Electronic Supplementary Information

A series of *N*-trinitromethyl-substituted polynitro-pyrazoles: high-energy-density materials with positive oxygen balances

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

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

$C_4H_5N_5O_4$	$F(000) = 192$
$M_r = 187.13$	$D_x = 1.749$ Mg m^{-3}
Monoclinic, *Pc*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.0966$ (8) Å	Cell parameters from 1157 reflections
$b = 12.015$ (2) Å	$\theta = 3.3–23.5°$
$c = 7.3348$ (15) Å	$\mu = 0.16$ mm^{-1}
$\beta = 100.207$ (6)°	$T = 170$ K
$V = 355.30$ (12) Å^3	Block, colourless
$Z = 2$	0.15 × 0.08 × 0.03 mm
Bruker D8 VENTURE diffractometer	990 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 0.1117 before and 0.0579 after correction. The Ratio of minimum to maximum transmission is 0.8623. The $\lambda/2$ correction factor is Not present.	$\theta_{max} = 27.7°$, $\theta_{min} = 3.3°$
$T_{min} = 0.643$, $T_{max} = 0.746$	$h = -5 \rightarrow 5$
4326 measured reflections	$k = -15 \rightarrow 15$
1482 independent reflections	$l = -9 \rightarrow 9$
Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.1338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.04$	$\Delta\rangle_{max} = 0.27$ e Å^{-3}
1482 reflections	$\Delta\rangle_{min} = -0.29$ e Å^{-3}
119 parameters	Absolute structure: Flack x determined using 340 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
2 restraints	Absolute structure parameter: -1.3 (10)
Primary atom site location: dual	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O4	0.8898 (10)	0.5532 (3)	0.6568 (6)	0.0343 (11)
O3	0.4836 (10)	0.4601 (3)	0.4898 (6)	0.0364 (11)
O2	0.5189 (12)	0.9895 (3)	0.3955 (6)	0.0424 (12)
O1	0.0841 (11)	0.9570 (3)	0.1843 (6)	0.0438 (13)
N5	0.1447 (12)	0.7386 (4)	0.2440 (6)	0.0280 (12)
N4	0.2275 (11)	0.6409 (4)	0.3187 (7)	0.0262 (12)
H4	0.131485	0.577980	0.277612	0.031*
N1	0.3125 (12)	0.9263 (4)	0.3044 (7)	0.0333 (14)
N3	0.6240 (10)	0.5488 (4)	0.5439 (6)	0.0262 (12)
N2	0.7849 (12)	0.8134 (4)	0.6261 (7)	0.0301 (12)
H2	0.857745	0.878317	0.594983	0.036*
C1	0.3467 (14)	0.8095 (4)	0.3484 (8)	0.0241 (13)
C3	0.4814 (13)	0.6482 (4)	0.4682 (7)	0.0222 (13)
C2	0.5670 (14)	0.7606 (5)	0.4977 (7)	0.0232 (12)
C4	0.9132 (15)	0.7736 (5)	0.8126 (8)	0.0337 (15)
H4A	1.112521	0.728777	0.811239	0.051*
H4B	0.744413	0.727997	0.856422	0.051*
H4C	0.968872	0.837359	0.895686	0.051*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O4	0.033 (2)	0.030 (2)	0.036 (3)	0.0083 (18)	-0.004 (2)	0.0023 (19)
O3	0.041 (3)	0.023 (2)	0.044 (3)	-0.0045 (18)	0.004 (2)	-0.0001 (19)
O2	0.054 (3)	0.026 (2)	0.041 (3)	-0.008 (2)	-0.009 (2)	0.0011 (19)
O1	0.053 (3)	0.031 (2)	0.039 (3)	0.014 (2)	-0.016 (3)	0.003 (2)
N5	0.028 (3)	0.026 (3)	0.028 (3)	0.002 (2)	-0.001 (2)	0.000 (2)
N4	0.030 (3)	0.020 (2)	0.027 (3)	-0.001 (2)	-0.001 (2)	0.000 (2)
N1	0.040 (3)	0.027 (3)	0.030 (3)	0.005 (2)	-0.001 (3)	0.001 (2)
N3	0.027 (3)	0.026 (3)	0.025 (3)	0.002 (2)	0.004 (3)	0.0028 (19)
N2	0.031 (3)	0.024 (2)	0.030 (3)	-0.004 (2)	-0.008 (2)	0.002 (2)
C1	0.025 (3)	0.020 (3)	0.026 (3)	0.003 (2)	0.002 (3)	-0.001 (2)
C3	0.023 (3)	0.020 (3)	0.023 (3)	0.003 (2)	-0.001 (3)	-0.001 (2)
C2	0.021 (3)	0.028 (3)	0.021 (3)	0.001 (2)	0.003 (3)	0.002 (3)
C4	0.038 (4)	0.030 (3)	0.029 (4)	-0.002 (3)	-0.008 (3)	-0.001 (3)

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

O4—N3	1.247 (5)	N3—C3	1.400 (7)
O3—N3	1.243 (6)	N2—H2	0.8800
O2—N1	1.240 (6)	N2—C2	1.337 (7)
O1—N1	1.223 (6)	N2—C4	1.456 (7)
N5—N4	1.314 (6)	C1—C2	1.417 (8)
N5—C1	1.331 (7)	C3—C2	1.403 (8)
N4—H4	0.8800	C4—H4A	0.9800
N4—C3	1.374 (7)	C4—H4B	0.9800
N1—C1	1.441 (7)	C4—H4C	0.9800
N4—N5—C1	104.1 (4)	N5—C1—C2	115.1 (5)
N5—N4—H4	123.9	C2—C1—N1	126.9 (5)
N5—N4—C3	112.2 (4)	N4—C3—N3	117.7 (5)
C3—N4—H4	123.9	N4—C3—C2	108.5 (5)
O2—N1—C1	116.5 (5)	N3—C3—C2	133.2 (5)
O1—N1—O2	124.4 (5)	N2—C2—C1	127.0 (5)
O1—N1—C1	119.1 (5)	N2—C2—C3	133.1 (5)
O4—N3—C3	118.8 (4)	C3—C2—C1	99.9 (5)
O3—N3—O4	123.3 (5)	N2—C4—H4A	109.5
O3—N3—C3	117.9 (4)	N2—C4—H4B	109.5
C2—N2—H2	116.9	N2—C4—H4C	109.5
C2—N2—C4	126.2 (5)	H4A—C4—H4B	109.5
C4—N2—H2	116.9	H4A—C4—H4C	109.5
N5—C1—N1	117.9 (5)	H4B—C4—H4C	109.5

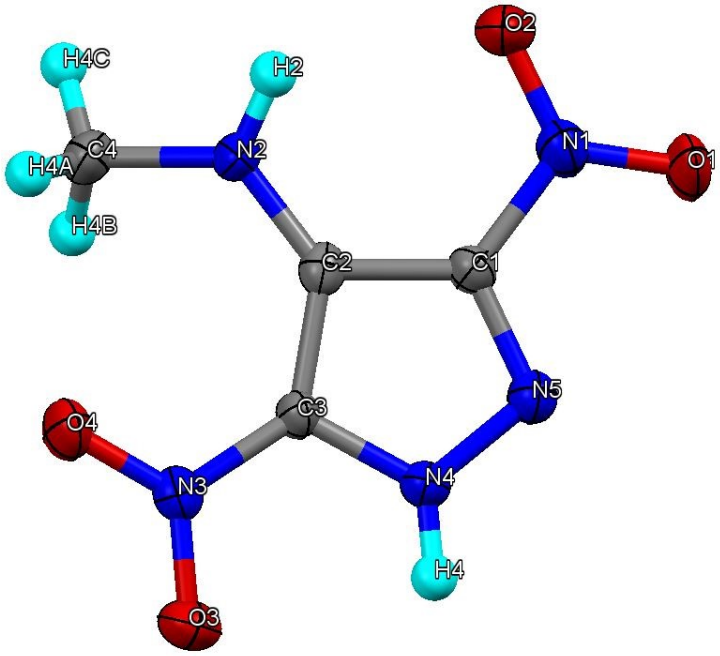


Fig. S1 Crystal structure of **2**.

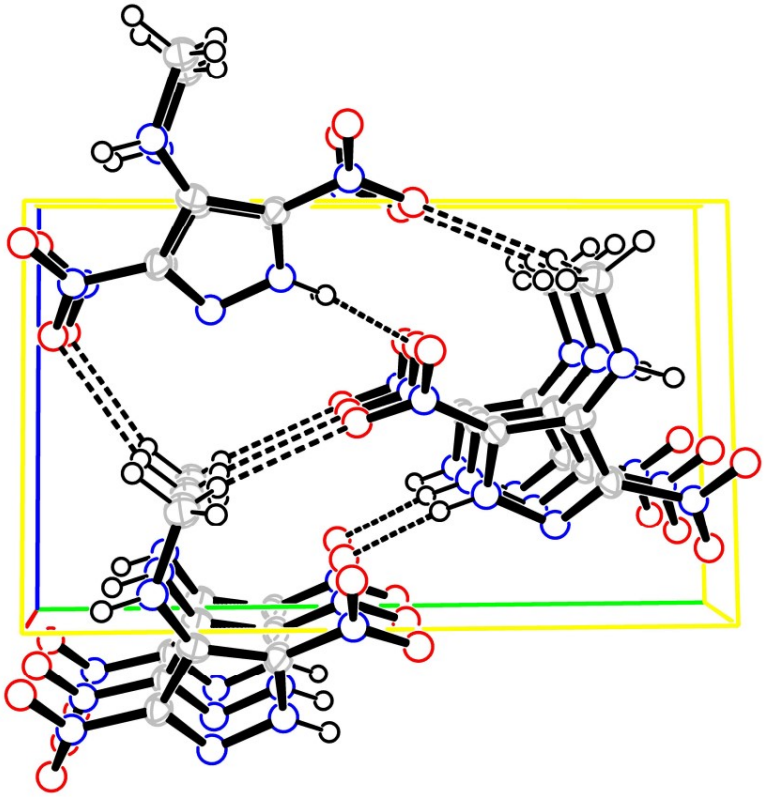


Fig. S2 Packing diagram of **2**.

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

Table S5. Crystal data, data collection, and refinement for **6**

$C_6H_5ClN_4O_5$	$F(000) = 504$
$M_r = 248.59$	$D_x = 1.774$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.292$ (3) Å	Cell parameters from 613 reflections
$b = 5.0976$ (10) Å	$\theta = 2.7–23.0°$
$c = 14.985$ (3) Å	$\mu = 0.43$ mm^{-1}
$\beta = 97.479$ (6)°	$T = 173$ K
$V = 931.0$ (3) Å^3	Block, colourless
$Z = 4$	0.28 × 0.15 × 0.12 mm
Bruker APEX-II CCD diffractometer	1492 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.041$
Absorption correction: multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0610 before and 0.0473 after correction. The Ratio of minimum to maximum transmission is 0.8967. The $\lambda/2$ correction factor is 0.00150.	$\theta_{max} = 26.4°$, $\theta_{min} = 1.7°$
$T_{min} = 0.668$, $T_{max} = 0.745$	$h = -15 \rightarrow 15$
5830 measured reflections	$k = -6 \rightarrow 6$
1886 independent reflections	$l = -18 \rightarrow 18$
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.042$	H-atom parameters constrained
$wR(F^2) = 0.122$	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1886 reflections	$\Delta\rangle_{max} = 0.28$ e Å^{-3}
146 parameters	$\Delta\rangle_{min} = -0.29$ e Å^{-3}
0 restraints	

Table S6. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **6**

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.35159 (6)	0.88010 (13)	0.95203 (4)	0.0320 (2)
O5	0.58919 (15)	0.3123 (4)	0.83730 (13)	0.0311 (5)

O4	0.57314 (16)	0.6545 (4)	0.92085 (13)	0.0380 (5)
O1	0.15622 (17)	0.6058 (4)	0.62957 (13)	0.0371 (5)
O2	0.05818 (15)	0.4519 (4)	0.81024 (15)	0.0405 (5)
N2	0.26850 (16)	0.3440 (4)	0.77247 (14)	0.0212 (5)
O3	0.11476 (17)	0.8326 (4)	0.86276 (14)	0.0403 (5)
N4	0.53515 (17)	0.4831 (4)	0.86843 (14)	0.0245 (5)
N3	0.37701 (16)	0.3089 (4)	0.78103 (13)	0.0215 (5)
N1	0.13005 (18)	0.6151 (4)	0.83291 (14)	0.0264 (5)
C5	0.3370 (2)	0.6401 (5)	0.87315 (15)	0.0215 (5)
C4	0.2423 (2)	0.5430 (5)	0.82599 (16)	0.0220 (5)
C6	0.4177 (2)	0.4827 (5)	0.84230 (16)	0.0206 (5)
C3	0.2016 (2)	0.1977 (5)	0.70151 (16)	0.0224 (5)
H3A	0.1384	0.1187	0.7264	0.027*
H3B	0.2458	0.0533	0.6807	0.027*
C2	0.1596 (2)	0.3699 (5)	0.62207 (17)	0.0240 (6)
C1	0.1232 (2)	0.2255 (6)	0.53699 (18)	0.0337 (7)
H1A	0.0677	0.3291	0.4995	0.051*
H1B	0.0917	0.0562	0.5511	0.051*
H1C	0.1862	0.1961	0.5044	0.051*

Table S7. Atomic displacement parameters (Å^2) for **6**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0426 (4)	0.0283 (4)	0.0240 (3)	0.0025 (3)	-0.0001 (3)	-0.0090 (3)
O5	0.0221 (10)	0.0336 (11)	0.0371 (11)	0.0018 (8)	0.0020 (8)	-0.0039 (9)
O4	0.0323 (11)	0.0417 (12)	0.0378 (11)	-0.0085 (9)	-0.0036 (9)	-0.0155 (9)
O1	0.0488 (13)	0.0230 (11)	0.0368 (11)	-0.0035 (9)	-0.0045 (10)	0.0010 (9)
O2	0.0215 (10)	0.0461 (13)	0.0537 (13)	0.0007 (10)	0.0044 (9)	-0.0037 (11)
N2	0.0181 (11)	0.0210 (11)	0.0235 (10)	-0.0004 (9)	-0.0013 (8)	-0.0019 (8)
O3	0.0400 (12)	0.0357 (12)	0.0456 (12)	0.0143 (10)	0.0071 (10)	-0.0097 (10)
N4	0.0239 (11)	0.0255 (12)	0.0233 (11)	-0.0030 (10)	-0.0001 (9)	-0.0005 (9)
N3	0.0193 (11)	0.0223 (11)	0.0221 (10)	-0.0014 (9)	-0.0002 (9)	-0.0020 (9)
N1	0.0237 (12)	0.0329 (13)	0.0225 (11)	0.0069 (11)	0.0030 (9)	0.0042 (10)
C5	0.0279 (14)	0.0188 (12)	0.0176 (11)	-0.0006 (11)	0.0017 (10)	-0.0005 (10)
C4	0.0223 (13)	0.0227 (13)	0.0209 (12)	0.0029 (11)	0.0020 (10)	0.0021 (10)
C6	0.0200 (12)	0.0208 (12)	0.0200 (12)	-0.0026 (10)	-0.0011 (10)	0.0008 (10)
C3	0.0193 (13)	0.0213 (13)	0.0254 (12)	-0.0024 (10)	-0.0021 (10)	-0.0025 (10)
C2	0.0203 (13)	0.0245 (14)	0.0270 (13)	-0.0042 (11)	0.0028 (11)	0.0011 (11)
C1	0.0390 (17)	0.0338 (16)	0.0264 (14)	-0.0069 (13)	-0.0024 (12)	-0.0014 (12)

Table S8. Geometric parameters (Å, º) for **6**

Cl1—C5	1.694 (2)	O3—N1	1.219 (3)
O5—N4	1.224 (3)	N4—C6	1.446 (3)
O4—N4	1.226 (3)	N3—C6	1.326 (3)
O1—C2	1.209 (3)	N1—C4	1.444 (3)
O2—N1	1.229 (3)	C5—C4	1.374 (4)
N2—N3	1.335 (3)	C5—C6	1.400 (3)
N2—C4	1.358 (3)	C3—C2	1.515 (3)
N2—C3	1.462 (3)	C2—C1	1.490 (4)
N3—N2—C4	110.8 (2)	C6—C5—Cl1	129.0 (2)
N3—N2—C3	117.54 (19)	N2—C4—N1	122.3 (2)
C4—N2—C3	131.0 (2)	N2—C4—C5	108.8 (2)
O5—N4—O4	124.8 (2)	C5—C4—N1	128.7 (2)
O5—N4—C6	117.9 (2)	N3—C6—N4	117.5 (2)
O4—N4—C6	117.3 (2)	N3—C6—C5	113.1 (2)
C6—N3—N2	105.00 (19)	C5—C6—N4	129.4 (2)
O2—N1—C4	117.8 (2)	N2—C3—C2	112.2 (2)
O3—N1—O2	125.3 (2)	O1—C2—C3	121.0 (2)
O3—N1—C4	116.9 (2)	O1—C2—C1	124.1 (3)
C4—C5—Cl1	128.7 (2)	C1—C2—C3	114.8 (2)
C4—C5—C6	102.3 (2)		

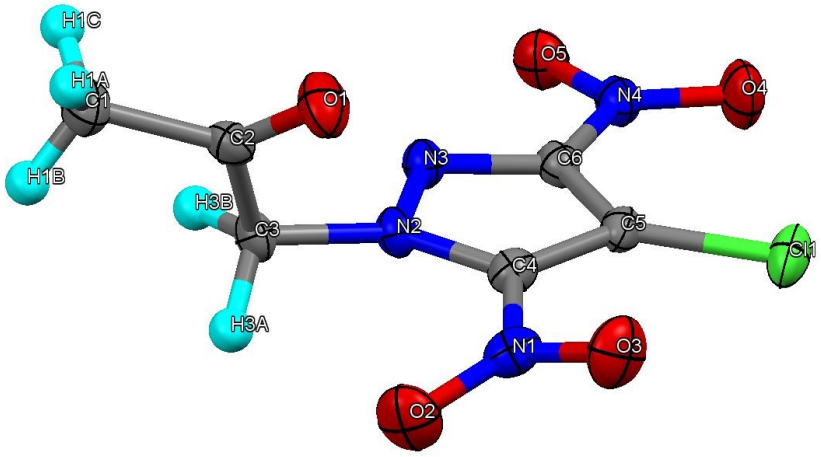


Fig. S3 Crystal structure of **6**.

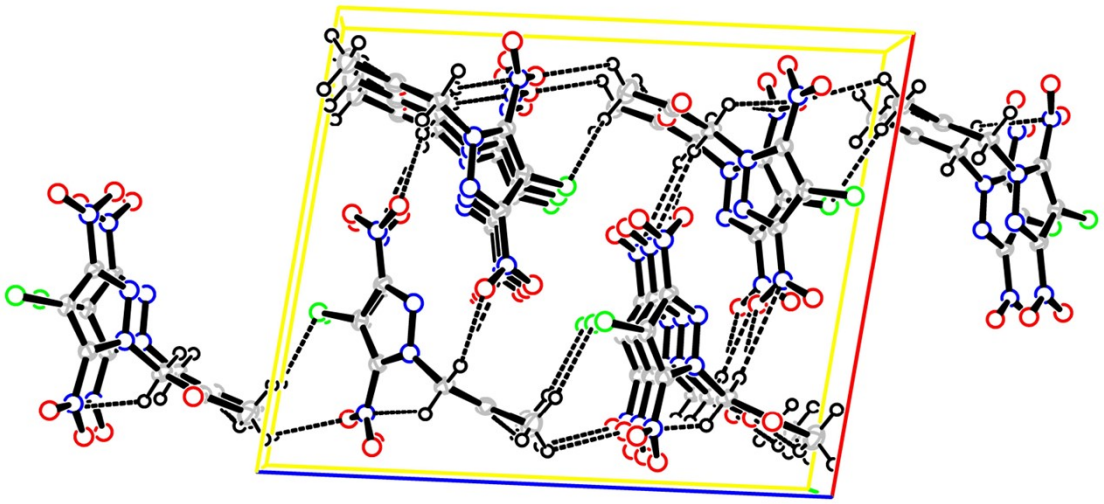


Fig. S4 Packing diagram of **6**.

3. Single-crystal X-ray diffraction analysis of **7**

Table S9. Crystal data, data collection, and refinement for **7**

$C_6H_7N_5O_5$	$F(000) = 472$
$M_r = 229.17$	$D_x = 1.701$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.4834$ (4) Å	Cell parameters from 1815 reflections
$b = 20.756$ (2) Å	$\theta = 3.6$–$26.2°$
$c = 9.7107$ (9) Å	$\mu = 0.15$ mm^{-1}
$\beta = 97.924$ (3)°	$T = 110$ K
$V = 895.02$ (15) Å^3	Block, colourless
$Z = 4$	0.12 × 0.08 × 0.05 mm
Bruker D8 VENTURE diffractometer	1219 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 0.1043 before and 0.0671 after correction. The Ratio of minimum to maximum transmission is 0.8090. The $\lambda/2$ correction factor is Not present.	$\theta_{max} = 26.4°$, $\theta_{min} = 2.3°$
$T_{min} = 0.603$, $T_{max} = 0.745$	$h = -5 \rightarrow 5$
8322 measured reflections	$k = -25 \rightarrow 24$
1823 independent reflections	$l = -12 \rightarrow 12$
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from

	neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.6589P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1823 reflections	$\Delta\rangle_{max} = 0.30$ e Å^{-3}
146 parameters	$\Delta\rangle_{min} = -0.33$ e Å^{-3}
0 restraints	

Table S10. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **7**

	x	*y*	*z*	U_{iso}*/U_{eq}
O001	0.6153 (4)	0.63370 (8)	0.2153 (2)	0.0226 (5)
O002	0.8442 (4)	0.78445 (8)	0.4709 (2)	0.0249 (5)
O003	1.1208 (4)	0.72375 (9)	0.35405 (19)	0.0239 (5)
O004	0.3055 (4)	0.61541 (9)	0.7941 (2)	0.0270 (5)
O005	0.4788 (5)	0.52107 (9)	0.7448 (2)	0.0301 (5)
N4	0.9045 (5)	0.61459 (10)	0.4733 (2)	0.0176 (5)
N5	0.7756 (5)	0.57314 (10)	0.5516 (2)	0.0189 (5)
N2	0.5085 (5)	0.72606 (10)	0.6614 (2)	0.0208 (5)
H2A	0.536272	0.765696	0.633666	0.025*
H2B	0.393734	0.718857	0.726404	0.025*
N3	0.9386 (5)	0.73138 (10)	0.4379 (2)	0.0207 (5)
N1	0.4602 (5)	0.57972 (11)	0.7295 (2)	0.0212 (5)
C2	0.6408 (6)	0.67668 (12)	0.6048 (3)	0.0175 (6)
C1	0.8292 (6)	0.67718 (12)	0.5017 (3)	0.0176 (6)
C4	0.8434 (6)	0.60136 (12)	0.2191 (3)	0.0191 (6)
C3	0.6232 (6)	0.61006 (12)	0.6306 (3)	0.0193 (6)
C5	1.0416 (6)	0.58888 (13)	0.3568 (3)	0.0201 (6)
H5A	1.073071	0.541922	0.369442	0.024*
H5B	1.240700	0.609273	0.355287	0.024*
C6	0.9476 (7)	0.57239 (14)	0.0939 (3)	0.0252 (7)
H6A	0.779216	0.570580	0.018090	0.038*
H6B	1.022613	0.528714	0.115822	0.038*
H6C	1.109638	0.598802	0.065387	0.038*

Table S11. Atomic displacement parameters (Å^2) for **7**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O001	0.0228 (11)	0.0211 (10)	0.0248 (11)	0.0017 (8)	0.0061 (9)	0.0011 (8)
O002	0.0338 (12)	0.0160 (10)	0.0269 (11)	0.0012 (8)	0.0111 (10)	-0.0024 (8)
O003	0.0257 (11)	0.0278 (11)	0.0212 (10)	-0.0023 (8)	0.0133 (10)	0.0003 (8)
O004	0.0299 (12)	0.0305 (11)	0.0240 (11)	0.0026 (9)	0.0157 (10)	-0.0009 (9)
O005	0.0371 (13)	0.0231 (12)	0.0327 (12)	-0.0009 (9)	0.0139 (10)	0.0057 (9)
N4	0.0200 (12)	0.0167 (12)	0.0176 (12)	-0.0001 (9)	0.0078 (10)	0.0001 (9)
N5	0.0206 (12)	0.0199 (12)	0.0175 (11)	-0.0005 (10)	0.0076 (10)	0.0011 (9)
N2	0.0241 (12)	0.0182 (12)	0.0221 (12)	0.0000 (10)	0.0107 (11)	-0.0020 (9)
N3	0.0209 (12)	0.0216 (13)	0.0202 (12)	-0.0009 (10)	0.0049 (11)	0.0000 (10)
N1	0.0218 (13)	0.0249 (14)	0.0176 (12)	-0.0014 (10)	0.0048 (11)	0.0025 (10)
C2	0.0172 (14)	0.0201 (14)	0.0154 (13)	-0.0012 (11)	0.0027 (12)	-0.0014 (10)
C1	0.0190 (14)	0.0168 (14)	0.0171 (13)	-0.0003 (11)	0.0030 (12)	-0.0002 (11)
C4	0.0240 (15)	0.0142 (14)	0.0202 (14)	-0.0041 (11)	0.0075 (13)	-0.0002 (11)
C3	0.0176 (14)	0.0210 (15)	0.0204 (14)	0.0007 (11)	0.0063 (12)	0.0019 (11)
C5	0.0231 (15)	0.0201 (14)	0.0190 (14)	0.0025 (11)	0.0095 (13)	-0.0003 (11)
C6	0.0303 (16)	0.0267 (16)	0.0202 (15)	0.0019 (13)	0.0089 (14)	-0.0022 (12)

Table S12. Geometric parameters (Å, º) for **7**

O001—C4	1.220 (3)	N3—C1	1.405 (3)
O002—N3	1.238 (3)	N1—C3	1.430 (3)
O003—N3	1.240 (3)	C2—C1	1.396 (4)
O004—N1	1.242 (3)	C2—C3	1.409 (4)
O005—N1	1.228 (3)	C4—C5	1.522 (4)
N4—N5	1.332 (3)	C4—C6	1.488 (4)
N4—C1	1.380 (3)	C5—H5A	0.9900
N4—C5	1.460 (3)	C5—H5B	0.9900
N5—C3	1.337 (3)	C6—H6A	0.9800
N2—H2A	0.8800	C6—H6B	0.9800
N2—H2B	0.8800	C6—H6C	0.9800
N2—C2	1.340 (3)		
N5—N4—C1	110.9 (2)	O001—C4—C5	120.4 (2)
N5—N4—C5	117.9 (2)	O001—C4—C6	123.6 (3)
C1—N4—C5	129.8 (2)	C6—C4—C5	116.0 (2)
N4—N5—C3	104.7 (2)	N5—C3—N1	118.8 (2)
H2A—N2—H2B	120.0	N5—C3—C2	114.5 (2)

C2—N2—H2A	120.0	C2—C3—N1	126.7 (2)
C2—N2—H2B	120.0	N4—C5—C4	111.2 (2)
O002—N3—O003	124.3 (2)	N4—C5—H5A	109.4
O002—N3—C1	116.4 (2)	N4—C5—H5B	109.4
O003—N3—C1	119.3 (2)	C4—C5—H5A	109.4
O004—N1—C3	116.7 (2)	C4—C5—H5B	109.4
O005—N1—O004	124.3 (2)	H5A—C5—H5B	108.0
O005—N1—C3	119.0 (2)	C4—C6—H6A	109.5
N2—C2—C1	129.4 (2)	C4—C6—H6B	109.5
N2—C2—C3	129.7 (2)	C4—C6—H6C	109.5
C1—C2—C3	100.9 (2)	H6A—C6—H6B	109.5
N4—C1—N3	123.7 (2)	H6A—C6—H6C	109.5
N4—C1—C2	109.0 (2)	H6B—C6—H6C	109.5
C2—C1—N3	127.2 (2)		

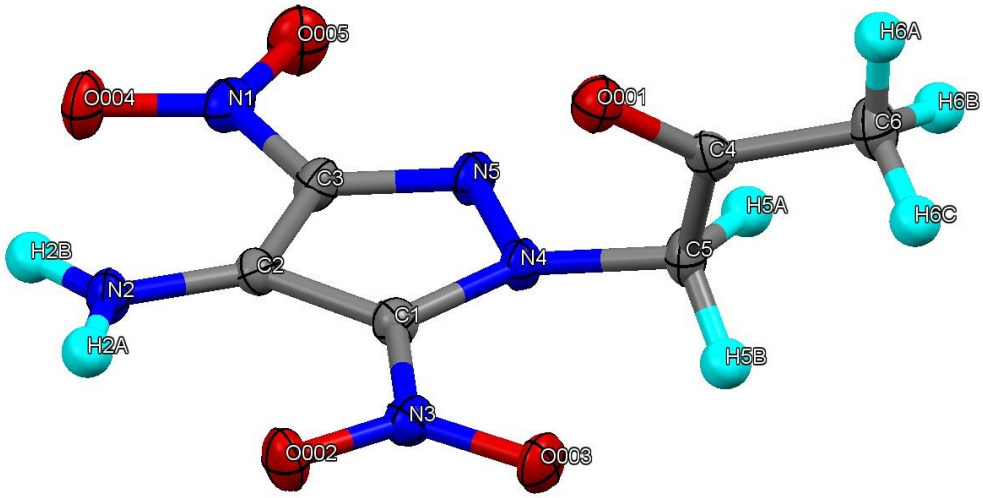


Fig. S5 Crystal structure of **7**.

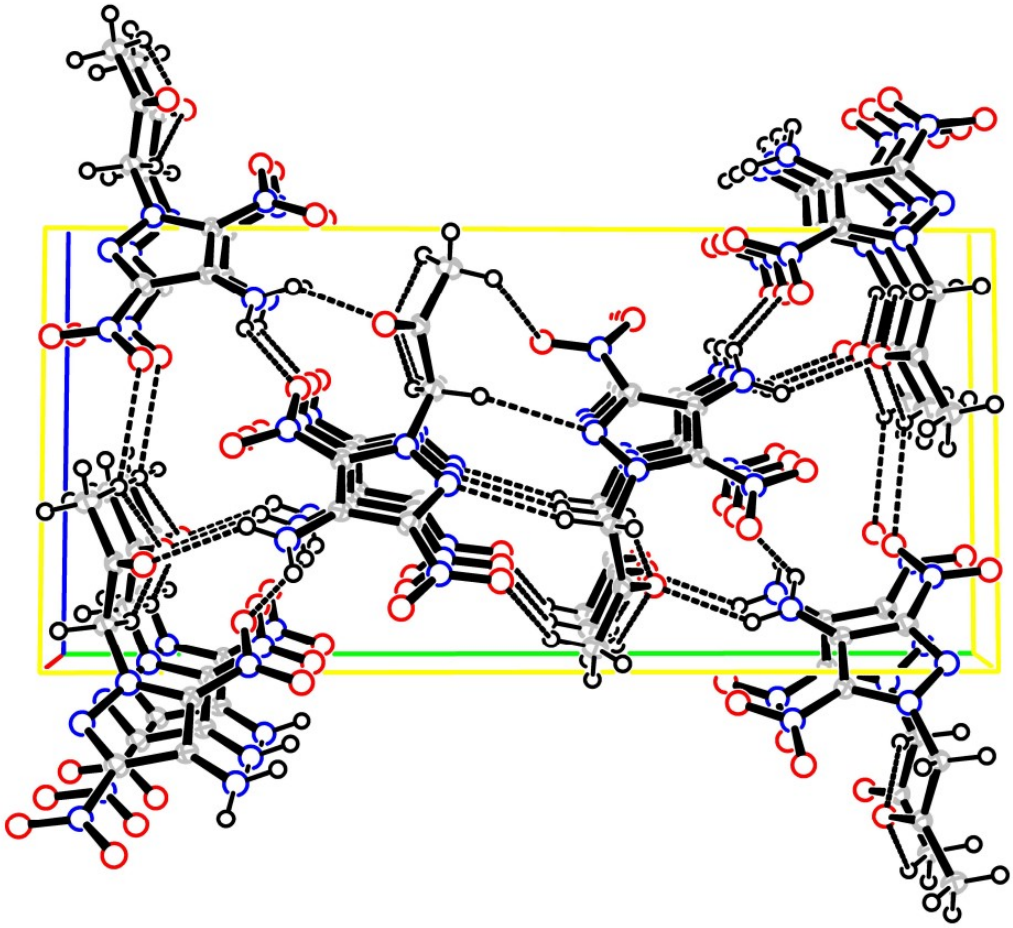


Fig. S6 Packing diagram of **7**.

4. Single-crystal X-ray diffraction analysis of **10**

Table S13. Crystal data, data collection, and refinement for **10**

$C_5H_3N_9O_{12}$	D_x = 1.894 Mg m^{-3}
M_r = 381.16	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, *Pbca*	Cell parameters from 1335 reflections
a = 6.2349 (6) Å	θ = 2.3–24.5°
b = 19.5174 (18) Å	μ = 0.19 mm^{-1}
c = 21.975 (2) Å	T = 150 K
V = 2674.1 (4) Å^3	Needle, colourless
Z = 8	0.12 × 0.04 × 0.02 mm
F(000) = 1536	
D8 VENTURE diffractometer	R_{int} = 0.076
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for	θ_{max} = 26.4°, θ_{min} = 2.1°

absorption correction. wR2(int) was 0.0761 before and 0.0492 after correction. The Ratio of minimum to maximum transmission is 0.5420. The λ/2 correction factor is Not present.	
T_{min} = 0.025, T_{max} = 0.045	h = -7→7
11892 measured reflections	k = -24→22
2702 independent reflections	l = -27→27
1507 reflections with $I > 2\sigma(I)$	
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.061	H-atom parameters constrained
$wR(F^2)$ = 0.162	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 3.7423P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max} < 0.001$
2702 reflections	$\Delta\rangle_{max}$ = 0.29 e Å^{-3}
245 parameters	$\Delta\rangle_{min}$ = -0.35 e Å^{-3}
243 restraints	

Table S14. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **10**

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O5	0.6469 (5)	0.72999 (14)	0.73647 (11)	0.0428 (7)	
O2	0.0352 (5)	0.74432 (15)	0.63050 (13)	0.0498 (8)	
O3	0.2280 (5)	0.76633 (16)	0.51430 (13)	0.0531 (8)	
O1	0.0986 (5)	0.84887 (14)	0.66011 (14)	0.0540 (8)	
N1	0.3717 (5)	0.78050 (14)	0.64072 (13)	0.0333 (7)	
N2	0.1555 (6)	0.79184 (17)	0.64343 (14)	0.0389 (8)	
N6	0.6764 (6)	0.67776 (16)	0.70768 (15)	0.0397 (8)	
N5	0.5862 (6)	0.61270 (15)	0.61551 (14)	0.0398 (8)	
N8	0.6171 (7)	0.51099 (17)	0.68123 (16)	0.0459 (9)	
N4	0.4714 (6)	0.61923 (16)	0.56339 (14)	0.0461 (9)	
N3	0.2663 (7)	0.7053 (2)	0.51542 (15)	0.0507 (10)	
O7	0.4690 (7)	0.53522 (16)	0.70664 (16)	0.0754 (12)	
O11	0.7078 (6)	0.45802 (15)	0.69257 (19)	0.0810 (12)	
O13	0.4862 (8)	0.46906 (17)	0.57489 (15)	0.0815 (13)	
C2	0.4378 (6)	0.71585 (17)	0.62133 (15)	0.0302 (8)	
C3	0.5674 (6)	0.67066 (17)	0.65105 (16)	0.0324 (8)	
O6	0.7944 (7)	0.63154 (16)	0.72303 (19)	0.0921 (15)	

N9	0.6504 (8)	0.50140 (19)	0.57071 (19)	0.0626 (12)	
C1	0.3880 (7)	0.68020 (19)	0.56717 (16)	0.0378 (9)	
O4	0.2166 (8)	0.66493 (19)	0.47614 (15)	0.0973 (16)	
O12	0.7817 (8)	0.5016 (2)	0.53072 (18)	0.0955 (15)	
C4	0.5137 (7)	0.83808 (18)	0.65413 (18)	0.0406 (10)	
H4A	0.473698	0.877398	0.628817	0.061*	
H4B	0.662330	0.825010	0.645375	0.061*	
H4C	0.500495	0.850469	0.697182	0.061*	
O10	1.0503 (6)	0.5153 (2)	0.6438 (2)	0.1064 (16)	
C5	0.6970 (7)	0.55013 (19)	0.6252 (2)	0.0464 (10)	
N7	0.9393 (8)	0.5604 (2)	0.6259 (3)	0.0987 (19)	
O8	1.0231 (14)	0.6134 (4)	0.6340 (6)	0.113 (4)	0.5
O9	0.9716 (11)	0.6117 (4)	0.5798 (4)	0.0596 (18)	0.5

Table S15. Atomic displacement parameters (Å^2) for **10**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O5	0.0457 (19)	0.0482 (16)	0.0344 (14)	0.0030 (14)	-0.0022 (13)	-0.0061 (12)
O2	0.0370 (18)	0.0577 (18)	0.0546 (17)	-0.0106 (15)	0.0029 (14)	-0.0061 (15)
O3	0.053 (2)	0.0565 (19)	0.0494 (17)	0.0050 (16)	-0.0062 (15)	0.0110 (14)
O1	0.049 (2)	0.0430 (16)	0.070 (2)	0.0142 (14)	0.0068 (17)	-0.0012 (15)
N1	0.0289 (18)	0.0298 (15)	0.0410 (17)	0.0000 (13)	-0.0006 (14)	-0.0002 (14)
N2	0.035 (2)	0.0407 (18)	0.0410 (18)	0.0047 (16)	0.0024 (15)	0.0032 (16)
N6	0.035 (2)	0.0357 (17)	0.0487 (19)	-0.0028 (16)	-0.0079 (16)	0.0034 (16)
N5	0.045 (2)	0.0292 (16)	0.0447 (18)	0.0039 (15)	0.0069 (16)	-0.0032 (14)
N8	0.050 (3)	0.0318 (18)	0.056 (2)	-0.0015 (17)	-0.0128 (19)	-0.0017 (16)
N4	0.065 (3)	0.0345 (18)	0.0382 (18)	-0.0052 (17)	0.0054 (18)	-0.0042 (15)
N3	0.061 (3)	0.056 (2)	0.0350 (18)	-0.007 (2)	-0.0052 (18)	0.0021 (17)
O7	0.106 (3)	0.0447 (18)	0.076 (2)	0.015 (2)	0.039 (2)	0.0124 (17)
O11	0.066 (3)	0.0352 (17)	0.142 (3)	0.0023 (17)	-0.032 (2)	0.0204 (19)
O13	0.129 (4)	0.052 (2)	0.064 (2)	-0.042 (2)	0.012 (2)	-0.0149 (17)
C2	0.032 (2)	0.0265 (17)	0.0318 (17)	-0.0034 (16)	0.0029 (16)	0.0033 (15)
C3	0.036 (2)	0.0286 (17)	0.0331 (18)	-0.0026 (17)	0.0023 (16)	0.0002 (15)
O6	0.093 (3)	0.0389 (17)	0.145 (3)	0.0192 (18)	-0.085 (3)	-0.014 (2)
N9	0.083 (4)	0.038 (2)	0.067 (3)	0.002 (2)	0.024 (2)	-0.0083 (19)
C1	0.049 (3)	0.036 (2)	0.0289 (18)	-0.0057 (19)	0.0037 (17)	0.0029 (16)
O4	0.173 (5)	0.067 (2)	0.0517 (19)	-0.013 (3)	-0.046 (3)	-0.0106 (17)
O12	0.118 (4)	0.082 (3)	0.086 (3)	0.032 (3)	0.057 (3)	0.003 (2)
C4	0.043 (3)	0.0300 (19)	0.049 (2)	-0.0065 (18)	0.006 (2)	-0.0037 (18)

O10	0.037 (3)	0.094 (3)	0.188 (5)	0.013 (2)	-0.009 (3)	-0.023 (3)
C5	0.037 (3)	0.0297 (19)	0.073 (3)	-0.0014 (17)	0.008 (2)	-0.0058 (18)
N7	0.044 (3)	0.041 (2)	0.212 (6)	-0.006 (2)	0.036 (3)	-0.029 (3)
O8	0.045 (5)	0.043 (4)	0.251 (12)	-0.017 (3)	0.043 (7)	-0.013 (6)
O9	0.036 (4)	0.047 (4)	0.095 (5)	-0.011 (3)	0.009 (4)	-0.033 (3)

Table S16. Geometric parameters (Å, º) for **10**

O5—N6	1.214 (4)	N4—C1	1.301 (5)
O2—N2	1.226 (4)	N3—C1	1.452 (5)
O3—N3	1.215 (4)	N3—O4	1.209 (4)
O1—N2	1.224 (4)	O13—N9	1.206 (6)
N1—N2	1.367 (5)	C2—C3	1.363 (5)
N1—C2	1.394 (4)	C2—C1	1.413 (5)
N1—C4	1.461 (5)	N9—O12	1.201 (5)
N6—C3	1.425 (5)	N9—C5	1.557 (6)
N6—O6	1.212 (4)	C4—H4A	0.9800
N5—N4	1.356 (5)	C4—H4B	0.9800
N5—C3	1.380 (4)	C4—H4C	0.9800
N5—C5	1.419 (5)	O10—N7	1.188 (6)
N8—O7	1.178 (5)	C5—N7	1.524 (7)
N8—O11	1.205 (4)	N7—O8	1.171 (8)
N8—C5	1.532 (6)	N7—O9	1.440 (10)
N2—N1—C2	116.8 (3)	C2—C3—N5	108.0 (3)
N2—N1—C4	117.7 (3)	O13—N9—C5	114.8 (4)
C2—N1—C4	125.4 (3)	O12—N9—O13	129.5 (5)
O2—N2—N1	118.1 (3)	O12—N9—C5	115.7 (5)
O1—N2—O2	125.4 (4)	N4—C1—N3	117.8 (3)
O1—N2—N1	116.5 (3)	N4—C1—C2	114.6 (4)
O5—N6—C3	117.7 (3)	C2—C1—N3	127.5 (4)
O6—N6—O5	124.9 (3)	N1—C4—H4A	109.5
O6—N6—C3	117.4 (3)	N1—C4—H4B	109.5
N4—N5—C3	110.9 (3)	N1—C4—H4C	109.5
N4—N5—C5	117.7 (3)	H4A—C4—H4B	109.5
C3—N5—C5	131.4 (4)	H4A—C4—H4C	109.5
O7—N8—O11	127.9 (4)	H4B—C4—H4C	109.5
O7—N8—C5	115.8 (3)	N5—C5—N8	113.1 (3)
O11—N8—C5	116.2 (4)	N5—C5—N9	108.6 (4)

C1—N4—N5	104.1 (3)	N5—C5—N7	111.8 (4)
O3—N3—C1	116.7 (3)	N8—C5—N9	104.7 (3)
O4—N3—O3	125.0 (4)	N7—C5—N8	112.3 (4)
O4—N3—C1	118.3 (4)	N7—C5—N9	105.8 (4)
N1—C2—C1	129.6 (3)	O10—N7—C5	118.9 (4)
C3—C2—N1	127.9 (3)	O10—N7—O9	131.9 (6)
C3—C2—C1	102.4 (3)	O8—N7—O10	110.1 (8)
N5—C3—N6	122.3 (3)	O8—N7—C5	124.0 (6)
C2—C3—N6	129.7 (3)	O9—N7—C5	102.9 (5)

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

Table S17. Crystal data, data collection, and refinement for **11**

$C_4ClN_7O_{10}$	$F(000) = 1360$
$M_r = 341.56$	$D_x = 1.960$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.840$ (2) Å	Cell parameters from 1257 reflections
$b = 12.1903$ (18) Å	$\theta = 2.3$–$20.7°$
$c = 14.668$ (2) Å	$\mu = 0.41$ mm^{-1}
$\beta = 110.697$ (4)°	$T = 173$ K
$V = 2315.0$ (6) Å^3	Block, colourless
$Z = 8$	0.19 × 0.12 × 0.11 mm
Bruker APEX-II CCD diffractometer	2876 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.086$
Absorption correction: multi-scan *SADABS2014*/5 (Bruker,2014/5) was used for absorption correction. wR2(int) was 0.0802 before and 0.0615 after correction. The Ratio of minimum to maximum transmission is 0.8994. The $\lambda/2$ correction factor is 0.00150.	$\theta_{max} = 27.6°$, $\theta_{min} = 1.7°$
$T_{min} = 0.671$, $T_{max} = 0.746$	$h = -17 \rightarrow 17$
18474 measured reflections	$k = -15 \rightarrow 15$
5239 independent reflections	$l = -17 \rightarrow 19$
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.128$	$\Delta\rangle_{max} = 0.36$ e Å^{-3}
$S = 0.97$	$\Delta\rangle_{min} = -0.37$ e Å^{-3}

5239 reflections	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
407 parameters	Extinction coefficient: 0.0104 (7)
404 restraints	

Table S18. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **11**

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl2	0.08822 (7)	0.01271 (7)	0.21187 (7)	0.0477 (3)	
Cl1	0.86231 (7)	0.30632 (9)	0.41845 (7)	0.0593 (3)	
O2	0.51624 (17)	0.29532 (17)	0.35240 (16)	0.0387 (6)	
O8	0.49814 (18)	0.01713 (18)	0.10809 (17)	0.0430 (6)	
O10	0.50027 (19)	0.26307 (19)	0.15544 (17)	0.0475 (6)	
N3	0.61700 (18)	0.13462 (18)	0.29261 (17)	0.0252 (6)	
O14	0.39455 (19)	0.41944 (19)	0.47961 (17)	0.0456 (6)	
N14	0.22321 (18)	0.29075 (19)	0.31618 (17)	0.0273 (6)	
N13	0.23157 (18)	0.23489 (19)	0.39884 (17)	0.0261 (6)	
O7	0.49060 (19)	-0.08216 (18)	0.22929 (18)	0.0507 (7)	
N2	0.68612 (19)	0.06253 (19)	0.28299 (17)	0.0285 (6)	
N4	0.6071 (2)	0.3134 (2)	0.36601 (19)	0.0338 (6)	
O1	0.6530 (2)	0.39731 (19)	0.39887 (18)	0.0528 (7)	
N6	0.49844 (19)	0.0028 (2)	0.1900 (2)	0.0333 (6)	
O12	0.11778 (19)	0.1928 (2)	0.08177 (16)	0.0540 (7)	
O5	0.5310 (2)	0.0615 (2)	0.41134 (19)	0.0543 (7)	
O11	0.1770 (2)	0.3534 (2)	0.13483 (17)	0.0580 (7)	
O13	0.2356 (2)	0.47398 (19)	0.4400 (2)	0.0612 (8)	
N5	0.4493 (2)	0.1966 (2)	0.17914 (19)	0.0330 (6)	
O9	0.35652 (18)	0.1874 (2)	0.1491 (2)	0.0605 (8)	
O21	0.1544 (2)	-0.03521 (19)	0.42676 (19)	0.0573 (7)	
N8	0.3054 (2)	0.4081 (2)	0.46758 (19)	0.0359 (7)	
N10	0.3720 (2)	0.2379 (2)	0.5579 (2)	0.0384 (7)	
O19	0.1044 (2)	0.2835 (2)	0.4884 (2)	0.0604 (8)	
N11	0.1547 (2)	0.2600 (2)	0.14612 (19)	0.0365 (7)	
N7	0.4669 (2)	0.0812 (2)	0.3329 (2)	0.0386 (7)	
O20	0.2247 (2)	0.0886 (2)	0.53581 (18)	0.0629 (8)	
O6	0.37449 (19)	0.0787 (2)	0.3097 (2)	0.0649 (8)	
O15	0.4028 (2)	0.2712 (2)	0.64054 (18)	0.0638 (8)	
N12	0.1888 (2)	0.0555 (2)	0.4517 (2)	0.0397 (7)	

O16	0.4133 (2)	0.1741 (2)	0.5221 (2)	0.0668 (8)	
O4	0.8588 (2)	-0.0386 (3)	0.2946 (2)	0.0719 (9)	
N9	0.1900 (2)	0.3095 (3)	0.5349 (2)	0.0489 (8)	
C3	0.6646 (2)	0.2272 (2)	0.3416 (2)	0.0270 (7)	
C7	0.1746 (2)	0.2224 (2)	0.2457 (2)	0.0263 (7)	
C5	0.1877 (2)	0.1323 (2)	0.3768 (2)	0.0283 (7)	
N1	0.8686 (2)	0.0532 (3)	0.3267 (2)	0.0502 (8)	
C1	0.7759 (2)	0.1105 (3)	0.3252 (2)	0.0320 (7)	
C6	0.1493 (2)	0.1206 (2)	0.2778 (2)	0.0286 (7)	
C4	0.5104 (2)	0.1079 (2)	0.2517 (2)	0.0254 (6)	
C8	0.2724 (2)	0.2915 (2)	0.4886 (2)	0.0297 (7)	
C2	0.7684 (2)	0.2151 (3)	0.3623 (2)	0.0329 (7)	
O3	0.9493 (2)	0.1026 (3)	0.3610 (3)	0.0914 (11)	
O17	0.2183 (5)	0.3727 (4)	0.6054 (4)	0.0684 (16)	0.67
O18	0.2214 (10)	0.3091 (9)	0.6267 (7)	0.063 (3)	0.33

Table S19. Atomic displacement parameters (Å^2) for **11**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl2	0.0472 (6)	0.0446 (5)	0.0494 (6)	-0.0146 (4)	0.0149 (5)	-0.0229 (4)
Cl1	0.0356 (5)	0.0803 (7)	0.0527 (7)	-0.0233 (5)	0.0041 (5)	-0.0105 (5)
O2	0.0349 (14)	0.0365 (13)	0.0434 (15)	0.0057 (10)	0.0121 (12)	-0.0049 (10)
O8	0.0479 (15)	0.0427 (13)	0.0369 (14)	-0.0005 (11)	0.0130 (13)	-0.0111 (11)
O10	0.0496 (16)	0.0395 (13)	0.0418 (15)	-0.0055 (12)	0.0016 (13)	0.0132 (11)
N3	0.0219 (13)	0.0248 (13)	0.0287 (14)	0.0036 (10)	0.0087 (12)	-0.0007 (10)
O14	0.0409 (15)	0.0514 (15)	0.0439 (15)	-0.0070 (12)	0.0141 (13)	0.0018 (11)
N14	0.0250 (14)	0.0299 (14)	0.0238 (14)	0.0018 (11)	0.0045 (12)	0.0005 (10)
N13	0.0263 (14)	0.0285 (13)	0.0222 (14)	0.0003 (11)	0.0069 (12)	-0.0028 (10)
O7	0.0633 (17)	0.0268 (12)	0.0642 (17)	-0.0037 (11)	0.0253 (15)	-0.0009 (11)
N2	0.0272 (14)	0.0333 (14)	0.0278 (15)	0.0115 (11)	0.0131 (13)	0.0059 (11)
N4	0.0446 (18)	0.0255 (14)	0.0304 (16)	0.0002 (13)	0.0120 (15)	-0.0009 (11)
O1	0.0627 (17)	0.0371 (14)	0.0572 (17)	-0.0139 (12)	0.0193 (14)	-0.0190 (12)
N6	0.0270 (15)	0.0266 (14)	0.0443 (18)	-0.0012 (11)	0.0100 (14)	-0.0026 (12)
O12	0.0571 (17)	0.0721 (18)	0.0250 (14)	-0.0031 (14)	0.0047 (13)	-0.0155 (12)
O5	0.0580 (18)	0.0660 (17)	0.0436 (16)	0.0038 (14)	0.0238 (15)	0.0132 (13)
O11	0.074 (2)	0.0603 (17)	0.0341 (15)	-0.0079 (15)	0.0121 (14)	0.0099 (12)
O13	0.0478 (16)	0.0352 (14)	0.0722 (19)	0.0124 (12)	-0.0141 (15)	-0.0110 (13)
N5	0.0284 (16)	0.0315 (14)	0.0323 (16)	0.0052 (12)	0.0024 (13)	-0.0038 (12)
O9	0.0242 (14)	0.0756 (19)	0.0688 (19)	0.0116 (13)	0.0005 (14)	0.0070 (15)

O21	0.0685 (19)	0.0337 (14)	0.0707 (19)	-0.0103 (13)	0.0258 (16)	0.0025 (12)
N8	0.0386 (18)	0.0328 (15)	0.0255 (15)	0.0009 (13)	-0.0019 (14)	-0.0079 (12)
N10	0.0402 (18)	0.0386 (16)	0.0280 (16)	-0.0019 (13)	0.0016 (14)	0.0027 (13)
O19	0.0335 (15)	0.090 (2)	0.0601 (19)	-0.0116 (14)	0.0196 (15)	-0.0223 (15)
N11	0.0260 (15)	0.0539 (18)	0.0264 (16)	0.0037 (13)	0.0054 (13)	-0.0028 (14)
N7	0.0394 (19)	0.0333 (15)	0.051 (2)	-0.0014 (13)	0.0253 (17)	-0.0015 (13)
O20	0.090 (2)	0.0578 (17)	0.0328 (15)	-0.0143 (15)	0.0112 (15)	0.0081 (12)
O6	0.0356 (15)	0.083 (2)	0.090 (2)	-0.0015 (14)	0.0384 (16)	0.0096 (16)
O15	0.068 (2)	0.0742 (19)	0.0278 (15)	0.0086 (15)	-0.0090 (14)	0.0014 (13)
N12	0.0410 (18)	0.0346 (15)	0.0436 (18)	0.0017 (14)	0.0151 (16)	0.0052 (13)
O16	0.0528 (18)	0.0664 (18)	0.0656 (19)	0.0288 (14)	0.0015 (15)	-0.0148 (15)
O4	0.0539 (19)	0.083 (2)	0.082 (2)	0.0318 (16)	0.0284 (17)	-0.0053 (17)
N9	0.0374 (19)	0.079 (2)	0.0340 (18)	0.0010 (17)	0.0168 (16)	-0.0177 (16)
C3	0.0252 (16)	0.0318 (16)	0.0207 (16)	-0.0014 (13)	0.0040 (14)	0.0006 (12)
C7	0.0207 (16)	0.0350 (17)	0.0203 (16)	0.0028 (13)	0.0038 (14)	-0.0058 (12)
C5	0.0235 (17)	0.0312 (16)	0.0305 (18)	-0.0012 (13)	0.0097 (15)	-0.0019 (13)
N1	0.0335 (19)	0.075 (2)	0.044 (2)	0.0179 (17)	0.0160 (16)	0.0069 (17)
C1	0.0220 (17)	0.0488 (19)	0.0255 (18)	0.0061 (14)	0.0089 (15)	0.0092 (14)
C6	0.0196 (16)	0.0344 (16)	0.0324 (18)	-0.0007 (13)	0.0098 (15)	-0.0105 (13)
C4	0.0237 (16)	0.0230 (14)	0.0305 (17)	0.0010 (12)	0.0109 (14)	-0.0006 (12)
C8	0.0270 (17)	0.0369 (17)	0.0218 (16)	0.0009 (13)	0.0044 (14)	-0.0054 (13)
C2	0.0249 (17)	0.0464 (19)	0.0242 (18)	-0.0055 (14)	0.0047 (15)	0.0055 (14)
O3	0.0234 (16)	0.126 (3)	0.119 (3)	0.0045 (17)	0.0176 (19)	-0.017 (2)
O17	0.073 (3)	0.091 (4)	0.048 (3)	-0.010 (3)	0.030 (3)	-0.039 (3)
O18	0.064 (6)	0.087 (7)	0.038 (4)	-0.004 (6)	0.019 (4)	-0.021 (5)

Table S20. Geometric parameters (Å, º) for **11**

Cl2—C6	1.673 (3)	N5—C4	1.543 (4)
Cl1—C2	1.687 (3)	O21—N12	1.209 (3)
O2—N4	1.221 (3)	N8—C8	1.557 (4)
O8—N6	1.213 (3)	N10—O15	1.204 (3)
O10—N5	1.204 (3)	N10—O16	1.192 (3)
N3—N2	1.343 (3)	N10—C8	1.540 (4)
N3—C3	1.375 (4)	O19—N9	1.182 (3)
N3—C4	1.420 (4)	N11—C7	1.461 (4)
O14—N8	1.191 (3)	N7—O6	1.202 (3)
N14—N13	1.359 (3)	N7—C4	1.548 (4)
N14—C7	1.313 (3)	O20—N12	1.224 (3)

N13—C5	1.378 (4)	N12—C5	1.439 (4)
N13—C8	1.415 (4)	O4—N1	1.203 (4)
O7—N6	1.208 (3)	N9—C8	1.535 (4)
N2—C1	1.313 (4)	N9—O17	1.238 (5)
N4—O1	1.211 (3)	N9—O18	1.260 (9)
N4—C3	1.437 (4)	C3—C2	1.368 (4)
N6—C4	1.543 (4)	C7—C6	1.415 (4)
O12—N11	1.218 (3)	C5—C6	1.366 (4)
O5—N7	1.203 (3)	N1—C1	1.454 (4)
O11—N11	1.206 (3)	N1—O3	1.211 (4)
O13—N8	1.210 (3)	C1—C2	1.405 (4)
N5—O9	1.206 (3)		
N2—N3—C3	111.4 (2)	O17—N9—C8	113.1 (4)
N2—N3—C4	118.5 (2)	O18—N9—C8	116.2 (6)
C3—N3—C4	130.0 (2)	N3—C3—N4	121.7 (3)
C7—N14—N13	104.1 (2)	C2—C3—N3	107.4 (3)
N14—N13—C5	110.7 (2)	C2—C3—N4	130.9 (3)
N14—N13—C8	117.7 (2)	N14—C7—N11	116.8 (3)
C5—N13—C8	131.2 (2)	N14—C7—C6	114.4 (3)
C1—N2—N3	104.5 (2)	C6—C7—N11	128.8 (3)
O2—N4—C3	117.1 (2)	N13—C5—N12	121.7 (3)
O1—N4—O2	125.7 (3)	C6—C5—N13	108.5 (3)
O1—N4—C3	117.2 (3)	C6—C5—N12	129.7 (3)
O8—N6—C4	115.0 (2)	O4—N1—C1	117.7 (3)
O7—N6—O8	128.8 (3)	O4—N1—O3	125.8 (3)
O7—N6—C4	116.1 (3)	O3—N1—C1	116.5 (3)
O10—N5—O9	127.8 (3)	N2—C1—N1	118.4 (3)
O10—N5—C4	115.9 (2)	N2—C1—C2	113.6 (3)
O9—N5—C4	116.2 (3)	C2—C1—N1	128.0 (3)
O14—N8—O13	129.4 (3)	C7—C6—Cl2	129.2 (2)
O14—N8—C8	116.0 (3)	C5—C6—Cl2	128.6 (2)
O13—N8—C8	114.6 (3)	C5—C6—C7	102.3 (2)
O15—N10—C8	116.0 (3)	N3—C4—N6	108.6 (2)
O16—N10—O15	127.5 (3)	N3—C4—N5	111.4 (2)
O16—N10—C8	116.3 (3)	N3—C4—N7	110.6 (2)
O12—N11—C7	116.3 (3)	N6—C4—N5	105.0 (2)
O11—N11—O12	125.9 (3)	N6—C4—N7	106.7 (2)
O11—N11—C7	117.8 (3)	N5—C4—N7	114.2 (2)

O5—N7—C4	115.0 (3)	N13—C8—N8	108.1 (2)
O6—N7—O5	128.1 (3)	N13—C8—N10	112.1 (2)
O6—N7—C4	116.8 (3)	N13—C8—N9	111.5 (3)
O21—N12—O20	125.6 (3)	N10—C8—N8	105.1 (2)
O21—N12—C5	117.9 (3)	N9—C8—N8	105.9 (2)
O20—N12—C5	116.6 (3)	N9—C8—N10	113.6 (2)
O19—N9—C8	117.1 (3)	C3—C2—Cl1	127.2 (3)
O19—N9—O17	127.3 (4)	C3—C2—C1	103.1 (3)
O19—N9—O18	120.9 (6)	C1—C2—Cl1	129.6 (2)

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

Table S21. Crystal data, data collection, and refinement for **12**

$C_4N_8O_9$	$F(000) = 608$
$M_r = 304.12$	$D_x = 1.927$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.4799$ (7) Å	Cell parameters from 2752 reflections
$b = 11.5935$ (9) Å	$\theta = 2.6–26.2°$
$c = 10.6812$ (8) Å	$\mu = 0.19$ mm^{-1}
$\beta = 93.431$ (3)°	$T = 170$ K
$V = 1048.20$ (14) Å^3	Block, colourless
$Z = 4$	0.12 × 0.05 × 0.03 mm
Bruker D8 VENTURE diffractometer	1543 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.050$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1080 before and 0.0517 after correction. The Ratio of minimum to maximum transmission is 0.9018. The $\lambda/2$ correction factor is Not present.	$\theta_{max} = 26.5°$, $\theta_{min} = 2.6°$
$T_{min} = 0.672$, $T_{max} = 0.745$	$h = -10\rightarrow10$
10845 measured reflections	$k = -14\rightarrow14$
2151 independent reflections	$l = -13\rightarrow13$
Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.8993P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.10$	$\Delta\rangle_{max} = 0.27$ e Å^{-3}

2151 reflections	$\Delta\rangle_{min}$ = -0.27 e Å^{-3}
190 parameters	

Table S22. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **12**

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.4398 (2)	0.44469 (15)	0.87363 (17)	0.0292 (4)
O2	0.8403 (2)	0.77159 (17)	0.7634 (2)	0.0385 (5)
O4	0.3848 (2)	0.36316 (17)	0.6030 (2)	0.0398 (5)
O6	0.1480 (3)	0.60227 (18)	0.8350 (2)	0.0413 (5)
N5	0.4056 (2)	0.57484 (18)	0.7073 (2)	0.0259 (5)
N2	0.7429 (3)	0.59210 (18)	0.9125 (2)	0.0250 (5)
N4	0.4780 (3)	0.66981 (18)	0.6561 (2)	0.0253 (5)
O9	0.2807 (3)	0.5341 (2)	0.4368 (2)	0.0457 (6)
O1	0.6730 (3)	0.84826 (19)	0.6267 (2)	0.0516 (6)
O8	0.1667 (3)	0.6809 (2)	0.5210 (2)	0.0518 (6)
N1	0.7138 (3)	0.77478 (19)	0.7029 (2)	0.0286 (5)
O7	-0.0101 (2)	0.5510 (2)	0.6771 (2)	0.0549 (7)
N6	0.2644 (3)	0.40139 (19)	0.6404 (2)	0.0308 (5)
N8	0.2316 (3)	0.5882 (2)	0.5231 (2)	0.0336 (6)
N7	0.1192 (3)	0.5662 (2)	0.7300 (2)	0.0342 (6)
N3	0.8416 (3)	0.5847 (2)	0.9848 (2)	0.0326 (6)
O5	0.1479 (3)	0.34990 (19)	0.6678 (3)	0.0566 (7)
C1	0.6048 (3)	0.6822 (2)	0.7271 (2)	0.0234 (6)
C2	0.6230 (3)	0.6002 (2)	0.8252 (2)	0.0234 (6)
C3	0.4866 (3)	0.5256 (2)	0.8162 (2)	0.0243 (6)
C4	0.2620 (3)	0.5356 (2)	0.6547 (2)	0.0251 (6)

Table S23. Atomic displacement parameters (Å^2) for **12**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0298 (10)	0.0276 (10)	0.0305 (10)	-0.0050 (8)	0.0047 (8)	0.0043 (8)
O2	0.0277 (11)	0.0415 (12)	0.0461 (13)	-0.0095 (9)	-0.0010 (10)	0.0041 (10)
O4	0.0372 (12)	0.0345 (11)	0.0482 (13)	0.0052 (10)	0.0085 (10)	-0.0058 (9)
O6	0.0455 (13)	0.0409 (12)	0.0387 (13)	0.0058 (10)	0.0119 (10)	-0.0054 (10)
N5	0.0242 (12)	0.0263 (11)	0.0270 (12)	-0.0069 (9)	0.0000 (9)	0.0029 (9)
N2	0.0247 (12)	0.0228 (11)	0.0279 (12)	-0.0025 (10)	0.0051 (10)	-0.0015 (10)
N4	0.0257 (12)	0.0225 (11)	0.0281 (12)	-0.0051 (9)	0.0044 (10)	0.0022 (9)

O9	0.0550 (14)	0.0512 (14)	0.0305 (12)	-0.0098 (11)	-0.0007 (10)	-0.0014 (10)
O1	0.0484 (14)	0.0417 (12)	0.0626 (15)	-0.0177 (11)	-0.0127 (12)	0.0267 (12)
O8	0.0486 (14)	0.0418 (13)	0.0635 (16)	0.0060 (11)	-0.0089 (12)	0.0149 (11)
N1	0.0259 (13)	0.0260 (12)	0.0341 (13)	-0.0057 (10)	0.0037 (10)	0.0000 (10)
O7	0.0233 (11)	0.0613 (16)	0.0802 (18)	-0.0042 (11)	0.0031 (12)	-0.0163 (13)
N6	0.0310 (13)	0.0278 (12)	0.0337 (13)	-0.0048 (11)	0.0040 (10)	-0.0014 (10)
N8	0.0290 (13)	0.0334 (13)	0.0373 (14)	-0.0074 (11)	-0.0068 (11)	0.0072 (11)
N7	0.0272 (13)	0.0287 (13)	0.0475 (16)	-0.0018 (10)	0.0089 (12)	-0.0040 (11)
N3	0.0269 (13)	0.0350 (13)	0.0355 (14)	-0.0041 (11)	-0.0017 (11)	0.0044 (11)
O5	0.0447 (13)	0.0365 (12)	0.0906 (19)	-0.0172 (11)	0.0209 (13)	-0.0051 (12)
C1	0.0244 (13)	0.0217 (13)	0.0244 (13)	-0.0035 (11)	0.0048 (11)	-0.0022 (10)
C2	0.0212 (13)	0.0244 (13)	0.0246 (13)	-0.0006 (11)	0.0011 (11)	-0.0010 (11)
C3	0.0255 (14)	0.0234 (13)	0.0242 (14)	-0.0009 (11)	0.0029 (11)	-0.0010 (11)
C4	0.0221 (13)	0.0246 (13)	0.0285 (14)	-0.0008 (11)	0.0012 (11)	0.0009 (11)

Table S24. Geometric parameters (Å, º) for **12**

O3—C3	1.201 (3)	O1—N1	1.214 (3)
O2—N1	1.219 (3)	O8—N8	1.206 (3)
O4—N6	1.203 (3)	N1—C1	1.450 (3)
O6—N7	1.208 (3)	O7—N7	1.216 (3)
N5—N4	1.389 (3)	N6—O5	1.205 (3)
N5—C3	1.433 (3)	N6—C4	1.563 (3)
N5—C4	1.387 (3)	N8—C4	1.540 (4)
N2—N3	1.108 (3)	N7—C4	1.535 (3)
N2—C2	1.341 (3)	C1—C2	1.417 (4)
N4—C1	1.287 (3)	C2—C3	1.443 (4)
O9—N8	1.209 (3)		
N4—N5—C3	115.7 (2)	O7—N7—C4	116.2 (2)
C4—N5—N4	119.9 (2)	N4—C1—N1	119.8 (2)
C4—N5—C3	124.4 (2)	N4—C1—C2	114.3 (2)
N3—N2—C2	179.5 (3)	C2—C1—N1	125.9 (2)
C1—N4—N5	103.3 (2)	N2—C2—C1	127.3 (2)
O2—N1—C1	115.6 (2)	N2—C2—C3	125.2 (2)
O1—N1—O2	125.7 (2)	C1—C2—C3	107.5 (2)
O1—N1—C1	118.6 (2)	O3—C3—N5	124.7 (2)
O4—N6—O5	128.5 (3)	O3—C3—C2	136.2 (3)
O4—N6—C4	114.5 (2)	N5—C3—C2	99.2 (2)

O5—N6—C4	117.0 (2)	N5—C4—N6	110.5 (2)
O9—N8—C4	116.4 (2)	N5—C4—N8	109.6 (2)
O8—N8—O9	128.7 (3)	N5—C4—N7	114.4 (2)
O8—N8—C4	114.9 (2)	N8—C4—N6	107.9 (2)
O6—N7—O7	127.4 (3)	N7—C4—N6	107.2 (2)
O6—N7—C4	116.4 (2)	N7—C4—N8	107.0 (2)

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

Table S25. Crystal data, data collection, and refinement for **13**

$C_4H_2N_8O_{10}$	$F(000) = 1296$
$M_r = 322.14$	$D_x = 1.895$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.6313$ (15) Å	Cell parameters from 4207 reflections
$b = 9.2702$ (8) Å	$\theta = 2.6–23.7°$
$c = 15.7637$ (14) Å	$\mu = 0.19$ mm^{-1}
$\beta = 98.696$ (3)°	$T = 193$ K
$V = 2258.0$ (4) Å^3	Block
$Z = 8$	0.12 × 0.11 × 0.1 mm
Bruker D8 VENTURE dual wavelength Mo/Cu diffractometer	5126 independent reflections
Radiation source: microfocus sealed X-ray tube, Incoatec Iμs DIAMOND	3391 reflections with $I > 2\sigma(I)$
Helios Multi-layer Optic monochromator	$R_{int} = 0.105$
Detector resolution: 7.41 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$
ω and ϕ scans	$h = -19 \rightarrow 20$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1199 before and 0.0845 after correction. The Ratio of minimum to maximum transmission is 0.8851. The λ/2 correction factor is Not present.	$k = -12 \rightarrow 10$
$T_{min} = 0.660$, $T_{max} = 0.746$	$l = -20 \rightarrow 20$
25214 measured reflections	
Refinement on F^2	Primary atom site location: dual
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H-atom parameters constrained
$wR(F^2) = 0.195$	$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 3.0392P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$

5126 reflections	$\Delta\rangle_{max}$ = 0.50 e Å^{-3}
398 parameters	$\Delta\rangle_{min}$ = -0.29 e Å^{-3}
0 restraints	

Table S26. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **13**

	x	*y*	*z*	U_{iso}*/U_{eq}
O20	0.73532 (17)	0.1582 (3)	0.24100 (19)	0.0344 (7)
O10	0.7421 (2)	0.6145 (3)	0.73330 (18)	0.0384 (7)
O9	0.7507 (2)	0.3906 (3)	0.69231 (19)	0.0397 (7)
N7	0.7620 (2)	0.5225 (3)	0.6836 (2)	0.0281 (7)
O2	0.9017 (2)	0.7579 (4)	0.39036 (19)	0.0463 (8)
O1	0.8759 (2)	0.9203 (3)	0.4844 (2)	0.0469 (8)
N3	0.8257 (2)	0.4757 (3)	0.55333 (19)	0.0265 (7)
O18	0.6395 (2)	-0.3233 (3)	0.3955 (2)	0.0453 (8)
N10	0.6867 (2)	0.0674 (3)	0.2641 (2)	0.0280 (7)
O6	0.67627 (19)	0.3490 (4)	0.5106 (2)	0.0437 (8)
O12	0.39446 (19)	0.3053 (4)	0.4085 (2)	0.0449 (8)
N15	0.49449 (19)	0.0961 (4)	0.3622 (2)	0.0268 (7)
N11	0.6344 (2)	-0.1937 (4)	0.3907 (2)	0.0291 (7)
O13	0.41067 (19)	-0.2022 (4)	0.3230 (2)	0.0488 (8)
O19	0.6954 (2)	-0.0642 (3)	0.2555 (2)	0.0440 (8)
O16	0.5145 (2)	-0.1128 (4)	0.1844 (2)	0.0504 (9)
O14	0.4866 (2)	-0.1826 (4)	0.4495 (2)	0.0469 (8)
N14	0.55675 (18)	0.0221 (3)	0.33035 (19)	0.0259 (7)
O7	0.8876 (2)	0.1292 (4)	0.6336 (2)	0.0512 (9)
O8	0.9252 (2)	0.3430 (4)	0.6764 (2)	0.0501 (8)
O4	0.8147 (2)	0.2453 (4)	0.40867 (19)	0.0489 (9)
N2	0.8564 (2)	0.5500 (4)	0.4906 (2)	0.0283 (7)
N6	0.8847 (2)	0.2574 (4)	0.6292 (2)	0.0316 (7)
N13	0.4754 (2)	-0.1780 (4)	0.3725 (2)	0.0315 (7)
O15	0.5546 (2)	-0.3231 (3)	0.2345 (2)	0.0466 (8)
N9	0.6301 (2)	0.3790 (3)	0.3015 (2)	0.0308 (7)
H9A	0.677746	0.378384	0.278075	0.037*
H9B	0.607318	0.461483	0.314371	0.037*
O3	0.94303 (19)	0.2656 (4)	0.4821 (2)	0.0477 (8)
O11	0.4829 (2)	0.4670 (4)	0.3723 (3)	0.0577 (10)
O5	0.7236 (2)	0.1361 (4)	0.5527 (2)	0.0512 (9)

O17	0.6826 (2)	-0.1086 (4)	0.4304 (2)	0.0552 (9)
N16	0.4598 (2)	0.3419 (4)	0.3812 (2)	0.0338 (8)
N5	0.7324 (2)	0.2622 (4)	0.5386 (2)	0.0325 (7)
N8	0.8022 (2)	0.8329 (4)	0.6291 (2)	0.0369 (8)
H8A	0.780179	0.831589	0.677318	0.044*
H8B	0.815343	0.915631	0.606970	0.044*
N4	0.8652 (2)	0.2729 (4)	0.4715 (2)	0.0320 (8)
N12	0.5416 (2)	-0.1959 (4)	0.2409 (2)	0.0317 (7)
N1	0.8783 (2)	0.7961 (4)	0.4576 (2)	0.0368 (8)
C6	0.5928 (2)	0.2562 (4)	0.3174 (2)	0.0233 (7)
C3	0.7993 (2)	0.5697 (4)	0.6139 (2)	0.0276 (8)
C5	0.6171 (2)	0.1161 (4)	0.3027 (2)	0.0246 (7)
C1	0.8501 (2)	0.6860 (4)	0.5121 (2)	0.0286 (8)
C4	0.8256 (2)	0.3246 (4)	0.5507 (2)	0.0277 (8)
C2	0.8154 (2)	0.7104 (4)	0.5900 (2)	0.0273 (8)
C7	0.5154 (2)	0.2322 (4)	0.3550 (2)	0.0260 (8)
C8	0.5547 (2)	-0.1294 (4)	0.3322 (2)	0.0262 (8)

Table S27. Atomic displacement parameters (Å^2) for **13**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O20	0.0347 (15)	0.0281 (16)	0.0443 (16)	-0.0045 (11)	0.0183 (12)	-0.0031 (12)
O10	0.0589 (18)	0.0274 (16)	0.0339 (15)	-0.0009 (13)	0.0229 (13)	-0.0058 (12)
O9	0.0638 (19)	0.0227 (15)	0.0379 (16)	-0.0097 (13)	0.0248 (14)	0.0004 (12)
N7	0.0389 (17)	0.0202 (17)	0.0276 (16)	-0.0030 (13)	0.0130 (13)	-0.0008 (13)
O2	0.0572 (19)	0.057 (2)	0.0286 (15)	-0.0101 (16)	0.0179 (13)	0.0074 (15)
O1	0.061 (2)	0.0255 (17)	0.058 (2)	-0.0062 (14)	0.0224 (16)	0.0063 (15)
N3	0.0363 (16)	0.0194 (16)	0.0262 (16)	-0.0027 (12)	0.0129 (12)	0.0021 (12)
O18	0.059 (2)	0.0246 (17)	0.0510 (19)	0.0078 (14)	0.0037 (15)	0.0031 (14)
N10	0.0287 (15)	0.0236 (17)	0.0346 (17)	0.0001 (12)	0.0143 (13)	-0.0022 (13)
O6	0.0375 (16)	0.0428 (19)	0.0507 (19)	0.0013 (13)	0.0060 (13)	0.0025 (15)
O12	0.0386 (16)	0.047 (2)	0.055 (2)	0.0141 (14)	0.0259 (14)	0.0064 (16)
N15	0.0283 (15)	0.0274 (17)	0.0266 (16)	0.0034 (12)	0.0107 (12)	0.0004 (13)
N11	0.0283 (16)	0.0290 (19)	0.0301 (17)	-0.0013 (13)	0.0045 (12)	0.0006 (14)
O13	0.0345 (16)	0.063 (2)	0.0496 (19)	-0.0142 (15)	0.0087 (14)	-0.0106 (17)
O19	0.0479 (17)	0.0236 (16)	0.069 (2)	0.0025 (13)	0.0345 (16)	-0.0065 (14)
O16	0.079 (2)	0.038 (2)	0.0320 (17)	0.0165 (17)	0.0024 (15)	0.0002 (14)
O14	0.0485 (18)	0.061 (2)	0.0352 (17)	0.0036 (15)	0.0187 (14)	0.0123 (15)
N14	0.0274 (15)	0.0216 (16)	0.0314 (17)	0.0017 (12)	0.0134 (12)	0.0009 (13)

O7	0.067 (2)	0.0233 (17)	0.061 (2)	0.0034 (14)	0.0031 (17)	0.0105 (15)
O8	0.059 (2)	0.039 (2)	0.0456 (19)	0.0008 (15)	-0.0120 (15)	-0.0079 (15)
O4	0.0514 (18)	0.068 (2)	0.0259 (15)	0.0060 (16)	0.0030 (13)	-0.0127 (15)
N2	0.0331 (16)	0.0284 (18)	0.0247 (15)	-0.0002 (13)	0.0091 (12)	0.0038 (14)
N6	0.0373 (18)	0.032 (2)	0.0256 (16)	-0.0017 (14)	0.0068 (13)	0.0006 (14)
N13	0.0333 (17)	0.0296 (19)	0.0337 (18)	-0.0033 (14)	0.0123 (14)	-0.0002 (14)
O15	0.078 (2)	0.0216 (16)	0.0410 (18)	0.0007 (14)	0.0128 (15)	-0.0045 (13)
N9	0.0373 (17)	0.0176 (16)	0.0405 (19)	0.0000 (13)	0.0157 (14)	0.0002 (14)
O3	0.0348 (16)	0.070 (2)	0.0419 (18)	0.0066 (15)	0.0172 (13)	-0.0002 (16)
O11	0.067 (2)	0.0241 (17)	0.092 (3)	0.0081 (15)	0.044 (2)	-0.0009 (17)
O5	0.0498 (19)	0.0271 (18)	0.079 (3)	-0.0060 (14)	0.0174 (17)	-0.0045 (16)
O17	0.054 (2)	0.039 (2)	0.064 (2)	-0.0074 (15)	-0.0170 (17)	-0.0011 (17)
N16	0.0382 (18)	0.0296 (19)	0.0369 (18)	0.0074 (14)	0.0166 (14)	0.0004 (15)
N5	0.0334 (17)	0.033 (2)	0.0330 (17)	-0.0020 (15)	0.0125 (13)	-0.0033 (15)
N8	0.054 (2)	0.0205 (18)	0.041 (2)	-0.0027 (15)	0.0206 (16)	0.0018 (15)
N4	0.0385 (19)	0.033 (2)	0.0266 (17)	0.0017 (14)	0.0128 (14)	-0.0015 (14)
N12	0.0359 (17)	0.034 (2)	0.0263 (17)	0.0016 (14)	0.0082 (13)	-0.0006 (14)
N1	0.0344 (17)	0.043 (2)	0.0344 (19)	-0.0049 (15)	0.0085 (14)	0.0105 (16)
C6	0.0259 (17)	0.0248 (19)	0.0199 (16)	0.0002 (13)	0.0057 (13)	-0.0013 (14)
C3	0.0320 (19)	0.027 (2)	0.0252 (18)	0.0011 (15)	0.0104 (15)	0.0021 (15)
C5	0.0294 (17)	0.0229 (19)	0.0239 (17)	-0.0004 (14)	0.0114 (14)	-0.0018 (14)
C1	0.0283 (18)	0.029 (2)	0.0299 (19)	-0.0037 (15)	0.0086 (15)	0.0069 (16)
C4	0.0345 (19)	0.025 (2)	0.0253 (18)	-0.0006 (15)	0.0096 (14)	-0.0028 (15)
C2	0.0298 (18)	0.0233 (19)	0.0297 (19)	0.0007 (14)	0.0080 (14)	0.0026 (15)
C7	0.0288 (18)	0.027 (2)	0.0241 (17)	0.0051 (14)	0.0088 (14)	-0.0007 (15)
C8	0.0320 (18)	0.0196 (19)	0.0296 (19)	-0.0017 (14)	0.0132 (15)	-0.0025 (15)

Table S28. Geometric parameters (Å, º) for **13**

O20—N10	1.225 (4)	O8—N6	1.202 (5)
O10—N7	1.230 (4)	O4—N4	1.198 (4)
O9—N7	1.246 (4)	N2—C1	1.313 (5)
N7—C3	1.390 (5)	N6—C4	1.557 (5)
O2—N1	1.224 (5)	N13—C8	1.544 (5)
O1—N1	1.229 (5)	O15—N12	1.203 (5)
N3—N2	1.351 (4)	N9—H9A	0.8800
N3—C3	1.400 (5)	N9—H9B	0.8800
N3—C4	1.401 (5)	N9—C6	1.320 (5)
O18—N11	1.205 (4)	O3—N4	1.204 (4)

N10—O19	1.238 (4)	O11—N16	1.229 (5)
N10—C5	1.398 (4)	O5—N5	1.202 (5)
O6—N5	1.223 (5)	N16—C7	1.439 (5)
O12—N16	1.214 (4)	N5—C4	1.552 (5)
N15—N14	1.349 (4)	N8—H8A	0.8800
N15—C7	1.312 (5)	N8—H8B	0.8800
N11—O17	1.200 (4)	N8—C2	1.324 (5)
N11—C8	1.553 (5)	N4—C4	1.550 (5)
O13—N13	1.202 (4)	N12—C8	1.551 (5)
O16—N12	1.204 (5)	N1—C1	1.445 (5)
O14—N13	1.200 (4)	C6—C5	1.383 (5)
N14—C5	1.402 (5)	C6—C7	1.443 (5)
N14—C8	1.405 (5)	C3—C2	1.391 (5)
O7—N6	1.191 (5)	C1—C2	1.433 (5)
O10—N7—O9	123.8 (3)	O3—N4—C4	115.1 (3)
O10—N7—C3	117.5 (3)	O16—N12—C8	114.4 (3)
O9—N7—C3	118.7 (3)	O15—N12—O16	127.6 (4)
N2—N3—C3	110.8 (3)	O15—N12—C8	117.8 (3)
N2—N3—C4	119.1 (3)	O2—N1—O1	126.7 (4)
C3—N3—C4	130.1 (3)	O2—N1—C1	117.9 (4)
O20—N10—O19	124.1 (3)	O1—N1—C1	115.4 (3)
O20—N10—C5	117.7 (3)	N9—C6—C5	129.6 (3)
O19—N10—C5	118.1 (3)	N9—C6—C7	129.2 (3)
C7—N15—N14	104.7 (3)	C5—C6—C7	101.1 (3)
O18—N11—C8	117.3 (3)	N7—C3—N3	123.0 (3)
O17—N11—O18	126.3 (4)	N7—C3—C2	128.7 (3)
O17—N11—C8	116.2 (3)	C2—C3—N3	108.3 (3)
N15—N14—C5	111.0 (3)	N10—C5—N14	122.7 (3)
N15—N14—C8	118.7 (3)	C6—C5—N10	128.9 (3)
C5—N14—C8	130.2 (3)	C6—C5—N14	108.4 (3)
C1—N2—N3	104.6 (3)	N2—C1—N1	118.9 (3)
O7—N6—O8	127.7 (4)	N2—C1—C2	115.1 (3)
O7—N6—C4	117.3 (3)	C2—C1—N1	125.9 (4)
O8—N6—C4	115.0 (3)	N3—C4—N6	112.2 (3)
O13—N13—C8	115.8 (3)	N3—C4—N5	111.9 (3)
O14—N13—O13	129.1 (3)	N3—C4—N4	109.5 (3)
O14—N13—C8	115.0 (3)	N5—C4—N6	112.4 (3)
H9A—N9—H9B	120.0	N4—C4—N6	104.8 (3)

C6—N9—H9A	120.0	N4—C4—N5	105.5 (3)
C6—N9—H9B	120.0	N8—C2—C3	129.0 (3)
O12—N16—O11	125.6 (3)	N8—C2—C1	129.9 (4)
O12—N16—C7	118.7 (3)	C3—C2—C1	101.1 (3)
O11—N16—C7	115.7 (3)	N15—C7—N16	119.0 (3)
O6—N5—C4	114.1 (3)	N15—C7—C6	114.8 (3)
O5—N5—O6	127.6 (4)	N16—C7—C6	126.1 (3)
O5—N5—C4	118.2 (3)	N14—C8—N11	112.1 (3)
H8A—N8—H8B	120.0	N14—C8—N13	108.8 (3)
C2—N8—H8A	120.0	N14—C8—N12	112.3 (3)
C2—N8—H8B	120.0	N13—C8—N11	105.4 (3)
O4—N4—O3	129.0 (3)	N13—C8—N12	105.4 (3)
O4—N4—C4	116.0 (3)	N12—C8—N11	112.3 (3)
O20—N10—C5—N14	179.0 (3)	O4—N4—C4—N3	-96.0 (4)
O20—N10—C5—C6	1.7 (6)	O4—N4—C4—N6	143.4 (4)
O10—N7—C3—N3	179.2 (3)	O4—N4—C4—N5	24.5 (5)
O10—N7—C3—C2	-2.2 (6)	N2—N3—C3—N7	177.5 (3)
O9—N7—C3—N3	-0.8 (6)	N2—N3—C3—C2	-1.3 (4)
O9—N7—C3—C2	177.8 (4)	N2—N3—C4—N6	117.1 (3)
N7—C3—C2—N8	2.7 (7)	N2—N3—C4—N5	-115.5 (3)
N7—C3—C2—C1	-177.4 (4)	N2—N3—C4—N4	1.1 (5)
O2—N1—C1—N2	4.8 (5)	N2—C1—C2—N8	178.9 (4)
O2—N1—C1—C2	-175.8 (4)	N2—C1—C2—C3	-1.0 (4)
O1—N1—C1—N2	-175.4 (4)	O15—N12—C8—N11	39.2 (4)
O1—N1—C1—C2	4.0 (6)	O15—N12—C8—N14	166.6 (3)
N3—N2—C1—N1	179.8 (3)	O15—N12—C8—N13	-75.1 (4)
N3—N2—C1—C2	0.3 (4)	N9—C6—C5—N10	-2.3 (7)
N3—C3—C2—N8	-178.7 (4)	N9—C6—C5—N14	-179.9 (4)
N3—C3—C2—C1	1.3 (4)	N9—C6—C7—N15	179.8 (4)
O18—N11—C8—N14	-178.8 (3)	N9—C6—C7—N16	2.2 (6)
O18—N11—C8—N13	62.9 (4)	O3—N4—C4—N3	84.3 (4)
O18—N11—C8—N12	-51.3 (4)	O3—N4—C4—N6	-36.3 (4)
O6—N5—C4—N3	18.9 (4)	O3—N4—C4—N5	-155.2 (3)
O6—N5—C4—N6	146.2 (3)	O11—N16—C7—N15	-179.6 (4)
O6—N5—C4—N4	-100.2 (4)	O11—N16—C7—C6	-2.2 (6)
O12—N16—C7—N15	-0.7 (5)	O5—N5—C4—N3	-165.1 (4)
O12—N16—C7—C6	176.7 (4)	O5—N5—C4—N6	-37.8 (5)
N15—N14—C5—N10	-177.7 (3)	O5—N5—C4—N4	75.9 (4)

N15—N14—C5—C6	0.1 (4)	O17—N11—C8—N14	5.1 (5)
N15—N14—C8—N11	-115.7 (3)	O17—N11—C8—N13	-113.1 (4)
N15—N14—C8—N13	0.5 (5)	O17—N11—C8—N12	132.7 (4)
N15—N14—C8—N12	116.7 (3)	N1—C1—C2—N8	-0.5 (7)
O13—N13—C8—N11	-146.0 (3)	N1—C1—C2—C3	179.6 (4)
O13—N13—C8—N14	93.6 (4)	C3—N3—N2—C1	0.6 (4)
O13—N13—C8—N12	-27.0 (4)	C3—N3—C4—N6	-61.7 (5)
O19—N10—C5—N14	-1.0 (6)	C3—N3—C4—N5	65.7 (5)
O19—N10—C5—C6	-178.3 (4)	C3—N3—C4—N4	-177.6 (4)
O16—N12—C8—N11	-144.8 (3)	C5—N14—C8—N11	61.5 (5)
O16—N12—C8—N14	-17.3 (4)	C5—N14—C8—N13	177.7 (3)
O16—N12—C8—N13	100.9 (4)	C5—N14—C8—N12	-66.1 (5)
O14—N13—C8—N11	35.8 (4)	C5—C6—C7—N15	-0.3 (4)
O14—N13—C8—N14	-84.6 (4)	C5—C6—C7—N16	-177.8 (4)
O14—N13—C8—N12	154.8 (3)	C4—N3—N2—C1	-178.4 (3)
N14—N15—C7—N16	178.0 (3)	C4—N3—C3—N7	-3.7 (6)
N14—N15—C7—C6	0.3 (4)	C4—N3—C3—C2	177.5 (4)
O7—N6—C4—N3	178.6 (3)	C7—N15—N14—C5	-0.2 (4)
O7—N6—C4—N5	51.5 (4)	C7—N15—N14—C8	177.5 (3)
O7—N6—C4—N4	-62.6 (4)	C7—C6—C5—N10	177.7 (4)
O8—N6—C4—N3	-4.7 (5)	C7—C6—C5—N14	0.1 (4)
O8—N6—C4—N5	-131.8 (4)	C8—N14—C5—N10	5.0 (6)
O8—N6—C4—N4	114.1 (4)	C8—N14—C5—C6	-177.3 (4)

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

Table S29. Crystal data, data collection, and refinement for **14**

$C_4ClN_7O_{10}$	$F(000) = 680$
$M_r = 341.56$	$D_x = 1.859$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 13.9214$ (7) Å	Cell parameters from 5926 reflections
$b = 6.9287$ (3) Å	$\theta = 2.9–27.2°$
$c = 13.9386$ (7) Å	$\mu = 0.39$ mm^{-1}
$\beta = 114.823$ (2)°	$T = 296$ K
$V = 1220.26$ (10) Å^3	Block, colourless
$Z = 4$	0.12 × 0.11 × 0.08 mm
Bruker D8 QUEST PHOTON 100 diffractometer	1831 reflections with $I > 2\sigma(I)$

Detector resolution: 10.42 pixels mm^{-1}	R_{int} = 0.031
ϕ and ω scans	θ_{max} = 25.0°, θ_{min} = 3.4°
Absorption correction: multi-scan *SADABS*	h = -15→16
T_{min} = 0.531, T_{max} = 0.746	k = -8→8
10861 measured reflections	l = -16→16
2136 independent reflections	
Refinement on F^2	0 restraints
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.118P)^2 + 0.818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.061	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.187	$\Delta\rangle_{max}$ = 0.76 e $Å^{-3}$
S = 1.09	$\Delta\rangle_{min}$ = -0.30 e $Å^{-3}$
2136 reflections	Extinction correction: *SHELXL2018*/1 (Sheldrick 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
200 parameters	Extinction coefficient: 0.054 (10)

Table S30. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for **14**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7808 (3)	0.4114 (5)	0.6219 (3)	0.0521 (9)
C2	0.8529 (3)	0.4078 (5)	0.7291 (3)	0.0464 (8)
C3	0.8161 (2)	0.5412 (5)	0.7775 (2)	0.0430 (8)
C4	0.6566 (3)	0.7557 (5)	0.7068 (3)	0.0496 (8)
Cl1	0.86687 (6)	0.61957 (12)	0.90697 (5)	0.0450 (4)
N1	0.7036 (2)	0.5323 (5)	0.6024 (2)	0.0525 (8)
N2	0.7264 (2)	0.6146 (4)	0.6992 (2)	0.0471 (7)
N3	0.7784 (3)	0.2903 (6)	0.5360 (3)	0.0710 (10)
N4	0.9478 (2)	0.2969 (5)	0.7736 (3)	0.0621 (9)
N5	0.7052 (3)	0.9581 (5)	0.7286 (3)	0.0593 (8)
N6	0.6197 (2)	0.7009 (5)	0.7929 (3)	0.0619 (9)
N7	0.5581 (3)	0.7666 (5)	0.6012 (3)	0.0663 (10)
O1	0.7926 (5)	0.3652 (7)	0.4675 (3)	0.1257 (19)
O2	0.7597 (4)	0.1209 (6)	0.5397 (4)	0.1143 (15)
O3	0.9745 (3)	0.2139 (6)	0.7124 (3)	0.1005 (12)
O4	0.9943 (3)	0.2869 (6)	0.8677 (3)	0.0958 (12)
O5	0.6090 (3)	0.5290 (5)	0.8020 (3)	0.0869 (10)
O6	0.6040 (3)	0.8285 (6)	0.8420 (3)	0.1010 (12)

O7	0.7988 (3)	0.9695 (4)	0.7579 (3)	0.0761 (9)
O8	0.6431 (3)	1.0889 (5)	0.7136 (3)	0.0922 (11)
O9	0.4788 (3)	0.6924 (7)	0.5983 (3)	0.1032 (13)
O10	0.5726 (3)	0.8510 (6)	0.5320 (3)	0.0912 (12)

Table S31. Atomic displacement parameters (Å^2) for **14**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.056 (2)	0.049 (2)	0.053 (2)	0.0074 (15)	0.0244 (17)	-0.0001 (15)
C2	0.0401 (16)	0.0427 (17)	0.053 (2)	0.0015 (13)	0.0163 (15)	0.0024 (14)
C3	0.0359 (15)	0.0454 (18)	0.0422 (17)	-0.0027 (13)	0.0110 (13)	0.0040 (14)
C4	0.0480 (18)	0.0458 (19)	0.052 (2)	0.0053 (14)	0.0179 (15)	-0.0037 (15)
Cl1	0.0430 (5)	0.0540 (6)	0.0313 (5)	-0.0003 (3)	0.0091 (3)	0.0019 (3)
N1	0.0542 (17)	0.0533 (18)	0.0421 (16)	0.0098 (13)	0.0125 (13)	-0.0046 (13)
N2	0.0435 (14)	0.0454 (16)	0.0482 (17)	0.0063 (11)	0.0152 (12)	-0.0028 (12)
N3	0.084 (2)	0.073 (3)	0.057 (2)	0.0252 (19)	0.0305 (19)	0.0002 (18)
N4	0.0430 (16)	0.061 (2)	0.074 (2)	0.0078 (14)	0.0161 (16)	0.0085 (17)
N5	0.067 (2)	0.0487 (19)	0.0613 (19)	0.0063 (16)	0.0263 (16)	0.0008 (15)
N6	0.0511 (18)	0.070 (2)	0.067 (2)	0.0050 (15)	0.0267 (16)	-0.0028 (17)
N7	0.058 (2)	0.064 (2)	0.059 (2)	0.0197 (16)	0.0078 (16)	-0.0056 (17)
O1	0.199 (5)	0.118 (4)	0.090 (3)	0.047 (3)	0.090 (4)	0.015 (2)
O2	0.162 (4)	0.079 (3)	0.119 (3)	-0.001 (2)	0.075 (3)	-0.037 (2)
O3	0.083 (2)	0.114 (3)	0.115 (3)	0.049 (2)	0.051 (2)	0.007 (2)
O4	0.073 (2)	0.095 (3)	0.082 (2)	0.0282 (18)	-0.0032 (17)	0.0067 (19)
O5	0.084 (2)	0.076 (2)	0.109 (3)	-0.0107 (17)	0.048 (2)	0.0125 (19)
O6	0.127 (3)	0.105 (3)	0.100 (3)	0.011 (2)	0.075 (3)	-0.013 (2)
O7	0.0671 (19)	0.0607 (18)	0.092 (2)	-0.0107 (14)	0.0252 (16)	0.0047 (15)
O8	0.106 (3)	0.0513 (18)	0.119 (3)	0.0223 (17)	0.047 (2)	-0.0055 (17)
O9	0.0517 (18)	0.112 (3)	0.112 (3)	-0.0005 (19)	0.0018 (17)	-0.015 (2)
O10	0.103 (3)	0.094 (3)	0.0585 (19)	0.048 (2)	0.0171 (18)	0.0125 (17)

Table S32. Geometric parameters (Å, º) for **14**

C1—N1	1.299 (5)	N1—N2	1.374 (4)
C1—C2	1.407 (5)	N3—O1	1.174 (5)
C1—N3	1.451 (5)	N3—O2	1.208 (6)
C2—C3	1.364 (5)	N4—O4	1.196 (5)
C2—N4	1.426 (5)	N4—O3	1.209 (5)
C3—N2	1.366 (4)	N5—O7	1.194 (4)

C3—Cl1	1.727 (3)	N5—O8	1.208 (5)
C4—N2	1.413 (4)	N6—O6	1.193 (5)
C4—N5	1.531 (5)	N6—O5	1.213 (5)
C4—N7	1.535 (5)	N7—O9	1.203 (5)
C4—N6	1.538 (5)	N7—O10	1.216 (5)
N1—C1—C2	113.1 (3)	C3—N2—C4	128.7 (3)
N1—C1—N3	118.0 (3)	N1—N2—C4	118.5 (3)
C2—C1—N3	128.7 (3)	O1—N3—O2	125.3 (4)
C3—C2—C1	105.4 (3)	O1—N3—C1	117.6 (4)
C3—C2—N4	128.4 (3)	O2—N3—C1	117.2 (4)
C1—C2—N4	126.1 (3)	O4—N4—O3	124.1 (4)
C2—C3—N2	105.3 (3)	O4—N4—C2	119.0 (4)
C2—C3—Cl1	131.0 (3)	O3—N4—C2	116.9 (3)
N2—C3—Cl1	123.6 (3)	O7—N5—O8	127.5 (4)
N2—C4—N5	112.8 (3)	O7—N5—C4	117.1 (3)
N2—C4—N7	109.1 (3)	O8—N5—C4	115.4 (3)
N5—C4—N7	106.7 (3)	O6—N6—O5	127.4 (4)
N2—C4—N6	110.6 (3)	O6—N6—C4	117.8 (4)
N5—C4—N6	109.6 (3)	O5—N6—C4	114.8 (3)
N7—C4—N6	107.7 (3)	O9—N7—O10	129.4 (4)
C1—N1—N2	103.4 (3)	O9—N7—C4	116.7 (4)
C3—N2—N1	112.7 (3)	O10—N7—C4	113.9 (4)
N1—C1—C2—C3	-1.1 (4)	N1—C1—N3—O2	-108.3 (5)
N3—C1—C2—C3	-176.0 (4)	C2—C1—N3—O2	66.5 (6)
N1—C1—C2—N4	-176.9 (3)	C3—C2—N4—O4	15.3 (6)
N3—C1—C2—N4	8.1 (7)	C1—C2—N4—O4	-169.9 (4)
C1—C2—C3—N2	0.3 (4)	C3—C2—N4—O3	-166.7 (4)
N4—C2—C3—N2	176.0 (3)	C1—C2—N4—O3	8.2 (6)
C1—C2—C3—Cl1	-177.4 (3)	N2—C4—N5—O7	-15.0 (5)
N4—C2—C3—Cl1	-1.7 (6)	N7—C4—N5—O7	-134.9 (3)
C2—C1—N1—N2	1.3 (4)	N6—C4—N5—O7	108.8 (4)
N3—C1—N1—N2	176.8 (3)	N2—C4—N5—O8	164.8 (4)
C2—C3—N2—N1	0.5 (4)	N7—C4—N5—O8	45.0 (4)
Cl1—C3—N2—N1	178.4 (2)	N6—C4—N5—O8	-71.3 (4)
C2—C3—N2—C4	179.0 (3)	N2—C4—N6—O6	146.3 (4)
Cl1—C3—N2—C4	-3.0 (5)	N5—C4—N6—O6	21.2 (5)
C1—N1—N2—C3	-1.1 (4)	N7—C4—N6—O6	-94.5 (4)

C1—N1—N2—C4	-179.8 (3)	N2—C4—N6—O5	-34.4 (4)
N5—C4—N2—C3	70.5 (4)	N5—C4—N6—O5	-159.5 (3)
N7—C4—N2—C3	-171.0 (3)	N7—C4—N6—O5	84.8 (4)
N6—C4—N2—C3	-52.7 (4)	N2—C4—N7—O9	104.0 (4)
N5—C4—N2—N1	-111.0 (3)	N5—C4—N7—O9	-133.8 (4)
N7—C4—N2—N1	7.5 (4)	N6—C4—N7—O9	-16.1 (5)
N6—C4—N2—N1	125.8 (3)	N2—C4—N7—O10	-76.0 (4)
N1—C1—N3—O1	70.2 (6)	N5—C4—N7—O10	46.2 (4)
C2—C1—N3—O1	-115.1 (5)	N6—C4—N7—O10	163.8 (3)

9. Single-crystal X-ray diffraction analysis of **15·2H$_2$O**

Table S33. Crystal data, data collection, and refinement for **15·2H$_2$O**

$C_4N_6O_9 \cdot 2(H_2O)$	$Z = 2$
$M_r = 312.13$	$F(000) = 316$
Triclinic, $P\bar{1}$	$D_x = 1.794$ Mg m^{-3}
$a = 7.6403$ (9) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.7898$ (8) Å	Cell parameters from 4206 reflections
$c = 11.2231$ (11) Å	$\theta = 3.0$–$26.8°$
$\alpha = 78.002$ (3)°	$\mu = 0.18$ mm^{-1}
$\beta = 80.654$ (3)°	$T = 296$ K
$\gamma = 62.508$ (3)°	Plate, colourless
$V = 577.88$ (11) Å^3	0.22 × 0.20 × 0.03 mm
Bruker D8 QUEST PHOTON 100 diffractometer	1961 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	$R_{int} = 0.028$
ϕ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan *SADABS*	$h = -9 \rightarrow 9$
$T_{min} = 0.631$, $T_{max} = 0.746$	$k = -10 \rightarrow 9$
8706 measured reflections	$l = -14 \rightarrow 14$
2639 independent reflections	
Refinement on F^2	6 restraints
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Only H-atom coordinates refined
$wR(F^2) = 0.147$	$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.5042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2639 reflections	$\Delta\rangle_{max} = 0.38$ e Å^{-3}

202 parameters	$\Delta\rangle_{min}$ = -0.37 e Å^{-3}

Table S34. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **15·2H$_2$O**

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.9612 (3)	0.7240 (3)	0.0761 (2)	0.0240 (5)
C2	0.7715 (3)	0.7555 (3)	0.0558 (2)	0.0259 (5)
C3	0.6757 (3)	0.7354 (3)	0.1737 (2)	0.0266 (5)
C4	0.7948 (4)	0.6591 (3)	0.3764 (2)	0.0299 (5)
N1	0.8187 (3)	0.6963 (3)	0.25047 (17)	0.0293 (4)
N2	0.9955 (3)	0.6881 (3)	0.19044 (17)	0.0288 (4)
N3	1.1174 (3)	0.7343 (3)	-0.01405 (17)	0.0295 (4)
N4	0.6931 (3)	0.7819 (3)	-0.05420 (18)	0.0301 (5)
N6	0.7630 (3)	0.8027 (3)	0.44295 (19)	0.0331 (5)
N7	0.7956 (3)	0.4813 (3)	0.42937 (18)	0.0331 (5)
O1	1.2850 (3)	0.6064 (3)	0.00065 (19)	0.0489 (5)
O2	1.0725 (3)	0.8684 (3)	-0.09956 (16)	0.0443 (5)
O3	0.8060 (3)	0.7482 (3)	-0.14808 (16)	0.0424 (5)
O4	0.5146 (3)	0.8306 (3)	-0.05326 (18)	0.0412 (5)
O5	0.8278 (3)	0.3628 (3)	0.35990 (18)	0.0458 (5)
O6	0.7649 (4)	0.4420 (3)	0.54070 (17)	0.0588 (6)
O7	0.7391 (4)	0.7795 (3)	0.55571 (17)	0.0539 (6)
O8	0.7664 (3)	0.9568 (3)	0.38450 (19)	0.0490 (5)
O9	0.5131 (3)	0.7385 (3)	0.21142 (16)	0.0371 (4)
O10	0.4755 (4)	0.3746 (4)	0.2479 (2)	0.0585 (6)
H10A	0.501 (6)	0.474 (5)	0.238 (4)	0.088*
H10B	0.384 (5)	0.384 (6)	0.306 (3)	0.088*
O11	0.1637 (4)	0.9556 (3)	0.3381 (2)	0.0620 (6)
H11A	0.278 (4)	0.902 (6)	0.294 (3)	0.093*
H11B	0.158 (6)	0.862 (5)	0.394 (3)	0.093*

Table S35. Atomic displacement parameters (Å^2) for **15·2H$_2$O**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0256 (11)	0.0194 (10)	0.0243 (11)	-0.0104 (8)	0.0031 (9)	-0.0006 (8)
C2	0.0275 (11)	0.0239 (10)	0.0249 (11)	-0.0110 (9)	0.0002 (9)	-0.0032 (8)
C3	0.0274 (12)	0.0253 (11)	0.0267 (11)	-0.0122 (9)	0.0021 (9)	-0.0053 (9)
C4	0.0400 (14)	0.0323 (12)	0.0210 (11)	-0.0205 (10)	0.0020 (10)	-0.0034 (9)

N1	0.0300 (11)	0.0387 (11)	0.0207 (9)	-0.0192 (9)	0.0026 (8)	-0.0014 (8)
N2	0.0295 (11)	0.0334 (10)	0.0247 (10)	-0.0178 (8)	0.0020 (8)	-0.0005 (8)
N3	0.0345 (11)	0.0290 (10)	0.0275 (10)	-0.0190 (9)	0.0047 (8)	-0.0032 (8)
N4	0.0400 (12)	0.0222 (9)	0.0294 (11)	-0.0148 (8)	-0.0047 (9)	-0.0023 (7)
N6	0.0373 (12)	0.0360 (11)	0.0322 (11)	-0.0232 (9)	0.0048 (9)	-0.0067 (9)
N7	0.0394 (12)	0.0305 (10)	0.0295 (11)	-0.0176 (9)	0.0005 (9)	-0.0023 (8)
O1	0.0288 (10)	0.0436 (11)	0.0596 (13)	-0.0128 (8)	0.0101 (9)	0.0040 (9)
O2	0.0537 (12)	0.0459 (11)	0.0319 (10)	-0.0284 (9)	0.0010 (8)	0.0089 (8)
O3	0.0597 (13)	0.0507 (11)	0.0234 (9)	-0.0312 (10)	0.0037 (8)	-0.0081 (8)
O4	0.0372 (11)	0.0386 (10)	0.0491 (11)	-0.0141 (8)	-0.0123 (8)	-0.0088 (8)
O5	0.0560 (13)	0.0341 (10)	0.0511 (12)	-0.0205 (9)	-0.0009 (9)	-0.0155 (8)
O6	0.1023 (18)	0.0429 (11)	0.0304 (11)	-0.0393 (12)	0.0076 (11)	0.0040 (8)
O7	0.0882 (17)	0.0658 (14)	0.0283 (10)	-0.0525 (13)	0.0107 (10)	-0.0163 (9)
O8	0.0631 (13)	0.0338 (10)	0.0550 (12)	-0.0302 (10)	0.0080 (10)	-0.0048 (9)
O9	0.0289 (9)	0.0430 (10)	0.0403 (10)	-0.0186 (8)	0.0080 (7)	-0.0100 (8)
O10	0.0734 (16)	0.0716 (15)	0.0473 (13)	-0.0479 (13)	0.0105 (11)	-0.0168 (11)
O11	0.0644 (15)	0.0491 (13)	0.0646 (15)	-0.0252 (11)	0.0138 (12)	-0.0067 (11)

Table S36. Geometric parameters (Å, º) for **15·2H$_2$O**

C1—N2	1.299 (3)	N3—O2	1.220 (3)
C1—C2	1.403 (3)	N4—O4	1.235 (3)
C1—N3	1.455 (3)	N4—O3	1.238 (3)
C2—N4	1.395 (3)	N6—O7	1.236 (3)
C2—C3	1.421 (3)	N6—O8	1.252 (3)
C3—O9	1.236 (3)	N7—O6	1.234 (3)
C3—N1	1.385 (3)	N7—O5	1.244 (3)
C4—N6	1.380 (3)	O10—H10A	0.863 (18)
C4—N1	1.382 (3)	O10—H10B	0.863 (18)
C4—N7	1.386 (3)	O11—H11A	0.887 (19)
N1—N2	1.388 (3)	O11—H11B	0.869 (18)
N3—O1	1.217 (3)		
N2—C1—C2	114.5 (2)	C1—N2—N1	102.84 (18)
N2—C1—N3	117.3 (2)	O1—N3—O2	124.3 (2)
C2—C1—N3	128.1 (2)	O1—N3—C1	117.34 (18)
N4—C2—C1	129.1 (2)	O2—N3—C1	118.34 (19)
N4—C2—C3	125.1 (2)	O4—N4—O3	122.4 (2)
C1—C2—C3	105.53 (19)	O4—N4—C2	118.5 (2)

O9—C3—N1	123.1 (2)	O3—N4—C2	119.0 (2)
O9—C3—C2	134.1 (2)	O7—N6—O8	120.7 (2)
N1—C3—C2	102.69 (19)	O7—N6—C4	122.1 (2)
N6—C4—N1	118.8 (2)	O8—N6—C4	117.1 (2)
N6—C4—N7	123.2 (2)	O6—N7—O5	121.2 (2)
N1—C4—N7	117.9 (2)	O6—N7—C4	121.6 (2)
C4—N1—C3	123.9 (2)	O5—N7—C4	117.3 (2)
C4—N1—N2	121.59 (19)	H10A—O10—H10B	110 (3)
C3—N1—N2	114.40 (18)	H11A—O11—H11B	106 (3)
N2—C1—C2—N4	-174.4 (2)	C4—N1—N2—C1	177.7 (2)
N3—C1—C2—N4	8.2 (4)	C3—N1—N2—C1	0.5 (2)
N2—C1—C2—C3	-0.4 (3)	N2—C1—N3—O1	45.7 (3)
N3—C1—C2—C3	-177.7 (2)	C2—C1—N3—O1	-137.0 (2)
N4—C2—C3—O9	-1.6 (4)	N2—C1—N3—O2	-135.0 (2)
C1—C2—C3—O9	-176.0 (2)	C2—C1—N3—O2	42.3 (3)
N4—C2—C3—N1	175.0 (2)	C1—C2—N4—O4	-171.6 (2)
C1—C2—C3—N1	0.6 (2)	C3—C2—N4—O4	15.4 (3)
N6—C4—N1—C3	-105.6 (3)	C1—C2—N4—O3	11.2 (3)
N7—C4—N1—C3	71.8 (3)	C3—C2—N4—O3	-161.8 (2)
N6—C4—N1—N2	77.5 (3)	N1—C4—N6—O7	179.5 (2)
N7—C4—N1—N2	-105.2 (3)	N7—C4—N6—O7	2.4 (4)
O9—C3—N1—C4	-0.8 (3)	N1—C4—N6—O8	-3.0 (3)
C2—C3—N1—C4	-177.9 (2)	N7—C4—N6—O8	179.8 (2)
O9—C3—N1—N2	176.4 (2)	N6—C4—N7—O6	1.0 (4)
C2—C3—N1—N2	-0.7 (2)	N1—C4—N7—O6	-176.2 (2)
C2—C1—N2—N1	-0.1 (2)	N6—C4—N7—O5	-179.3 (2)
N3—C1—N2—N1	177.58 (17)	N1—C4—N7—O5	3.5 (3)

10.NMR spectra

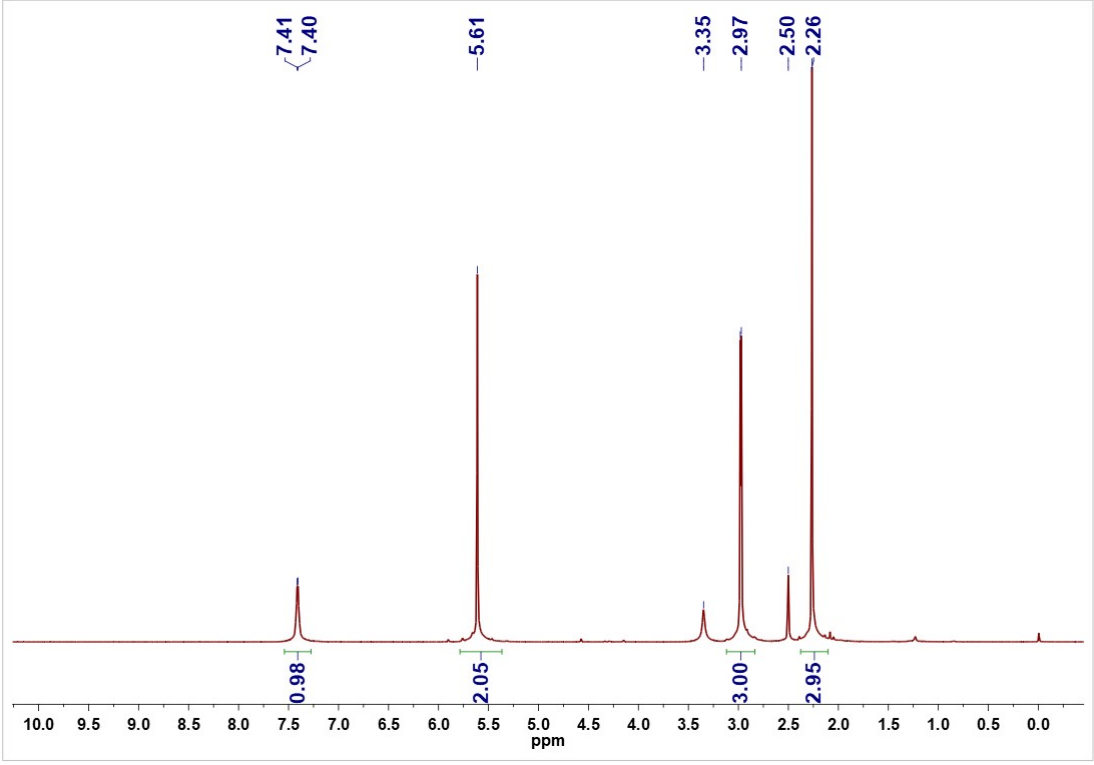


Fig. S7 ^{1}H NMR spectrum of **5** in d_6-DMSO.

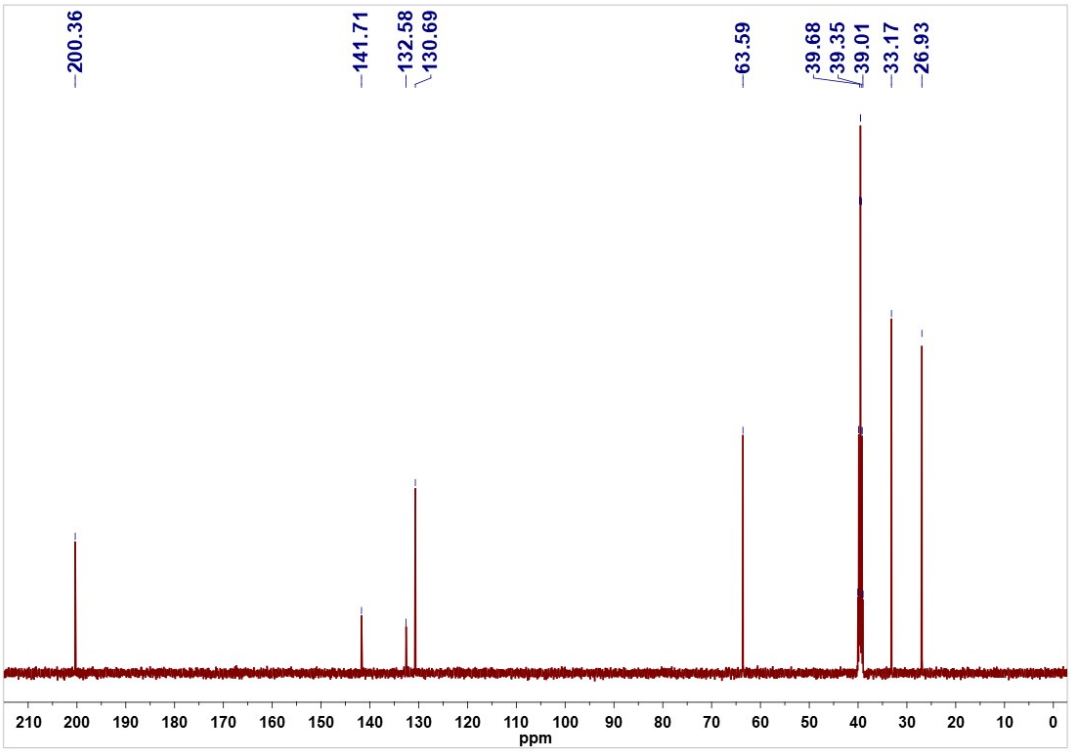


Fig. S8 ^{13}C NMR spectrum of **5** in d_6-DMSO.

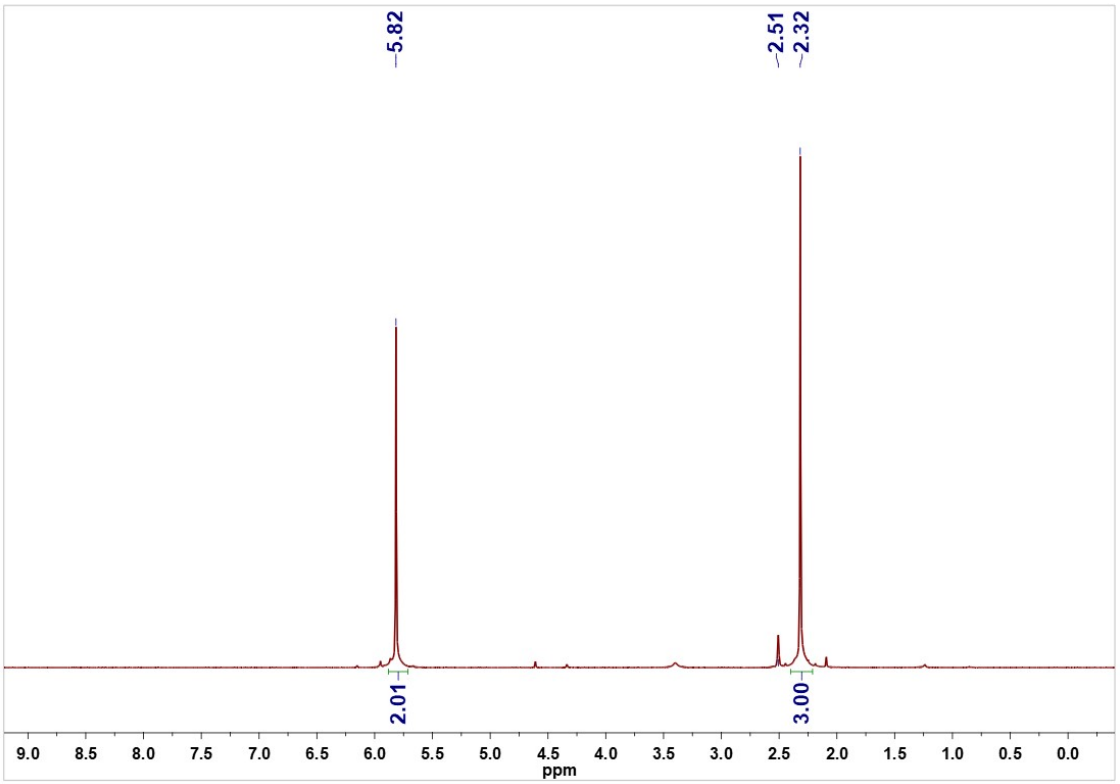


Fig. S9 ^{1}H NMR spectrum of **6** in d_6-DMSO.

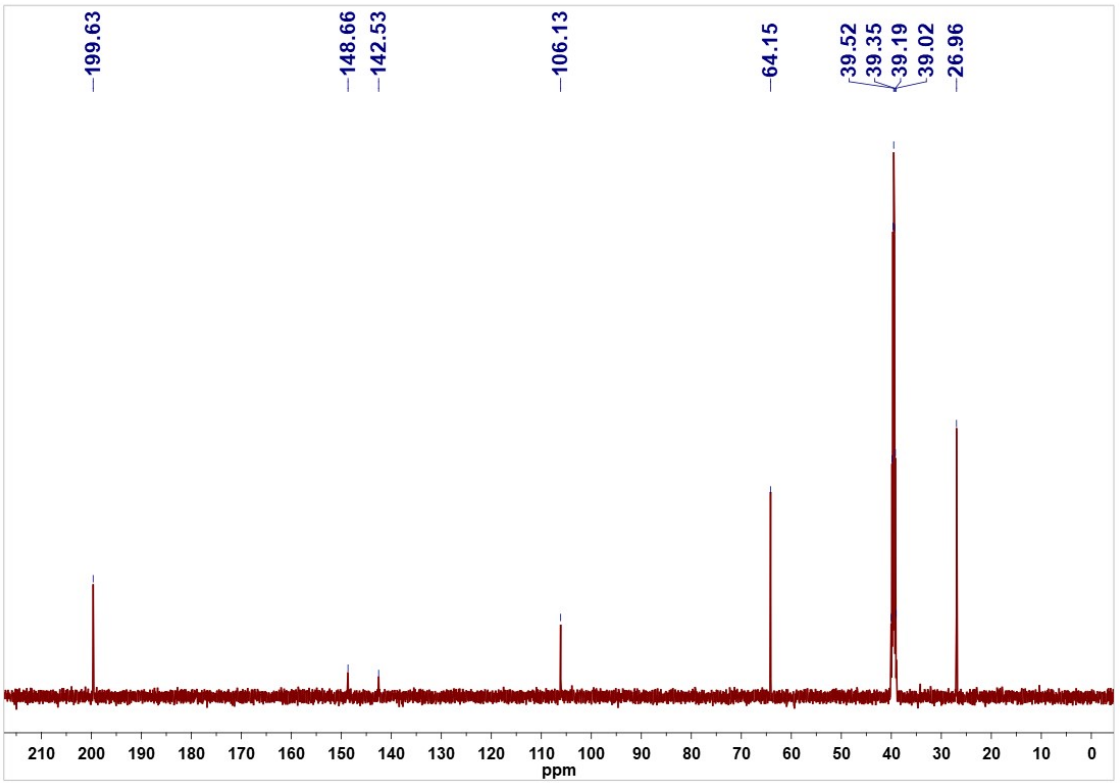


Fig. S10 ^{13}C NMR spectrum of **6** in d_6-DMSO.

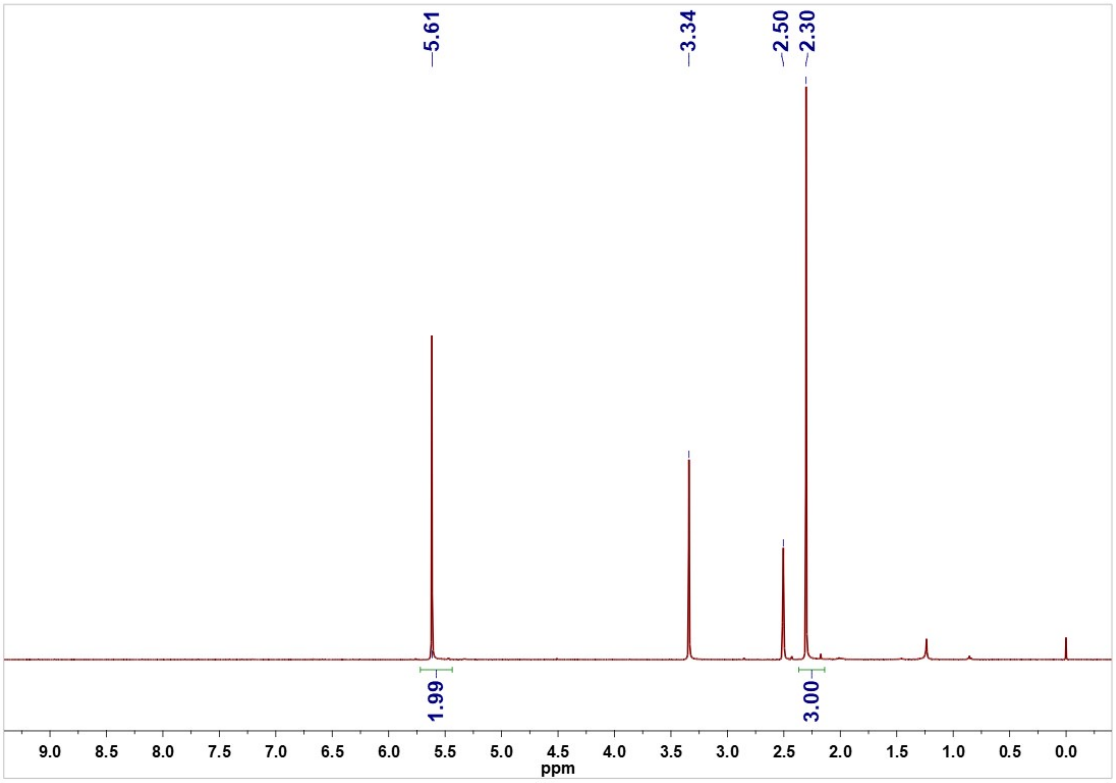


Fig. S11 ^{1}H NMR spectrum of **8** in d_6-DMSO.

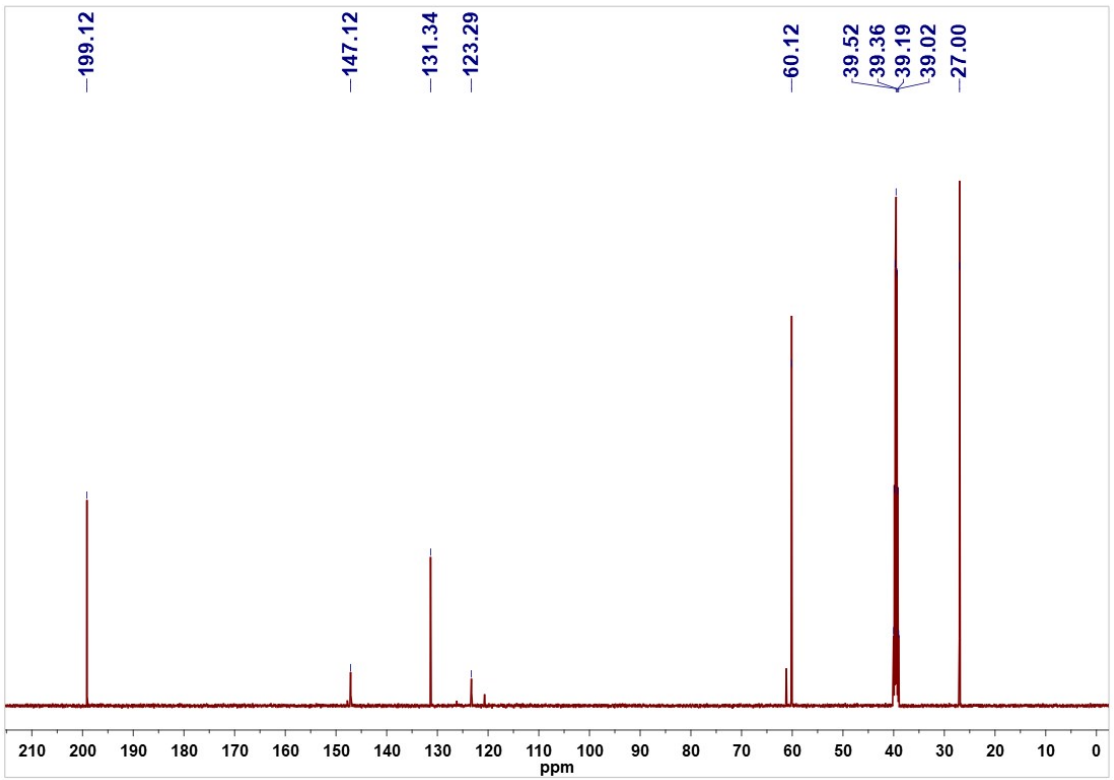


Fig. S12 ^{13}C NMR spectrum of **8** in d_6-DMSO.

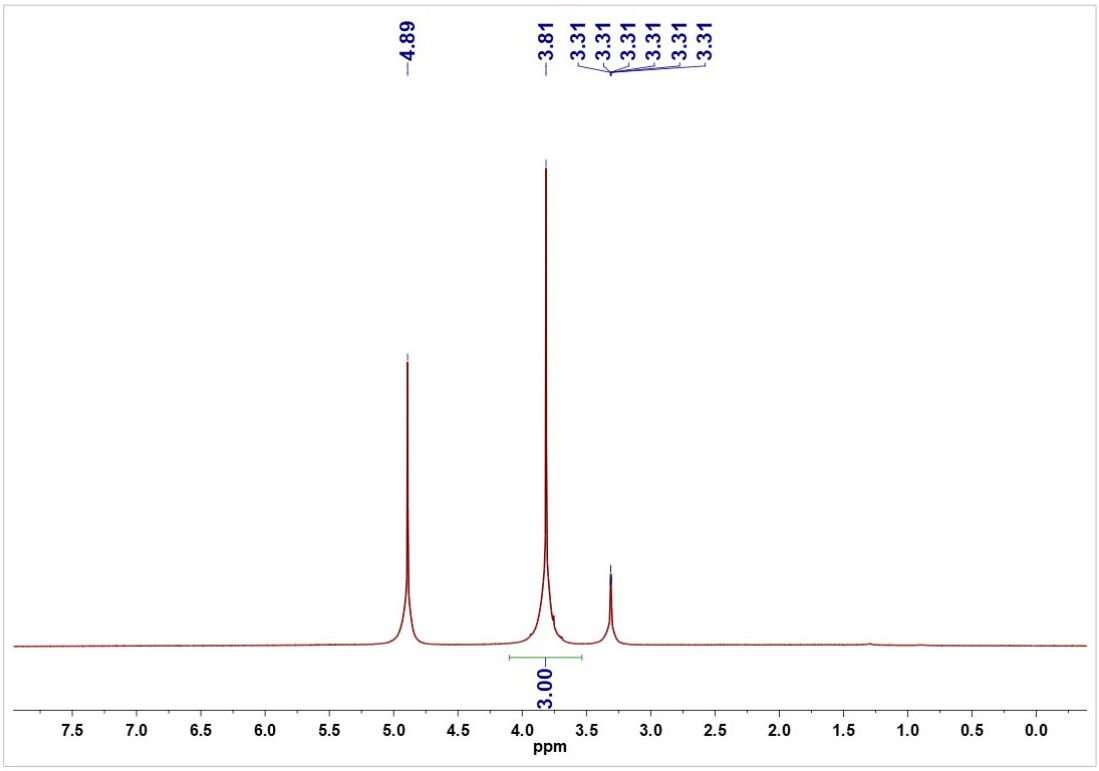


Fig. S13 ^{1}H NMR spectrum of **10** in CD_3OD.

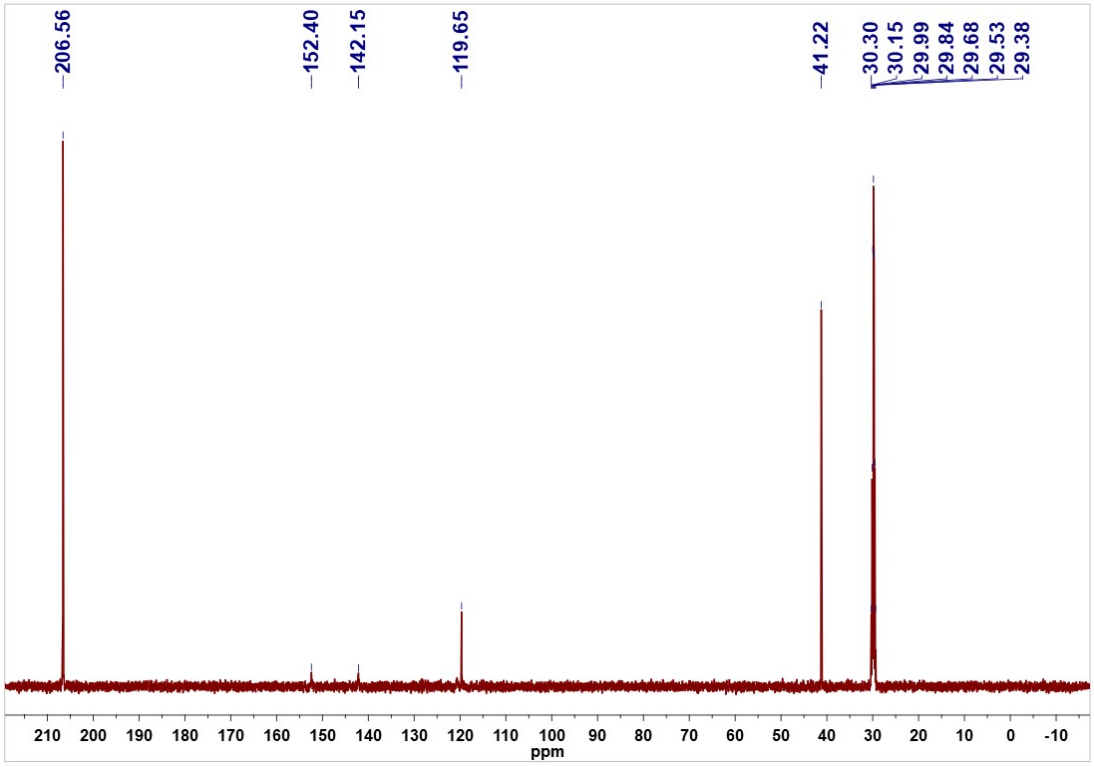


Fig. S14 ^{13}C NMR spectrum of **10** in d_6-Acetone.

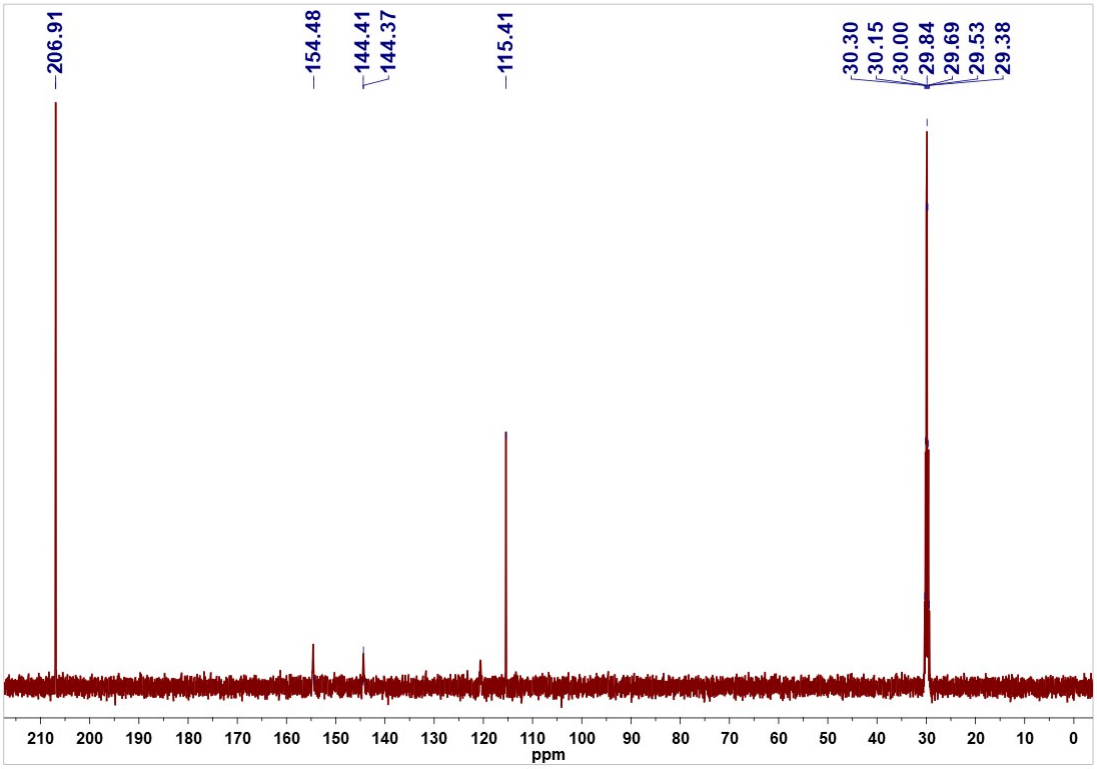


Fig. S15 ^{13}C NMR spectrum of **11** in d_6-Acetone.

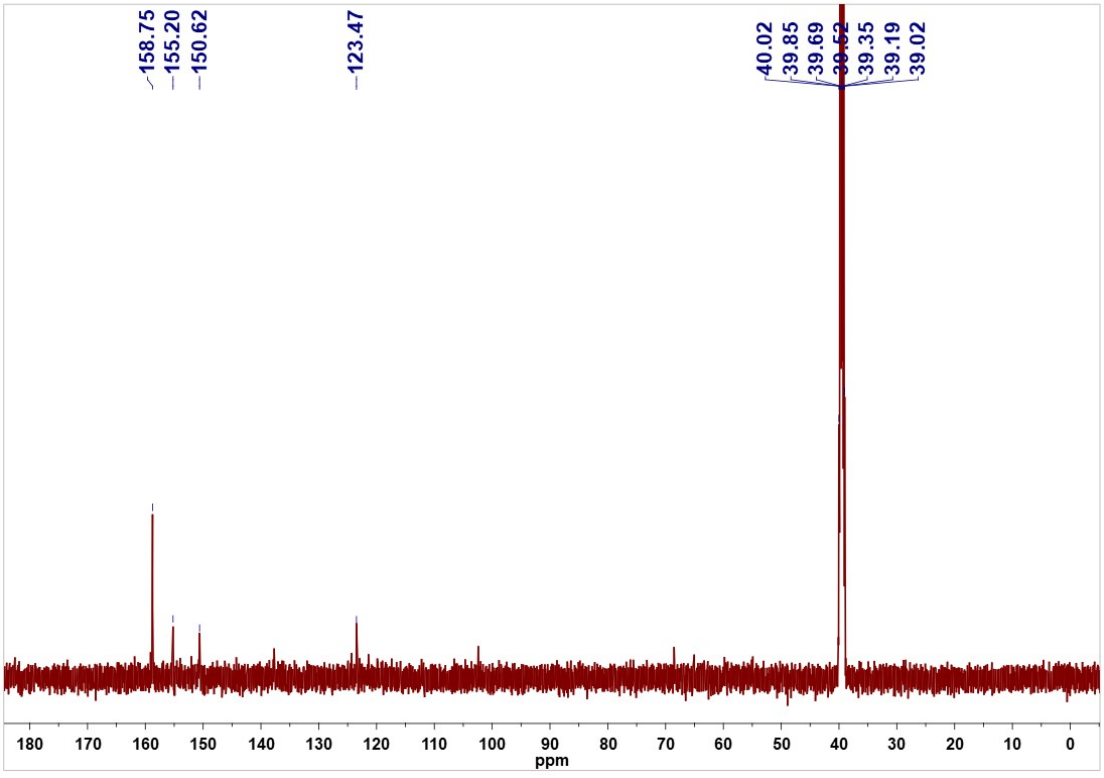


Fig. S16 ^{13}C NMR spectrum of **12** in d_6-DMSO.

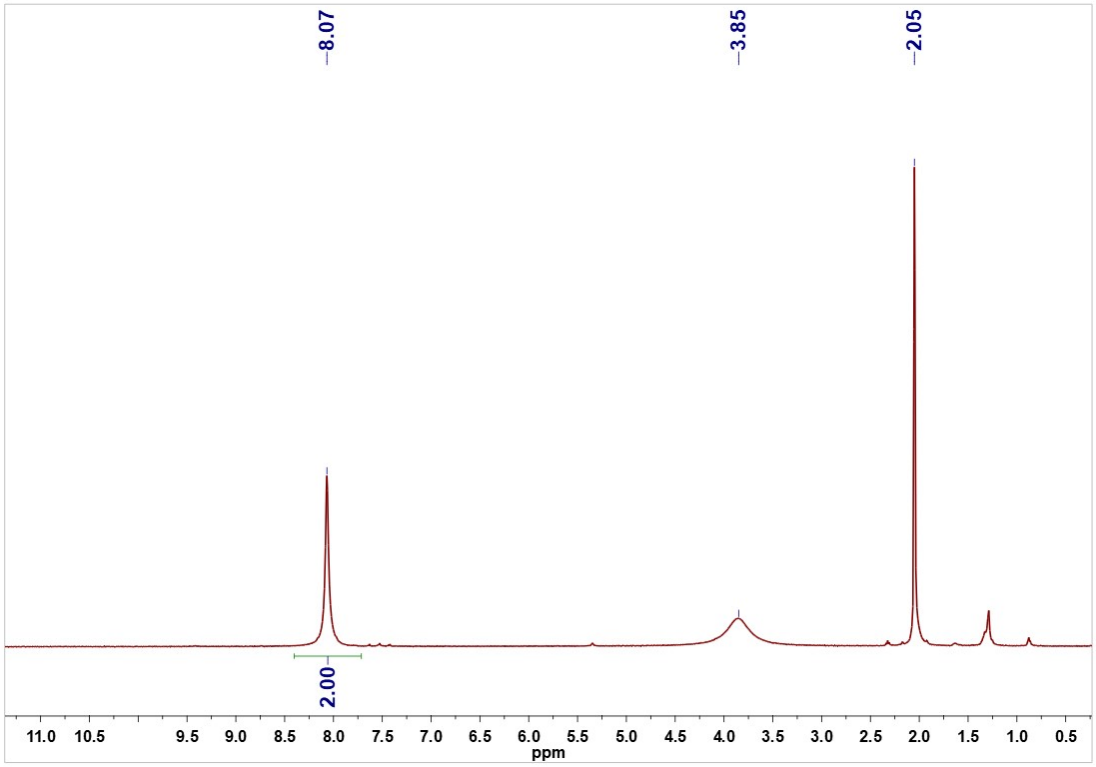


Fig. S17 ^{1}H NMR spectrum of **13** in d_6-Acetone.

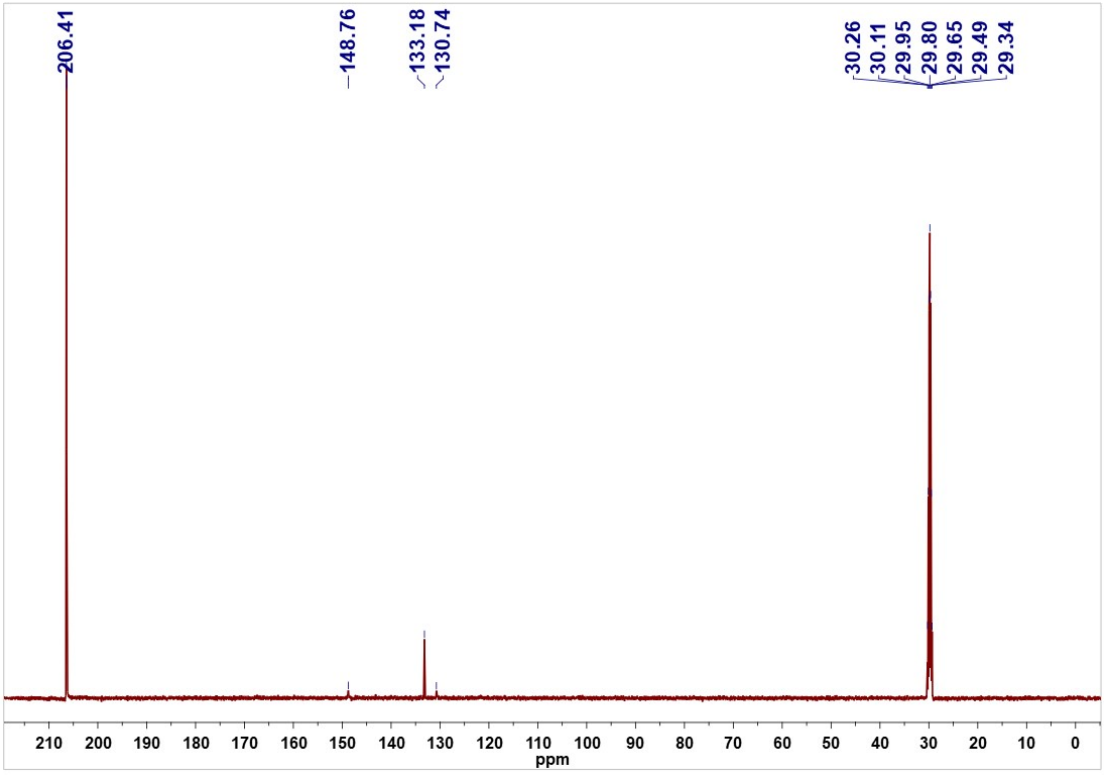


Fig. S18 ^{13}C NMR spectrum of **13** in d_6-Acetone.

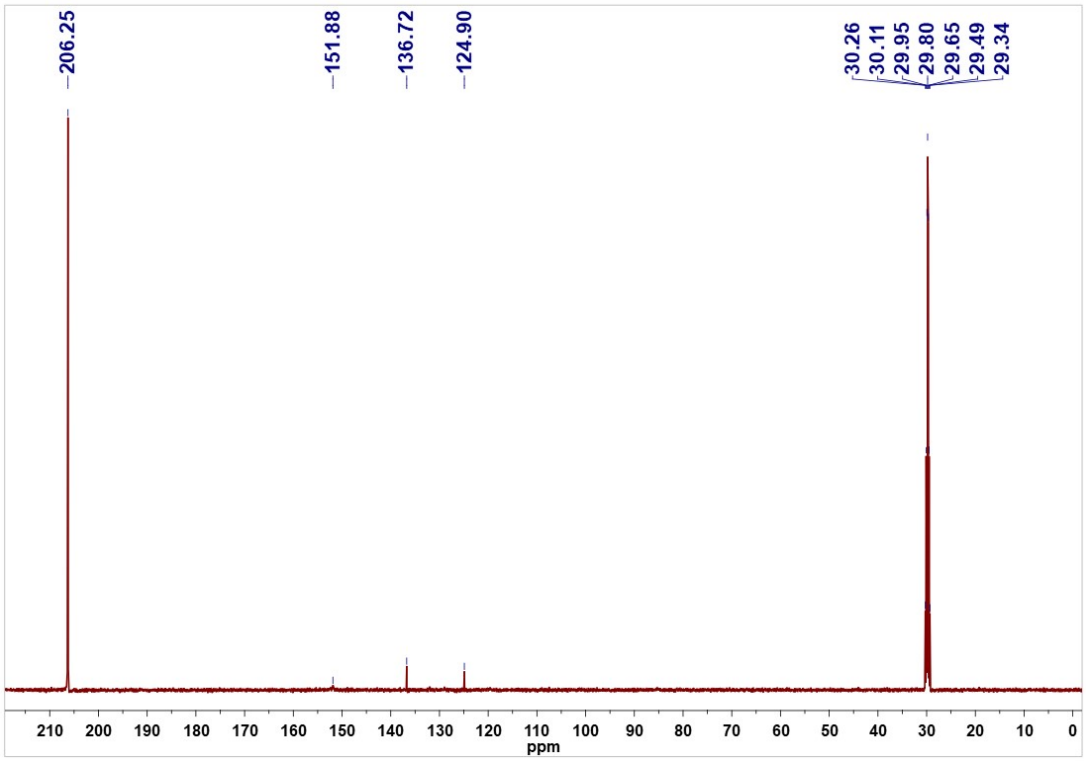


Fig. S19 ^{13}C NMR spectrum of **14** in d_6-Acetone.

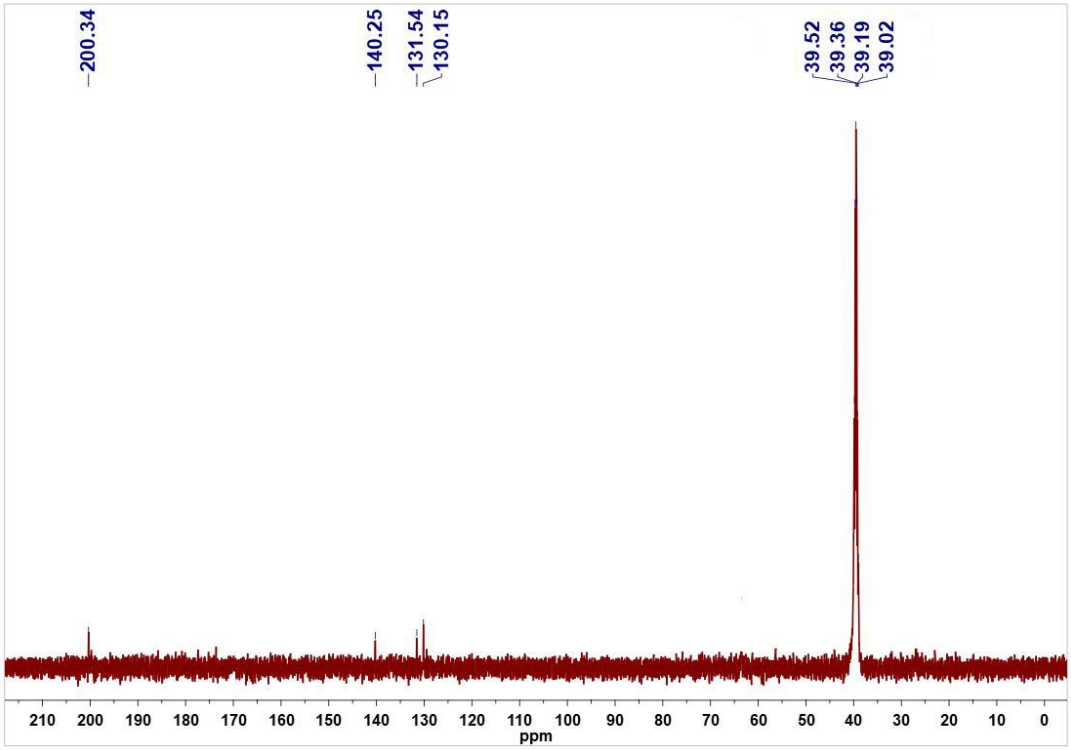


Fig. S20 ^{13}C NMR spectrum of **15** in d_6-DMSO.

11.IR spectra

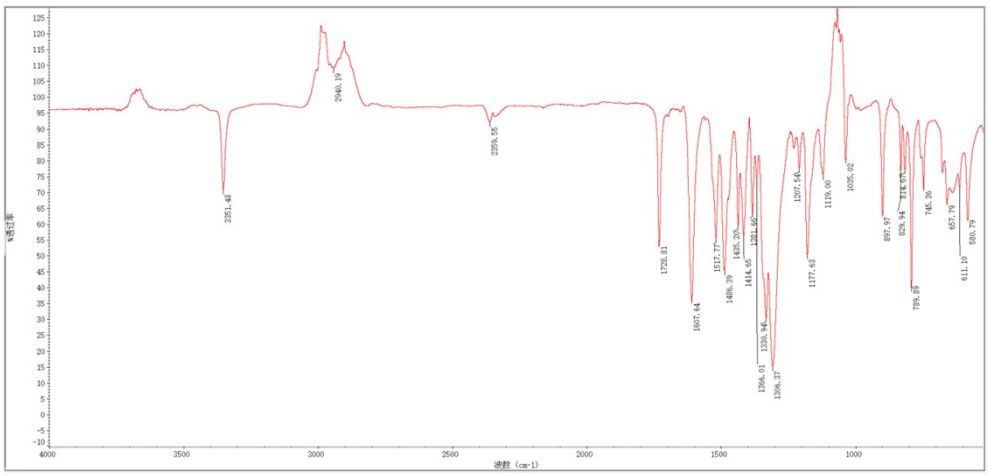


Fig. S21 IR spectrum of **5**.

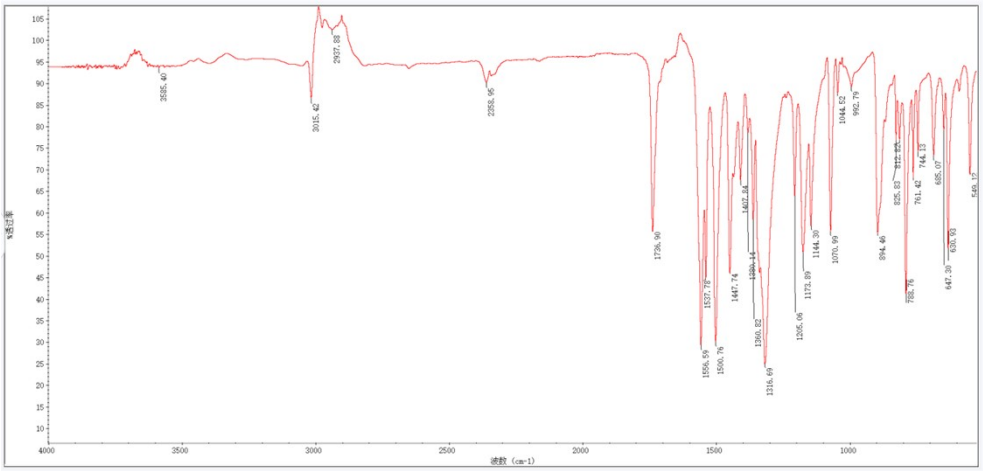


Fig. S22 IR spectrum of **6**.

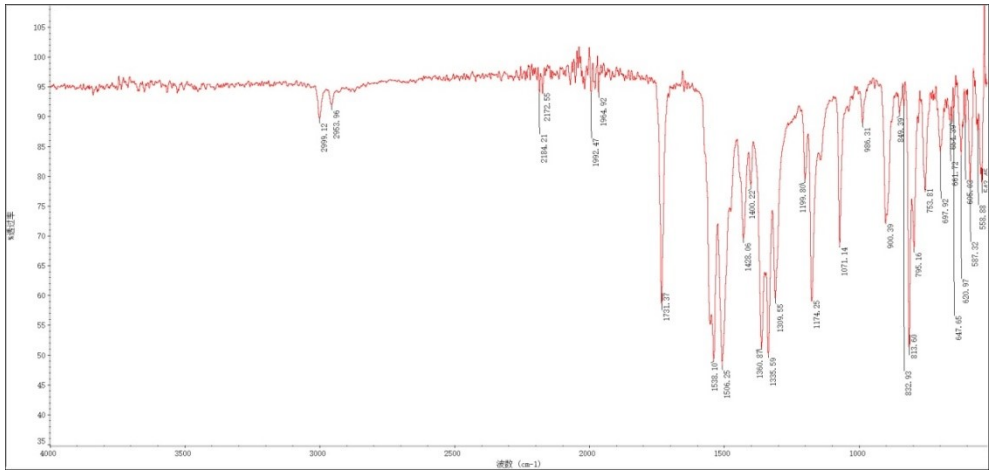


Fig. S23 IR spectrum of **8**.

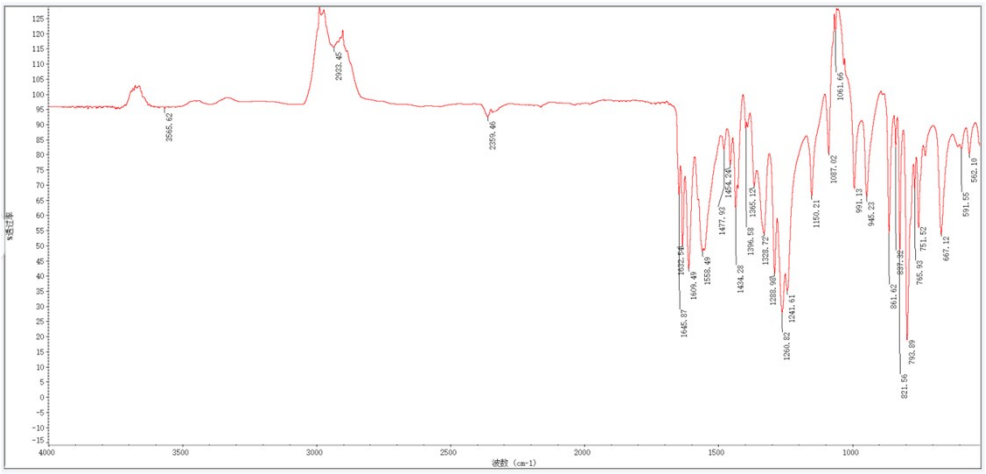


Fig. S24 IR spectrum of **10**.

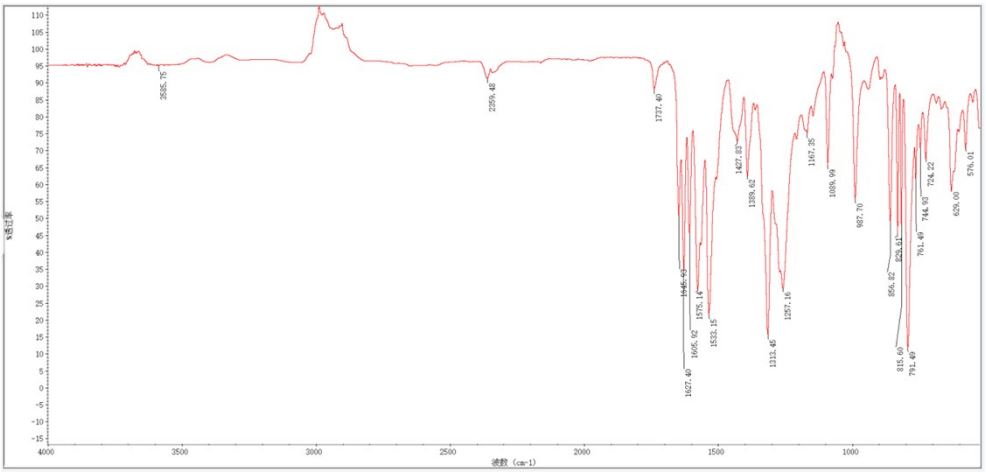


Fig. S25 IR spectrum of **11**.

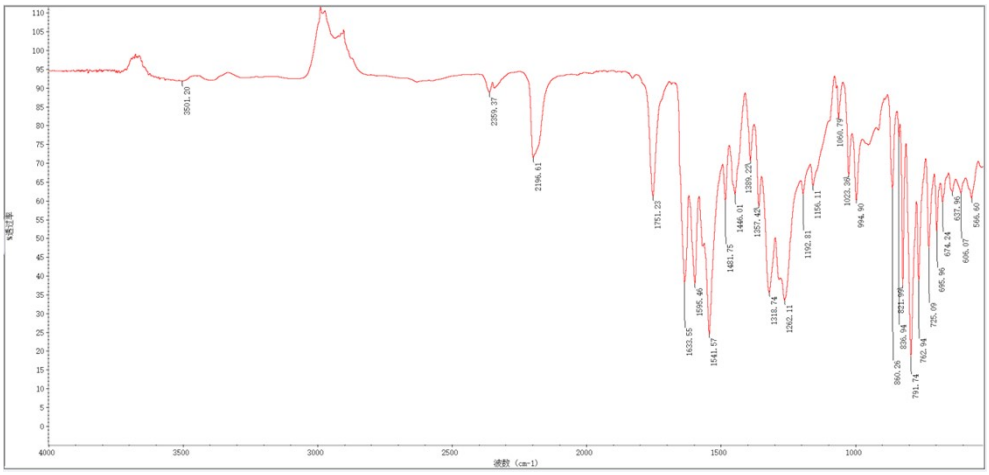


Fig. S26 IR spectrum of **12**.

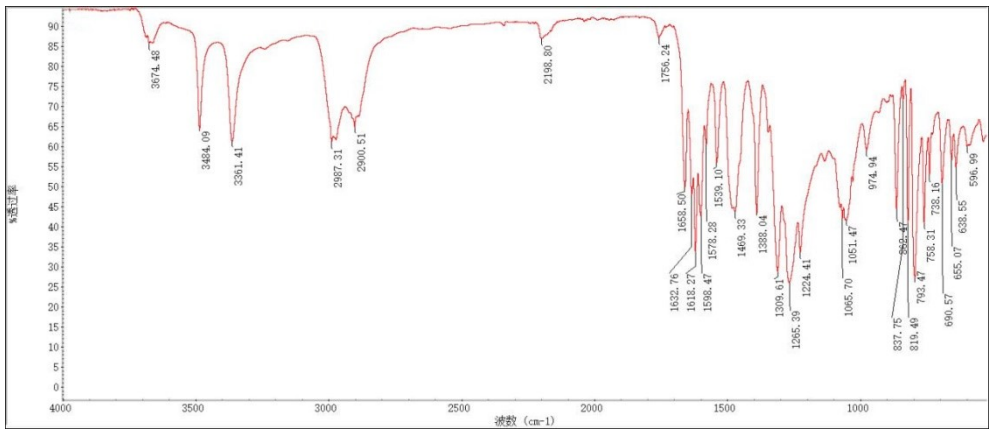


Fig. S27 IR spectrum of **13**.

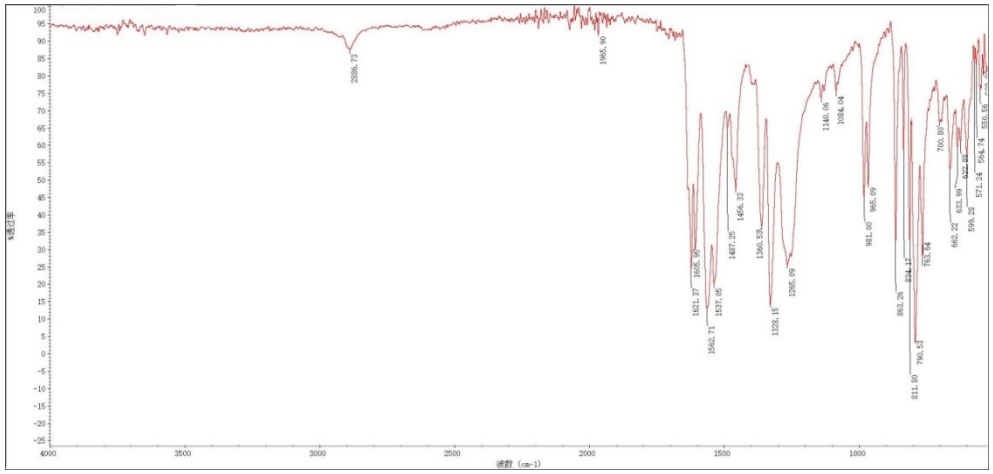


Fig. S28 IR spectrum of **14**.

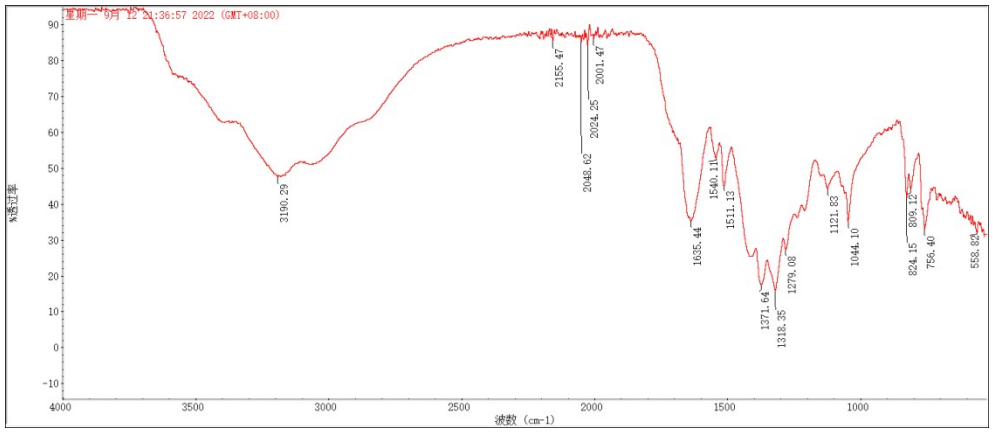


Fig. S29 IR spectrum of **15**.

12.General methods

12.1 Calculation details

All of the *ab initio* calculations involved in this work were carried out using the Gaussian 09 suite of programs.[1] The geometric optimization and frequency analyses of the structures are based on available single-crystal structures 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. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibration frequencies analysis.

An isodesmic reaction processes is designed to screen the values of heat of formation for gas. So heats of formation of molecules can be given in terms of eq (1)[2]:

$$R(NO_2)_n + nCH_4 \rightarrow RH_n + nCH_3NO_2 \quad (1)$$

According to Hess' law of constant heat summation condensed-phase heats of formation can be determined.[3]

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

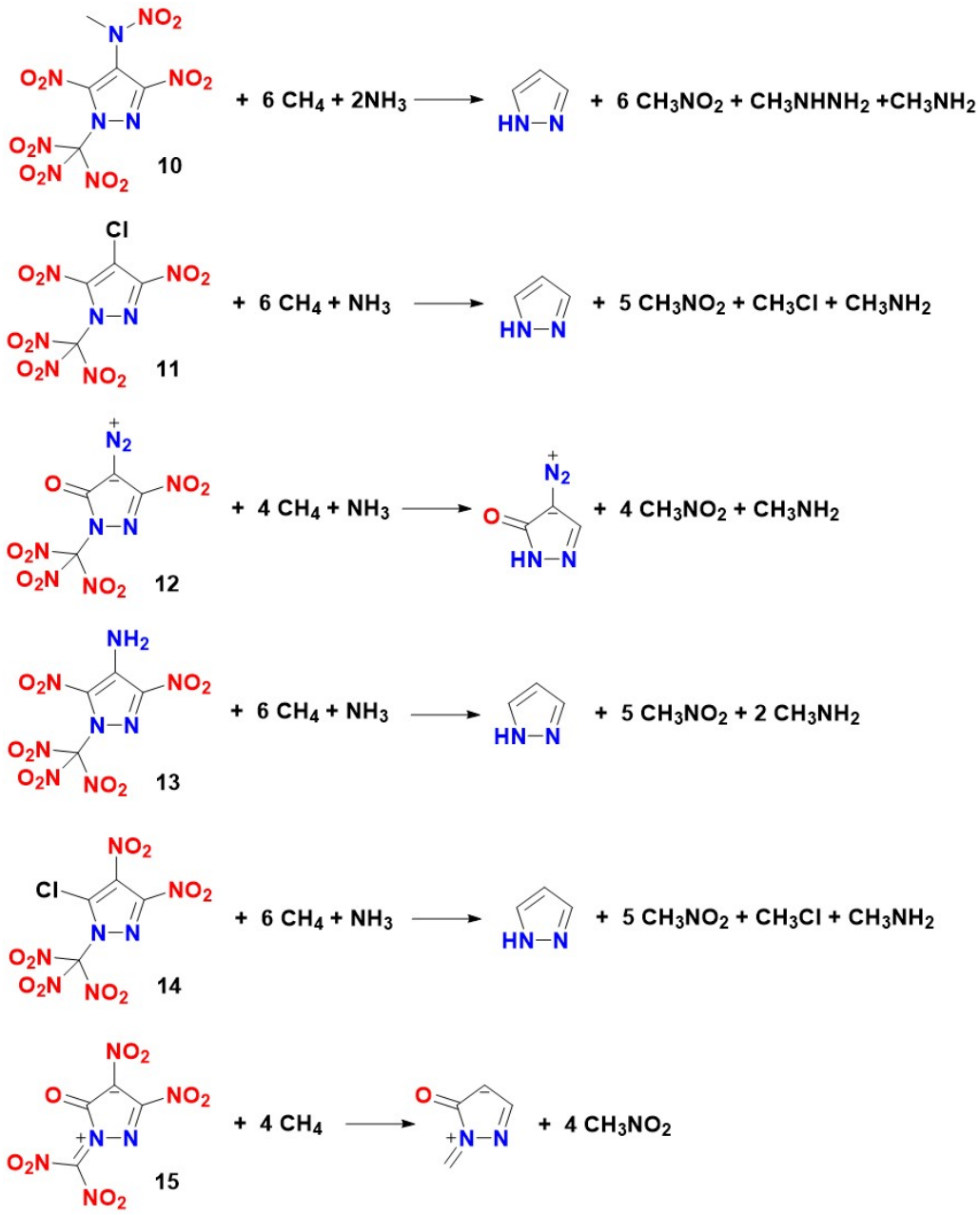
The enthalpy of sublimation can be represented as eq (3) and on the basis of the predicted electrostatic potential of a molecule.[4]

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

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.[4a]

Table S37. *Ab* initio computational values of 10-15

Comp.	E_0/ a.u.	ZPE/ kJ mol^{-1}	H_T/ kJ mol^{-1}	ΔH(gas)/ kJ mol^{-1}	ΔH(sublimation)/ kJ mol^{-1}	ΔH(solid)/ kJ mol^{-1}
10	-1587.106971	398.52	65.57	734.11	217.44	516.67
11	-1747.538475	253.64	54.25	631.80	174.33	457.47
12	-1266.951699	248.28	51.38	645.93	166.18	479.75
13	-1343.343292	323.10	53.99	559.24	169.32	389.92
14	-1747.537170	253.16	54.87	635.37	178.99	456.38
15	-1157.444710	218.59	49.07	543.69	157.14	386.55



Scheme S1. Isodesmic reactions for **10**-**15**.

12.2 Caution!

Although we have not encountered any difficulties in preparing these new energetic materials, manipulations must be carried out by using standard safety precaution. Leather coat, ear protection, latex gloves, and face shield are strongly recommended for the experimental operation. All compounds should be handled with extreme care.

12.3 Characterization methods

All reagents and solvents were purchased from Energy Chemical, Sigma-Aldrich, and Aladdin as analytical grade and were used as received. ^{1}H and ^{13}C spectra were recorded using a 500 MHz (Bruker AVANCE III 500) nuclear magnetic resonance spectrometer

operating at 500 and 125.72 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si as external standard. DSC plots were acquired on a differential scanning calorimeter (NETZSCH DSC 204 F1 Phoenix) at a scan rate of 5 °C min^{-1} in perforated Al containers under a nitrogen flow of 60 mL min^{-1}. IR spectra were recorded on a Thermo Nicolet iS10 spectrometer equipped with a Thermo Scientific Smart iTR diamond ATR accessory. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. Densities were measured at 25 °C with a Micromeritics AccuPyc II 1345 gas pycnometer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

12.4 X-ray crystallography

The single-crystal X-ray diffraction measurements for all the compounds were conducted on a Bruker Smart Apex II or Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator at 150-296 K. An Oxford Cobra low-temperature device was used to maintain the low temperature. Integration and scaling of intensity data was accomplished using the SAINT program[5]. The structures were solved by intrinsic using SHELXT2015[6] and refinement was carried out by a full-matrix least-squares technique using SHELXL2015[7]. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS[8].

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