# Supporting Information

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## 1. The crystallographic data

**Table S1.** X-ray data and parameters of compounds **5** and **7**.

| | 5 | 7 |
|---|---|---|
| Chemical formula | $C_6H_8N_8O_8$ | $C_4H_6N_6O_5$ |
| Formula mass | 320.20 | 218.15 |
| Crystal system | triclinic | orthorhombic |
| a/Å | 6.6754(11) | 9.155(2) |
| b/Å | 8.1836(13) | 7.2579(17) |
| c/Å | 11.2567(17) | 23.291(5) |
| α/° | 94.152(4) | 90 |
| β/° | 104.263(4) | 90 |
| γ/° | 104.096(4) | 90 |
| Volume/Å$^3$ | 572.28(16) | 1547.6(6) |
| Temperature/K | 173 | 173 |
| Space group | *P*-1 | *Pbca* |
| Z | 2 | 8 |
| Radiation type | Mo-Ka | Mo-Ka |
| μ/mm$^{-1}$ | 0.172 | 0.171 |
| Density$_{calcd}$/g cm$^{-3}$ | 1.858 | 1.873 |
| F(000) | 328 | 896 |
| 2Θ range for data collection/° | 3.8 to 55 | 3.6 to 55.6 |
| Index ranges | -8/8;-10/9; -14/14 | -11:11; -9:9; -30:30 |
| Reflections collected | 5180 | 8402 |
| Independent reflections | 2558 | 1788 |
| R$_{int}$ | 0.036 | 0.072 |
| Data/restraints/ parameters | 2558/0/199 | 1788/163/154 |
| R$_1$ / wR$_2$ [all data] | 0.0832/0.1935 | 0.0856/0.1540 |
| R$_1$ / wR$_2$ [I > 2σ(I)] | 0.0616/0.1956 | 0.0568/0.1603 |
| Goodness-of-fit on F$^2$ | 1.07 | 1.05 |
| CCDC number | 1886018 | 1886043 |

**Table S2.** The existed HBs interaction in structure of compound **7**

| D-H···A | D-H(Å) | H···A(Å) | D···A(Å) | D-H···A(°) |
|---|---|---|---|---|
| N3—H3···O2 | 0.8800 | 1.9700 | 2.593(3) | 127 |
| N3—H3···O1 | 0.8800 | 2.2900 | 3.070(5) | 147 |
| N3—H3···O1A | 0.8800 | 2.2200 | 2.946(4) | 140 |
| N5—H5···O4 | 0.8800 | 1.9200 | 2.574(3) | 130 |
| N5—H5···O5 | 0.8800 | 2.2600 | 2.923(3) | 132 |
| C3—H3A···O2 | 0.9900 | 2.4700 | 3.370(3) | 151 |
| C4—H4A···O5 | 0.9900 | 2.5900 | 3.374(3) | 137 |
| C4—H4A···N6 | 0.9900 | 2.6100 | 3.327(4) | 130 |

## 2. Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] Based on the method of isodesmic reactions (Scheme S1), gas-phase heats of formation of the neutral compounds were computed. The gas-phase enthalpies of the building-block molecules were obtained by using the atomization method with the G2 ab initio calculations. Then the remaining task is to determine the solid-state heats of formation for the synthesized compounds.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation.
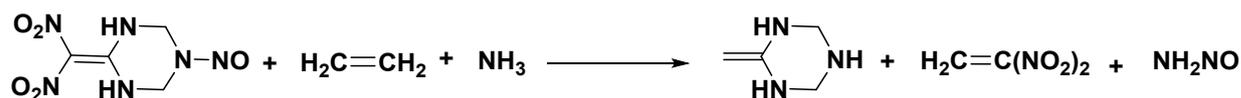
$$\Delta H_f = \Delta H_f(g) - \Delta H_{sub} \quad (1)$$

On the basis of the literature,[2] the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{sub} = 188/J\ mol^{-1}K^{-1} \times T\ (2)$$

The detailed principle can be consulted from literatures[1-4].
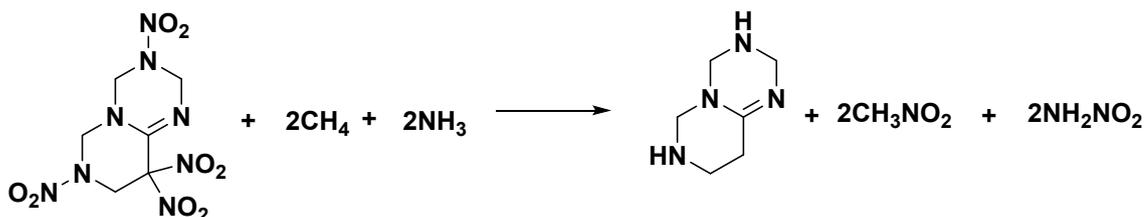
**Scheme S1.** Isodesmic reactions

## 3. Mechanism study

We proposed a possible reaction mechanism for the formation of derivative **5**. In this mechanism, the derivative **4** first reacted with the 100% $HNO_3$ to generate the nitramine compound **8** with a resonance structure of **8'** (Scheme S2). Also, in 100% $HNO_3$, the $NO_2^+$ was formed by an ionization equilibrium as shown in Scheme 1.1, and $H_3O^+$ also formed as well in this equilibrium process. Then, the nitramine compound **8** partly hydrolyzed to generate the diol compound **9** and FOX-7. In the presence of 100% nitric acid, diol **9** could be readily pronated and the further elimination of **10** gave rise to the iminium ion **11**. The coordination of $ZnCl_2$ with gem-dinitro group resulted to the resonance structures **12** and **12'** which played as an activated nucleophilic reagent to attack the iminium ion **11**. The resulting intermediate **13** could undergo the similar tautomerization to yield iminium cation **14**, whereas the subsequent intramolecular cyclization was successfully completed to form the fuse-ring compound **5**.
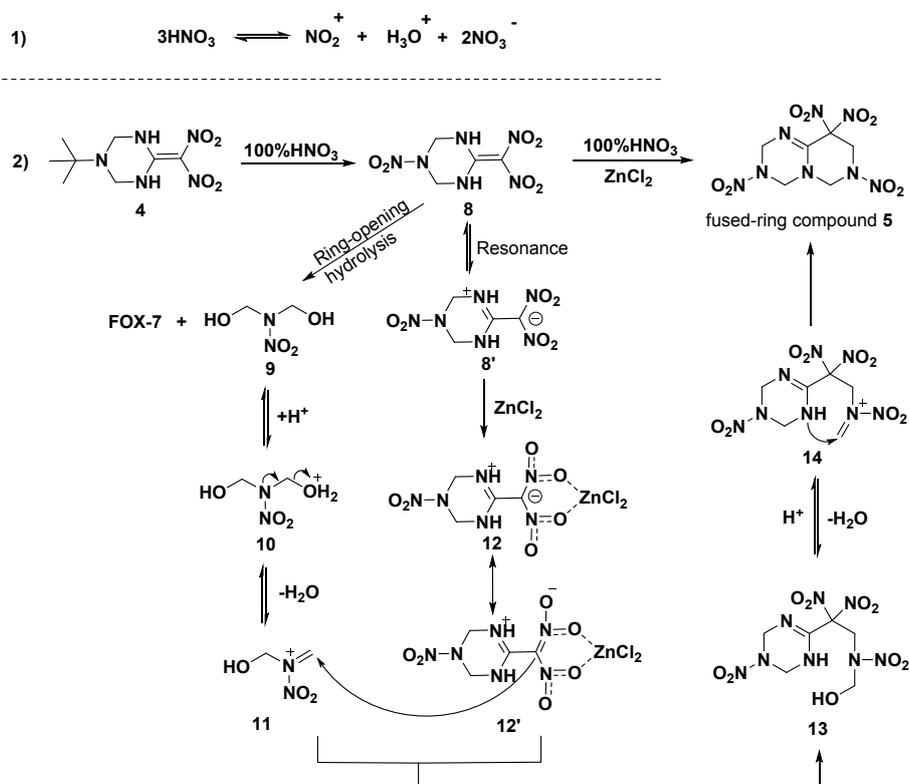


**Scheme S2**. The possible mechanism for the formation of fused-ring compound **5**.

**4. Experimental Section**

Safety precautions. Although no explosion or detanation happened during the synthesis, characterization and handling of the compounds described in this work, all manipulations must be carried out by using appropriate standard safety precautions like face shield, leather coat and leather gloves. Mechanical actions involving scratching or scraping must be avoided.

**Hexahydro-1-tert-butyl-4-dinitromethylene-1,3,5-triazine(1)** were prepared according to the literature procedures.[5,6]
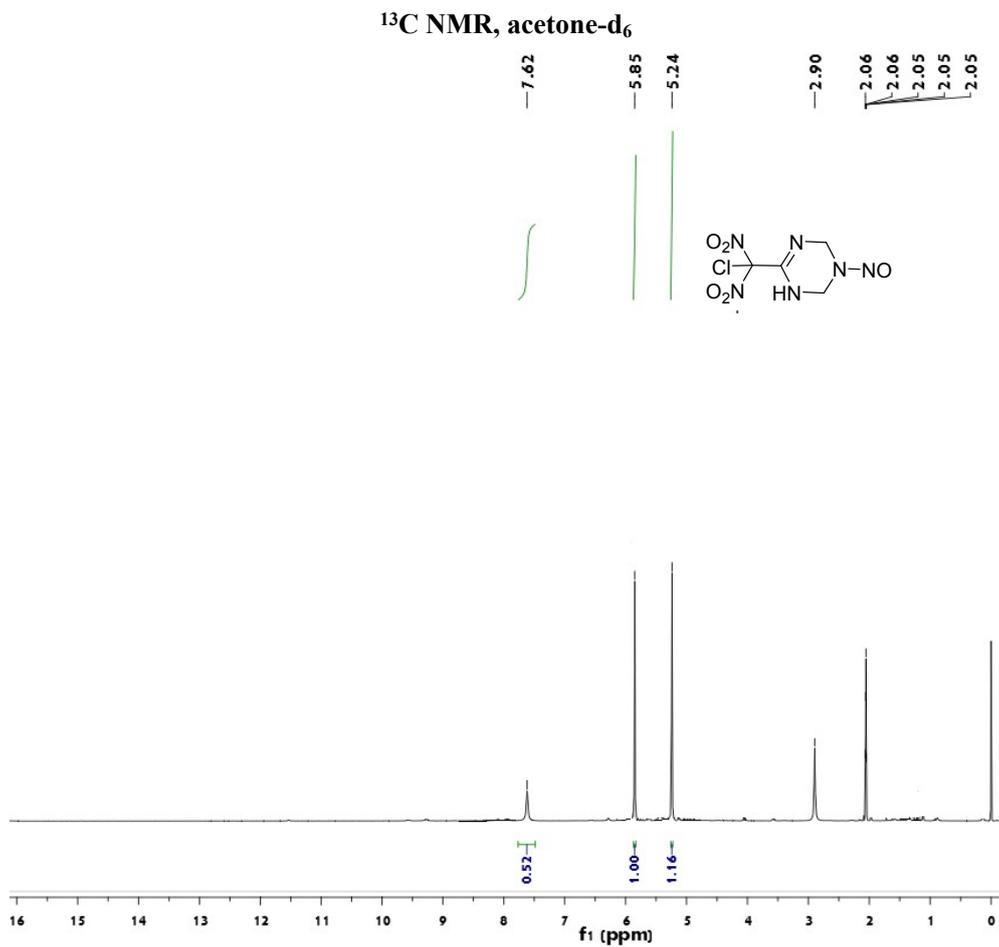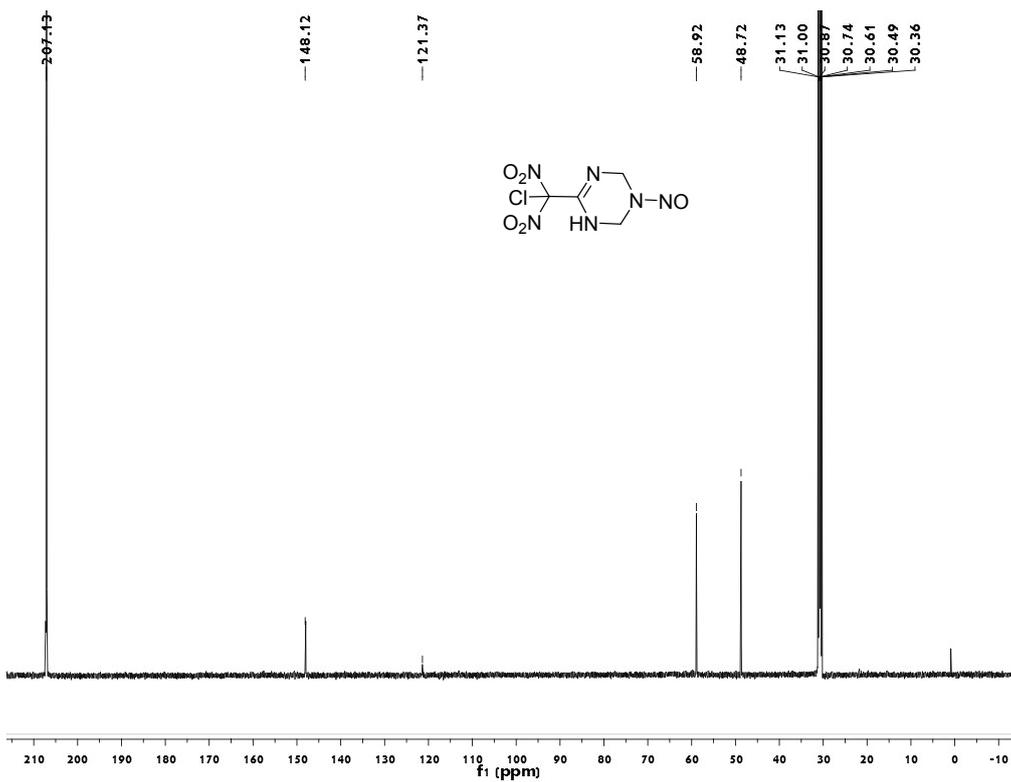
**4,8,10,10-tetranitrobicyclo[4.4.0]-1,3,5,7-aza-1-decene (5).** To 2 mL of fuming nitric acid at 0°C, **I** (0.245 g, 1 mmol) was added portion wise over a 10 min period, followed by one portion addition of $ZnCl_2$ (0.409 g, 3 mmol). The reaction was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A light yellow solid formed was filtrated, washed with water and dried in air to give **5** (0.085 g, 26.4 %). $^1H$ NMR (600 MHz, $CD_3COCD_3$): $\delta_H$ = 5.56 (2H, s), 5.58 (2H, s), 5.67 (4H, d) ppm; $^{13}C$ NMR (151MHz, $CD_3COCD_3$): $\delta_C$ = 51.90, 61.02, 63.17, 64.44, 111.38, 144.84 ppm; IR (KBr): $\nu$ = 3061, 3048, 3030, 3019, 2971, 2905, 2843, 1658, 1601, 1580, 1558, 1507, 1469, 1457, 1434, 1414, 1383, 1371, 1342, 1279, 1221, 1181, 1151, 1120, 1073, 1041, 1015, 985, 964, 949, 928, 861, 818, 798, 772, 761, 732, 678, 667, 649, 627, 610, 534, 484, 425 cm$^{-1}$; elemental analysis calcd (%) for $C_6H_8N_8O_8$ (320.18): C 22.51, H 2.52, N 35.00, found: C 22.41, H 2.60, N 34.24.
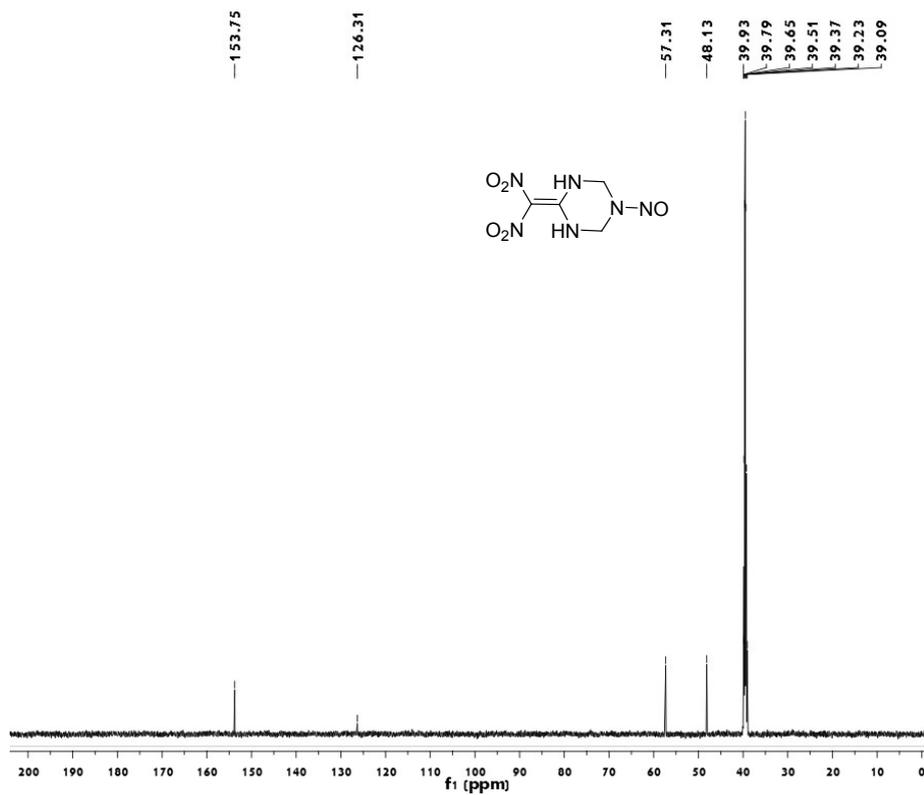
**6-(chlorodinitromethyl)-3-nitroso-1,2,3,4-tetrahydro-1,3,5-triazine (6).** To 2 mL of 95 % nitric acid at 0°C, **1** (0.245 g, 1 mmol) was added portionwise over a 10 min period, followed by one portion addition of $NH_4Cl$ (0.156 g, 3 mmol). The reaction was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A white solid formed was filtrated, washed with water and dried in air to give **6** (0.161 g, 63.6%). $^1H$ NMR (600 MHz, $CD_3COCD_3$) : $\delta_H$ = 5.24 (2H, s), 5.85 (2H, s), 7.62 (1H, s) ppm; $^{13}C$ NMR (151MHz, $CD_3COCD_3$): $\delta_C$ = 48.72, 58.92, 121.37, 148.12 ppm; IR (KBr): $\nu$ = 3202, 2992, 1662, 1622, 1595, 1511, 1475, 1456, 1434, 1369, 1346, 1321, 1291, 1257, 1210, 1129, 1066, 1028, 990, 959, 948, 931, 829, 815, 787, 725, 647, 540, 503, 433 cm$^{-1}$; elemental analysis calcd (%) for $C_4H_5N_6O_5Cl$ (252.57): C 19.02, H 2.00, N 33.27, found: C 18.97, H 2.03, N 33.21.

**4-(dinitromethylene)-1-nitroso-1,3,5-triazinane (7). 6** (0.253 g, 1 mmol) was dissolved in methanol (5 mL), potassium iodide (0.2 g, 1.2 mmol) was added portionwise, and the mixture was stirred for 12 h at room temperature. The precipitate formed was collected by filtration, washed with water and dried in the air to give **7** (0.197 g, 80.2%). $^1H$ NMR (600 MHz, DMSO-$d_6$) : $\delta_H$ = 5.30 (2H, s), 6.03 (2H, s), 10.79 (2H, s) ppm; $^{13}C$ NMR (151MHz, DMSO-$d_6$): $\delta_C$ = 48.13, 57.31, 126.31, 153.75 ppm; IR (KBr): $\nu$ = 3236, 3027, 2961, 2923, 2852, 1583, 1510, 1473, 1451, 1360, 1320, 1261, 1177, 1125, 1032, 1012, 852, 815, 780, 750, 704, 676, 575, 542 cm$^{-1}$; elemental analysis calcd (%) for $C_4H_6N_6O_5$ (218.13): C 22.03, H 2.77, N 38.53, found: C 22.01, H 2.81, N 38.43.
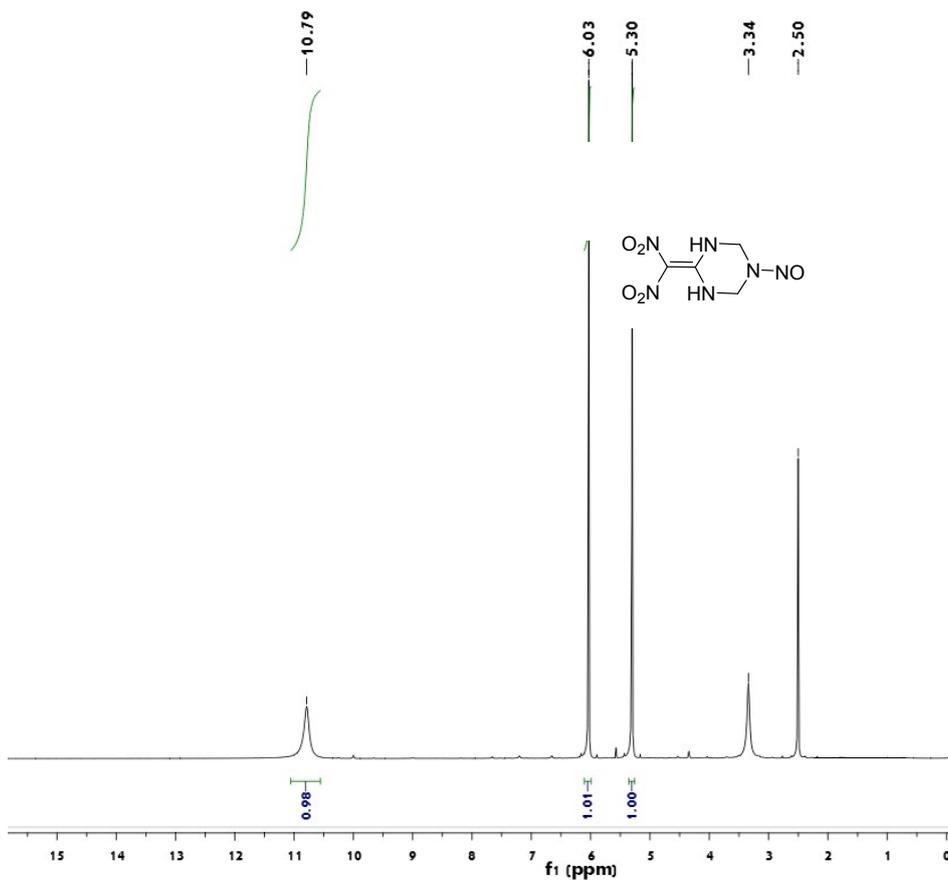
## 5. References

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## 6. NMR spectroscopy



**¹³C NMR, acetone-d₆**



**¹H NMR, acetone-d₆**

7

207.13
148.12
121.37
58.92
48.72
31.13
31.00
30.87
30.74
30.61
30.49
30.36

**$^{13}$C NMR, acetone-d$_6$**



7.62
5.85
5.24
2.90
2.06
2.06
2.05
2.05
2.05

0.52
1.00
1.16

**$^1$H NMR, acetone-d$_6$**

8

**13C NMR, DMSO-d₆**

Peaks: 153.75, 126.31, 57.31, 48.13, 39.93, 39.79, 39.65, 39.51, 39.37, 39.23, 39.09



**1H NMR, DMSO-d₆**

Peaks: 10.79, 6.03, 5.30, 3.34, 2.50

Integrations: 0.98, 1.01, 1.00