

**Tunable Dimroth rearrangement of versatile 1,2,3-triazoles  
towards high-performance energetic materials**

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Complete List of Authors:	Shreeve, Jean'ne; University of Idaho, Department of Chemistry Feng, Shangbiao; Beijing Institute of Technology, Chemistry Yin, Ping; Beijing Institute of Technology, Materials Science and Engineering He, Chunlin; Beijing Institute of Technology, State Key Laboratory of Explosion Science and Technology Pang, Si-Ping; Beijing Institute of Technology,

## Tunable Dimroth rearrangement of versatile 1,2,3-triazoles towards high-performance energetic materials

 Shangbiao Feng,<sup>[a,b,c]</sup> Ping Yin,<sup>\* [a,b,c]</sup> Chunlin He,<sup>[a,b,c]</sup> Siping Pang,<sup>\* [a]</sup> and Jean'ne M. Shreeve<sup>\*[b]</sup>

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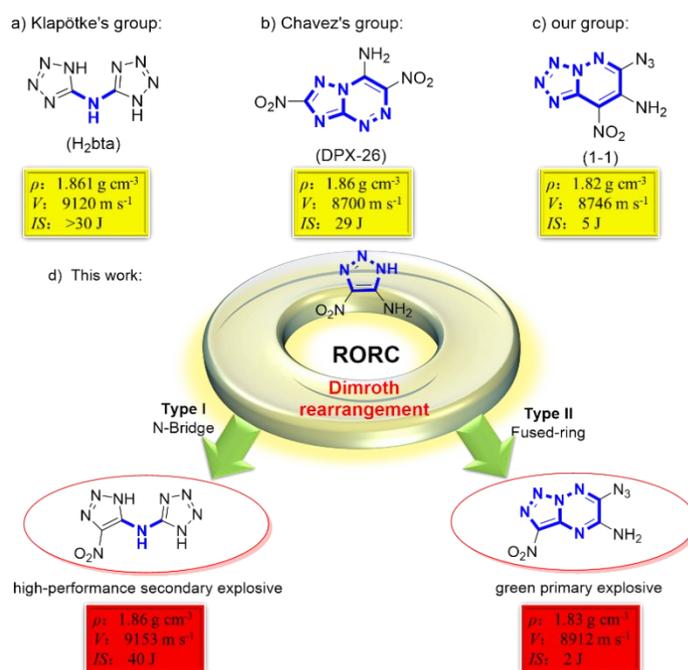
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A highly efficient strategy of two different types of nitrogen-rich heterocyclic energetic compounds, featuring a single NH-bridge (-NH-) and a fused ring, was demonstrated by virtue of Dimroth rearrangement reactions using 4-amino-5-nitro-1,2,3-triazole as the precursor. Various nitrogen-rich compounds and their salts were prepared via this transformation and fully characterized using multinuclear NMR spectroscopy, IR, elemental analysis, and single crystal X-ray structuring. Their key properties, such as decomposition temperatures, densities, detonation velocities and pressures, and impact sensitivities, were obtained from theoretical calculations or experimental measurements. With different task-specific explosives, the representative energetic compounds **6b** and **18** exhibit great potential as high performance insensitive energetic materials and organic primary explosives, respectively. This work gives the classic Dimroth rearrangement new vitality to access diversified task-specific energetic materials.

### Introduction

The field of high energy density materials (HEDMs) has witnessed rapid development in military and civilian research systems.<sup>[1]</sup> Traditional HEDMs, such as RDX and TNT play irreplaceable roles in most currently used munitions. With a goal of balancing energy and stability, smart assembly of novel energetic backbones and functionalized groups is the first priority in structural innovation on a molecular level. However, unlike for most chemical materials, new synthetic methodologies for highly energetic moieties are still ongoing issues in the community of HEDMs.

Compared to the widely investigated building block azo-bridge (-N=N-), the NH-bridge (-NH-) in energetic compounds benefit from inter- or intramolecular hydrogen bonding interactions, which contributes greatly to the efficient crystal packing, and makes the compounds less sensitive toward external stimuli. However, traditional construction of such a structural motif via transition metal catalyzed cross coupling strategy is not suitable for nitrogen-rich heterocycles due to deactivation resulting from catalyst poisoning.<sup>[2]</sup> Other than from cross coupling reactions, in-situ construction of NH-bridged energetics employ an acid-catalyzed cycloaddition of sodium azide and sodium dicyanamide to give 5,5'-bis(1H-tetrazolyl)amine (**H<sub>2</sub>bta·H<sub>2</sub>O**) as the monohydrate. A



**Fig. 1** Nitrogen-rich heterocyclic energetic compounds with single NH-bridge (-NH-) and fused ring structures.

dehydration process at elevated temperature and reduced pressure gives the anhydrous product which exhibits good performance ( $d$ , 1.861 g cm<sup>-3</sup>,  $D_v$ , 9120 m s<sup>-1</sup>,  $IS$  >30 J) (Fig. 1a).<sup>[3]</sup> In addition, the ionic derivatives of H<sub>2</sub>bta exhibit excellent overall detonation properties superior to HMX.<sup>[4]</sup>

Fused nitrogen-rich heterocycles are attractive targets in preparation of HEDMs for their conjugated systems and coplanar structures that enhance heats of formation and

<sup>a</sup> School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, (P. R. China).

<sup>b</sup> Department of Chemistry, University of Idaho, Moscow, ID 83844-2343 United States. E-mail: jshreeve@uidaho.edu

<sup>c</sup> Beijing Institute of Technology Chongqing Innovation Center, Chongqing, 401120 (P. R. China)

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thermal stabilities.<sup>[5]</sup> In 2016, Chavez's group developed a cyclization reaction of 3-amino-5-nitro-1,2,4-triazole and nitroacetonitrile with sodium nitrite and hydrochloric acid to obtain a fused triazolo-triazine bicycle (**DPX-26**) which displays favorable energetic performance comparable to RDX but with excellent insensitivity (Fig. 1b).<sup>[6]</sup> A fused ring that is functionalized by an azido group always produces primary explosive with good performance, like ICM-103.<sup>[7]</sup> Recently, we reported a metal-free explosive **1-1**, which shows a superior detonation performance ( $d$ , 1.82 g cm<sup>-3</sup>,  $D_v$  = 8746 m s<sup>-1</sup>) compared to commercial primary explosives (Fig. 1c).<sup>[8]</sup>

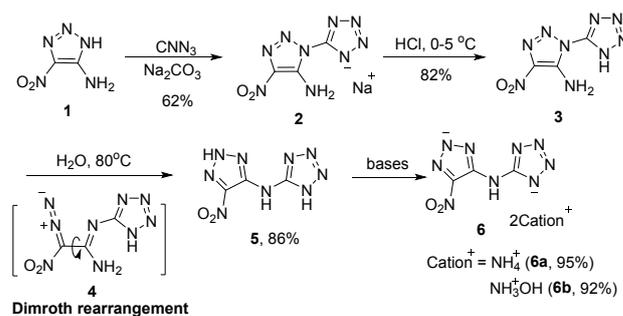
With three catenated nitrogen atoms, the 1,2,3-triazole ring has a high heat of formation comparable to furoxan and higher than the isomeric 1,2,4-triazole. However, limited to the characteristics of synthesis, functionalization and selectivity difficulties, 1,2,3-triazole-based energetic compounds have been less explored compared to other azoles, e.g., pyrazole, imidazole, tetrazole and 1,2,4-triazole.<sup>[9]</sup> Given this background, it is worthwhile exploring 1,2,3-triazole-based nitrogen-rich energetic compounds with a single NH-bridge (-NH-) and fused ring structures. The Dimroth rearrangement (DR) is a great tool for the translocation of two heteroatoms in heterocyclic compounds via a ring opening, ring closing (RORC) process which was first performed over 120 years ago. Many groups have used this reaction as a synthetic method or as an explanation for a mechanism.<sup>[10]</sup> Unfortunately, this reaction has received little attention in the field of HEDMs.

Inspired and encouraged by these excellent works and considering the good performance of 1,2,3-triazole, we now report a highly efficient strategy to synthesize two different types of nitrogen-rich heterocyclic energetic compounds with single NH-bridge (-NH-) and fused ring structures using a common precursor, 4-amino-5-nitro-1,2,3-2H-triazole, via a heat or acid-catalyzed Dimroth rearrangement reaction (Fig. 1d).

## Results and discussion

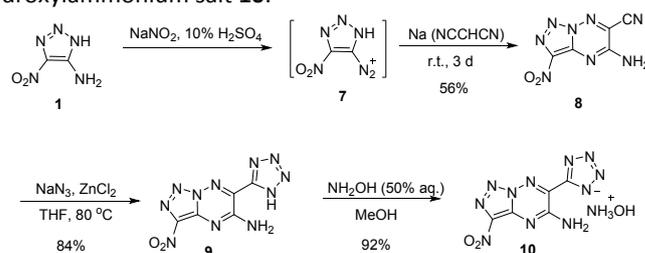
### Synthetic procedures

As the common precursor for the series of new compounds, 4-amino-5-nitro-1,2,3-2H-triazole **1** was prepared from previous methods.<sup>[11]</sup> The target single NH-bridge type compound **5** was obtained efficiently in 3 steps from precursor **1**. First, **1** was treated with cyanogen azide under basic conditions to give tetrazole derivative **2** as a sodium salt (Scheme 1). This can be transformed into neutral compound **3** by reaction with hydrochloric acid. Then compound **5** was obtained in good yield via intermediate **4** through a RORC process at 80 °C. Finally, **5** was reacted with ammonia or aqueous hydroxylamine in methanol which leads to the different energetic salts **6a** or **6b**.



**Scheme 1** Synthesis of N-tetrazole 1,2,3-triazole (**3**) and derivatives from Dimroth rearrangement (**5-6**).

After completing the single NH-bridged compounds **5-6**, the synthesis of fused ring structures was undertaken by diazotization of the common precursor **1** to produce an intermediate diazonium species **7** (Scheme 2). Subsequent addition of sodium malononitrile led to triazolo-triazine bicyclic compound **8** in one pot with good yield after reaction for 3 days at room temperature. Compound **8** was not the expected ordinary cyclic product when X-ray crystal structure was obtained, but surprisingly instead there was a cyclization/rearrangement cascade reaction in this transformation. Furthermore, compound **8** can be further transformed into tetrazole derivative **9** in good yield, which reacted with aqueous hydroxylamine in ethanol to give the hydroxylammonium salt **10**.

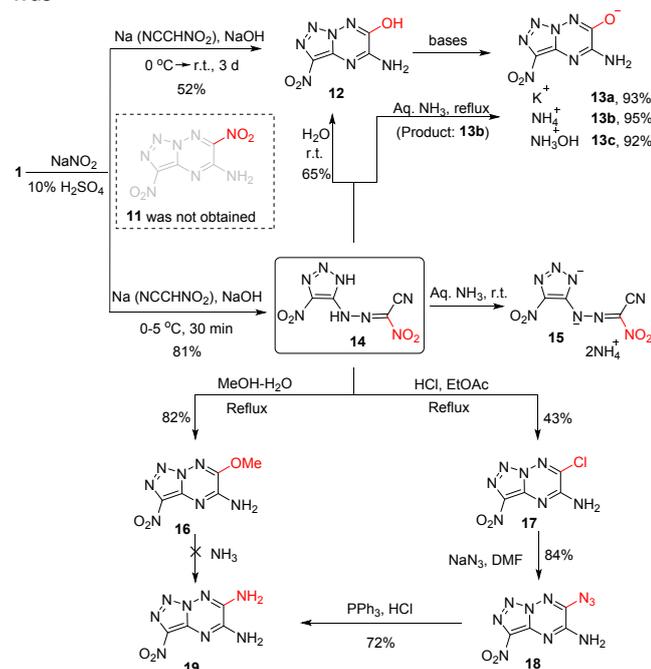


**Scheme 2** 6-Tetrazolo-5-amino-3-nitro [1,2,3]triazolo[1,5-b][1,2,4]triazine (**9**) and ionic derivative (**10**).

Considering that the vicinal C-nitro/C-amino partner in HEDMs can stabilize the molecule and increase density for there is a strong intramolecular hydrogen bond,<sup>[12]</sup> an attempt was made to change malononitrile into nitroacetonitrile in this cascade reaction under standard conditions to obtain compound **11** (Scheme 3). However, only the hydroxylated compound **12** was isolated. This is caused by the nitro group as a good leaving group under standard conditions and the hydroxy group can easily replace it. Compound **12** can be further converted to different energetic salts (**13a-c**) by reaction with corresponding bases. However, when the reaction temperature was maintained at 0 to 5 °C and the reaction time reduced to 30 minutes, a non-cyclized product **14** was isolated. This may result from the strong electron-withdrawing ability of the nitro group which can affect the cyclization process. This result also provides a glimpse into the reaction mechanism. It is noteworthy that **14** could be transformed into different salts (**13b** and **15**) at different reaction temperatures.

Many attempts to obtain **11** from **14** were explored. However, only hydroxy-, methoxy- and chloro-substituted fused-ring compounds (**12**, **16** and **17**) were formed, respectively. In order

to further improve the performance, the azide derivative **18** was

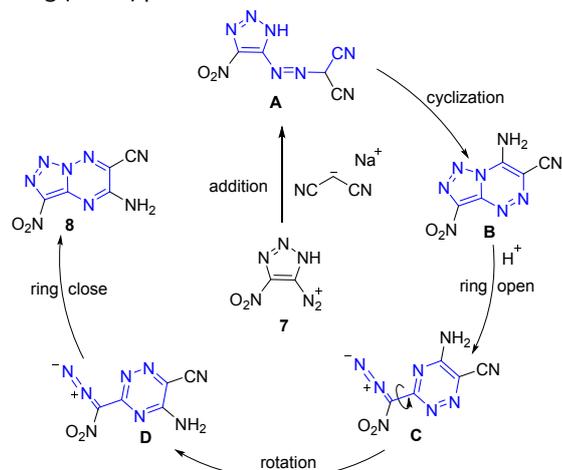


**Scheme 3** Cyclization and rearrangement of 5-amino-4-nitro-1,2,3-triazole (**1**) with nitroacetonitrile.

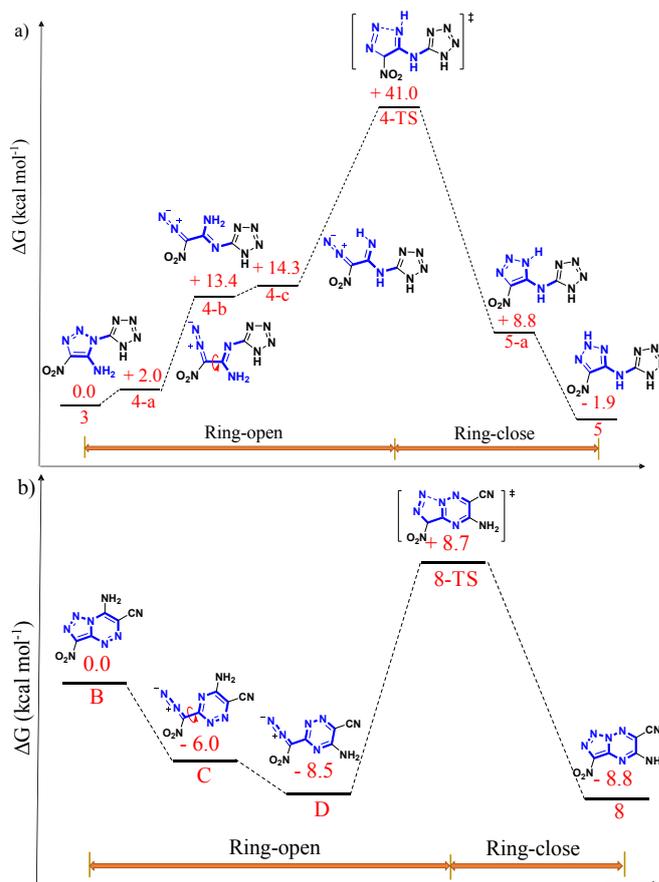
obtained from **17**. It reacted with a reductant to give the vicinal diamino compound **19**, which could not be obtained directly from **16**.

#### Mechanism study

On the basis of the experimental results and previous plausible mechanism for this key cascade reaction is depicted in Scheme 4. The sequence would be initiated through the addition to the diazonium intermediate **7** by malononitrile leading to diazo compound **A**, which cyclizes rapidly to form the bicyclic intermediate **B**. Subsequently, **B** gives the final product **8** via a ring-opening, carbon-carbon bond rotation and ring-closing (RORC) process under acidic conditions.



**Scheme 4** Possible reaction mechanism.



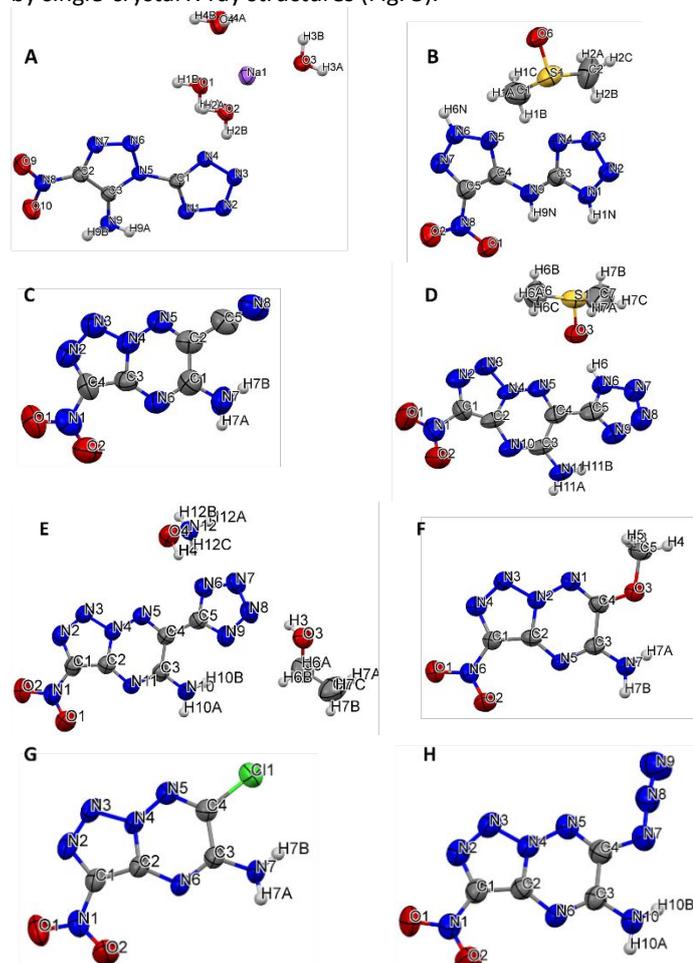
**Fig. 2** Energy profiles at M062X/ 6-31G(d,p) level in kcal mol<sup>-1</sup> of mechanism of Dimroth rearrangement.

Density functional theory (DFT) calculations of two types of Dimroth rearrangement reactions were carried out for the detailed mechanism using the M062X functional (Fig. 2). According to the calculation results (see the Electronic Supplementary Information (ESI) for details), ring-opening of triazole under the heating conditions results to intermediate **4-a** ( $\Delta G = +2.0$  kcal mol<sup>-1</sup>). Then, a rotation of the carbon-carbon bond gives **4-b** with an energy barrier of 11.4 kcal mol<sup>-1</sup>, which undergoes a further tautomerization to form intermediate **4-c**. The sequence ring-closing reaction via the transition state **4-TS** ( $\Delta G = +26.7$  kcal mol<sup>-1</sup>) gives the intermediate **5-a**. Finally the isomerization occurs to afford the final product **5** and this step is exergonic by 10.7 kcal/mol. The rate-limiting reaction energy barrier is about +26.7 kcal mol<sup>-1</sup>, which rationalize this ring-opening/ring-closing process requires a reaction temperature of 80 °C. (Fig. 2a).

For the fused ring intermediate **B**, according to the calculation, the ring-opening and carbon-carbon bond rotation processes can occur spontaneously at room temperature to give the intermediate **C** and **D**, which are exergonic by 6 kcal mol<sup>-1</sup> and 8.5 kcal mol<sup>-1</sup>, respectively. As a result, **B** cannot be isolated in the experiment. The rate-limiting reaction energy barrier is just +17.2 kcal mol<sup>-1</sup> from **D** to **8-TS**, that is why the tandem reaction can be finished at room temperature. The final thermodynamically stable product **8** can be easily obtained via transition state **8-TS** (Fig. 2b).

## Structure

The structures of the new compounds are supported by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and IR spectroscopy, and elemental analysis. Compounds **2**, **5**, **8**, **9**, **10**, **16**, **17** and **18** were further confirmed by single-crystal X-ray structures (Fig. 3).



**Fig. 3** (a) Molecular structure of **2**• $\text{H}_2\text{O}$ . (b) Molecular structure of **5**• $\text{DMSO}$ . (c) Molecular structure of **8**. (d) Molecular structure of **9**• $\text{DMSO}$ . (e) Molecular structure of **10**• $\text{C}_2\text{H}_5\text{OH}$ . (f) Molecular structure of **16**. (g) Molecular structure of **17**. (h) Molecular structure of **18**.

## Physical and Detonation Properties.

The key physicochemical properties were fully investigated to acquire a comprehensive evaluation of the 1,2,3-triazole based energetic compounds (Table 1).

A quick evaluation of detonation properties for the new energetic compounds was carried out using Explo 5 (version 6.02) program based on density, formula and heat of formation. The NH-bridged type, **5** and its hydroxylammonium salt **6b** are featured with outstanding detonation velocity ( $D_v$ , **5**,  $9153 \text{ m s}^{-1}$ ; **6b**,  $9483 \text{ m s}^{-1}$ ) and detonation pressure ( $P$ , **5**,  $33.71 \text{ GPa}$ ; **6b**,  $34.75 \text{ GPa}$ ) which is similar to HMX and superior to RDX. Among fused triazole-triazine compounds, **18** exhibits the highest detonation velocity of  $8912 \text{ m s}^{-1}$  and detonation pressure of  $32.27 \text{ GPa}$ , which is superior to commercial primary explosives DDNP ( $D_v = 6900 \text{ m s}^{-1}$  and  $P = 24.7 \text{ GPa}$ ).

Although NH-bridged and fused types both give rise to great detonation properties, the further sensitivity tests noted

diversified performance in the presence of external mechanic stimuli. While all of the NH-bridged compounds (**5**, **6a** and **6b**) are insensitive to impact or friction [impact sensitivity (IS),  $40 \text{ J}$ ; friction sensitivity (FS),  $360 \text{ N}$ ]. Except for compound **19**, fused type compounds (**9**, **10**, **13c**, **17-18**) exhibit more sensitive

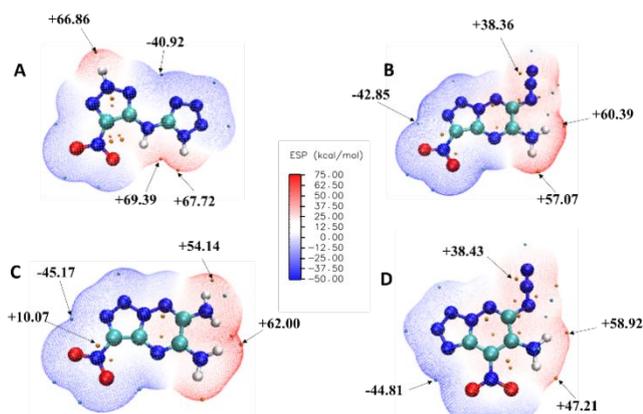
**Table 1** Physicochemical properties of 1,2,3-triazole-based energetic compounds.

Comp.	$T_d^a$ [°C]	$d^b$ [g cm $^{-3}$ ]	$\Delta H_f^c$ [kJ g $^{-1}$ ]	$v_D^d$ [m s $^{-1}$ ]	$P^e$ [GPa]	$IS^f$ [J]	$FS^g$ [N]
<b>3</b>	233	1.75	2.72	8600	28.63	30	360
<b>5</b>	308	1.86	2.80	9153	33.71	40	360
<b>6a</b>	245	1.64	1.52	8696	25.93	40	360
<b>6b</b>	242	1.80	1.74	9482	34.75	40	360
<b>8</b>	196	1.80	3.03	8344	27.38	15	360
<b>9</b>	240	1.77	3.07	8423	27.29	5	360
<b>10</b>	181	1.68	2.85	8357	25.97	4	216
<b>13c</b>	202	1.74	1.11	8442	27.70	20	360
<b>17</b>	218	1.90	1.96	8013	26.58	5	160
<b>18</b>	166	1.83	3.52	8912	32.27	2	10
<b>19</b>	256	1.81	2.12	8623	28.36	30	360
<b>1-1</b> <sup>h</sup>	163	1.82	3.65	8746	31.5	5	120
DDNP <sup>i</sup>	157	1.72	1.53	6900	24.7	1	24.7
RDX <sup>j</sup>	204	1.80	0.32	8795	34.9	7	120
HMX <sup>j</sup>	287	1.90	0.25	9144	39.2	7	120

[a] Decomposition temperature (onset). [b] Density measured by gas pycnometer ( $25^\circ\text{C}$ ). [c] Heat of formation. [d] Detonation velocity (calculated with Explo5 v6.02). [e] Detonation pressure (calculated with Explo5 v6.02). [f] Impact sensitivity. [g] Friction sensitivity. [h] Ref. [8]. [i] Ref. [13]. [j] Ref. [14].

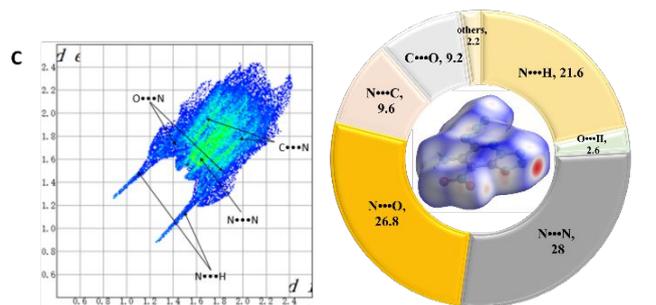
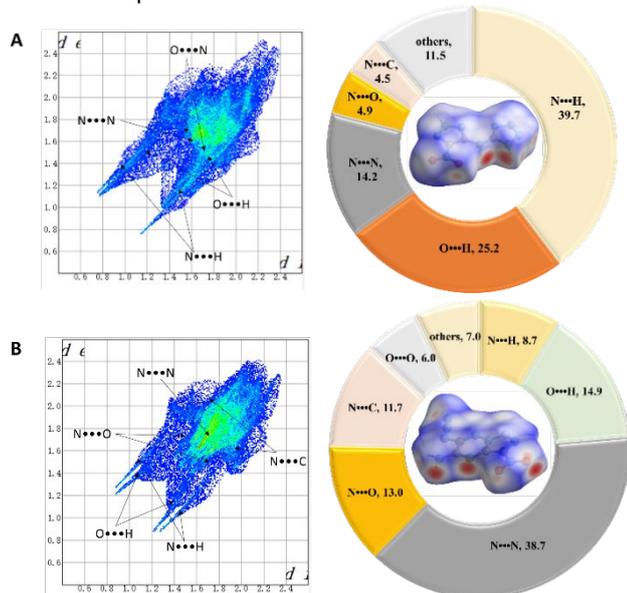
features, especially for the azido-functionalized [1,2,3]triazolo[1,5-b][1,2,4]triazine **18** (IS,  $2\text{J}$ ; FS,  $10 \text{ N}$ ). On the basis of these data, **5** and **6b** have the potential of application as highly insensitive secondary explosives. In contrast, the very sensitive **18** is similar to compound **1-1** may be explored as a candidate for nonmetallic primary explosive.

The calculated electrostatic potential (ESP) is a good tool to explain the changes of molecular stability.<sup>[15]</sup> The ESP plots of compounds **5**, **18**, **19** and **1-1** were evaluated by using Multiwfn (Fig. 4).<sup>[16]</sup> In energetic compounds, the sensitivities are closely related to their surface ESPs. The larger electropositive areas and higher ESP values often result in high sensitivities.<sup>[17]</sup> For NH-bridged compound **5**, the electronegative areas (blue region) and electropositive areas (red region) have a symmetrical arrangement (Fig. 4a), that is much different with fused compounds **18** (Fig. 4b) and **19** (Fig. 4c). The azido group of **18** results in a strong positive potentials over its right portion. Comparing with its isomeride **1-1**, **18** exhibits higher ESP maximum values, especially in amino group areas ( $+57.07$  vs  $+47.21$ ). Therefore, **18** is more sensitive towards impact stimuli than other analogous fused energetics.



**Fig. 4** ESP-mapped molecular vdW surface of **5(a)**, **18(b)**, **19(c)** and **1-1(d)**. The minimum and maximum of ESP are marked as blue and red points, respectively.

To gain additional insight into the relationship between structure and physical properties, the Hirshfeld surface plots and two dimensional fingerprint spectra of **5**, **18** and **1-1** in the crystal structures are investigated (Fig. 5). Red dots indicate intermolecular strong interactions which locate on the side faces of the plate. The relative contribution of the contacts are reflected in regular 2D fingerprint plots. The major interactions are N $\cdots$ H (39.7%), O $\cdots$ H (25.2%), and N $\cdots$ N (14.2%) for **5**. To compounds **18** and **1-1**, N $\cdots$ H (8.7%), O $\cdots$ H (14.9%), N $\cdots$ N (38.7%) and N $\cdots$ O (13%) for **18** and N $\cdots$ H (21.6%), O $\cdots$ H (2.6%), N $\cdots$ N (28%) and N $\cdots$ O (26.8%) for **1-1**. That is to say, the total contact associated with hydrogen bonding interaction is 64.9% (**5**), 23.9% (**18**) and 24.2% (**1-1**), respectively. The striking difference rationalizes outstanding insensitive feature of **5** in comparison to other compounds.



**Fig. 5.** 2D fingerprint plots and Hirshfeld surfaces in crystal stacking for **5(a)**, **18(b)** and **1-1(c)**. The pie graphs for **5**, **18** and **1-1** show the percentage contributions of the individual atomic contacts to the Hirshfeld surface.

## Conclusions

In conclusion, two significant types of energetic materials, including NH-bridged azole and [1,2,3]triazolo[1,5-b][1,2,4]triazine were achieved by virtue of the classic organic named reaction, i.e., Dimroth rearrangement. More importantly, the newly prepared compounds with different structural types exhibit great potential as insensitive high-performance explosives and green primary explosives, respectively. The NH-bridged compound **5** and its ionic derivative **6b** are evaluated with high detonation performance and low sensitivity. As a new energetic fused ring, [1,2,3]triazolo[1,5-b][1,2,4]triazine is more sensitive to external stimuli and the representative compound **18** could be explored as a potential green primary explosive. This work highlights the designable Dimroth rearrangement reaction as a useful toolbox to construct versatile energetic backbones and task-specific HEDMs.

## Experimental section

**Caution!** Although we have encountered no difficulties in preparing these nitrogen-rich compounds in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided!

### General information.

**General.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 300 MHz, 400 MHz or 500 MHz nuclear magnetic resonance spectrometers. Chemical shifts for  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra are reported relative to  $\text{Me}_4\text{Si}$  or deuterated solvents. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Melting and decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q10) at a scan rate of  $5\text{ }^\circ\text{C min}^{-1}$ . Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester. IR spectra were recorded using KBr pellets with a Biorad Model 3000 FTS spectrometer. Densities were determined at room temperature by employing a

Micromeritics AccuPyc 1330 gas pycnometer. The DFT calculations of mechanism were performed with Gaussian 09 package at M062X/6-31G(d,p) level.

**Synthesis.** *Synthesis of 2•H<sub>2</sub>O.* To a solution of **1** (129.0 mg, 1.0 mmol) and sodium carbonate (53.0 mg, 0.5 mmol) in distilled water (5.0 mL) freshly prepared cyanogen azide (~3.0 mmol in 5.0 mL acetonitrile) was added at 0~5 °C. The mixture was slowly warmed up to room temperature and stirred for 24 h. Most of the solvent was removed by blowing air over the liquid surface. Compound **2•H<sub>2</sub>O** was collected by filtration, washed by cold water, and dried in vacuum (grey solid, 147.0 mg, 62% yield).

**2•H<sub>2</sub>O:** T<sub>d</sub>=227 °C; <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO) δ 7.98 (s, 2H); <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO) δ 156.4, 140.6, 136.1; IR (KBr pellet): 3377, 3263, 1655, 1545, 1463, 1428, 1383, 1334, 1302, 1235, 1127, 1072, 1025, 981, 845, 759, 737, 697, 583, 459; Elemental analysis (%) calcd for C<sub>3</sub>H<sub>2</sub>N<sub>9</sub>NaO<sub>2</sub>•H<sub>2</sub>O (237.03) C, 15.20; H, 1.70; N, 53.17; found: C, 14.82; H, 2.23; N, 53.14.

*Synthesis of 3•H<sub>2</sub>O.* Compound **2•H<sub>2</sub>O** (0.5 mmol, 119.0 mg) was added to ice-cold 10% HCl aqueous solution (5.0 mL) and the mixture was stirred at 0~5 °C for 30 min. The precipitate was isolated by filtration and dried in vacuum, giving **3•H<sub>2</sub>O** (yellowish solid, 82% yield). The crude product of **3•H<sub>2</sub>O** contain a small amount of isomers.

**3•H<sub>2</sub>O:** T<sub>d</sub>=233 °C; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN) δ 7.33 (s, 2H); <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO) δ 154.2, 141.9, 135.7; IR (KBr pellet): 3576, 3403, 3336, 3256, 3213, 1663, 1572, 1492, 1458, 1377, 1349, 1319, 1291, 1241, 1209, 1165, 1126, 1068, 1023, 977, 960, 839, 760, 743, 701, 579, 491, 459; Elemental analysis (%) calcd for C<sub>3</sub>H<sub>3</sub>N<sub>9</sub>O<sub>2</sub>•H<sub>2</sub>O (215.05) C, 16.75; H, 2.34; N, 58.60; found: C, 16.56; H, 2.40; N, 58.26.

*Synthesis of 5.* The suspension of **3•H<sub>2</sub>O** (1.0 mmol, 215.0 mg) in distilled water (10.0 mL) was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered and the filter cake was washed by water and cold ethanol, then dried in vacuum to yield **5** (yellow solid, 86% yield).

**5:** T<sub>d</sub>=308 °C; <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ 7.07 (br, 1H); <sup>13</sup>C NMR (75 MHz, *d*<sub>6</sub>-DMSO) δ 153.2, 139.4, 137.9; IR (KBr pellet): 3458, 2794, 1630, 1589, 1533, 1483, 1386, 1351, 1319, 1254, 1180, 1153, 1030, 1008, 975, 867, 816, 764, 592, 467, 408; Elemental analysis (%) calcd for C<sub>3</sub>H<sub>3</sub>N<sub>9</sub>O<sub>2</sub> (197.04) C, 18.28; H, 1.53; N, 63.95; found: C, 17.74; H, 1.95; N, 63.08.

*Synthesis of 6.* Ammonia (7.0 N in methanol, 0.5 mL) or hydroxylamine (50 wt. % in H<sub>2</sub>O, 0.13 mL) was added to a solution of **5** (1.0 mmol, 197.0 mg) in methanol (5 mL). The obtained mixture was stirred for 1 h at room temperature, the solvent was removed by rotary evaporation and the residue was dried in vacuum to give **6a-6b** (**6a**, yellow solid, 95% yield; **6b**, yellow solid, 92% yield).

**6a:** T<sub>d</sub>=245 °C; <sup>1</sup>H NMR (300 MHz, *d*<sub>6</sub>-DMSO) δ 7.31 (s, 8H); <sup>13</sup>C NMR (75 MHz, *d*<sub>6</sub>-DMSO) δ 158.6, 145.2, 139.1; IR (KBr pellet): 3439, 3231, 1719, 1604, 1477, 1421, 1350, 1311, 1289, 1238, 1219, 1153, 1077, 1020, 969, 863, 818, 760, 748, 703; Elemental Analysis (%) calcd for C<sub>3</sub>H<sub>9</sub>N<sub>11</sub>O<sub>2</sub> (231.10): C, 15.59; H, 3.92; N, 66.65; found: C, 15.54; H, 4.06; N, 64.64.

**6b:** T<sub>d</sub>=242 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 9.49 (br, 8H); <sup>13</sup>C NMR (500 MHz, *d*<sub>6</sub>-DMSO) δ 154.2, 141.9, 139.1; IR (KBr pellet):

3121, 3039, 2707, 1611, 1542, 1490, 1449, 1369, 1236, 1156, 1028, 970, 861, 824, 759, 697, 663, 597; Elemental Analysis (%) calcd for C<sub>3</sub>H<sub>9</sub>N<sub>11</sub>O<sub>4</sub> (263.08): C, 13.69; H, 3.45; N, 58.54; found: C, 12.98; H, 3.95; N, 57.7.

*Synthesis of 8.* To an ice-cold suspension of **1** (129.0 mg, 1.0 mmol) in 20.0 mL 10% H<sub>2</sub>SO<sub>4</sub>, sodium nitrite (104.0 mg, 1.5 mmol) in distilled water (5.0 mL) was added dropwise. The mixture was warmed up to ~20 °C until a yellowish transparent solution was formed. A mixture of malononitrile (198.0 mg, 3.0 mmol) in distilled water (2.0 mL) was added dropwise into the as-prepared solution of diazonium salt at 0-5 °C. The final reaction was stirred at room temperature for 3 days. The final mixture was filtered, washed by water and dried in vacuum, giving **8** as a yellowish solid (56% yield).

**8:** T<sub>d</sub>=196 °C; <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO) δ 9.78 (s, 1H), 9.10 (s, 1H); <sup>13</sup>C NMR (125 MHz, *d*<sub>6</sub>-DMSO) δ 153.5, 136.1, 134.7, 122.8, 111.4; IR (KBr pellet): 3561, 3484, 3371, 3117, 1679, 1601, 1506, 1480, 1411, 1339, 1327, 1280, 1232, 1131, 1062, 869, 800, 767, 759, 652, 628, 508, 490, 443; Elemental Analysis (%) calcd for C<sub>5</sub>H<sub>2</sub>N<sub>8</sub>O<sub>2</sub> (206.03): C, 29.14; H, 0.98; N, 54.36; found: C, 28.96; H, 1.00; N, 52.40.

*Synthesis of 9.* To a solution of **8** (1.0 mmol, 206.0 mg) in 5 mL THF was added NaN<sub>3</sub> (1.5 mmol, 98.0 mg) and ZnCl<sub>2</sub> (1.2 mmol, 163.0 mg). The reaction mixture was heated to 80 °C and refluxed overnight. Then the resulting mixture was cooled to room temperature and acidified to pH 1-2 with 20% HCl. The precipitate formed was collected and dried in vacuum, giving **9** as a yellow solid (84% yield).

**9:** T<sub>d</sub>=248 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 12.01 (s, 1H), 9.94 (s, 1H), 9.02 (s, 1H); <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO) δ 153.1, 152.3, 136.7, 134.7, 131.6; IR (KBr pellet): 3318, 3172, 1652, 1608, 1522, 1492, 1419, 1320, 1273, 1137, 1078, 869, 829, 691, 656; Elemental Analysis (%) calcd for C<sub>5</sub>H<sub>3</sub>N<sub>11</sub>O<sub>2</sub> (249.05): C, 24.10; H, 1.21; N, 61.84; found: C, 23.23; H, 0.99; N, 59.51.

*Synthesis of 10.* Hydroxylamine (50 wt. % in H<sub>2</sub>O, 0.13 mL) was added to a solution of **9** (1.0 mmol, 249.0 mg) in ethanol (5.0 mL). The obtained mixture was stirred for 1 h at room temperature, the solvent was removed by rotary evaporation and the residue was dried in vacuum to give **10** (yellowish solid, 92% yield).

**10:** T<sub>d</sub>=192 °C; <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 10.24 (s, 2H), 10.07 (s, 3H), 9.67 (s, 1H); <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO) δ 156.0, 154.0, 136.8, 135.2, 134.2; IR (KBr pellet): 3299, 3156, 1646, 1608, 1500, 1413, 1331, 1267, 1128, 1075, 1002, 867, 819, 740, 707; Elemental Analysis (%) calcd for C<sub>5</sub>H<sub>6</sub>N<sub>12</sub>O<sub>3</sub> (282.07): C, 21.28; H, 2.14; N, 59.57; found: C, 21.41; H, 2.62; N, 58.00.

*Synthesis of 12•H<sub>2</sub>O:* Method A: To an ice-cold suspension of **1** (129.0 mg, 1.0 mmol) in 20.0 mL 10% H<sub>2</sub>SO<sub>4</sub>, sodium nitrite (104.0 mg, 1.5 mmol) in distilled water (5.0 mL) was added dropwise. The mixture was warmed up to ~20 °C until a yellowish transparent solution was formed. A mixture of nitroacetonitrile (258.0 mg, 3.0 mmol) and sodium hydroxide (120.0 mg, 3.0 mmol) in distilled water (2.0 mL) was added dropwise into the as-prepared solution of diazonium salt at 0-5 °C. The final reaction was stirred at room temperature for 3 days to give **12•H<sub>2</sub>O** as a yellow precipitate (112.0 mg, 52% yield from **1**), which could be filtered from the aqueous solution.

Method B: Same procedure as method A except that the mixing temperature of diazonium salt and nitroacetonitrile was kept at  $-10\text{ }^{\circ}\text{C}$  and the reaction was stirred at the same temperature for 1 h. Compound **14**•4H<sub>2</sub>O was filtered, washed by a small amount of ice-cold water (<1.0 mL) and dried in vacuum as a yellow solid (242.0 mg, 81% yield). The cyclization reaction from freshly prepared **14**•4H<sub>2</sub>O to **12**•H<sub>2</sub>O could be carried out in distilled water (2.0 mL) at room temperature for 3 days, giving a yield of 65%.

**12**•H<sub>2</sub>O:  $T_d=118\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $d_6$ -DMSO)  $\delta$  9.05 (s, 1H), 8.29 (s, 1H), 5.67 (s, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $d_6$ -DMSO)  $\delta$  150.9, 150.0, 136.8, 132.4; IR (KBr pellet): 3338, 3305, 3163, 1882, 1650, 1591, 1541, 1410, 1302, 1168, 1069, 877, 808, 788, 778, 756, 723, 702, 673, 624, 601, 526, 488, 460; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>3</sub>N<sub>7</sub>O<sub>3</sub>•H<sub>2</sub>O (215.04): C, 22.33; H, 2.34; N, 45.58; found: C, 22.25; H, 2.38; N, 45.42.

*Synthesis of 13a-13c.* Potassium carbonate (0.5 mmol, 69.0 mg), ammonia (7.0 N in methanol, 0.5 mL), or hydroxylamine (50 wt. % in H<sub>2</sub>O, 0.15 mL) was added to a solution of **12**•H<sub>2</sub>O (1.0 mmol, 215.0 mg) in methanol (5.0 mL). The obtained mixture was stirred for 3 h at  $40\text{ }^{\circ}\text{C}$ , the solvent was removed by rotary evaporation and the residue was dried in vacuum to give **13a-13c** (**13a**, 93% yield; **13b**, 95% yield; **13c**, 92% yield).

**13a**:  $T_d=269\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $d_6$ -DMSO)  $\delta$  8.26 (s, 1H), 7.49 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $d_6$ -DMSO)  $\delta$  155.3, 154.3, 137.0, 129.7; IR (KBr pellet): 3417, 3308, 3168, 3031, 1658, 1612, 1585, 1524, 1463, 1409, 1380, 1345, 1296, 1237, 1154, 1090, 925, 878, 805, 756, 716, 700, 604, 485, 466, 404; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>2</sub>KN<sub>7</sub>O<sub>3</sub> (234.99): C, 20.43; H, 0.86; N, 41.69; found: C, 19.91; H, 1.05; N, 39.98.

**13b**:  $T_d=193\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $d_6$ -DMSO)  $\delta$  8.30 (s, 1H), 7.52 (s, 1H), 7.17 (br, 4H);  $^{13}\text{C NMR}$  (100 MHz,  $d_6$ -DMSO)  $\delta$  155.3, 154.3, 137.0, 129.8; IR (KBr pellet): 3423, 3082, 3031, 1653, 1594, 1383, 1346, 1296, 1239, 1156, 1092, 929, 877, 804, 773, 757, 721, 700, 670, 607, 487, 469, 404; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>6</sub>N<sub>8</sub>O<sub>4</sub> (214.06): C, 22.44; H, 2.82; N, 52.33; found: C, 22.12; H, 2.94; N, 51.02.

**13c**:  $T_d=202\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (400 MHz,  $d_6$ -DMSO)  $\delta$  8.91 (s, 4H), 8.34 (s, 1H), 7.55 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $d_6$ -DMSO)  $\delta$  155.3, 154.3, 137.0, 129.8; IR (KBr pellet): 3422, 1654, 1588, 1522, 1445, 1406, 1383, 1347, 1297, 1239, 1156, 1092, 929, 878, 804, 757, 700, 607, 469; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>6</sub>N<sub>8</sub>O<sub>3</sub> (230.05): C, 20.88; H, 2.63; N, 48.69; found: C, 20.43; H, 2.51; N, 48.42.

*Synthesis of 15.* Compound **14**•4H<sub>2</sub>O can be stabilized by ionizing with aqueous ammonia at room temperature and boiling temperature, resulting **15** or **13b**, respectively.

**14**•4H<sub>2</sub>O:  $T_d=117\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $d_6$ -DMSO)  $\delta$  8.07 (br, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $d_6$ -DMSO)  $\delta$  146.6, 142.3, 124.1, 110.9; IR (KBr pellet): 3430, 3251, 2931, 2862, 1565, 1458, 1397, 1376, 1309, 1248, 1210, 1136, 977, 906, 846, 796, 763, 749, 737, 679, 619, 523, 494, 413; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>2</sub>N<sub>8</sub>O<sub>4</sub>•4H<sub>2</sub>O (298.06): C, 16.11; H, 3.38; N, 37.58; found: C, 15.71; H, 2.61; N, 37.01.

**15**:  $T_d=136\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO)  $\delta$  7.27 (br, 8H);  $^{13}\text{C NMR}$  (75 MHz,  $d_6$ -DMSO)  $\delta$  151.9, 145.9, 122.1, 112.7;

Elemental analysis (%) calcd for C<sub>4</sub>H<sub>8</sub>N<sub>10</sub>O<sub>4</sub> (260.17) C, 18.47; H, 3.10; N, 53.84; found: C, 18.44; H, 3.313; N, 52.93.

*Synthesis of 16.* A solution of **14**•4H<sub>2</sub>O (1.0 mmol, 312.0 mg) in MeOH (5.0 mL) and H<sub>2</sub>O (5.0 mL) was heated up to reflux for 1 h. The work-out procedure was same as that of **17**, resulting to **16** (white solid, 82% yield).

**16**:  $T_d=202\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO)  $\delta$  9.26 (s, 1H), 8.54 (s, 1H), 4.13 (s, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $d_6$ -DMSO)  $\delta$  149.8, 149.3, 136.7, 132.8, 56.2; IR (KBr pellet): 3416, 3315, 3245, 3201, 1632, 1597, 1533, 1455, 1448, 1434, 1399, 1357, 1329, 1300, 1253, 1151, 1085, 1061, 968, 903, 871, 799, 759, 733, 704, 671, 651, 611, 599, 484, 413; Elemental Analysis (%) calcd for C<sub>5</sub>H<sub>5</sub>N<sub>7</sub>O<sub>3</sub> (211.05): C, 28.44; H, 2.39; N, 46.44; found: C, 28.10; H, 2.64; N, 45.74.

*Synthesis of 17.* To a saturated hydrochloride solution in ethyl acetate (10.0 mL) **14**•4H<sub>2</sub>O (1.0 mmol, 312.0 mg) was added and the reaction was kept reflux for 30 min. The solvent was removed by rotary evaporation and 2.0 ml of ice-cold water was added. The suspension was treated with ultrasound at room temperature for 5 min. Then the precipitate was collected by filtration and dried in vacuum to give **17** (White solid, 57% yield). Using concentrated hydrochloric acid instead of HCl-EtOAc resulted in a yield of 43%.

**17**:  $T_d=218\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (500 MHz,  $d_6$ -DMSO)  $\delta$  9.65 (s, 1H), 8.78 (s, 1H);  $^{13}\text{C NMR}$  (125 MHz,  $d_6$ -DMSO)  $\delta$  152.8, 140.2, 136.1, 134.3; IR (KBr pellet): 3313, 3221, 3158, 1597, 1650, 1561, 1520, 1489, 1409, 1346, 1311, 1309, 1276, 1193, 1117, 869, 843, 795, 762, 726, 698; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>2</sub>ClN<sub>7</sub>O<sub>2</sub> (215.00): C, 22.29; H, 0.94; N, 45.49; found: C, 21.59; H, 0.98; N, 44.31. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calculated for C<sub>4</sub>H<sub>3</sub>ClN<sub>7</sub>O<sub>2</sub><sup>+</sup>: 216.0031, found: 216.0030.

*Synthesis of 18.* To a solution of **17** (1.0 mmol, 216.0 mg) in 2.0 mL DMF was added NaN<sub>3</sub> (1.5 mmol, 98.0 mg). The reaction mixture was stirred at room temperature for 1 h and then the mixture was poured into water (10 mL). The precipitate formed was collected, washed with water, and dried in vacuum to yield **18** (white solid, 84% yield).

**18**:  $T_d=166\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO)  $\delta$  9.36 (s, 1H), 8.42 (s, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $d_6$ -DMSO)  $\delta$  149.8, 142.1, 136.6, 133.7; IR (KBr pellet): 3357, 3310, 3222, 3189, 2713, 2187, 2157, 1655, 1567, 1593, 1537, 1515, 1407, 1352, 1326, 1301, 1159, 1123, 1069, 929, 872, 803, 755, 701, 646, 530, 446; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>2</sub>N<sub>10</sub>O<sub>2</sub> (222.04): C, 21.63; H, 0.91; N, 63.06; found: C, 21.81; H, 1.11; N, 63.11. HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calculated for C<sub>4</sub>H<sub>3</sub>N<sub>10</sub>O<sub>2</sub><sup>+</sup>: 223.0435, found: 223.0434.

*Synthesis of 19.* To a solution of **18** (1.0 mmol, 222.0 mg) in acetone (3.0 mL) triphenylphosphine (1.2 mmol, 315.0 mg) was added at  $0-5\text{ }^{\circ}\text{C}$ . The mixture was stirred for 2 h at room temperature and the solvent was removed by rotary evaporation. Concentrated hydrochloric acid (1.0 mL) and ethanol (3.0 mL) was added and then the mixture was stirred at  $50\text{ }^{\circ}\text{C}$  for 1 h. After the reaction was cooled down, the precipitate was filtered, washed by water and ethanol to give **19** (white solid, 72% yield).

**19**:  $T_d=256\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $d_6$ -DMSO)  $\delta$  9.13 (br, 1H), 7.93 (br, 1H), 7.51 (s, 2H);  $^{13}\text{C NMR}$  (125 MHz,  $d_6$ -DMSO)  $\delta$  148.9, 144.1, 136.9, 130.7; IR (KBr pellet): 3421, 3329, 3233, 3186,

1667, 1644, 1596, 1541, 1515, 1419, 1348, 1321, 1305, 1259, 1172, 1112, 1078, 902, 876, 806, 758, 709, 652, 513; Elemental Analysis (%) calcd for C<sub>4</sub>H<sub>4</sub>N<sub>8</sub>O<sub>2</sub> (196.05): C, 24.50; H, 2.06; N, 57.13; found: C, 23.96; H, 2.36; N, 56.51.

### Conflicts of interest

There are no conflicts to declare.

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