Supporting Information

New green energetic materials based on monosubstituted pyrazole-tetrazine and perchlorates thereof

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Section 1. Materials and instrumentations

The chemicals and reagents were purchased commercially and were used as received without any further purification. Solvents were purified according to standard procedures. Elemental analysis (C, H, N) was performed with a Vario EL IIIFully-Automatic Trace Element Analyzer. Fourier Transform Infrared Spectroscopy (FT-IR) spectra was recorded on an IRPrestige-21 spectrometer using KBr pellets from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

DMPTzDATr(1). Yield 63%; **EA:** found (calc): C 39.56 (39.56), H 4.00 (4.03), N 56.42 (56.41); **IR** (**KBr,** cm^{-1}): ν= 3286, 3174, 3051, 2917, 1650, 1578, 1462, 1382, 1074, 1045, 955, 702, 564; **Mass spec:** 274.10 [$C_9H_{12}N_{11}^+$], 272.15[$C_9H_{12}N_{11}^-$].

PyrTzSCZ(2). Yield 73%; **EA:** found (calc): C 32.55 (32.58), H 3.14 (3.17), N 57.08 (57.01); **IR** (**KBr,** cm^{-1}): ν= 3395, 3189, 3145, 2979, 1679, 1538, 1476, 1400, 1191, 1035, 948, 799, 597, 546. **Mass spec:** 222.05 [$C_6H_8N_9O^+$], 220.10 [$C_6H_6N_9O^-$].

DMPTzDATrClO$_4$(3). Yield 89%; **EA:** found (calc): C 28.87 (28.92), H 3.28 (3.21), N 41.19 (41.23); **IR** (**KBr,** cm^{-1}): ν= 3575, 3351, 3122, 1615, 1532, 1500, 1416, 1352, 1303, 1100, 1073, 1055, 1042, 976, 839, 779, 615, 556, 508. **Mass spec:** 274.20 [$C_9H_{12}N_{11}^+$], 272.20 [$C_9H_{10}N_{11}^-$].

DMPTzHATrClO$_4$·H$_2$O(4). Yield 86%; **EA:** found (calc): C 26.55 (26.57), H 3.67 (3.69), N 41.36 (41.33); **IR** (**KBr,** cm^{-1}): ν= 3547, 3354, 3280, 2744, 1694, 1622, 1586, 1548, 1495, 1567, 1287, 1209, 1088, 968, 929, 623, 566. **Mass spec:** 289.20 [$C_9H_{13}N_{12}^+$], 287.20 [$C_9H_{11}N_{12}^-$].

PyrTzSCZClO$_4$(5). Yield 81%; **EA:** found (calc): C 22.44 (22.40), H 2.51 (2.49), N 39.15 (39.19); **IR** (**KBr,** cm^{-1}): ν= 3396, 3315, 3187, 3147, 3038, 2975, 1676, 1545, 1475, 1422, 1401, 1196, 1074, 1036, 954, 940, 800, 605, 554. **Mass spec:** 222.20 [$C_6H_8N_9O^+$], 220.07 [$C_6H_6N_9O^-$].

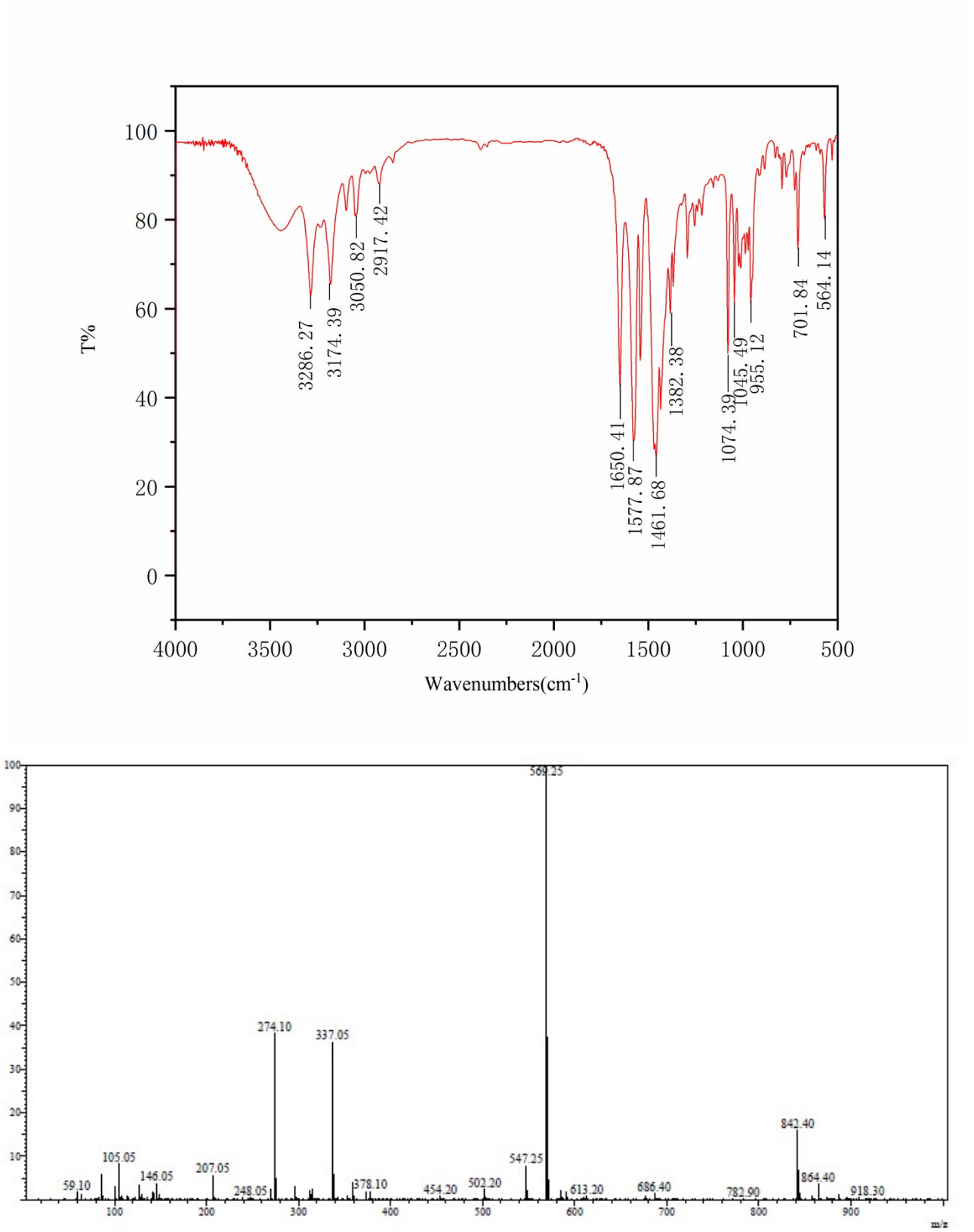

Figure S1. IR (top) and MS (bottom) Spectrum of **1**.

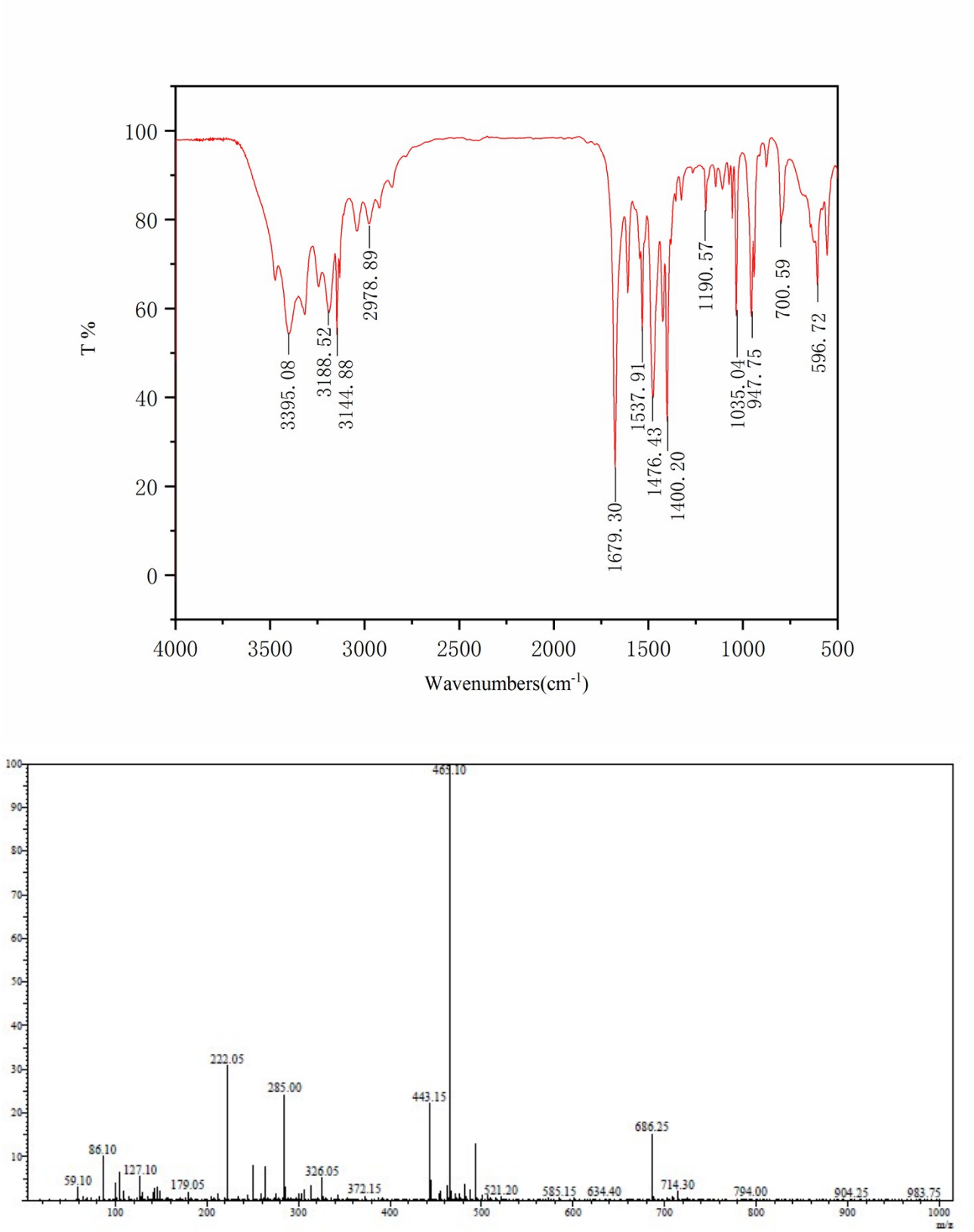

Figure S2. IR (top) and MS (bottom) Spectrum of **2**.

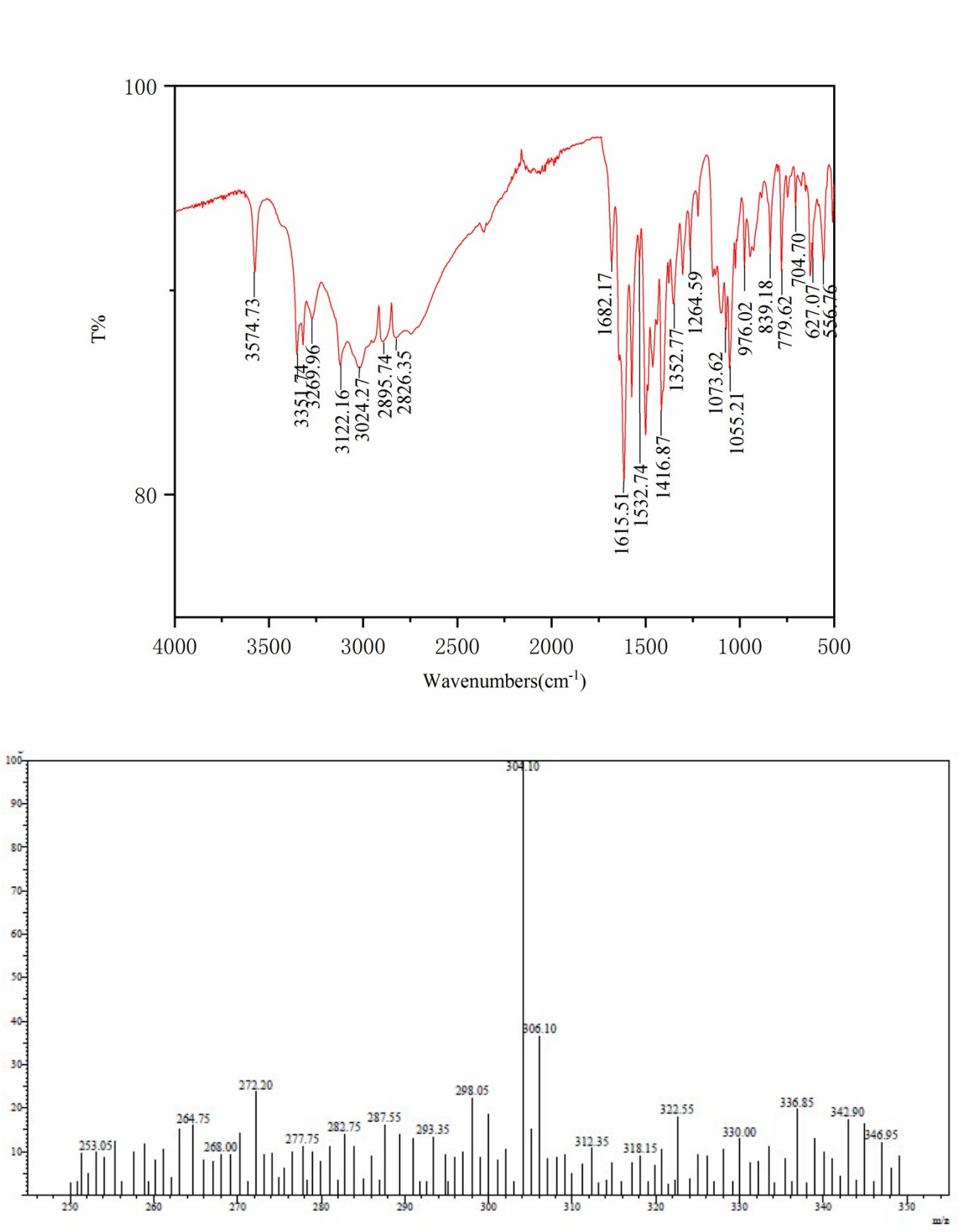

Figure S3. IR (top) and MS (bottom) Spectrum of **3**.

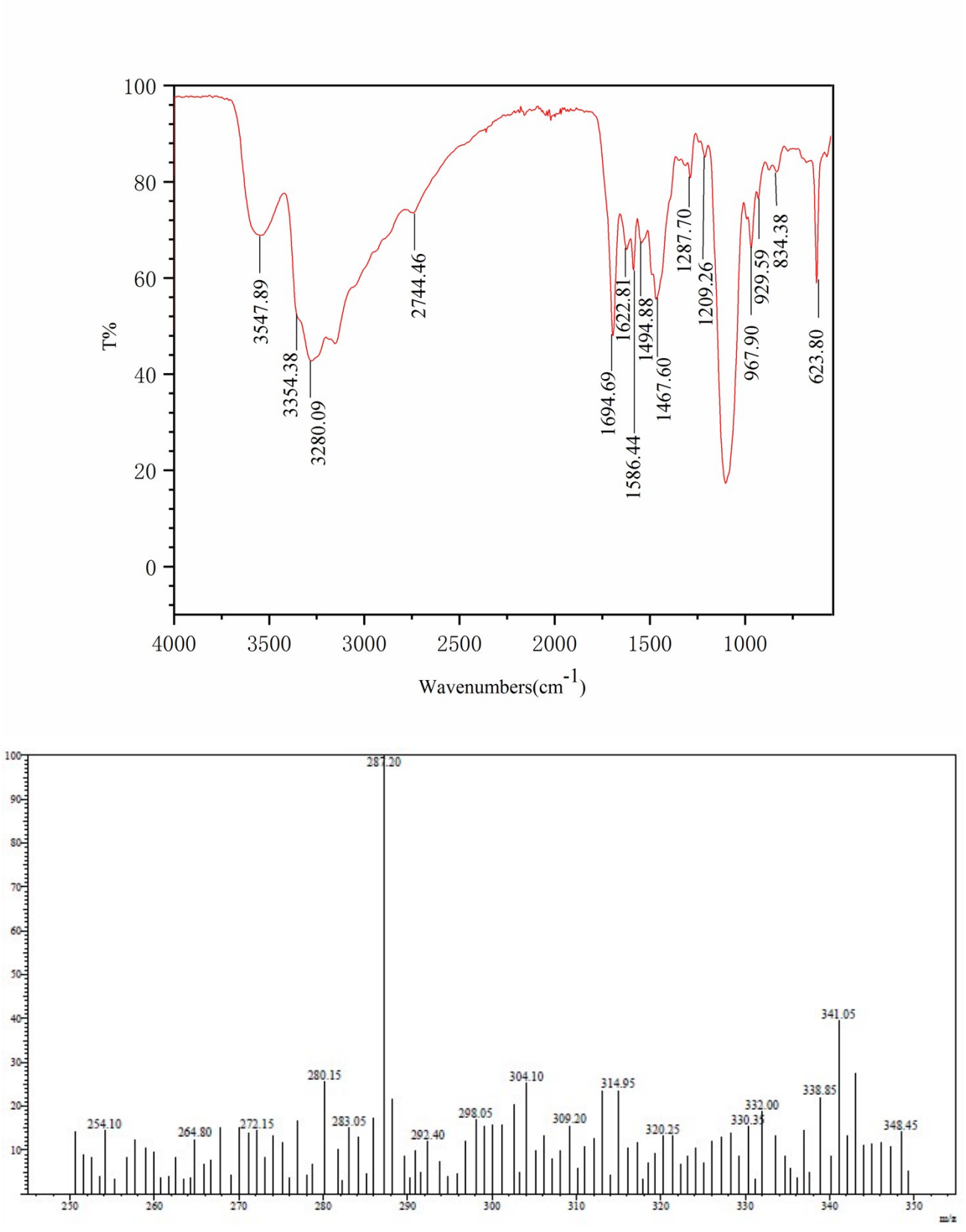

Figure S4. IR (top) and MS (bottom) Spectrum of **4**.

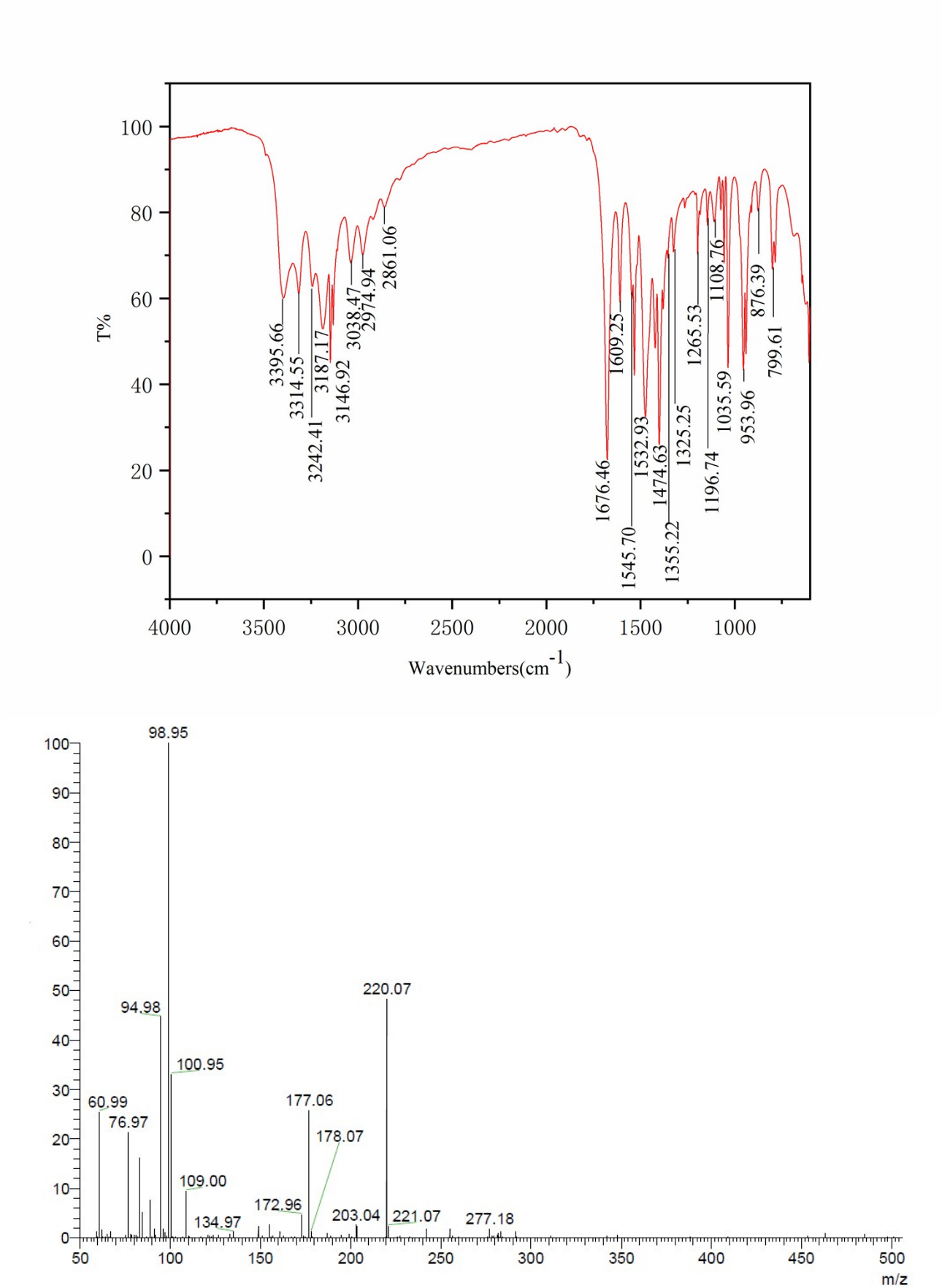

Figure S5. IR (top) and MS (bottom) Spectrum of **5**.

Section 2. X-ray crystallography

The obtained signal crystal of five novel nitrogen-rich energetic materials were used in the X-ray diffraction study. Crystallographic data and experimental details for structure analyses are summarized in **Table S1** to **Table S10**.

Table S1. Selected bond lengths for compound **1**

Bond length (Å)							
N1-N4	1.398(7)	N11-C8	1.334(8)	N5-C1	1.326(6)	N8-N9	1.305(7)
N1-C1	1.366(7)	N4-H4A	0.8400	N5-C3	1.338(6)	C7-C8	1.407(8)
N1-C2	1.387(7)	N4-H4B	0.8400	N6-N7	1.321(7)	C8-C9	1.492(7)
N2-N3	1.399(7)	C5-C6	1.481(9)	N6-C3	1.364(7)	C2-H2	0.9300
N2-C1	1.349(6)	N5-H5	0.8400	N7-C4	1.315(7)	C5-H5A	0.9600
N3-C2	1.297(8)	C6-C7	1.365(9)				

Table S2. Selected dihedral angles for compound **1**

Dihedral angle (º)							
N4-N1-C1-N2	177.6(5)	N3-N2-C1-N1	-0.4(7)	C3-N6-N7-C4	-1.3(8)	N9-N8-C4-N10	-176.9(5)
N4-N1-C1-N5	-0.1(9)	N3-N2-C1-N2	177.0(6)	N7-N6-C3-N5	-173.1(5)	N8-N9-C3-N5	173.0(5)
C2-N1-C1-N2	0.4(7)	N3-N2-C1-N3	0.1(7)	N7-N6-C3-N9	9.7(8)	N8-N9-C3-N6	-9.7(8)
C2-N1-C1-N5	-177.3(6)	N3-N2-C1-N4	-179.3(5)	N6-N7-C4-N8	-7.3(9)	C4-N10-N11-C8	178.4(5)
N4-N1-C2-N3	-177.4(5)	N3-N2-C1-N5	3.7(10)	N6-N7-C4-N10	176.9(5)	C6-N10-N11-C8	-0.7(6)
C1-N1-C2-N3	-0.4(7)	N3-N2-C1-N6	-0.7(8)	C4-N8-N9-C3	1.3(8)	N11-N10-C4-N7	3.5(8)
C1-N2-N3-C2	0.2(7)	N3-N2-C1-N7	176.7(5)	N9-N8-C4-N7	7.3(9)	N11-N10-C4-N8	-172.8(5)

Table S3. Selected bond lengths for compound **2**

Bond length (Å)							
N1-C1	1.322(3)	N3-C2	1.351(3)	N6-N7	1.318(3)	O1-C1	1.232(3)
N1-H1A	0.86	N3-H3	0.86	N7-C2	1.333(3)	C4-C5	1.340(3)
N1-H1B	0.86	N4-N5	1.316(3)	N8-C4	1.347(3)	C4-H4	0.93
N2-C1	1.371(3)	N4-C2	1.344(3)	N8-N9	1.358(2)	C5-C6	1.384(3)
N2-N3	1.390(2)	N5-C3	1.327(3)	N8-C3	1.395(3)	C5-H5	0.93
N2-H2	0.86	N6-C3	1.317(3)	N9-C6	1.315(3)	C6-H6	0.93

Table S4. Selected dihedral angles for compound **2**

Dihedral angle (º)							
C1-N2-N3-C2	78.4(3)	N6-N7-C2-N4	-4.3(3)	N7-N6-C3-N8	-178.35(18)	N9-N8-C4-C5	0.4(3)
C2-N4-N5-C3	-0.8(3)	N6-N7-C2-N3	177.89(19)	N4-N5-C3-N6	-3.3(3)	C3-N8-C4-C5	177.9(2)
C3-N6-N7-C2	0.2(3)	N5-N4-C2-N7	4.7(3)	N4-N5-C3-N8	178.77(18)	N8-C4-C5-C6	-0.4(3)
C4-N8-N9-C6	-0.3(3)	N5-N4-C2-N3	-177.50(19)	C4-N8-C3-N6	-1.0(3)	N8-N9-C6-C5	0.0(3)
C3-N8-N9-C6	-178.0(2)	N2-N3-C2-N7	-7.4(3)	N9-N8-C3-N6	176.29(19)	C4-C5-C6-N9	0.2(3)
N3-N2-C1-O1	-158.6(2)	N2-N3-C2-N4	174.59(19)	C4-N8-C3-N5	177.1(2)		
N3-N2-C1-N1	23.0(3)	N7-N6-C3-N5	3.7(3)	N9-N8-C3-N5	-5.6(3)		

Table S5. Selected dihedral angles for compound **3**

Bond length (Å)							
Cl1-O2	1.19(4)	N1-H1	0.86	N6-N7	1.323(4)	C2-H2	0.9300
Cl1-O1	1.38(6)	N2-C1	1.291(4)	N6-C3	1.325(4)	C5-C6	1.412(5)
Cl1-O4	1.39(6)	N3-C2	1.326(4)	N7-C4	1.345(4)	C5-C8	1.485(5)
Cl1-O3	1.405(15)	N3-C1	1.378(4)	N8-C4	1.309(4)	C6-C7	1.354(5)
Cl1-O4	1.42(2)	N3-N5	1.412(4)	N8-N9	1.328(4)	C6-H6	0.9300
Cl1-O2	1.435(18)	N4-C1	1.355(4)	N9-C3	1.335(4)	C7-C9	1.498(5)
Cl1-O3	1.45(3)	N4-C3	1.378(4)	N10-N11	1.379(4)	C8-H8A	0.9600
Cl1-O1	1.53(3)	N4-H4	0.86	N10-C4	1.393(4)	C8-H8B	0.9600
N1-C2	1.306(4)	N5-H5A	0.89	N10-C7	1.400(4)	C8-H8C	0.9600
N1-N2	1.364(4)	N5-H5B	0.89	N11-C5	1.335(4)	C9-H9A	0.9600

Table S6. Selected dihedral angles for compound **3**

Dihedral angle (º)							
C2-N1-N2-C1	0.6(4)	N5-N3-C1-N2	179.5(3)	C1-N4-C3-N6	173.4(3)	N10-N11-C5-C6	1.0(4)
C3-N6-N7-C4	1.8(5)	C2-N3-C1-N4	-179.2(3)	C1-N4-C3-N9	-5.9(6)	N10-N11-C5-C8	-178.4(3)
C4-N8-N9-C3	0.9(6)	N5-N3-C1-N4	-0.4(6)	N9-N8-C4-N7	-3.8(6)	N11-C5-C6-C7	-0.9(5)
C4-N10-N11-C5	176.5(3)	N2-N1-C2-N3	-0.2(4)	N9-N8-C4-N10	176.3(3)	C8-C5-C6-C7	178.5(4)
C7-N10-N11-C5	-0.8(4)	C1-N3-C2-N1	-0.2(4)	N6-N7-C4-N8	2.4(6)	C5-C6-C7-N10	0.4(4)
N1-N2-C1-N4	179.2(3)	N5-N3-C2-N1	-179.2(3)	N6-N7-C4-N10	-177.8(3)	C5-C6-C7-C9	-179.8(4)
N1-N2-C1-N3	-0.7(4)	N7-N6-C3-N9	-4.8(6)	N11-N10-C4-N8	178.9(3)	N11-N10-C7-C6	0.2(4)
C3-N4-C1-N2	-10.0(6)	N7-N6-C3-N4	175.9(3)	C7-N10-C4-N8	-4.4(6)	C4-N10-C7-C6	-176.6(4)
C3-N4-C1-N3	169.8(3)	N8-N9-C3-N6	3.4(6)	N11-N10-C4-N7	-1.0(5)	N11-N10-C7-C9	-179.6(3)
C2-N3-C1-N2	0.6(4)	N8-N9-C3-N4	-177.3(3)	C7-N10-C4-N7	175.7(3)	C4-N10-C7-C9	3.6(6)

Table S7. Selected dihedral angles for compound **4**

Bond length (Å)							
Cl1-O4	1.383(4)	N5-C1	1.372(6)	N9-N10	1.371(5)	C3-C4	1.401(7)
Cl1-O3	1.396(4)	N5-N6	1.378(4)	N9-H9	0.8600	C3-C6	1.499(7)
Cl1-O2	1.409(4)	N5-C5	1.380(6)	N10-C9	1.274(6)	C4-C5	1.344(7)
Cl1-O1	1.417(4)	N6-C3	1.319(6)	N11-C8	1.343(5)	C4-H4	0.9300
N1-N2	1.299(5)	N7-C2	1.348(6)	N11-C9	1.374(6)	C5-C7	1.504(7)
N1-C2	1.351(5)	N7-N8	1.386(5)	N11-N12	1.391(5)	C6-H6A	0.9600
N2-C1	1.338(6)	N7-H7	0.8600	N12-H12B	0.8900	C6-H6B	0.9600
N3-N4	1.328(5)	N8-C8	1.320(6)	N12-H12C	0.8899	C6-H6C	0.9600
N3-C1	1.328(5)	N8-H8	0.8600	O5-H5C	0.8500	C7-H7A	0.9600
N4-C2	1.314(5)	N9-C8	1.311(6)	O5-H5D	0.8499	C7-H7B	0.9600

Table S8. Selected dihedral angles for compound **4**

Dihedral angle (º)							
C2-N1-N2-C1	-0.6(6)	N6-N5-C1-N3	165.7(4)	N5-N6-C3-C4	-0.7(5)	N10-N9-C8-N8	176.7(5)
C1-N3-N4-C2	0.7(6)	C5-N5-C1-N3	-13.1(7)	N5-N6-C3-C6	179.3(4)	N10-N9-C8-N11	-1.5(5)
C1-N5-N6-C3	-178.0(4)	N6-N5-C1-N2	-14.2(6)	N6-C3-C4-C5	0.2(6)	N7-N8-C8-N9	-5.0(7)
C5-N5-N6-C3	1.0(5)	C5-N5-C1-N2	166.9(4)	C6-C3-C4-C5	-179.8(5)	N7-N8-C8-N11	172.8(4)
C2-N7-N8-C8	-95.1(5)	N3-N4-C2-N7	177.1(4)	C3-C4-C5-N5	0.5(5)	C9-N11-C8-N9	1.5(5)
C8-N9-N10-C9	0.8(6)	N3-N4-C2-N1	-1.8(6)	C3-C4-C5-C7	179.1(5)	N12-N11-C8-N9	175.9(4)
N4-N3-C1-N2	0.3(7)	N8-N7-C2-N4	12.3(7)	C1-N5-C5-C4	178.0(5)	C9-N11-C8-N8	-176.8(4)
N4-N3-C1-N5	-179.7(4)	N8-N7-C2-N1	-168.7(4)	N6-N5-C5-C4	-1.0(5)	N12-N11-C8-N8	-2.4(7)
N1-N2-C1-N3	-0.4(7)	N2-N1-C2-N4	1.7(6)	C1-N5-C5-C7	-0.8(8)	N9-N10-C9-N11	0.2(6)
N1-N2-C1-N5	179.6(4)	N2-N1-C2-N7	-177.2(4)	N6-N5-C5-C7	-179.7(4)	C8-N11-C9-N10	-1.1(6)

TableS9.Selected dihedral angles for compound **5**

Bond length (Å)							
Cl1-O5	1.434(7)	N2-C1	1.340(9)	N5-C3	1.338(9)	N9-C6	1.335(9)
Cl1-O4	1.449(6)	N2-N3	1.396(8)	N6-N7	1.324(9)	N9-H9	0.8600
Cl1-O2	1.450(6)	N2-H2	0.8600	N6-C3	1.369(10)	O1-C1	1.298(9)
Cl1-O3	1.452(6)	N3-C2	1.372(9)	N7-C2	1.386(9)	C4-C5	1.376(12)
N1-C1	1.299(10)	N3-H3	0.900	N8-N9	1.363(9)	C4-H4	0.9300
N1-H1A	0.8600	N4-N5	1.336(9)	N8-C4	1.369(10)	C5-C6	1.446(11)
N1-H1B	0.8600	N4-C2	1.350(10)	N8-C3	1.375(10)	C5-H5	0.9300

Table S10. Selected dihedral angles for compound **5**

Dihedral angle (°)							
Cl1-O5	1.434(7)	N2-C1	1.340(9)	N5-C3	1.338(9)	N9-C6	1.335(9)
Cl1-O4	1.449(6)	N2-N3	1.396(8)	N6-N7	1.324(9)	N9-H9	0.8600
Cl1-O2	1.450(6)	N2-H2	0.8600	N6-C3	1.369(10)	O1-C1	1.298(9)
Cl1-O3	1.452(6)	N3-C2	1.372(9)	N7-C2	1.386(9)	C4-C5	1.376(12)
N1-C1	1.299(10)	N3-H3	0.9000	N8-N9	1.363(9)	C4-H4	0.9300
N1-H1A	0.8600	N4-N5	1.336(9)	N8-C4	1.369(10)	C5-C6	1.446(11)
N1-H1B	0.8600	N4-C2	1.350(10)	N8-C3	1.375(10)	C5-H5	0.9300

Section 3. Computational structural considerations

Electrostatic potential (ESP) and natural bond orbitals (NBO) and of compounds **1** and **2** were calculated using the density functional theory with B3LYP/6-311++G** method. The ESP maps of compound **1-2** are given in **Figure S6** and **Figure S7**, respectively. The blue color represents positive electrostatic potential represent while the red color represents negative electrostatic potential, and the white color represents zero potential. The calculated NBO charges for compounds **1** and **2** are displayed in **Table S11** and **Table S12**.

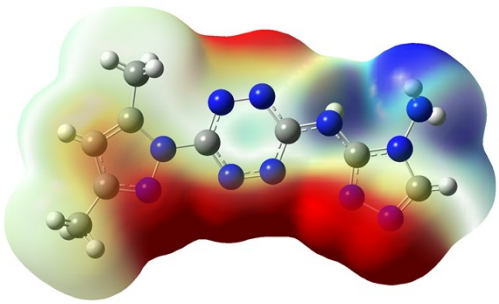

Figure S6. ESP map of compound **1**.

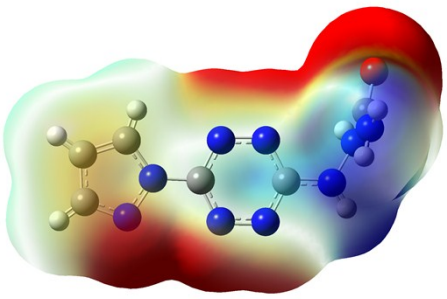

Figure S7. ESP map of compound **2**.

Table S11. Natural Population Analysis for compound **1**

Charge(e)							
N1	-0.23025	N9	-0.1904	H17	0.15519	C25	-0.30917
N2	-0.31683	N10	-0.1812	C18	0.51207	H26	0.18185
N3	-0.26058	N11	-0.2396	C19	0.52977	C27	0.23243
N4	-0.59621	N12	-0.2182	C20	-0.5638	C28	-0.56608
H5	0.34333	N13	-0.2298	H21	0.1944	H29	0.19054
H6	0.35231	N14	-0.2991	H22	0.20347	H30	0.19812
N7	-0.59143	C15	0.49579	H23	0.21037	H31	0.20455
H8	0.36071	C16	0.18795	C24	0.23995		

Table S12. Natural Population Analysis for compound **2**

Charge(e)							
N1	-0.72368	H7	0.35548	N13	-0.2603	H19	0.18688
H2	0.36072	N8	-0.23562	O14	-0.65255	C20	-0.26611
H3	0.34319	N9	-0.16976	C15	0.79684	H21	0.18025
N4	-0.4232	N10	-0.21206	C16	0.49629	C22	0.03193
H5	0.34938	N11	-0.25106	C17	0.50153	H23	0.16201
N6	-0.39663	N12	-0.19672	C18	0.02319		