Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Nitramino-functionalized Tetracyclic Oxadiazoles as Energetic Materials with High Performance and High stability

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General Methods

All reagents were purchased from Energy Chemical of analytical grade and were used as supplied, if not stated otherwise. ^{1}H, ^{13}C spectra were recorded using a 500 MHz (Bruker AVANCE III 500) nuclear magnetic resonance spectrometer operating at 500 and 50.69 MHz, respectively. Chemical shifs in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si as external standards. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 ml min^{-1}. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer.

Safety Precautions

Although none of the energetic materials described herein have exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices.

Experimental section

N,N'-([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))dinitramide **(2)**. Compound **1** (3.04 g, 10 mmol) was added slowly in 95% HNO_3 (6 ml) at 0 °C. After 1 hour, the mixture was poured in ice water (200 ml) and the insoluble matter precipitates out. The precipitate was filtered to get compound **2** (2.88 g, yield: 73.0 %). Light yellow solids. T_d: 84 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 7.08 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.84, 159.74, 152.87, 141.94 ppm. IR (KBr): υ 3471, 2728, 1979, 1690, 1621, 1595, 1514, 1460, 1321, 1237, 1167, 1038, 977, 872, 800, 761, 679 cm^{-1}. Elemental analysis for $C_8H_2N_{12}O_8$ (394.18): calcd C 24.38, H 0.51, N 42.64%. Found: C 24.53, H 0.57, N 42.42%.

General methods for preparing compounds 3-14:

28% aqueous aqueous ammonia (1.20 g, 20 mmol), 98% hydrazine monohydrate (1.02 g, 20 mmol), 50% hydroxylamine solution (1.32 g, 20 mmol), 3,5-diamino-1,2,4-triazole (1.98 g, 20 mmol), guanidine carbonate (1.80 g, 10 mmol), aminoguanidine bicarbonate (2.68 g, 20 mmol), 4-amino-1,2,4-triazole (1.66 g, 20 mmol), 3-amino-1,2,4-triazole (1.66 g, 20 mmol), carbohydrazide (0.91 g, 10 mmol), 4-Amino-3-hydrazino-1,2,4-triazole (1.15 g, 10 mmol), sodium hydroxide (0.8 g, 20 mmol), and potassium hydroxide (1.12 g, 20 mmol) were added slowly into the **2** (3.94 g, 10 mmol) acetonitrile (20 ml) solution respectively. The precipitate was filtered to get energetic salts 3-14.

Diammonium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) **(3)**. Yellow solids (3.67 g, yield: 85.7%). T_d: 215 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 7.14 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.48, 160.67, 158.23, 141.36 ppm. IR (KBr): υ 3600, 3194, 1596, 1525, 1503, 1411, 1288, 1184, 1138, 1040, 971, 911, 820, 778, 767 cm^{-1}. Elemental analysis for $C_8H_8N_{14}O_8$ (428.24): calcd C 22.44, H 1.88, N 45.79%. Found: C 22.27, H 1.76, N 45.94%.

Dihydrazium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) **(4)**. Yellow solids (3.95 g, yield: 86.3%). T_d: 225 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 7.09 (br) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.45, 160.64, 158.04, 141.25 ppm. IR (KBr): υ 3184, 1595, 1526, 1501, 1431, 1365, 1283, 1176, 1136, 1039, 970, 911, 876, 820, 766, 737 cm^{-1}. Elemental analysis for $C_8H_{10}N_{16}O_8$ (458.27): calcd C 20.97, H 2.20, N 48.90%. Found: C 20.77, H 2.11, N 49.03%.

Dihydroxylammonium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) **(5)**. Yellow solids (3.83 g, yield: 82.9%). T_d: 187 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 9.98 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.44, 160.67, 158.21, 141.39 ppm. IR (KBr): υ 2952, 2725, 1599, 1525, 1503, 1433, 1391, 1284, 1176, 1136, 1010, 972, 918, 820, 766, 737 cm^{-1}. Elemental analysis for $C_8H_8N_{14}O_{10}$ (460.24): calcd C 20.88, H 1.75, N 42.61%. Found: C 20.73, H 1.61, N 42.74%.

Di(3,5-diamino-1,2,4-triazolium) ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl)) bis(nitroamide) **(6)**. Yellow solids (5.02 g, yield: 84.8%). T_d: 225 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 6.96 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.42, 160.69, 158.33, 151.25, 141.45 ppm. IR (KBr): υ 3293, 3159, 2756, 1694, 1651, 1595, 1524, 1415, 1384, 1303, 1175, 1018, 971, 914, 875, 767, 715 cm^{-1}. Elemental analysis for $C_{12}H_{12}N_{22}O_8$ (592.34): calcd C 24.33, H 2.04, N 52.02%. Found: C 24.46, H 1.98, N 51.93%.

Diguanidinium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) **(7)**. Yellow solids (4.19 g, yield: 81.9%). T_d: 263 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 6.97 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.43, 160.67, 158.20, 157.98, 141.42 ppm. IR (KBr): υ 3404, 3340, 3255, 3196, 1652, 1601, 1517,

1498, 1413, 1388, 1286, 1187, 1139, 1044, 970, 911, 819 cm^{-1}. Elemental analysis for $C_{10}H_{12}N_{18}O_8$ (512.32): calcd C 23.44, H 2.36, N 49.21%. Found: C 23.57, H 2.43, N 49.03%.

Di(aminoguanidinium) ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) **(8)**. Yellow solids (4.67 g, yield: 86.1%). T_d: 228 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 8.60 (s), 7.26 (s), 6.68 (s), 4.68 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.45, 160.59, 158.81, 158.31, 141.46 ppm. IR (KBr): υ 3446, 3308, 3202, 1662, 1588, 1525, 1497, 1425, 1290, 1171, 1132, 1040, 968, 920, 837, 819,766 cm^{-1}. Elemental analysis for $C_{10}H_{14}N_{20}O_8$ (542.35): calcd C 22.15, H 2.60, N 51.65%. Found: C 22.02, H 2.61, N 51.74%.

Di(4-amino-1,2,4-triazolium) ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) **(9)**. Yellow solids (4.73 g, yield: 84.2%). T_d: 221 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 9.50 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.48, 160.59, 157.75, 144.09, 141.42 ppm. IR (KBr): υ 3583, 3320, 3122, 3011, 1592, 1500, 1424, 1398, 1261, 1216, 1154, 963, 938, 863, 811, 767, 715 cm^{-1}. Elemental analysis for $C_{12}H_{10}N_{20}O_8$ (562.34): calcd C 25.63, H 1.79, N 49.82%. Found: C 25.51, H 1.72, N 50.01%.

Di(4-amino-1,2,4-triazolium) ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) **(10)**. Yellow solids (4.69 g, yield: 83.4%). T_d: 218 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 8.29 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.41, 160.70, 158.25, 150.84, 141.41, 139.35 ppm. IR (KBr): υ 3418, 3182, 2767, 1692, 1592, 1516, 1498, 1427, 1315, 1177, 1016, 969, 948, 910, 874, 840, 711 cm^{-1}. Elemental analysis for $C_{12}H_{10}N_{20}O_8$ (562.34): calcd C 25.63, H 1.79, N 49.82%. Found: C 25.46, H 1.71, N 49.96%.

Carbonic dihydrazidinium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis (nitroamide) **(11)**. Yellow solids (4.00 g, yield: 82.6%). T_d: 191 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 10.32 (s), 8.33 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.45, 160.62, 157.96, 156.78, 141.46 ppm. IR (KBr): υ 3501, 2950, 2743, 1755, 1591, 1564, 1523, 1434, 1289, 1173, 1137, 1014, 970, 920, 880, 827, 766 cm^{-1}. Elemental analysis for $C_9H_8N_{16}O_9$ (484.27): calcd C 22.32, H 1.67, N 46.28%. Found: C 22.27, H 1.71, N 46.43%.

4-Amino-3-hydrazino-1,2,4-triazolium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-iyl))bis(nitroamide) **(12)**. Yellow solids (4.34 g, yield: 85.4%). T_d: 198 °C. ^{1}H NMR (500 MHz, d6-DMSO): δ 9.81 (s) ppm. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.45, 160.79, 158.22, 152.70, 142.83, 141.38 ppm. IR (KBr): υ 3366, 3190, 1741, 1703, 1643, 1594, 1519, 1424, 1323, 1174, 1133, 1084, 1038, 970, 914, 826, 766 cm^{-1}. Elemental analysis for $C_{10}H_8N_{18}O_8$ (508.29): calcd C 23.63, H 1.59, N 49.60%. Found: C 23.51, H 1.64, N 49.75%.

Disodium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) **(13)**. Yellow solids (3.68 g, yield: 3.68%). T_d: 303 °C. ^{1}H NMR (500 MHz, d6-DMSO): No peak. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.42, 160.68, 158.23, 141.37 ppm. IR (KBr): υ 3508, 3367, 1677, 1593, 1519, 1499, 1435, 1344, 1312, 1178, 1138, 1042, 970, 916, 875, 823, 714 cm^{-1}. Elemental analysis for $C_8Na_2N_{12}O_8$ (438.14): calcd C 21.93, N 38.36%. Found: C 21.78, N 38.48%.

Dipotassium ([5,5'-bi(1,2,4-oxadiazole)]-3,3'-diylbis(1,2,5-oxadiazole-4,3-diyl))bis(nitroamide) **(14)**. Yellow solids (3.92 g, yield: 83.3%). T_d: 274 °C. ^{1}H NMR (500 MHz, d6-DMSO): No peak. ^{13}C NMR (500 MHz, d6-DMSO): δ 163.49, 160.65, 158.11, 141.20 ppm. IR (KBr): υ 3448, 2183, 1595, 1499, 1429, 1384, 1287, 1173, 1132, 1037, 970, 911, 870, 815, 777, 740, 715 cm^{-1}. Elemental analysis for $C_8K_2N_{12}O_8$ (470.36): calcd C 20.43, N 35.74%. Found: C 20.59, N 35.56%.

X-ray crystallography detail

A colorless sheet crystal (**2**·2H_2O) of dimensions 0.35×0.21×0.03 mm^3, a light yellow sheet crystal (**5**) of dimensions 0.31×0.12×0.02 mm^3, and a light yellow column crystal (**6**·2H_2O) of dimensions 0.27×0.14×0.13 mm^3, a light yellow block crystal (**9**) of dimensions 0.20×0.18×0.17 mm^3, a light yellow plate crystal (**10**) of dimensions 0.22×0.17×0.08 mm^3, a yellow sheet crystal (**11**·H_2O) of dimensions 0.32×0.19×0.02 mm^3, and a light yellow needle crystal (**14**) of dimensions 0.15×0.08×0.05 mm^3 were mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 173 K. Corrections for Lorentz and polarization effects and for absorption (ψ scan) were applied. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares calculation on F2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically. All hydrogens were placed in calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they were attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations.

Table S1 Crystallographic data for **2**·2H_2O, **5**, **6**·2H_2O, and **9**.

Compound	**2**·2H_2O	**5**	**6**·2H_2O	**9**
Formula	$C_8H_2N_{12}O_8$·2H_2O	$C_8H_8N_{14}O_{10}$	$C_{12}H_{12}N_{22}O_8$·2H_2O	$C_{12}H_{10}N_{20}O_8$
M_w	430.25	460.28	628.47	562.40
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	P21/c	P21/c	P21/c
a [Å]	4.5145(4)	14.701(3)	7.0523(7)	8.0468(5)
b [Å]	12.0237(11)	4.1634(7)	19.0738(19)	16.0227(10)
c [Å]	28.870(3)	14.1870(19)	9.4159(12)	8.3828(4)
α[°]	90	90	90	90
β[°]	90	110.503(7)	111.758(4)	105.085(2)
γ[°]	90	90	90	90
V [$Å^3$]	1567.1(3)	813.3(2)	1176.3(2)	1043.56(10)
Z	4	2	2	2
T [K]	173	173	173	173
λ [Å]	0.71073	0.71073	0.71073	0.71073
P_{calcd} [g cm^{-3}]	1.822	1.880	1.774	1.790
μ [mm^{-1}]	0.167	0.171	0.154	0.153
F(000)	872	468	644	572
θ range[°]	2.82-25.13	2.96-24.37	3.16-25.32	2.91-25.34
Index ranges	-4 ≤ h ≤5	-17 ≤ h ≤ 17	-8 ≤ h ≤ 6	-9 ≤ h ≤ 9
	-14 ≤ k ≤ 14	-4 ≤ k ≤ 4	-22 ≤ k ≤ 22	-19 ≤ k ≤ 19
	-34 ≤ l ≤ 34	-17 ≤ l ≤ 14	-11 ≤ l ≤ 11	-9 ≤ l ≤ 10
Data/restraints/ parameters	1436/2/145	1451/7/157	2139/9/223	1882/1/190
GOF on F2	1.041	1.047	1.019	1.026
R[$F^2 > 2\sigma(F^2)$]	0.0431	0.0606	0.0562	0.0369
wR(F^2)	0.0991	0.1195	0.0909	0.0837

Table S2 Crystallographic data for **10**, **11**·H_2O, and **14**.

Compound	**10**	**11**·H_2O	**14**
Formula	$C_{12}H_{10}N_{20}O_8$	$C_9H_8N_{16}O_9 \cdot H_2O$	$C_8K_2N_{12}O_8$
M_w	562.40	502.33	470.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/c	P21/c	P-1
a [Å]	11.9711(12)	28.666(3)	4.7645(6)
b [Å]	6.8493(6)	4.5532(5)	6.9326(8)
c [Å]	13.2618(12)	14.0610(16)	12.4985(14)
α[°]	90	90	100.528(4)
β[°]	102.882(3)	95.658(4)	105.085(2)
γ[°]	90	90	108.417(4)
V [$Å^3$]	1060.02(17)	1826.3(3)	382.35(8)
Z	2	4	1
T [K]	173	173	173
λ [Å]	0.71073	0.71073	0.71073
P_{calcd} [g cm^{-3}]	1.762	1.827	2.043
μ [mm^{-1}]	0.150	0.164	0.703
F(000)	572	1024	234
θ range[°]	3.15-25.27	3.11-25.06	3.17-25.29
Index ranges	$-14 \le h \le 14$	$-34 \le h \le 31$	$-5 \le h \le 4$
	$-6 \le k \le 8$	$-4 \le k \le 5$	$-8 \le k \le 8$
	$-15 \le l \le 15$	$-16 \le l \le 16$	$-15 \le l \le 14$
Data/restraints /parameters	1920/0/193	1614/90/202	1381/0/136
GOF on F2	1.048	1.051	1.047
$R[F^2 > 2\sigma(F^2)]$	0.0453	0.0629	0.0419
$wR(F^2)$	0.0942	0.1414	0.0791

Crystal structures

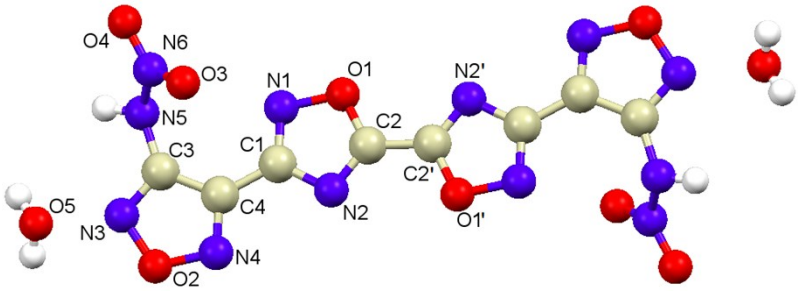


Figure S1 Crystal structures for **2**·2H_2O.

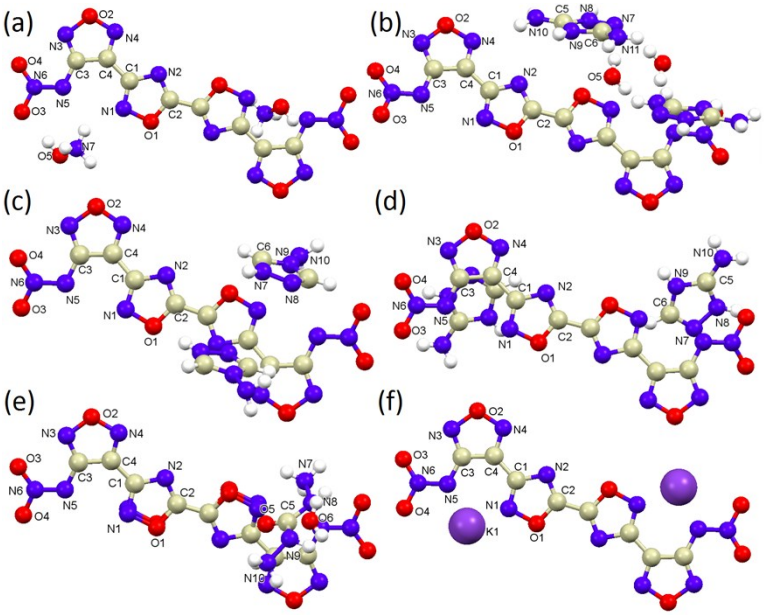


Figure S2 Crystal structures for **5**, **6**·2H_2O, **9**, **10**, **11**·H_2O, and **14**.

Hydrogen-bonding interactions

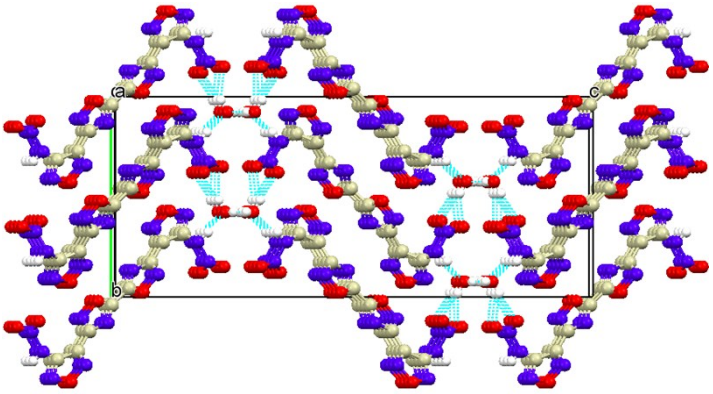


Figure S3 Hydrogen bonds for **2**·2H_2O.

Table S3 Hydrogen bonds for **2**·2H_2O.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O5-H5A···O3	0.826	2.017	2.843	176.69
N5'-H5'···O5	0.906	1.828	2.724	169.22
O5-H5B···O5'	0.823	1.908	2.730	177.33

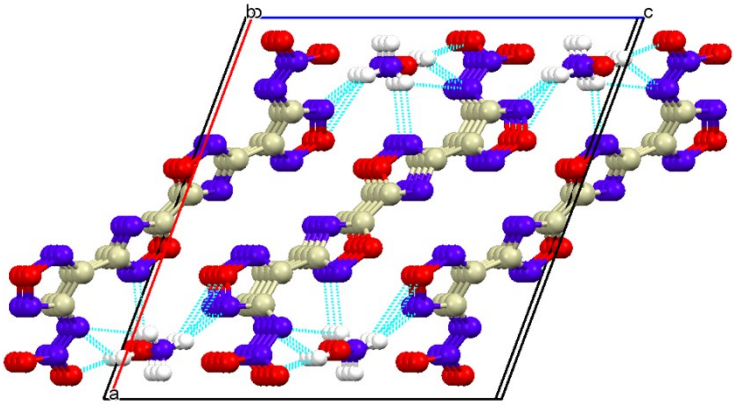


Figure S4 Hydrogen bonds for **5**.

Table S4 Hydrogen bonds for **5**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O5-H5···O3	0.826	1.849	2.674	178.10
N7-H7A···N1	0.920	2.302	3.078	141.88
N7-H7A···N5	0.920	2.407	3.079	129.92
N7-H7B···N3	0.915	2.019	2.898	160.43
N7'-H7C'···O3'	0.929	1.982	2.815	148.16

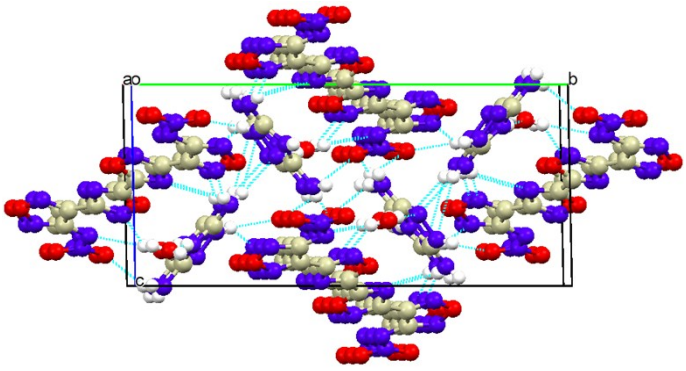


Figure S5 Hydrogen bonds for **6**·2H_2O.

Table S5 Hydrogen bonds for **6**·2H_2O.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
O5-H5C···N7	0.837	2.072	2.905	173.77
O5-H5D···N5	0.817	2.459	3.218	155.04
N10-H10A···N4	0.854	2.312	3.146	165.50
N10-H10B···N7'	0.846	2.229	3.018	155.20
N9-H9A···O5'	0.828	1.843	2.663	170.31
N11-H11A···O3'	0.844	2.235	2.889	134.34
N8-H8A···N3'	0.823	2.199	2.877	139.84
N8-H8A···O4'	0.823	2.197	2.867	138.62

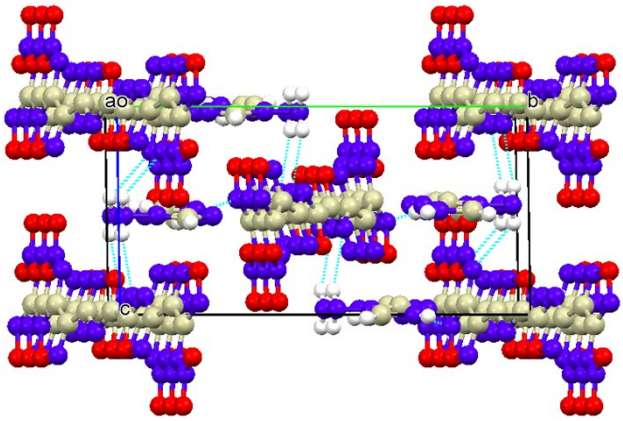


Figure S6 Hydrogen bonds for **9**.

Table S6 Hydrogen bonds for **9**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
N10-H10A···N2	0.886	2.465	3.208	141.74
N7-H7A···N3	0.831	2.184	3.012	174.25

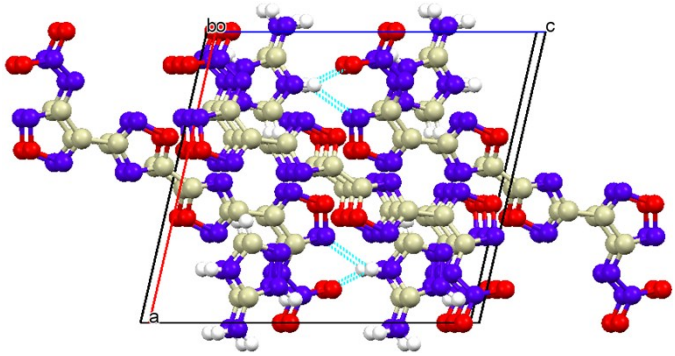


Figure S7 Hydrogen bonds for **10**.

Table S7 Hydrogen bonds for **10**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
N9-H9A···N3	0.825	2.275	2.974	142.73
N9-H9A···O4	0.825	2.149	2.856	143.82
N10'-H10A'···O4	0.876	2.128	2.892	145.49
N10'-H10B'···O3'	0.826	2.334	3.084	149.79
N10'-H10B'···N5'	0.826	2.296	3.039	149.79

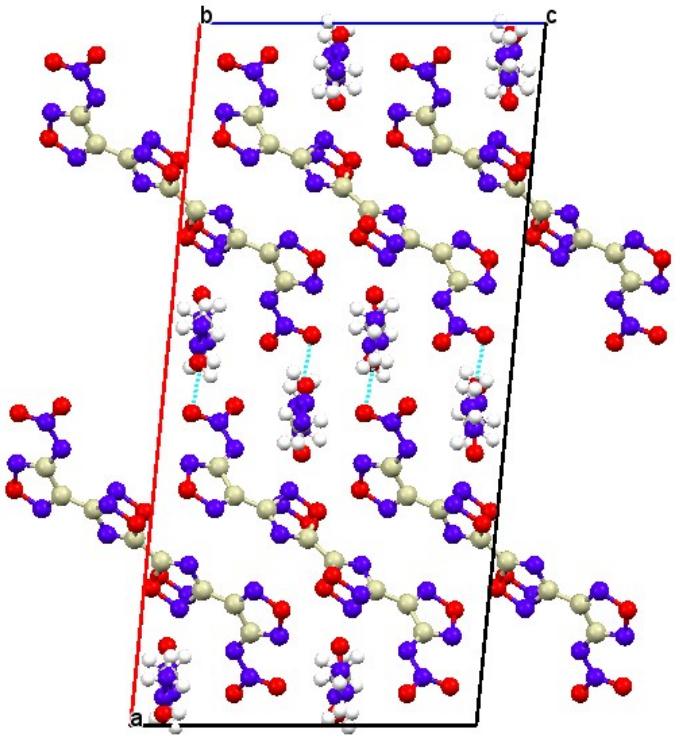


Figure S8 Hydrogen bonds for **11**·H_2O.

Table S8 Hydrogen bonds for **11**·H_2O.

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
N8-H8A···O3	0.846	2.260	3.087	165.76

Data for N5-N6 (N-NO_2)

Table S9 Bond-dissociation energies for N5-N6 in different compounds.

Compd	2	5	6	9	10	11	14
Value/kJ mol^{-1}	159.7	381.5	367.9	310.7	321.4	314.5	377.6

Table S10 Bond lengths for N5-N6 in different compounds.

Compd	2	5	6	9	10	11	14
Length/Å	1.390	1.324	1.328	1.336	1.311	1.312	1.321

Table S11 Torsion angles N6-N5-C3-C4 for in different compounds.

Compd	2	5	6	9	10	11	14
Torsion angle/°	69.03	175.78	177.24	172.33	168.06	177.70	179.32

Bond lengths and angles

Table S12 Bond lengths (Å) and bond angles (°) for **2**·2H_2O.

C1 N1 1.306(3)	C3 N3 1.302(3)	N4 O2 1.384(2)
C1 N2 1.377(3)	C3 N5 1.397(3)	N5 N6 1.390(3)
C1 C4 1.457(3)	C3 C4 1.433(3)	N5 H5 0.91(3)
C2 N2 1.288(3)	C4 N4 1.298(3)	N6 O4 1.212(3)
C2 O1 1.340(3)	N1 O1 1.404(2)	N6 O3 1.223(3)
C2 C2 1.459(4)	N3 O2 1.373(3)	O5 H5A 0.826(16)
O5 H5B 0.823(17)		
N1 C1 N2 115.5(2)	N4 C4 C1 122.0(2)	C3 N5 H5 117.5(17)
N1 C1 C4 120.6(2)	C3 C4 C1 129.6(2)	O4 N6 O3 126.9(2)
N2 C1 C4 124.0(2)	C1 N1 O1 103.16(18)	O4 N6 N5 115.6(2)
N2 C2 O1 115.4(2)	C2 N2 C1 100.7(2)	O3 N6 N5 117.5(2)
N2 C2 C2 128.1(3)	C3 N3 O2 105.37(18)	C2 O1 N1 105.24(17)
O1 C2 C2 116.5(3)	C4 N4 O2 105.81(19)	N3 O2 N4 111.07(16)
N3 C3 N5 120.7(2)	N6 N5 C3 116.1(2)	H5A O5 H5B 109(3)
N3 C3 C4 109.3(2)	N6 N5 H5 109.1(16)	N4 C4 C3 108.4(2)
N5 C3 C4 129.8(2)		

Table S13 Bond lengths (Å) and bond angles (°) for **5**.

C1 N1 1.307(5)	C3 N5 1.374(5)	N6 O4 1.245(4)
C1 N2 1.385(5)	C3 C4 1.435(6)	N6 O3 1.286(4)
C1 C4 1.458(5)	C4 N4 1.299(5)	N7 O5 1.409(5)
C2 N2 1.290(5)	N1 O1 1.408(4)	N7 H7A 0.92(2)
C2 O1 1.340(5)	N3 O2 1.402(4)	N7 H7B 0.92(2)
C2 C2 1.452(7)	N4 O2 1.369(4)	N7 H7C 0.93(2)
C3 N3 1.315(5)	N5 N6 1.324(4)	O5 H5 0.826(19)
N1 C1 N2 115.0(3)	N4 C4 C1 118.7(4)	O5 N7 H7A 107(2)
N1 C1 C4 122.8(3)	C3 C4 C1 131.0(4)	O5 N7 H7B 107(3)
N2 C1 C4 122.2(4)	C1 N1 O1 103.4(3)	H7A N7 H7B 111(2)
N2 C2 O1 115.3(3)	C2 N2 C1 100.9(3)	O5 N7 H7C 113(2)
N2 C2 C2 127.3(5)	C3 N3 O2 105.0(3)	H7A N7 H7C 109(2)
O1 C2 C2 117.3(5)	C4 N4 O2 105.2(3)	H7B N7 H7C 110(2)
N3 C3 N5 131.3(4)	N6 N5 C3 115.9(3)	C2 O1 N1 105.3(3)
N3 C3 C4 108.0(4)	O4 N6 O3 119.3(3)	N4 O2 N3 111.5(3)
N5 C3 C4 120.8(3)	O4 N6 N5 125.1(3)	N7 O5 H5 101(4)
N4 C4 C3 110.3(4)	O3 N6 N5 115.6(3)	

Table S14 Bond lengths (Å) and bond angles (°) for **6**·2H_2O.

C1 N1 1.309(3)	C5 N8 1.321(3)	N6 O4 1.240(2)
C1 N2 1.378(3)	C5 N10 1.326(3)	N6 O3 1.259(3)

C1 C4 1.459(3)	C5 N9 1.345(3)	N7 N8 1.405(3)
C2 N2 1.289(3)	C6 N7 1.305(3)	N8 H8A 0.82(2)
C2 O1 1.341(3)	C6 N11 1.348(3)	N9 H9A 0.83(2)
C2 C2 1.455(5)	C6 N9 1.368(3)	N10 H10A 0.854(17)
C3 N3 1.316(3)	N1 O1 1.408(3)	N10 H10B 0.846(18)
C3 N5 1.376(3)	N3 O2 1.402(3)	N11 H11A 0.844(17)
C3 C4 1.441(3)	N4 O2 1.371(3)	N11 H11B 0.856(18)
C4 N4 1.300(3)	N5 N6 1.328(3)	O5 H5C 0.837(18)
O5 H5D 0.817(17)		
N1 C1 N2 115.4(2)	N8 C5 N10 126.4(2)	O3 N6 N5 115.48(19)
N1 C1 C4 123.4(2)	N8 C5 N9 106.8(2)	C6 N7 N8 103.24(19)
N2 C1 C4 121.2(2)	N10 C5 N9 126.8(2)	C5 N8 N7 111.0(2)
N2 C2 O1 115.0(2)	N7 C6 N11 125.1(2)	C5 N8 H8A 126.7(19)
N2 C2 C2 127.4(3)	N7 C6 N9 112.0(2)	N7 N8 H8A 117.5(19)
O1 C2 C2 117.6(3)	N11 C6 N9 122.8(2)	C5 N9 C6 106.9(2)
N3 C3 N5 131.4(2)	C1 N1 O1 102.92(18)	C5 N9 H9A 124.9(18)
N3 C3 C4 107.6(2)	C2 N2 C1 101.1(2)	C6 N9 H9A 128.2(18)
N5 C3 C4 121.0(2)	C3 N3 O2 105.81(19)	C5 N10 H10A 120.4(18)
N4 C4 C3 109.9(2)	C4 N4 O2 105.94(19)	C5 N10 H10B 117.8(19)
N4 C4 C1 119.0(2)	N6 N5 C3 115.34(19)	H10A N10 H10B 117(3)
C3 C4 C1 131.0(2)	O4 N6 O3 120.5(2)	C6 N11 H11A 116.9(18)
C2 O1 N1 105.56(17)	O4 N6 N5 124.0(2)	C6 N11 H11B 115.7(19)
N4 O2 N3 110.74(17)	H5C O5 H5D 108(3)	H11A N11 H11B 122(3)

Table S15 Bond lengths (Å) and bond angles (°) for **9**.

C1 N1 1.302(2)	C4 N4 1.299(2)	N4 O2 1.371(2)
C1 N2 1.381(2)	C5 N8 1.298(3)	N5 N6 1.336(2)
C1 C4 1.460(3)	C5 N9 1.359(3)	N6 O4 1.249(2)
C2 N2 1.291(2)	C5 H5 0.9500	N6 O3 1.251(2)
C2 O1 1.336(2)	C6 N7 1.302(3)	N7 N8 1.371(2)
C2 C2 1.454(4)	C6 N9 1.330(2)	N7 H7A 0.831(16)
C3 N3 1.320(2)	C6 H6 0.9500	N9 N10 1.409(2)
C3 N5 1.373(2)	N1 O1 1.4093(19)	N10 H10A 0.89(2)
C3 C4 1.440(2)	N3 O2 1.410(2)	N10 H10B 0.89(2)
N1 C1 N2 115.08(16)	N8 C5 H5 124.5	O3 N6 N5 115.43(15)
N1 C1 C4 121.93(16)	N9 C5 H5 124.5	C6 N7 N8 112.06(17)
N2 C1 C4 122.99(15)	N7 C6 N9 106.22(17)	C6 N7 H7A 129.0(16)
N2 C2 O1 115.27(16)	N7 C6 H6 126.9	N8 N7 H7A 118.9(16)
N2 C2 C2 128.1(2)	N9 C6 H6 126.9	C5 N8 N7 103.53(17)
O1 C2 C2 116.6(2)	C1 N1 O1 103.45(13)	C6 N9 C5 107.23(16)
N3 C3 N5 132.20(17)	C2 N2 C1 101.01(15)	C6 N9 N10 123.78(16)
N3 C3 C4 107.98(16)	C3 N3 O2 104.89(14)	C5 N9 N10 128.96(16)

N5 C3 C4 119.75(16)	C4 N4 O2 105.62(14)	N9 N10 H10A 109.0(14)
N4 C4 C3 110.16(16)	N6 N5 C3 115.50(15)	N9 N10 H10B 106.9(14)
N4 C4 C1 120.66(16)	O4 N6 O3 121.42(15)	H10A N10 H10B 105(2)
C3 C4 C1 129.15(16)	O4 N6 N5 123.14(15)	N4 O2 N3 111.33(13)
N8 C5 N9 110.96(18)	C2 O1 N1 105.18(13)	

Table S16 Bond lengths (Å) and bond angles (°) for **10**.

C1 N1 1.305(3)	C5 N10 1.325(3)	N5 N6 1.311(3)
C1 N2 1.380(3)	C5 N8 1.328(3)	N6 O4 1.256(2)
C1 C4 1.470(3)	C5 N9 1.337(3)	N6 O3 1.271(3)
C2 N2 1.289(3)	C6 N7 1.292(3)	N7 N8 1.382(3)
C2 O1 1.336(3)	C6 N9 1.358(4)	N8 H8A 0.91(3)
C2 C2 1.465(5)	C6 H6 0.9500	N9 H9A 0.82(3)
C3 N3 1.313(3)	N1 O1 1.410(2)	N10 H10A 0.88(3)
C3 N5 1.374(3)	N3 O2 1.395(2)	N10 H10B 0.83(3)
C3 C4 1.434(3)	N4 O2 1.373(2)	C4 N4 1.301(3)
N1 C1 N2 115.4(2)	N10 C5 N9 127.6(3)	C5 N8 H8A 126.1(16)
N1 C1 C4 122.9(2)	N8 C5 N9 105.5(2)	N7 N8 H8A 121.7(16)
N2 C1 C4 121.7(2)	N7 C6 N9 112.4(3)	C5 N9 C6 107.2(2)
N2 C2 O1 115.2(2)	N7 C6 H6 123.8	C5 N9 H9A 125(2)
N2 C2 C2 128.3(3)	N9 C6 H6 123.8	C6 N9 H9A 128(2)
O1 C2 C2 116.5(3)	C1 N1 O1 102.90(18)	C5 N10 H10A 117(2)
N3 C3 N5 130.2(2)	C2 N2 C1 100.9(2)	C5 N10 H10B 120(2)
N3 C3 C4 107.9(2)	C3 N3 O2 105.48(18)	H10A N10 H10B 115(3)
N5 C3 C4 121.7(2)	C4 N4 O2 105.34(19)	C2 O1 N1 105.50(17)
N4 C4 C3 110.0(2)	N6 N5 C3 116.1(2)	N4 O2 N3 111.22(16)
N4 C4 C1 119.2(2)	O4 N6 O3 119.7(2)	C6 N7 N8 102.9(2)
C3 C4 C1 130.8(2)	O4 N6 N5 124.1(2)	C5 N8 N7 112.0(2)
N10 C5 N8 126.8(2)	O3 N6 N5 116.21(19)	

Table S17 Bond lengths (Å) and bond angles (°) for **11**·H_2O.

C1 N1 1.342(7)	N4 O2 1.369(4)	C5 N9 1.383(7)
C1 N1' 1.344(8)	N5 N6 1.312(4)	N8 N10 1.260(10)
C1 N2 1.352(4)	N6 O3 1.244(4)	N8 H8A 0.85(2)
C1 C4 1.452(5)	N6 O4 1.263(4)	N9 N10 1.426(10)
C2 N2 1.265(4)	O1 N1 1.401(8)	N9 N7 1.574(11)
C2 O1 1.357(7)	N7 N10 0.277(13)	N9 H9A 0.9001
C2 O1' 1.365(7)	N7 N8 1.424(10)	N10 N7 0.277(13)
C2 C2 1.447(7)	N7 N9 1.574(11)	N10 N8 1.260(10)
C3 N3 1.306(4)	N7 H7A 0.8999	N10 H10A 0.8999
C3 N5 1.376(4)	N7 H7B 0.9000	N10 H10B 0.9000
C3 C4 1.437(5)	N7 H7C 0.9002	N10 H10C 0.9000
C4 N4 1.295(4)	C5 O5 1.207(8)	O1' N1' 1.411(9)

N3 O2 1.399(4) O6 H6E 0.8500	C5 N8 1.367(7)	O6 H6D 0.8499
N1 C1 N2 112.8(4)	C2 O1 N1 106.0(5)	N8 C5 N9 113.7(6)
N1' C1 N2 111.8(4)	C1 N1 O1 102.0(5)	N10 N8 C5 119.6(6)
N1 C1 C4 120.2(4)	N10 N7 N8 49(4)	N10 N8 N7 9.6(7)
N1' C1 C4 119.9(4)	N10 N7 N9 53(4)	C5 N8 N7 111.4(6)
N2 C1 C4 124.4(3)	N8 N7 N9 101.2(6)	N10 N8 H8A 91(5)
N2 C2 O1 112.4(4)	N10 N7 H7A 140.2	C5 N8 H8A 138(5)
N2 C2 O1' 113.0(4)	N8 N7 H7A 112.9	N7 N8 H8A 101(5)
N2 C2 C2 130.4(4)	N9 N7 H7A 115.8	C5 N9 N10 108.9(5)
O1 C2 C2 115.3(5)	N10 N7 H7B 110.2	C5 N9 N7 99.9(5)
O1' C2 C2 114.2(5)	N8 N7 H7B 109.0	N10 N9 N7 9.0(6)
N3 C3 N5 131.1(3)	N9 N7 H7B 108.2	C5 N9 H9A 109.1
N3 C3 C4 108.7(3)	H7A N7 H7B 109.4	N10 N9 H9A 110.9
N5 C3 C4 120.2(3)	N10 N7 H7C 62.4	N7 N9 H9A 115.4
N4 C4 C3 109.4(3)	N8 N7 H7C 109.4	N7 N10 N8 121(4)
N4 C4 C1 120.7(3)	N9 N7 H7C 9.1	N7 N10 N9 118(4)
C3 C4 C1 129.8(3)	H7A N7 H7C 108.0	N8 N10 N9 119.1(7)
C2 N2 C1 103.4(3)	H7B N7 H7C 108.0	N7 N10 H10A 6.1
C3 N3 O2 104.8(3)	O5 C5 N8 122.8(5)	N8 N10 H10A 126.6
C4 N4 O2 105.8(3)	O5 C5 N9 123.5(5)	N9 N10 H10A 111.6
N6 N5 C3 117.3(3)	H10A N10 H10C 108.2	N7 N10 H10B 107.2
O3 N6 O4 120.3(3)	H10B N10 H10C 108.2	N8 N10 H10B 37.7
O3 N6 N5 124.1(3)	C2 O1' N1' 104.5(5)	N9 N10 H10B 110.6
O4 N6 N5 115.5(3)	C1 N1' O1' 102.9(5)	H10A N10 H10B 109.3
N4 O2 N3 111.3(2)	H6D O6 H6E 121.1	N7 N10 H10C 103.9
N9 N10 H10C 108.9	N8 N10 H10C 70.8	

Table S18 Bond lengths (Å) and bond angles (°) for **14**.

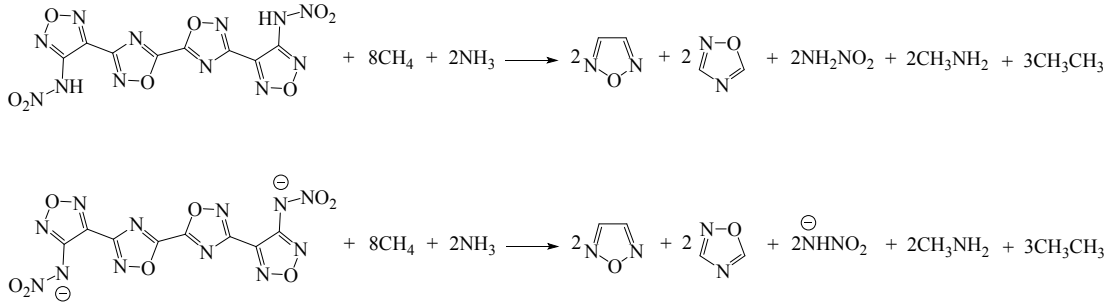
C1 N1 1.311(4)	K1 O4 2.665(3)	N3 O2 1.411(3)
C1 N2 1.380(4)	K1 O3 2.722(2)	N3 K1 2.859(3)
C1 C4 1.459(5)	K1 O3 2.766(2)	N4 O2 1.376(3)
C2 N2 1.289(4)	K1 N3 2.858(3)	N5 N6 1.321(4)
C2 O1 1.340(4)	K1 O2 2.857(3)	N6 O3 1.248(3)
C2 C2 1.465(6)	K1 N5 2.894(3)	N6 O4 1.266(3)
C3 N3 1.317(4)	K1 O4 2.970(2)	N6 K1 3.265(3)
C3 N5 1.378(4)	K1 N1 3.037(3)	O2 K1 2.857(3)
C3 C4 1.445(4)	K1 N6 3.265(3)	O3 K1 2.722(2)
C4 N4 1.305(4)	K1 O4 3.404(3)	O3 K1 2.766(2)
K1 K1 4.3682(17)	K1 N6 3.445(3)	O4 K1 2.665(3)
N1 O1 1.412(3)	O4 K1 2.970(2)	
N1 C1 N2 115.2(3)	O3 K1 N3 54.59(7)	O4 K1 N1 131.27(7)

N1 C1 C4 122.6(3)	O3 K1 N3 124.59(8)	O4 K1 N6 100.47(8)
N2 C1 C4 122.2(3)	O4 K1 O2 144.55(7)	O3 K1 N6 93.11(7)
N2 C2 O1 115.6(3)	O3 K1 O2 70.47(8)	O3 K1 N6 21.94(7)
N2 C2 C2 127.7(4)	O3 K1 O2 92.80(8)	N3 K1 N6 141.51(8)
O1 C2 C2 116.7(4)	N3 K1 O2 83.77(8)	O2 K1 N6 106.36(7)
N3 C3 N5 131.5(3)	O4 K1 N5 74.21(8)	N5 K1 N6 85.55(7)
N3 C3 C4 108.2(3)	O3 K1 N5 154.13(9)	O4 K1 N6 22.81(6)
N5 C3 C4 120.2(3)	O3 K1 N5 101.63(7)	N1 K1 N6 144.47(7) .
N4 C4 C3 110.1(3)	N3 K1 N5 132.80(8)	O4 K1 O4 102.78(7)
N4 C4 C1 119.6(3)	O2 K1 N5 85.09(8)	O3 K1 O4 122.32(7)
C3 C4 C1 130.3(3)	O4 K1 O4 78.50(7)	O3 K1 O4 63.63(6)
O4 K1 O3 131.16(8)	O3 K1 O4 112.39(7)	N3 K1 O4 159.23(8)
O4 K1 O3 119.08(8)	O3 K1 O4 44.39(7)	O2 K1 O4 76.50(7)
O3 K1 O3 72.14(8)	N3 K1 O4 146.77(8)	N5 K1 O4 39.78(6)
O4 K1 N3 89.51(8)	O2 K1 O4 123.21(7)	O4 K1 O4 53.55(8)
O3 N6 N5 124.1(3)	N5 K1 O4 73.69(7)	N1 K1 O4 92.37(7)
O4 N6 N5 116.1(3)	O4 K1 N1 76.94(8)	N6 K1 O4 53.14(6)
O3 N6 K1 55.93(15)	O3 K1 N1 115.53(8)	O4 K1 N6 82.79(7)
O4 N6 K1 65.43(15)	O3 K1 N1 152.73(9)	O3 K1 N6 143.61(8)
N5 N6 K1 167.8(2)	N3 K1 N1 73.94(8)	O3 K1 N6 79.86(7)
O3 N6 K1 139.5(2)	O2 K1 N1 67.74(8)	N3 K1 N6 154.57(8)
O4 N6 K1 77.49(16)	N5 K1 N1 59.41(7)	O2 K1 N6 88.55(7)
N5 N6 K1 54.84(15)	N6 K1 K1 62.09(5)	N5 K1 N6 21.90(6)
K1 N6 K1 116.09(8)	C1 N1 O1 103.2(2)	O4 K1 N6 54.85(6)
C2 O1 N1 105.1(2)	C1 N1 K1 118.0(2)	N1 K1 N6 80.71(7)
N4 O2 N3 111.7(2)	O1 N1 K1 117.83(18)	N6 K1 N6 63.91(8)
N4 O2 K1 114.68(18)	C2 N2 C1 100.9(3)	O4 K1 N6 21.30(6)
N3 O2 K1 107.28(17)	C3 N3 O2 104.8(2)	O4 K1 K1 41.79(5)
N6 O3 K1 145.3(2)	C3 N3 K1 133.4(2)	O3 K1 K1 131.34(6)
N6 O3 K1 102.12(18)	O2 N3 K1 117.74(17)	O3 K1 K1 79.08(6)
K1 O3 K1 107.86(8)	C4 N4 O2 105.1(3)	N3 K1 K1 124.31(7)
N6 O4 K1 159.4(2)	N6 N5 C3 116.2(3)	O2 K1 K1 150.40(6)
N6 O4 K1 91.76(17)	N6 N5 K1 103.26(18)	N5 K1 K1 69.08(6)
K1 O4 K1 101.50(7)	C3 N5 K1 119.7(2)	O4 K1 K1 36.71(5)
N6 O4 K1 81.21(16)	O3 N6 O4 119.8(3)	N1 K1 K1 108.10(6)
K1 O4 K1 102.78(7)	O4 K1 K1 74.39(5)	N6 K1 K1 58.94(5)
K1 O4 K1 126.45(8)		

Theoretical study

For organic compounds

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs. 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 were optimized with no constraints imposed under default convergence criteria. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibrational frequency analysis. The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

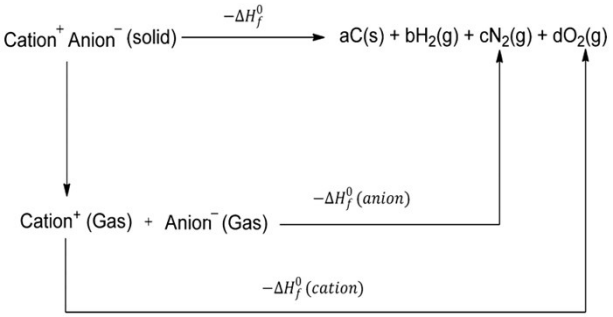


Scheme S1 Isodesmic reactions for calculating heats of formation for **2** and $\mathbf{2}^{2-}$.

Table S19 Enthalpies of the gas-phase species.

Compound	ΔH_f(kJ mol^{-1})
methane	-74.6
ammonia	-45.9
1,2,5-oxadiazole	196.78
1,2,4-oxadiazole	75
nitramide	-3.9
nitramide anion	-84.0
aminomethane	-22.5
ethane	-84

For energetic salt , the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S2). The number is simplified by equation 2:



Scheme S2 Born−Haber Cycle for the formation of energetic salts.

$$\Delta H_f(\text{salt, 298 K}) = \Delta H_f(\text{cation, 298K}) + \Delta H_f(\text{anion, 298K}) - \Delta H_L \quad (1)$$

in which ΔH_L can be predicted by using the formula suggested by Jenkins, et al.(equation 2):

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

In this equation, n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively.

The equation for lattice potential energy U_{pot}(equation 3) has the form:

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

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJmol^{-1}cm) and δ (kJmol^{-1}) are assigned literature values.

IR spectra

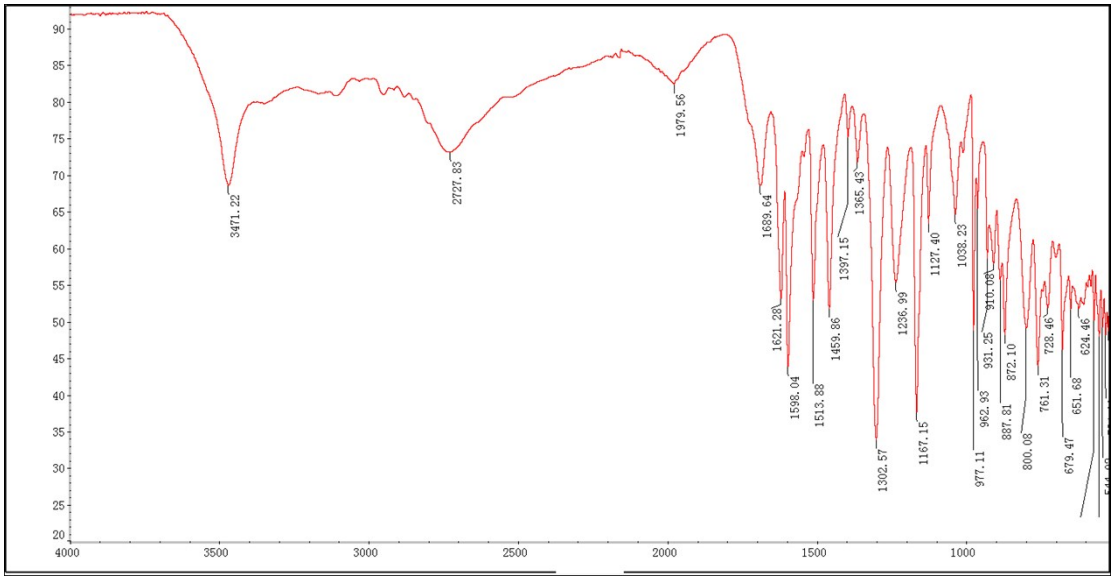


Figure S9 IR spectra for **2**.

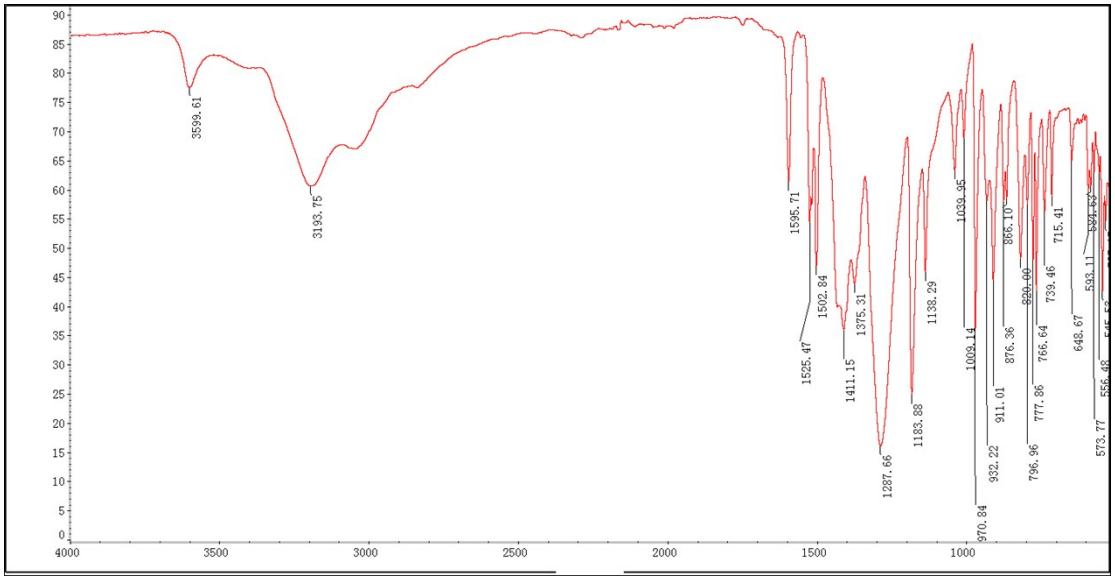


Figure S10 IR spectra for **3**.

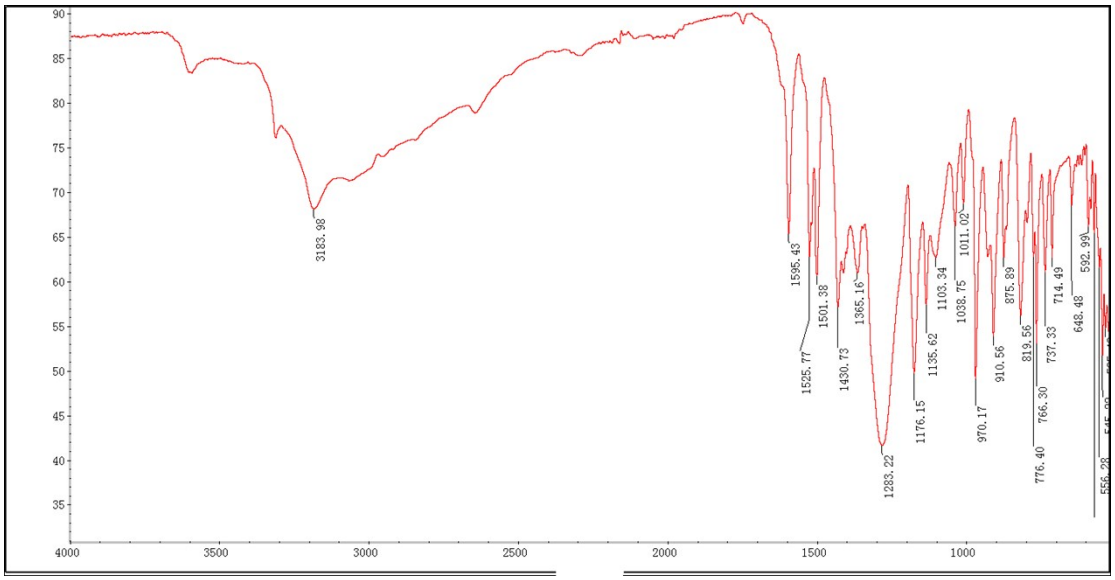


Figure S11 IR spectra for **4**.

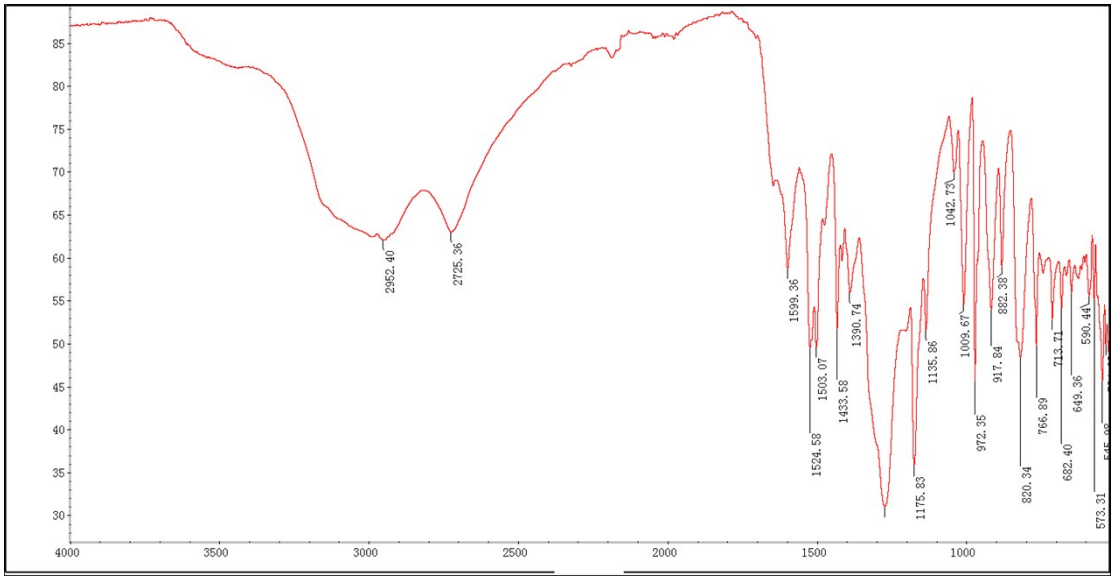


Figure S12 IR spectra for **5**.

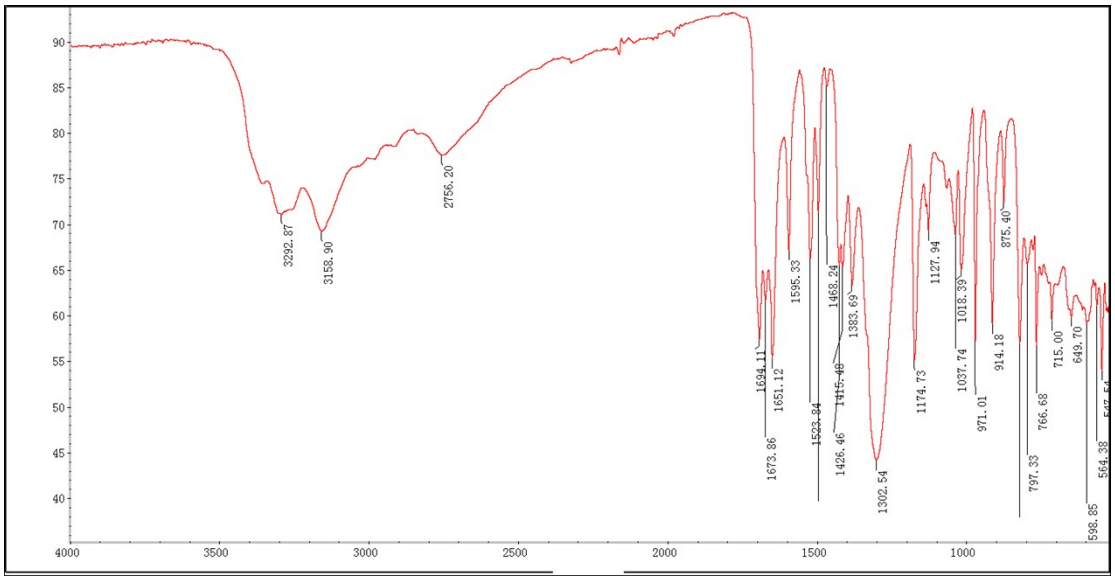


Figure S13 IR spectra for **6**.

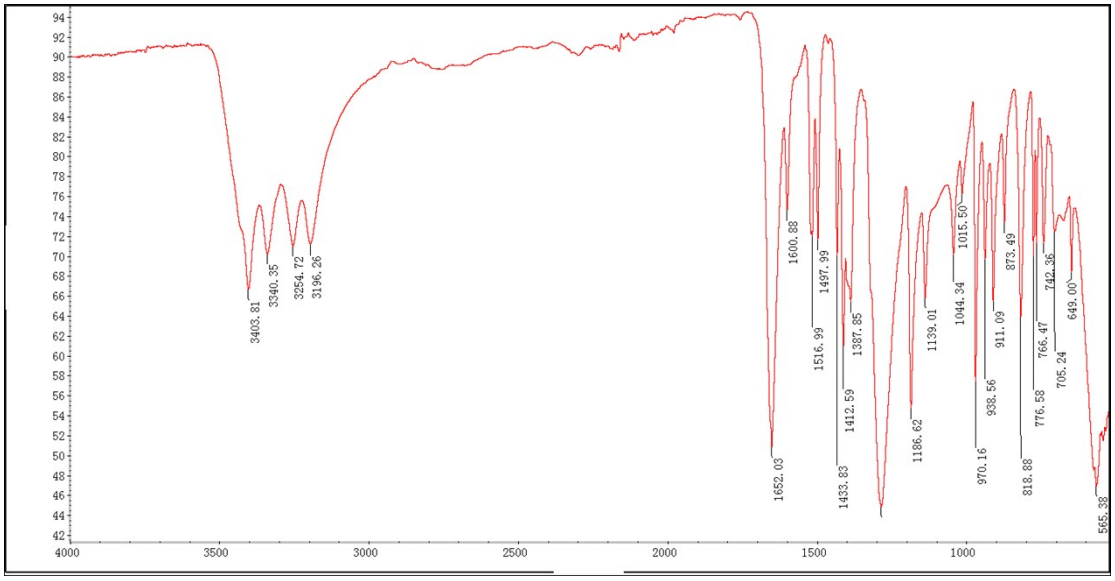


Figure S14 IR spectra for **7**.

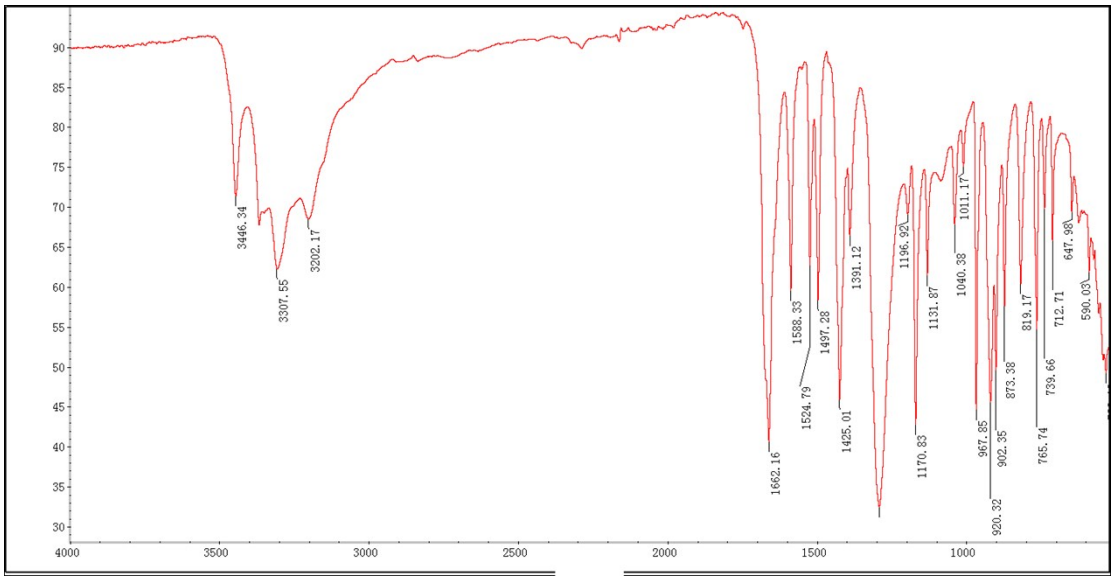


Figure S15 IR spectra for **8**.

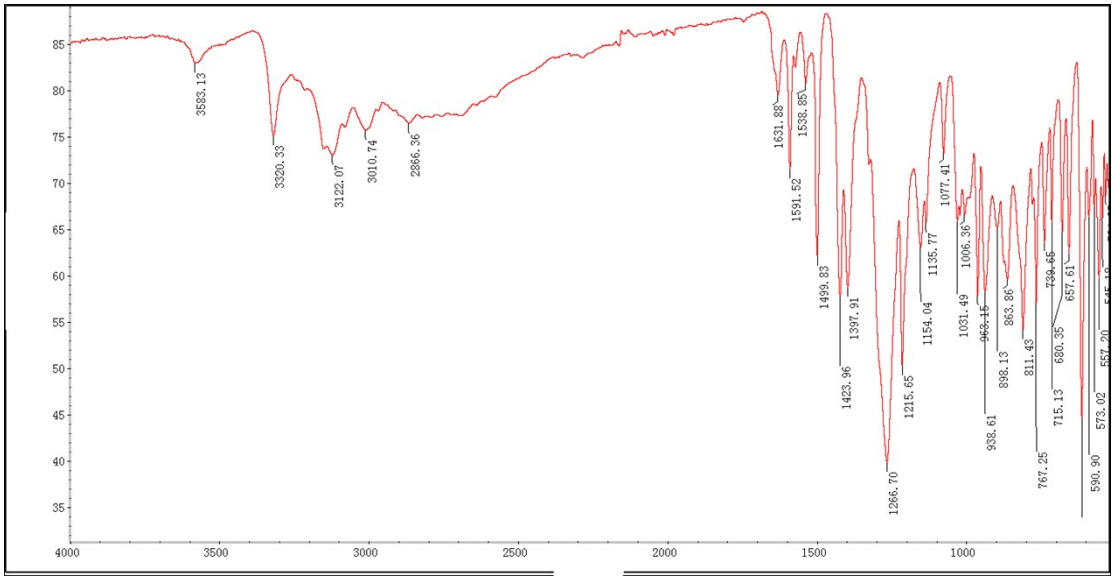


Figure S16 IR spectra for **9**.

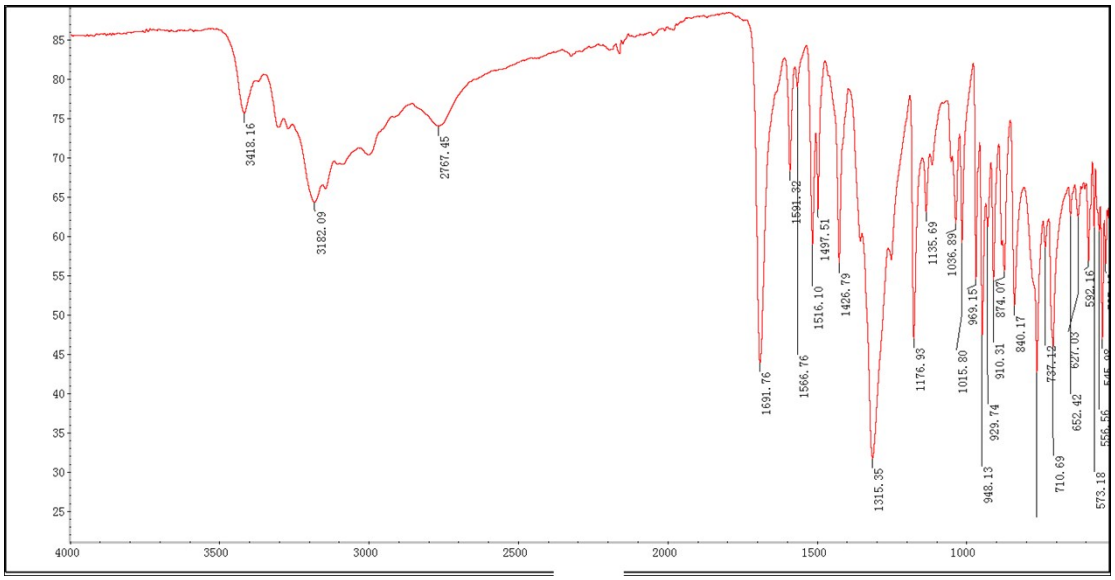


Figure S17 IR spectra for **10**.

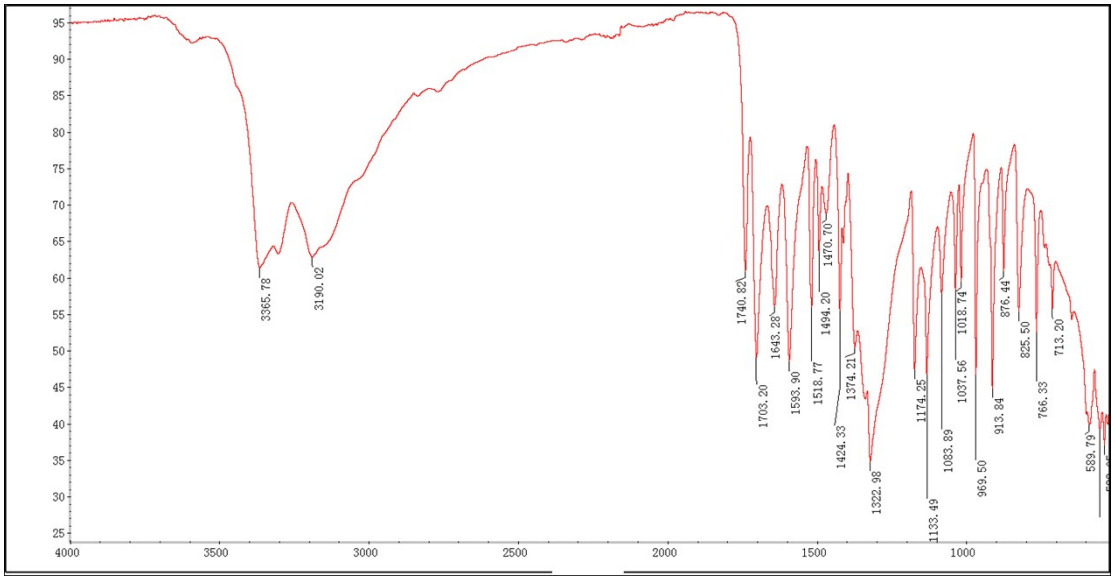


Figure S18 IR spectra for **11**.

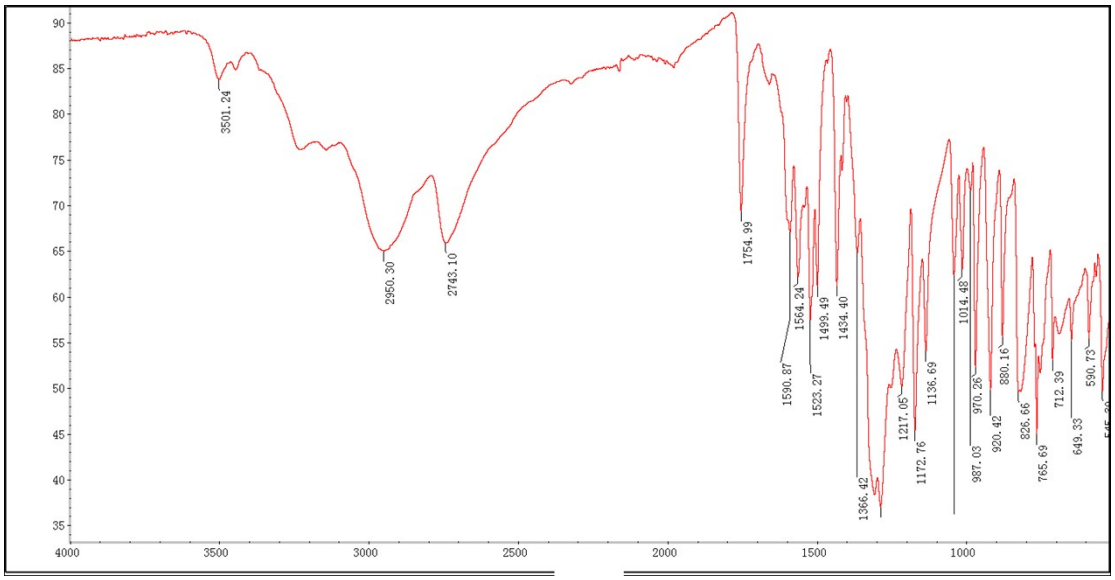


Figure S19 IR spectra for **12**.

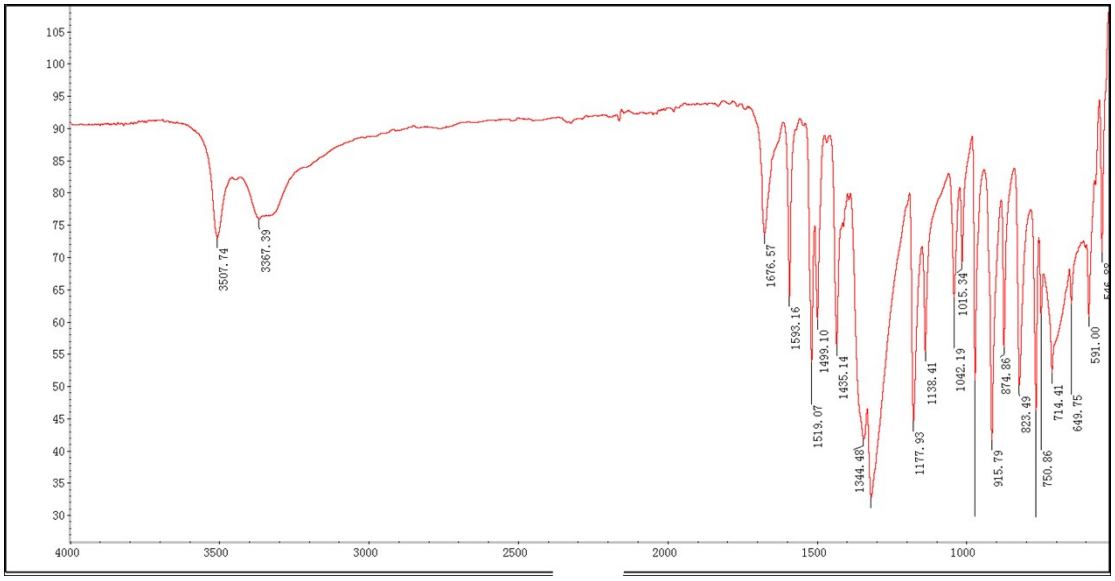


Figure S20 IR spectra for **13**.

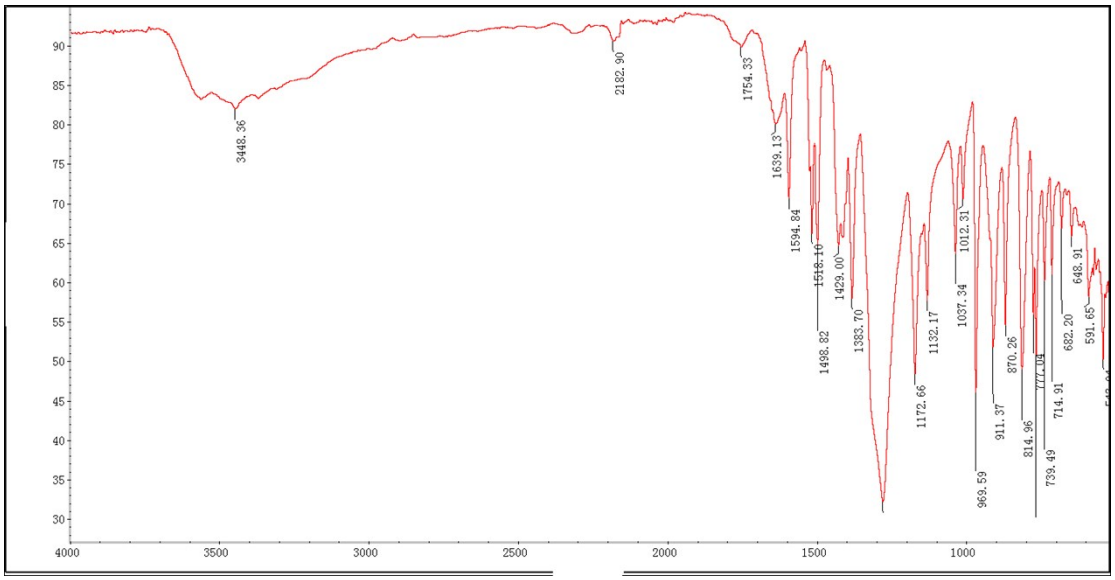


Figure S21 IR spectra for **14**.