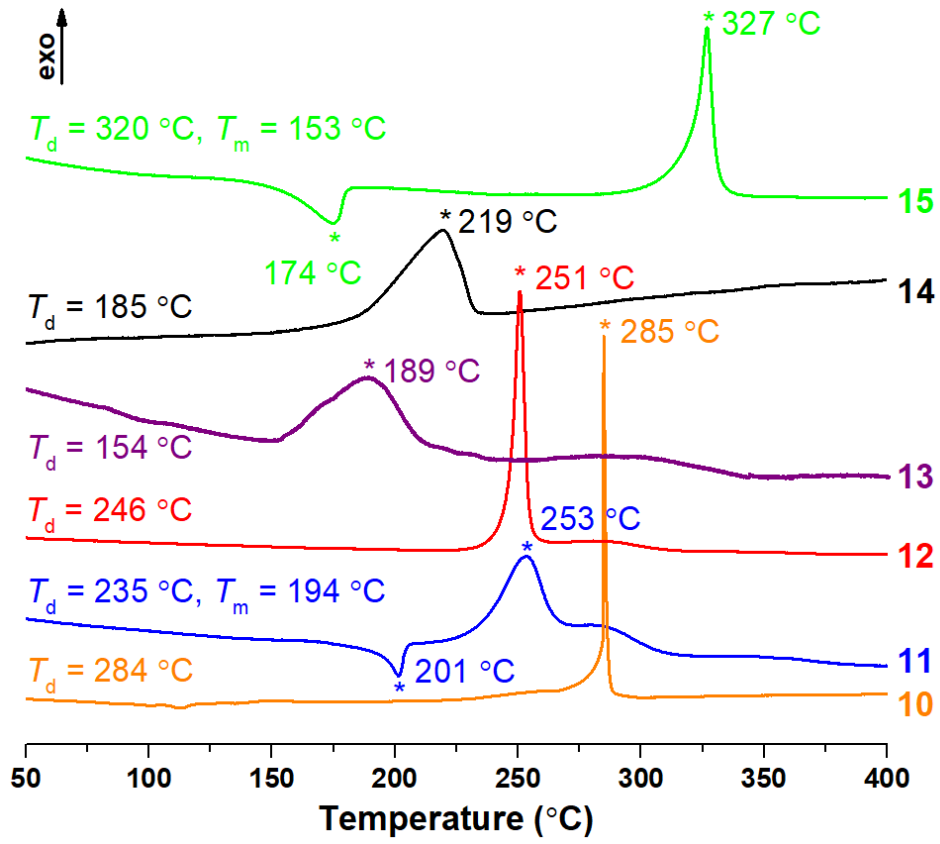


Fig. S62 DSC curves of **10**-**15** under nitrogen with a heating rate of 5 °C min^{-1}.

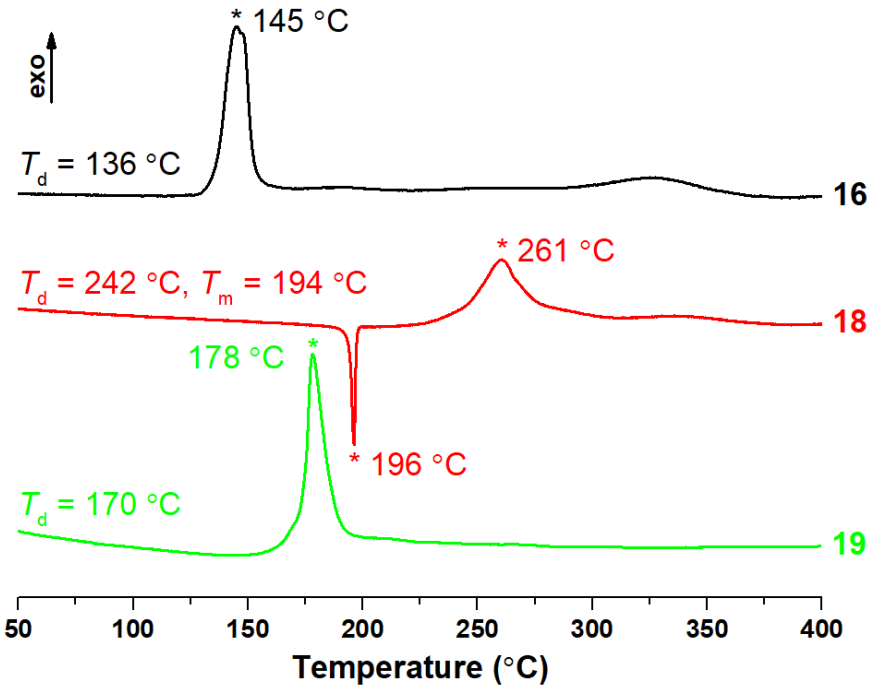


Fig. S63 DSC curves of **16**, **18**, **19** under nitrogen with a heating rate of 5 °C min^{-1}.

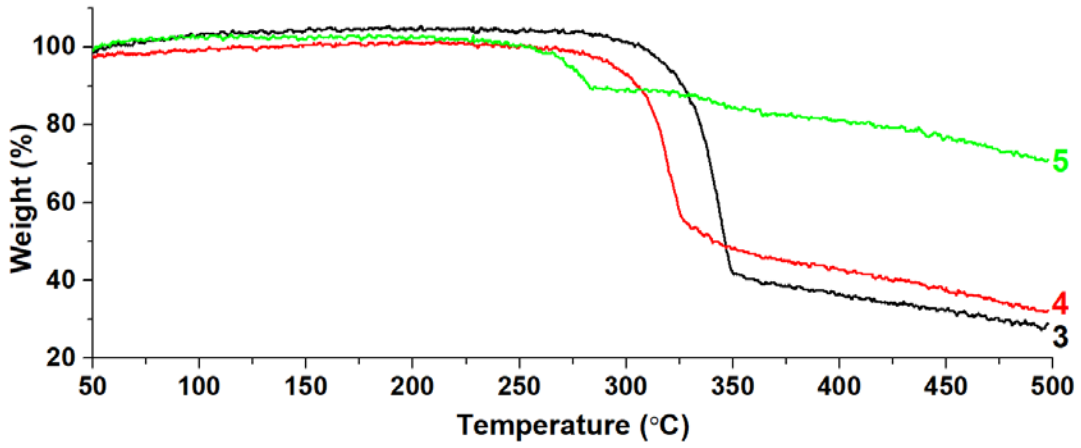


Fig. S64 TG curves of **3-5** under nitrogen with a heating rate of 5 ^{o}C min^{-1}.

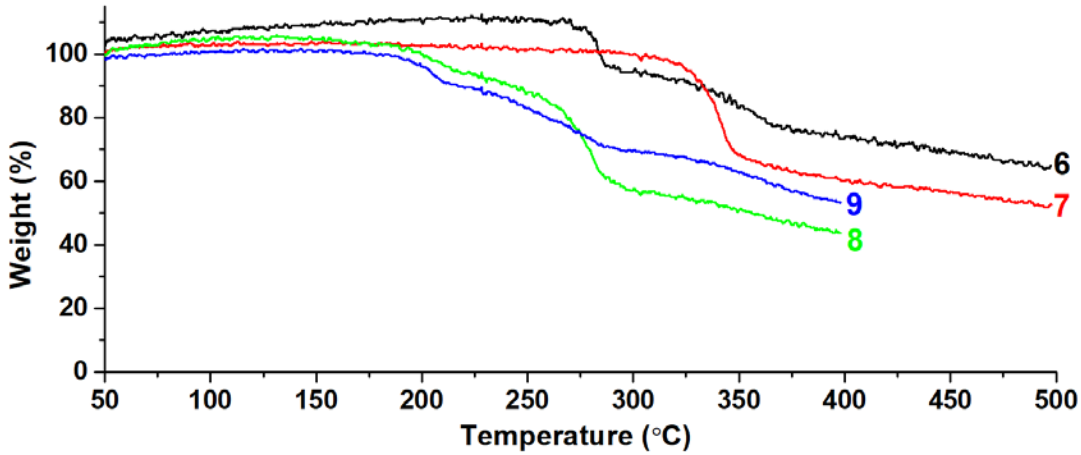


Fig. S65 TG curves of **6-9** under nitrogen with a heating rate of 5 ^{o}C min^{-1}.

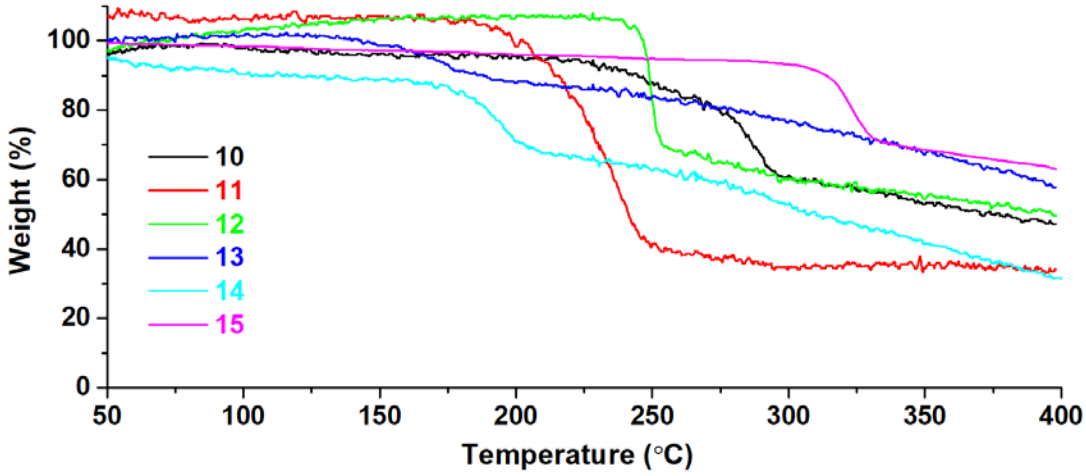


Fig. S66 TG curves of **10-15** under nitrogen with a heating rate of 5 ^{o}C min^{-1}.

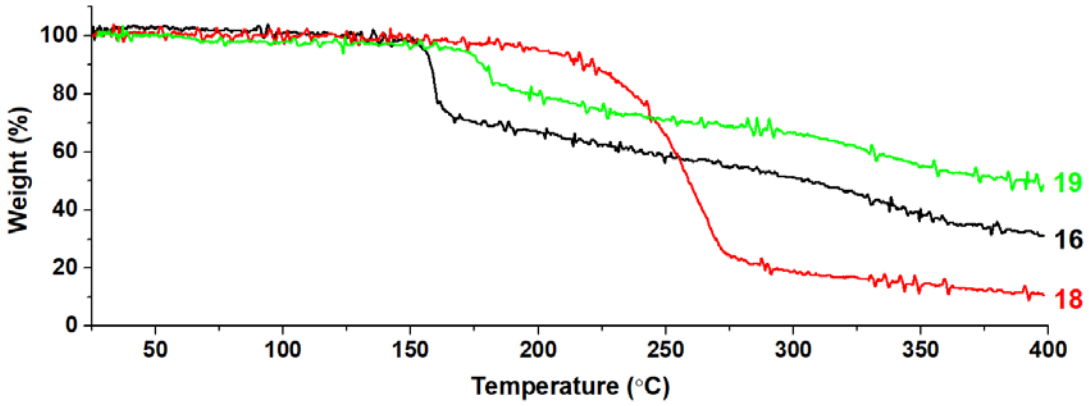


Fig. S67 TG curves of **16**, **18**, **19** under nitrogen with a heating rate of 5 ^{o}C min^{-1}.

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