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Strategy for Extending the Nitrogen Chain: the Bis(1,2,3-triazole) Formation Reaction from Tosylhydrazones and N-Amino Azole

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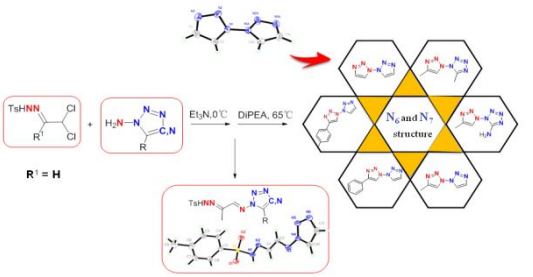
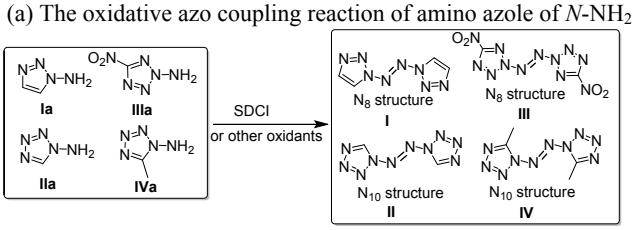


ABSTRACT: A facile and versatile synthesis strategy for the bis(1,2,3-triazole) formation reaction was developed from tosylhydrazones and *N*-amino (*N*-NH_2) azole instead of *C*-amino amine derivatives. The novel energetic compounds containing the bicycle catenated six-nitrogen chain (N_6) and the first example of N_7 neutral compounds were synthesized in a moderate or high yield. The possible mechanism of bis(1,2,3-triazole) formation reaction based on amino azole of *N*-NH_2 was verified by the X-ray crystal structure of key intermediates. In addition, four energetic compounds **4aa, 4ba, 4ac** and **4ad** containing N_6 and N_7 structure possess acceptable decomposition temperature(150.1-201.6 °C) and moderate calculated detonation performances(6850-7727 m/s). Among them, **4aa** (N_6 structure) and **4ad** (N_7 structure) could be used as melt-cast explosive candidate and the gas generation agent candidate, respectively. This type of nitrogen-nitrogen bonding formation opens a new method for discovery of novel high-nitrogen energetic compounds containing catenated multiple nitrogen atoms especially odd number nitrogen compounds.

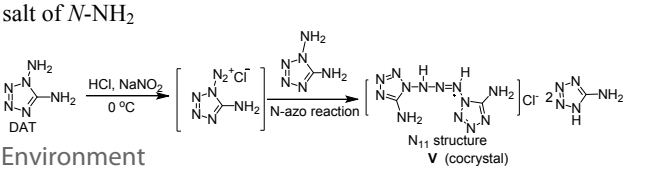
INTRODUCTION

High nitrogen compounds that contain long catenated nitrogen chains (N_n) have attracted considerable attention in the research field of propellants, explosives, and gas generant due to their high heat of formation and clean decomposed product of nitrogen gas.[1] However, a serious lack of nitrogen - nitrogen bond forming reactions has hindered the development of energetic compounds containing catenated N-N bonds. Although the oxidative azo coupling of the *C*-NH_2 functionality have been fully investigated and well documented, that of *N*-NH_2 instead of *C*-NH_2 functionality is relatively unexplored. In 2010, the oxidative azo coupling of amino azole of *N*-NH_2 was developed to create a rather long chain of catenated tetrazene structure (N-N=N-N linkage) by the group of Pang S. P.[2] Followed this effective method was applied sequentially in synthesizing of 2,2'-azobis(5-nitrotetrazole) (**III**)[3] with catenated N_8 structure, 1,1'-azobistetrazole (**II**)[4] and 1,1'-azobis(5-methyltetrazole) (**IV**)[5] with N_{10} structure(Scheme 1, a). Unfortunately, these compounds are extremely sensitive to mechanical stimulation and physical unstable in solution, which limits their application. And this method is confined to the synthesis of catenated even nitrogen chains only. In 2013, our group achieved the first example of azo coupling reaction between the diazonium salt of *N*-NH_2 and amine derivative to form the longest nitrogen chain (N_{11}) containing triazene structure (N=N-NH linkage) (Scheme 1, b).[6] Unfortunately, this method has not been exploited further due to strict operation condition and instability of triazene structure. Although high nitrogen compounds containing longer catenated nitrogen own higher heat of formation, compounds with large number of directly linked nitrogen atoms are sensitive,thermally unstable and physically unstable. Based on combination properties of the synthetic N_n compounds, the compound with catenated nitrogen atom (n = 6-8) was supposed to be the ideal energetic materials candidate.[7] The compound containing the continuous odd number nitrogen chain (n≥6) was scarcely reported due to limitation of existing nitrogen-nitrogen formation reaction.

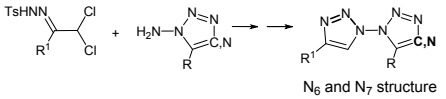
(a) The oxidative azo coupling reaction of amino azole of *N*-NH_2



(b) *N*-azo reaction between amine derivative and its diazonium salt of *N*-NH_2



(c) This work: the bistriazole formation reaction from tosylhydrazones and amino azole of *N*-NH_2。



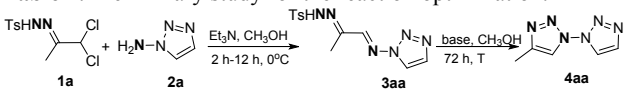
Scheme 1 Various routes to prepare compounds that contain long catenated nitrogen chains.

In 1986, Sakai et al. have first described the facile synthesis of triazoles from *α*,*α*-dichlorotosylhydrazones and primary amines of *C*-NH_2 instead of energetic azides.[8] Despite of the evident potential of this reaction, it has less investigated and infrequent applications.[9] If the amino group is connected to the nitrogen atom in the azole rings (*N*-NH_2), such reaction could result in a rather long chain of catenated nitrogen. And yet, this extended nitrogen chain reaction had rarely reported and exploited due to low reaction activity of *N*-amino azoles.[10] Herein, we employed the bis(1,2,3-triazole) formation reaction from tosylhydrazones and *N*-amino (*N*-NH_2) azole instead of the primary amine(*C*-NH_2) based Sakai reaction to synthesize some novel nitrogen chains compounds with N_6 structure or an unreported N_7 structure (Scheme 1, c). This approach could also be applied to extend the nitrogen chain for high-nitrogen systems from both academic and practical considerations.

RESULTS AND DISCUSSION

In a preliminary set of experiments, we studied the reaction of *α*,*α*-dichlorotosylhydrazones(**1a**) with the amino azole of *N*-NH_2, 1-amino-1,2,3-triazole (**2a**), in the presence of alkaline reagents by using one-step method following the triazole formation reaction based on primary amines (*C*-NH_2) reported.[9a] However, the isolation of 4-methyl-1,1'-bi(1,2,3-triazole) (**4aa**) was very difficult since the yield is very low with many unknown byproducts. To our delight, a modification of two-step method led to the formation of **4aa**,

Table 1: Preliminary study for the reaction optimization.[a]



Entry	Base	Substrate: base	T/°C	Yield %
1	DiPEA[b]	1:2.4	rt	80
2	t-BuOK	1:2.4	rt	75
3	Et_3N	1:2.4	rt	70
4	DABCO[c]	1:2.4	rt	65
5	DBU[d]	1:2.4	rt	32
6	Et_2NH	1:2.4	rt	53
7	L-proline	1:2.4	rt	-
8	K_2CO_3	1:2.4	rt	-
9	CH_3ONa	1:2.4	rt	59
10	CH_3CH_2ONa	1:2.4	rt	54
11	DiPEA	1:2.4	35	84
12	DiPEA	1:2.4	50	85
13	DiPEA	1:2.4	65	89
14	DiPEA	1:3.6	65	95

[a] Reaction conditions: **3aa** (0.5 mmol), base (1.2 mmol or 1.8 mmol)/ CH_3OH (2 mL) were stirred in another 4 mL of CH_3OH for 72 h. [b] DiPEA = N,N-diisopropylethylamine. [c] DABCO = 1,4-diazabicyclo[2.2.2]octane. [d] DBU = 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine.

which was easily separated by column chromatography in the improved synthetic pathway. A 91% yield of intermediate **3aa** could be precipitated from the reaction mixture of **1a** and **2a** in presence of Et_3N. So we turned our attention to investigate the second step reaction of the formation of bis(1,2,3-triazole) **4aa** by utilizing various alkali in methanol at room temperature. The addition of base *L*-proline and K_2CO_3 afford no product (Table1, entries 7-8). When *t*-BuOK, Et_3N, DABCO, DBU, Et_2NH, CH_3ONa, CH_3CH_2ONa as bases were used, the bis(1,2,3-triazole) **4aa** were obtained in moderate yield in the range of 32-75% (Table 1, entries 2-6, 9-10). In contrast, DiPEA presents the highest activity in methanol with 80% yield of **4aa** (Table 1, entry 1), which indicating that DiPEA was the most favorable base among those examined for further studies. The reaction condition was further optimized for **3aa** as a model substrate to find the appropriate reaction temperature of 65 °C, methanol as solvent and 1: 2.4 of molar ratios of **3aa** to DiPEA, which can afford **4aa** in high yield of 95%(Table 1, entry 14).

This result encouraged us to investigate further the bis(1,2,3-triazole) formation reaction of tosylhydrazones and amino azole of *N*-NH_2 to examine the scope on the basis of the optimal conditions established. However, *α*,*α*-dichlorotosylhydrazone **1c** as key start material could not be obtained from 2,2-dichloro-1-phenylethanone and tosylhydrazine. Instead, the *N*-substituted triazole **1c**' was isolated according to the Sakai and Westermann's reported.[8, 9a] When we attempted to synthesize the **1c** by the addition the catalyst $TiCl_4$ following Lam's method, the isolation of **1c** with column chromatography could not be accomplished due to low yield and many byproducts.[9b] To our delight, the modification reaction condition such as catalyst loading, substrate ratio could afford **1c** in a improved yield of 66%, which is precipitated and easily separated from the reaction mixture. This method also works for other *α*,*α*-dichlorotosylhydrazone substrate, which makes the *N*-amino azoles-based bis(1,2,3-triazole) formation reaction possible. As can be seen from Table 2, the two-step reaction of various *α*,*α*-dichlorotosylhydrazone **1** and *N*-amino azoles **2a** proceeds smoothly to afford intermediate **3** and product **4** in yield of 84-92% and 75-95%, respectively. The benzene rings with electron-withdrawing groups of F, Cl, Br and electron-donating -CH_3 groups showed good reactivity in a 77-90% yield (Table2, entries 5-7). When 4-amino-1,2,4-triazole (**2b**) react with *α*,*α*-dichlorotosylhydrazone **1a** and **1c**, the two-step reaction proceeds smoothly and forms trizoles **4ab** and **4cb** in good yield (Table2, entries 8-9). It is worth

mentioning that **4ac** and **4ad** with N_7 structure was successfully accomplished. This is the first synthesize example of N_7 neutral compound (Table2, entries 10-11).

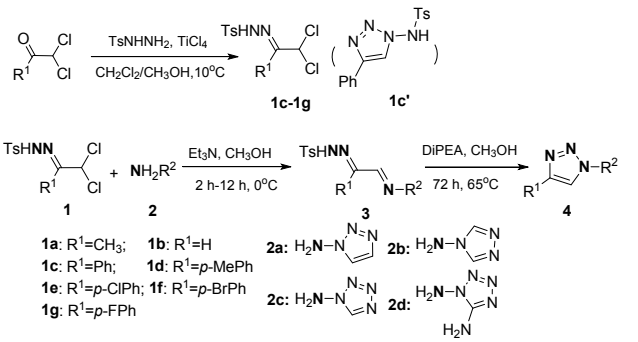
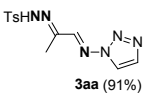
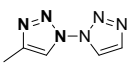
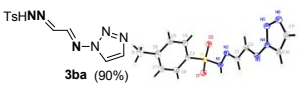
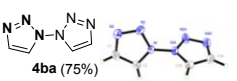
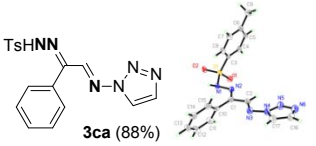
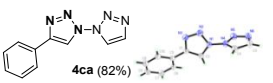
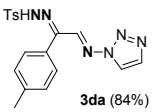
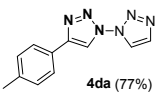
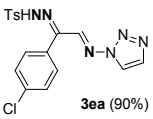
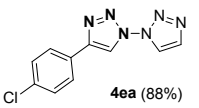
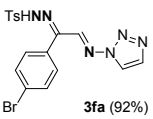
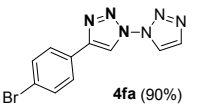
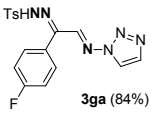
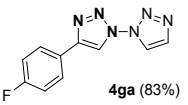
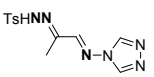
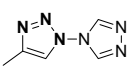
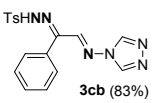
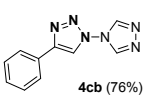
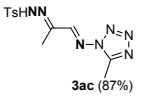
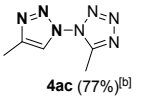
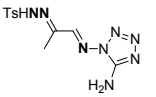
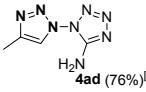
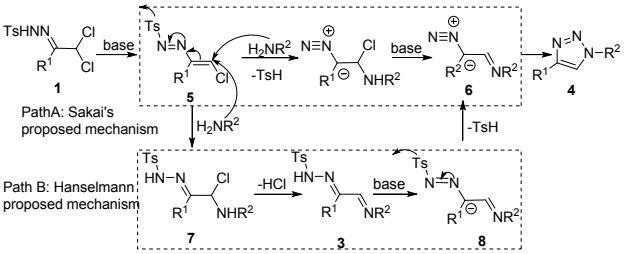


Table 2*:* Scope of substrates.[a]

Entry	Intermediate **3**	Product **4**
1	 **3aa** (91%)	 **4aa** (95%)
2	 **3ba** (90%)	 **4ba** (75%)
3	 **3ca** (88%)	 **4ca** (82%)
4	 **3da** (84%)	 **4da** (77%)
5	 **3ea** (90%)	 **4ea** (88%)
6	 **3fa** (92%)	 **4fa** (90%)
7	 **3ga** (84%)	 **4ga** (83%)
8	 **3ab** (83%)	 **4ab** (88%)
9	 **3cb** (83%)	 **4cb** (76%)
10	 **3ac** (87%)	 **4ac** (77%)[b]
11	 **3ad** (85%)	 **4ad** (76%)[b]

[a] Unless otherwise mentioned, reaction conditions: **3aa** (0.5 mmol), DiPEA (1.8 mmol)/CH_3OH (2 mL) were stirred in another 4 mL of CH_3OH at 65 °C for 72 h. [b] room temperature.

Although primary amines (*C*-NH_2) based the triazole formation reaction has been investigated, the mechanism of the reaction remains ambiguous due to lack of structure proof for key intermediate. Sakai suggested a general mechanism for the formation of 1,2,3-triazole (Scheme 2, Path A).[8] The *α*,*α*-dichlorotosylhydrazone was deprotonated to vinyldiazine **5**. Subsequent amine addition and *p*-toluenesulfinic acid elimination in **5** formed iminoethane-diazonium **6**, which was then intramolecular cyclized to triazole after deprotonation. Hanselmann et al. proposed another possible mechanism (Scheme 2, Path B), wherein amine is added to vinyldiazine **5**, but the tosyl group is retained without elimination.[9c] In order to verify the mechanism for the *N*-amino azoles-based bistriazole formation reaction, the key intermediate **3ba** (Table 2, entry 2) and **3ca** (Table 2, entry 3) were further confirmed by single-crystal X-ray structure analyses. Based on the structure of intermediate **3**, the bistriazole formation reaction *α*,*α*-dichlorotosylhydrazones and amino azole of *N*-NH_2 were verified to follow the Hanselmann's proposed mechanism.



Scheme 2. Two possible mechanisms for the triazole formation reaction.

Table 3: Comparison of detonation properties of some energetic compounds with **4aa**, **4ba**, **4ac** and **4ad**.

Comp-ounds	**4aa** (N_6)	**4ba** (N_6)	**4ac** (N_7)	**4ad** (N_7)	**I** (N_8)[h]	**IV** (N_{10})[i]	**V** (N_{11})[i]	TNT[k]
T_m[a] (°C)	74.1	132	76.6	75.2	-	-	143	81
T_d[b] (°C)	201.6	185.3	168.5	150.1	193.8	127.2	230.5	295
ρ[c] (g/cm³)	1.414	1.515	1.466	1.517	1.62	1.482	1.563	1.65
V[d] (L/kg)	682	705	713	753	-	-	-	-
D[e] (m/s)	6850	7208	7342	7724	7764	7320	7220	6881
P[f] (GPa)	15.17	17.54	17.73	20.31	25.24	20.99	21.17	19.5
$\Delta_f H_m$[j] (kJ/mol)	628.32	664.92	699.62	747.17	962.27	986.05	1499.01	-295
FS(J)	18	17	13	14	4	-	10	15
IS(N)	260	290	270	250	-	-	160	353

ESD[l](J)	0.52	0.43	0.33	0.38	-	-	0.32	-
Dmix[m] (m/s)	7515	7750	7725	7878	-	-	-	7585
Pmix[m] (GPa)	22.9	25.02	24.51	25.52	-	-	-	26.47

[a]Melting point. [b] Temperature of decomposition. [c] Density measured by gas pycnometer at 25 °C, except **4ba**, the density from single crystal X-ray diffraction. [d] Gas volume after detonation. [e] Detonation velocity. [f] Detonation pressure. [g] Calculated molar enthalpy of formation. . [h] Ref. [2]. [i] Ref. [5]. [j] Ref. [6]. [k] TNT = trinitrotoluene.Ref. [14].[l]Electrostatic discharge sensitivity.[m] Compounds(50.4%) mixed with AP(39.1%) and fluororubber($(C_2F_2H_2)_{0.8}(C_3F_6)_{0.2}$)(10.5%).

The detonation parameters of compounds containing long catenated nitrogen atom chains were predicted based on the measured density and the heat of formation using the EXPLO5 program (version 6.01).[11] The results were listed in Table 3. The heat of formation (HOF) plays an important role in evaluating the performance of energetic materials. Compounds **4aa** and **4ba** (N_6 structure) exhibits positive heats of formation of 628.32 and 664.92 kJ/mol(Table 3, entries 1-2), respectively. In contrast, compounds **4ac** and **4ad** (N_7 structure) possess higher heats of formation of 699.62 kJ/mol and 747.17 kJ/mol(Table 3, entries 3-4). The calculated volumes of detonation gases at standard temperature pressure are between 682 kg/L and 753 kg/L. compound **4ad** has the highest volumes of detonation gases of 753 kg/L, which could be the potential gas generation agent candidate.

The thermal decomposition of **4aa** and **4ba** with N_6 structure occurs at 201.6 °C and 185.3 °C, which is higher than that of **4ac** (168.5 °C) and **4ad** (150.1°C) with N_7 structure, respectively (see Supplementary Figure S47-S48). It is worth pointing out that **4aa** decomposes at 201.6 °C, which is 127.5 °C higher than its melting point (74.1 °C) (Table 3, entry 1), thus indicating that it can be candidate as melt-cast explosive. As we can see from the Table 3, the larger the number of directly linked nitrogen atoms, the more HOF and the less thermal stability are, which is attributed to a large number of N=N, N-N bonds within their structure. Owing to the high heat of formation, the detonation velocity of compound **4ba** (7208 m/s), **4ac** (7342 m/s) and **4ad** (7724 m/s) is superior to that of TNT (6881 m/s). The detonation properties of the mixture of **4aa**, **4ba**, **4ac** , **4ad** , TNT(50.4%for each one) , ammonium perchlorate(39.1%) and fluororubber($(C_2F_2H_2)_{0.8}(C_3F_6)_{0.2}$) (10.5%)were caclulatedand.The detonation velocity of a mixture of **4ad** with 39.4% ammonium perchlorate was increased to 7878m/s, which is higher than that of TNT mixed with the same amount of ammonium perchlorate (7585m/s),demonstrating that **4ad** is very competitive.

CONCLUSIONS

In conclusion, novel nitrogen chain compounds, which has an N_6 structure and an unreported N_7 structure, were designed and synthesized through a facile two-step reaction from tosylhydrazones and amino azole of *N*-NH_2.Importantly, X-ray crystal structure for intermediate revealed a convincing evidence for the mechanism of amino azole-based the bistriazole formation reaction. This N-N bonding-forming reaction provides a new efficient method for the discovery of novel high-nitrogen energetic compounds.

EXPERIMENT SECTION

Caution: Although we have not encountered any difficulties in preparing these new energetic materials, manipulations must be carried out by using standard safety precautions. Leather coat, ear protection, latex gloves, and face shield are strongly recommended for the experimental operation. All compounds should be handled with extreme care.

General Information

All commerical available reagents and solvents (analytical grade) were used as supplied without further purification unless otherwise stated. For chromatography, 100-200 and 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance III 300MHz Digital NMR Spectrometer and a Bruker Avance 75 instrument. NMR acquisitions were performed at 295 K unless otherwise noted. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 High resolution mass spectra were obtained using an Agilent 6210 Series TOFLC-MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. The decomposition point was recorded on a DSC823^e at a heating rate of 5 °C·min^{-1} in closed Al containers with a nitrogen flow of 30 mL·min^{-1}.

Data for **3ba**, **4ba**, **3ca** and **4ca** were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low temperature device was used to keep the crystals at a constant 173 K during data collection. Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0]. Data Reduction was performed using *SAINT* [v7.68A] and *XPREP* [v2008/2] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1]. The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

α, α-dichlorotosylhydrazones **1a**[12] and **1b**[13] were synthesized according to the literatures procedures.

N'-(2,2-dichloro-1-methylethylidene)-4-methylbenzenesulfonohydrazide (1a). White solid (6.10 g); Yield: 90%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm:9.6 (s,1H), 7.8 (d, *J*=8.22 Hz, 2H), 7.4 (d, *J*=8.25 Hz,2H),

6.5 (s, 1H) . ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm:151.3, 144.9, 137.0, 130.3, 128.6,73.9, 21.0,10.7.

N'-(2,2-dichloroethylidene)-4-methylbenzenesulfonohydrazide (1b). White solid (5.64 g); Yield: 83%.^{1}H NMR (300 MHz, Acetone-d_6) δ ppm:8.34 (s, 1H), 7.81 (d, *J*=8.19Hz, 2H), 7.36 (d, *J*=8.07, 2H), 7.21 (d, *J*=7.47Hz, 1H), 2.40 (d, *J*=7.44Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 144.9, 143.4, 134.4, 129.9, 127.8, 77.3, 67.3.

General procedure for preparation of α,α-dichlorotosylhydrazones (1c-1g):

$TsNHNH_2$ (2.79 g, 15.0 mmol) was swollen in a mixture containing 20 mL CH_3OH and 1.5 mL of $TiCl_4$ (1 mol/L) in CH_2Cl_2 for 1 h at room temperature. The intermeidiate α,α-dichloroacetophenones (23.0 mmol) was added and the reaction mixture was then stirred at 10 °C for 12 h. The precipitate was collected by filtration and washed consecutively with CH_3OH, and dried overnight in a vacuum oven at 40 °C. The yield of the product was around 56-67% in general.

N'-(2,2-dichloro-1-phenylethylidene)-4 methylbenzenesulfonohydrazide (1c). White solid (3.54 g); Yield: 66%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm: 9.67 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.53 (m, 3H), 7.40 (m, 4H), 6.85 (s, 1H), 2.44 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 151.1, 145.0, 137.0, 131.3, 130.4, 130.4, 129.8, 129.1, 128.7, 72.9, 21.5. Anal. Calcd for $C_{16}H_{16}N_2O_2SCl_2$: C, 51.76; H, 4.34; N, 7.55; S, 8.64.. Found: C, 51.77; H, 4.33; N, 7.54; S, 8.66..

N'-(2,2-dichloro-1-(p-tolyl)ethylidene)-4-methylbenzenesulfonohydrazide (1d). White solid (3.11 g); Yield: 56%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm: 9.62 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 1H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 151.2, 145.0, 141.4, 137.4, 130.4, 130.4, 130.0, 128.7, 126.2, 73.1, 21.5, 21.4. Anal. Calcd for $C_{17}H_{18}N_2O_2SCl_2$: C, 52.99; H, 4.71; N, 7.27; S, 8.32.. Found: C, 52.97; H, 4.74; N, 7.26; S, 8.33..

N'-(2,2-dichloro-1-(4-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1e). White solid (3.82 g); Yield: 65%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm: 9.85 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H) , 7.57 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 2.4 Hz, 2H), 7.39 (d, *J* = 2.7 Hz, 2H), 6.86 (s, 1H), 2.43 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 149.7, 145.0, 137.0, 132.1, 130.4, 130.1, 129.3, 128.6, 127.9, 72.7, 21.5. Anal. Calcd for $C_{16}H_{15}N_2O_2SCl_3$: C, 47.37; H, 3.73; N, 6.90; S, 7.90.. Found: C, 47.35; H, 4.75; N, 7.28; S, 8.31..

N'-(1-(4-bromophenyl)-2,2-dichloroethylidene)-4-methylbenzenesulfonohydrazide (1f). White solid (4.35 g); Yield: 67%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm: 9.86 (s, 3H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H) 7.34 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 2.42 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 206.4, 149.8, 145.1, 136.9, 133.0, 132.2, 130.4, 128.6, 128.3, 125.3, 72.7, 21.5. Anal. Calcd for $C_{16}H_{15}N_2O_2SCl_2Br$: C, 42.69; H, 3.36; N, 6.22; S, 7.12.. Found: C, 42.64; H, 3.38; N, 6.20; S, 7.13.

N'-(2,2-dichloro-1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1g). White solid (3.46 g); Yield: 62%. ^{1}H NMR (300 MHz, Acetone-d_6) δ ppm: 9.79 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.44 (m, 4H), 7.28 (t, 2H), 6.83 (s, 1H), 2.41 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, Acetone-d_6) δ ppm: 166.2, 145.0, 145.0, 137.0, 132.8, 130.4, 128.6, 125.3, 117.0, 116.7, 72.9, 21.5. Anal. Calcd for $C_{16}H_{15}N_2O_2SCl_2F$: C, 49.37; H, 3.88; N, 7.20; S, 8.24.. Found: C, 49.35; H, 3.90; N, 7.21; S, 8.23.

N-amino azoles **2a**,[4] **2b**,[5] **2c**[6] and **2d**[7] were synthesized according to the literatures procedures.

A solution of Et_3N (0.22 g, 2.2 mmol) in 10 mL methanol was added to a suspension of amino azoles (**2**, 2.0 mmol) and α,α-dichlorotosylhydrazone (**1**, 2.0 mmol), the reaction was stirred for 2-12 h at 0 °C. The precipitate was collected by filtration and washed consecutively with CH_3OH, then filtered and dried at 40 °C in vacuum. The yield of compounds **3** was around 83%-92% in general.

N'-(1-((1H-1,2,3-triazol-1-yl)imino)propan-2-ylidene)-4-methylbenzenesulfonohydrazide (3aa). 0.56 g of **3aa** was obtained as light yellow solid from the reaction of **1a** (0.59 g, 2.0 mmol) and **2a** (0.17 g, 2.0 mmol) for 12 h. Yield: 91.0%. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 11.61 (s, 1H), 8.62 (d, *J* = 7.8 Hz, 2H), 7.88 (s,1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 155.6, 149.2, 144.0, 135.8, 134.1, 129.8, 127.5, 121.6, 21.1, 11.4. Anal. Calcd for $C_{12}H_{14}N_6O_2S$: C, 47.05; H, 4.61; N, 27.43; S, 10.47.. Found: C, 47.02; H, 4.63; N, 27.44; S, 10.45..

N'-(2-((1H-1,2,3-triazol-1-yl)imino)ethylidene)-4-methylbenzenesulfonohydrazide (3ba). 0.52 g of **3ba** was obtained as white solid from the reaction of **1b** (0.56 g, 2.0 mmol) and **2a** (0.17 g, 2.0 mmol) for 2 h. Yield: 90%. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 12.35 (s, 1H), 8.78 (d, *J* = 8.4, 1H), 8.22 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 153.0, 143.6, 141.3, 135.5, 133.5, 129.37, 126.9, 121.7, 21.0. Anal. Calcd for $C_{11}H_{12}N_6O_2S$: C, 45.20; H, 4.14; N, 28.75; S, 10.97.. Found: C, 45.24; H, 4.13; N, 28.77; S, 10.98..

N'-(1-((4H-1,2,4-triazol-4-yl)imino)propan-2-ylidene)-4-methylbenzenesulfonohydrazide (3ab). 0.51 g of **3ab** was obtained as light yellow solid from the reaction of **1a** (0.59 g, 2.0 mmol) and **2b** (0.17 g, 2.0 mmol) for 12 h; Yield: 83%. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 11.58 (s, 1H), 9.17 (s, 2H), 8.51 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 2.08 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 156.2, 149.8, 143.9, 139.2, 136.0, 129.8, 127.8, 21.0, 11.3. Anal. Calcd for $C_{12}H_{14}N_6O_2S$:

C, 47.05; H, 4.61; N, 27.43; S, 10.47.. Found: C, 47.02; H, 4.59; N, 27.46; S, 10.44..

4-methyl-N'-(1-((5-methyl-1H-tetrazol-1-yl)imino)propan-2-lidene)benzenesulfonohydrazide (3ac). 0.56 g of **3ac** as light yellow solid was obtained from the reaction of **1a** (0.59 g, 2.0 mmol) and **2c** (0.20 g, 2.0 mmol) for 4 h. Yield: 87%. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 11.73 (s, 1H), 8.57 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.1 Hz), 2.55 (s, 3H), 2.38 (s, 3H), 2.12 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 157.4, 150.5, 148.7, 144.1, 135.7, 129.8, 127.5, 21.1, 11.3, 8.2. Anal. Calcd for $C_{12}H_{15}N_7O_2S$: C, 44.85; H, 4.71; N, 30.51; S, 9.98.. Found: C, 44.83; H, 4.69; N, 30.52; S, 9.95..

N'-(1-((5-amino-1H-tetrazol-1-yl)imino)propan-2-ylidene)-4-methylbenzenesulfonohydrazide (3ad). 0.55 g of 3ad was obtained as yellow solid from the reaction of **1a** (0.59 g, 2.0 mmol) and **2d** (0.20 g, 2.0 mmol) for 8 h. Yield: 85%. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 11.46 (s, 1H), 8.33 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1Hz, 2H), 7.24 (s, 2H), 2.37 (s, 3H), 2.13 (s, 3H). ^{13}C {1H} NMR (75 MHz, DMSO-d6) δ ppm: 152.8, 152.3, 149.8, 143.9, 135.8, 129.8, 127.5, 21.1, 11.2. Anal. Calcd for $C_{11}H_{14}N_8O_2S$: C, 40.99; H, 4.38; N, 34.76; S, 9.95.. Found: C, 41.02; H, 4.39; N, 34.74; S, 9.98..

To a suspension of intermediate compounds **3** (0.5 mmol) in methanol (4 mL) was added dropwise a solution of DiPEA (0.23 g, 1.8 mmol) in 2 mL of methanol at 65 °C or room temperature (only for **4ac** and **4ad)**. The reaction turned clear slowly and stirring was continued for 72 h. After completion of the reaction, all volatiles were removed under reduced pressure. The residue was purified by column chromatography using petroleum/ethyl acetate ether (petroleum ether/ethyl acetate = 1/1) as the eluent. The yield of compounds **4** was around 75%-95% in general.

4-methyl-1,1'-bi(1,2,3-triazole) (4aa). White solid (0.071 g); Yield: 95%. DSC: m.p 74.1 °C, $T_{d,\ onset}$ = 160.8 °C, $T_{d,\ peak}$ = 201.6 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.01 (d, J = 1.2 Hz, 1H), 8.73 (s, 1H), 8.15 (d, J = 0.9 Hz, 1H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 142.7, 133.7, 126.6, 123.5, 10.65. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_5H_7N_6$ 151.0732; Found: 151.0730. IR (KBr): 3162, 3146, 1550, 1475, 1227, 1004, 805, 623 cm^{-1}.

1,1'-bi(1,2,3-triazole) (4ba). White solid (0.051 g); Yield: 75%. DSC: m.p 132.0 °C, $T_{d,\ onset}$ = 155.2 °C $T_{d,\ peak}$ = 185.3 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm: 9.04 (d, J = 1.2 Hz, 1H), 8.17 (d, J = 1.2 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 133.8, 126.5. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_4H_5N_6$ 137.0575; Found: 137.0597. IR (KBr): 3137, 3117, 1480, 1405, 1279, 1013, 939, 805, 602 cm^{-1}.

4-phenyl-1,1'-bi(1,2,3-triazole) (4ca). Light yellow solid (0.087 g); Yield: 82%. DSC: m.p 140.1 °C, $T_{d,\ onset}$ = 155.3 °C, $T_{d,\ peak}$ = 185.2 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.51 (s, 1H), 9.10 (d, J = 0.3 Hz, 1H), 8.20 (d, J = 1.2 Hz, 1H), 7.97 (d, J = 6.0 Hz, 2H), 7.57-7.43 (m, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 146.3, 133.8, 129.2, 129.0, 126.4, 125.5, 122.6. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{10}H_9N_6$ 213.0888; Found: 213.0890. IR (KBr): 3133, 1476, 1218, 1011, 811, 751, 682 cm^{-1}.

4-(*p*-tolyl)-1,1'-bi(1,2,3-triazole) (4da). White solid (0.087 g); Yield: 77%. DSC: m.p 106.7 °C, $T_{d,\ onset}$ = 147.5 °C, $T_{d,\ peak}$ = 179.2 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.44 (s, 1H), 9.08 (s, 1H), 8.19 (s, 1H), 7.86 (d, J = 6.0 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 146.4, 138.7, 133.8, 129.8, 126.4, 126.3, 125.5, 122.2, 21.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{11}H_{11}N_6$ 227.1045; Found: 227.1044. IR (KBr): 3094, 1500, 1256, 1003, 795, 505 cm^{-1}.

4-(4-chlorophenyl)-1,1'-bi(1,2,3-triazole) (4ea). White solid (0.108 g); Yield: 88%. DSC: m.p 142.7 °C, $T_{d,\ onset}$ = 155.4 °C, $T_{d,\ peak}$ = 187.8 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.56 (s, 1H), 9.10 (d, J = 1.2 Hz, 1H), 8.20 (d, J = 1.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 145.2, 133.8, 133.6, 129.3, 127.9, 127.2, 126.4, 123.0. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{10}H_8ClN_6$ 247.0499, 249.0469; Found: 247.0494, 249.0464. IR (KBr): 3150, 3117, 1473, 1237, 1094, 1013, 798, 757, 512 cm^{-1}.

4-(4-bromophenyl)-1,1'-bi(1,2,3-triazole) (4fa). White solid (0.131 g); Yield: 90%. DSC: m.p 157.1 °C, $T_{d,\ onset}$ = 166.8 °C, $T_{d,\ peak}$ = 188.1 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.53 (s, 1H), 9.06 (s, 1H), 8.19 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 145.4, 134.0, 132.3.0, 128.3, 127.6, 126.5, 123.0, 122.4. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{10}H_8BrN_6$ 290.9993, 292.9973; Found: 290.9966, 291.9971. IR (KBr): 3122, 1486, 1402, 1242, 998, 781, 500 cm^{-1}.

4-(4-fluorophenyl)-1,1'-bi(1,2,3-triazole) (4ga). White solid (0.095 g); Yield: 83%. DSC: m.p 122.2 °C, $T_{d,\ onset}$ = 157.8 °C, $T_{d,\ peak}$ = 189.8 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.50 (s, 1H), 9.09 (s, 1H), 8.20 (s, 1H), 8.00 (m, 2H), 7.39 (m, 2H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 166.0, 145.4, 133.8, 127.6, 126.4, 125.6, 122.5, 116.4, 116.1. HRMS (ESI-TOF) m/z: [M+Cl]$^-$ Calcd for $C_{10}H_8FN_6Cl$ 265.0404; Found : 265.0401. IR (KBr): 3143, 1626, 1555, 1497, 1221, 1156, 1090, 1017, 836, 815, 777, 610, 509 cm^{-1}.

4-methyl-1-(4H-1,2,4-triazol-4-yl)-1H-1,2,3-triazole (4ab). White solid (0.066 g); Yield: 88%. DSC: m.p 120.4 °C, $T_{d,\ onset}$ = 185.0 °C, $T_{d,\ peak}$ = 223.8 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.30 (s, 2H), 8.58 (s, 1H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 142.3, 142.1, 123.7, 10.6. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_5H_7N_6$ 151.0732; Found: 151.0729. IR (KBr): 3182, 3121, 1566, 1520, 1075, 1020, 612 cm^{-1}.

4-phenyl-1-(4H-1,2,4-triazol-4-yl)-1H-1,2,3-triazole (4cb). White solid (0.080 g); Yield: 76%. DSC: $T_{d,\ onset}$ = 203.5 °C, $T_{d,\ peak}$ = 210.4 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ ppm: 9.41 (s, 1H), 9.36 (s, 1H), 7.93 (d, J

= 7.5 Hz, 2H), 7.54 (t, 2H), 7.46 (t, 2H). ^{13}C {^1H} NMR (75 MHz, DMSO-d_6) δ ppm: 146.0, 142.1, 129.2, 129.0, 125.3, 122.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_9N_6$ 213.0888; Found: 213.0890. IR (KBr): 3100, 3065, 1468, 1177, 1045, 1018, 966, 762, 700, 586 cm^{-1}.

5-methyl-1-(4-methyl-1H-1,2,3-triazol-1-yl)-1H-tetrazole (4ac). White solid (0.063 g); Yield: 77%. DSC: m.p 76.6 °C, $T_{d,\ onset}$ = 134.8 °C, $T_{d,\ peak}$ = 168.5 °C. ^1H NMR (300 MHz, DMSO-d_6) δ ppm: 8.65 (s, 1H), 2.46 (s, 3H), 2.40 (s, 3H).^{13}C {^1H} NMR (75 MHz, DMSO-d_6) δ ppm: 152.5, 143.3, 123.7, 10.7, 7.7. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_5H_7N_7Na$ 188.0660; Found: 188.0663. IR(KBr): 3151, 3115, 1545, 1452, 1358, 1322, 1220, 1126, 1017, 959, 815, 613 cm^{-1}.

1-(4-methyl-1H-1,2,3-triazol-1-yl)-1H-tetrazol-5-amine (4ad). Red brown solid (0.063 g); Yield: 76%. DSC: m.p 75.2 °C, $T_{d,\ onset}$ = 129.7 °C, $T_{d,\ peak}$ = 150.1 °C.^1H NMR (300 MHz, DMSO-d_6) δ ppm: 8.59 (s, 1H), 7.67 (s, 2H), 2.36 (s, 3H). ^{13}C {^1H} NMR (126 MHz, DMSO-d_6) δ ppm: 153.8, 142.9, 124.1, 10.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_4H_7N_8$ 167.0793; Found: 167.0797. IR(KBr): 3369, 3285, 3165, 3109, 1667, 1538, 1410, 1272, 1215, 1126, 1017, 976, 802, 591cm^{-1}.

ASSOCIATED CONTENT

Supporting Information:concise list of types of data or files found in the SI

Optimization of Reaction Conditions for Preparation 4**aa** from 3**aa**; Computation Details; X-ray Structural Analysis of 3**ba**, 4**ba**, 3**ca** and 4**ca**.; NMR Spectra for New Compounds; DSC Curves of Compounds 4**aa**-4**ga**, 4**ab**-4**ad**.

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Notes

The authors declare no competing financial interest.

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