Synthesis of Thermally Stable Energetic 1,2,3-Triazole Derivatives

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Abstract: Various thermally stable enpolynitro-aryl-1,2,3-triazoles ergetic have been synthesized through Cu-catalyzed [3+2] cycloaddition reactions between their corresponding azides and alkynes, followed by nitration. These compounds were characterized by analytical and spectroscopic methods and the solid-state structures of most of these compounds have been determined by using X-ray diffraction techniques. Most of the polynitro-bearing triazole derivatives decomposed within the range 142-319°C and their heats of formation and crystal densities were determined from computational studies. By using the Kamlet-Jacobs

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empirical relation, their detonation velocities and pressures were calculated from their heats of formation and crystal densities. Most of these newly synthesized compounds exhibited high positive heats of formation, good thermal stabilities, reasonable densities, and acceptable detonation properties that were comparable to those of TNT.

Introduction

Formidable challenges remain in the development of less sensitive and thermally stable energetic materials because this process requires a detailed investigation into the design of N- and O-rich molecules, the determination of their energy content through computational studies, as well as the demonstration of reliable strategies for their synthesis.^[1] Therefore, the synthesis of small organic molecular frameworks that have high N- and O-content as thermally stable energetic materials from readily available precursors is always desirable.^[2] In general, the presence of benzene moieties in the form of energetic polynitroarenes lowers the hygroscopic nature of a material, as well as its synthetic cost; this group also decreases the sensitivity of the material to impact, shock, and friction.^[3] Five-membered azole heterocycles behave as a source of energy owing to their high N content.^[4] Therefore, nitrogen-rich aromatic-triazole-based energetic materials have invariably been used in civil and military applications, such as in aerospace propellants, smoke-free pyrotechnic fuels, fire extinguishers, and so on.^[5,1g] In essence, 1,2,3-triazoles are considered to be one of the most promising backbones for the fabrication of high-

performance explosives because they possess high positive heats of formation, owing to their N-N and C-N bonds and ring strain.^[6,1g] In addition, the aromatic nature of the triazole moiety makes the molecule thermally stable. Unfortunately, most of the better-performing energetic materials are practically unsuitable for safe handling, whereas materials with lower sensitivity do not show good-enough performance with respect to the benchmark explosives.^[7] Apart from a high positive heat of formation, a high oxygen balance and high density improve the detonation performance of a material and make the molecule a better-performing energetic material. In general, the incorporation of nitro groups into a molecular backbone enhances the oxygen balance and density.^[8]

Herein, we report the synthesis of various N-benzyl-/aryland/or pyridyl-tethered 1,2,3-triazoles by using the known Cu-catalyzed [3+2] cycloaddition reaction between their corresponding azides and terminal alkynes. Nitration on these precursors delivered a wide range of nitro-rich 1,2,3triazole derivatives as thermally stable energetic materials. The solid-state structures of most of these newly synthesized compounds were elucidated by using X-ray diffraction techniques.

Results and Discussion

The development of simple and efficient approaches for the creation of triazole skeletons in small molecular entities has always attracted considerable attention.^[9] Importantly, the Cu-catalyzed [3+2] cycloaddition reaction between an azide and an alkyne, termed the "click reaction", is a reliable synthetic strategy for the efficient formation of 1,2,3-triazole skeletons in high yields with affordable cost and high regioselectivity.^[10] Herein, we report the synthesis of nitro-rich

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benzyl-/aryl- and pyridyl-tethered 1,2,3-triazoles as new thermally stable energetic materials.

In general, electron-rich azides (dipoles) and electronpoor alkynes (dipolarophiles) favor the cycloaddition reaction, whereas steric bulk on the acetylene retards the rate of the reaction.^[11] It has been reported that the cycloaddition reaction of electron-rich dipolarophiles proceeds well in water and in protic solvents.^[12] The base-mediated deprotection of the C–Si bond occurs smoothly in protic solvent at ambient temperature.^[13] With these facts in mind, the cycloaddition reactions between readily accessible benzyl azides and electron-rich TMS-acetylene (1) were carried out under the previously reported conditions involving sodium ascorbate, CuSO₄, and K₂CO₃ as a base in MeOH/water at room temperature for 24 h (Table 1).^[14] Benzyl azides were pre-

Table 1. CuI-catalyzed 1,3-dipolar cycloaddition of benzyl azides and TMS-acetylene $(1)^{\rm [a]}$

	Na a Na a CuS Me R	$S \longrightarrow (1)$ Base ascorbate $O_4:5H_2O$ OH/H_2O T, 24 h	3 N-N. N +		N M TMS
Entry	2	R	Base	Yield [9	6] ^[b]
				3	4
1	2 a	Н	K ₂ CO ₃	92	3
2	2b	$4-NO_2$	K_2CO_3	87	0
3	2 c	3-NO ₂	KOAc	83	9
4	2 d	$2-NO_2$	K_2CO_3	53	0
5	2 e	4-OMe	K_2CO_3	92	0
6	2 f	3-OMe	K_2CO_3	79	0
7	2 g	2-OMe	K ₂ CO ₃	52	0

[a] All reactions were carried out with azide (1.0 equiv), TMS-acetylene (1.5 equiv), base (potassium carbonate or potassium acetate, 1.2 equiv), sodium ascorbate (0.4 equiv), and $CuSO_4$ -5H₂O (0.2 equiv) in a mixture of MeOH/water (1:1, 0.5 mL for 1 mmol) at room temperature for 24 h. [b] Yield of isolated product.

pared from the commercially available benzyl bromides by nucleophilic displacement with NaN3 in DMSO in almost quantitative yields.^[15] The electronically neutral benzyl azide 2a reacted smoothly with 1 to give compound 3a in 92% yield; the corresponding TMS-substituted 1,2,3-triazole 4a was also isolated in trace amounts (Table 1, entry 1). An activated aryl azide that had a nitro group at the 4-position on the phenyl ring underwent cycloaddition with 1, thereby producing compound 3b in 87% yield (Table 1, entry 2). A poor yield of compound 3c was obtained when the reaction of 3-nitrobenzyl azide (2c) with 1 was conducted under the optimized conditions. Interestingly, KOAc was found to be suitable as the base and the desired compound, 3c, was isolated in 83% yield (Table 1, entry 3). Sterically demanding 2-nitro-substituted benzyl azide 2d reacted poorly with compound 1 and only afforded compound 3d in moderate yield, with a fair amount of recovered unreacted compound 2d. A similar trend of reactivity and selectivity was observed in the reactions of MeO-substituted benzyl azides 2e-2g with 1 under the optimized conditions, thus delivering their corresponding products, **3e–3g**, in good-to-excellent yields (Table 1, entries 5–7).

With a series of triazole-based molecules in hand, the nitrations of compounds 3a-3g were independently performed in either a mixture of 70% HNO₃ and 98% H₂SO₄ (Conditions A) or 95% HNO3 and 98% H2SO4 (Conditions B), as shown in Equation (1). Table 2 summarizes the nitration reactions of the N-benzyl-substituted-1,2,3-triazoles (3). At first, compound 3a was heated under conditions A at 120°C for 24 h. Nitro-rich regioisomeric products 5a-8a were detected and purified easily by column chromatography on silica gel in an overall 83% yield (Table 2, entry 1). In non-polar trinitro-bearing compound 5a, which was isolated in 15% yield, the two nitro groups were substituted at the o- and p-positions on the N-benzyl ring, whilst the other nitro group was inserted at the 4-position of the triazole moiety. As expected, the o,p-dinitro-substituted compound 6a was isolated in 39% yield as the major product. Interestingly, the m,m- and m,p-dinitro substituted compounds 7a and 8a, respectively, were also isolated, albeit in poor yields. The factors that were responsible to the formation of these unlikely meta-substituted products (7a and 8a) remain unclear. The introduction of more nitro groups onto the molecular framework usually enhances the density and detonation properties of a compound. Therefore, we speculate that the use of 95% HNO₃ in the nitration reactions could influence the formation of the tetranitro substituted products. Therefore, the nitration of compound 3a was carried out under conditions B at 100 °C. Although compound 3a was completely consumed within 12 h, products 5a-8a were exclusively formed (Table 2, entry 1), as observed previously.



Next, the nitration reactions of nitro-substituted triazoles 3b-3d were independently conducted under conditions A and B. The products, **5a** (12%), **6a** (70%), and **8a** (11%), were obtained from 3b under conditions A at 120°C, whereas the same reaction under conditions B at 70 °C gave compounds 6a and 8a in good overall yields (Table 2, entry 2). Similarly, the nitrations of compound 3c under conditions A or B delivered 7a and 8a as the major and minor products, respectively (Table 2, entry 3). Compound 6a was exclusively obtained from the nitration of o-nitro-substituted triazole **3d** under both sets of conditions (Table 2, entry 4). Thus, variously substituted nitro-containing products (6a, 7a, and 8a) can be directly prepared from 3 in good yields. In general, electron-rich aromatic compounds undergo electrophilicsubstitution reactions with ease. Therefore, we anticipated that the OMe group on the aryl moiety in benzyl triazoles would facilitate the introduction of more nitro groups onto the aromatic skeleton. Thus, the nitration of 4-OMe-susbti-

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Entry	3	<i>T</i> [°C]	<i>t</i> [h]	Polynitro derivatives of benzyl-1,2,3-triazoles ^[c]					
				NO ₂ N, N, N NO ₂		O ₂ N NO ₂ NO ₂ N			
				5a	6a	7 a	8a		
1	3a	120 ^[a]	24 ^[a]	15	39	20	9		
		$100^{[b]}$	12 ^[b]	14	35	25	10		
2	3 b	120 ^[a]	24 ^[a]	12	70	_	11		
		70 ^[b]	6 ^[b]	_	64	_	13		
3	3c	80 ^[a]	12 ^[a]	_	_	60	25		
		60 ^[b]	$10^{[b]}$	_	_	62	30		
4	3 d	60 ^[a]	8 ^[a]	_	88	_	-		
		45 ^[b]	6 ^[b]	_	93	_	-		
5	3e	RT ^[a]	2 ^[a]	_	_	H_3CO NO_2 NO_2	_		
		RT ^[b]	2 ^[b]		-	9 (71 ^[a] , 76 ^[b])	-		
6	3 f	RT ^[a]	2 ^[a]		_	_	-		
		RT ^[b]	2 ^[b]	10 (75 ^[a] , 81 ^[b])	-		_		
7	3g	$\mathrm{RT}^{[a]}$	6 ^[a]	_	_		_		
_		RT ^[b]	2 ^[b]	_	-	11 (48 ^[a] , 64 ^[b])	-		

Table 2. Nitration reactions of triazoles 3.

[a] Mixture of 70 % HNO3 and 98 % H₂SO4. [b] Mixture of 95 % HNO3 and 98 % H₂SO4. [c] Yield of isolated product.

tuted triazole 3e was independently carried out under conditions A and B; the di-*ortho*-nitro-substituted product 9 was exclusively isolated in good yield (Table 2, entry 5). Gratifyingly, the trinitration product, 10, was obtained in 81% yield when *m*-methoxy-bearing triazole 3f was exposed to conditions B at RT for 2 h (Table 2, entry 6). On the other hand, the sterically demanding compound 3g delivered the *o.p*-dinitration product (11) as a thick liquid in moderate yield (Table 2, entry 7). These results reveal that conditions B are more mild than conditions A. In addition, more reactive and highly productive nitration reactions are observed under conditions B in comparison to conditions A. X-ray diffraction analysis confirmed the structures of compounds **5a**, **6a**, **7a**, **8a**, and **9**, as depicted in Figure 1.

Next, we turned our attention to exploring the nitration reactions of aryl-1,2,3-triazoles and the synthesis of various polynitroaryl triazoles. We anticipate that these nitro-containing N-aryl triazoles would show better energetic proper-



Figure 1. Molecular structures of compounds 5a, 6a, 7a, 8a, 9, 20, 21, 22, and 25a; thermal ellipsoids are set at 30% probability and hydrogen atoms are unlabeled for clarity.

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ties compared to their corresponding nitro-substituted *N*benzyl triazoles, because of their lower carbon content. In addition, the presence of the triazole skeleton on the aryl ring (C–N bond) would facilitate the electrophilic-nitration process.

The Cu-catalyzed cycloaddition reaction between an aryl azide and TMS-acetylene (1) is a reliable method for the synthesis of aryl triazoles (Table 3).^[14] Aryl azides are easily

Table 3. [3+2] Cycloaddition reactions between aryl azides and TMS-acetylene. $\ensuremath{^{[a]}}$



[a] All reactions were carried out with azide (1.0 equiv), TMS-acetylene (1.5 equiv), base (potassium carbonate or potassium acetate, 1.2 equiv), sodium ascorbate (0.4 equiv), and $CuSO_4$ - $5H_2O$ (0.2 equiv) in a mixture of MeOH/water (1:1, 0.5 mL for 1 mmol) at room temperature for 24 h. [b] Yield of isolated product.

accessible in good yields from their corresponding commercially available aryl amines, through diazotization followed by azide substitution.^[15] The reaction between phenyl azide (12a) and 1 was successfully conducted under previously optimized conditions (sodium ascorbate, CuSO₄, and K₂CO₃ as a base in MeOH/water at room temperature) and the product 13a was isolated in 66% yield (Table 3, entry 1). p/m-Nitro/methoxy-substituted aryl azides efficiently underwent cycloaddition with 1, thereby delivering triazoles 13b,c and 13e,f in good to excellent yields (Table 3, entries 2-3 and 5-6). However, the cycloaddition reactions of ortho-substituted aryl azides 12d and 12g were successfully performed in the presence of KOAc as the base: their corresponding 1-substituted-1,2,3-triazoles 13d and 13g were isolated in moderate yields and TMS-bearing 1,4-disubstituted-triazoles 14d and 14g were also formed in fairly good amounts (Table 3, entries 4 and 7). The desilylation of compounds 14d and 14g with K₂CO₃ in MeOH readily gave their corresponding products 13d and 13g.^[13]

The nitration of *N*-aryl-substituted 1,2,3-triazoles was independently examined under conditions A and B (Table 4). Our attempts to nitrate compound 13a under conditions A were unsuccessful; however, heating compound 13a at reflux under conditions B gave mono-nitro derivatives 15and 16 in poor yields (Table 4, entry 1). The *m,p*-dinitro-substituted product (17) and trinitro benzene (18) were ob-



[a] Mixture of 95 $\%~HNO_3$ and 98 $\%~H_2SO_4.$ [b] Yield of isolated product is shown in parenthesis.

tained in poor yields when compound 13c was reacted under conditions B at 160 °C (Table 4, entry 2). Unfortunately, cleavage of the C-N linkage of the aryl triazole was observed when the reaction was conducted in strong acids at higher temperatures.^[16] The presence of a nitro group at the ortho/para position with respect to the triazole made the aryl ring highly electron deficient and, therefore, compounds 13b and 13d failed to undergo nitration under both sets of conditions, even when the reaction was performed at elevated temperatures. Therefore, we investigated the nitration reactions of electron-rich methoxy-substituted aryl triazoles. Owing to the o- and p-directing nature of the OMe group, nitration of 4-MeO-substituted phenyl triazole 13e exclusively produced the di-ortho-nitro-containing product 19 in 85% yield under conditions B at room temperature (Table 4, entry 3). A regioisomeric mixture of o,p-dinitrosubstituted products 20 and 21 was obtained from the nitration of 3-OMe-substituted triazole 13 f in good overall yield (Table 4, entry 4). The sterically encumbered compound 13g delivered 22 in 82% yield when the reaction was carried out under conditions B at room temperature for 2 h. Unfortunately, our efforts to achieve the tri- and/or tetranitro-substi-

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tuted aryl triazole were futile. The structures of compounds **20**, **21**, and **22** were confirmed by single-crystal X-ray analysis (Figure 1).

Heat of formation (HOF) is a valuable factor that determines the nature and efficiency of highly energetic materials.^[6] Our synthesized polynitro-1,2,3-triazole derivatives (**5a-11** and **15-22**) all showed positive HOFs that varied from 197–401 kJ mol⁻¹. These results reveal that the 1,2,3-triazole skeleton is beneficial to a positive HOF value. Therefore, we believe that the incorporation of more triazole rings would enhance the heat of formation of the molecule. The fact that a pyridine moiety contributes more energy than a benzene ring is well-established.^[17] Based on this information, new molecular entities **24**, in which two triazole skeletons are attached onto a pyridine template, were proposed and their synthesis was initiated through a cycloaddition reaction between 2,6-bis(azidomethyl)-pyridine (**23**) and the corresponding alkynes (Table 5). The precursor **23**

Table 5. Synthesis of bis-1,2,3-triazoles from their corresponding azides and alkynes.^[a]



[a] All reactions were carried out with azide (1.0 equiv), TMS-acetylene (3.0 equiv), base (potassium carbonate or potassium acetate, 2.4 equiv), sodium ascorbate (0.8 equiv), and $CuSO_4$ -5H₂O (0.4 equiv) in a mixture of MeOH/water (1:1, 1 mL for 1 mmol) at room temperature for 24 h. [b] Yield of isolated product.

was obtained from the commercially available 2,6bis(bromomethyl)pyridine by the nucleophilic displacement of bromide by NaN₃ in good yield.^[18] The cycloaddition of compound **23** to TMS-acetylene (**1**) under the optimized conditions gave **24a** in 74% yield at room temperature (Table 5, entry 1). Similarly, the reaction between compound **23** and propargyl propionate (**1**') in the presence of KOAc afforded **24b** in excellent yield (Table 5, entry 2).

Our efforts to nitrate compound **24a** failed, even when the reaction was performed at high temperatures under conditions A and B. Presumably, the protonation of the pyridine-N atom by the acids hindered the electrophilic nitration of the pyridine moiety. However, the oxidation of compound **24a** with mCPBA in CHCl₃ at 70 °C delivered the corresponding *N*-oxide product **25a** in 35 % yield (Table 6, entry 1). X-ray diffraction studies establish the structure of **25a** (Figure 1).

A recent report by Shreeve and co-workers^[19] inspired us to introduce more nitro groups onto the methylene hydrogen atoms of compound **24b**. However, we noted the formation of the mono-nitro derivative of compound **24b** under

Table 6. Synthesis of pyridine-*N*-oxides **25a** and **25b**.



[[]a] Yield of isolated product. [b] Nitration failed, even at high temperature.

conditions B at room temperature. Subsequently, the purified nitro-containing product was reacted with mCPBA at room temperature and the desired *N*-oxide product **25b** was isolated in 41 % yield over two steps (Table 6, entry 2).

X-ray crystallography: Single crystals were grown by the slow evaporation of solutions of **5a**, **6a**, **7a**, **8a**, **9**, **20**, **21**, **22**, and **25a** in EtOAc at room temperature and atmospheric pressure. The structures of **5a**, **6a**, **7a**, **8a**, **9**, **20**, **21**, **22**, and **25a** were unambiguously elucidated by single-crystal X-ray diffraction analysis. The molecular structures of **5a**, **6a**, **7a**, **8a**, **9**, **20**, **21**, **22**, and **25a** are shown in Figure 1. Compounds **5a**, **7a**, **8a**, **9**, **20**, and **25a** crystallized in monoclinic space groups $P2_1$, $P2_1/n$, $P2_1/c$, $P2_1/n$, $P2_1/c$, and C2/c, with cell volumes of 557.09(10), 1016.72(14), 1074.68(14), 1240.45(14), 2316.6(6), and 1182.7(4) Å³, respectively, whereas **6a**, **21**, and **22** crystallized in the orthorhombic space group $P2_12_12_1$ with cell volumes of 1075.07(12), 1112.8(8), 1141(4) Å³, respectively. The crystallographic data of all of these compounds are detailed in Table 7.

This work demonstrates the synthesis of polynitrobenzyl-(5a-11), polynitro-N-aryl- (15-22), and polynitropyridylcontaining triazoles (25a and 25b). Essential parameters, such as heat of formation (HOF), density (ρ), detonation velocity (D), and detonation pressure (P), determine the nature and efficiency of energetic materials. Table 8 summarizes the energetic properties of these materials. The HOF is indicative of the energy content of high-energy materials; the newly synthesized triazole derivatives showed positive HOFs, that is, in the range 197–683 kJ mol⁻¹. Of the benzylsubstituted triazole derivatives, compound 5a possessed the highest HOF (390.3 kJ mol⁻¹), owing to the presence of three nitro groups in the molecular backbone. Compound 5a showed better density and performance than the other nitro-bearing benzyl derivatives 6a-8a and 9-11, because it contained one more nitro group than the latter compounds. Changes in the positions of the nitro groups in the molecular structure did not affect the HOF values, as observed in compounds 6a, 7a, and 8a. Similar trends were observed in polynitro-N-aryl-triazole derivatives 19-22. Of the triazole derivatives, pyridyl-based compound 25 a showed the higher HOF, which can be attributed to the presence of triazole

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Table 7. Crystallographic data for compounds 5a, 6a, 7a, 8a, 9, 20, 21, 22, and 25a.

Compound	5a	6a	7a	8a	9	20	21	22	25 a
CCDC	895107	895108	895109	895110	896656	895111	895112	895113	895114
formula	$C_9H_5N_6O_6$	$C_9H_7N_5O_4$	$C_9H_7N_5O_4$	$C_9H_7N_5O_4$	$C_{10}H_9N_5O_5$	$C_9H_7N_5O_5$	$C_9H_7N_5O_5$	$C_9H_7N_5O_5$	$C_{11}H_{11}N_7O_1$
$M_{ m w}$	293.19	249.20	249.20	249.20	279.22	265.20	265.20	265.20	257.27
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_1/n$	$P2_{1}/c$	$P2_1/n$	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	C2/c
<i>T</i> [K]	100	298	100	293	293 K	298	298	298	298
a [Å]	5.5245(6)	5.5436(4)	10.0567(8)	8.6097(7)	11.6392(8)	10.8498(16)	5.6454(18)	5.554(3)	14.179(3)
b [Å]	5.5719(6)	11.9190(8)	9.2416(7)	11.3982(8)	5.4843(3)	12.1869(18)	13.486(7)	12.461(6)	7.7450(17)
c [Å]	18.1323(19)	16.2706(10)	10.9434(9)	11.0544(7)	19.6637(14)	18.249(3)	14.616(5)	16.49(6)	10.792(2)
α [°]	90	90	90	90	90	90	90	90	90
β [°]	93.521(2)	90	91.5180(10)	97.843(7)	98.790(7)	106.253(2)	90	90	93.667 (4)
γ [°]	90	90	90	90	90	90	90	90	90
Ζ	2	4	4	4	4	8	4	4	4
V [Å ³]	557.09(10)	1075.07(12)	1016.72(14)	1074.68(14)	1240.45(14)	2316.6(6)	1112.8(8)	1141(4)	1182.7(4)
$D_{\rm calc} [\rm g cm^{-3}]$	1.748	1.540	1.628	1.540	1.495	1.521	1.583	1.544	1.445
$\mu [{ m mm}^{-1}]$	0.151	1.077	0.132	0.125	0.123	0.127	0.132	0.129	0.102
total reflns	5787	3071	8988	4709	3255	20797	3131	2165	5768
unique reflns	2177	1851	1763	2408	2811	3933	2095	1451	1137
observed	2098	1700	1603	1687	1688	3303	1545	1264	901
reflns									
$R_1[I > 2\sigma(I)]$	0.0355	0.0381	0.0350	0.0450	0.0733	0.0682	0.0366	0.0889	0.0504
wR_2 [all]	0.0879	0.0982	0.0806	0.1282	0.2306	0.1823	0.0835	0.2440	0.1245
GOF	1.114	1.073	1.088	0.863	1.241	1.122	0.968	1.082	1.126
diffractometer	SMART	Xcalibur	SMART	SMART	Xcalibur	SMART	Xcalibur	Xcalibur	Xcalibur
	APEX	Gemini Eos	APEX	APEX	Gemini Eos	APEX	Gemini Eos	Gemini Eos	Gemini Eos
	CCD	CCD	CCD	CCD	CCD	CCD	CCD	CCD	CCD

Table 8. Energetic properties of the 1,2,3-triazole derivatives.

Compound	$OB^{[a]}$	$ ho^{ ext{[b]}}$	$D^{[c]}$	$P^{[d]}$	M.p. ^[e]	$T_{d}^{[f]}$	HOF ^[g]
	[%]	$[g \text{ cm}^{-3}]$	$[\mathrm{km}\mathrm{s}^{-1}]$	[GPa]	[°C]	[°C]	[kJ mol ⁻¹
5a	-81.6	1.64	6.99	20.07	195	256	390.3
		(1.75)					
6a	-112.4	1.53	6.26	15.73	145	220	381.9
		(1.54)					
7a	-112.4	1.53	6.27	15.77	131	312	364.8
		(1.63)					
8a	-112.4	1.58	6.47	17.16	88	215	387.0
		(1.54)					
9	-111.7	1.54	5.92	14.08	90	170	232.6
		(1.49)					
10	-83.8	1.61	6.50	17.52	-	237	224.2
11	-111.7	1.53	5.90	14.08	-	209	197.4
15	-143.0	1.49	5.15	10.46	197	271	401.6
16	-143.0	1.48	5.13	10.33	92	259	383.2
17	-98.6	1.57	6.20	15.69	125	268	394.9
19	-99.5	1.57	6.37	16.59	-	319	263.1
20	-99.5	1.58	6.40	16.82	168	221	263.1
		(1.52)					
21	-99.5	1.59	6.41	16.89	200	230	253.5
		(1.58)					
22	-99.5	1.57	6.34	16.41	-	152	253.5
		(1.54)					
25 a	-164.8	1.38	4.42	7.32	62	228	682.8
		(1.44)					
25 b	-117.2	1.49	5.75	13.05	110	142	585.7

[a] Oxygen balance. [b] Calculated density; the experimental crystal density is shown in parentheses. [c] Velocity of detonation. [d] Detonation pressure. [e] Melting point. [f] Decomposition temperature. [g] Heat of formation.

and pyridine rings in its molecular structure. In general, pyridine contributes $140.12 \text{ kJ mol}^{-1}$ energy, whereas benzene offers only $82.84 \text{ kJ mol}^{-1}$; thus, the *N*-oxide-bearing pyri-

dine-triazole molecules 25a and 25b possess higher HOFs.^[17] Density is a primary physical parameter that determines the detonation performance of a molecule. The detonation velocity increases with packing density and the detonation pressure varies proportionally with respect to the square of the density. The densities of the triazole derivatives were in the range $1.38-1.64 \text{ g cm}^{-3}$. As evident in Table 8, the predicted densities (from their cvff force fields) closely matched their observed crystal densities. The incorporation of nitro groups into a framework improves its density. As a consequence, a noticeable variation in density was clearly visible between compounds 16 and 17; a similar trend was observed among compounds 5a and 6a, 9 and 10, and 25 a and 25 b. The velocity of detonation (D) is a function of the energy that is produced by explosive decomposition. The density, heat of formation, and atomic composition can be integrated into an empirical formula to predict the performance of a proposed explosive. The detonation velocity and detonation pressure of the triazole derivatives were computed by Kamlet-Jacobs empirical equations and the results are shown in Table 8. Detonation performance mainly depends on the crystal density, whereas, the contribution of the HOF to the detonation properties is negligible. For example, compounds 25a and 25b show poor detonation performance, apart from their high HOFs. Of the synthesized triazole derivatives, compound 5a demonstrated the best performance, owing to its high crystal density. Thus, compound **5a** possessed $D = 6.99 \,\mathrm{km \, s^{-1}}$ and $P \approx 20.07 \,\mathrm{GPa}$. The thermal stabilities of the triazole derivatives were determined by DSC-TGA measurements. The triazole derivatives decomposed in the range 142-319°C. Interestingly, compounds **7a** and **19** showed good thermal stabilities $(>300 \,^{\circ}\text{C})$. Compounds **10**, **11**, **19**, and **22** decomposed without melting. Owing to a large variation in their melting $(<92 \,^{\circ}\text{C})$ and decomposition temperatures $(>170 \,^{\circ}\text{C})$, compounds **8a**, **9**, **16**, and **25a** could be useful as melt-cast explosives.

Conclusion

In summary, a wide variety of new thermally stable nitrorich benzyl-/aryl- and pyridyl-tethered 1,2,3-triazole-based energetic materials have been efficiently synthesized through a cycloaddition reaction between their corresponding readily available benzyl-/aryl- and pyridyl-tethered azides and commercially available alkynes, followed by nitration of the triazole derivatives; the molecules were thoroughly characterized by analytical and spectroscopic methods. The structures of most of these newly synthesized molecules were determined by using X-ray diffraction analysis. Most of the nitro derivatives of 1,2,3-triazoles decomposed in the range 142-319°C; therefore, these molecules are considered to be thermally stable energetic materials. Most of these compounds exhibited moderate detonation performance: Compound **5a** $(P=20.07 \text{ GPa}, D=6.99 \text{ km s}^{-1})$ showed comparable detonation properties to TNT (P =19.5 GPa, $D = 6.88 \text{ km s}^{-1}$). Our predicted results revealed that the synthesized compounds possessed high positive HOFs; in particular, the pyridyl-tethered nitro derivative showed a HOF of 682.8 kJ mol⁻¹. Some of these molecules might be useful as melt-cast explosives and energetic oxidizers, owing to their low melting points and high thermal stabilities. Fabrication of complex structures with more triazole moieties on pyridine templates is currently being pursued in our laboratory.

Experimental Section

Caution! Working with azides should always be done carefully. Organic azides, in particular those of low molecular weight or with high nitrogen content, are potentially explosive. Heat, light, and pressure can cause decomposition of the azides. Any experiments in which azides are to be heated in the presence of copper should involve the use of a blast shield. All nitro derivatives of 1,2,3-triazoles are dangerous when heating at high temperature. We prepared all of these compounds on the milligram scale. None of the compounds described herein exploded or were detonated during the course of this research; in any case, these materials should be handled with care by using proper safety precautions. Safety shields, safety glasses, face shields, leather gloves, and protective clothing, such as leather suits and ear plugs, must be worn. Ignoring safety precautions can lead to serious injury.

General: Unless otherwise noted, all of the chemicals were purchased from Sigma Aldrich Ltd. and used as received. All of the reactions were performed in oven-dried round-bottomed flasks. Commercial-grade solvents were distilled prior to use. Column chromatography was performed on either 100–200 Mesh or 230–400 Mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of the spots on the TLC plates was accomplished with UV light (254 nm) and with staining in an I₂ chamber. ¹H NMR and ¹³C NMR spectra were

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recorded at 400 MHz and 101 MHz, respectively, with the solvent resonance as an internal standard (¹H NMR: CDCl₃ at δ =7.26 ppm, [D₆]DMSO at δ =2.50 and 3.50 ppm; ¹³C NMR: CDCl₃ at δ =77.0 ppm, [D₆]DMSO at δ =44.0 ppm). IR spectra are reported in cm⁻¹. LCMS spectra were obtained with an ionization voltage of 70ev; data are reported in the form of m/z (intensity relative to base peak=100). Elemental analysis was carried out on a FLASH EA 1112 analyzer. Melting points and decomposition temperatures (DTA) were determined by using DSC–TGA measurements. Single-crystal X-ray data were collected at 298 K on SMART APEX CCD and Xcalibur Gemini Eos CCD single-crystal diffractometers by using graphite-monochromated Mo_{Ka} radiation (0.71073 Å).

X-ray crystallography: X-ray reflections for compounds **5a**, **7a**, **8a**, and **20** were collected on a Bruker SMART APEX CCD diffractometer that was equipped with a graphite monochromator and a Mo K α fine-focus sealed tube (λ =0.71073 Å). Data integration was done by using SAINT.^[20] The intensities of the absorption were corrected by using SADABS.^[21] Structure solution and refinement were carried out by using Bruker SHELX-TL.^[22] X-ray reflections for compounds **6a**, **9**, **21**, **22**, and **25a** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer by using Mo K α radiation. Data reduction was performed by using CrysAlisPro (version 1.171.33.55). The OLEX2–1.0^[23] and SHELX-TL 97 programs were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically and the C–H hydrogen atoms were placed at fixed positions.

CCDC-895107 (5a), CCDC-895108 (6a), CCDC-895109 (7a), CCDC-895110 (8a), CCDC-896565 (9), CCDC-895111 (20), CCDC-895112 (21), CCDC-895113 (22), and CCDC-895114 (25a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical study: Density function theory (DFT) has been universally applied to study energetic materials and has been shown to be reliable. Electronic-structure calculations were performed with the Gaussian 09 suite.^[24] The geometries of the molecules were calculated at the B3LYP level in conjugation with the 6-311G** basis set.[25] The optimized geometries were submitted to the polymorph module of the Material studio suite for density calculations by using the CVFF force field^[26] The heats of formation of the triazole derivatives were obtained by using semi-empirical methods (Austin Model 1 (AM1), Parameterization Method 3 (PM3), and Parameterization Method 6 (PM6)).^[27] The detonation properties (D and P) of the compounds were evaluated by using the Kamlet-Jacobs equations,^[28] based on their predicted densities and HOFs, according to Equations (2) and (3), where D is detonation velocity (km s⁻¹), P is the detonation pressure (GPa), N is the number of moles of gaseous detonation products per gram of explosives, M is the average molecular weight of the gaseous products, Q is the chemical energy of detonation (cal g⁻¹), which is defined as the difference between the HOFs of the products and the reactants, and ρ is the density of the explosive (gcm⁻³):

$$D = 1.01 (NM^{0.5}Q^{0.5})^{0.5} (1+1.30\rho_{\rm o})$$
⁽²⁾

$$P = 1.55\rho_0^2 N M^{0.5} Q^{0.5} \tag{3}$$

General procedure for the cycloaddition reaction: A mixture of the azide (1.0 equiv), trimethylsilyl (TMS)-acetylene (1.5 equiv), potassium carbonate (1.2 equiv), CuSO₄ (0.2 equiv), and sodium ascorbate (0.4 equiv) was dissolved in MeOH/water (1:1, 5 mL for 10 mmol) in a 20 mL vial. The vial was sealed with a screw cap and the resulting mixture was stirred rapidly at RT for 24 h. Upon completion of the reaction, aqueous ammonium hydroxide (5%) was added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with EtOAc (3 times). The combined extracts were washed with water (twice) and brine and dried over Na₂SO₄. The solvent was filtered off and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.

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According to this above-mentioned procedure, known triazole compounds **3a-3g**, **4a**, and **13a-13g** were prepared in good-to-excellent yields.

2,6-Bis((1*H***-1,2,3-triazol-1-yl)methyl)pyridine (24 a)**: M.p. 65–68 °C; $R_{\rm f}$ = 0.57 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.65–7.54 (m, 5H), 7.02 (d, *J*=7.6 Hz, 2H), 5.57 ppm (s, 4H); ¹³C NMR (101 MHz, CDCl₃): δ = 154.6, 138.6, 134.1, 124.5, 121.7, 54.9 ppm; IR (KBr): $\tilde{\nu}$ =1591, 1454, 1217, 1087, 1028, 800, 765, 690 cm⁻¹; MS (EI): m/z (%): 242 (100) [*M*+1]⁺, 214 (19), 186 (14), 173 (8), 145 (16); elemental analysis calcd (%) for C₁₁H₁₁N₇: C 54.76, H 4.60, N 40.64; found: C 54.63, H 4.68, N 40.52.

Diethyl-2,2'-(1,1'-(pyridine-2,6-diylbis(methylene))bis(1H-1,2,3-triazole-4,1-diyl)) diacetate (24b): $R_{\rm f}$ =0.56 (EtOAc); ¹H NMR (400 MHz, CDCl₃): δ =7.72 (s, 2H), 7.66 (t, *J*=8.0 Hz, 1H), 7.11 (d, *J*=7.6 Hz, 2H), 5.59 (s, 4H), 5.17 (s, 4H), 2.28 (q, *J*=7.6 Hz, 4H), 1.06 ppm (t, *J*=7.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ =173.7, 154.3, 142.7, 138.4, 124.7, 121.5, 57.1, 54.6, 26.9, 8.60 ppm; IR (neat): $\tilde{\nu}$ =2982, 1738, 1462, 1182, 1051, 781 cm⁻¹; MS (EI): m/z (%): 414 (45) [*M*+1]⁺, 436 (100) [*M*+Na]⁺; elemental analysis calcd (%) for C₁₉H₂₃N₇O₄: C 55.20, H 5.61, N 23.72; found: C 55.36, H 5.65, N 23.65.

General procedure for the synthesis of compounds 5a–11: A mixture of 98% sulfuric acid (15 mL) and 70% nitric acid (10 mL) was added to compound 3 (12 mmol) at 0°C and the reaction was carried out under the respective conditions shown in the Table 2. Upon completion, the reaction mixture was cooled by the addition of ice and neutralized with a saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with the minimum amount of EtOAc (3×20 mL). The combined extracts were washed with water (2×20 mL) and brine (25 mL) and dried over Na₂SO₄. The solvent was filtered off and evaporated under vacuum. The crude residue was purified by column chromatography on silica gel to afford the desired nitration products in good overall yields. A similar procedure was adopted for the nitration reactions that were carried out with a mixture of 95% nitric acid and 98% sulfuric acid.

1-(2,4-Dinitrobenzyl)-4-nitro-1H-1,2,3-triazole (5a): 0.58 g, 15% Yield; colorless solid; m.p. 195°C; DTA=256°C (exotherm); $R_{\rm f}$ =0.60 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =9.38 (s, 1 H), 8.84 (s, 1 H), 8.52 (d, *J*=8.0 Hz, 1 H), 7.50 (d, *J*=8.8 Hz, 1 H), 6.22 ppm (s, 2 H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =153.5, 143.2, 134.9, 130.9, 124.1, 57.6 ppm; IR (KBr): $\tilde{\nu}$ =3412, 3092, 1518, 1342, 1086, 1047, 829, 723 cm⁻¹; MS (EI): *m/z* (%): 295 (100) [*M*+1]⁺, 282 (6), 250 (60), 231 (14), 181 (4), 73 (48); elemental analysis calcd (%) for C₉H₆N₆O₆: C 36.74, H 2.06, N 28.57; found: C 36.85, H 2.01, N 28.64.

1-(2,4-Dinitrobenzyl)-1H-1,2,3-triazole (6a): 1.23 g, 39% Yield; colorless solid; m.p. 152°C; DTA = 220°C (exotherm); R_f =0.28 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.82 (d, J=2.4 Hz, 1H), 8.52 (dd, J=2.4, 8.8 Hz, 1H), 8.23 (s, 1H), 7.85 (s, 1H), 7.11 (d, J=8.8 Hz, 1H), 6.14 ppm (s, 2H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =147.8, 147.6, 138.4, 138.3, 134.3, 131.6, 131.5, 128.8, 126.6, 120.8, 50.0 ppm; IR (KBr): $\tilde{\nu}$ =3132, 1608, 1535, 1346, 1221, 1070, 839, 729 cm⁻¹; MS (EI): m/z (%): 250 (100) [M+1]⁺, 195 (3), 181 (3); elemental analysis calcd (%) for C₉H₇N₅O₄: C 43.38, H 2.83, N 28.11; found: C 43.32, H 2.85, N 28.26.

1-(3,5-Dinitrobenzyl)-1H-1,2,3-triazole (7a): 0.62 g, 20% Yield; colorless solid; m.p. 131 °C; DTA = 312 °C (exotherm); $R_{\rm f}$ =0.20 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.78 (s, 1 H), 8.59 (s, 2 H), 8.33 (s, 1 H), 7.81 (s, 1 H), 5.95 ppm (s, 2 H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =148.7, 140.6, 134.3, 129.1, 126.1, 118.8, 51.3 ppm; IR (KBr): $\tilde{\nu}$ =3140, 3076, 1547, 1346, 1072, 929, 800, 729 cm⁻¹; MS (EI): *m/z* (%): 250 (100) [*M*+1]⁺, 234 (5), 220 (3), 177 (5), 121 (3), 89 (9); elemental analysis calcd (%) for C₉H₇N₅O₄: C 43.38, H 2.83, N 28.11; found: C 43.51, H 2.88, N 28.07.

1-(3,4-Dinitrobenzyl)-1H-1,2,3-triazole (8a): 0.31 g, 9% Yield; yellow semi-solid; m.p. 88°C; DTA=215°C (exotherm); $R_{\rm f}$ =0.10 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.30 (s, 1H), 8.23 (d, J=8.4 Hz, 1H), 8.18 (s, 1H), 7.81 (s, 1H), 7.77 (d, J=8.4 Hz, 1H), 5.89 ppm (s, 2H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =143.8, 142.5, 141.8, 134.3, 133.9, 126.7, 126.1, 125.3, 51.5 ppm; IR (KBr): $\tilde{\nu}$ =2928, 1541, 1369, 1219, 1026, 846, 804 cm⁻¹; MS (EI): m/z (%): 250 (100)

 $[M+1]^+$, 202 (19), 192 (3), 172 (5), 159 (3); elemental analysis calcd (%) for $C_9H_7N_5O_4$: C 43.38, H 2.83, N 28.11; found: C 43.45, H 2.81, N 28.05.

1-(4-Methoxy-3,5-dinitrobenzyl)-1*H***-1,2,3-triazole (9)**: 1.12 g, 71 % Yield; yellow solid; m.p. 90 °C; DTA =170 °C (exotherm); $R_{\rm f}$ =0.51 (*n*-hexane/EtOAc, 1:1) ¹H NMR (400 MHZ, [D₆]DMSO): δ =7.98 (s, 2H), 7.79 (s, 1H), 7.72 (s, 1H), 5.69 (s, 2H), 3.98 ppm (s, 3H); ¹³C NMR (400 MHz, [D₆]DMSO): δ =147.6, 145.3, 134.6, 131.9, 128.6, 124.4, 64.9, 51.7 ppm; IR (KBr): $\tilde{\nu}$ =3113, 1537, 1348, 1269, 1082, 979, 717 cm⁻¹; MS (EI): *m/z* (%): 280 (100) [*M*+1]⁺, 211 (45), 102 (28), 70 (26); elemental analysis calcd (%) for C₁₀H₉N₅O₅: C 43.02, H 3.25, N 25.08; found: C 43.15, H 3.31, N 25.19.

1-(4-Methoxy-3,5-dinitrobenzyl)-4-nitro-1H-1,2,3-triazole (10): 1.02 g, 75 % Yield; yellow solid; DTA = 237 °C (exotherm); R_f =0.71 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.96 (s, 1H), 8.84 (s, 1H), 8.80 (s, 1H), 5.88 (s, 2H), 4.28 ppm (s, 3H); ¹³C NMR (101 MHz, [D₆]DMSO): δ = 160.2, 151.3, 138.5, 132.1, 131.8, 127.5, 124.9, 123.2, 50.7, 46.9 ppm; IR (KBr): $\bar{\nu}$ = 3111, 1610, 1591, 1531, 1352, 1074, 792, 688 cm⁻¹; MS (EI): m/z (%): 325 (100) $[M+1]^+$, 116 (22), 102 (20), 84 (38), 70 (22); elemental analysis calcd (%) for C₁₀H₈N₆O₇: C 37.05, H 2.49, N 25.92; found: C 37.12, H 2.55, N 25.86.

1-(2-Methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (11): 0.21 g, 48 % Yield; yellow solid; DTA=209 °C (exotherm); $R_{\rm f}$ =0.67 (*n*-hexane/EtOAc, 3:7); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.78 (d, J=2.4 Hz, 1H), 8.36 (d, J=2.0 Hz, 1H), 8.26 (s, 1H), 7.79 (s, 1H), 5.85 (s, 2H), 3.88 ppm (s, 3H); ¹³C NMR(101 MHz, [D₆]DMSO): δ =156.2, 142.9, 142.6, 134.1, 134.0, 129.4, 126.2, 122.1, 63.7, 47.7 ppm; IR (neat): $\tilde{\nu}$ =1608, 1539, 1481,1346, 1265, 1091, 985 cm⁻¹; MS (EI): m/z (%): 281 (19) $[M+1]^+$, 280 (100) $[M]^+$, 235 (7), 207 (8), 162 (5), 116 (9), 84 (16); elemental analysis calcd (%) for C₁₀H₉N₅O₅: C 43.02, H 3.25, N 25.08; found: C 43.11, H 3.19, N 25.15.

General procedure for the synthesis of compounds 15–22: A mixture of 98% sulfuric acid (15 mL) and 95% nitric acid (10 mL) was added to compound 13 (12 mmol) at 0°C and the reaction was carried out under the respective conditions shown in the Table 4. Upon completion, the reaction mixture was cooled by the addition of ice and neutralized with a saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with the minimum amount of EtOAc (3×20 mL). The combined extracts were washed with water (2×20 mL) and brine (25 mL) and dried over Na₂SO₄. The solvent was filtered off and evaporated under vacuum. The crude residue was purified by column chromatography on silica gel to afford the desired nitration products in good overall yields.

1-(3,4-Dinitrophenyl)-1H-1,2,3-triazole (17): 0.19 g, 18% Yield; brown solid; m.p. 125 °C; DTA = 268 °C (exotherm); $R_{\rm f}$ =0.48 (*n*-hexane/EtOAc, 2:1); ¹H NMR (400 MHz, CDCl₃): δ =9.10 (br s, 1H), 9.03 (br d, J= 4.0 Hz, 2H), 8.31 (br s, 1H), 7.99 ppm (br s, 1H); ¹³C NMR (101 MHz, CDCl₃): δ =149.3, 138.6, 135.8, 121.9, 120.1, 117.9 ppm; IR (KBr): $\tilde{\nu}$ = 3084, 2961, 1635, 1558, 1261, 1024, 798 cm⁻¹; MS (EI): m/z (%): 234 (38) [M-1]⁺, 228 (31), 206 (100), 183 (16), 87 (7); elemental analysis calcd (%) for C₈H₅N₅O₄: C 40.86, H 2.14, N 29.78; found: C 40.75, H 2.18, N 29.71.

1-(4-Methoxy-3,5-dinitrophenyl)-1H-1,2,3-triazole (19): 1.10 g, 85% Yield; yellow solid; DTA=319°C (exotherm); R_t =0.57 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =9.03 (s, 1H), 8.91 (s, 2H), 8.06 (s, 1H), 4.00 ppm (s, 3H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =146.1, 145.4, 135.6, 132.2, 124.5, 121.3, 65.1 ppm; IR (KBr): $\tilde{\nu}$ =3157, 1541, 1346, 1271, 1053, 783 cm⁻¹; MS (EI): *m*/*z* (%): 266 (21) [*M*+1]⁺, 265 (100) [*M*], 250 (39), 236 (26), 221 (13), 205 (5); elemental analysis calcd (%) for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41; found: C 40.82, H 2.61, N 26.31.

1-(3-Methoxy-2,6-dinitrophenyl)-1H-1,2,3-triazole (20): 0.49 g, 33 % Yield; yellow solid; m.p. 168 °C; DTA = 221 °C (exotherm); R_f =0.65 (*n*-hexane/EtOAc, 4:6); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.68 (br s, 1H), 8.63 (d, J=9.6 Hz, 1H), 8.01 (s, 1H), 7.86 (d, J=9.6 Hz, 1H), 4.13 ppm (s, 3H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =155.2, 137.7, 137.0, 134.6, 130.2, 128.9, 124.9, 116.7, 59.0 ppm; IR (KBr): $\tilde{\nu}$ =3124, 1614, 1342, 1078, 989, 794, 652 cm⁻¹; MS (EI): *m/z* (%): 266 (58) [*M*+1]⁺, 242 (26), 226 (83), 210 (100), 194 (91), 163 (72), 149 (85); elemental anal-

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ysis calcd (%) for $C_9H_7N_5O_5{:}$ C 40.76, H 2.66, N 26.41; found: C 40.71, H 2.59, N 26.35.

1-(3-Methoxy-2,4-Dinitrophenyl)-1H-1,2,3-triazole (21): 0.69 g, 46 % Yield; yellow solid; m.p. 200 °C; DTA = 230 °C (exotherm); $R_{\rm f}$ =0.40 (*n*-hexane/EtOAc, 7:3); ¹H NMR (400 MHz, CDCl₃): δ =8.88 (s, 1H), 8.77 (br s, 1H), 8.05 (br s, 1H), 7.87 (s, 1H), 4.11 ppm (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ =155.9, 138.3, 136.0, 134.7, 134.3, 127.3, 124.1, 114.4, 59.1 ppm; IR (KBr): $\tilde{\nu}$ =3097, 1620, 1531, 1350, 1232, 1072, 806 cm⁻¹; MS (EI): m/z (%): 266 (68) [*M*+1]⁺, 242 (45), 226 (57), 210 (72), 194 (92), 164 (100), 149 (72); elemental analysis calcd (%) for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41; found: C 40.85, H 2.63, N 26.35.

1-(2-Methoxy-3,5-dinitrophenyl)-1H-1,2,3-triazole (22): 1.24 g, 82 % Yield; yellow solid; DTA=152 °C (exotherm); $R_{\rm f}$ =0.57 (*n*-hexane/EtOAc, 1:1); ¹H NMR (400 MHz, CDCl₃): δ =8.98–8.95 (m, 1 H), 8.80 (br s, 1 H), 8.69 (s, 1 H), 8.07 (s, 1 H), 3.63 ppm (s, 3 H); ¹³C NMR (101 MHz, CDCl₃): δ =151.5, 144.0, 142.4, 134.8, 132.1, 127.8, 126.1, 125.7, 121.9, 63.4 ppm; IR (KBr): $\tilde{\nu}$ =3155, 1547, 1350, 1261, 1049, 978, 733 cm⁻¹; MS (EI): m/z (%): 266 (58) $[M+1]^+$, 223 (23), 129 (56), 116 (12), 97 (100), 74 (6); elemental analysis calcd (%) for C₉H₇N₅O₅: C 40.76, H 2.66, N 26.41; found: C 40.65, H 2.69, N 26.52.

General procedure for the formation of the N-oxides: A solution of the bistriazole-containing pyridine (24) (1.0 equiv) and *m*-chloroperbenzoic acid (mCPBA, 1.5 equiv) in CHCl₃ (2 mL for 1 mmol) was placed in a 10 mL screw-capped vial. The vial was sealed and the mixture was stirred at 70 °C for 48 h. Upon completion of the reaction, the mixture was cooled and dissolved in water. The organic layer was separated and the aqueous layer was extracted with Et₂O (twice). The combined extracts were washed with water and brine and dried over Na₂SO₄. The solvent was filtered off and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel. The desired *N*-oxide products were obtained in good yields.

2,6-Bis((1*H***-1,2,3-triazol-1-yl)methyl)pyridine 1-oxide (25 a):** 0.08 g, 35% Yield; colorless solid; m.p. 62°C; DTA=228°C (exotherm); $R_{\rm f}$ =0.68 (CHCl₃/MeOH, 9:1); ¹H NMR (400 MHz, CDCl₃): δ =7.94 (s, 2H), 7.78 (s, 2H), 7.27 (br s, 1H), 7.12 (d, *J*=8.0 Hz, 2H), 5.87 ppm (s, 4H); ¹³C NMR (101 MHz, CDCl₃): δ =145.8, 134.2, 125.9, 125.6, 125.4, 48.4 ppm; IR (KBr): $\tilde{\nu}$ =2852, 1693, 1417, 1350, 1217, 1028, 808 cm⁻¹; MS (EI): *m/z* (%): 258 (100) [*M*+1]⁺, 242 (16), 230 (14), 174 (11), 145 (8); elemental analysis calcd (%) for C₁₁H₁₁N₇O₅: C 51.36, H 4.31, N 38.11; found: C 51.28, H 4.26, N 38.29.

2,6-Bis((4-(nitromethyl)-1*H***-1,2,3-triazol-1-yl)methyl)pyridine 1-oxide (25b):** 0.04 g, 41 % Yield; pale-yellow solid; m.p. 110 °C; DTA = 142 °C (exotherm); R_f =0.72 (CHCl₃/MeOH, 9:1); ¹H NMR (400 MHz, [D₆]DMSO): δ =8.14 (s, 2H), 7.38–7.27 (m, 3H), 5.79 (s, 4H), 5.58 ppm (s, 4H); ¹³C NMR (101 MHz, [D₆]DMSO): δ =145.0, 139.6, 126.8, 126.7, 126.0, 65.6, 48.8 ppm; IR (KBr): $\tilde{\nu}$ =2924, 1724, 1641, 1385, 1261, 1111, 1022, 850, 796 cm⁻¹; MS (EI): m/z (%): 375 (100) [*M*]⁺, 374 (100) [*M*-1]⁺, 356 (13), 343 (5), 327 (24); elemental analysis calcd (%) for C₁₃H₁₃N₉O₅: C 41.60, H 3.49, N 33.59; found: C 41.75, H 3.56, N 33.41.

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