Supporting Information

for

Comprehensive energetic modifications of peptides for high-performance amphoteric compounds

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1. General Methods

All reagents were purchased from Energy Chemical of analytical grade and were used as supplied, if not stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Bruker 400 MHz and 101 MHz, respectively. Chemical shifts were reported in parts per million (ppm) and relative to Me4Si as external standards. DSC was performed in closed Al containers with a nitrogen flow of 50 mL min-1 using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 10 °C min^{-1}.

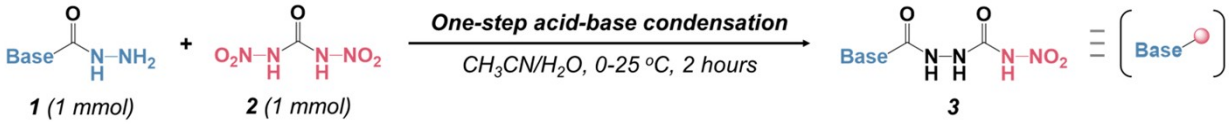
Infrared spectra (IR) were obtained using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. at 25 °C. Elemental analyses of C/H/N were investigated on a vario EL III CHNOS elemental analyzer. Impact sensitivity and friction sensitivity of samples are measured by using the standard BAM methods. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer.

2. Safety Precautions

All the new compounds in this manuscript are powerful explosives, and should be handled with extreme care using the best safety practices.

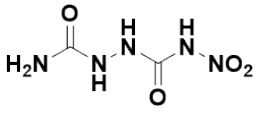
3. Experimental procedures

General procedure for the synthesis of compounds 3a-3p.



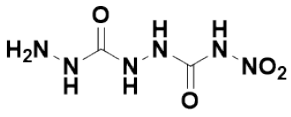
At 0-25 °C, to a 10 mL single-necked flask, 2.0 mL acetonitrile and 1.0 mL water were added and mixed well, compound 2 (1,3-dinitrourea, 1.0 mmol, 150 mg) was added and stirred for 5 min and then compound 1 (1.0 mmol) was added, and after the system was stabilized, the reaction was held for 2 h and then filtered. The filter cake was washed by 1.0 mL of cold acetonitrile and dried.

Representative example



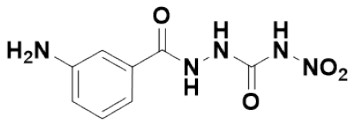
3a, HNNC-NH_2

N-nitrohydrazine-1,2-dicarboxamide (3a, HNNC-NH_2): Yield 70.2%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.48 (s, 2H), 8.54 (s, 1H), 6.54 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 158.06, 153.78ppm. IR (KBr): 3488, 3381, 3302, 3054, 1682, 1608, 1530, 1380, 1339, 1295, 1206, 1140, 1077, 1009, 967, 877, 784, 762, 735, 690, 614, 520 cm^{-1}. HRMS (ESI): Mass calcd for $C_2H_4N_5O_4$ [M-H]$^-$: 162.0269; found: 162.0262. Elemental analysis for $C_2H_5N_5O_4$ (163.09). Calcd: C 14.73; H 3.09; N 42.94%. Found: C 14.77; H 3.13; N 42.91%.



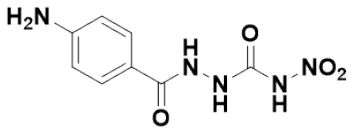
3b, HNNC

2-(hydrazinecarbonyl)-N-nitrohydrazine-1-carboxamide (3b, HNNC): Yield 88.7%, white solid. ^{1}H NMR (400 MHz, D_2O): No Found. ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.03, 160.36 ppm. IR (KBr): 3332, 3247, 3005, 1667, 1578, 1496, 1367, 1334, 1300, 1259, 1231, 1117, 1049, 1005, 983, 843, 786, 759, 648, 577 cm^{-1}. HRMS (ESI): Mass calcd for $C_2H_5N_6O_4$ [M-H]$^-$: 177.0378; found: 177.0378. Elemental analysis for $C_2H_6N_6O_4$ (178.11). Calcd: C 13.49; H 3.40; N 47.19%. Found: C 13.45; H 3.43; N 47.16%.



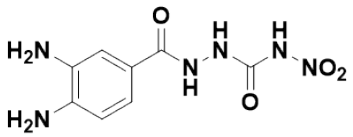
3c

2-(3-aminobenzoyl)-N-nitrohydrazine-1-carboxamide (3c): Yield 85.2%, brown-white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.20 (t, 1H), 7.12 (t, 1H), 7.04 (d, 1H), 6.86 (dd, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.93, 153.75, 147.72, 131.48, 129.42, 118.87, 115.66, 113.60 ppm. IR (KBr): 3326, 2960, 1682, 1628, 1582, 1537, 1486, 1430, 1319, 1188, 1092, 1002, 948, 882, 816, 782, 742, 680, 548 cm^{-1}. HRMS (ESI): Mass calcd for $C_8H_8N_5O_4$ [M-H]$^-$: 238.0582; found: 238.0579. Elemental analysis for $C_8H_9N_5O_4$ (239.19). Calcd: C 40.17; H 3.79; N 29.28%. Found: C 40.15; H 3.76; N 29.30%.



3d

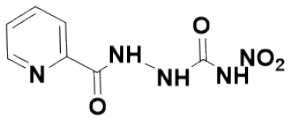
2-(4-aminobenzoyl)-N-nitrohydrazine-1-carboxamide (3d): Yield 84.3%, powder white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.52 (s, 1H), 8.85 (s, 2H), 7.58 (d, 2H), 6.58 (d, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.48, 153.74, 153.15, 129.47, 116.82, 112.79 ppm. IR (KBr): 3427, 3353, 3231, 3092, 1724, 1708, 1605, 1544, 1508, 1399, 1322, 1304, 1178, 1074, 1017, 877, 850, 780, 721, 684, 613 cm^{-1}. HRMS (ESI): Mass calcd for $C_8H_8N_5O_4$ [M-H]$^-$: 238.0582; found: 238.0578. Elemental analysis for $C_8H_9N_5O_4$ (239.19). Calcd: C 40.17; H 3.79; N 29.28%. Found: C 40.19; H 3.77; N 29.26%.



3e

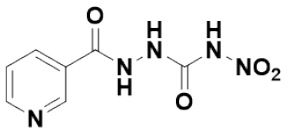
2-(3,4-diaminobenzoyl)-N-nitrohydrazine-1-carboxamide (3e): Yield 77.1%, black solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.14 (d, 1H), 7.06 (dd, 1H), 6.56 (d, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 166.92, 153.72, 140.61, 132.29, 119.13, 118.40, 114.73, 113.08 ppm. IR (KBr): 3433, 3363, 3276, 2956, 1708, 1616, 1504, 1429, 1317, 1193, 1093, 1006, 956, 879, 836, 783, 758, 735, 681, 557, 521 cm^{-1}. HRMS (ESI): Mass calcd for $C_8H_9N_6O_4$[M-H]$^-$: 253.0691; found: 253.0688. Elemental analysis for

$C_8H_{10}N_6O_4$ (254.21). Calcd: C 37.80; H 3.97; N 33.06%. Found: C 37.82; H 3.94; N 33.02%.



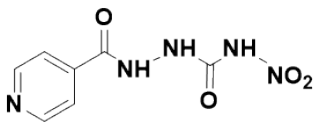
3f

N-nitro-2-picolinoylhydrazine-1-carboxamide (3f): Yield 82.3%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (s, 1H), 11.00 (s, 2H), 8.72 (d,1H), 8.10-8.02 (m, 2H), 7.71 (ddd, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.60, 153.59, 149.18, 147.50, 138.35, 128.01, 122.96 ppm. IR (KBr): 3424, 3228, 2971, 2752, 1704, 1654, 1603, 1522, 1499, 1473, 1431, 1364, 1294, 1235, 1110, 1035, 1008, 941, 818, 788, 757, 736, 701, 663, 628, 561, 505 cm^{-1}. HRMS (ESI): Mass calcd for $C_7H_6N_5O_4$ [M-H]$^-$: 224.0425; found: 224.0420. Elemental analysis for $C_7H_7N_5O_4$ (225.16). Calcd: C 37.34; H 3.13; N 31.10%. Found: C 37.31; H 3.16; N 31.05%.



3g

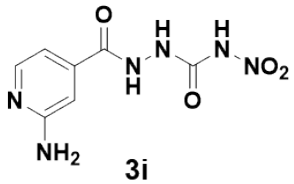
2-nicotinoyl-N-nitrohydrazine-1-carboxamide (3g): Yield 79.5%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.18 (s, 1H), 10.95 (s, 2H), 9.03 (dd, 1H), 8.82 (dd, 1H), 8.26 (dt, 1H), 7.63 (ddd, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 164.72, 153.68, 152.96, 148.28, 136.11, 126.84, 124.17 ppm. IR (KBr): 3282, 3056, 1712, 1670, 1598, 1541, 1506, 1461, 1422, 1362, 1315, 1203, 1177, 1148, 1087, 1030, 976, 954, 884, 828, 781, 736, 701, 686, 635 cm^{-1}. HRMS (ESI): Mass calcd for $C_7H_6N_5O_4$ [M-H]$^-$: 224.0425; found: 224.0422. Elemental analysis for $C_7H_7N_5O_4$ (225.16). Calcd: C 37.34; H 3.13; N 31.10%. Found: C 37.36; H 3.13; N 31.07%.



3h

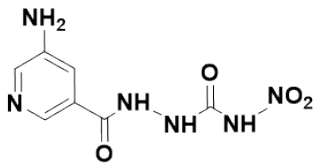
2-isonicotinoyl-N-nitrohydrazine-1-carboxamide (3h): Yield 78.2%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 3H), 8.83-8.80 (m, 2H), 7.82-7.78 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-

d_6): δ 164.42, 153.68, 150.27, 138.60, 121.57 ppm. IR (KBr): 3307, 3072, 1705, 1673, 1637, 1599, 1520, 1480, 1425, 1320, 1281, 1234, 1181, 1090, 996, 955, 891, 838, 786, 754, 681 cm^{-1}. HRMS (ESI): Mass calcd for $C_7H_8N_5O_4$ $[M+H]^+$: 226.0571; found: 226.0571. Elemental analysis for $C_7H_7N_5O_4$ (225.16). Calcd: C 37.34; H 3.13; N 31.10%. Found: C 37.38; H 3.17; N 31.06%.



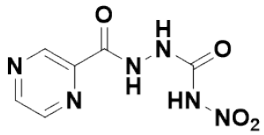
3i

2-(2-aminoisonicotinoyl)-N-nitrohydrazine-1-carboxamide (3i): Yield 79.3%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, 1H), 7.16 (s, 1H), 7.01 (d, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.88, 156.12, 153.78, 144.78, 140.42, 110.53, 109.06 ppm. IR (KBr): 3322, 3200, 1668, 1629, 1525, 1476, 1440, 1286, 1246, 1195, 1079, 995, 877, 820, 784, 737, 685, 562 cm^{-1}. HRMS (ESI): Mass calcd for $C_7H_9N_6O_4$ $[M+H]^+$: 241.0680; found: 241.0680. Elemental analysis for $C_7H_8N_6O_4$ (240.18). Calcd: C 35.01; H 3.36; N 34.99%. Found: C 35.04; H 3.32; N 34.96%.



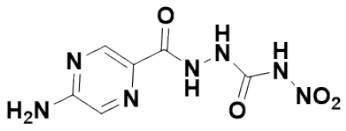
3j

2-(5-aminonicotinoyl)-N-nitrohydrazine-1-carboxamide (3j): Yield 84.3%, gray solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (s, 1H), 8.09 (s, 1H), 7.44 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 164.43, 153.25, 145.55, 136.69, 133.80, 128.94, 119.97 ppm. IR (KBr): 3417, 3337, 3320, 3235, 2962, 2875, 1667, 1628, 1593, 1582, 1443, 1360, 1327, 1294, 1265, 1166, 1109, 1023, 988, 939, 909, 894, 876, 843, 805, 727, 682, 626, 550 cm^{-1}. HRMS (ESI): Mass calcd for $C_7H_9N_6O_4$ $[M+H]^+$: 241.0680; found: 241.0678. Elemental analysis for $C_7H_8N_6O_4$ (240.18). Calcd: C 35.01; H 3.36; N 34.99%. Found: C 34.97; H 3.38; N 35.02%.



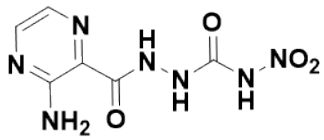
3k

N-nitro-2-(pyrazine-2-carbonyl)hydrazine-1-carboxamide (3k): Yield 81.5%, yellowish-white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 10.95 (s, 2H), 9.24 (d, 1H), 8.96 (d, 1H), 8.81 (dd, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.53, 153.61, 148.83, 143.99, 142.80 ppm. IR (KBr): 3355, 3000, 1712, 1602, 1508, 1462, 1449, 1406, 1375, 1315, 1282, 1209, 1177, 1163, 1086, 1058, 1022, 870, 780, 739, 686, 543 cm^{-1}. HRMS (ESI): Mass calcd for $C_6H_5N_6O_4$ [M-H]$^-$: 225.0378; found: 225.0372. Elemental analysis for $C_6H_6N_6O_4$ (226.15). Calcd: C 31.87; H 2.67; N 37.16%. Found: C 31.85; H 2.63; N 37.12%.



3l

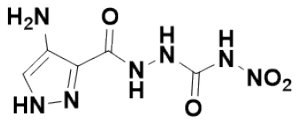
2-(5-aminopyrazine-2-carbonyl)-N-nitrohydrazine-1-carboxamide (3l): Yield 82.4%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.81 (s, 3H), 8.54 (d, 1H), 7.89 (d, 1H), 7.38 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.57, 157.99, 153.78, 143.75, 131.11, 130.13 ppm. IR (KBr): 3442, 3319, 3217, 1647, 1609, 1582, 1519, 1476, 1408, 1362, 1300, 1249, 1114, 1014, 954, 898, 760, 682, 631, 508 cm^{-1}. HRMS (ESI): Mass calcd for $C_6H_6N_7O_4$ [M-H]$^-$: 240.0487; found: 240.04478. Elemental analysis for $C_6H_7N_7O_4$ (241.17). Calcd: C 29.88; H 2.93; N 40.66%. Found: C 29.84; H 2.97; N 40.65%.



3m

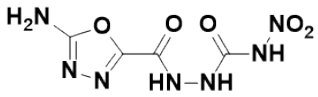
2-(3-aminopyrazine-2-carbonyl)-N-nitrohydrazine-1-carboxamide (3m): Yield 84.2%, orange solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (s, 3H), 8.28 (d, 1H), 7.87 (d, 1H), 7.49 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 165.19, 155.10, 153.71, 148.04, 131.55, 123.63 ppm. IR (KBr): 3431, 3378, 3310, 3047, 1706, 1682, 1613, 1565, 1512, 1436, 1400, 1323, 1296, 1181, 1087, 1026, 966, 858, 784, 739, 691, 521 cm^{-1}. HRMS (ESI): Mass calcd for $C_6H_6N_7O_4$ [M-H]$^-$: 240.0487; found: 240.0480. Elemental

analysis for $C_6H_7N_7O_4$ (241.17). Calcd: C 29.88; H 2.93; N 40.66%. Found: C 29.92; H 2.91; N 40.68%.



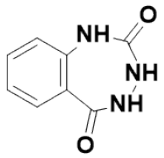
3n

2-(4-amino-1H-pyrazole-3-carbonyl)-N-nitrohydrazine-1-carboxamide (3n): Yield 68.8%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.78, 153.81, 131.27, 129.68 118.42 ppm. IR (KBr): 3308, 3092, 2941, 1666, 1614, 1547, 1342, 1183, 1147, 1024, 974, 945, 745, 612 cm^{-1}. HRMS (ESI): Mass calcd for $C_5H_6N_7O_4$ [M-H]$^-$: 228.0487; found: 228.0486. Elemental analysis for $C_5H_7N_7O_4$ (229.16). Calcd: C 26.21; H 3.08; N 42.79%. Found: C 26.18; H 3.05; N 42.77%.



3o

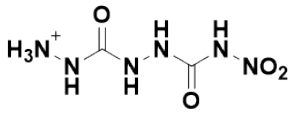
2-(5-amino-1,3,4-oxadiazole-2-carbonyl)-N-nitrohydrazine-1-carboxamide (3o): Yield 88.7%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (s, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 164.66, 153.78, 153.31, 152.06 ppm. IR (KBr): 3342, 3262, 3022, 2782, 2621, 1661, 1633, 1584, 1567, 1541, 1427, 1354, 1317, 1180, 1160, 1111, 1044, 972, 924, 881, 752, 729, 635, 547, 526 cm^{-1}. HRMS (ESI): Mass calcd for $C_4H_4N_7O_5$ [M-H]$^-$: 230.0279; found: 228.0270. Elemental analysis for $C_4H_5N_7O_5$ (231.13). Calcd: C 20.79; H 2.18; N 42.42%. Found: C 20.76; H 2.20; N 42.47%.



3p

3,4-dihydro-1H-benzo[e][1,2,4]triazepine-2,5-dione (3p): Yield 91.4%, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (s, 3H), 7.45 (dd, 1H), 7.19 (ddd, 1H), 6.74 (dd, 1H), 6.56-6.50 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.63, 153.72, 149.99, 132.73, 128.10, 116.64, 114.86, 111.62 ppm. IR (KBr): 3492, 3377, 3222, 2988, 1652, 1617, 1579, 1552, 1451, 1402, 1302, 1230, 1154, 1079, 1014, 963,

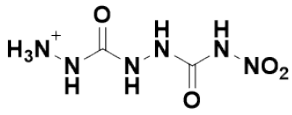
898, 784, 749, 700, 531 cm^{-1}. HRMS (ESI): Mass calcd for $C_8H_6N_3O_2$ $[M-H]^-$: 176.0466; found: 176.0457. Elemental analysis for $C_8H_7N_3O_2$ (177.16). Calcd: C 54.24; H 3.98; N 23.72%. Found: C 54.20; H 4.01; N 23.68%.



NO_3^-

4

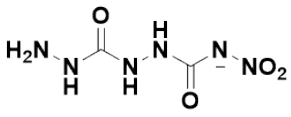
[HNNC$^+$][NO_3^-] (4): The HNNC (0.178 g, 1 mmol) was dispersed into 5 ml of water at 0-5 °C, slowly added into HNO_3 solution with a mass fraction of 68% of equal molar ratio, reacted at room temperature for 8 h, and then filtered to obtain the liquid, which was slowly evaporated in a quiet place (about 1−2 days). Collect a crystal sample of **4** (0.188 g, 0.78 mmol). Yield 78.0%, colorless ccrystal. ^{1}H NMR (400 MHz, D_2O): No Found. ^{13}C NMR (101 MHz, D_2O): δ 157.72, 152.13 ppm. IR (KBr): 3425, 3220, 2971, 2169, 1598, 1528, 1477, 1427, 1343, 1297, 1242, 1066, 763, 681, 586 cm^{-1}. Elemental analysis for $C_2H_7N_7O_7$ (241.12). Calcd: C 9.96; H 2.93; N 40.66%. Found: C 9.92; H 2.91; N 40.68%.



ClO_4^-

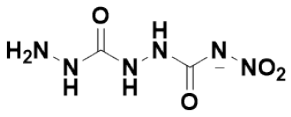
5

[HNNC$^+$][ClO_4^-] (5): The HNNC(0.178 g, 1 mmol) was dispersed into 5 ml of water at 0-5 °C, slowly added into $HClO_4$ solution with a mass fraction of 70% of equal molar ratio, reacted at room temperature for 8 h, and then filtered to obtain the liquid, which was slowly evaporated in a quiet place (about 1−2 days). Collect a crystal sample of **5** (0.223 g, 0.80 mmol). Yield 80.0 %, colorless crystal. ^{1}H NMR (400 MHz, D_2O) No Found. ^{13}C NMR (101 MHz, D_2O): δ 157.82, 152.68 ppm. IR (KBr): 3462, 3288, 2972, 2707, 1958, 1717, 1692, 1636, 1594, 1542, 1501, 1448, 1381, 1345, 1211, 1078, 963, 836, 790, 752, 702, 642, 601, 515 cm^{-1}. Elemental analysis for $C_2H_7ClN_6O_8$ (278.56). Calcd: C 8.62; H 2.53; Cl 12.73; N 30.17%. Found: C 8.65; H 2.50; Cl 12.71; N 30.12%.



6 NH_4^+

[HNNC$^-$][NH_4^+] (6): The HNNC(0.178 g, 1 mmol) was dispersed into 5 ml of water at 0-5 ^oC, slowly added into ammonia liquor solution with a mass fraction of 30% of equal molar ratio, reacted at room temperature for 8 h, and then filtered to obtain the liquid, which was slowly evaporated in a quiet place (about 1−2 days). Collect a crystal sample of **6** (0.117 mg, 0.60 mmol). Yield 60.0%, colorless crystal. ^1H NMR (400 MHz, D_2O) No Found. ^{13}C NMR (101 MHz, D_2O): δ 162.65, 161,12 ppm. IR (KBr): 3851, 3331, 3207, 1636, 1584, 1536, 1490, 1442, 1335, 1239, 1158, 1068, 1025, 983, 943, 879, 843, 770, 732, 583 cm^{-1}. Elemental analysis for $C_2H_9N_7O_4$ (195.14). Calcd: C 12.31; H 4.65; N 50.25%. Found: C 12.28; H 4.62; N 50.21%.



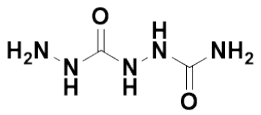
7 NH_3OH^+

[HNNC$^-$][NH_3OH^+] (7): The HNNC (0.178 g, 1 mmol) was dispersed into 5 ml of water at 0-5 °C, and then slowly added to an equal molar ratio of 50% hydroxylamine solution at room temperature for 8 h, after which the filtrate was filtered, and the solution was slowly evaporated in a quiet place (about 1−2 days). Collect crystal samples 6 (0.149 g，0.71 mmol). Yield 70.6%, colorless crystal. ^1H NMR (400 MHz, D_2O) No Found. ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.60, 155.04 ppm. IR (KBr): 3333, 3250, 2976, 1665, 1561, 1496, 1366, 1333, 1301, 1204, 1115, 1048, 1004, 982, 842, 786, 759, 641, 575 cm^{-1}. Elemental analysis for $C_2H_9N_7O_5$ (211.14). Calcd: C 11.38; H 4.30; N 46.44%. Found: C 11.34; H 4.31; N 46.41%.

3a, HNNC-NH_2

N-nitrohydrazine-1,2-dicarboxamide (HNNC-NH_2): Yield 70.2%, white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 10.48 (s, 2H), 8.54 (s, 1H), 6.54 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6): δ 158.06, 153.78ppm. IR (KBr): 3488, 3381, 3302, 3054, 1682, 1608, 1530, 1380, 1339, 1295, 1206, 1140, 1077,

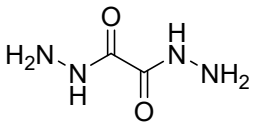
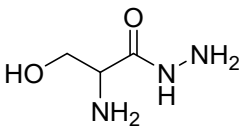
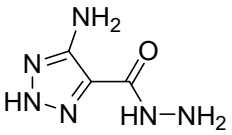
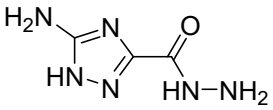
1009, 967, 877, 784, 762, 735, 690, 614, 520 cm^{-1}. HRMS (ESI): Mass calcd for $C_2H_4N_5O_4$ $[M-H]^-$: 162.0269; found: 162.0262. Elemental analysis for $C_2H_5N_5O_4$ (163.09). Calcd: C 14.73; H 3.09; N 42.94%. Found: C 14.77; H 3.13; N 42.91%.



HNNC-NO_2

2-(Hydrazinecarbonyl)hydrazine-1-carboxamide (NHHC-NO_2): The HNNC (1.78 g, 10 mmol) is dispersed into 5 ml water at 0-5 °C. Slowly add 85% hydrazine hydrate solution (1.25 g, 20 mmol), stir the mixture at 30 °C for 2 h, and then cool the mixture to 0 °C to obtain a white solid (0.28 g, 2.10 mmol). Yield 21%, white solid. ^{1}H NMR (400 MHz, D_2O) No Found. ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.03, 160.36 ppm. IR (KBr): 3308, 3092, 2941, 1666, 1614, 1547, 1342, 1183, 1147, 1024, 974, 945, 745, 612 cm^{-1}. Elemental analysis for $C_2H_7N_5O_2$ (133.11). Calcd: C 18.05; H 5.30; N 52.61%. Found: C 18.01; H 5.33; N 52.65%.

Substrates that do not undergo acid-base condensation

4. Spectrum Analysis

4.1 ^{1}H and ^{13}C NMR Spectra

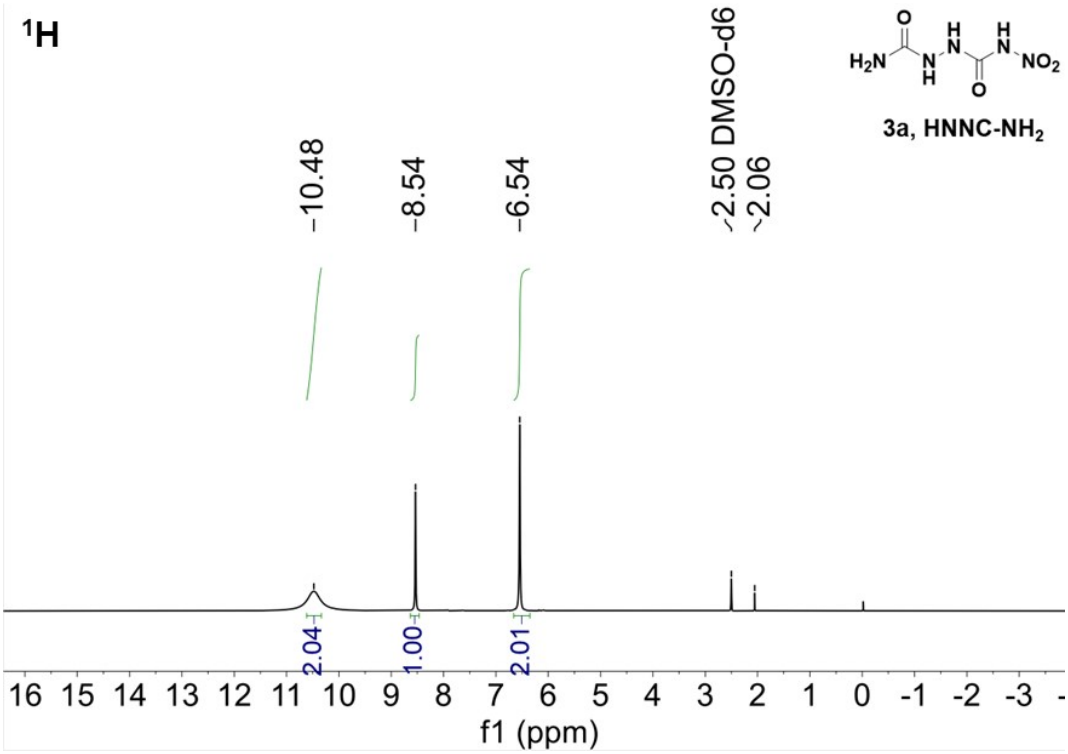


Figure S1. ^{1}H NMR of **HNNC-NH$_2$ (3a)** in DMSO-d$_6$.

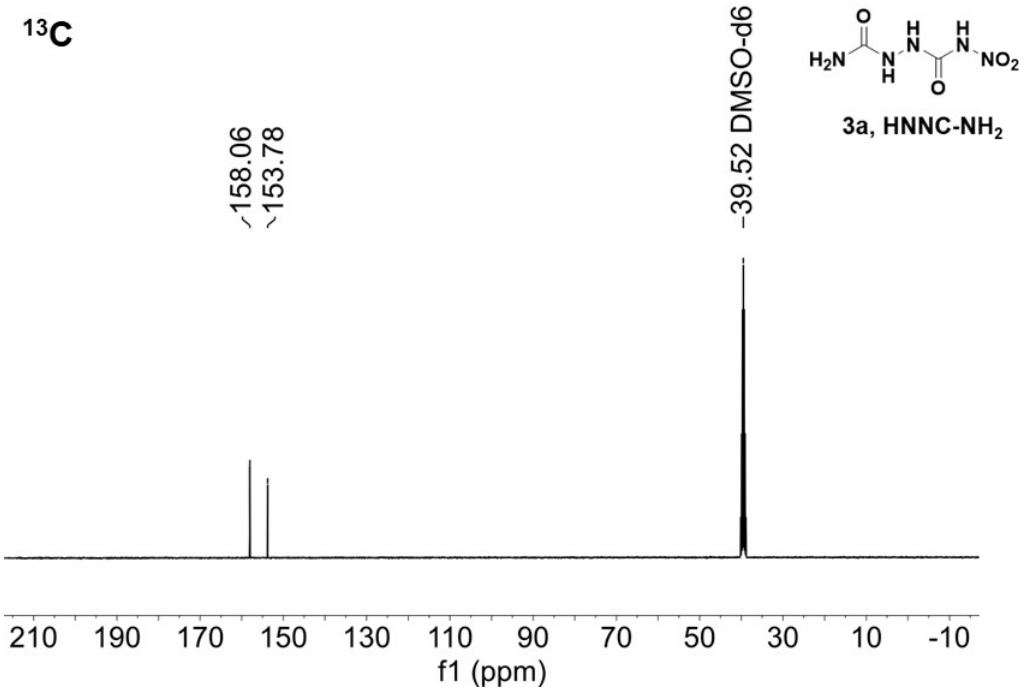


Figure S2. ^{13}C NMR of **HNNC-NH$_2$ (3a)** in DMSO-d$_6$.

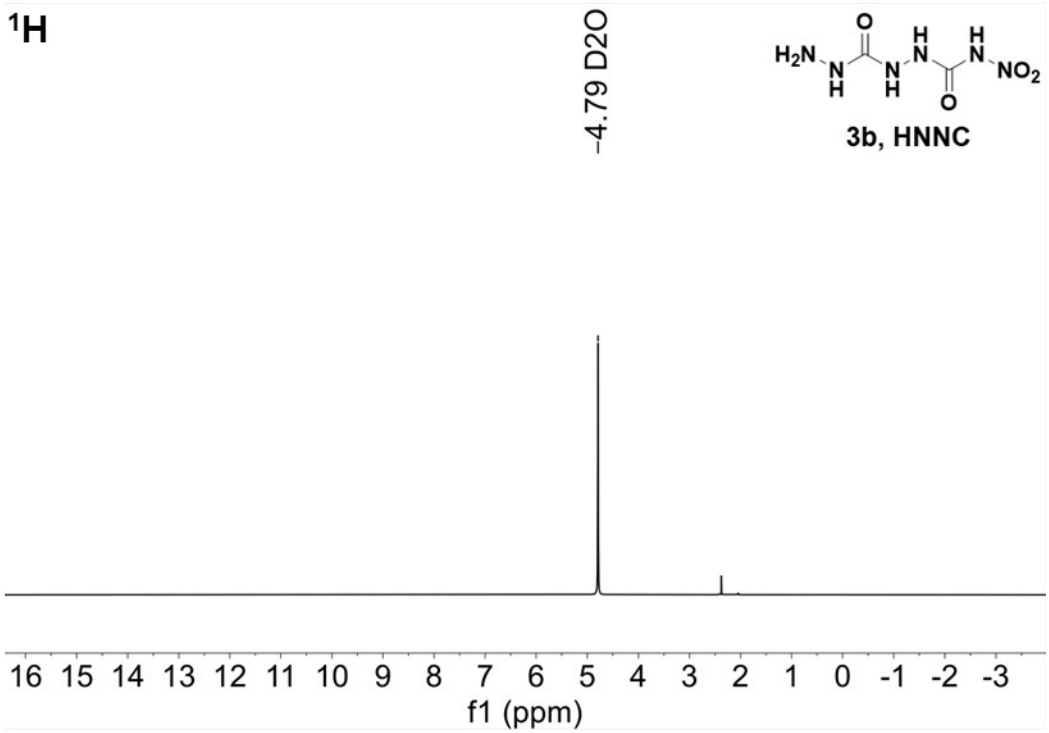


Figure S3. ^{1}H NMR of **HNNC (3b)** in D_2O.

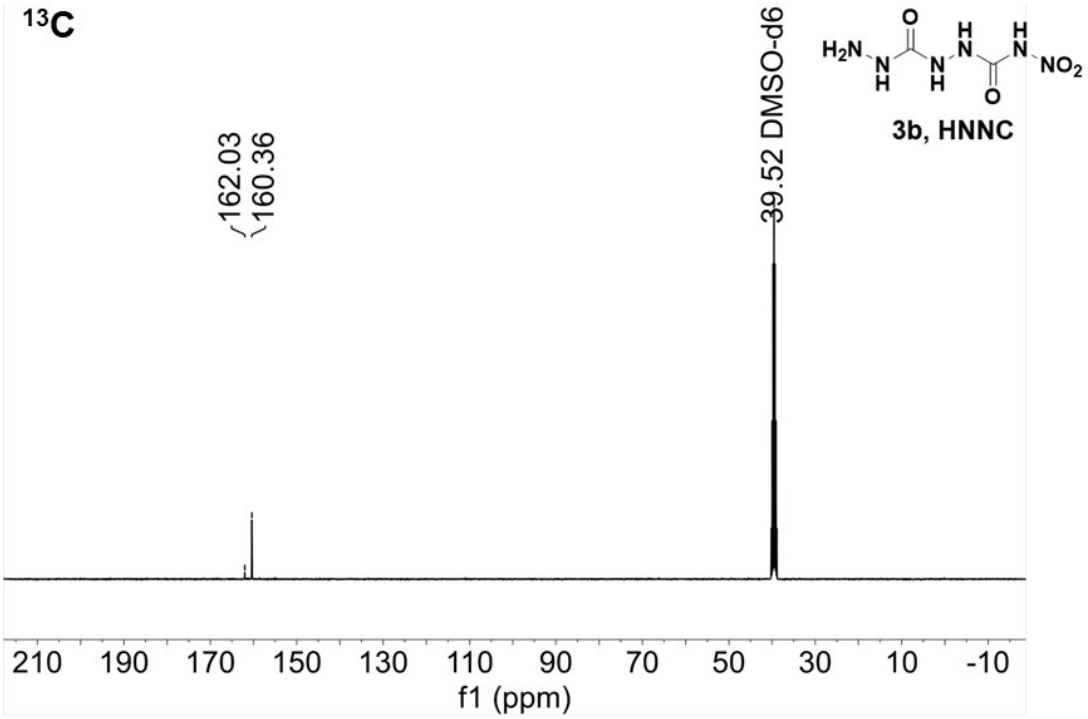


Figure S4 ^{13}C NMR of **HNNC (3b)** in DMSO-d_6.

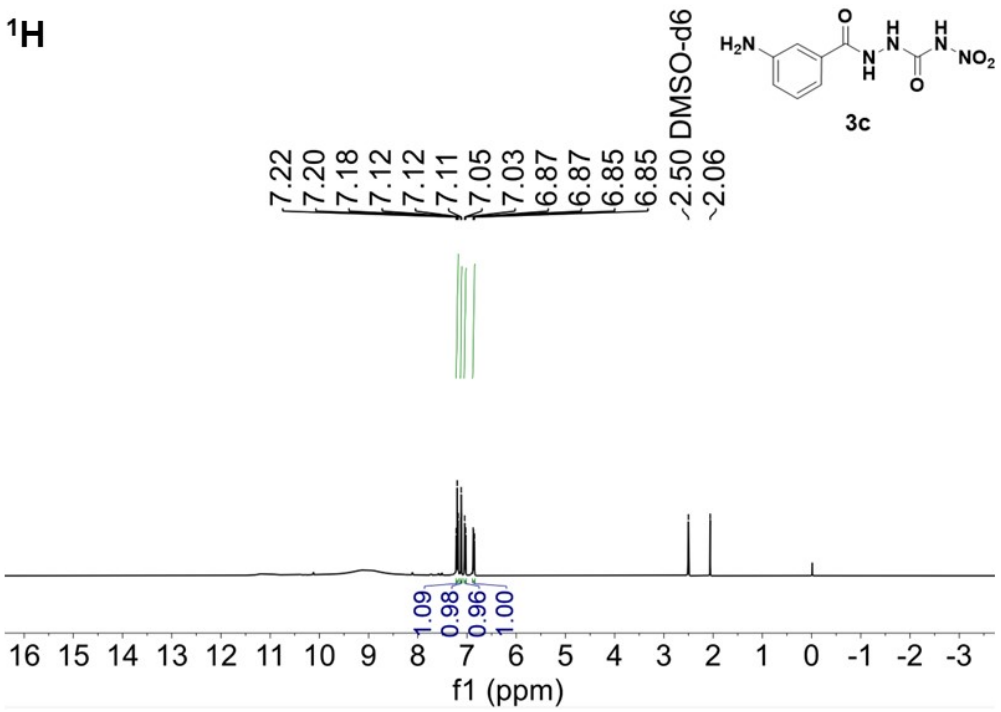


Figure S5. ^{1}H of **3c** in DMSO-d_6.

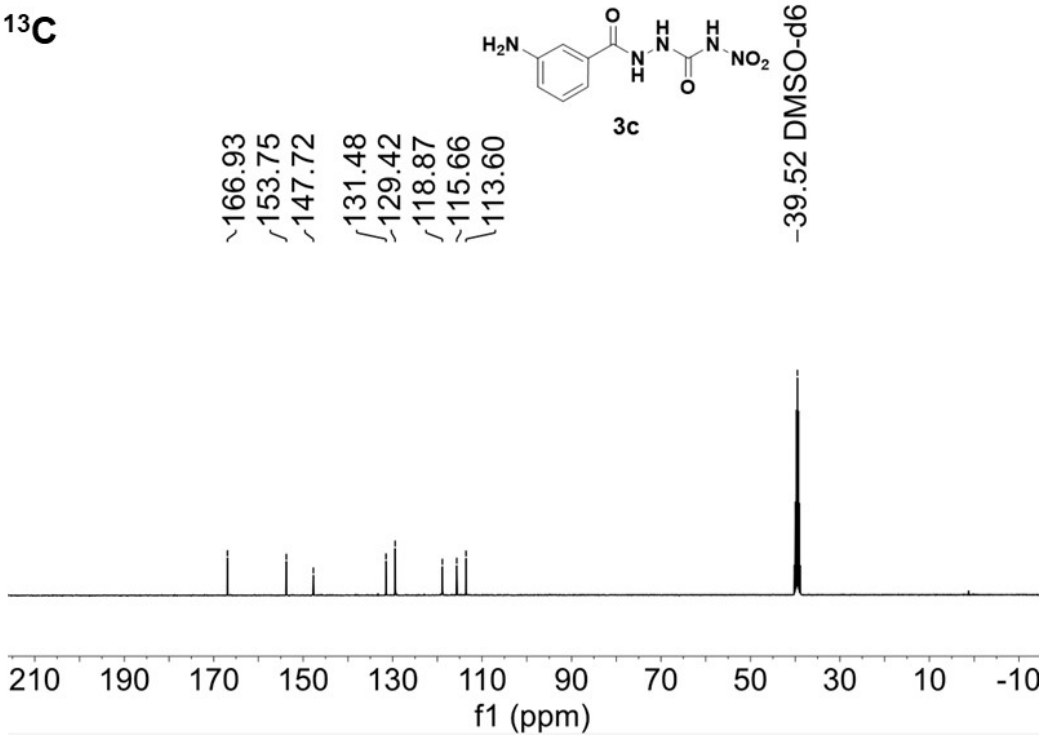


Figure S6. ^{13}C NMR of **3c** in DMSO-d_6.

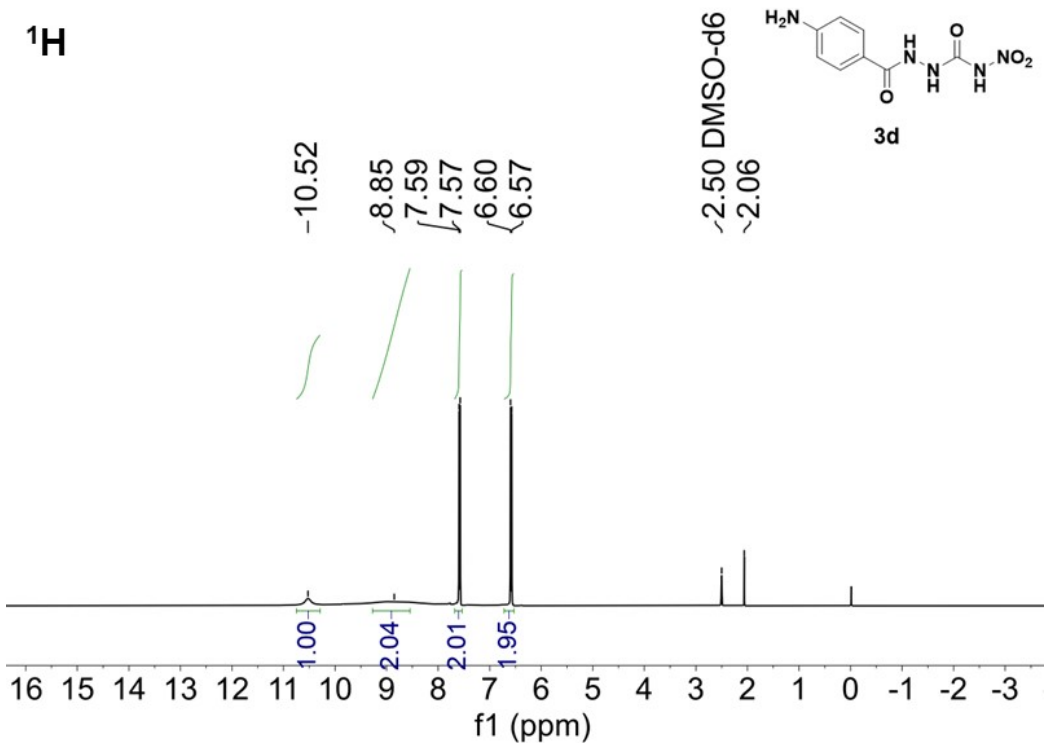


Figure S7. ^{1}H NMR of **3d** in DMSO-d_6.

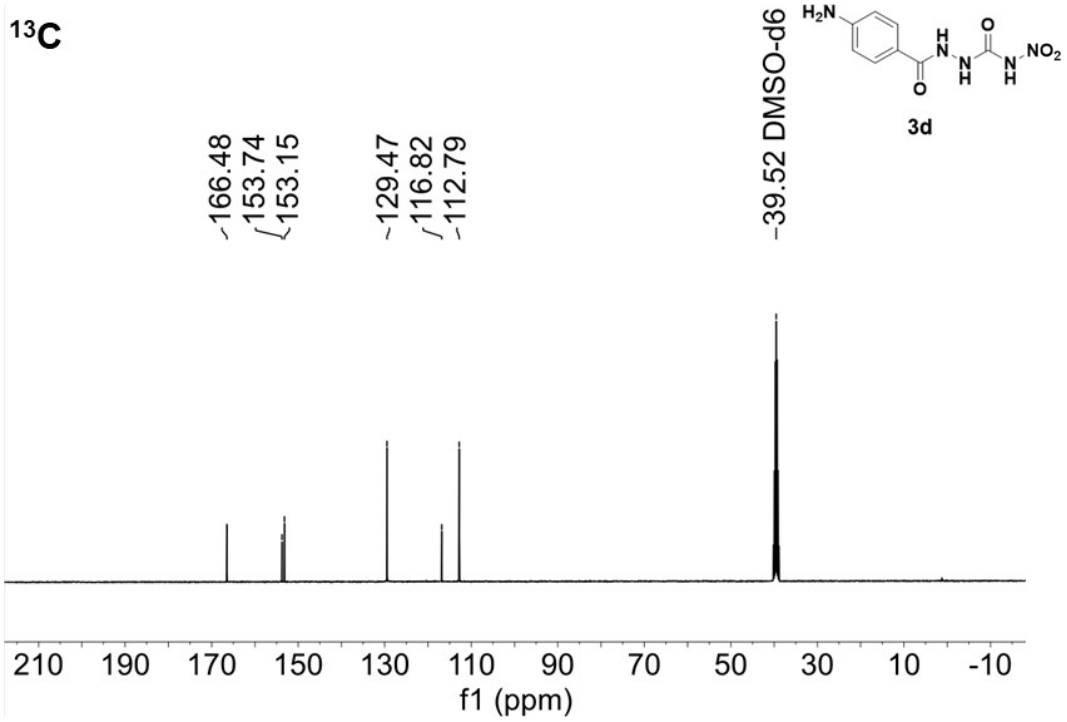


Figure S8. ^{1}H NMR of **3d** in DMSO-d_6.

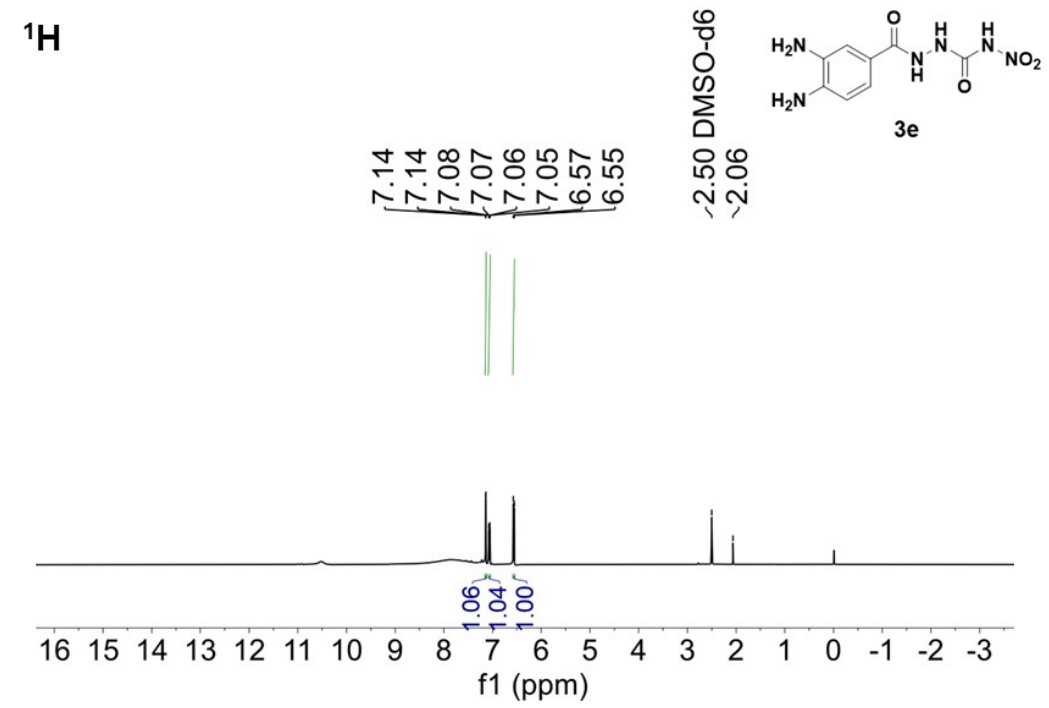


Figure S9. ^{1}H NMR of **3e** in DMSO-d_6.

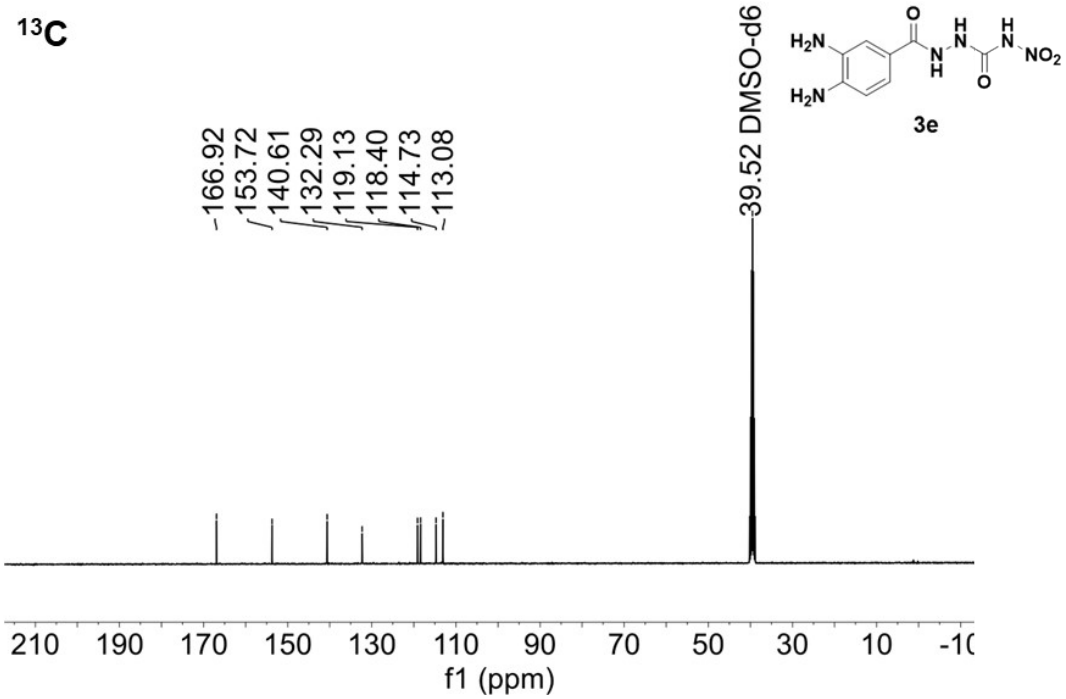


Figure S10. ^{13}C NMR of **3e** in DMSO-d_6.

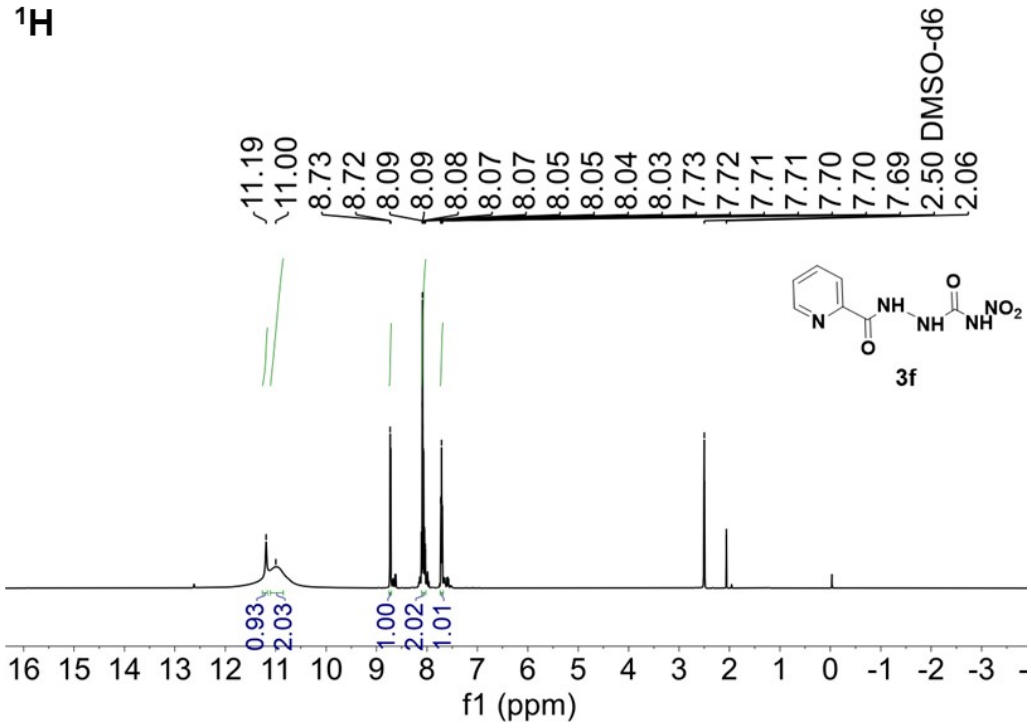


Figure S11. ^{1}H NMR of **3f** in DMSO-d_6.

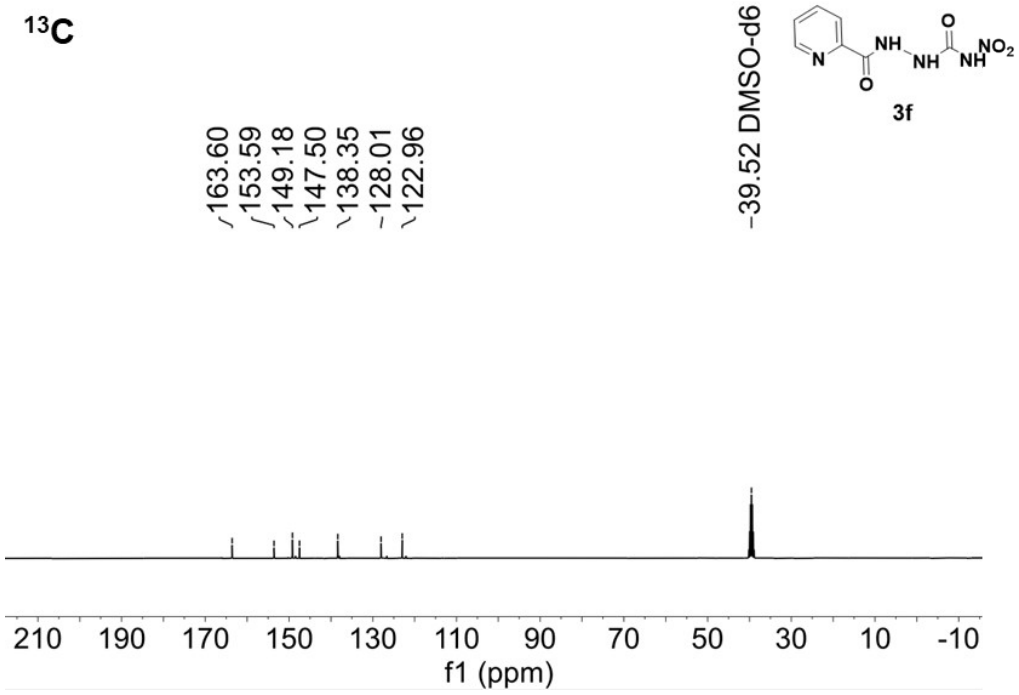


Figure S12. ^{13}C NMR of **3f** in DMSO-d_6.

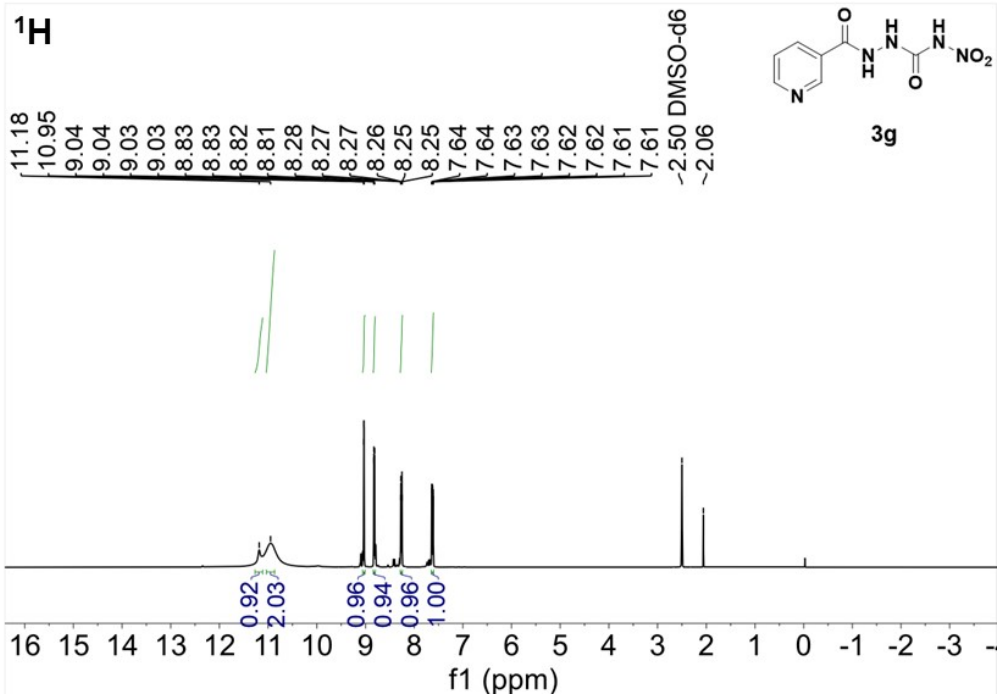


Figure S13. ^{1}H NMR of **3g** in DMSO-d_6.

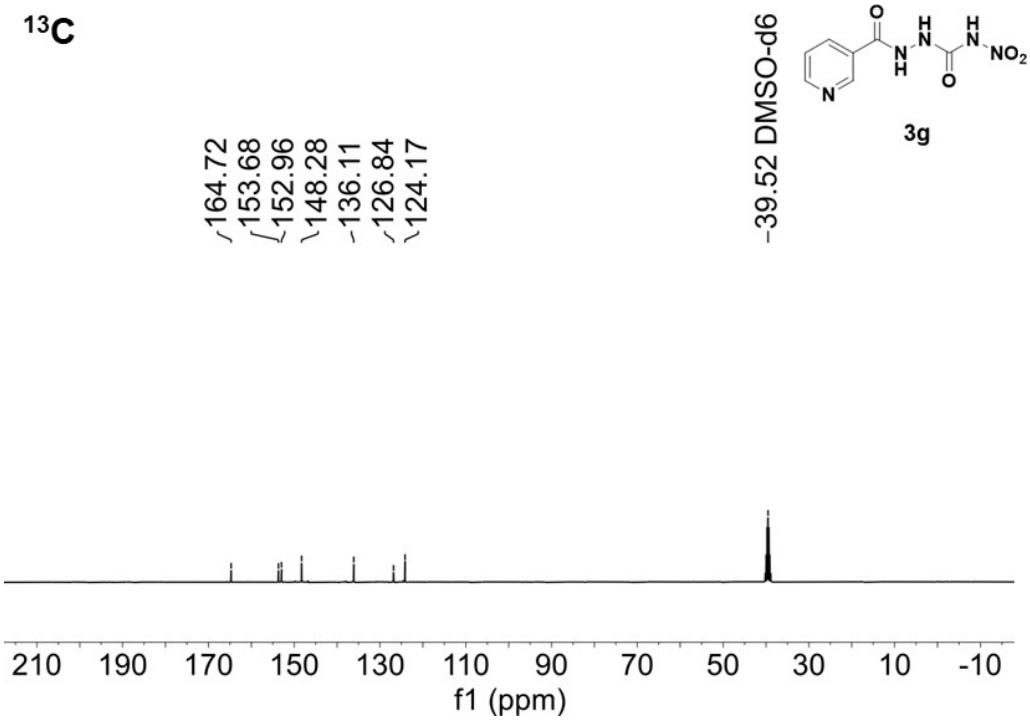


Figure S14. ^{13}C NMR of **3g** in DMSO-d_6.

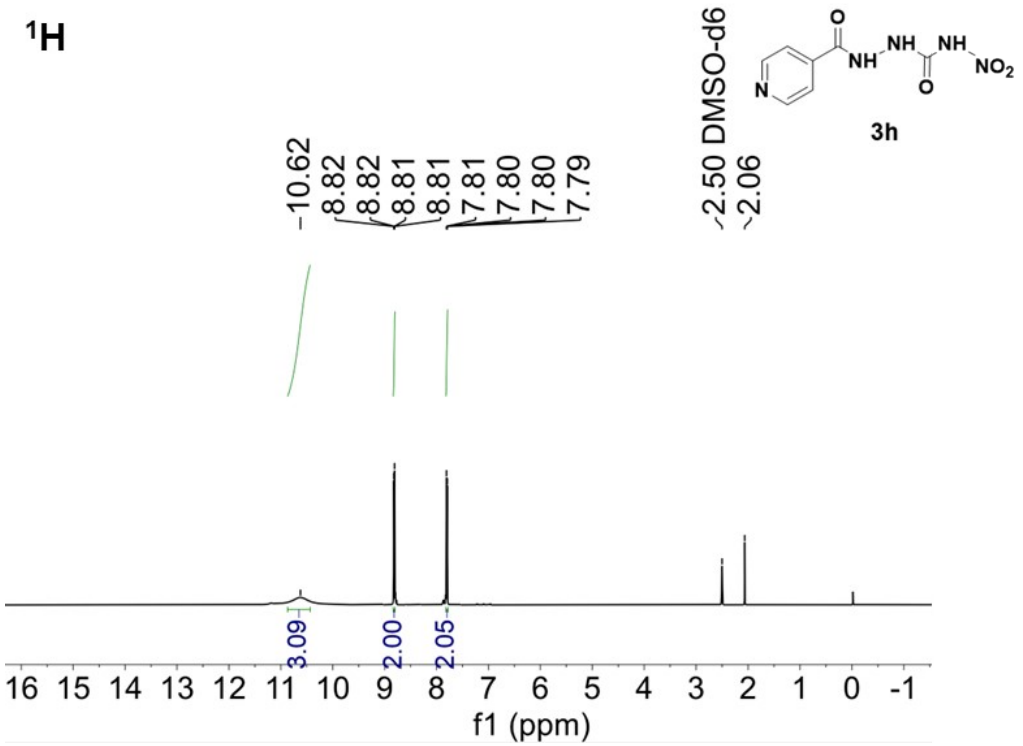


Figure S15. ^{1}H NMR of **3h** in DMSO-d_6.

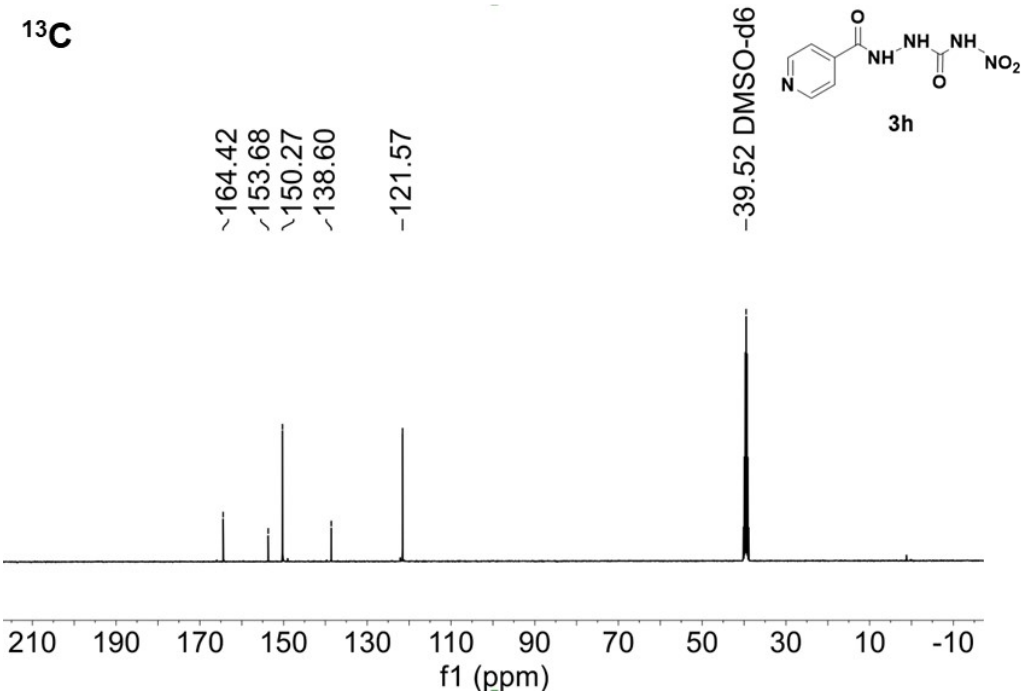


Figure S16. ^{13}C NMR of **3h** in DMSO-d_6.

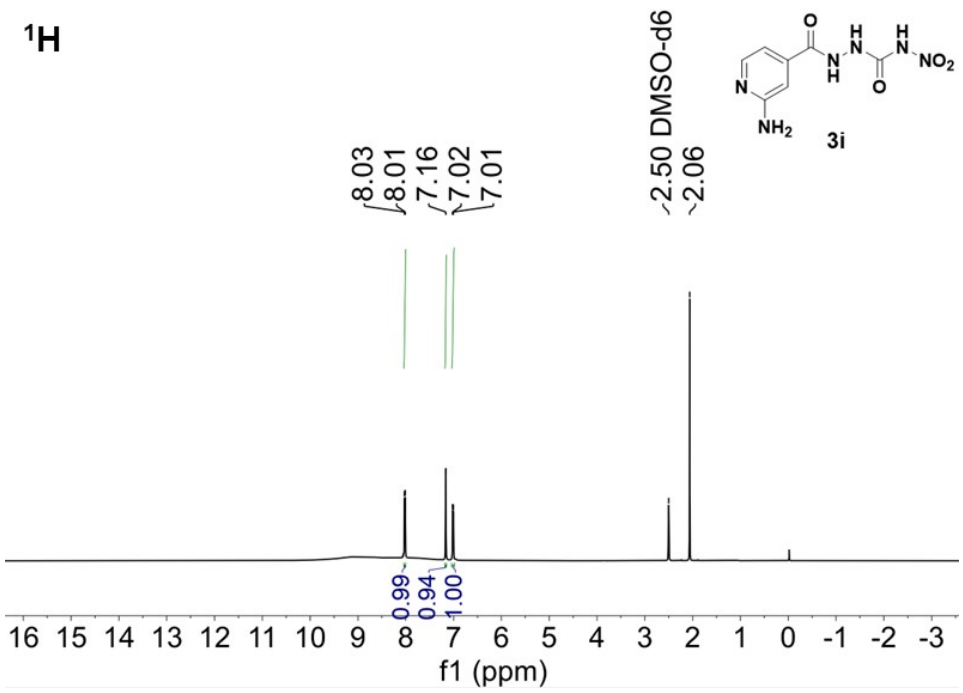


Figure S17. ^{1}H NMR of **3i** in DMSO-d_6.

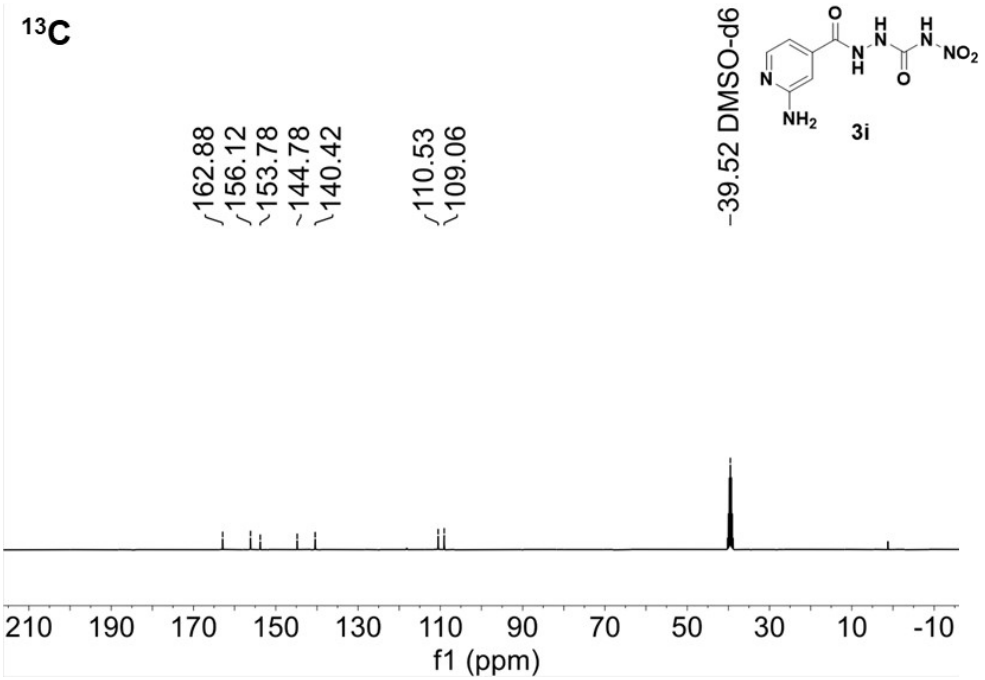


Figure S18. ^{13}C NMR of **3i** in DMSO-d_6.

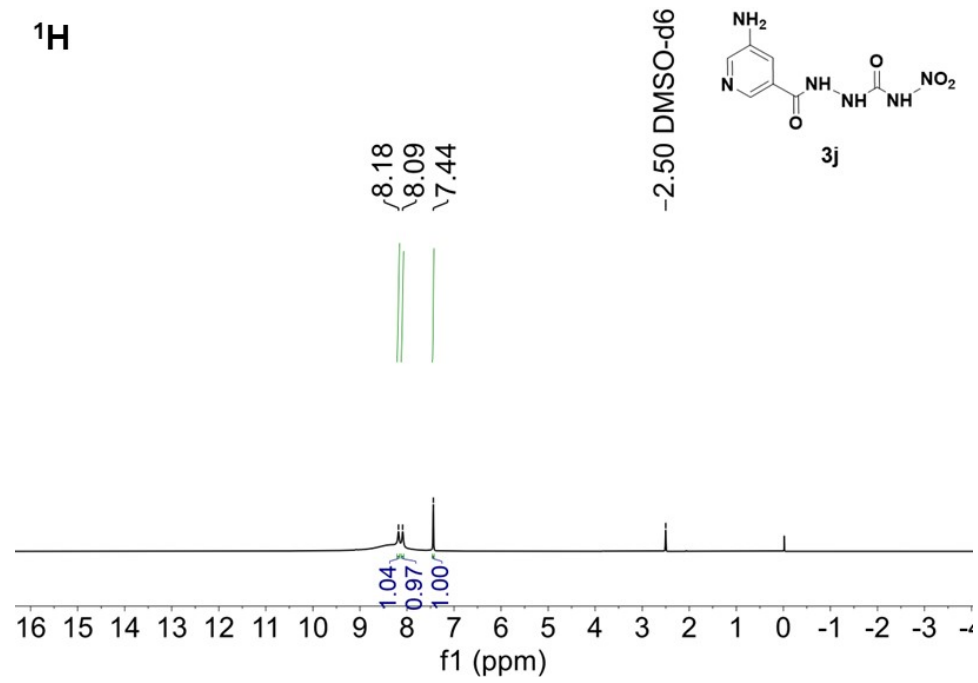


Figure S19. ^{1}H NMR of **3j** in DMSO-d_6.

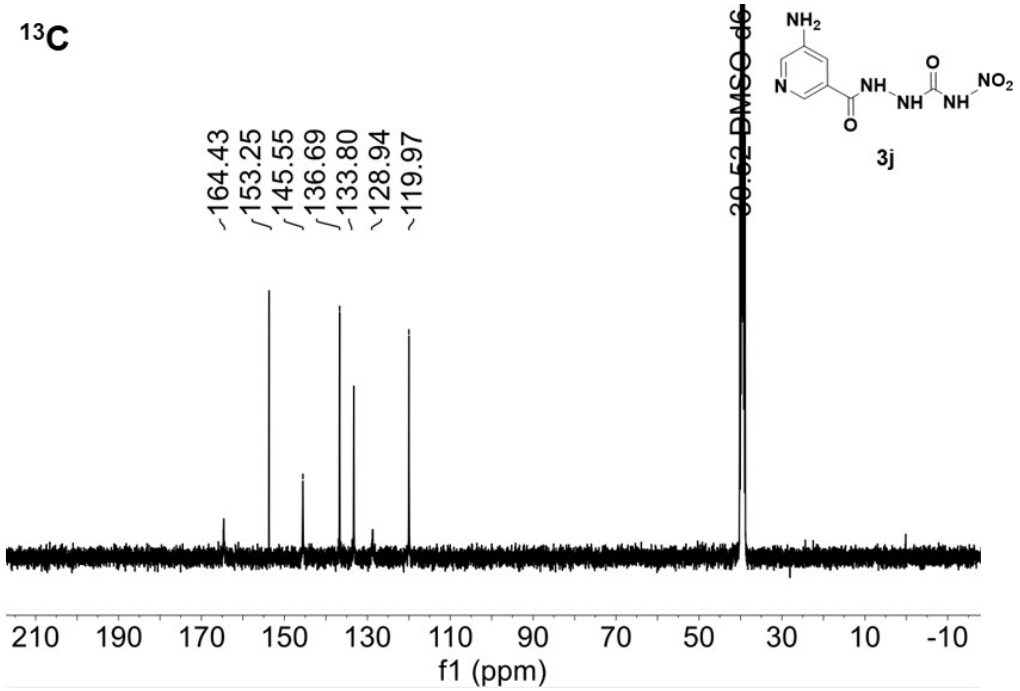


Figure S20. ^{13}C NMR of **3j** in DMSO-d_6.

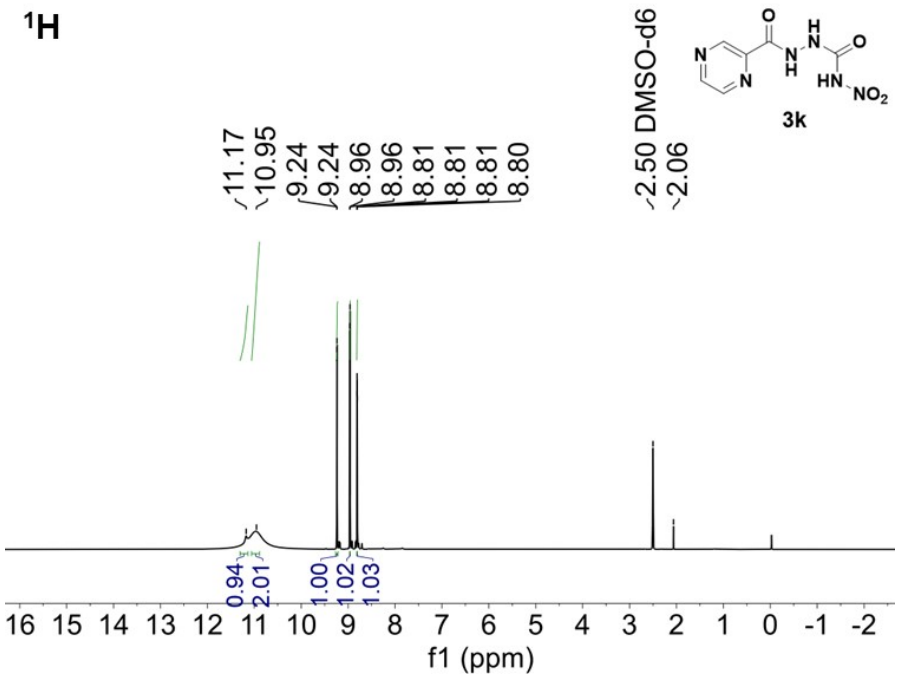


Figure S21. ^{1}H NMR of **3k** in DMSO-d_6.

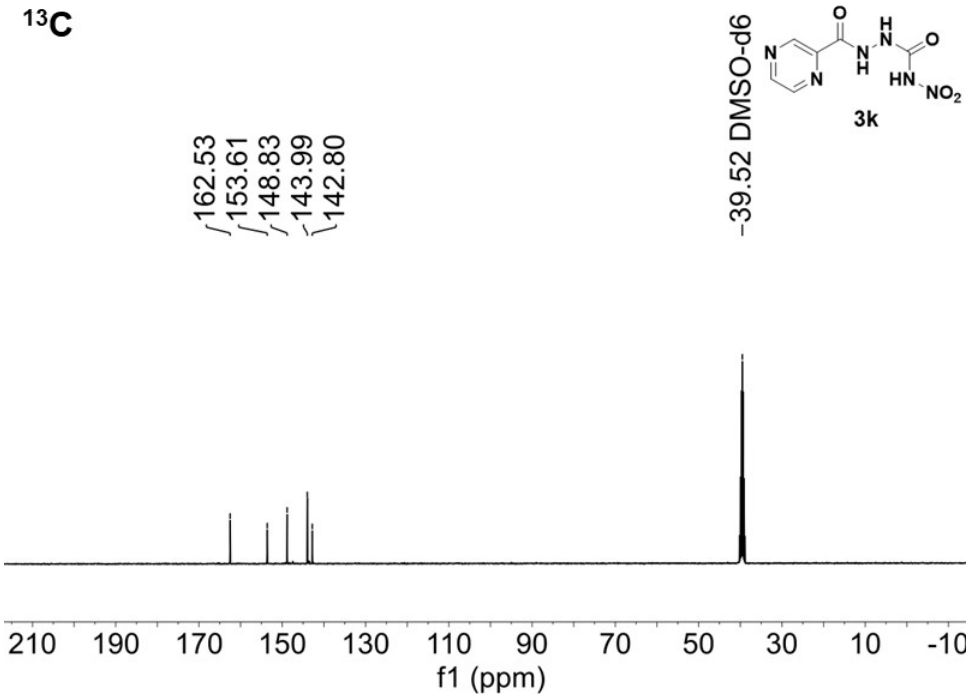


Figure S22. ^{13}C NMR of **3k** in DMSO-d_6.

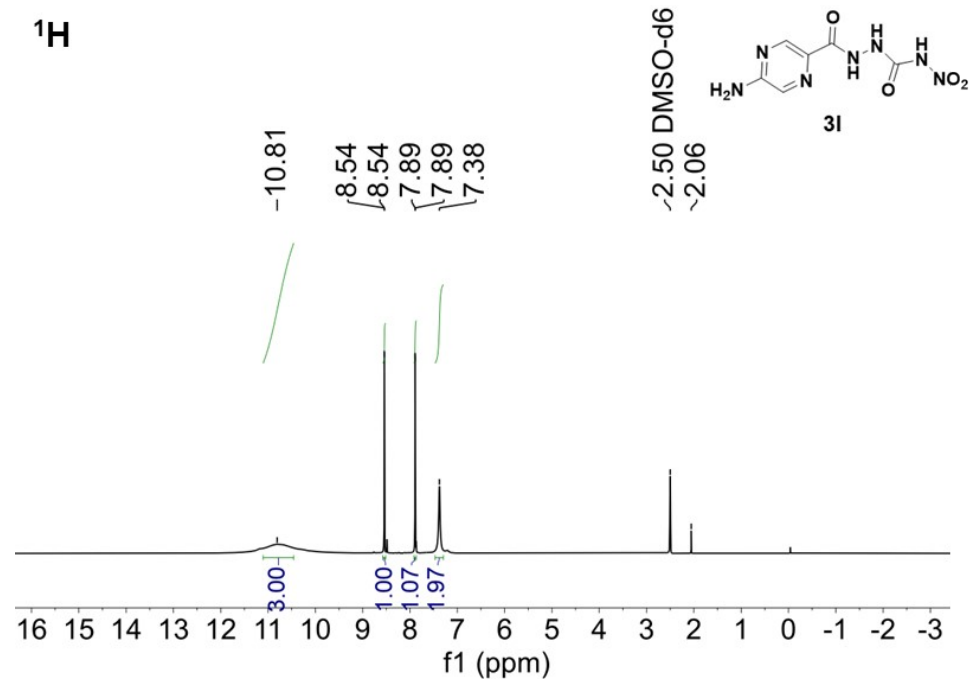


Figure S23. ^{1}H NMR of **3l** in DMSO-d_6.

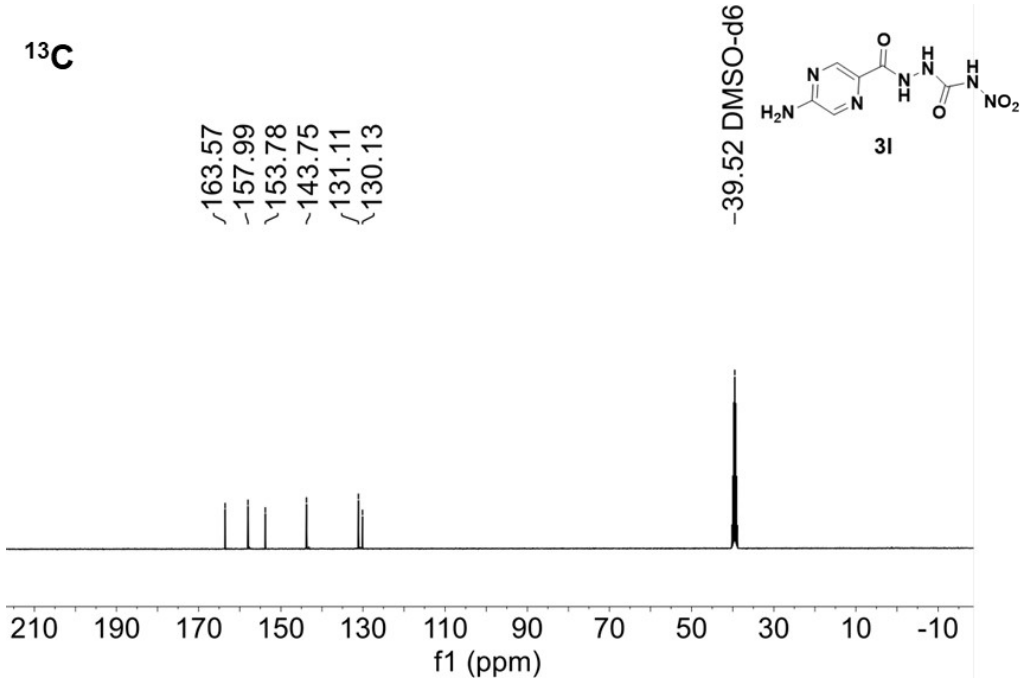


Figure S24. ^{13}C NMR of **3l** in DMSO-d_6.

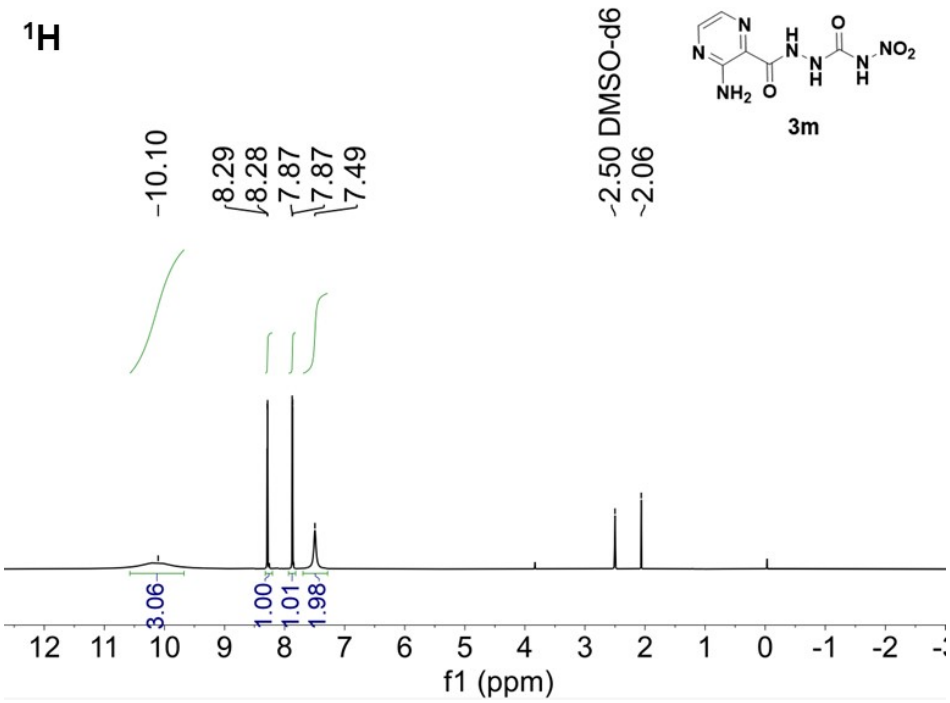


Figure S25. ^{1}H NMR of **3m** in DMSO-d_6.

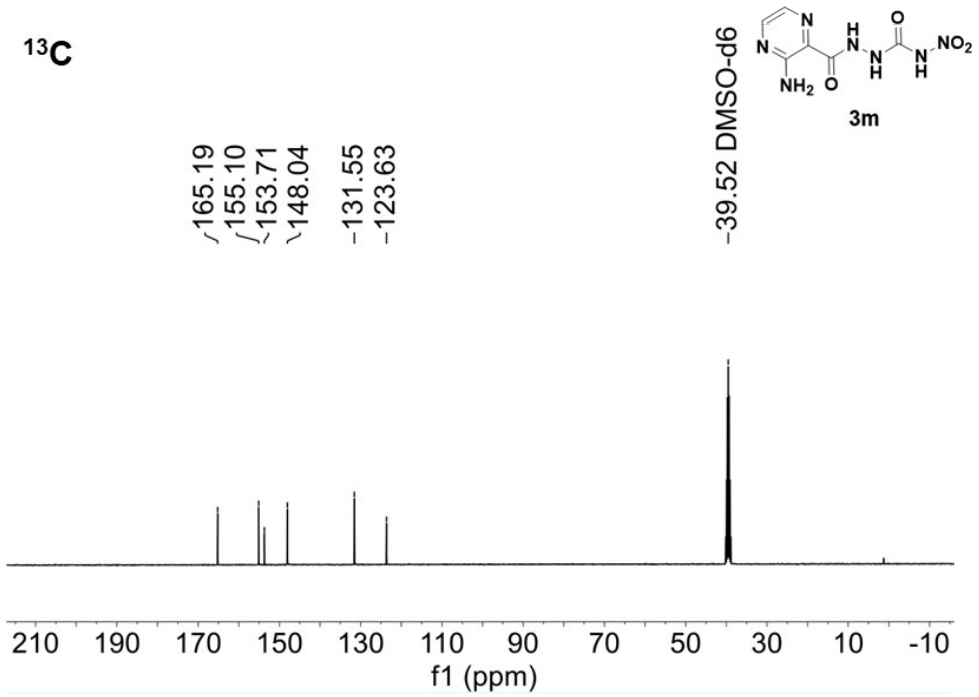


Figure S26. ^{13}C NMR of **3m** in DMSO-d_6.

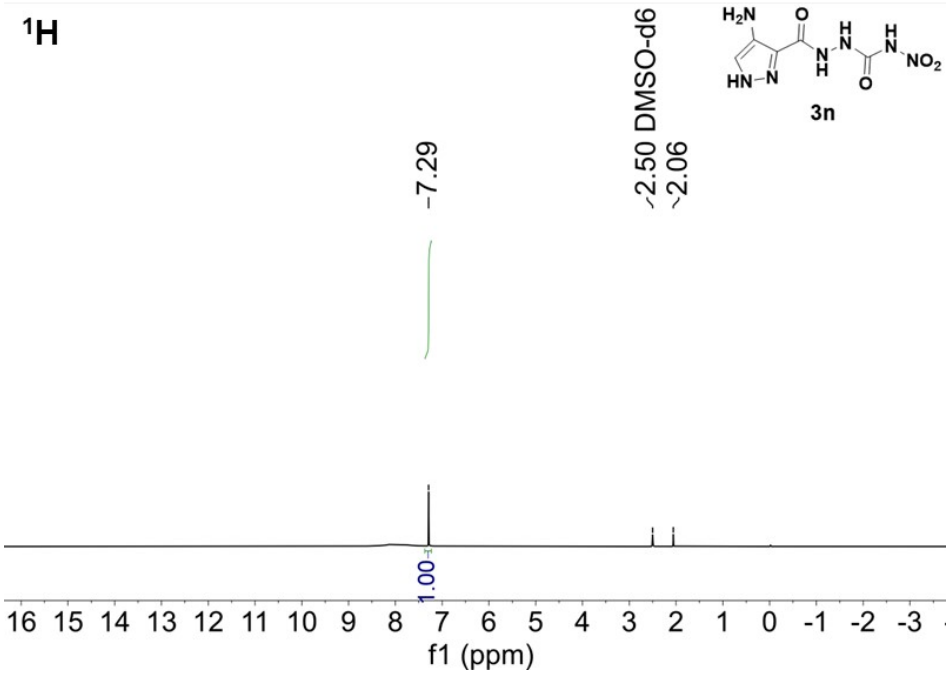


Figure S27. ^{1}H NMR of **3n** in DMSO-d_6.

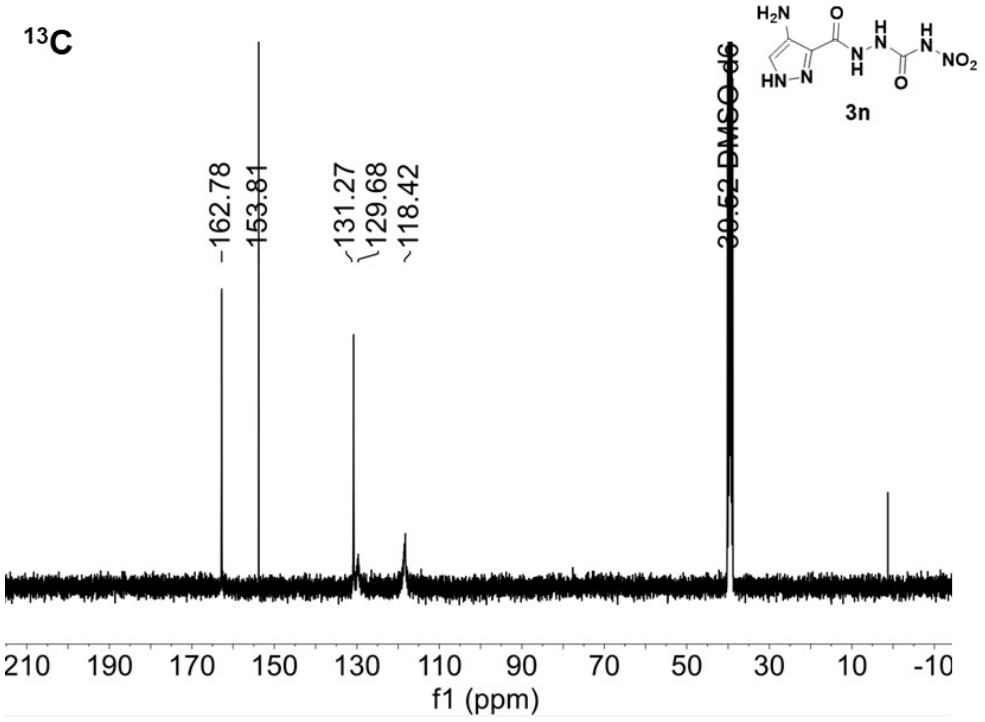


Figure S28. ^{13}C NMR of **3n** in DMSO-d_6.

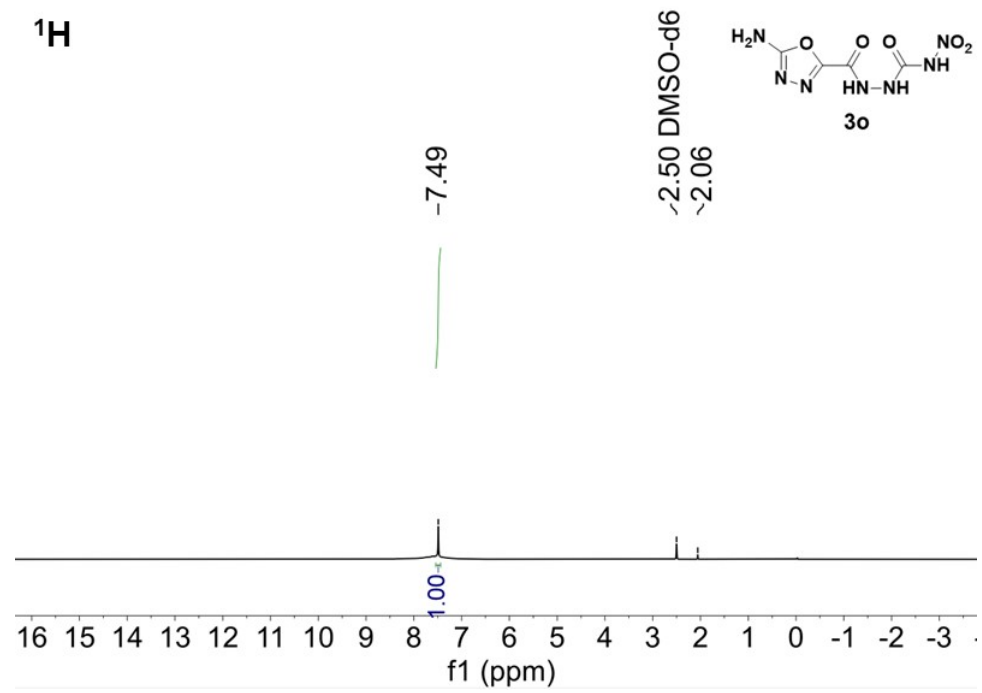


Figure S29. ^{1}H NMR of **3o** in DMSO-d_6.

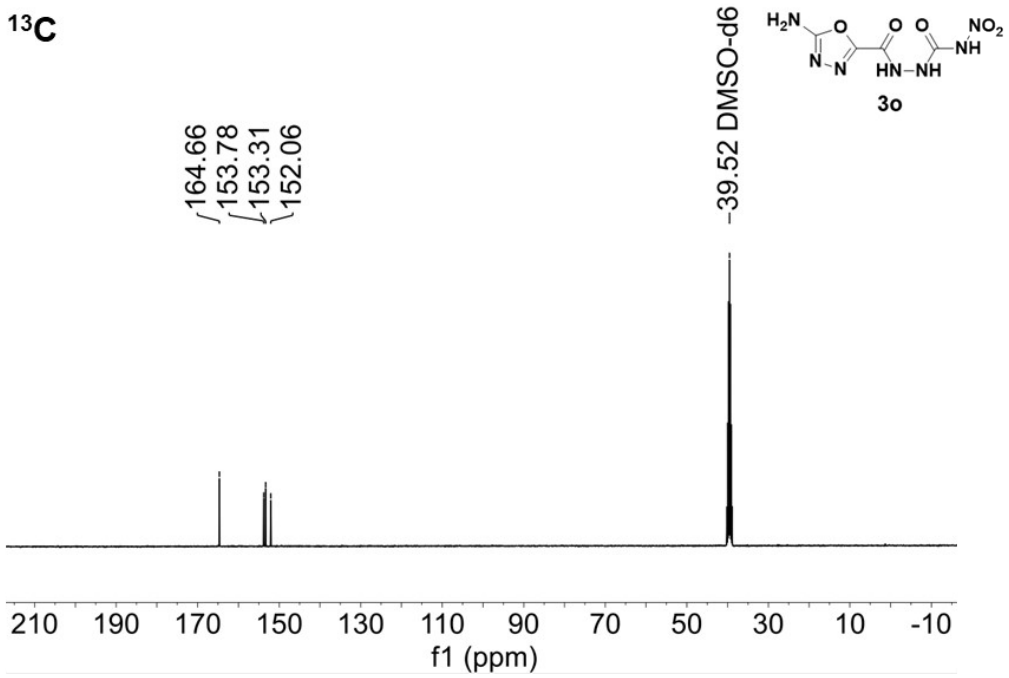


Figure S30. ^{13}C NMR of **3o** in DMSO-d_6.

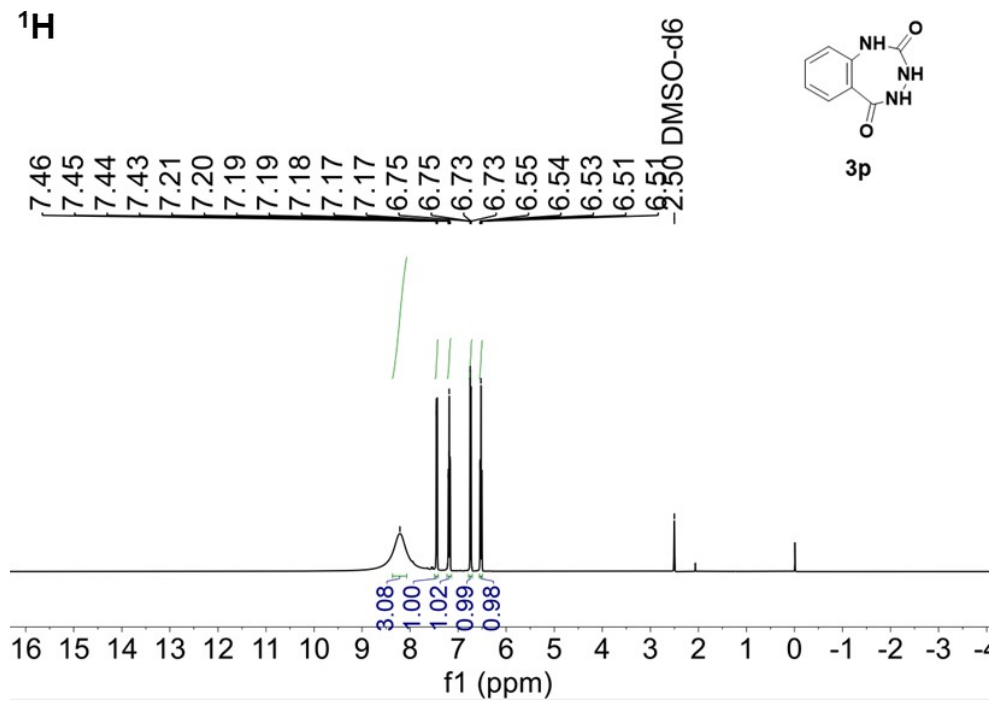


Figure S31. ^{1}H NMR of **3p** in DMSO-d_6.

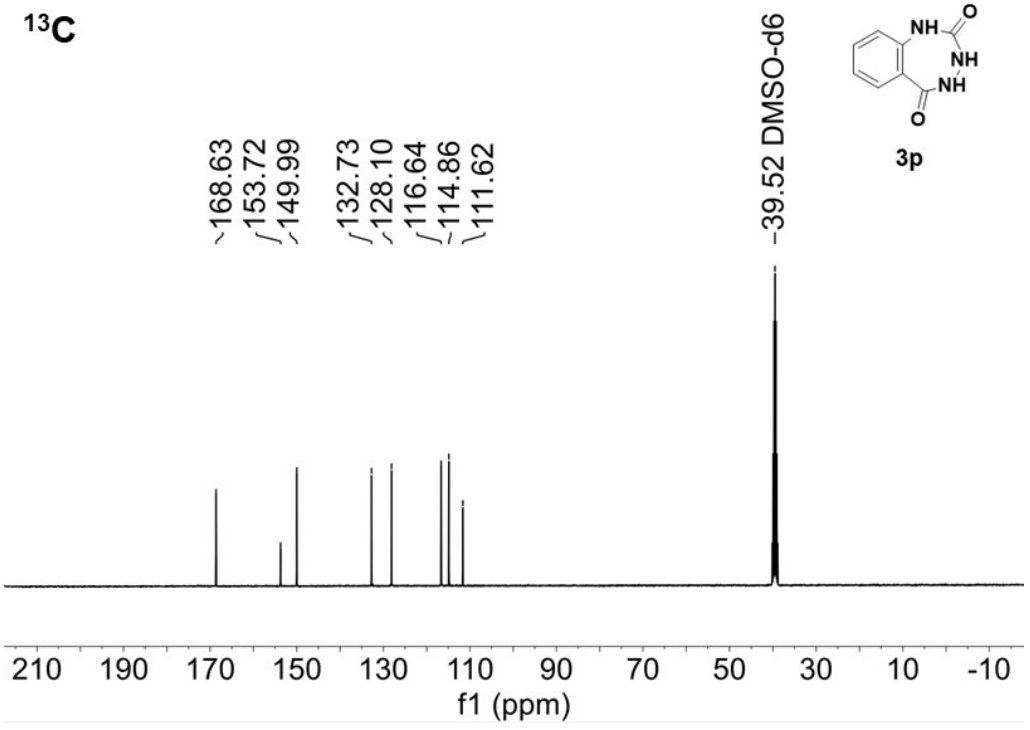


Figure S32. ^{13}C NMR of **3p** in DMSO-d_6.

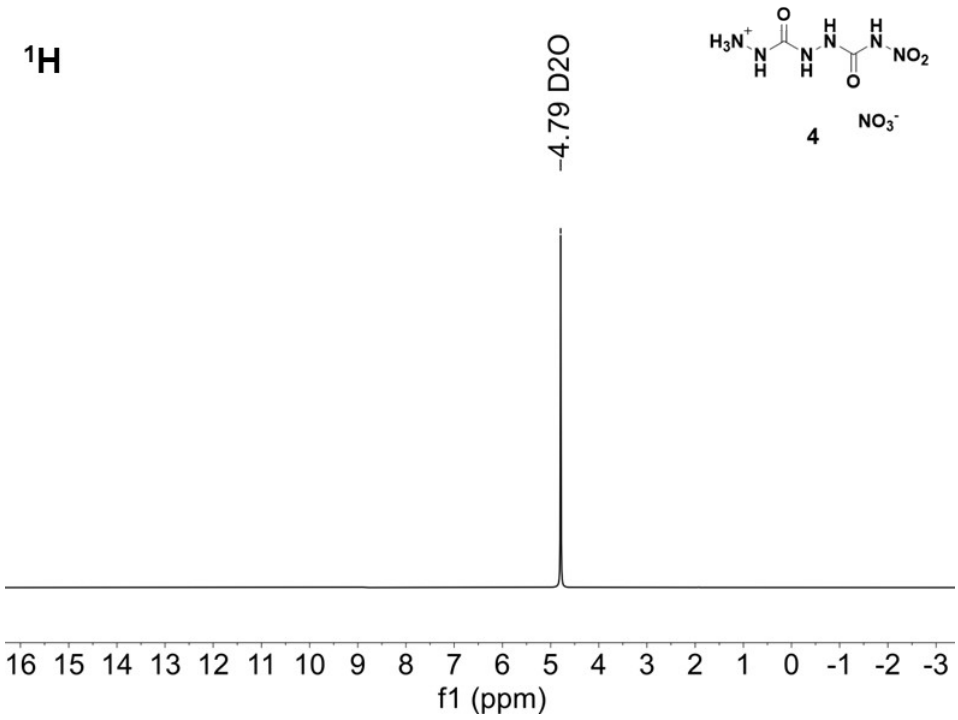


Figure S33. ^{1}H NMR of **4** in D_2O.

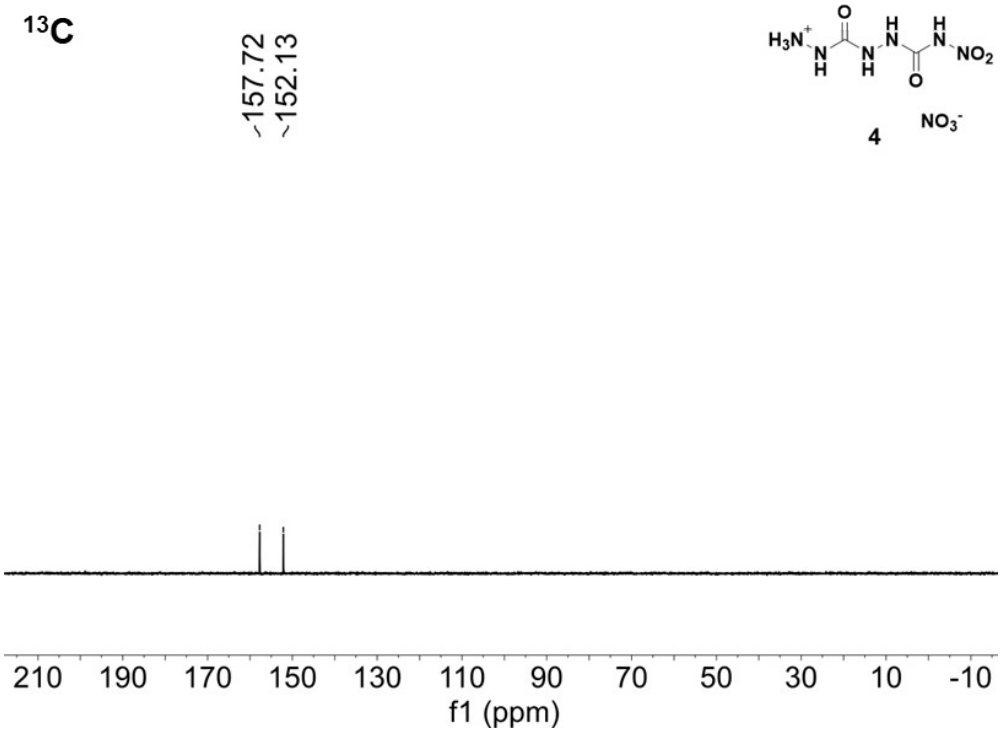


Figure S34. ^{13}C NMR of **4** in D_2O.

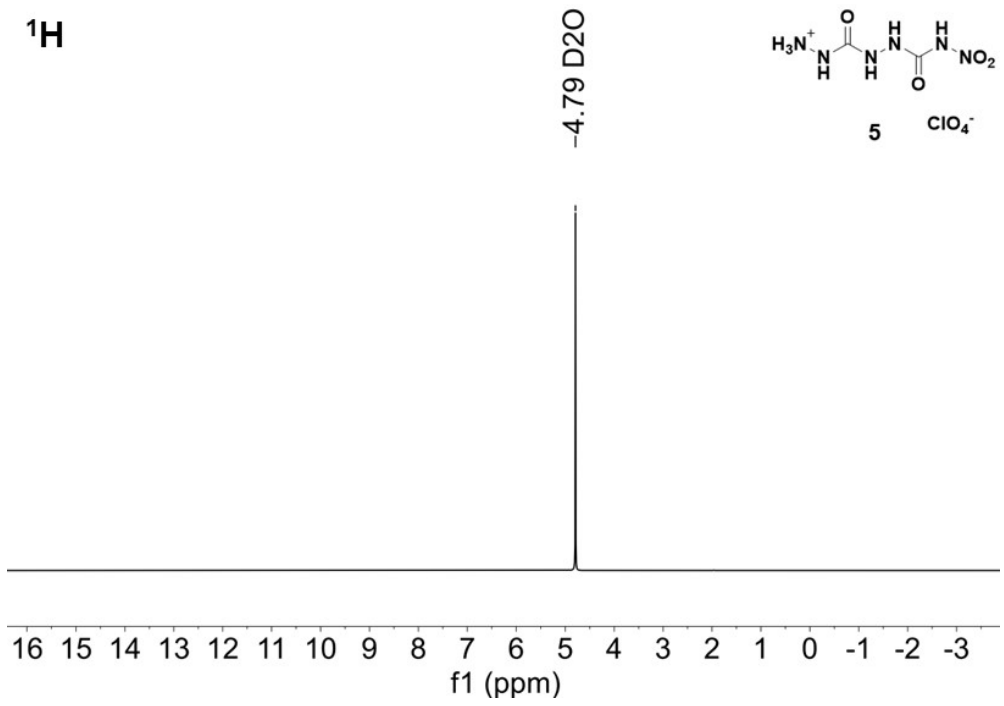


Figure S35. ^{1}H NMR of **5** in D_2O.

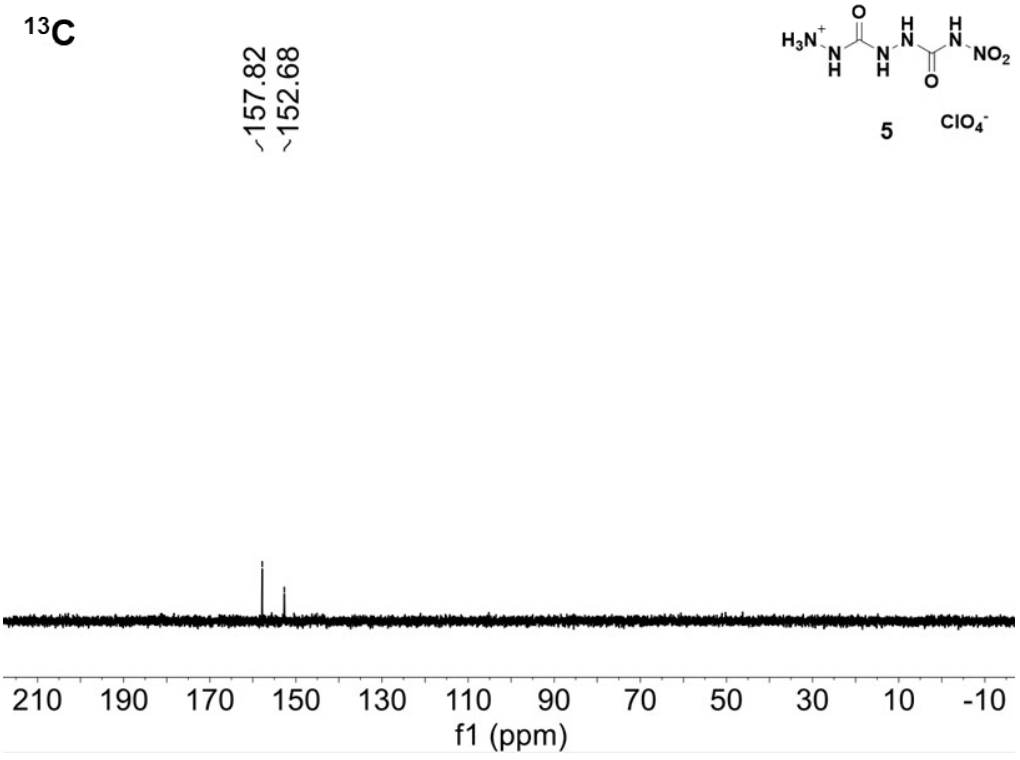


Figure S36. ^{13}C NMR of **5** in D_2O.

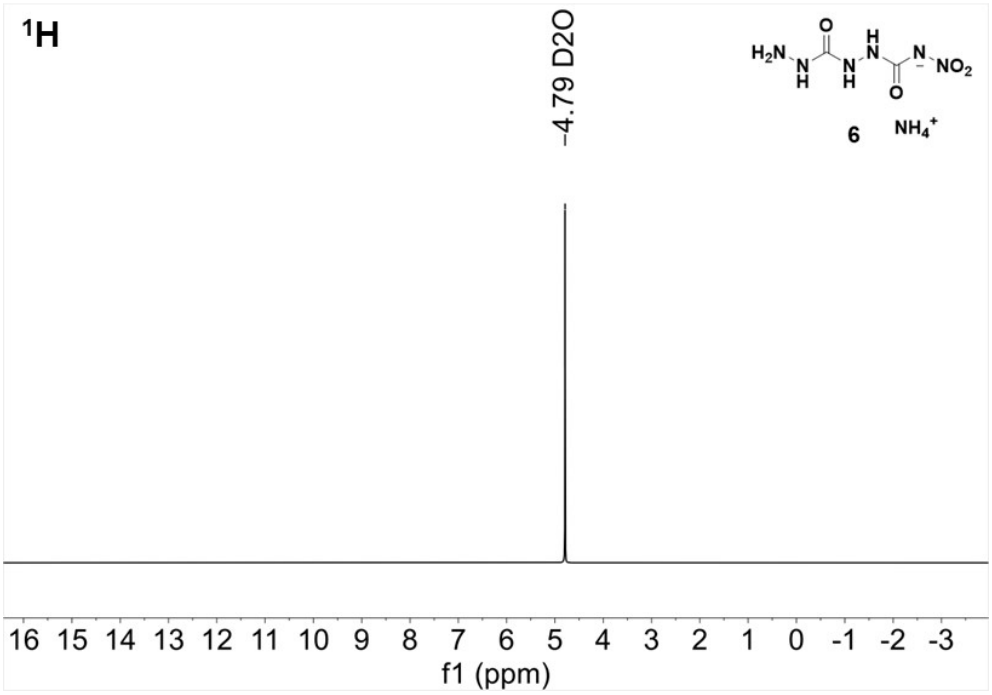


Figure S37. ^{1}H NMR of **6** in D_2O.

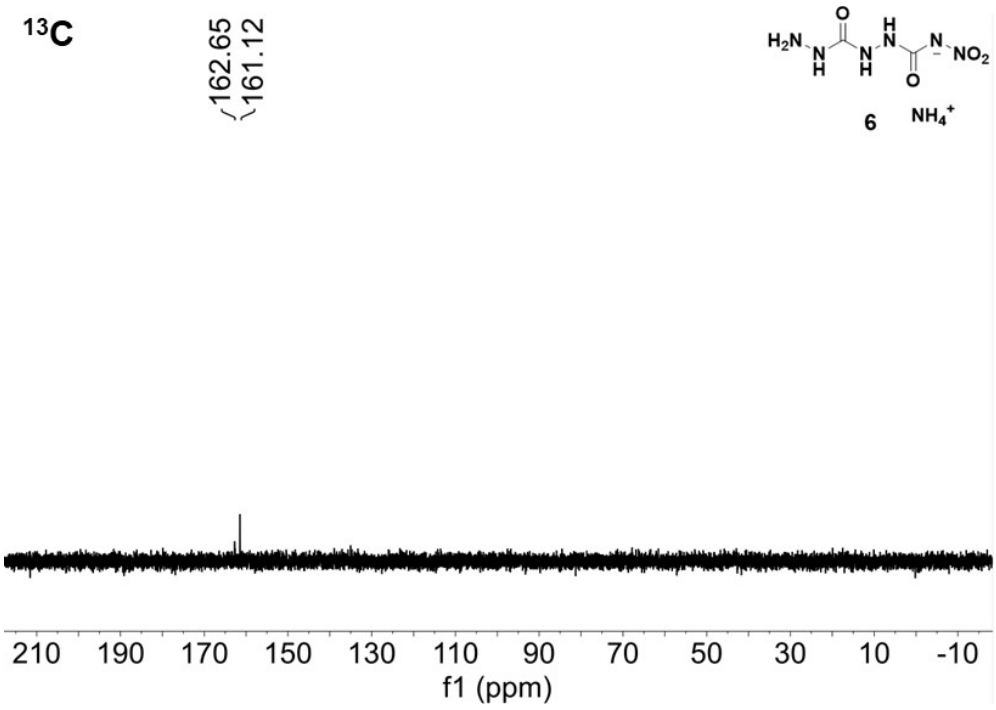


Figure S38. ^{13}C NMR of **6** in D_2O.

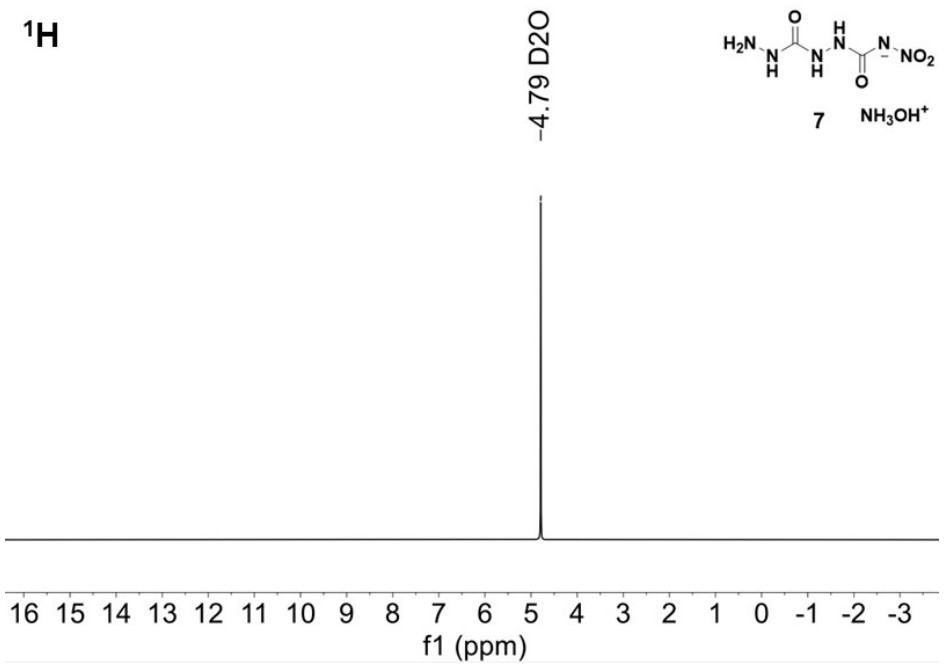


Figure S39. ^{1}H NMR of **7** in D_2O.

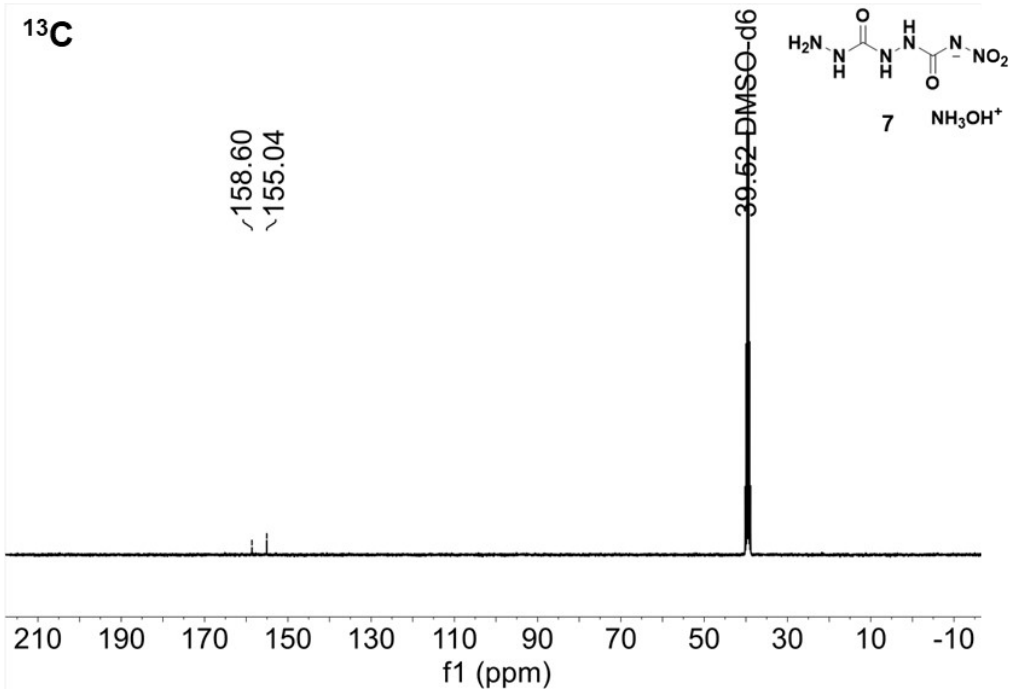


Figure S40. ^{13}C NMR of **7** in DMSO-d_6.

Figure S41. ^{1}H NMR of **HNNC-NH$_2$ (3a)** in DMSO-d$_6$.

Figure S42. ^{13}C NMR of **HNNC-NH$_2$ (3a)** in DMSO-d$_6$.

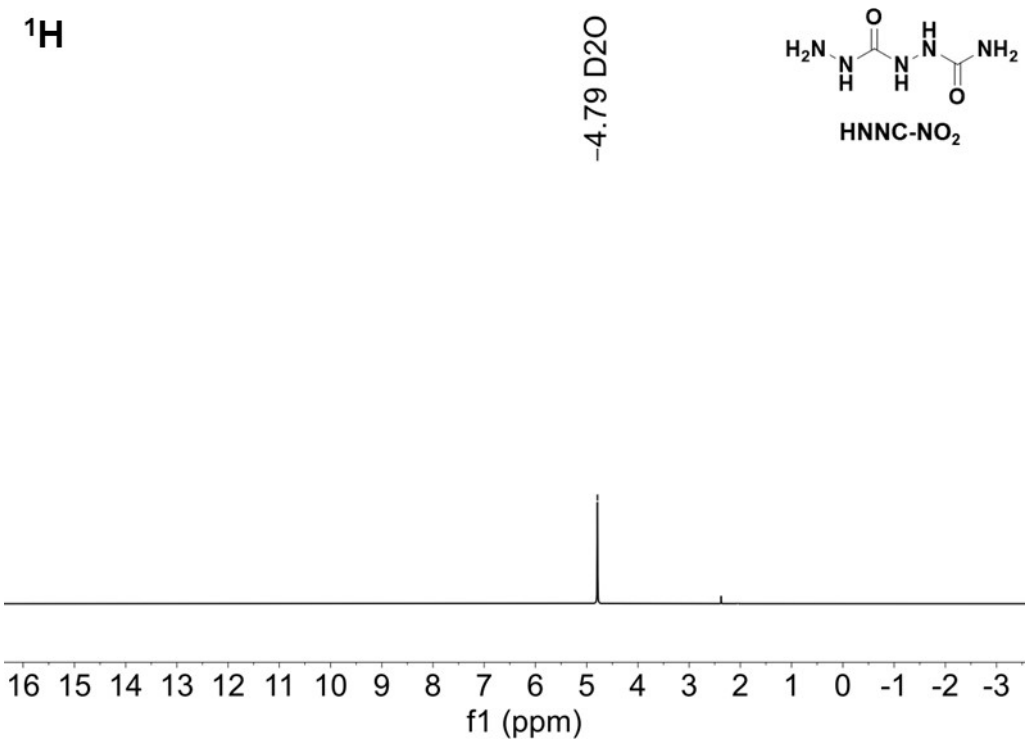


Figure S43. ^{1}H NMR of **HNNC-NO_2** in D_2O.

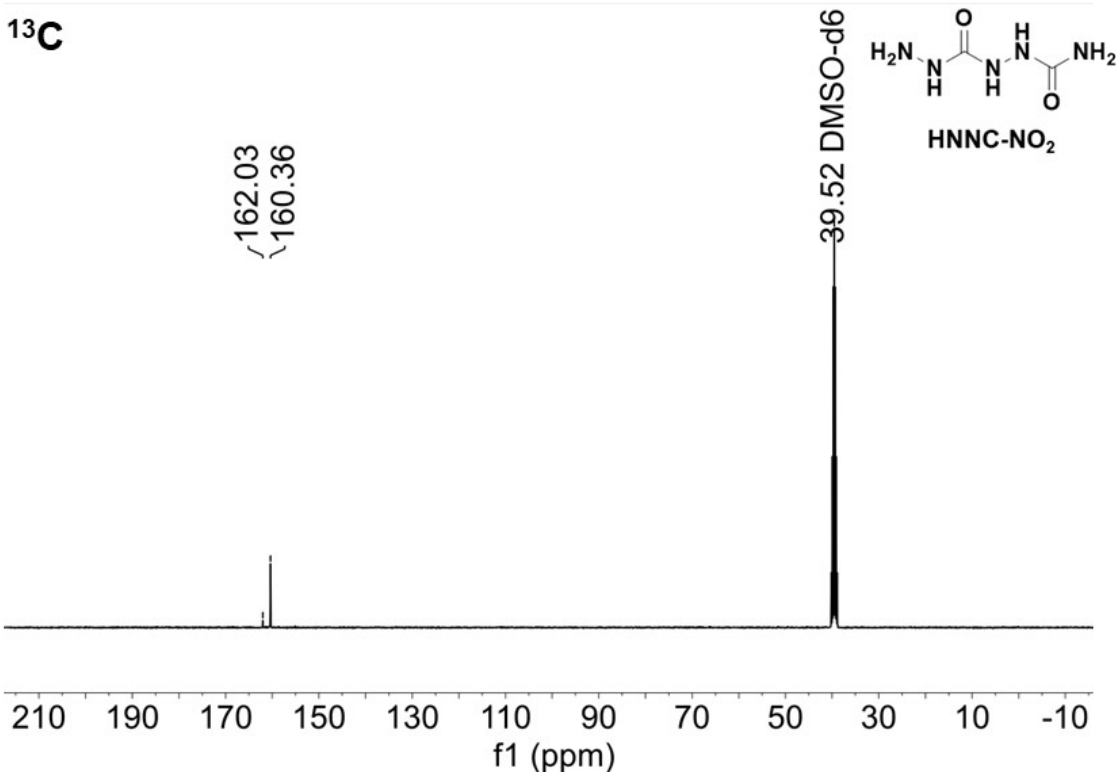


Figure S44. ^{13}C NMR of **HNNC-NO_2** in DMSO-d_6.

4.2 IR Spectra

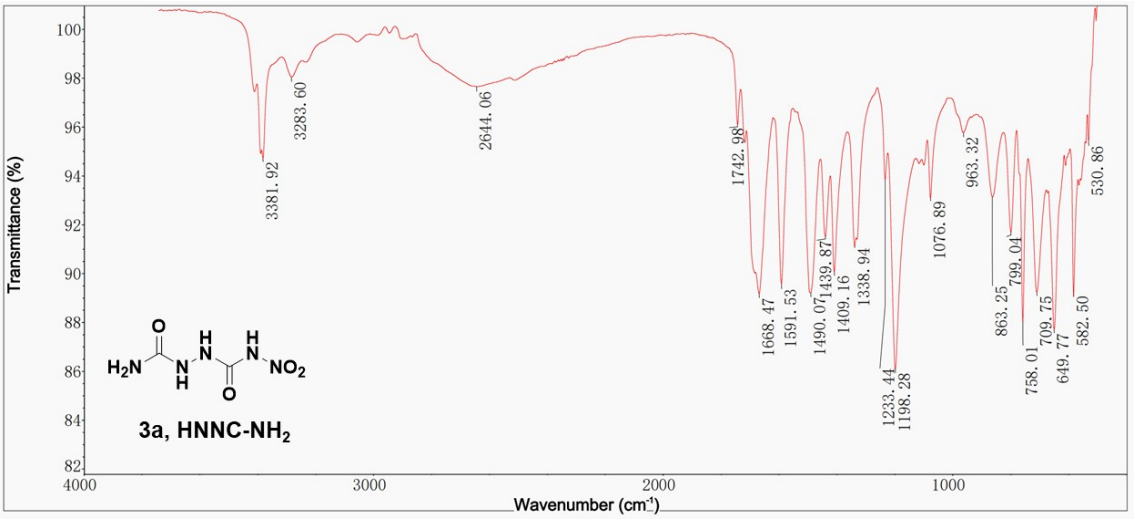


Figure S45. IR spectrum of **HNNC-NH$_2$ (3a)**.

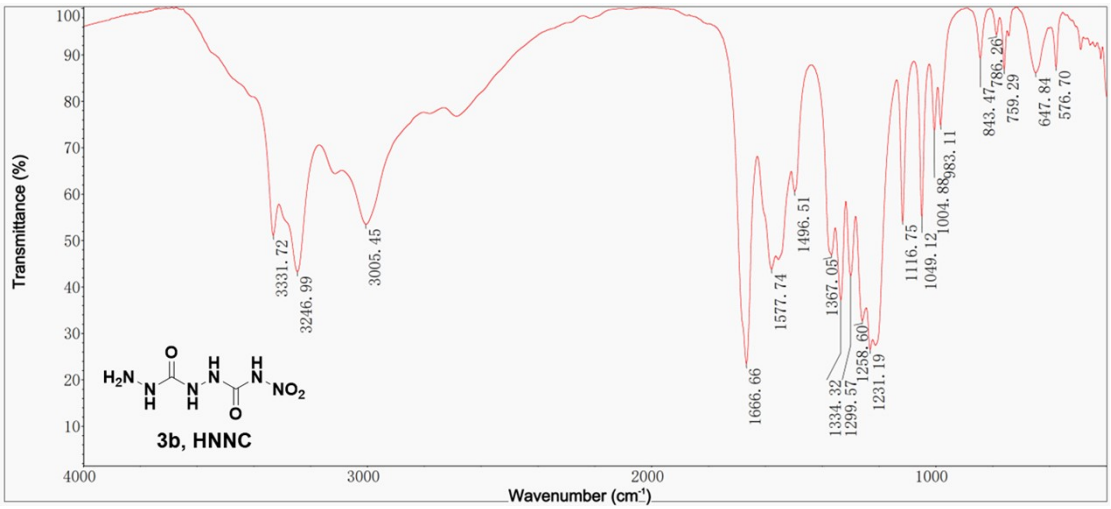


Figure S46. IR spectrum of **HNNC (3b)**.

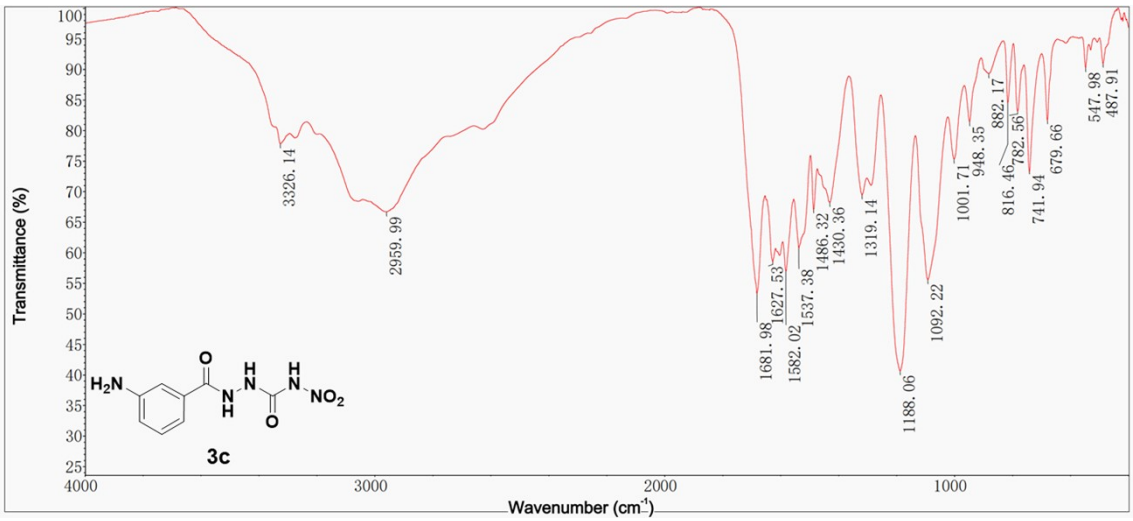


Figure S47. IR spectrum of **3c**.

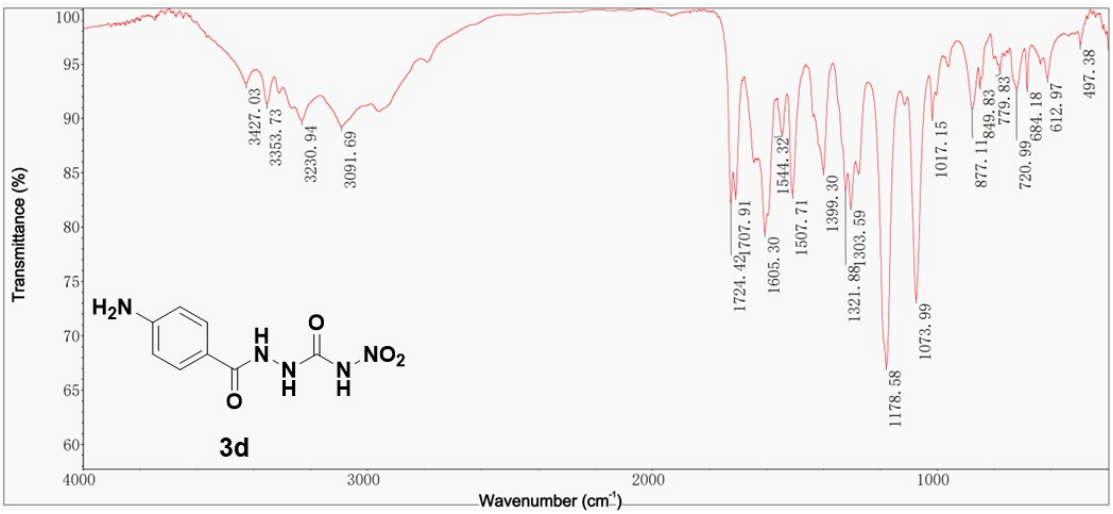


Figure S48. IR spectrum of **3d**.

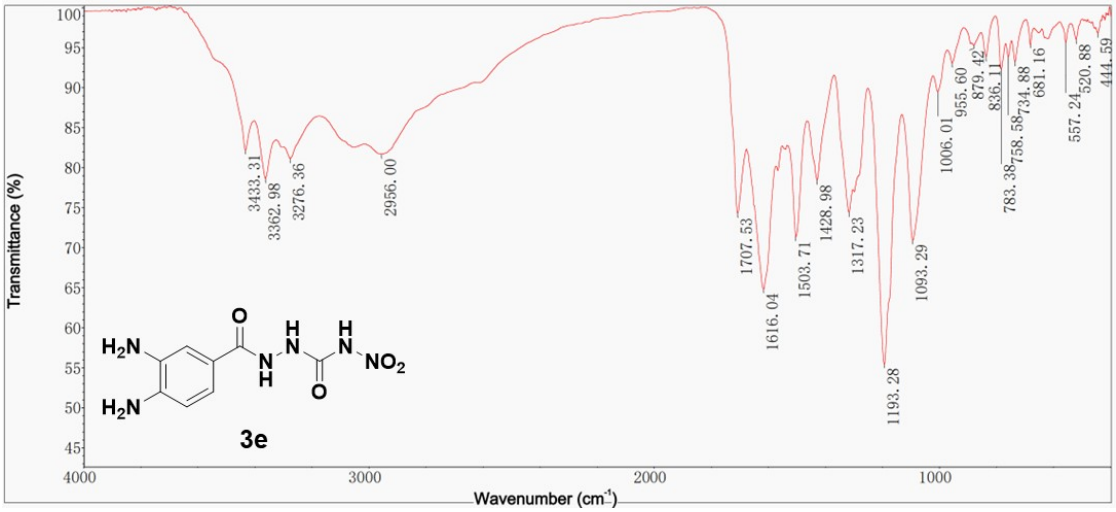


Figure S49. IR spectrum of **3e**.

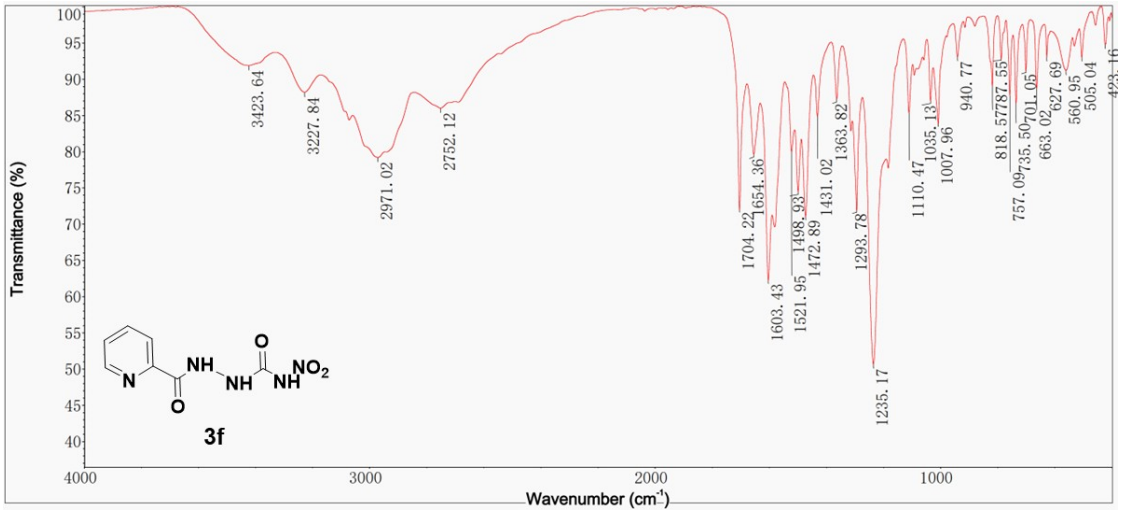


Figure S50. IR spectrum of **3f**.

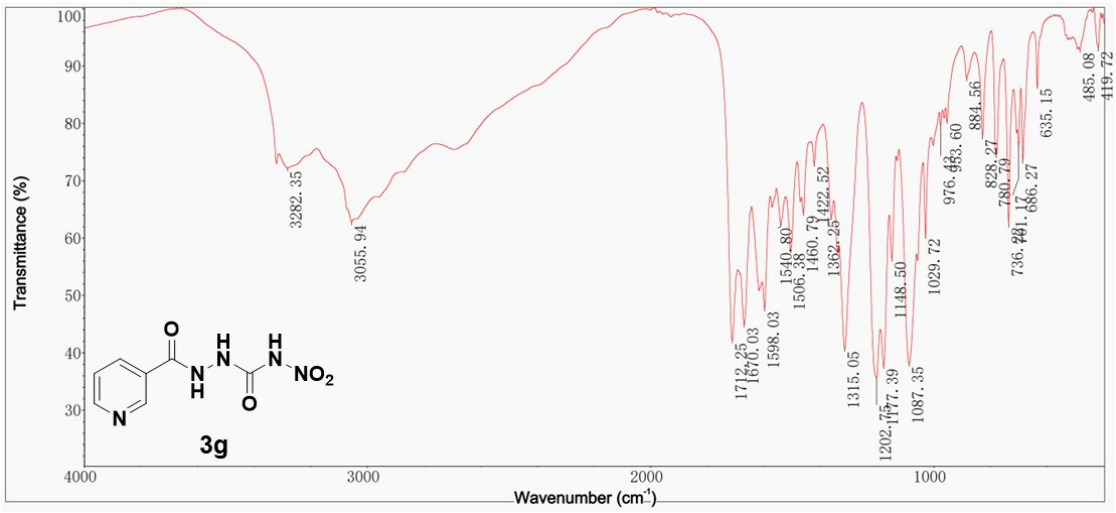


Figure S51. IR spectrum of **3g**.

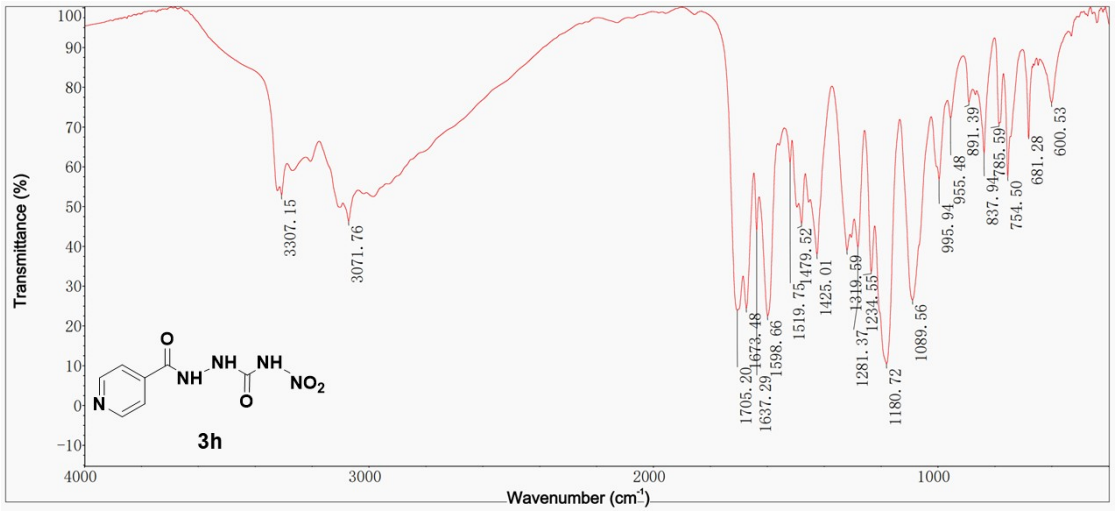


Figure S52. IR spectrum of **3h**.

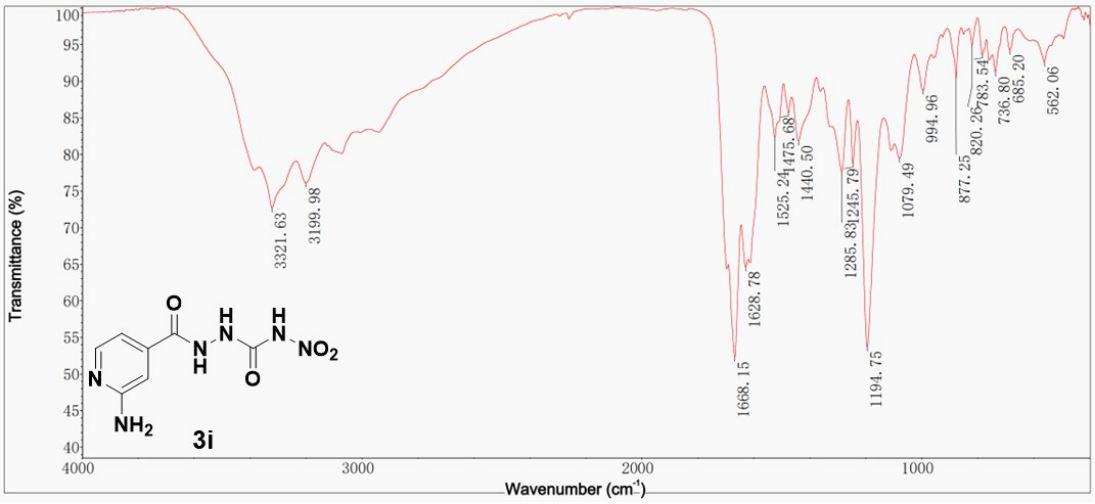


Figure S53. IR spectrum of **3i**.

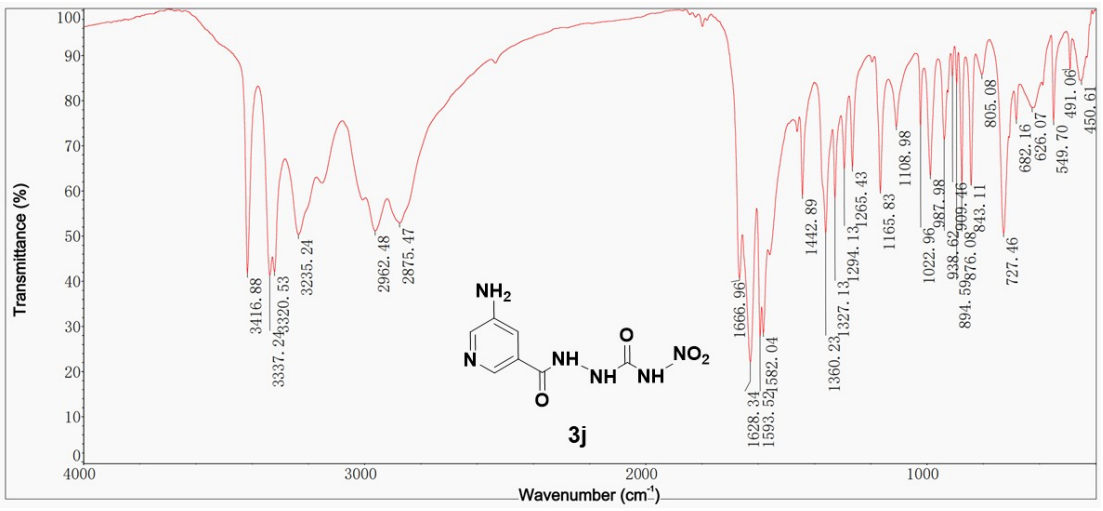


Figure S54. IR spectrum of **3j**.

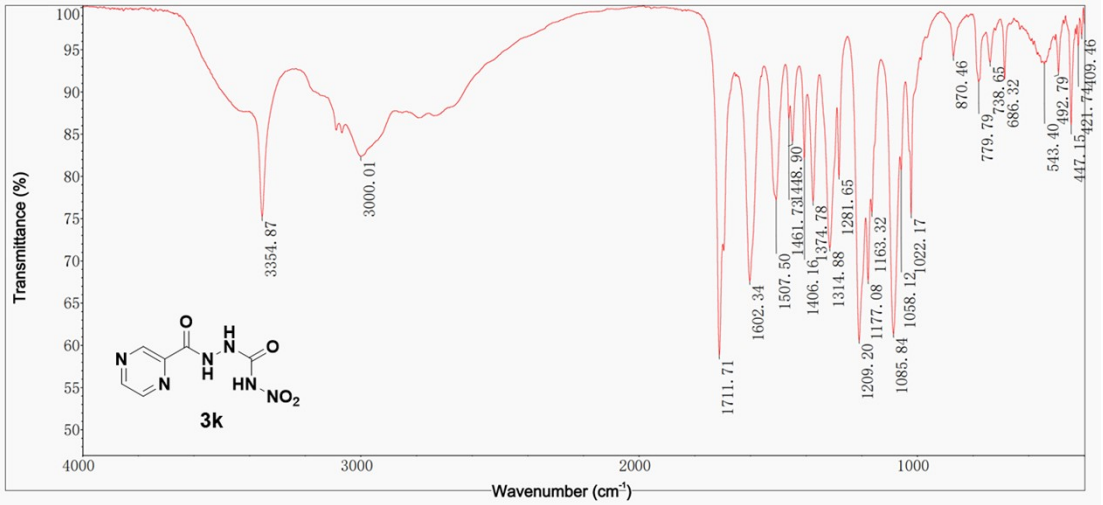


Figure S55. IR spectrum of **3k**.

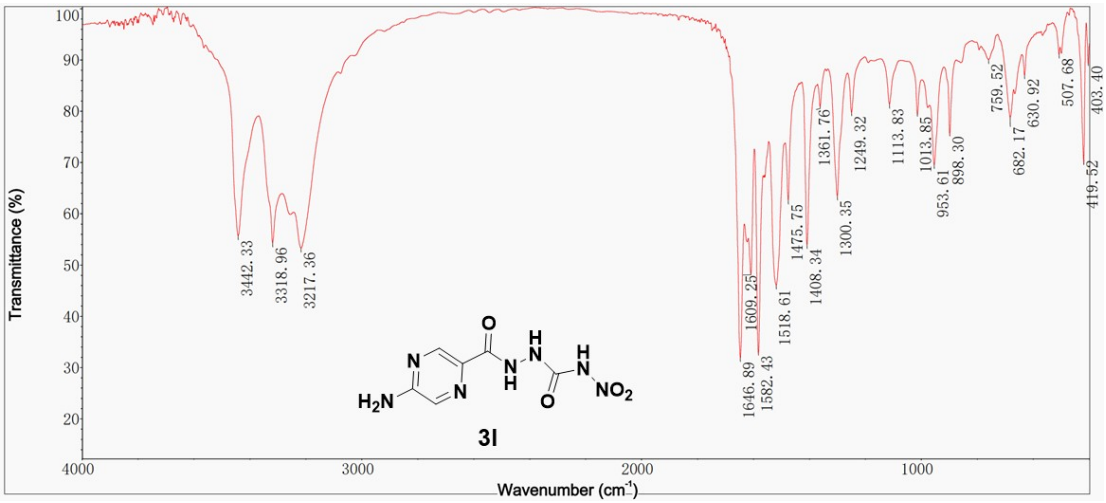


Figure S56. IR spectrum of **3l**.

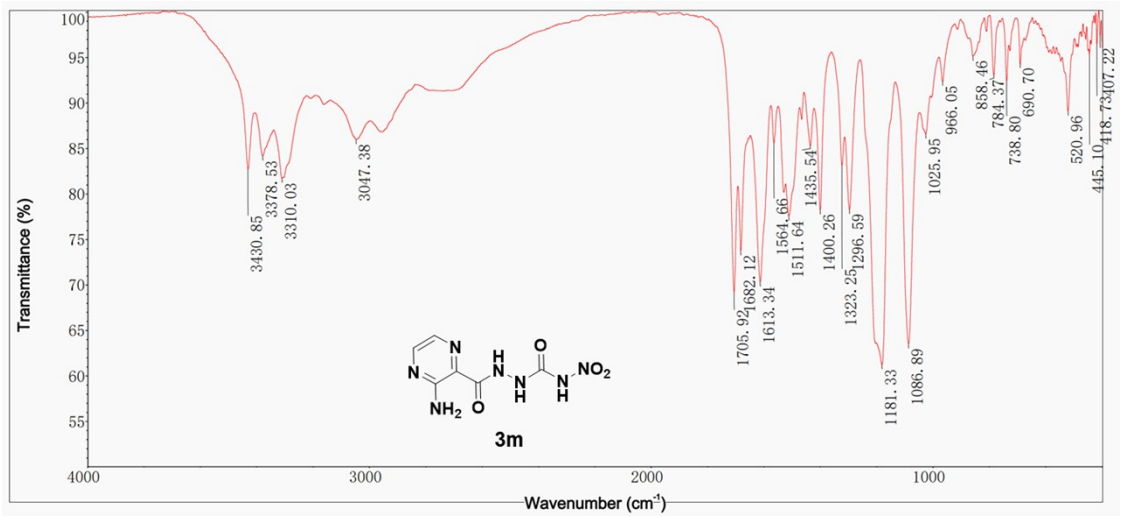


Figure S57. IR spectrum of **3m**.

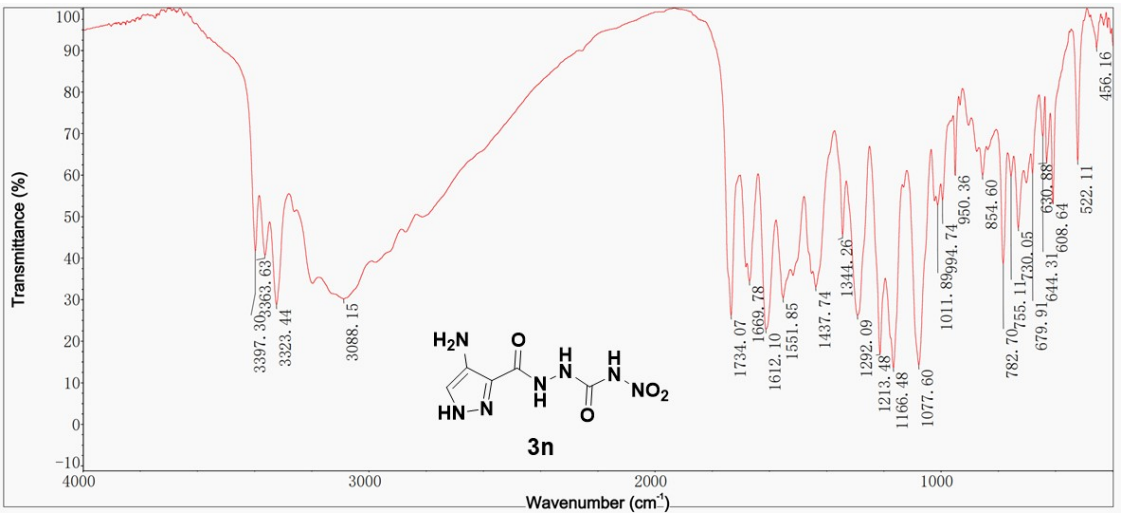


Figure S58. IR spectrum of **3n**.

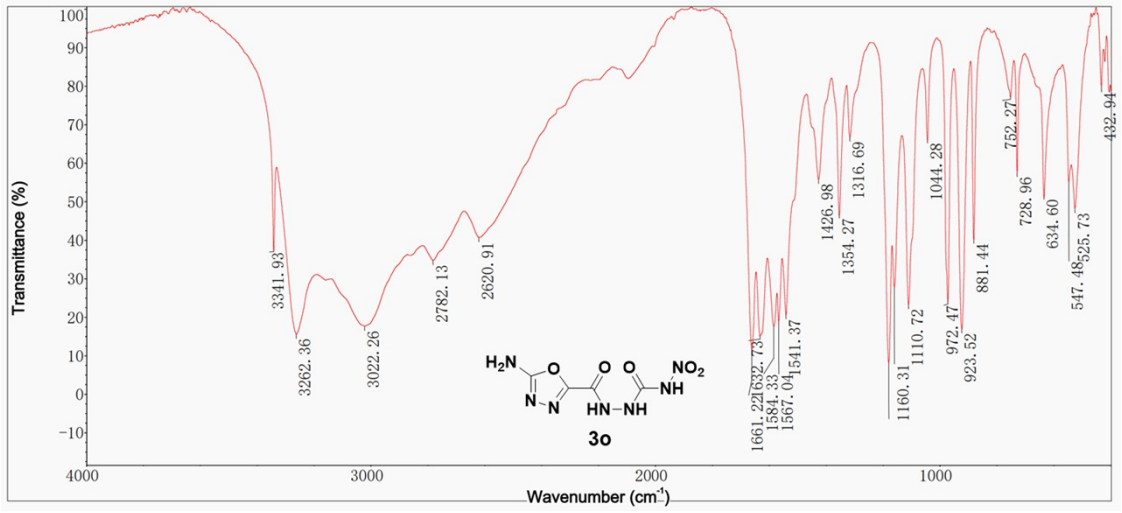


Figure S59. IR spectrum of **3o**.

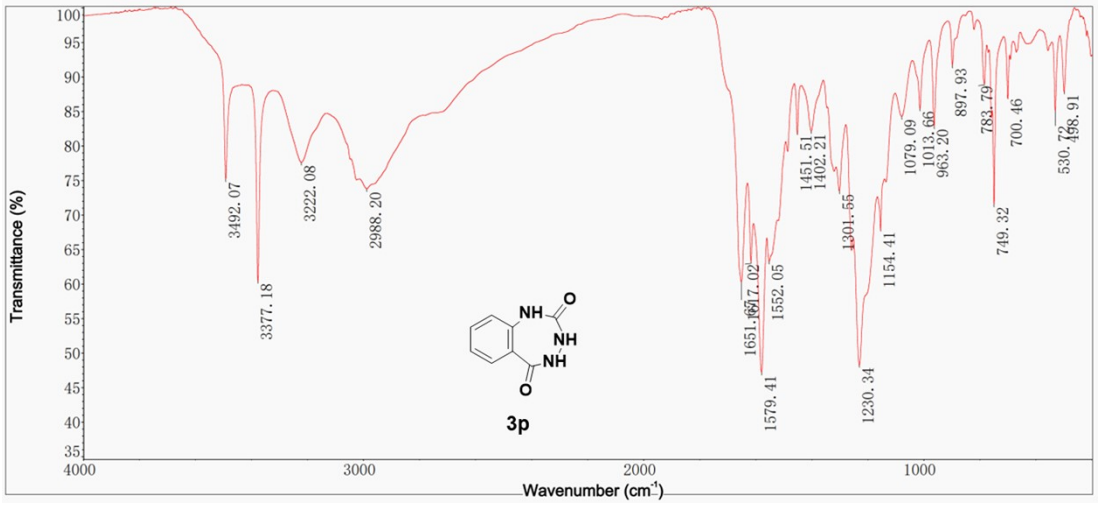


Figure S60. IR spectrum of **3p**.

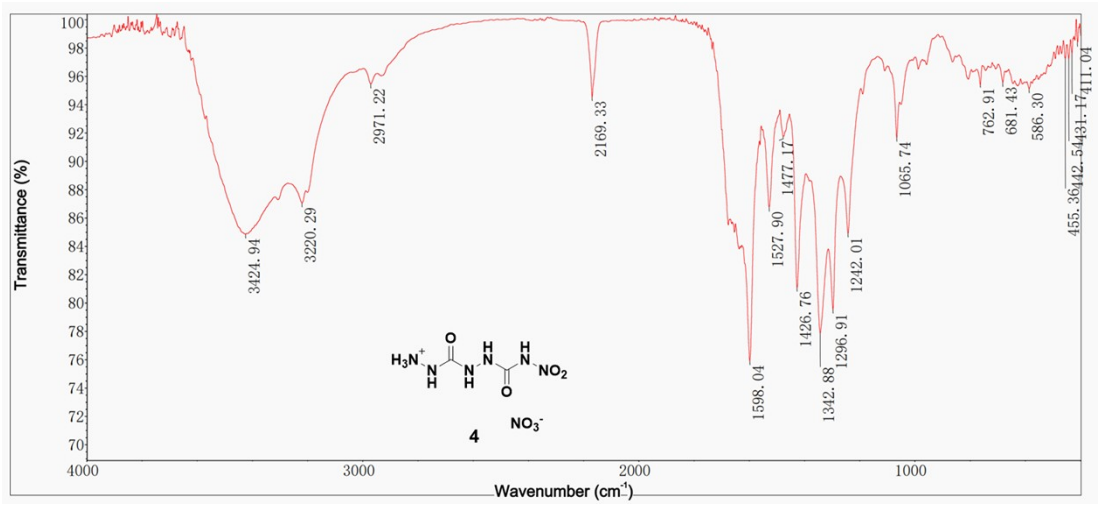


Figure S61. IR spectrum of **4**.

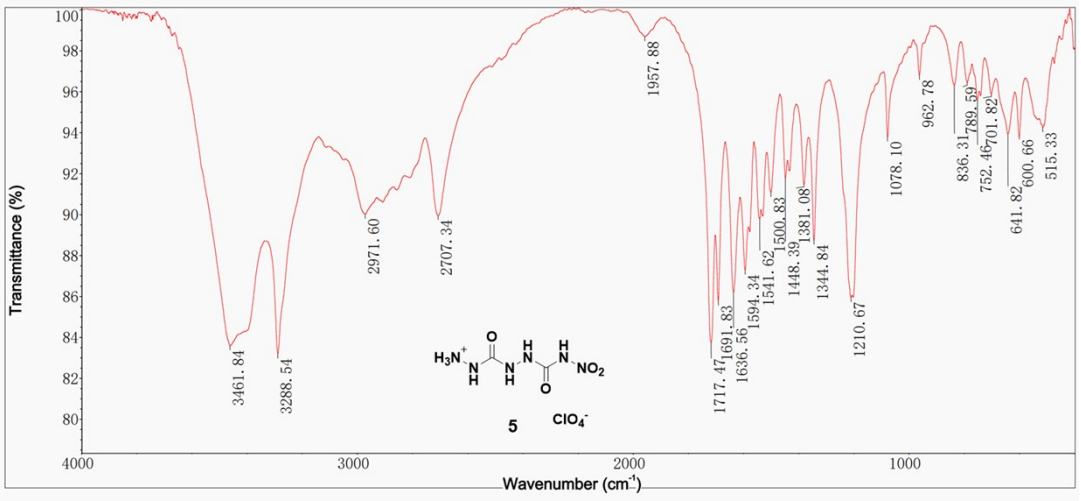


Figure S62. IR spectrum of **5**.

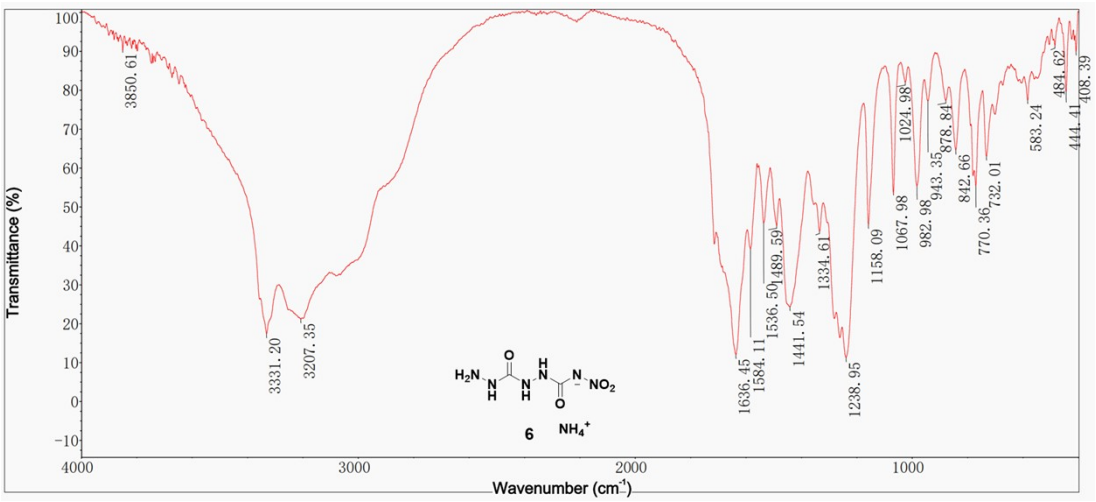


Figure S63. IR spectrum of **6**.

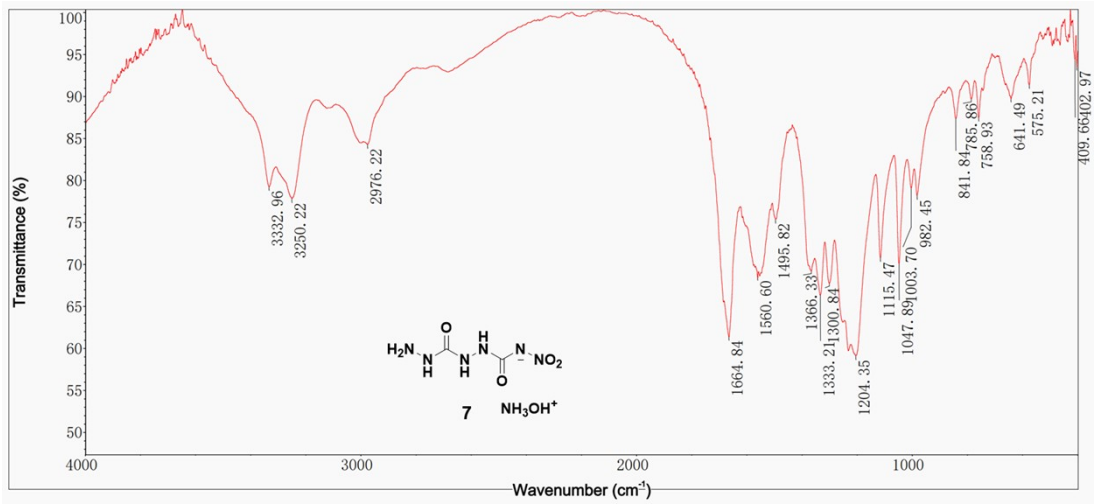


Figure S64. IR spectrum of **7**.

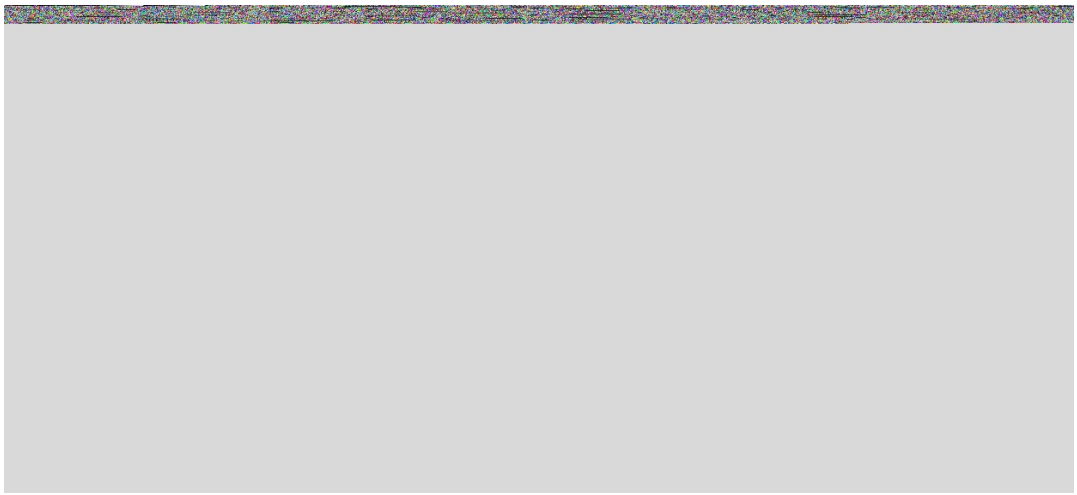


Figure S65. IR spectrum of **HNNC-NH_2 (3a)**.

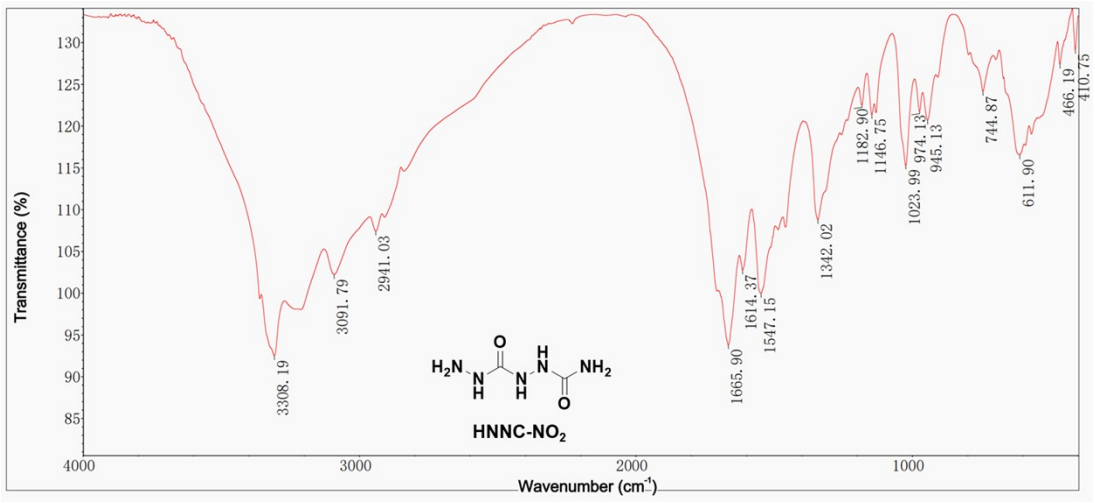


Figure S66. IR spectrum of **HNNC-NO_2**.

4.3 HRMS Spectra

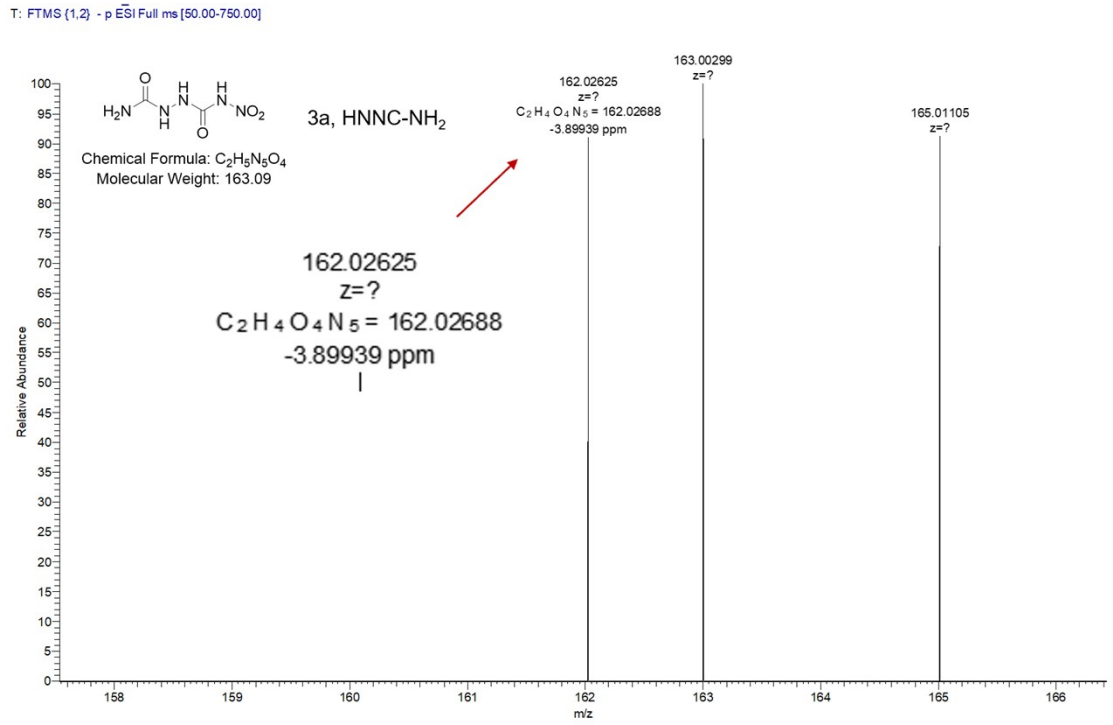


Figure S67. HRMS spectrum of **HNNC-NH$_2$ (3a)**

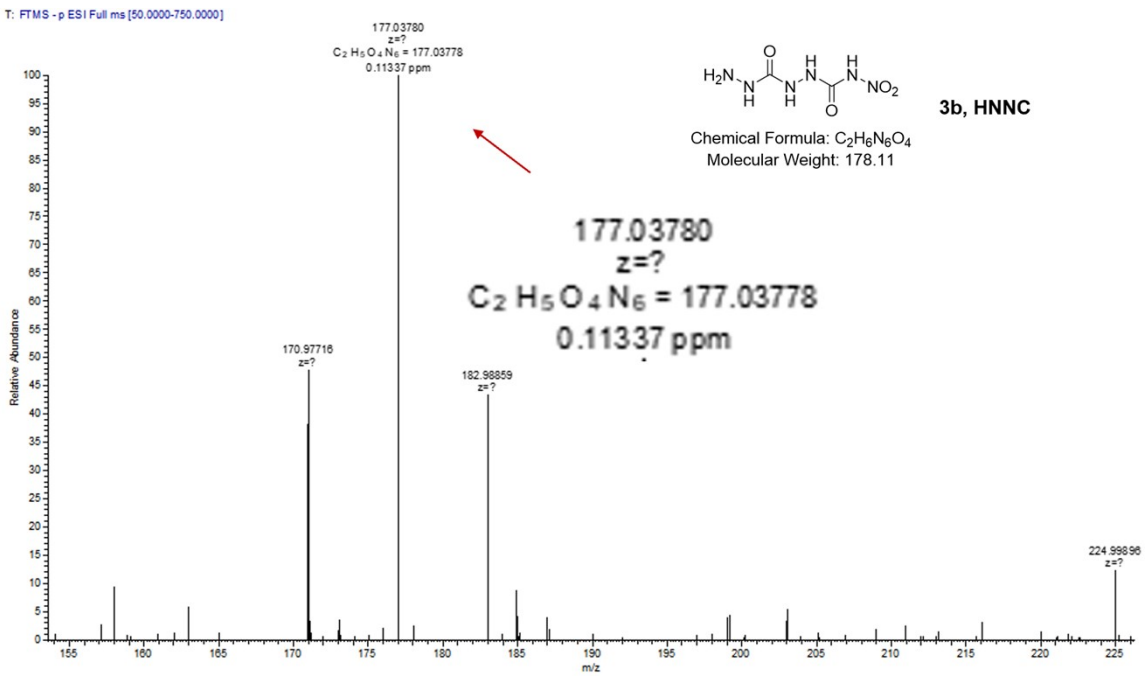


Figure S68. HRMS spectrum of **HNNC (3b)**.

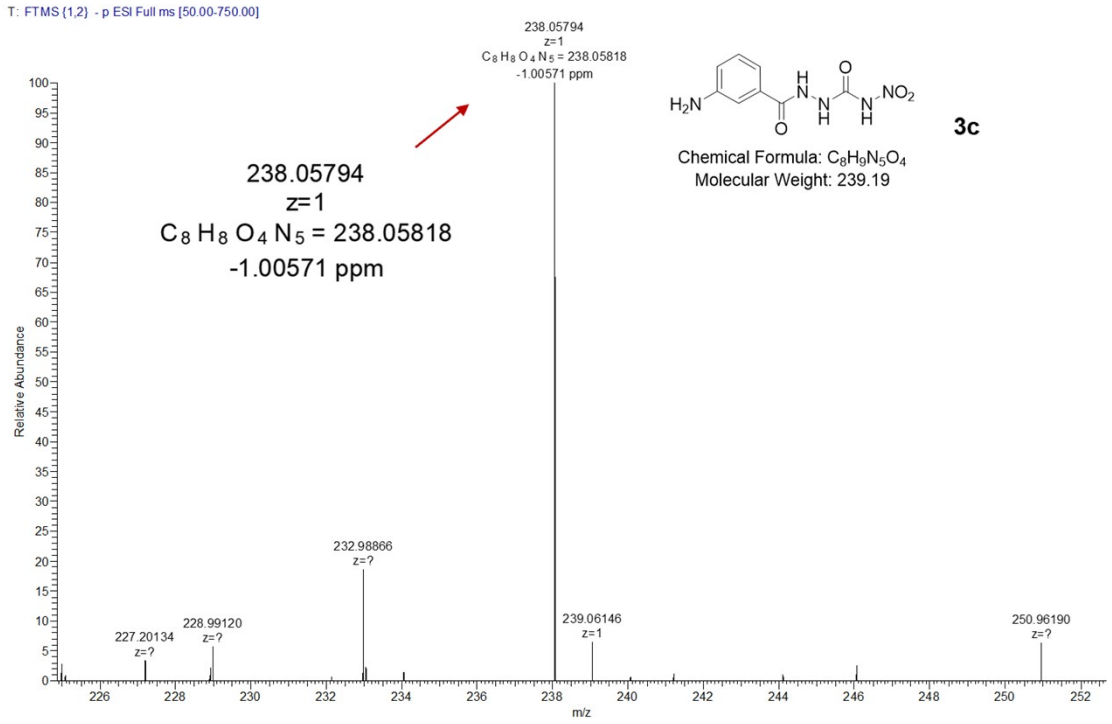


Figure S69. HRMS spectrum of **3c**.

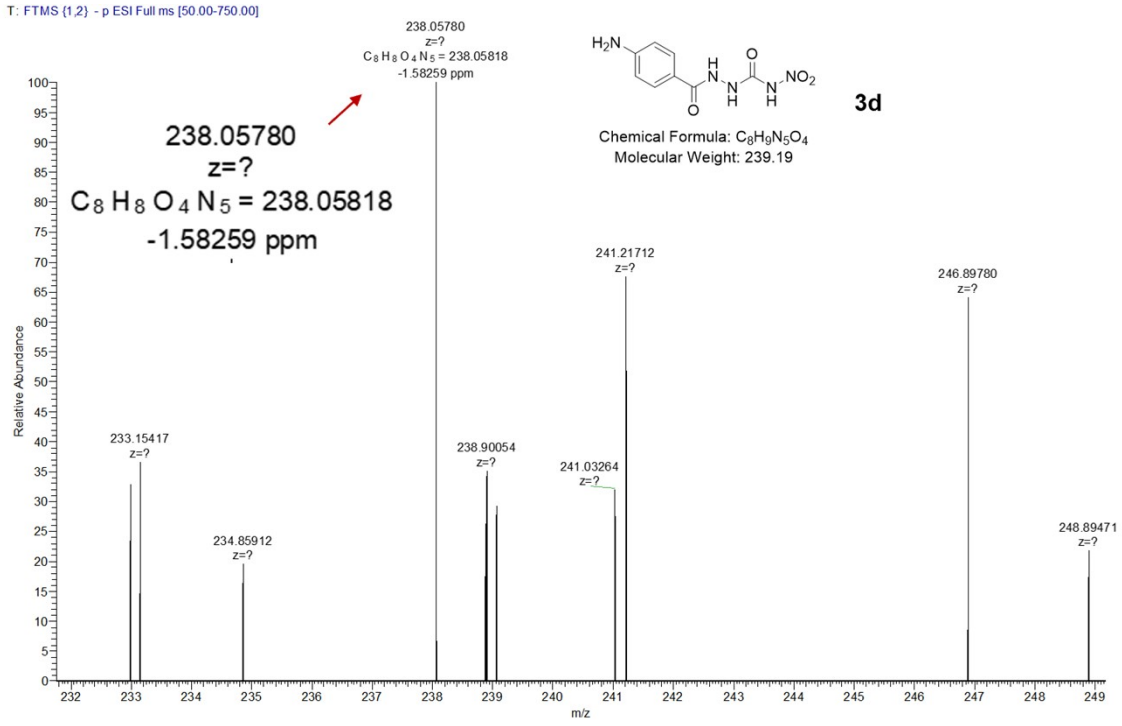


Figure S70. HRMS spectrum of **3d**.

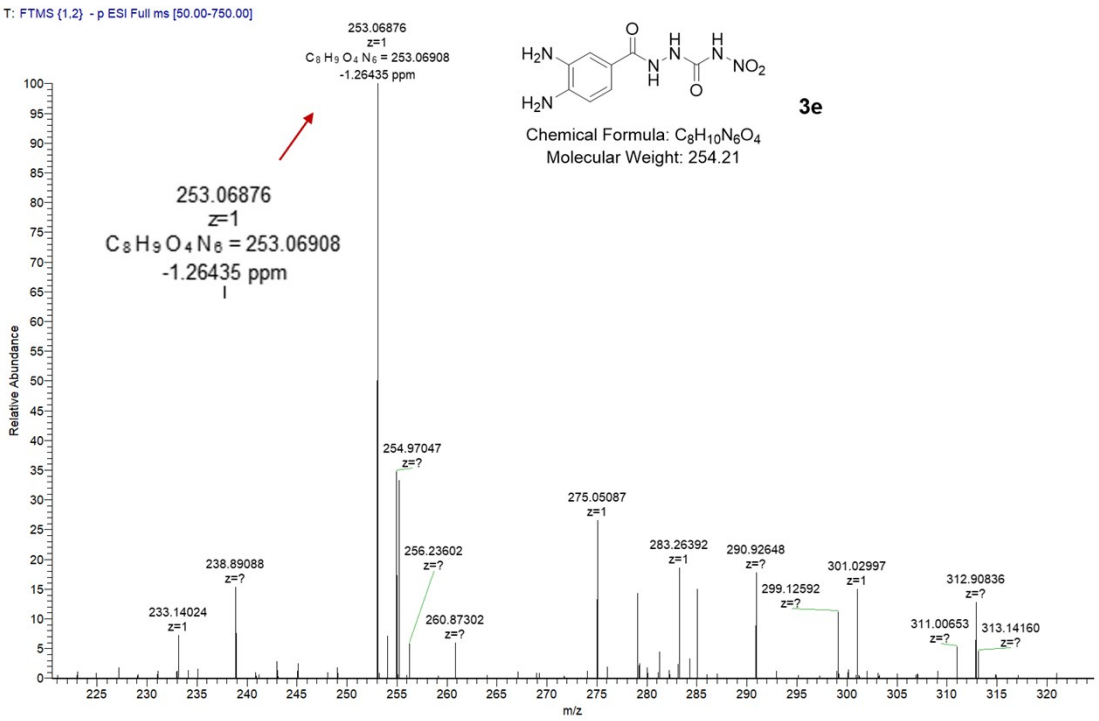


Figure S71. HRMS spectrum of **3e**.

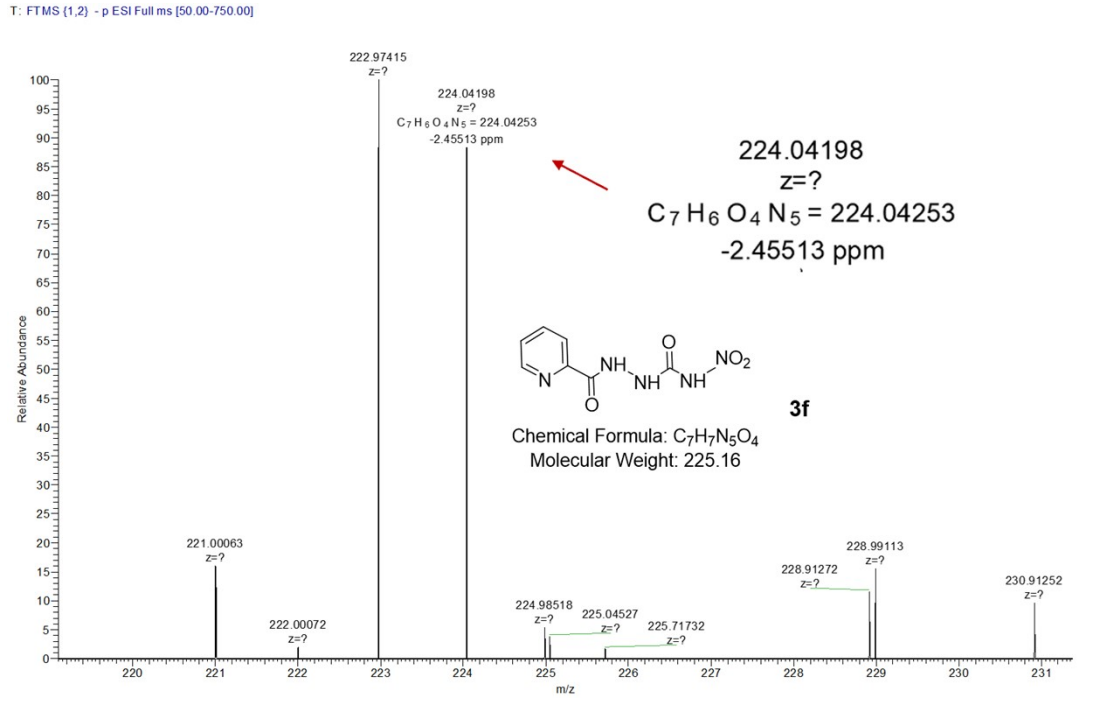


Figure S72. HRMS spectrum of **3f**.

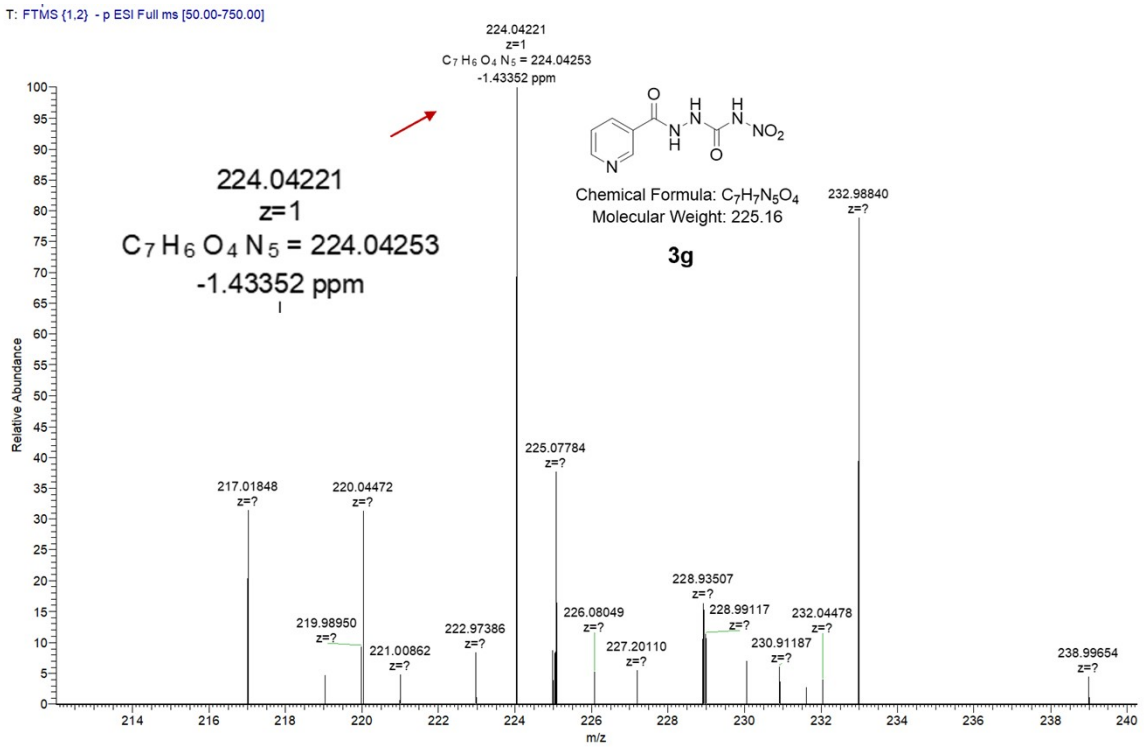


Figure S73. HRMS spectrum of **3g**.

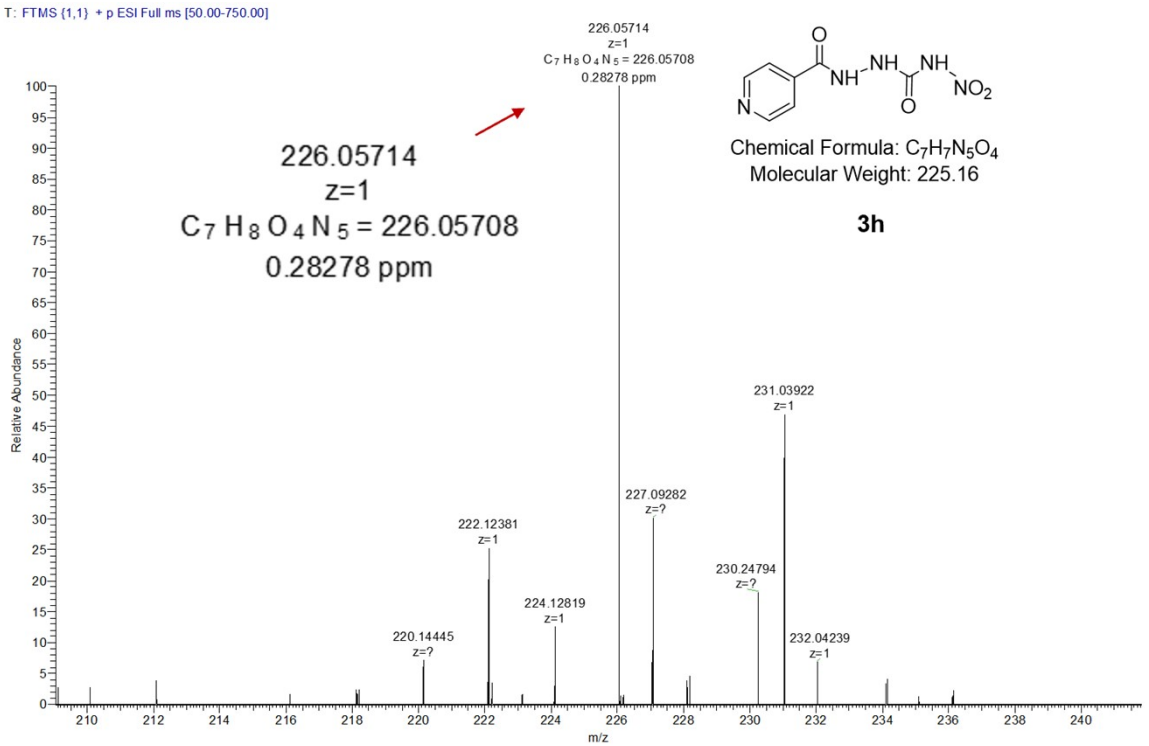


Figure S74. HRMS spectrum of **3h**.

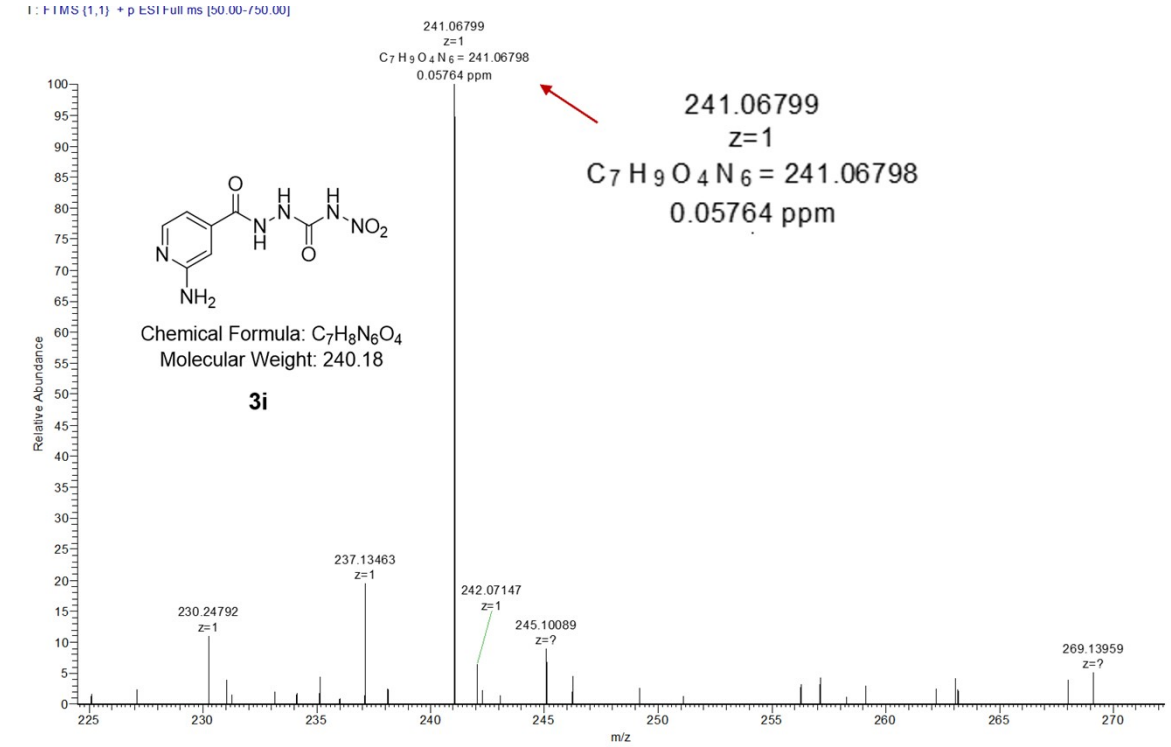


Figure S75. HRMS spectrum of **3i**.

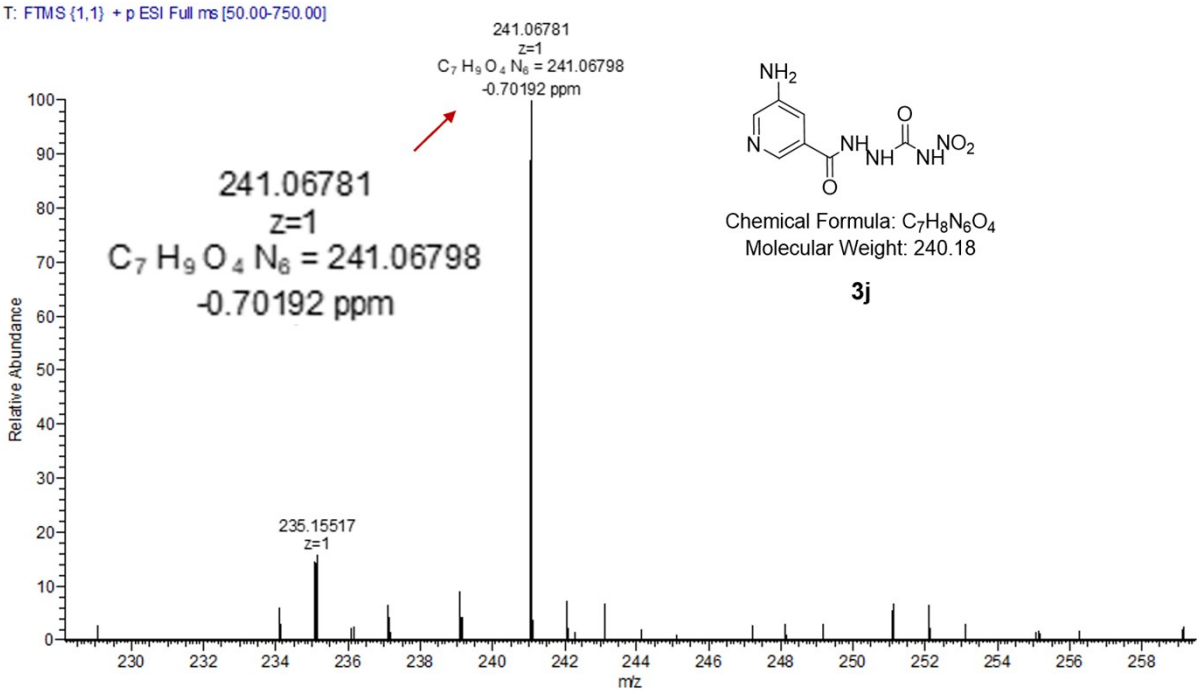


Figure S76. HRMS spectrum of **3j**.

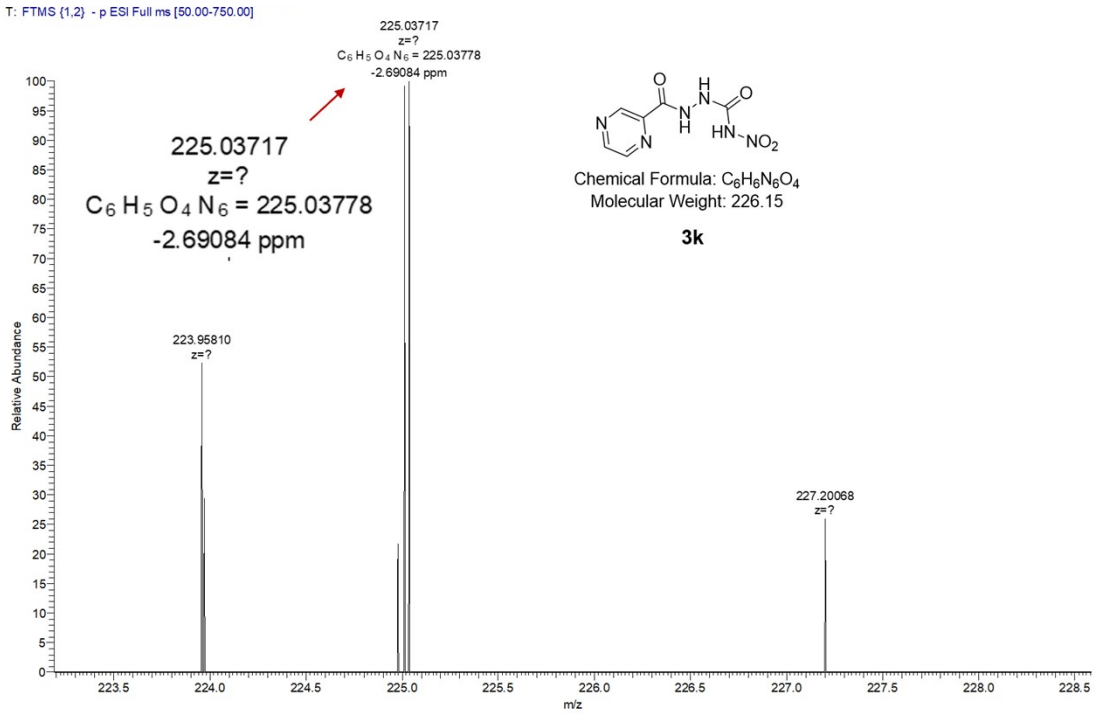


Figure S77. HRMS spectrum of **3k**.

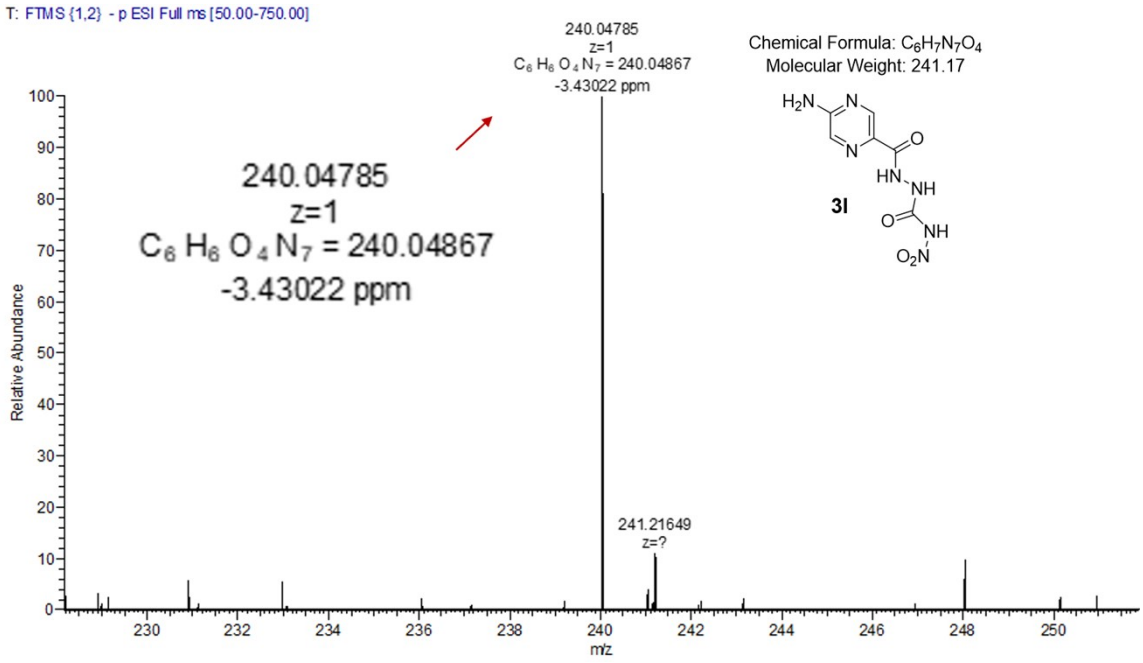


Figure S78. HRMS spectrum of **3l**.

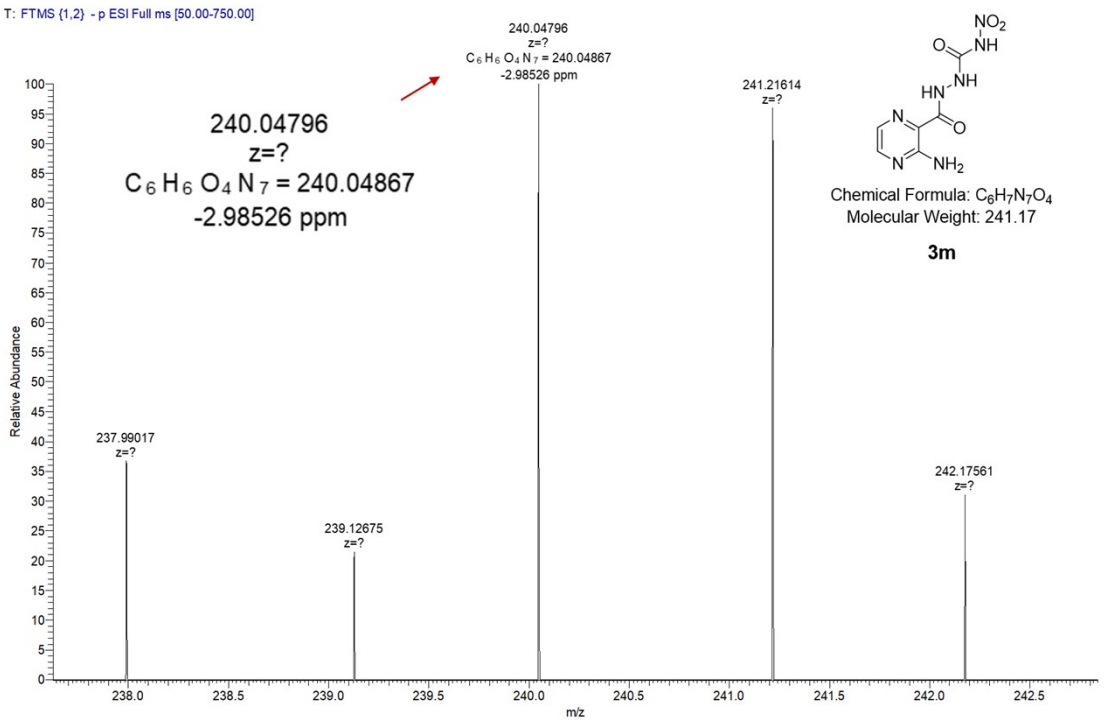


Figure S79. HRMS spectrum of **3m**.

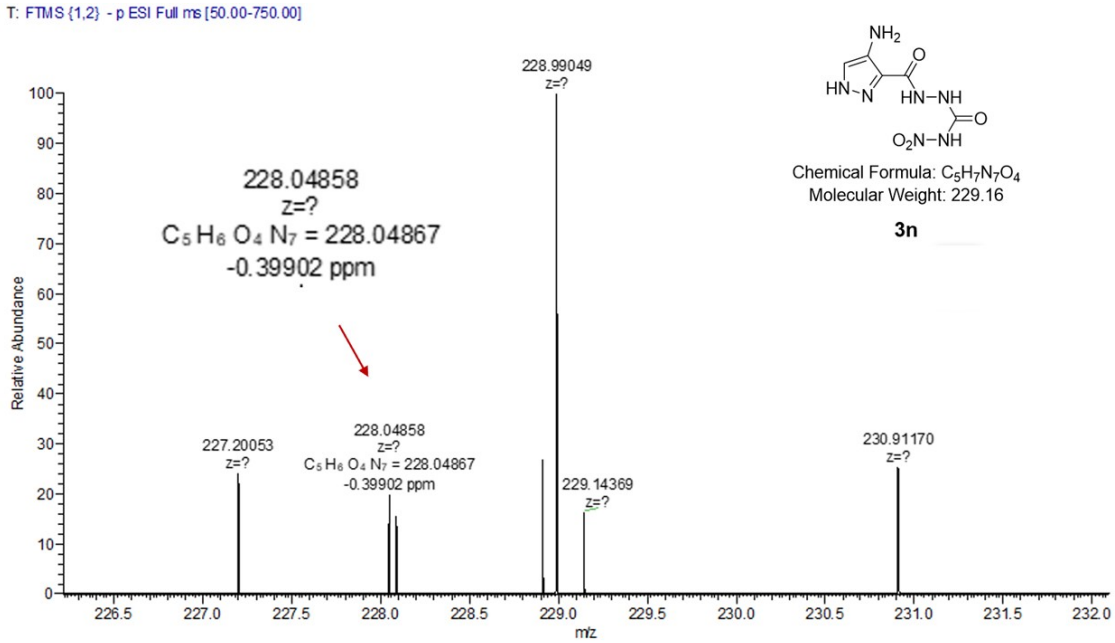


Figure S80. HRMS spectrum of **3n**.

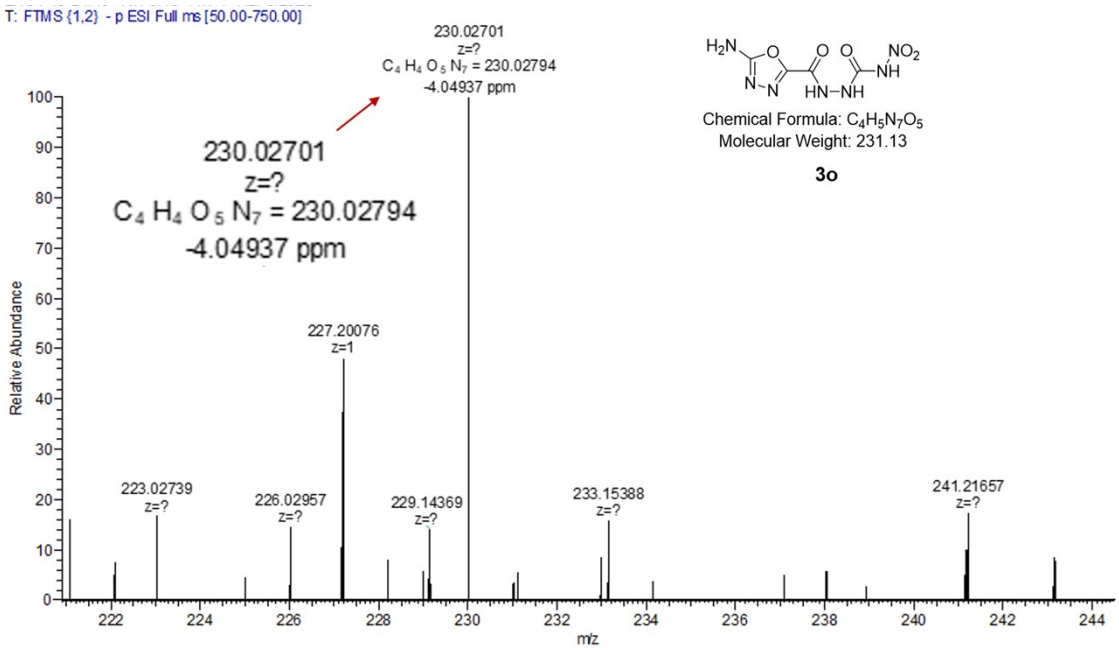


Figure S81. HRMS spectrum of **3o**.

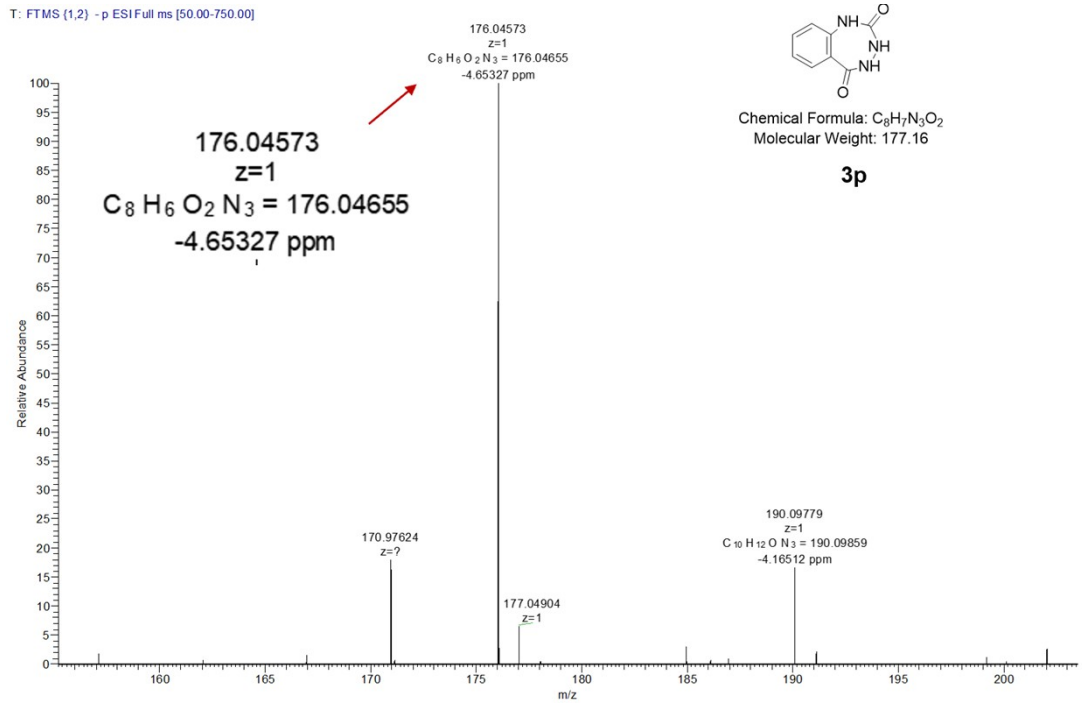


Figure S82. HRMS spectrum of **3p**.

5. Crystal Structures

5.1 X-ray crystallography details

A colorless block crystal (**HNNC-NH_2, 3a**) of dimensions 0.20×0.20×0.20 mm^3, a colorless block crystal (**HNNC, 3b)** of dimensions 0.13×0.12×0.11 mm^3, a colorless block crystal **7** of dimensions 0.20×0.20×0.20 mm^3, and a colorless block crystal (**HNNC-NO_2**) of dimensions 0.20×0.20×0.20 mm^3 were mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 296 K. A colorless block crystal (**3f**) of dimensions 0.15×0.08×0.05 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 1.34139 Å) at 298 K. A colorless block crystal (**3h**) of dimensions 0.11×0.04×0.02 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ =1.34139 Å) at 296 K. A colorless block crystal (**3j**) of dimensions 0.11×0.04×0.02 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ =1.54178 Å) at 173 K. A colorless block crystal (**3p**) of dimensions 0.11×0.04×0.02 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ =0.71073 Å) at 173 K. A colorless block crystal (**4**) of dimensions 0.11×0.04×0.02 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ =0.71073 Å) at 170 K. The structure was solved by intrinsic phasing approachs using ShelXT and refined with ShelXL-2014/2019. All hydrogen atoms on carbon are treated using theoretical hydrogenation. As for hydrogen atom treatment, all hydrogen atoms on nitrogen and oxygen are treated using Fourier hydrogenation. All single crystals are obtained by preparing a saturated aqueous solution of the compound and slowly evaporating the water.

Due to the inability to obtain higher-quality crystals of compound 7, the data were cropped to reflect the data resolution. The specific parameters are as follows: resolution of 0.94 (2θ = 44.4 degrees). This cut resulted in the following values: R1 of 8.45%, wR2 of 25.97%, I/σ of 7.6, and Rint of 10.02%. Moreover, EXTI has been integrated into the refinement process, and responses to the CheckCIF Alert A/B have also been included. Relevant plots of I/sigma and R merge versus resolution are as follows:

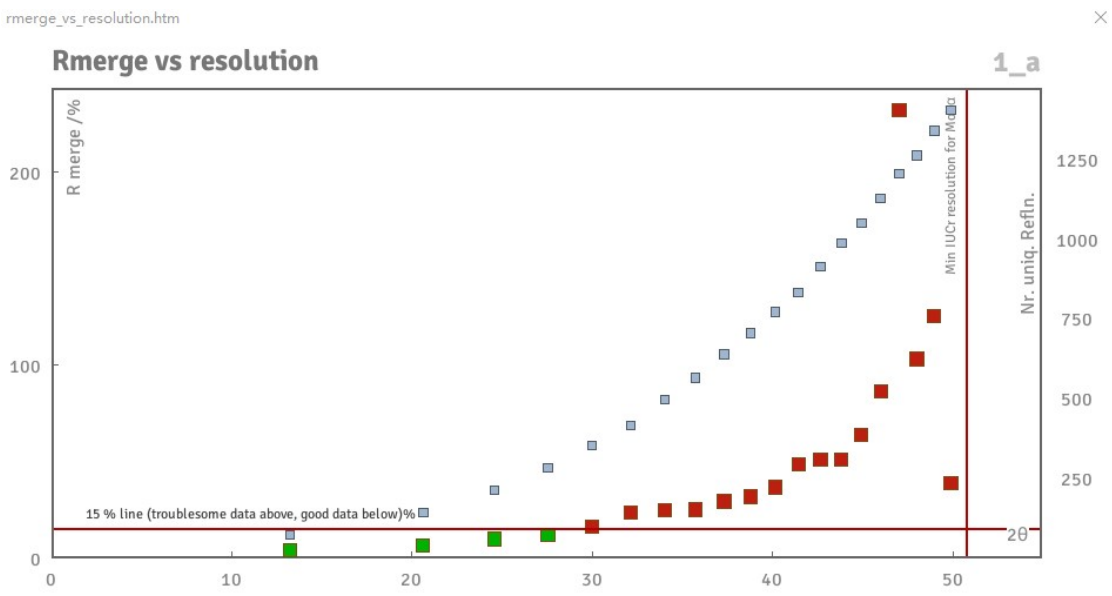

rmerge_vs_resolution.htm
Rmerge vs resolution
1_a
R merge /%
Nr. uniq. Refln.
Min IUCr resolution for Mo
15 % line (troublesome data above, good data below)%
2θ
0
100
200
250
500
750
1000
1250
0
10
20
30
40
50

Table S1. Crystallographic data for **HNNC-NH_2 (3a), HNNC (3b) and 3f**.

Compound	**HNNC-NH_2, 3a**	**HNNC, 3b**	**3f**
CCDC Number	2454803	2454624	2454625
Formula	$C_2H_5N_5O_4$	$C_2H_6N_6O_4$	$C_{14}H_{16}N_{10}O_9$
M_w	163.11	178.13	468.37
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 2/c	P 21/n	C 2/c
a [Å]	18.7573(12)	9.547(2)	24.934(2)
b [Å]	4.7917(3)	4.6558(12)	5.2983(5)
c [Å]	14.1888(8)	14.643(4)	15.9811(15)
α[°]	90	90	90
β[°]	109.606(2)	107.474(3)	107.988(4)
γ[°]	90	90	90
V [$Å^3$]	1201.34(13)	620.8(3)	2008.0(3)
Z	8	4	4
T [K]	296	296	298
λ [Å]	0.71073	0.71073	1.34139
P_{calcd}[g cm^{-3}]	1.804	1.906	1.549
μ [mm^{-1}]	0.169	0.177	0.727
F(000)	672	368	968.0
θ range[°]	2.305-25.071	2.274-27.523	5.101-52.955
Index ranges	-22 ≤ h ≤ 22	-12 ≤ h ≤ 9	-29 ≤ h ≤ 20
	-5 ≤ k ≤ 5	-6 ≤ k ≤ 5	-6 ≤ k ≤ 6
	-16 ≤ l ≤ 16	-16 ≤ l ≤ 19	-19 ≤ l ≤ 17
Data/restraints/parameters	1060/1/112	1407/1/121	1746/6/161
GOF on F2	1.103	1.071	1.047
R[F^2> 2σ(F^2)]	0.0368	0.0473	0.0572
wR(F^2)	0.1006	0.1293	0.1734

Table S2. Crystallographic data for **3h, 3j,** and **3p**.

Compound	**3h**	**3j**	**3p**
CCDC Number	2454626	2454623	2454627
Formula	$C_7H_9N_5O_5$	$C_7H_8N_6O_4$	$C_8H_9N_3O_3$
M_w	243.19	240.19	195.18
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	P 41	P 21/c	C 2/c
a [Å]	5.0977(3)	4.8878(2)	34.234(6)
b [Å]	5.0977(3)	27.3100(13)	3.7532(6)
c [Å]	39.382(4)	7.1034(4)	30.453(6)
α[°]	90	90	90
β[°]	90	105.629(4)	121.052(5)
γ[°]	90	90	90
V [Å^3]	1023.40(16)	913.15(8)	3352.1(10)
Z	4	4	16
T [K]	296	173	173
λ [Å]	1.34139	1.54178	0.71073
P_{calcd}[g cm^{-3}]	1.578	1.747	1.547
μ [mm^{-1}]	0.751	1.265	0.121
F(000)	504.0	496.0	1632.0
θ range[°]	3.906-56.967	3.236-63.736	2.383-26.397
Index ranges	-6 ≤ h ≤ 4	-5 ≤ h ≤ 5	-42 ≤ h ≤ 42
	-5 ≤ k ≤ 6	-31 ≤ k ≤ 31	-4 ≤ k ≤ 4
	-49 ≤ l ≤ 36	-8 ≤ l ≤ 8	-35 ≤ l ≤ 38
Data/restraints/parameters	1824/1/158	1500/0/154	3404/0/275
GOF on F2	1.039	1.071	1.028
R[F^2> 2σ(F^2)]	0.0359	0.0591	0.0591
wR(F^2)	0.0971	0.1623	0.1514

Table S3. Crystallographic data for **4, 7,** and **HNNC-NO_2**.

Compound	**4**	**7**	**HNNC-NO_2**
CCDC Number	2454628	2454629	2454630
Formula	$C_2H_7N_7O_7$	$C_2H_9N_7O_5$	$C_2H_7N_5O_2$
M_w	241.15	211.16	133.13
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	P 21	P -1	P n a 21
a [Å]	4.7316(2)	4.918(4)	9.1713(12)
b [Å]	8.2172(4)	8.996(7)	4.7459(8)
c [Å]	10.9255(4)	9.996(9)	12.745(2)
α[°]	90	74.35(2)	90
β[°]	98.713(1)	76.761(17)	90
γ[°]	90	78.785(16)	90
V [$Å^3$]	419.89(3)	410.4(6)	554.74(15)
Z	2	2	4
T [K]	170	296	296
λ [Å]	0.71073	0.71073	0.71073
P_{calcd}[g cm^{-3}]	1.907	1.709	1.594
μ [mm^{-1}]	0.187	0.160	0.137
F(000)	248.0	220.0	280.0
θ range[°]	3.115-26.364	2.805-22.210	3.197-25.063
Index ranges	-5 ≤ h ≤ 5 -10 ≤ k ≤ 10 -13 ≤ l ≤ 13	-5 ≤ h ≤ 5 -9 ≤ k ≤ 8 -10 ≤ l ≤ 10	-10 ≤ h ≤ 10 -5 ≤ k ≤ 5 -13 ≤ l ≤ 15
Data/restraints/parameters	1694/8/154	1026/0/130	893/3/88
GOF on F2	1.055	0.974	1.031
R[F^2> 2σ(F^2)]	0.1003	0.0845	0.0475
wR(F^2)	0.0406	0.2597	0.1324

5.2 Bond lengths and angles

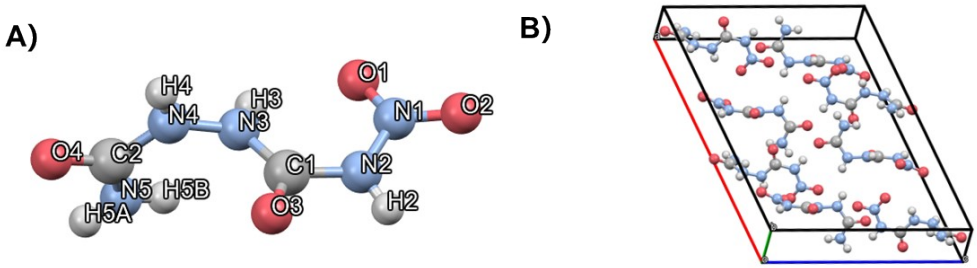


Figure S83. A) Crystal structure of **HNNC-NH$_2$, 3a**; B) Packing diagram of **HNNC-NH$_2$, 3a**.

Table S4. Bond lengths (Å) and bond angles (°) for **HNNC-NH$_2$, 3a**.

Bond lengths		
C1 N2 1.408(2)	C2 O4 1.242(2)	N3 N4 1.381(2)
C1 N3 1.344(3)	N1 N2 1.356(2)	N3 H3 0.81(3)
C1 O3 1.206(2)	N1 O1 1.219(2)	N4 H4 0.83(2)
C2 N4 1.361(2)	N1 O2 1.227(2)	N5 H5A 0.8600
C2 N5 1.319(3)	N2 H2 0.908(17)	N5 H5B 0.8600
Bond angles		
N3 C1 N2 118.82(17)	O1 N1 O2 124.26(16)	N4 N3 H3 117.5(17)
O3 C1 N2 116.12(17)	O2 N1 N2 115.93(17)	C2 N4 N3 121.46(18)
O3 C1 N3 125.06(18)	C1 N2 H2 118.1(15)	C2 N4 H4 117.4(16)
N5 C2 N4 118.18(17)	N1 N2 C1 126.16(16)	N3 N4 H4 118.8(16)
O4 C2 N4 118.86(18)	N1 N2 H2 112.3(16)	C2 N5 H5A 120.0
O4 C2 N5 122.94(17)	C1 N3 N4 118.33(18)	C2 N5 H5B 120.0
O1 N1 N2 119.80(15)	C1 N3 H3 121.6(17)	H5A N5 H5B 120.0

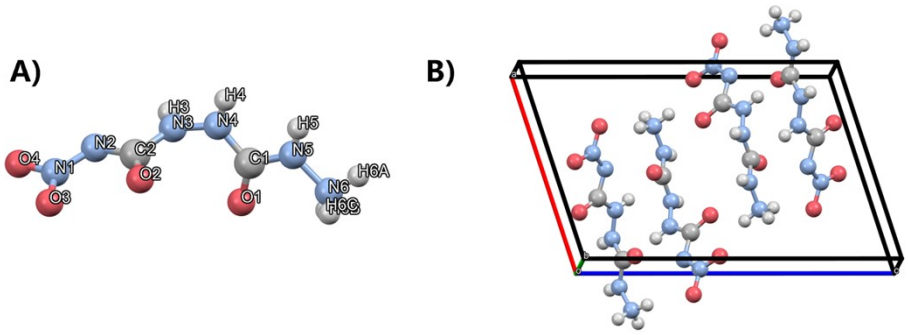


Figure S84. A) Crystal structure of **HNNC, 3b**; B) Packing diagram of **HNNC, 3b**

Table S5. Bond lengths (Å) and bond angles (°) for **HNNC, 3b**.

Bond lengths (**HNNC, 3b)**

O1 C1 1.224(2)	N6 H6A 0.91(3)	C2 N3 1.358(3)
N1 N2 1.297(3)	N6 H6B 0.92(3)	N3 H3 0.8600
N1 O3 1.222(2)	N6 N5 1.405(3)	N3 N4 1.373(2)
N1 O4 1.272(2)	N6 H6C 0.91(3)	N4 H4 0.8600
C1 N4 1.344(3)	O2 C2 1.223(2)	N5 H5 0.8600
C1 N5 1.359(3)	N2 C2 1.384(3)	
Bond angles (**HNNC, 3b)**		
O3 N1 N2 126.3(2)	H6B N6 H6C 108(3)	C2 N3 H3 119.6
O3 N1 O4 117.76(19)	N5 N6 H6A 106.2(19)	C2 N3 N4 120.89(17)
O4 N1 N2 115.93(17)	N5 N6 H6B 113(2)	N4 N3 H3 119.6
O1 C1 N4 124.91(19)	N5 N6 H6C 113.6(18)	C1 N4 N3 119.85(18)
O1 C1 N5 121.8(2)	N1 N2 C2 118.17(18)	C1 N4 H4 120.1
N4 C1 N5 113.25(18)	O2 C2 N2 131.1(2)	N3 N4 H4 120.1
H6A N6 H6B 110(3)	O2 C2 N3 122.1(2)	C1 N5 N6 116.14(18)
H6A N6 H6C 107(2)	N3 C2 N2 106.84(17)	C1 N5 H5 121.9
N6 N5 H5 121.9		

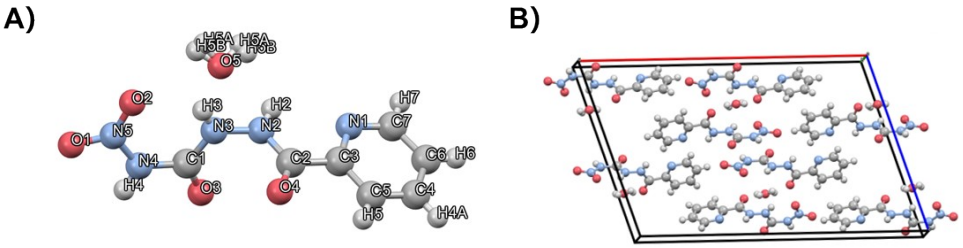


Figure S85. A) Crystal structure of **3f**; B) Packing diagram of **3f**.

Table S6. Bond lengths (Å) and bond angles (°) for **3f**.

Bond lengths		
O4 C2 1.216(3)	C3 N1 1.340(3)	N4 H4 1.03(3)
O3 C1 1.224(3)	C3 C4 1.370(3)	C4 H4A 0.9300
N3 H3 0.8600	N1 C7 1.336(3)	C7 H7 0.9300
N3 N2 1.377(3)	N2 H2 0.81(3)	C7 C6 1.369(4)
N3 C1 1.333(3)	C5 H5 0.9300	C6 H6 0.9300
O2 N5 1.219(3)	C5 C4 1.377(3)	O5 H5A 0.85(6)
C2 C3 1.493(3)	C5 C6 1.370(3)	O5 H5A 0.8500
C2 N2 1.346(3)	N4 C1 1.403(3)	O5 H5B 0.850(3)
O1 N5 1.227(3)	N4 N5 1.360(3)	O5 H5B 0.8500
Bond angles		

N2 N3 H3 121.2	C6 C5 H5 120.7	N1 C7 H7 118.0
C1 N3 H3 121.2	C6 C5 C4 118.7(2)	N1 C7 C6 124.0(2)
C1 N3 N2 117.5(2)	C1 N4 H4 115.8(18)	C6 C7 H7 118.0
O4 C2 C3 121.8(2)	N5 N4 C1 128.5(2)	C5 C6 H6 120.6
O4 C2 N2 123.0(2)	N5 N4 H4 114.9(17)	C7 C6 C5 118.7(3)
N2 C2 C3 115.26(18)	O3 C1 N3 124.0(2)	C7 C6 H6 120.6
N1 C3 C2 117.1(2)	O3 C1 N4 116.0(2)	H5A O5 H5A 86.2
N1 C3 C4 123.6(2)	N3 C1 N4 119.9(2)	H5A O5 H5B 104.5
C4 C3 C2 119.3(2)	O2 N5 O1 125.6(2)	H5A O5 H5B 78.6
C7 N1 C3 116.1(2)	O2 N5 N4 120.4(2)	H5A O5 H5B 104.5
N3 N2 H2 122(2)	O1 N5 N4 114.0(2)	H5B O5 H5A 78.6
C2 N2 N3 121.1(2)	C3 C4 C5 118.8(2)	H5B O5 H5B 175.8
C2 N2 H2 116(2)	C3 C4 H4A 120.6	
C4 C5 H5 120.7	C5 C4 H4A 120.6	

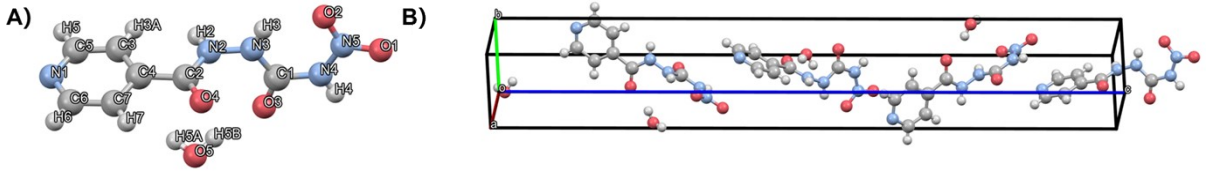


Figure S86. A) Crystal structure of **3h**; B) Packing diagram of **3h**.

Table S7. Bond lengths (Å) and bond angles (°) for **3h**.

Bond lengths		
O1 N5 1.216(4)	N3 H3 0.8600	C4 C7 1.365(6)
O2 N5 1.217(4)	N3 C1 1.344(4)	C5 H5 0.9300
O3 C1 1.211(4)	N4 H4 0.8600	C6 H6 0.9300
O4 C2 1.223(4)	N4 N5 1.340(4)	C6 C7 1.387(6)
N1 C5 1.319(5)	N4 C1 1.394(4)	C7 H7 0.9300
N1 C6 1.308(5)	C2 C4 1.507(5)	O5 H5A 0.8505
N2 H2 0.8600	C3 H3A 0.9300	O5 H5B 0.8494
N2 N3 1.381(4)	C3 C4 1.351(5)	
N2 C2 1.342(5)	C3 C5 1.374(6)	
Bond angles		
C6 N1 C5 116.4(3)	O2 N5 N4 120.2(3)	C3 C4 C7 117.0(3)
N3 N2 H2 119.7	O3 C1 N3 124.8(3)	C7 C4 C2 118.1(3)
C2 N2 H2 119.7	O3 C1 N4 116.5(3)	N1 C5 C3 124.0(4)

C2 N2 N3 120.7(3)	N3 C1 N4 118.6(3)	N1 C5 H5 118.0
N2 N3 H3 120.4	O4 C2 N2 123.0(3)	C3 C5 H5 118.0
C1 N3 N2 119.2(3)	O4 C2 C4 120.7(3)	N1 C6 H6 118.5
C1 N3 H3 120.4	N2 C2 C4 116.2(3)	N1 C6 C7 123.1(4)
N5 N4 H4 115.8	C4 C3 H3A 120.2	C7 C6 H6 118.5
N5 N4 C1 128.3(3)	C4 C3 C5 119.7(4)	C4 C7 C6 119.8(4)
C1 N4 H4 115.8	C5 C3 H3A 120.2	C4 C7 H7 120.1
O1 N5 O2 124.2(3)	C3 C4 C2 124.9(3)	C6 C7 H7 120.1
O1 N5 N4 115.6(3)	C3 C4 C7 117.0(3)	H5A O5 H5B 104.5

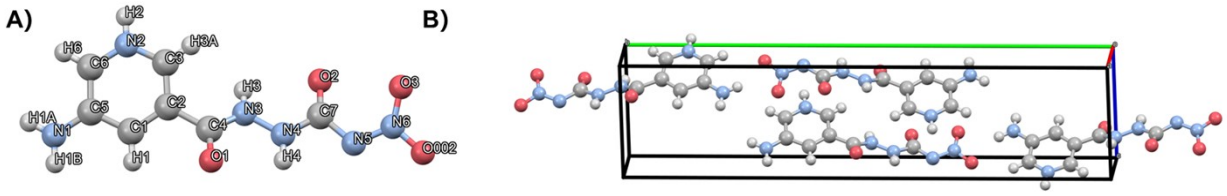


Figure S87. A) Crystal structure of **3j**; B) Packing diagram of **3j**.

Table S8. Bond lengths (Å) and bond angles (°) for **3j**.

Bond lengths		
O1 C4 1.225(4)	N2 C3 1.340(4)	C2 C3 1.378(5)
O002 N6 1.252(3)	N2 C6 1.333(4)	C1 H1 0.9500
O2 C7 1.227(4)	N5 N6 1.320(4)	C1 C5 1.407(4)
O3 N6 1.249(4)	N5 C7 1.386(4)	C5 C6 1.392(5)
N4 H4 0.8800	N1 H1A 0.8800	C3 H3A 0.9500
N4 N3 1.389(3)	N1 H1B 0.8800	C6 H6 0.9500
N4 C7 1.353(4)	N1 C5 1.352(4)	N2 H2 0.8800
N3 H3 0.8800	C4 C2 1.498(4)	
N3 C4 1.334(4)	C2 C1 1.382(4)	
Bond angles		
N3 N4 H4 120.2	O2 N6 N5 115.9(3)	N1 C5 C1 121.7(3)
C7 N4 H4 120.2	O3 N6 O002 119.0(3)	N1 C5 C6 121.7(3)
C7 N4 N3 119.7(3)	O3 N6 N5 124.9(3)	C6 C5 C1 116.6(3)
N4 N3 H3 121.1	O1 C4 N3 121.5(3)	N2 C3 C2 118.0(3)
C4 N3 N4 117.8(3)	O1 C4 C2 121.5(3)	N2 C3 H3A 121.0
C4 N3 H3 121.1	N3 C4 C2 116.9(3)	C2 C3 H3A 121.0
C3 N2 H2 118.0	C1 C2 C4 117.7(3)	O2 C7 N4 120.2(3)
C6 N2 H2 118.0	C3 C2 C4 121.9(3)	O2 C7 N5 130.9(3)

C6 N2 C3 124.0(3)	C3 C2 C1 120.2(3)	N4 C7 N5 108.6(3)
N6 N5 C7 116.9(3)	C2 C1 H1 119.7	N2 C6 C5 120.6(3)
H1A N1 H1B 120.0	C2 C1 C5 120.5(3)	N2 C6 H6 119.7
C5 N1 H1A 120.0	C5 C1 H1 119.7	C5 C6 H6 119.7
C5 N1 H1B 120.0		

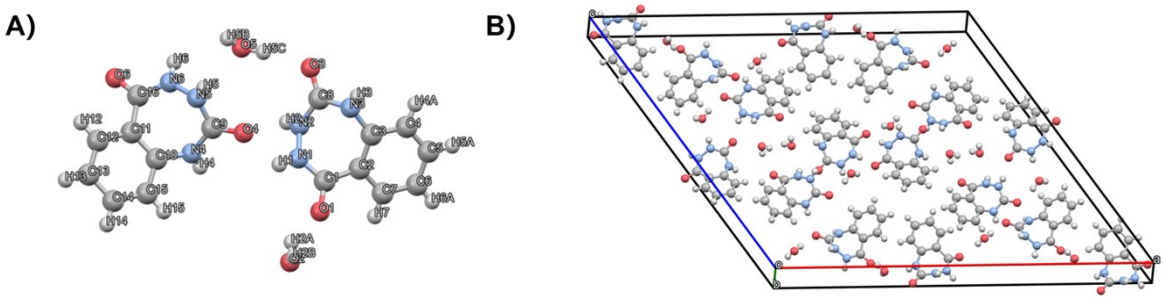


Figure S88. A) Crystal structure of **3p**; B) Packing diagram of **3p**.

Table S9. Bond lengths (Å) and bond angles (°) for **3p**.

Bond lengths		
O6 C16 1.249(3)	N5 H5 0.99(4)	C12 C13 1.376(4)
O3 C8 1.234(3)	N2 N1 1.401(3)	C10 C15 1.393(4)
O4 C9 1.233(3)	N2 C8 1.351(4)	C4 H4A 0.9500
O1 C1 1.245(3)	N2 H2 0.87(3)	C4 C3 1.393(4)
O5 H5B 0.8700	N1 H1 0.8800	C4 C5 1.371(4)
O5 H5C 0.8700	N1 C1 1.327(4)	C13 H13 0.9500
N4 C10 1.421(4)	O2 H2A 0.8699	C13 C14 1.380(4)
N4 C9 1.371(4)	O2 H2B 0.8701	C15 H15 0.9500
N4 H4 0.99(3)	C11 C12 1.389(4)	C15 C14 1.378(4)
N6 H6 0.8800	C11 C10 1.399(4)	C7 H7 0.9500
N6 N5 1.403(3)	C11 C16 1.473(4)	C7 C6 1.374(4)
N6 C16 1.332(4)	C2 C3 1.399(4)	C14 H14 0.9500
N3 C3 1.416(4)	C2 C7 1.401(4)	C5 H5A 0.9500
N3 C8 1.371(4)	C2 C1 1.472(4)	C5 C6 1.379(4)
N3 H3 0.96(3)	C12 H12 0.950	C6 H6A 0.9500
N5 C9 1.359(4)		
Bond angles		
H5B O5 H5C 104.5	C3 C2 C7 119.1(3)	O6 C16 C11 121.3(3)
C10 N4 H4 114.1(18)	C3 C2 C1 123.2(3)	N6 C16 C11 119.2(3)
C9 N4 C10 122.5(3)	C7 C2 C1 117.3(3)	C12 C13 H13 120.3

C9 N4 H4 112.1(19)	C11 C12 H12 119.5	C12 C13 C14 119.5(3)
N5 N6 H6 117.5	C13 C12 C11 121.0(3)	C14 C13 H13 120.3
C16 N6 H6 117.5	C13 C12 H12 119.5	C10 C15 H15 119.8
C16 N6 N5 125.1(2)	C11 C10 N4 123.8(2)	C14 C15 C10 120.3(3)
C3 N3 H3 111(2)	C15 C10 N4 116.9(3)	C14 C15 H15 119.8
C8 N3 C3 121.9(3)	C15 C10 C11 119.2(3)	C2 C7 H7 119.4
C8 N3 H3 119(2)	C3 C4 H4A 119.7	C6 C7 C2 121.2(3)
N6 N5 H5 113(2)	C5 C4 H4A 119.7	C6 C7 H7 119.4
C9 N5 N6 120.8(3)	C5 C4 C3 120.6(3)	O1 C1 N1 119.9(3)
C9 N5 H5 113(2)	C2 C3 N3 123.3(3)	O1 C1 C2 121.4(3)
N1 N2 H2 113(2)	C4 C3 N3 117.7(3)	N1 C1 C2 118.6(3)
C8 N2 N1 122.5(3)	C4 C3 C2 118.9(3)	C13 C14 H14 119.7
C8 N2 H2 120(2)	O4 C9 N4 120.9(3)	C15 C14 C13 120.6(3)
N2 N1 H1 118.1	O4 C9 N5 121.2(3)	C15 C14 H14 119.7
C1 N1 N2 123.9(3)	N5 C9 N4 117.8(3)	C4 C5 H5A 119.4
C1 N1 H1 118.1	O3 C8 N3 121.7(3)	C4 C5 C6 121.1(3)
H2A O2 H2B 104.5	O3 C8 N2 122.2(3)	C6 C5 H5A 119.4
C12 C11 C10 119.3(3)	N2 C8 N3 116.0(3)	C7 C6 C5 119.0(3)
C12 C11 C16 117.1(3)	O6 C16 N6 119.4(3)	C7 C6 H6A 120.5
C10 C11 C16 123.4(3)	C5 C6 H6A 120.5	

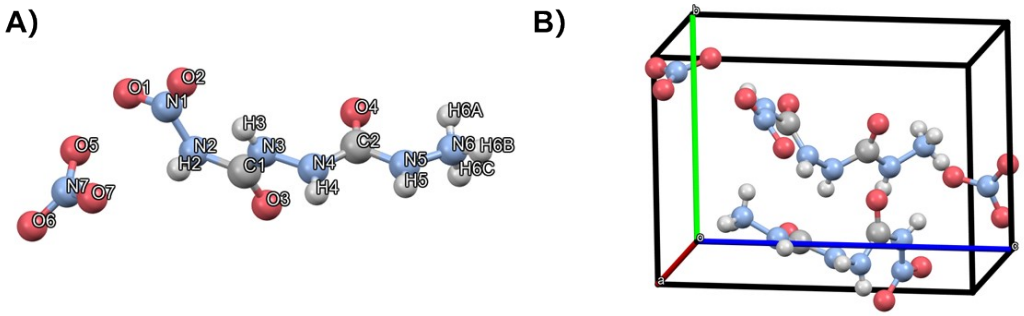


Figure S89. A) Crystal structure of **4**; B) Packing diagram of **4**.

Table S10. Bond lengths (Å) and bond angles (°) for **4**.

Bond lengths		
O6 N7 1.259(4)	N1 N2 1.359(5	N6 H6C 0.89(3)
O4 C2 1.215(5)	N3 H3 0.8800	N5 H5 0.8800
O5 N7 1.250(5)	N3 N4 1.380(5)	N5 C2 1.364(5)
O2 N1 1.236(5)	N3 C1 1.337(6)	N4 H4 0.8800
O1 N1 1.218(4)	N6 H6A 0.8859	N4 C2 1.360(5)
O3 C1 1.216(5)	N6 H6B 0.8858	N2 C1 1.410(5)

O7 N7 1.244(4)	N6 N5 1.418(5)	N2 H2 0.86(3)
Bond angles		
O5 N7 O6 119.7(3)	H6A N6 H6C 115.4	C2 N4 H4 121.1
O7 N7 O6 120.6(3)	H6B N6 H6C 104.5	N1 N2 C1 128.5(3)
O7 N7 O5 119.7(3)	N5 N6 H6A 109.6	N1 N2 H2 114(4)
O2 N1 N2 119.0(3)	N5 N6 H6B 110.0	C1 N2 H2 118(4)
O1 N1 O2 124.8(4)	N5 N6 H6C 108(4)	O3 C1 N3 125.7(4)
O1 N1 N2 116.2(3)	N6 N5 H5 122.1	O3 C1 N2 116.5(4)
N4 N3 H3 121.1	C2 N5 N6 115.8(3)	N3 C1 N2 117.8(4)
C1 N3 H3 121.1	C2 N5 H5 122.1	O4 C2 N5 122.9(3)
C1 N3 N4 117.9(4)	N3 N4 H4 121.1	O4 C2 N4 124.6(4)
H6A N6 H6B 108.9	C2 N4 N3 117.8(3)	N4 C2 N5 112.5(4)

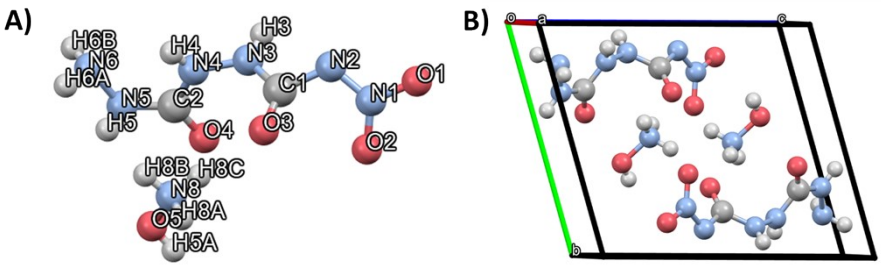


Figure S90. (a) Crystal structure of **7**; (b) Packing diagram of **7**.

Table S11. Bond lengths (Å) and bond angles (°) for **7**.

Bond lengths		
C1 N2 1.397(10)	C2 N5 1.307(10)	N1 O2 1.243(7)
C1 N3 1.341(10)	C2 O4 1.245(9)	N3 H3 0.8600
C1 O3 1.231(8)	N1 N2 1.304(9)	N3 N4 1.375(8)
C2 N4 1.339(10)	N1 O1 1.251(8)	N4 H4 0.8600
N5 H5 0.8600	N6 H6B 0.8900	N8 H8A 0.8900
N5 N6 1.403(9)	O5 H5A 0.8200	N8 H8B 0.8900
N6 H6A 0.8900	O5 N8 1.395(8)	N8 H8C 0.8900
Bond angles		
N3 C1 N2 110.0(7)	C1 N3 H3 119.3	N5 N6 H6B 109.1
O3 C1 N2 126.7(8)	C1 N3 N4 121.5(6)	H6A N6 H6B 109.5
O3 C1 N3 123.1(7)	N4 N3 H3 119.3	N8 O5 H5A 109.5
N5 C2 N4 115.6(8)	C2 N4 N3 120.8(7)	O5 N8 H8A 109.5
O4 C2 N4 122.2(7)	C2 N4 H4 119.6	O5 N8 H8B 109.5

O4 C2 N5 122.2(8)	N3 N4 H4 119.6	O5 N8 H8C 109.5
O1 N1 N2 116.5(7)	C2 N5 H5 119.6	H8A N8 H8B 109.5
O2 N1 N2 124.6(7)	C2 N5 N6 120.9(7)	H8A N8 H8C 109.5
O2 N1 O1 118.7(7)	N6 N5 H5 119.6	H8B N8 H8C 109.5
N1 N2 C1 115.1(7)	N5 N6 H6A 108.7	

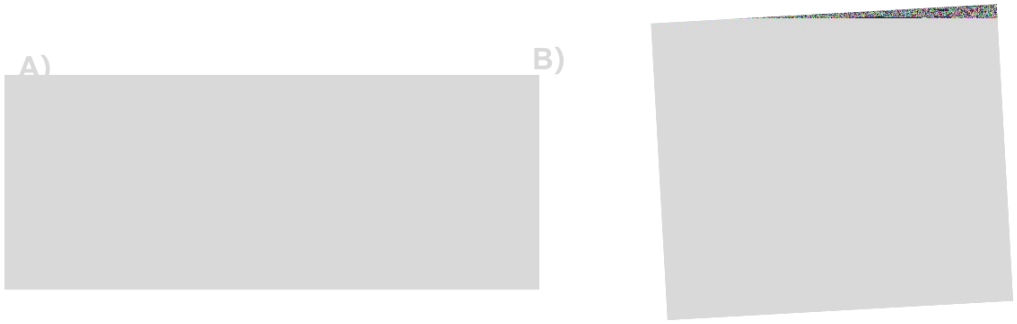


Figure S91. A) Crystal structure of **HNNC-NH_2**; B) Packing diagram of **HNNC-NH_2**.

Table S12. Bond lengths (Å) and bond angles (°) for **HNNC-NH_2, 3a**.

Bond lengths		
C1 N2 1.408(2)	C2 O4 1.242(2)	N3 N4 1.381(2)
C1 N3 1.344(3)	N1 N2 1.356(2)	N3 H3 0.81(3)
C1 O3 1.206(2)	N1 O1 1.219(2)	N4 H4 0.83(2)
C2 N4 1.361(2)	N1 O2 1.227(2)	N5 H5A 0.8600
C2 N5 1.319(3)	N2 H2 0.908(17)	N5 H5B 0.8600
Bond angles		
N3 C1 N2 118.82(17)	O1 N1 O2 124.26(16)	N4 N3 H3 117.5(17)
O3 C1 N2 116.12(17)	O2 N1 N2 115.93(17)	C2 N4 N3 121.46(18)
O3 C1 N3 125.06(18)	C1 N2 H2 118.1(15)	C2 N4 H4 117.4(16)
N5 C2 N4 118.18(17)	N1 N2 C1 126.16(16)	N3 N4 H4 118.8(16)
O4 C2 N4 118.86(18)	N1 N2 H2 112.3(16)	C2 N5 H5A 120.0
O4 C2 N5 122.94(17)	C1 N3 N4 118.33(18)	C2 N5 H5B 120.0
O1 N1 N2 119.80(15)	C1 N3 H3 121.6(17)	H5A N5 H5B 120.0

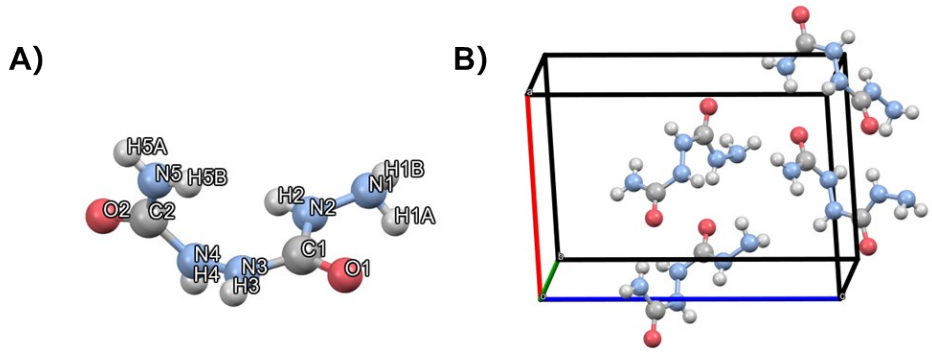


Figure S92. (a) Crystal structure of **HNNC-NO$_2$**; (b) Packing diagram of **HNNC-NO$_2$**.

Table S13. Bond lengths (Å) and bond angles (°) for **HNNC-NO$_2$**.

Bond lengths		
C1 N2 1.338(7)	C2 O2 1.236(6)	N3 H3 0.8600
C1 N3 1.358(8)	N1 H1A 0.903(14)	N3 N4 1.376(6)
C1 O1 1.242(6)	N1 H1B 0.906(14)	N4 H4 0.8600
C2 N4 1.369(8)	N1 N2 1.393(8)	N5 H5A 0.8600
C2 N5 1.333(8)	N2 H2 0.8600	N5 H5B 0.8600
Bond angles		
N2 C1 N3 117.1(5)	N2 N1 H1A 111(5)	N4 N3 H3 119.6
O1 C1 N2 123.0(6)	N2 N1 H1B 106(5)	C2 N4 N3 121.8(5)
O1 C1 N3 119.9(5)	C1 N2 N1 122.3(5)	C2 N4 H4 119.1
N5 C2 N4 118.4(5)	C1 N2 H2 118.8	N3 N4 H4 119.1
O2 C2 N4 118.1(6)	N1 N2 H2 118.8	C2 N5 H5A 120.0
O2 C2 N5 123.4(6)	C1 N3 H3 119.6	C2 N5 H5B 120.0
H1A N1 H1B 104(7)	C1 N3 N4 120.8(5)	H5A N5 H5B 120.0

6. Quantum Computing Analysis

6.1 Heat of formation

Theoretical calculations were performed by using the Gaussian 16 (Revision A.03) suite of programs. [1] Gas phase heats of formation (HOF) of the title compounds were computed based on an isodesmic reaction. The isodesmic reaction processes, in which the types and quantities of bonds broken and formed remain identical before and after the reaction, were used with the application of the bond separation reaction (BSR) rules. The isodesmic reactions used to derive the heat of formation (HOF) are shown in **Scheme S1**.

The geometric optimization and frequency analyses of the HNNC, its cation ($HNNC^+$), its anion ($HNNC^-$), HNNC-NH_2, and HNNC-NO_2 were calculated using B3LYP/6-31+G** level, and the energy was calculated at the MP2/6-311++G** level. The heats of formation for 3n, 3o and complex structures were obtained by atomization using G2 ab initio method.[2] The enthalpy of sublimation was calculated by using Trouton's rule.[3] Solid state heats of formation of the resulting compounds were calculated with equation (1) in which $T_{m/d}$ is the melting temperature or decomposition temperature.

$$\Delta H_{f(solid)} = \Delta H_{f(g)} - \Delta H_{sub} = \Delta H_{f(g)} - 188[J\ mol^{-1}] \times T_{m/d}$$

Scheme S1. Isodesmic reactions for calculating heats of formation for **HNNC, its cation (HNNC$^+$), its anion (HNNC$^-$), HNNC-NH_2,** and **HNNC-NO_2**, respectively.

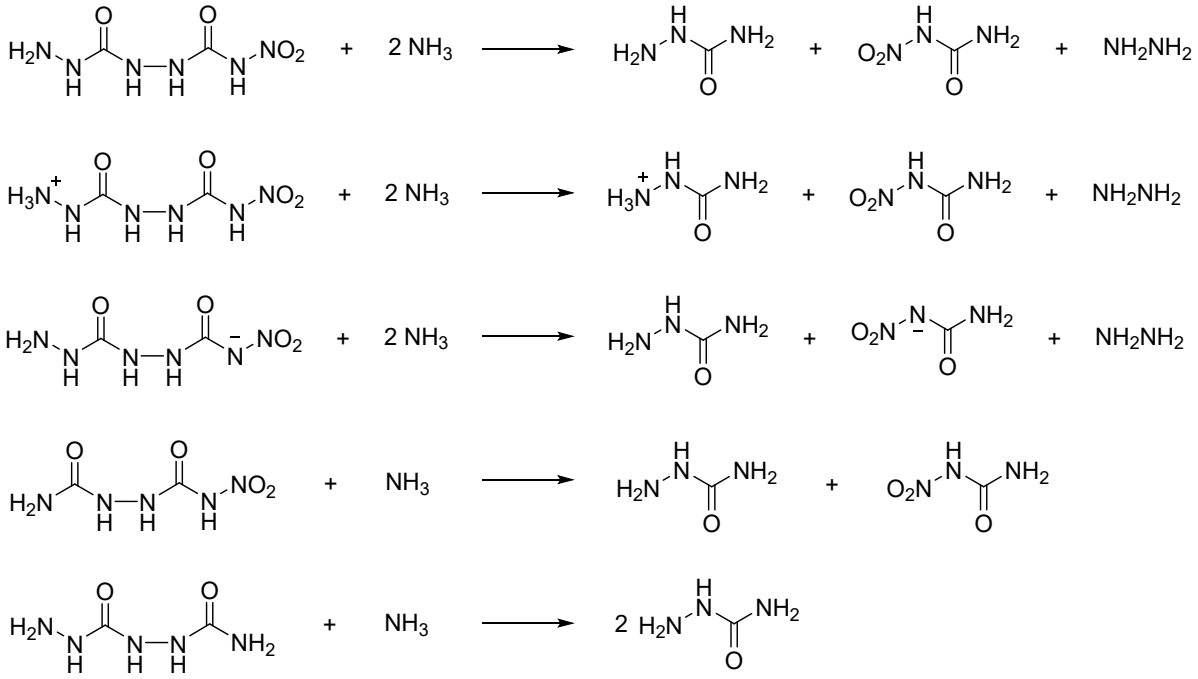


Table S14. Calculated Total Energy (E_0), Zero Point Energy (ZPE) and values of Thermal Correction (H_{corr}) of the compounds.

Compound	ZPE/a.u.	H_{corr}/a.u.	E_0/a.u.
HNNC	0.126574	0.139980	-707.5265112
HNNC$^+$	0.140833	0.153470	-707.8797045
HNNC$^-$	0.114077	0.126720	-707.0046489
HNNC-NH_2	0.109697	0.121685	-652.3527278
HNNC-NO_2	0.124547	0.135783	-503.4740461
NH_3	0.034372	0.038190	-56.4154643
Hydrazinecarboxamide	0.080473	0.087208	-279.9336074
Hydrazinecarboxamide$^+$	0.094054	0.100506	-280.2844449
1-nitrourea	0.065716	0.073450	-428.8266934
1-nitrourea$^-$	0.052983	0.059958	-428.2894699
NH_2NH_2	0.053393	0.057595	-111.593707

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

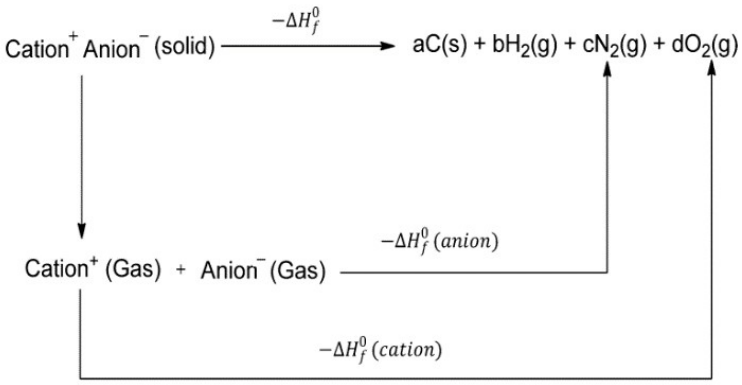


Table S15. Heats of formation of the compounds.

Compound	kJ mol^{-1}	kJ g^{-1}
HNNC	-195.4	-1.10
4	-300.0	-1.25
5	-209.5	-0.75
6	-169.1	-0.87
7	-122.3	-0.60
HNNC-NH_2	-342.1	-2.10
HNNC-NO_2	-294.2	-2.21

6.2 Packing coefficient

In this study, the packing coefficient was calculated according to equation PC=$\sum V_m/V_c$, V_m means the volume enclosed through a surface with an assigned electronic density. The electronic density was calculated at the B3LYP/6-311+G(d,p) theory level, and 0.003 a.u. density was adopted for the V_m calculation.[4] V_c means the unit cell volume.

As shown in **Table S94**, molecules **HNNC**, **HNNC-NH_2** and **HNNC-NO_2** have the different molecular weight and different molecular volume (135.66 ,121.32 and 110.03 Å^3). Simultaneously, their densities are quite different with the value of 1.906, 1.804 and 1.594 g cm^{-3}, respectively. As supported by the X-ray data, although their repeated number of asymmetric units in one unit cell (Z) are the same, their unit cell volumes are different, which means the compactness of their packing is different, with the packing coefficient of 87.4% ,80.8% and 79.3%, respectively.

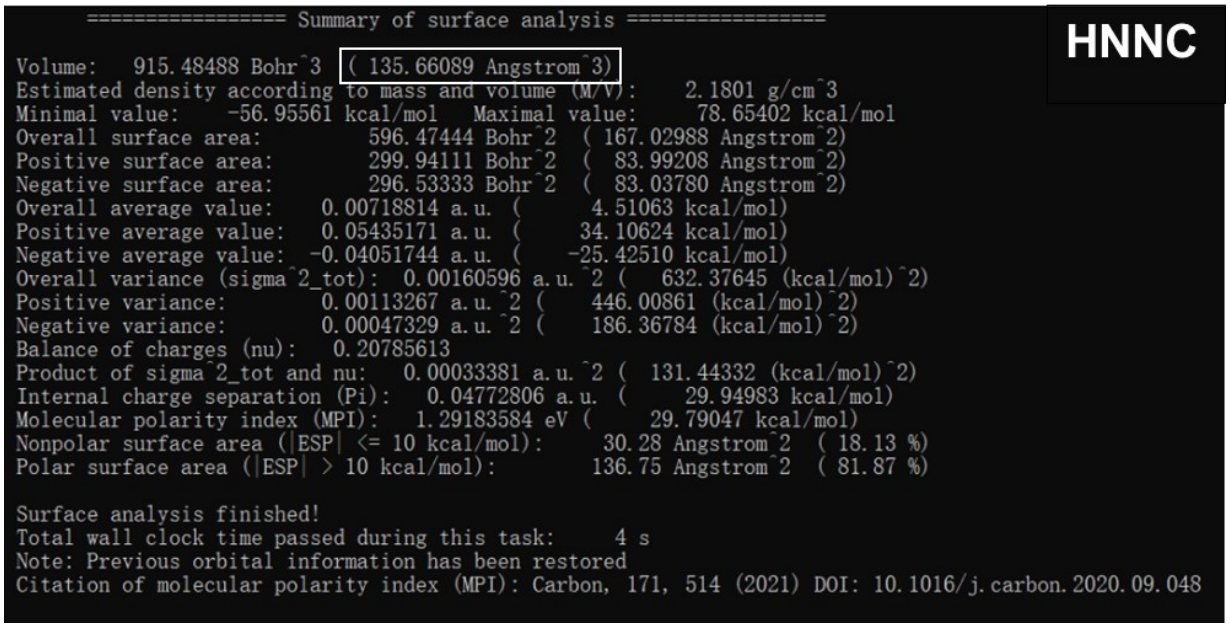


Figure S93. Molecular volumes of HNNC.

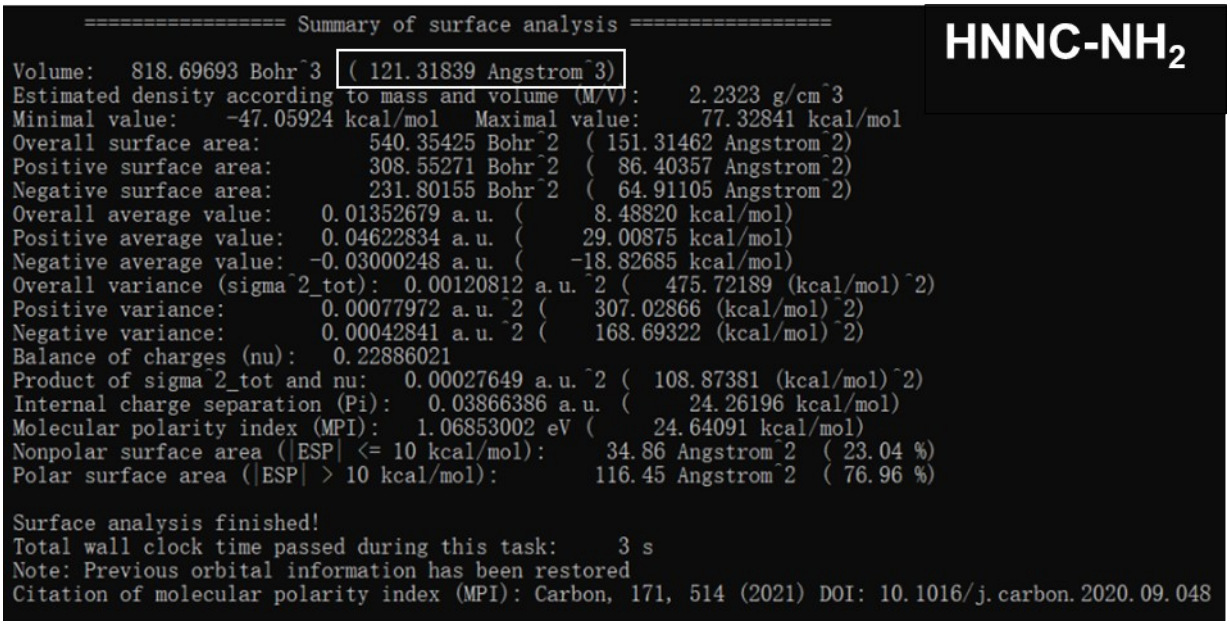


Figure S94. Molecular volumes of HNNC-NH_2.

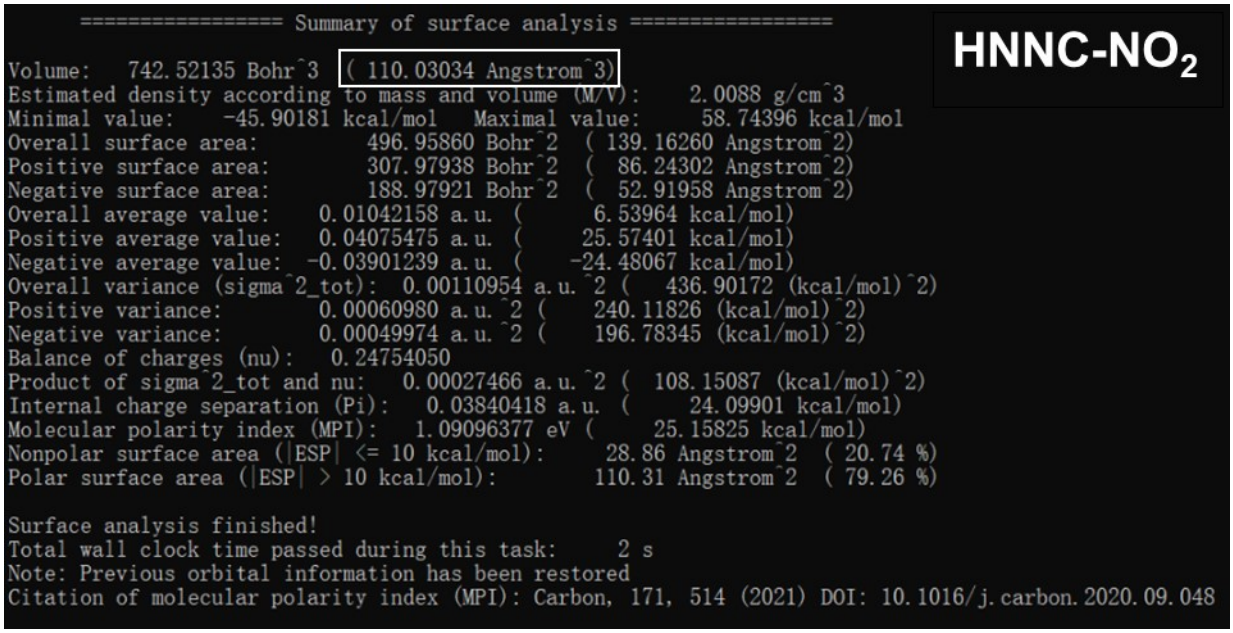


Figure S95. Molecular volumes of HNNC, HNNC-NH_2 and HNNC-NO_2.

The experimental results show that the density of **HNNC** is higher than that of **HNNC-NH_2** and **HNNC-NO_2**. This can be explained by the fact that the filling coefficient of **HNNC** (87.4%) is higher than that of **HNNC-NH_2** (80.8%) and **HNNC-NO_2** (79.3%). The above analysis shows that the molecular filling coefficient has a very important effect on the density of the compound, and a higher filling coefficient may lead to a higher molecular density.

Table S16. Packing coefficient of HNNC, HNNC-NH_2 and HNNC-NO_2.

Compound	d[a]	V_m[b]	Z[c]	V_c[d]	PC[e]
HNNC	1.906	135.66	4	620.8	87.4%
HNNC-NH_2	1.804	121.32	8	1201.34	80.8%
HNNC-NO_2	1.594	110.03	4	554.74	79.3%

[a] Crystal Density: **HNNC**, **HNNC-NH_2** and **HNNC-NO_2** at 296 K, g cm^{-3}. [b] Molecular volume calculated by using Gaussian 16 and Multiwfn programs, $Å^3$. [c] Repeated number of asymmetric units in the unit cell; [d] Unit cell volume, $Å^3$; [e] Packing coefficient, %.

7. Thermal stability

The thermal stability plots of HNNC are shown in the main article.

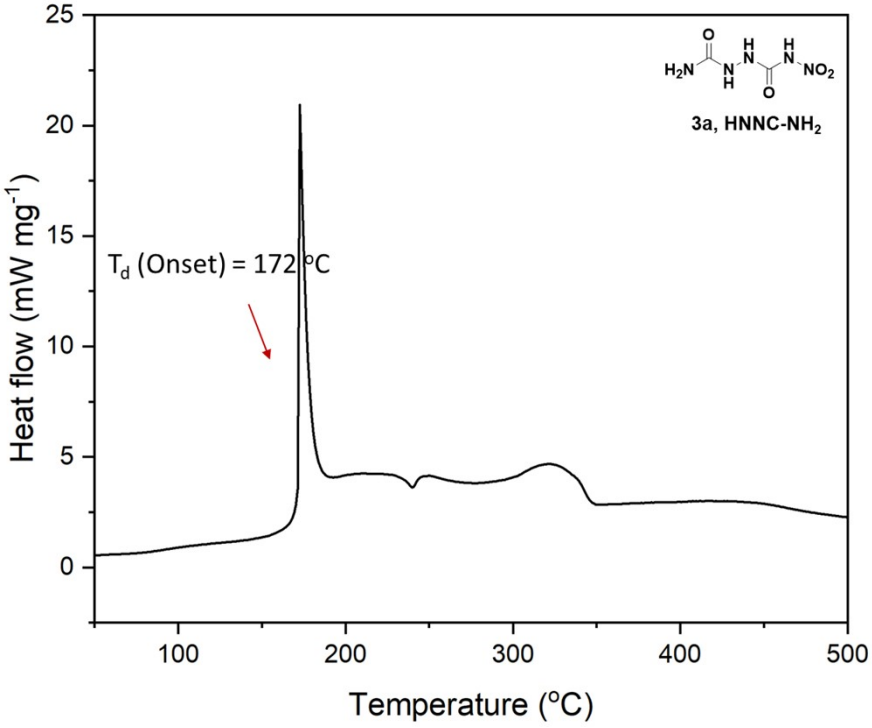


Figure S96. DSC curve of **HNNC-NH_2**.

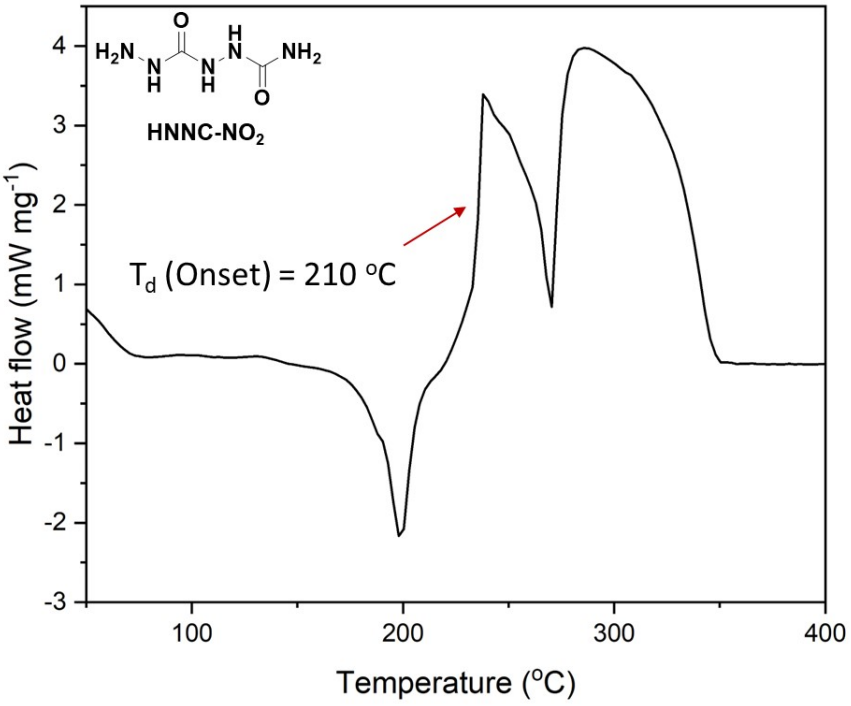


Figure S97. DSC curve of **HNNC-NO_2**.

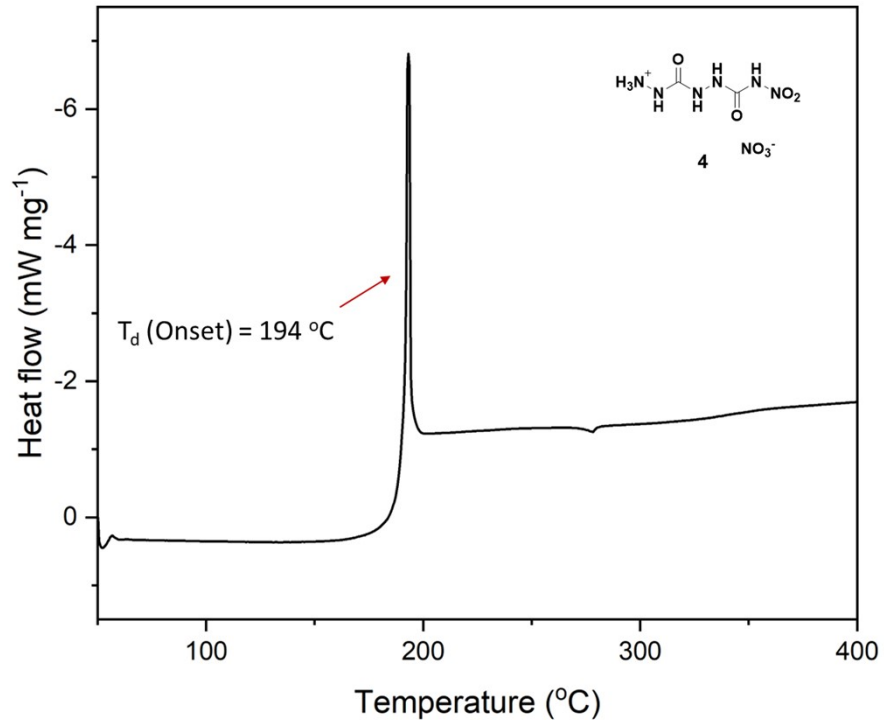


Figure S98. DSC curve of **4**.

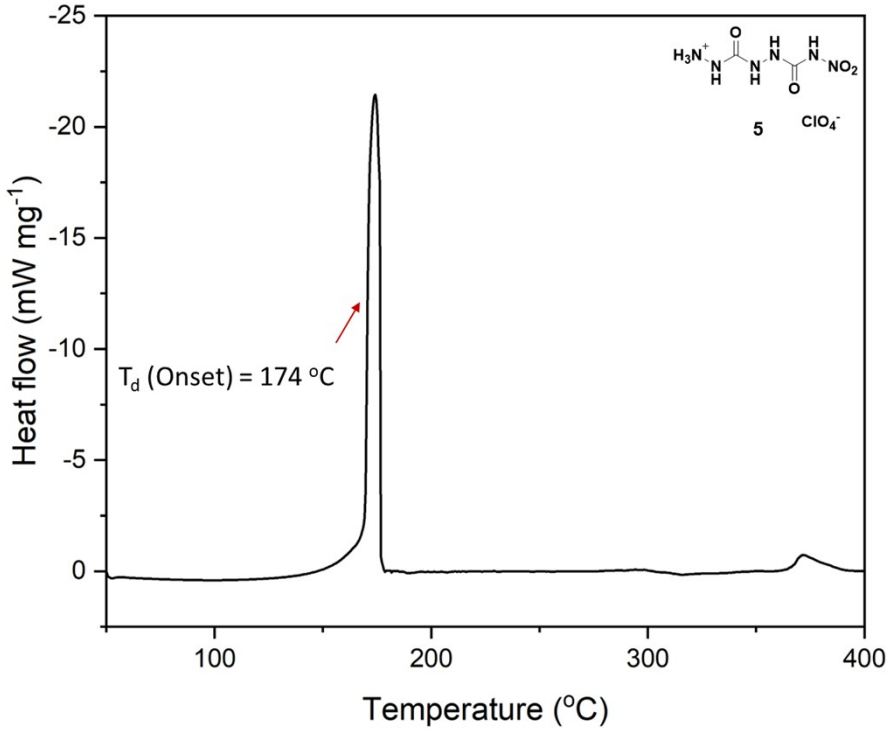


Figure S99. DSC curve of **5**.

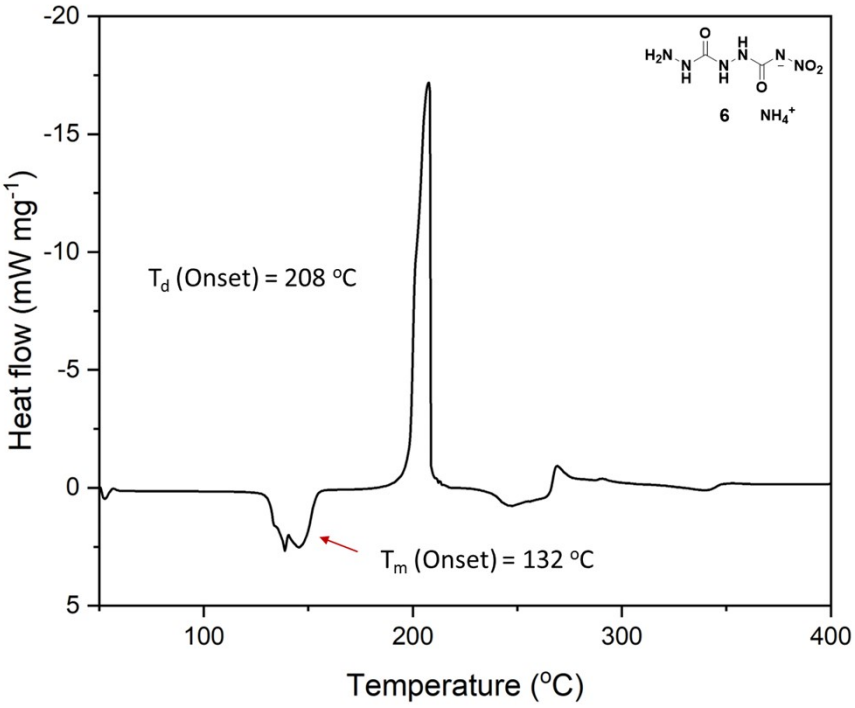


Figure S100. DSC curve of **6**.

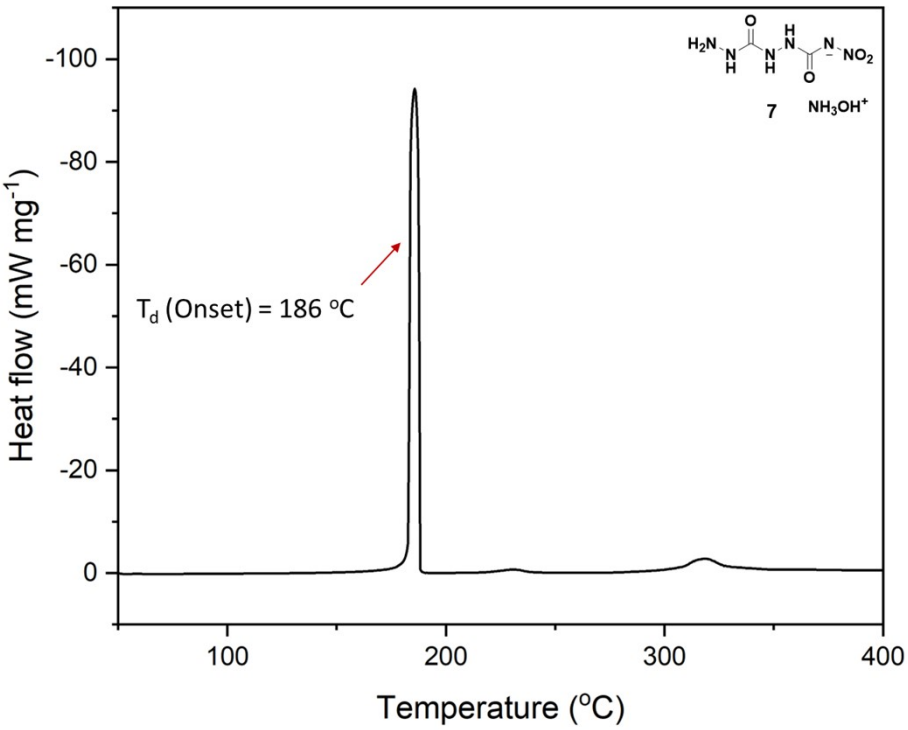


Figure S101. DSC curve of **7**.

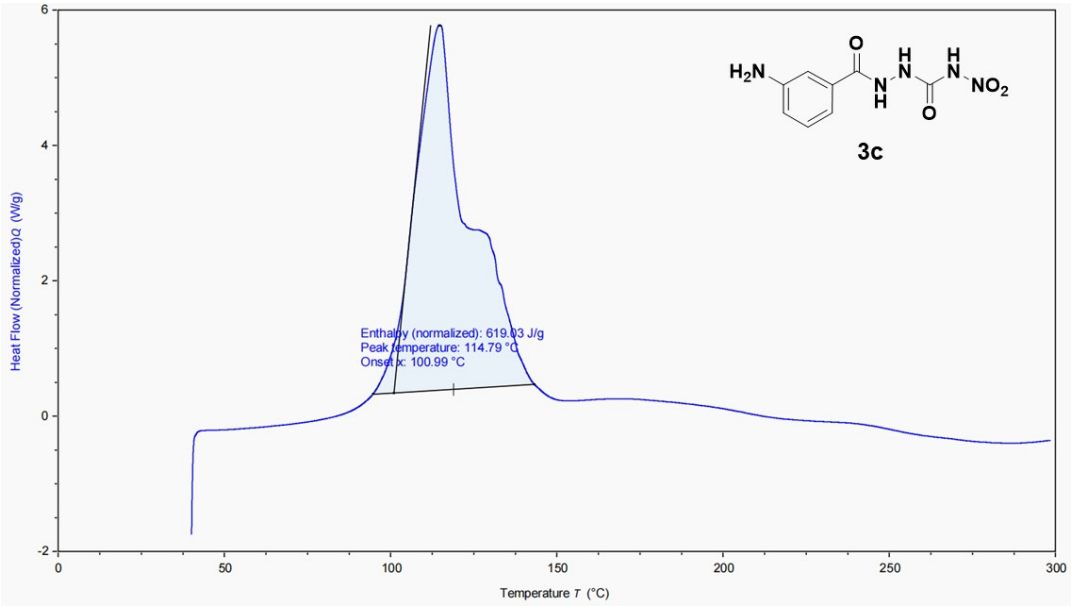


Figure S102. DSC curve of **3c.**

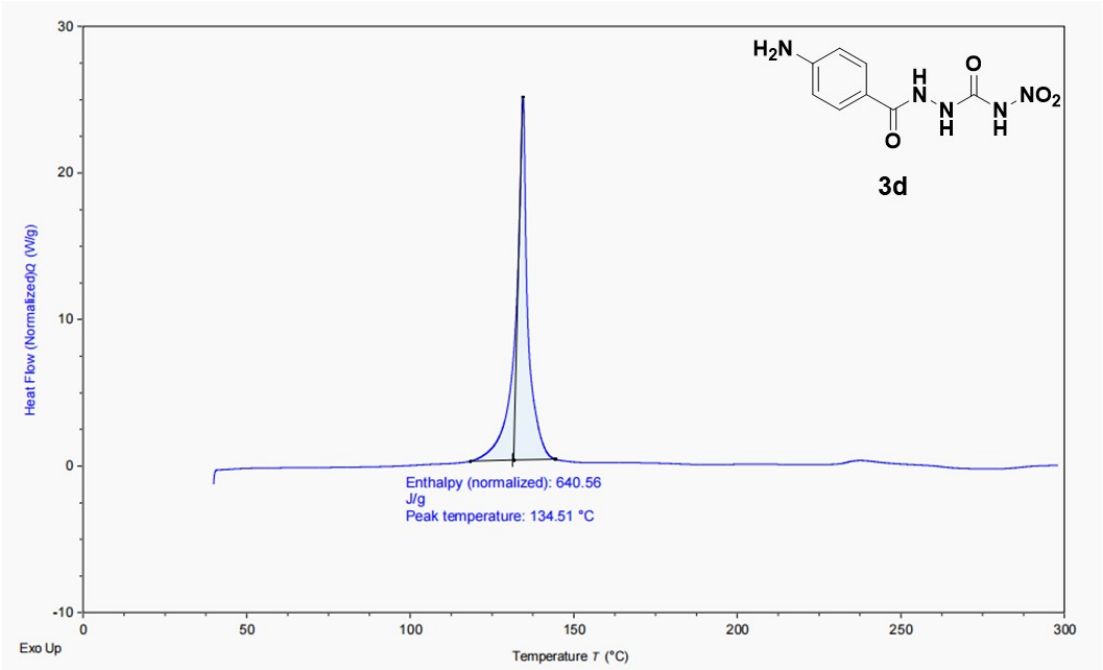


Figure S103. DSC curve of **3d.**

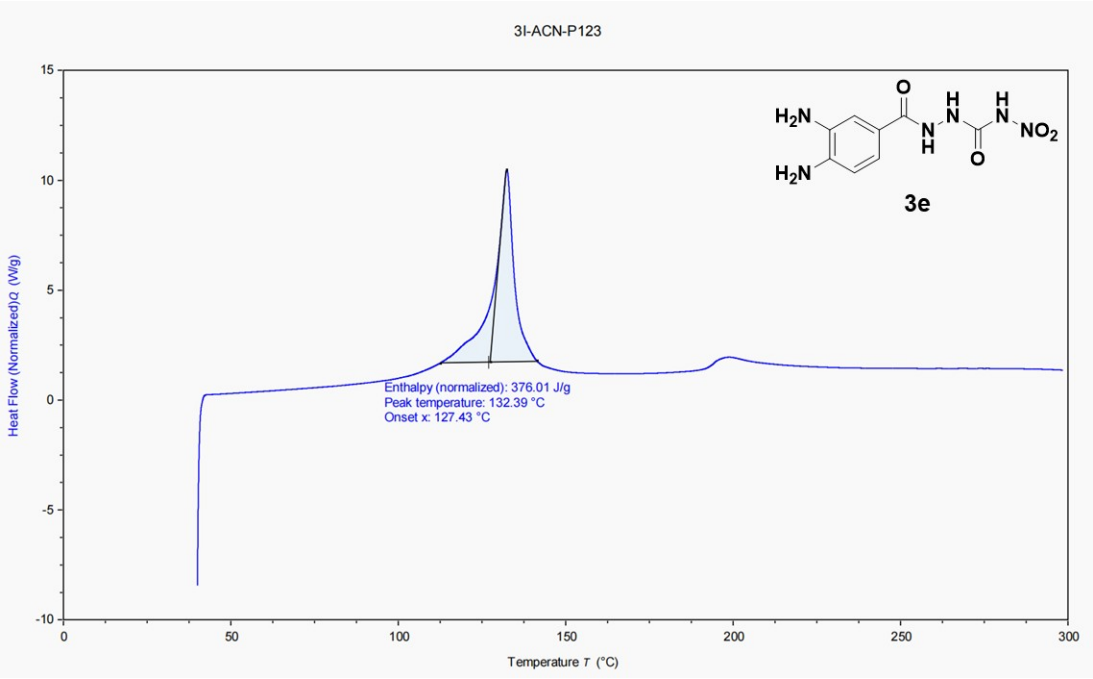


Figure S104. DSC curve of **3e.**

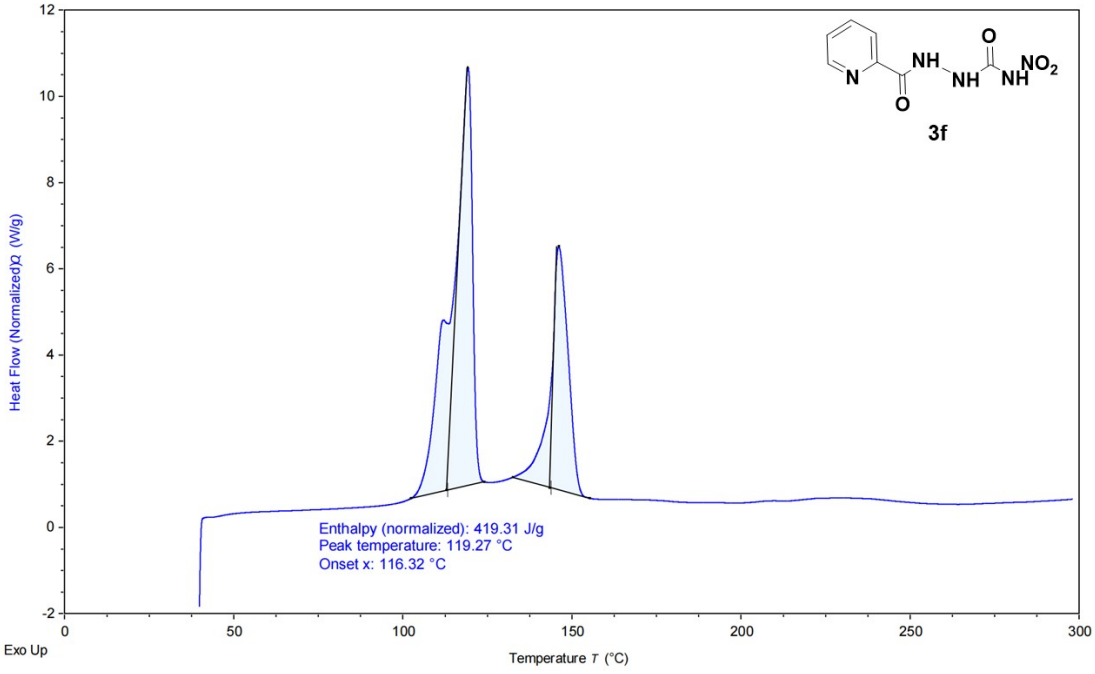


Figure S105. DSC curve of **3f.**

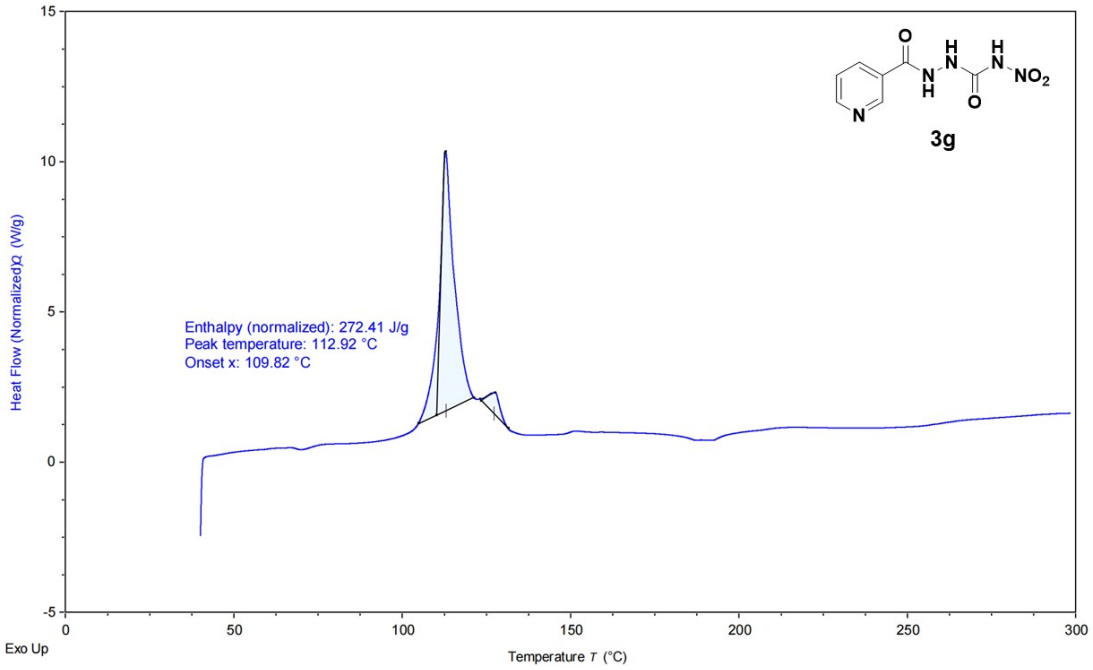


Figure S106. DSC curve of **3g.**

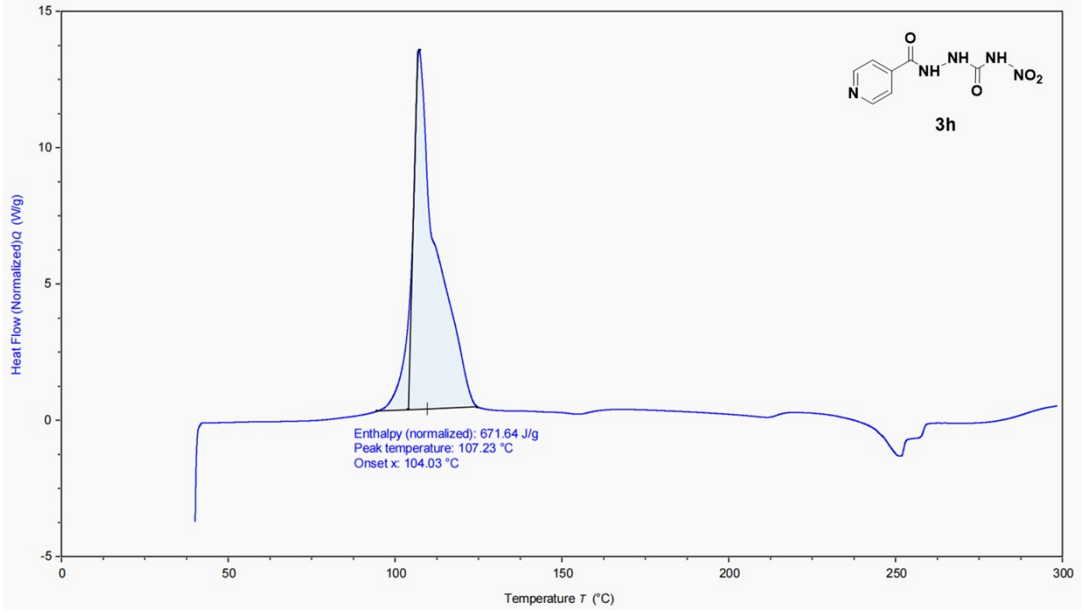


Figure S107. DSC curve of **3h.**

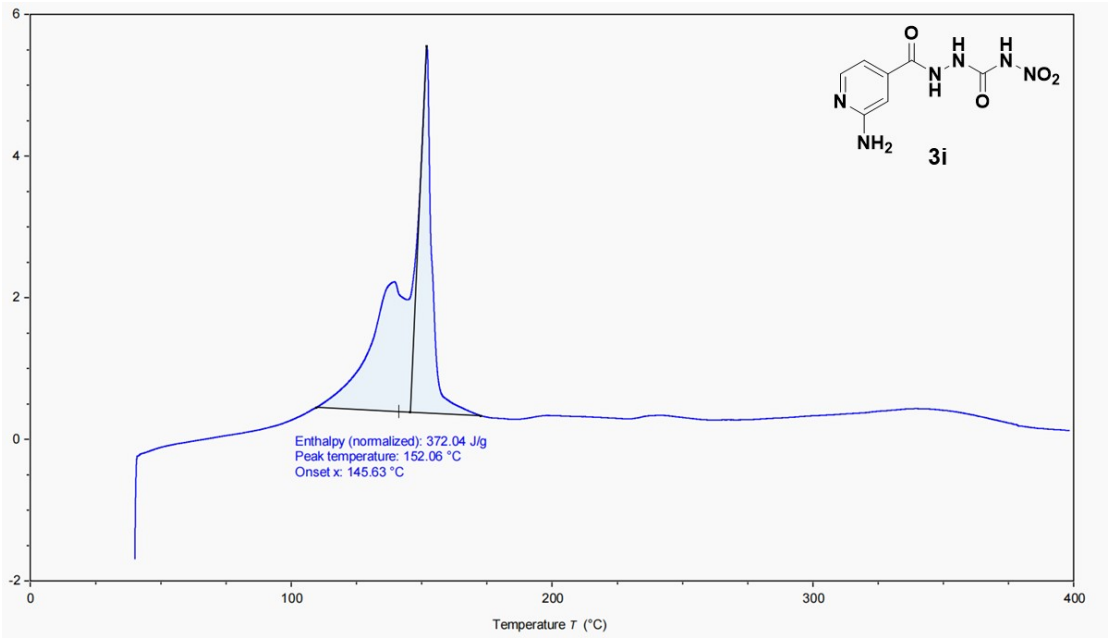


Figure S108. DSC curve of **3i.**

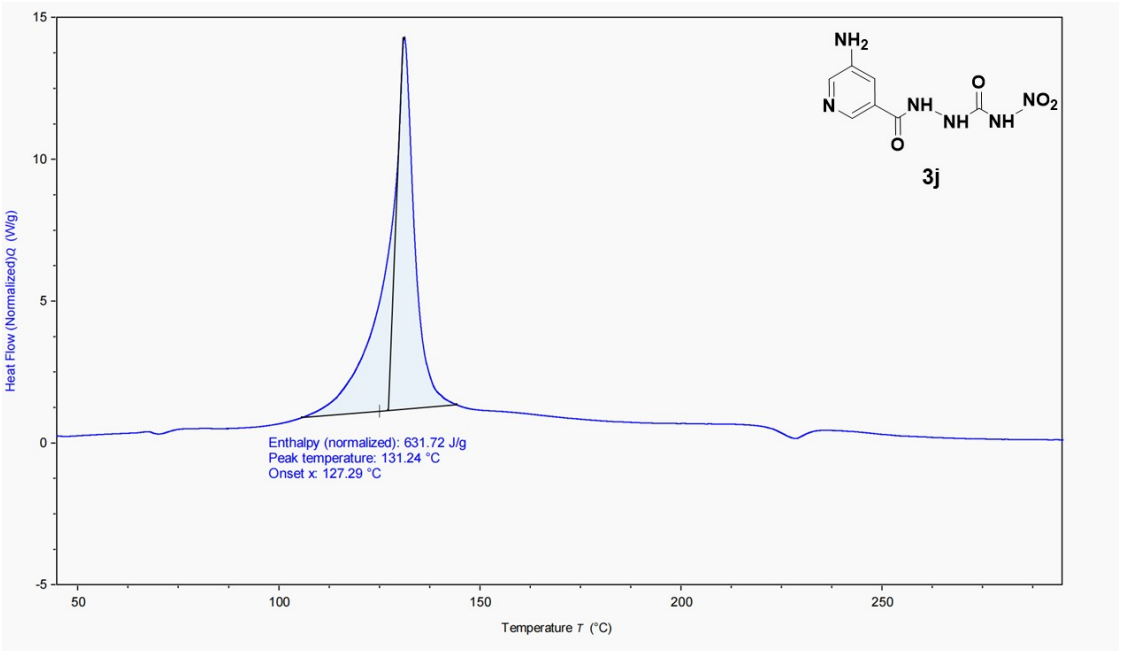


Figure S109. DSC curve of **3j.**

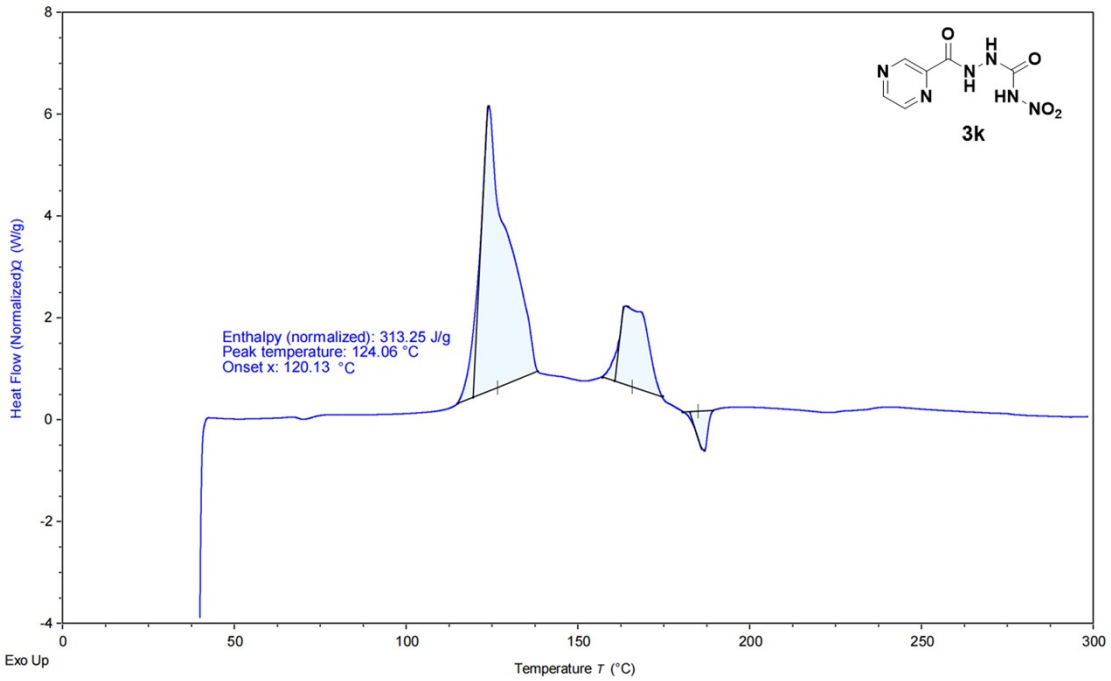


Figure S110. DSC curve of **3k.**

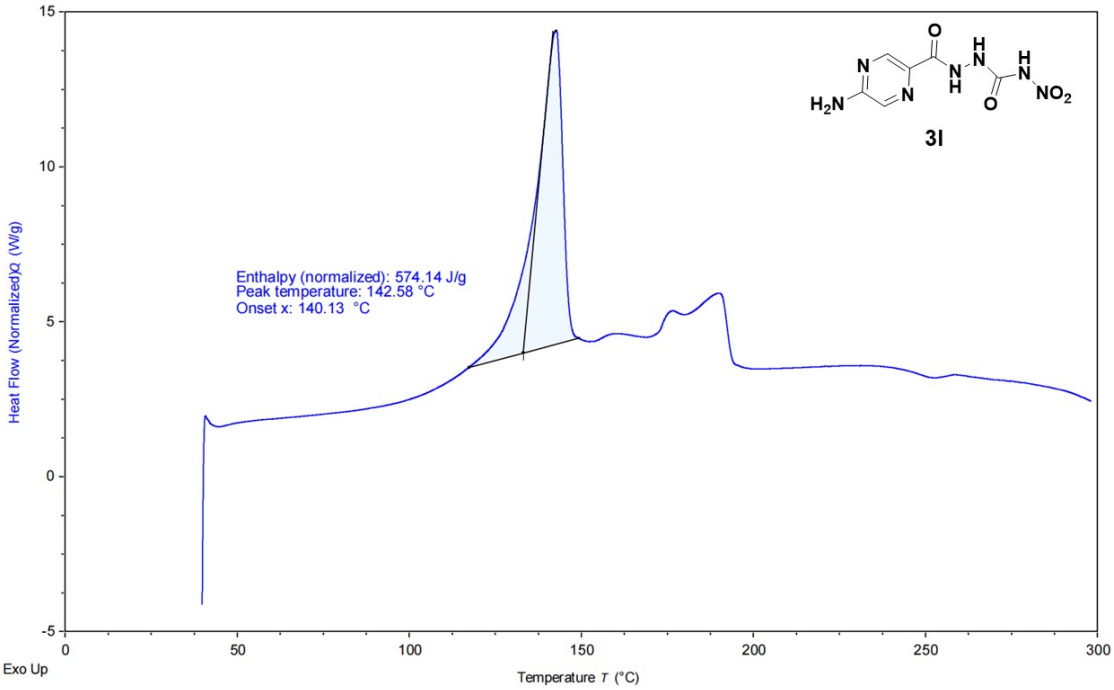


Figure S111. DSC curve of **3l.**

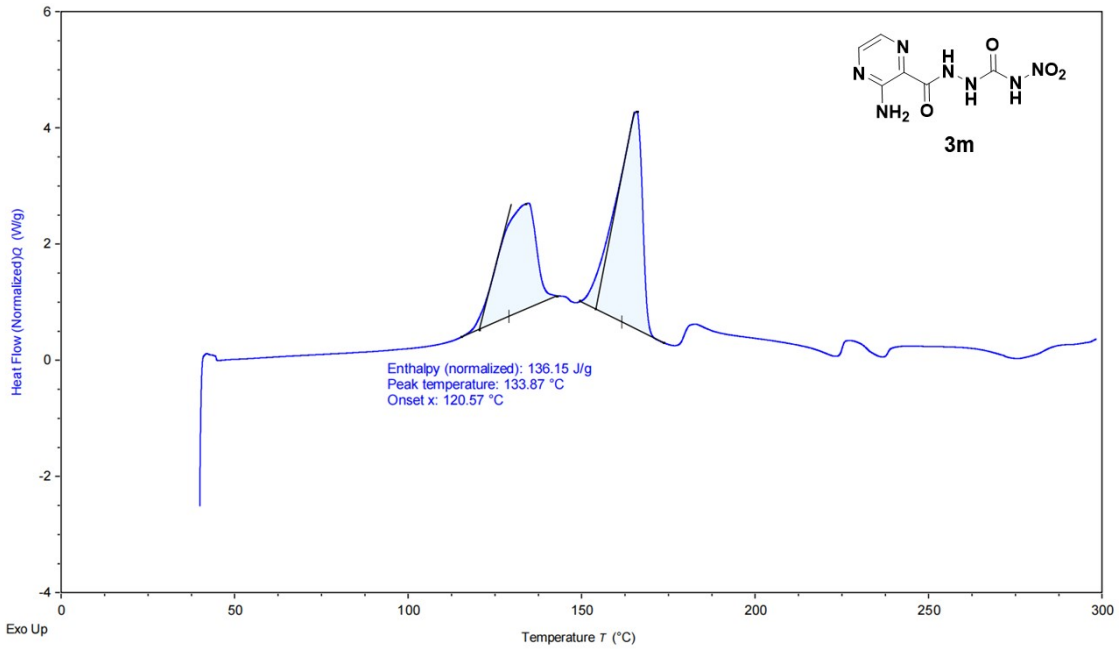


Figure S112. DSC curve of **3m.**

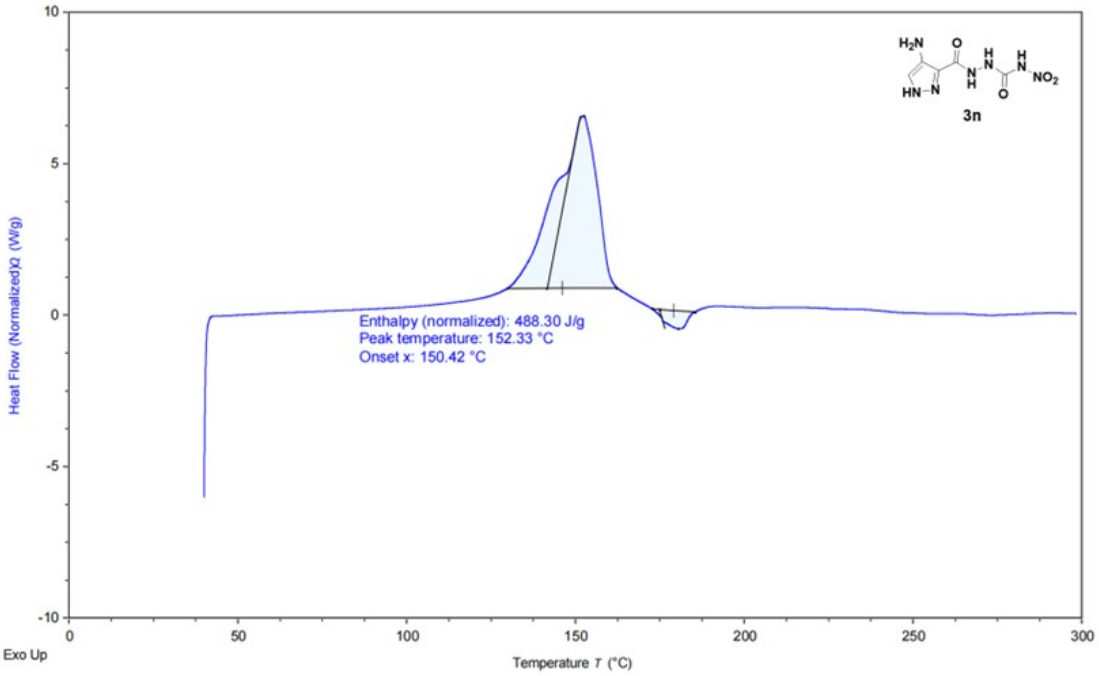


Figure S113. DSC curve of **3n.**

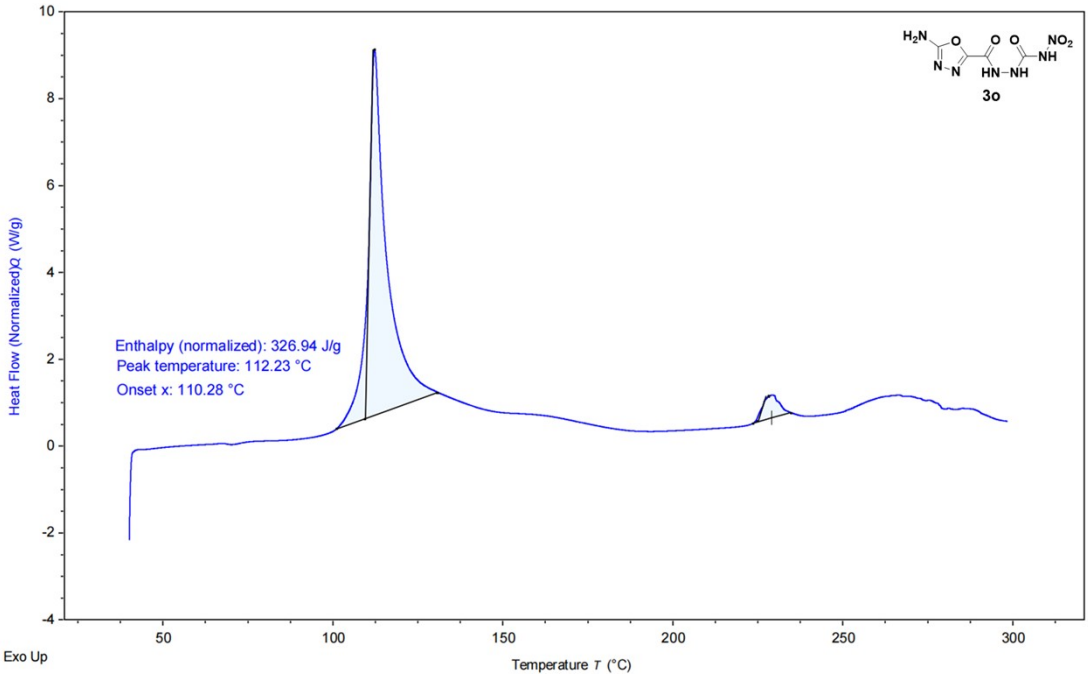


Figure S114. DSC curve of **3o.**

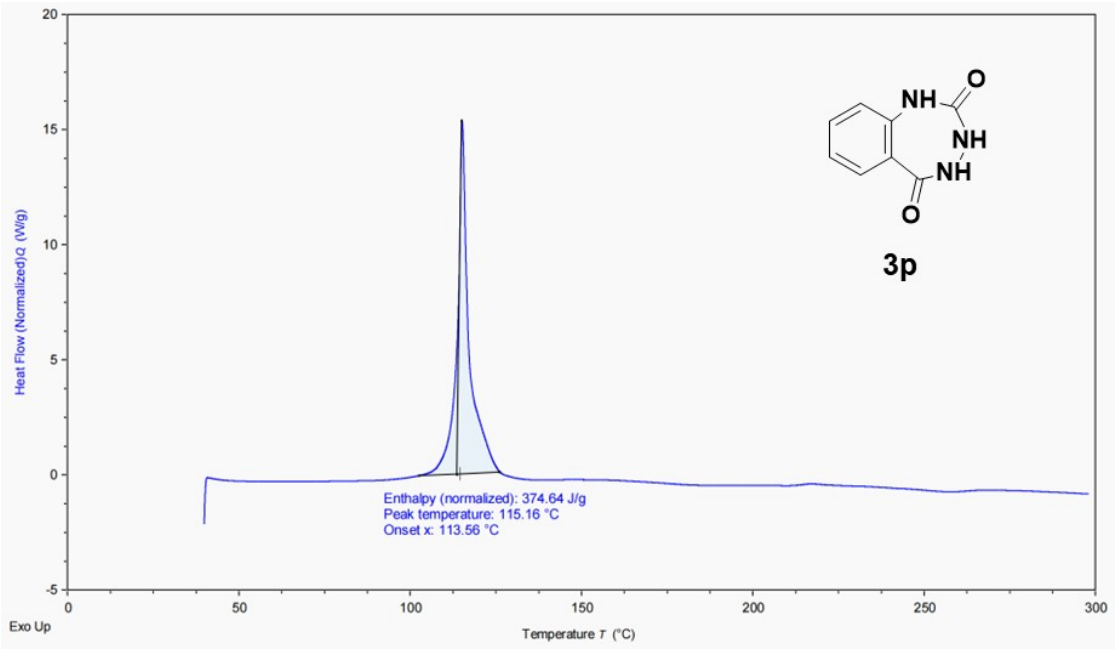


Figure S115. DSC curve of **3p.**

8. References

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