Received: 20 December 2023 | Revised: 15 February 2024 | Accepted: 4 March 2024

DOI: 10.1002/jhet.4803

RESEARCH ARTICLE

JOURNAL OF HETEROCYCLIC CHEMISTRY WILEY

N-Azidoethyl azoles through *N*-alkylation under highly harmonized reaction conditions: Synthesis, characterization, and complexation as energetic coordination compounds

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Funding information
Office of Naval Research, Grant/Award Number: ONR N00014-19-1-2078; Strategic Environmental Research and Development Program, Grant/Award Number: W912HQ19C0033; Ludwig Maximilian University (LMU); EMTO GmbH

Abstract

Organic azides are universally important in many areas of chemistry, particularly in organic synthesis. The availability of these azides often depends on specific transfer reagents and reaction conditions, or only work with certain substrates. Customizable transfer reagents offer a safe and direct pathway to desired compounds, thereby increasing the availability of *N*-alkyl-azides. In an effort to streamline the synthesis and broaden the scope of *N*-azidoethyl-containing molecules, three different versatile azidoethyl transfer reagents were synthesized and a uniform reaction protocol with azoles as substrates, including imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, and tetrazole was established. The resulting azidoethyl-azoles were further used as ligands for energetic coordination compounds in an effort to create new lead-free primary explosives. A comprehensive characterization of the transfer reagents, the azidoethyl-containing products, and energetic coordination compounds was conducted using multinuclear nuclear magnetic resonance (NMR), elemental analysis, mass spectrometry, and infrared spectroscopy (IR). Furthermore, their thermal stability and sensitivity toward friction and impact were determined as well as the detonation properties were calculated by using the EXPLO5 code.

1 | INTRODUCTION

Parts of this work were published on the NTREM 2023 conference [1,2]. Azides have been shown to be indispensable since the discovery of organic azides by Griess [3] and the first isolation of the azide anion by Curtius [4]. A large amount of applications have been found for azide-containing molecules, which are now essential in a wide range of applications, including biology [5], chemistry [6], medicine [7, 8], and materials science [9]. Azides can be used in substitution- and addition-reactions as well as for functional group

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This paper is dedicated to Prof. i.R. Dr. Ingo-Peter Lorenz on the occasion of his 80th birthday.

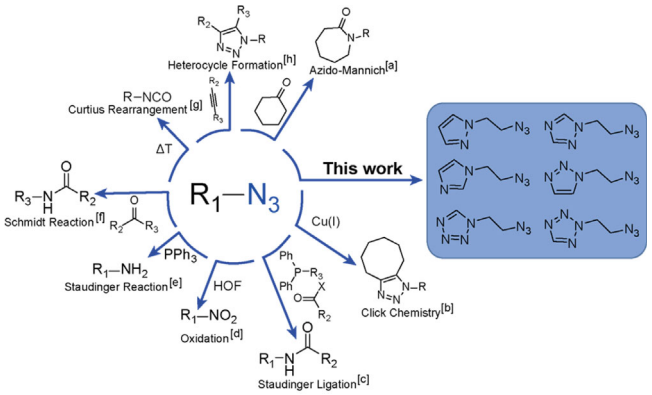


FIGURE 1 The versatility of organic azides in synthesis [6, 10–19].

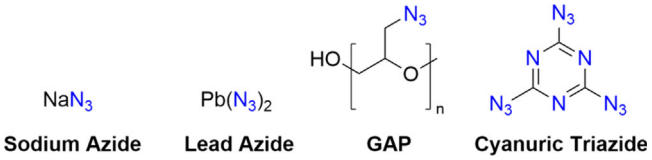
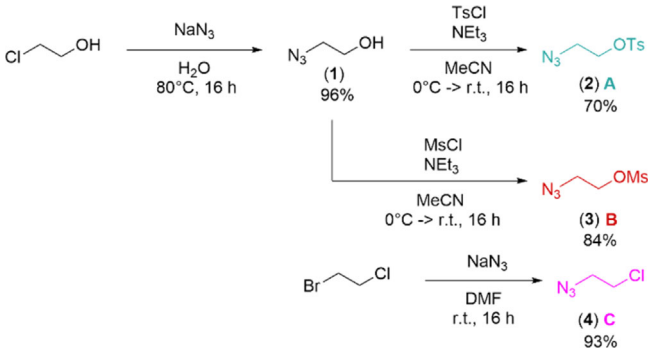


FIGURE 2 Examples for azides with use as energetic materials [23, 25].

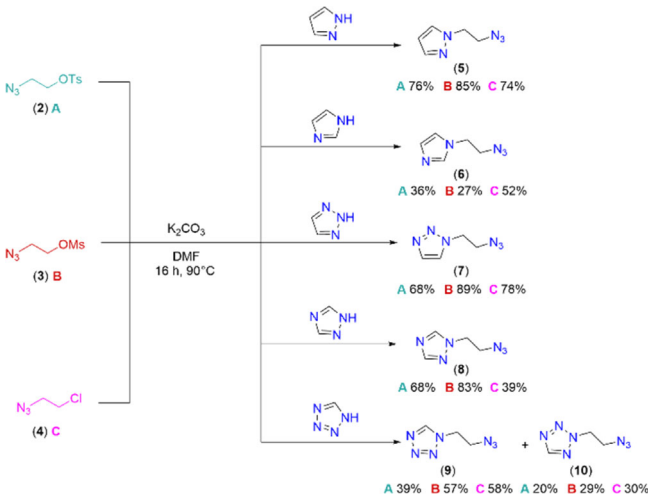
transformations as either targets or starting materials. From these compounds, a variety of functional groups can be obtained including otherwise difficult to access reactive species such as nitrenes and nitrenium ions, as shown in Figure 1 [6, 10–13]. Possible azide reactions can be seen in Figure 1 and include the azido-Mannich reaction [14], Staudinger ligation [15] as well as the Staudinger reaction [16], direct oxidation to nitro derivatives [17], the Schmidt reaction [18], and starting from acyl azides the Curtius rearrangement [19]. In recent years, the use as building blocks in traditional organic chemistry for cycloadditions of nitrogen rich azoles such as tetrazole or triazole has gained a lot of attraction. The concept of click chemistry, introduced by Sharpless, refers to a set of reactions characterized by their reliability, ease of use, low production of by-products, and ability to generate high yields of often nitrogen-rich products under mild conditions [20, 21].

In the field of applied energetic materials, azides also have a well-established history (Figure 2). Sodium azide, the most common representative, has the advantage of being a cheap and easy to handle source of the azide anion for synthesis but is also used itself as gas generating agent airbags [22]. Lead azide is still widely used as primary explosive, cyanuric triazide is easily prepared from cyanuric chloride and acts as initiator, and glycidyl azide polymer (GAP) is an energetic polymer that has use as an energetic binder [23–25].

wOther compounds containing the azidomethyl functionality, like in GAP, have already been of research interest in recent years as possible energetic plasticizers [26], primary explosives [27, 28], and melt-castable alternatives to trinitrotoluene [29]. However, the presence of the azidomethyl group can induce heightened sensitivity to mechanical stimuli, posing challenges for practical applications in certain scenarios. Lengthening the alkyl chain from methyl to ethyl can help to make the compounds more insensitive, while still profiting from the high heat of formation, that an azido group contributes [12]. Also, when comparing 1-azidomethyl-tetrazole with 1-azidoethyl-tetrazole (1-AET) a decrease in melting temperature can be observed, as the ethyl derivative is a liquid at room temperature compared to the *N*-azidomethyl derivative which melts at 54°C [27, 30]. Extending the alkyl chain length in the right system can result in achieving a melting point within the suitable range for melt castable energetic materials [26]. Given the significance of the azido functionality in organic synthesis in general and more specifically in the field of energetic materials, a reliable method of introducing the functional group is essential. The most important way of introducing azides is via nucleophilic substitution from halides, sulfonates, sulfites, or groups of similar properties [31]. A straightforward introduction of the azide functionality along with an alkyl chain can be accomplished with the use of an azidoalkyl transfer [32]. This effectively reduces the number of reaction steps required to obtain new compounds, while providing the safety benefit of adding the explosophoric group at the end of the synthesis route. *N*-alkylation has been performed under many different reaction conditions and with many different bases, but the lack of uniform reaction conditions hinders the development of new compounds. In some cases, alkylation is also preferred because of the accessibility of desired products. The aforementioned 1-AET can be selectively obtained from 2-azidoethylamine, however 2-(2-azidoethyl)-tetrazole (2-AET) is not available through this reaction route [30]. Alkyl transfer offers a practical method of obtaining previously uncharacterized but promising compounds such as 2-AET. Transfer reactions in general are of considerable importance in chemical synthesis due to the ability to efficiently introduce alkyl groups onto diverse substrates [33, 34]. During the development of these unified conditions, the goal of extending the reaction protocol to higher substituted azoles was set and already achieved for several nitropyrazole derivatives [35]. This facile route allows access to a multitude of new *N*-azidoethyl azoles, which can then be used as neat compounds or further used as ligands for energetic coordination compounds (ECCs). This opens the possibility to slightly alter their coordination sphere, leading to homologous ECCs with different



SCHEME 1 Synthesis of the azidoethyl transfer reagents **2**–**4**.



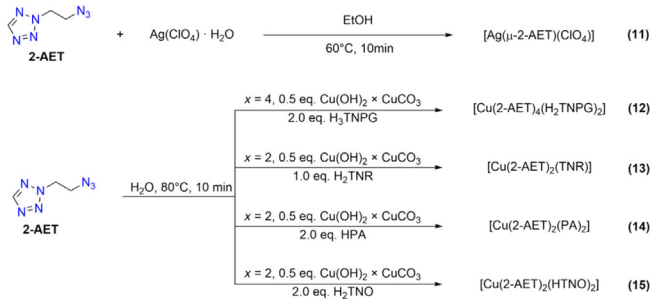
SCHEME 2 Synthesis of the azideoethyl containing azoles **5**–**10** under universal reaction conditions using the transfer reagents **2**–**4**.

mechanical properties [36, 37]. Recent publications have underlined their potential to serve as nontoxic alternatives for lead azide, yet an ideal alternative is still to be found [38, 39].

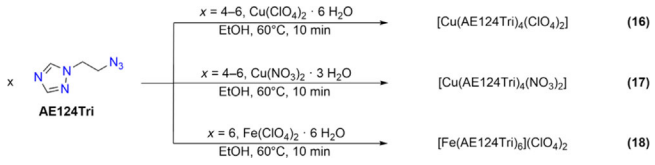
In this paper, we present a simple synthetic strategy to obtain the *N*-azidoethyl moiety via a standardized reaction protocol that is applicable to all common *N*-unsubstituted azoles and can be extended to higher substituted heterocycles as required. The primary objective of this work was to establish a versatile reaction protocol, thereby improving the feasibility of screening for novel compounds. In addition, some of the promising new compounds were tested as ligands in ECCs with different metal cations and anions as well as co-ligands, in an effort to create nontoxic, lead-free energetic materials as new primary explosives.

2 | RESULTS AND DISCUSSION

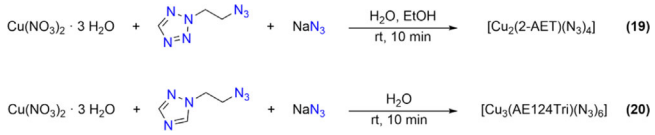
The azidoethyl transfer reagents 2-azidoethyl-4-methyl benzenesulfonate (**2**), 2-azidoethyl-methylsulfonate (**3**),



SCHEME 3 Synthesis of energetic coordination compounds **11**–**15** with 2-AET as ligand.



SCHEME 4 Energetic coordination compounds **16**–**18** obtained by combination of the AE124Tri ligand with copper(II) perchlorate or nitrate and iron(II) perchlorate.



SCHEME 5 Synthesis of the copper(II) azides **19** and **20**.

and 1-azido-2-chloroethane (**4**) were prepared according to modified literature and reacted with several unsubstituted azoles to yield the corresponding azidoethyl derivatives [40, 41]. The synthesis can be divided into three separate parts: First, the synthesis of the transfer reagents **2**–**4** (Scheme 1). Second, the application of the transfer reagents on unsubstituted azoles to obtain compounds **5**–**10** (Scheme 2). Third, the synthesis of ECCs using compounds **8**–**10** as ligands (Schemes 3–5).

The starting material for transfer reagents **2** and **3**, 2-azidoethan-1-ol (**1**), was synthesized based on a modified literature procedure [41]. Commercially available 2-chloroethanol was treated with sodium azide in water at 80°C to perform a chloride-azide exchange reaction and yield the corresponding azidoethanol **1** in excellent yields. The transfer reagents **2** and **3** were prepared according to the literature [40, 41]. The alcohol functionality was reacted with *p*-toluenesulfonyl chloride or methanesulfonyl chloride, resulting in the tosylation or mesylation of the respective hydroxy group, yielding compounds **2** and **3** as transfer reagents. Compound **4** was obtained similarly to azidoethanol by bromide to azide exchange reaction of 1-bromo-2-chloroethanol in

TABLE 1 Reaction conditions investigated for the transfer reaction.

Azole	*T* (°C)	*t* (h)	Base	Solvent	Yield (%)
Pyrazole	90	16	K_2CO_3	DMF	85[a]
Pyrazole	100	16	K_2CO_3	DMF	88[a]
Pyrazole	90	16	$KHCO_3$	DMF	79[a]
Pyrazole	90	16	Cs_2CO_3	DMF	np[a]
Pyrazole	90	4	K_2CO_3	DMF	11[a]
Pyrazole	90	16	K_2CO_3	MeCN	np[a]
Pyrazole	90	16	K_2CO_3	DMF/H_2O	np[a]
Imidazole	90	16	K_2CO_3	DMF	52[b]
Imidazole	70	16	K_2CO_3	DMF	63[b]
1,2,3-Triazole	90	16	K_2CO_3	DMF	89[a]
1,2,3-Triazole	70	16	K_2CO_3	DMF	58[a]
1,2,4-Triazole	90	16	K_2CO_3	DMF	83[a]
1,2,4-Triazole	70	16	K_2CO_3	DMF	64[a]
Tetrazole[c]	90	16	K_2CO_3	DMF	62[b]
Tetrazole[c]	90	16	NEt_3	DMF	53[b]
Tetrazole[c]	90	16	LiOH	DMF	52[b]
Tetrazole[c]	80	16	K_2CO_3	DMF	np[b]

[a]2-Azidoethyl-methylsulfonate (**3**) as transfer reagent.
[b]2-Azidoethyl-4-methylbenzenesulfonate (**2**) as transfer reagent.
[c]Overall yield of both isomers before column chromatography determined through NMR spectroscopy.

dimethylformamide (DMF) at room temperature. The following azidoethyl transfer reactions were carried out in a standardized reaction protocol. The unsubstituted azoles were dissolved in DMF and reacted with the respective transfer reagents **2**–**4** with 1.5 eq potassium carbonate as base at 90°C for 16 h.

Through this reaction, the products 1-(2-azidoethyl)-pyrazole (**5**) (AEPy), 1-(2-azidoethyl)-imidazole (**6**) (AEIm), 1-(2-azidoethyl)-1,2,3-triazole (**7**) (AE123Tri), 1-(2-azidoethyl)-1,2,4-triazole (**8**) (AE124Tri), and 1-(2-azidoethyl)-tetrazole (**9**) (1-AET) as well as 2-(2-azidoethyl)-tetrazole (2-AET) (**10**) were obtained with the use of three different transfer reagents as depicted in Scheme 2. No other isomer for both triazole derivatives **7** and **8** were observed. One factor at a time optimization reactions were carried out to test different bases, solvent systems, and reaction temperatures and times. In order to ensure the viability of this reaction for a wide range of substrates, the goal of the optimization was identifying reaction conditions that can ensure successful reaction with any commonly used azole. For optimization of yield and efficiency of single reactions of interest, a more detailed approach like using design of experiment is recommended [42]. The results can be seen in Table 1. Pyrazole and tetrazole were chosen as substrates for base and solvent optimization, the temperatures were tested individually for each heterocycle. K_2CO_3, $KHCO_3$, Cs_2CO_3, NEt_3, and LiOH were tested as bases with K_2CO_3 giving the best results. DMF and a water-DMF mixture as well as acetonitrile were investigated as solvent systems, but DMF resulted less side product formation and less failed reactions. Reaction temperatures were ranged from 70 to 100°C. For optimized yields 90°C was confirmed as the best temperature, but it is worth noting that different temperatures gave better yields for certain heterocycles, such as 70°C for imidazole.

It has been previously reported that 1-AET can act as a ligand in ECCs with copper, silver, zinc, and iron as central metal ions and with common anions like nitrate or perchlorate [27]. This allows that the energetic properties of the ligand itself, as well as its complexation behavior, to be studied and compared with 1-AET. As seen in Scheme 3, 2-AET coordinated to silver(I) perchlorate and the nitroaromatic copper(II) salts in the expected stoichiometry, similar to 1-AET [30]. While [Ag(μ-2-AET)(ClO_4)] was obtained by combining ethanolic solutions of the ligand and silver perchlorate, the nitroaromatic ECCs were prepared by stirring a suspension of the respective neutral nitrophenol derivative with basic copper carbonate in water until a clear solution was obtained. The addition of 2-AET, followed by stirring at elevated temperatures allowed the formation of the ECCs, which precipitated upon cooling to room temperature until the yield stagnated within few days.

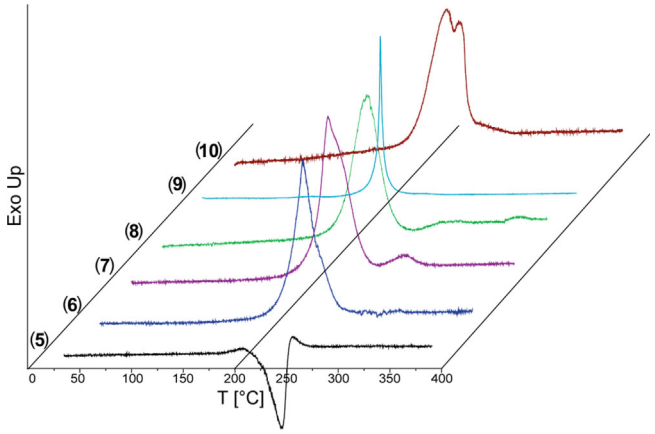


FIGURE 3 DTA plots of compounds **5**–**10** with a heating rate of 5°C min^{-1}.

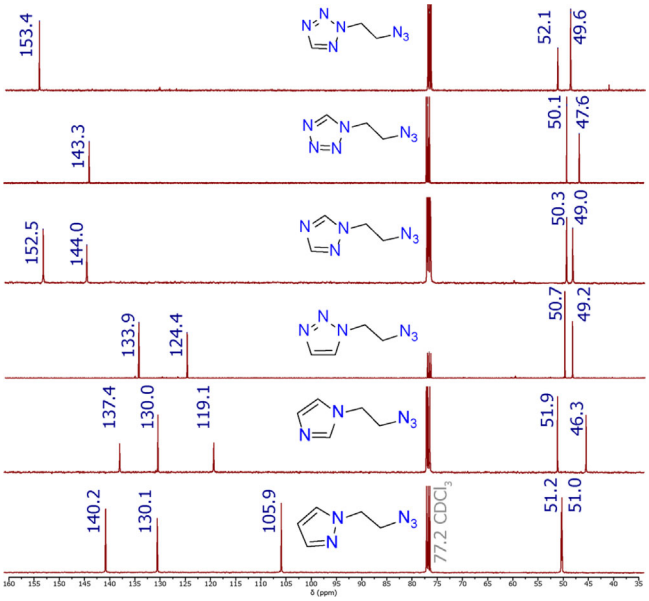


FIGURE 4 ^{13}C NMR spectra of compounds **5**–**10** measured in $CDCl_3$.

The reaction scheme for the formation of the ECCs with the AE124Tri ligand can be seen in Scheme 4. This ligand allows the formation of ECCs with an improved ratio of ligand to anion, and therefore a better trade-off between fuel and oxidizing agent, like in the cases of [Cu(AE124Tri)$_4$(ClO$_4$)$_2$] and [Cu(AE124Tri)$_4$(NO$_3$)$_2$].

A potential use for ECCs is their application as successors of lead azide and lead styphnate, which are to be banned in the EU for civil application in detonators [43, 44]. If the exemption, which expires in April 2026, is not extended, this could lead to a serious demand for alternatives. ECCs based on copper azide might be one possible alternative for such an application, as existing plants could most likely be used with only minor adjustments. Therefore, [Cu$_2$(2-AET)(N$_3$)$_4$] (**19**) and [Cu$_3$(AE124Tri)$_2$(N$_3$)$_6$] (**20**) were synthesized and evaluated as potential candidates, as seen in Scheme 5. Their synthesis was conducted by straightforward precipitation from aqueous solutions of copper(II) nitrate trihydrate and ligand by addition of sodium azide. In the case of **19**, a small amount of ethanol had to be added to improve the solubility of the ligand. Attempts without the addition of EtOH lead to the precipitation of neat Cu(N$_3$)$_2$, which represents an even more serious safety thread than **19** [45].

2.1 | Characterization

Differential thermal analysis (DTA) of the compounds was determined with an OZM Research DTA 552-Ex instrument with a heating rate of 5°C min^{-1} in open test tubes. All compounds show thermal stability in the expected range of ~200°C with the lowest thermally stable being the 1-AET (**9**) with an onset of decomposition of 193°C and the highest thermal stability for 1-(2-azidoethyl)-1,2,3-triazole (**7**) 214°C. An exception is AEPy (**5**) that evaporates at 216°C. Increasing the heating rate to 10°C min^{-1} allows to indentify the decomposition temperature at 225°C. The thermal behavior can be seen in Figure 3.

To screen new molecules efficiently, highly specific characterization methods are required. Azides show a strong asymmetric vibration resulting in a vibrational band in the region of 2100 cm^{-1}, which can be used to confirm a newly introduced azide group [46].

Additionally, ^1H and ^{13}C NMR spectroscopy are particularly useful to see if the reaction was successful (Figure 4). The resonances can be divided into two groups. The newly introduced ethyl groups were assigned upfield and the ring positions shifted downfield. The shifts of the CH_2 groups belonging to the ethyl functionality range from 3.63 to 4.93 ppm for ^1H NMR and from 46.3 to 51.9 ppm in the ^{13}C NMR. The second set of resonances, shifted downfield, range from 6.22 to 9.44 ppm for the ^1H-NMR and 105.9 to 153.4 ppm for the carbon atoms in the ^{13}C-NMR. This allows easy evaluation as the CH_2-resonances are clearly distinguishable from the starting materials and a slight shift in the aromatic positions indicates a successful alkylation for the ring signals.

2.2 | Physicochemical properties

The presented azidoethyl azoles **5**–**10** can be classified as potential energetic materials and were therefore investigated for their energetic properties. As expected, products

TABLE 2 Physicochemical properties and EXPLO5 V7.01.01 calculation results of compounds **5**–**10**.

Compound	5	6	7	8	9	10
Formula	$C_5H_7N_5$	$C_5H_7N_5$	$C_4H_6N_6$	$C_4H_6N_6$	$C_3H_5N_7$	$C_3H_5N_7$
M (g mol^{-1})	137.15	137.15	138.13	138.13	139.12	139.12
IS (J)[a]	>40	>40	>40	>40	9	3
FS (N)[b]	>360	>360	>360	>360	>360	>360
ρ (g cm^{-3})[c]	1.08	1.18	1.21	1.22	1.25	1.26
N (%)[d]	51.07	51.07	60.8	60.8	70.5	70.5
T_{dec} (°C)[e]	216	210	214	197	193	201
$\Delta_f H°$ (kJ mol^{-1})[f]	420.9	383.7	510.8	442.9	592.8	568.6
EXPLO5 V7.01.01[g]						
$-\Delta_{Ex} U^0$ (kJ kg^{-1})[h]	3380	3141	3948	3495	4452	4292
T_{det} (K)[i]	2889	2070	2560	2359	2974	2889
P_{CJ} (GPa)[j]	7.1	8.5	10.8	10.4	13.2	13.1
V_{det} (m s^{-1})[k]	5311	5706	6217	6110	6677	6670

[a]Impact sensitivity (BAM drophammer [1 of 6]).
[b]Friction sensitivity (BAM friction tester [1 of 6]).
[c]Determined pycnometrically.
[d]Nitrogen content.
[e]Decomposition temperature; melting point (DTA; $\beta = 5°C\ min^{-1}$).
[f]Calculated enthalpy of formation.
[g]EXPLO5 Version V7.01.01 [51].
[h]Energy of explosion.
[i]Detonation temperature.
[j]Detonation pressure at Chapman–Jouguet point.
[k]Detonation velocity.

with adjacent nitrogens as in pyrazole and 1,2,3-triazole have a higher heat of formation than their respective isomers imidazole and 1,2,4-triazole [47, 48]. Due to the high influence of the density on the detonation parameters, 1-(2-azidoethyl)-imidazole (**6**) outperforms 1-(2-azidoethyl)-pyrazole (**5**) although the heat of formation is lower. Among the synthesized azoles, the tetrazole derivatives **9** and **10** show the highest values for detonation velocity, which can be attributed to their high heat of formation, density, and high nitrogen content. According to the "Recommendations on the Transport of Dangerous Goods," [49] all compounds are insensitive toward friction and only 1-AET (**9**) and 2-AET (**10**) show sensitivity toward impact. While 2-AET is more thermally stable (201–193°C), 1-AET shows a lower sensitivity toward impact (9–3 J). This trend has previously been observed for other 1-tetrazole and 2-tetrazole isomers, reinforcing the idea that tetrazole isomers have different advantages that can be used based on the needs for application [50] (Table 2).

Table 3 shows that all ECCs that carry the 2-AET ligand can be characterized as very sensitive toward impact. Except for compound **11** they are more sensitive toward friction compared to the respective ECC that contains the 1-AET ligand. It is of no surprise that ECCs that carry the AE124Tri ligand instead of 1-AET, are significantly less sensitive to mechanical stimuli due to the lower enthalpy of formation of the ligand, and therefore in sum, of the ECC [48]. Compounds **11** and **13** proved to undergo detonative behavior under the confined conditions of the hot needle test. Therefore, those two ECCs were selected for initiation experiments with pentaerythritol tetranitrate as main charge within self-assembled detonators that contain net explosive quantities of 250 mg.

The outcomes of the performance tests of compounds **11**–**20** can be found in Table 4. To test the performance of the ECCs as primary explosives in detonator setups, 200 mg of pentaerythriol tetranitrate (PETN) (<100 μm) were pressed in a copper shell (diameter: 7 mm, length: 88 mm), by lowering a weight of 8 kg on top. The shell was then placed on a copper witness plate with a thickness of 1 mm. Then 50 mg of the respective ECC was loosely filled on top of the PETN and a type A electric igniter was crimped to the shell. In the case of compound **11**, **19**, and **20**, positive initiation of the PETN, indicated by penetration of the witness plate (Figure 5), was feasible. The ignitability of colored compounds by laser was tested by pressing 25 mg of sample into a polycarbonate primer cap with a force of 1.5 kN. The surface was then

TABLE 3 Sensitivities of compounds **11**–**20** against external stimuli in comparison with literature-known analogs which carry the 1-AET ligand.

Compound	No.	Tendo[a] (°C)	Texo[b] (°C)	IS[c] (J)	FS[d] (N)	ESD[e] (mJ)	HP[f]	HN[g]
$[Ag(\mu\text{-}2\text{-}AET)(ClO_4)]$	**11**	151[h]	151[h]	<1	0.6	13	det.	det.
$[Ag(1\text{-}AET)](ClO_4)$ [30]		-	165	<1	0.6	65	det.	det.
$[Cu(2\text{-}AET)_4(H_2TNPG)_2]$	**12**	-	145	<1	54	250	def.	def.
$[Cu(1\text{-}AET)_4(H_2TNPG)_2]$ [30]		-	121	1.5	84	84	def.	def.
$[Cu(2\text{-}AET)_2(TNR)]$	**13**	151[h]	151[h]	<1	30	200	def.	det.
$[Cu(1\text{-}AET)_2(TNR)]$ [30]		-	177	<1	240	123	def.	def.
$[Cu(2\text{-}AET)_2(PA)_2]$	**14**	-	169	2	192	160	def.	dec.
$[Cu(1\text{-}AET)_2(PA)_2]$ [30]		-	183	3	252	226	def.	def.
$[Cu(2\text{-}AET)_2(HTNO)_2]$	**15**	-	141	<1	80	160	def.	def.
$[Cu(1\text{-}AET)_2(HTNO)_2]$ [52]		-	191	<1	>360	90	def.	dec.
$[Cu(AE124Tri)_4(ClO_4)_2]$	**16**	-	171	<1	108	50	def.	dec.
$[Cu(1\text{-}AET)_6](ClO_4)_2$[44]		135	158	<1	15	368	def.	det.
$[Cu(AE124Tri)_4(NO_3)_2]$	**17**	117, 153	179	35	>360	42	dec.	dec.
$[Cu(1\text{-}AET)_2(H_2O)(NO_3)_2]$ [30]		94, 121	152	10	108	840	def.	def.
$[Fe(AE124Tri)_6](ClO_4)_2$	**18**	128[h]	128[h]	7.5	120	160	def.	dec.
$[Fe(1\text{-}AET)_6](ClO_4)_2$[44]		-	151	3	3.75	65	det.	det.
$[Cu_2(2\text{-}AET)(N_3)_4]$	**19**	-	143	<1	<0.1	2.5	det.	det.
$[Cu_3(AE124Tri)_2(N_3)_6]$	**20**	-	112	<1	0.2	2.5	det.	det.
$[Cu(1\text{-}AET)(N_3)_2]$ [45]		-	131	<1	<0.1	1.1	det.	det.

[a]Onset temperature of endothermic event in the DTA (heating rate of 5°C min^{-1}), indicating a melting point of the compound.
[b]Onset of exothermic event in the DTA.
[c]Impact sensitivity (BAM drophammer [1 of 6]).
[d]Friction sensitivity (BAM friction tester [1 of 6]).
[e]Electrostatic discharge device (OZM XSpark10).
[f]Hot plate test (det.: detonation, def.: deflagration, dec.: decomposition).
[g]Hot needle test (det.: detonation, def.: deflagration, dec.: decomposition).
[h]Endo-to-exo-transition.

TABLE 4 Outcomes of the PETN and laser initiation experiments.

			Laser parameter[b]			
Compound	No.	PETN initiation[a]	7 A, 15 ms	7 A, 30 ms	8 A, 30 ms	10 A, 30 ms
$[Ag(\mu\text{-}2\text{-}AET)(ClO_4)]$	**11**	pos.	-	-	-	-
$[Cu(2\text{-}AET)_4(H_2TNPG)_2]$	**12**	-	-	-	neg.	det.
$[Cu(2\text{-}AET)_2(TNR)]$	**13**	neg.	-	-	neg.	det.
$[Cu(2\text{-}AET)_2(PA)_2]$	**14**	-	-	-	-	def.
$[Cu(2\text{-}AET)_2(HTNO)_2]$	**15**	-	-	-	-	neg.
$[Cu(AE124Tri)_4(ClO_4)_2]$	**16**	-	det.	det.	-	-
$[Cu(AE124Tri)_4(NO_3)_2]$	**17**	-	-	-	-	neg.
$[Fe(AE124Tri)_6](ClO_4)_2$	**18**	-	dec.	-	-	dec.
$[Cu_2(2\text{-}AET)(N_3)_4]$	**19**	pos.	-	-	-	-
$[Cu_3(AE124Tri)_2(N_3)_6]$	**20**	pos.	-	-	-	-

[a]pos.: positive, neg.: negative, -: not performed, PETN: pentaerythriol tetranitrate.
[b]Operating parameters: voltage $U = 4$ V, current $I = 7$–10 A, pulse length $\tau = 15$–30 ms, theoretical maximal output power $P_{max} = 45$ W, wavelength $\lambda = 915$ nm (det.: detonation, def.: deflagration, dec.: decomposition, neg.: negative).

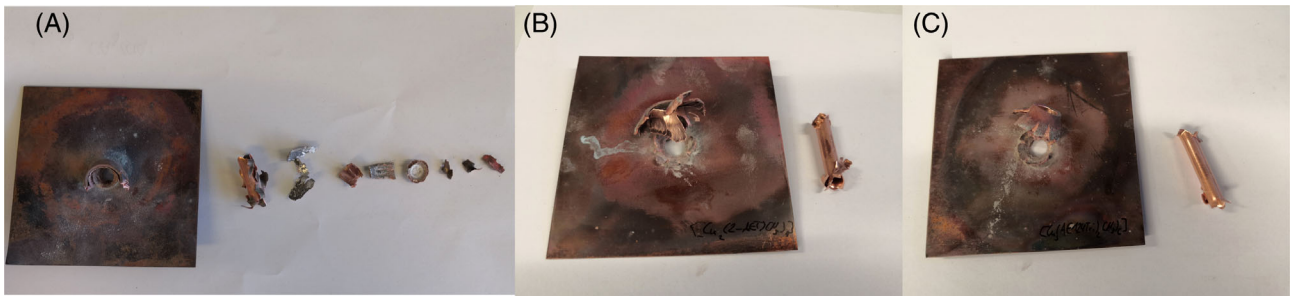


FIGURE 5 Outcomes of the initiation by (a) [Ag(μ-2-AET)(ClO_4)], (b) [Cu_2(2-AET)(N_3)$_4$], and (c) [Cu_3(AE124Tri)$_2$(N_3)$_6$].

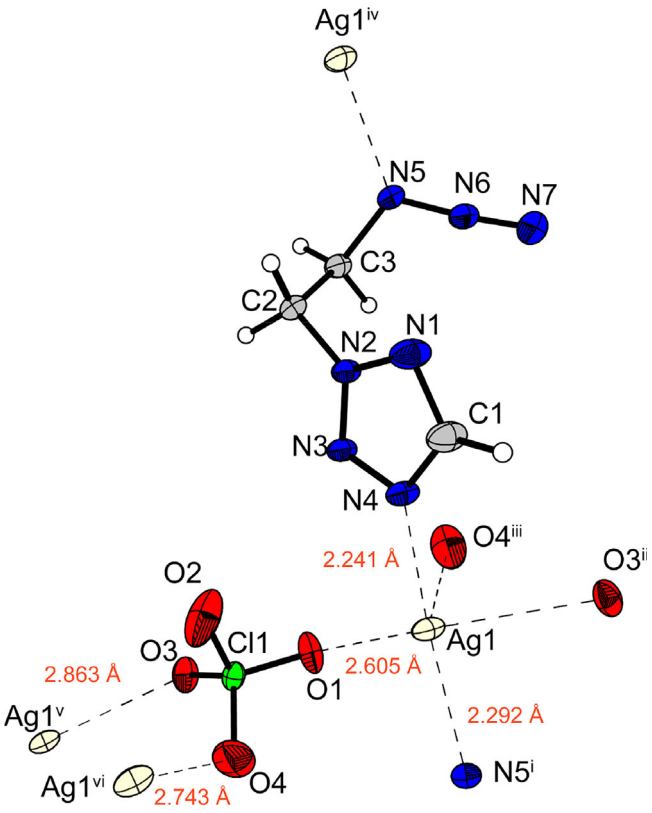


FIGURE 6 Coordination polymer of [Ag(μ-2-AET)(ClO_4)]. Selected bond lengths [Å]: Ag1–O1 2.6049(16), Ag1–N4 2.2405(17), Ag1–N5^{i} 2.2917(17); Selected bond angles [°]: O1–Ag1–N4 103.17 (6), O1–Ag1–N5^{i} 93.17(5), N4–Ag1–N5^{i} 156.94(6); Symmetry codes: (i) $-x, -1/2 + y, 3/2 - z$, (ii) $-1 + x, 1/2 - y, 1/2 + z$, (iii) $x, 1/2 - y, 1/2 + z$, (iv) $-x, 1/2 + y, 3/2 - z$, (v) $1 + x, 1/2 - y, -1/2 + z$, (vi) $x, 1/2 - y, -1/2 + z$.

sealed with UV-curable adhesive. The samples were irradiated by a 45 W InGaAs laser ($\lambda = 915$ nm) operating in single-pulse mode. Additional information on the setup can be found in the Supporting Information. Compounds **13**, **14**, and **16** showed detonative behavior during irradiation under certain specification. The detailed settings can be seen in the Supporting Information. For safety reasons, **19** and **20** were not tested in this setup. Their high sensitivities against mechanical manipulation do not allow manual compression of any kind. Such handling, if necessary, should only be done under increased safety standards and by trained professionals only.

2.3 | Crystal structures

Figure 6 shows the crystal structure of [Ag(μ-2-AET)(ClO_4)] including some bond distances of interest. Unlike [Ag(1-AET)](ClO_4), which crystallized in the triclinic space group $P-1$ with a calculated density of 2.470 g cm^{-3} (173 K) [30], the ECC produced from the 2-isomer crystallized in the monoclinic space group $P2_1/c$ with a slightly lower density of 2.412 g cm^{-3} (173 K). A direct comparison shows that [Ag(1-AET)](ClO_4) forms a one-dimensional polymeric network in which the 1-azidoethyl ligand is the linking unit. In the case of [Ag(μ-2-AET)(ClO_4)], the bond distances to the silver(I) atom are shortened in comparison and the perchlorate ion takes a major role in building a three-dimensional coordination network. The slightly lower theoretical maximum density can be explained by the formation of pores within the three-dimensional structure.

The coordination spheres of (a) [Cu(2-AET)$_4$(H_2TNPG)$_2$], (b) [Cu(2-AET)$_2$(TNR)], (c) [Cu(2-AET)$_2$(PA)$_2$], and (d) [Cu(2-AET)$_2$(HTNO)$_2$] are shown in Figure 7. While all four compounds crystallized in the triclinic space group $P-1$, only three of them showed densities close to 1.8 g cm^{-3} at the respective temperature. It was not possible to perform a low-temperature x-ray measurement of [Cu(2-AET)$_2$(HTNO)$_2$], due to cracking of the single crystals at reduced temperatures. The crystal structure was therefore determined at room temperature, leading to increased sizes of the thermal ellipsoids. In all cases, coordination was observed as expected for Cu(II) compounds. The crystal structures all feature Jahn–Teller-like distorted octahedral coordination spheres.

The crystal structure of [Cu(AE124Tri)$_4$(ClO_4)$_2$] is shown in Figure 8. The compound crystallized in the triclinic space group $P-1$ with a density of 1.717 g cm^{-3} at 100 K. Unlike its structural relative 1-AET, the copper(II)

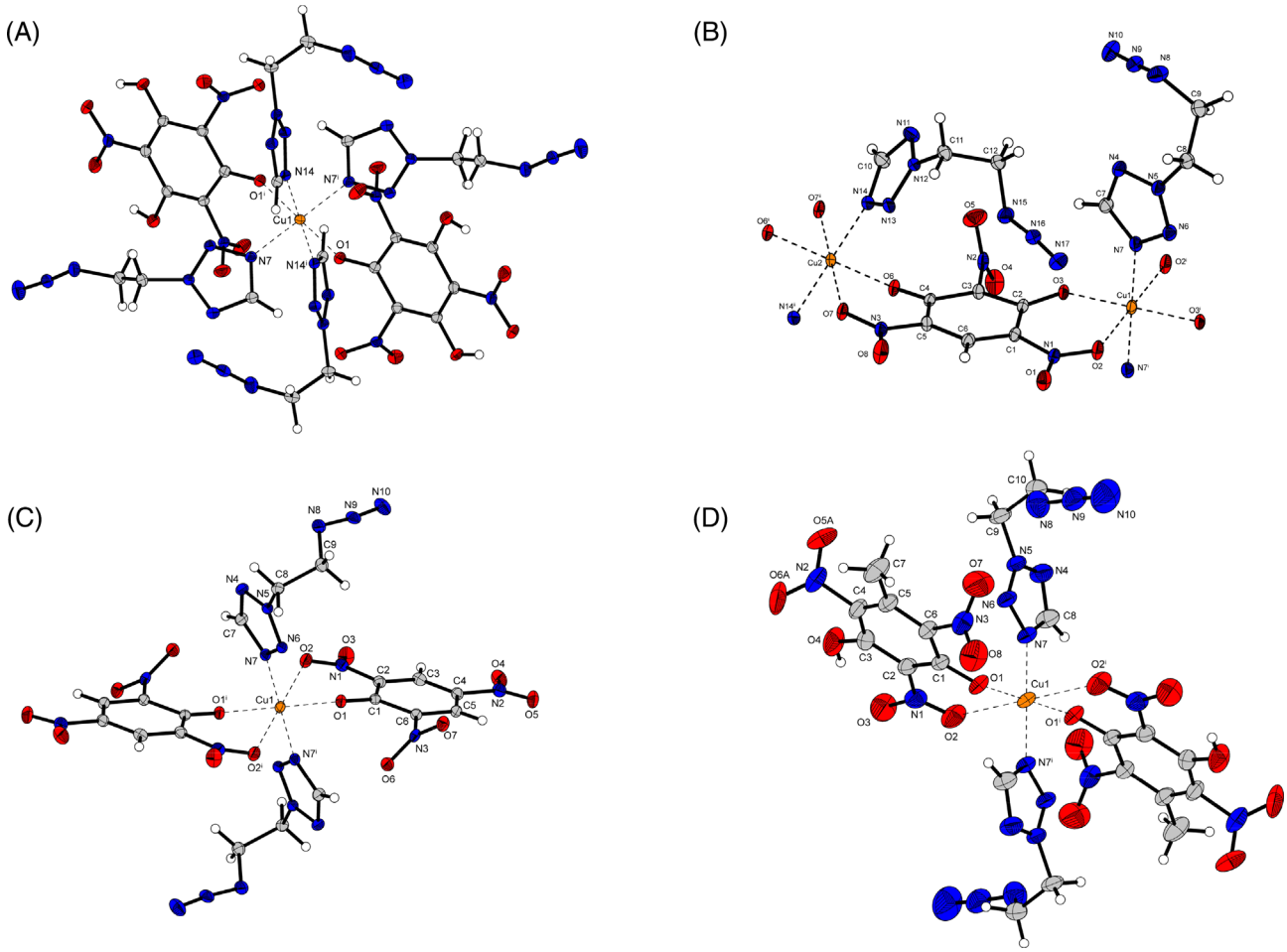


FIGURE 7 (a) Crystal structure of $[Cu(2\text{-}AET)_4(H_2TNPG)_2]$. Selected bond lengths [Å]: Cu1–O1 2.3345(15), Cu1–N7 2.0227(18), Cu1–N14 2.0156(18); Selected bond angles [°]: O1–Cu1–N7 84.23(6), O1–Cu1–N14 89.16(7); Symmetry codes: (i) $1-x, 1-y, 1-z$. (b) Crystal structure of $[Cu(2\text{-}AET)_2(TNR)]$. Selected bond lengths [Å]: Cu1–O2 2.3077(17), Cu1–O3 1.9341(15), Cu1–N7 2.0202(18), Cu2–O6 1.9396(16), Cu2–O7 2.3094(17), Cu2–N14 2.0164(18); Selected bond angles [°]: O2–Cu1–O3 82.88(6), O2–Cu1–N7 92.59(6), O3–Cu1–N7 89.00(7), O6–Cu2–O7 81.14(6), O6–Cu2–N14 87.56(7); Symmetry codes: (i) $1-x, 1-y, -z$, (ii) $2-x, 1-y, 1-z$. (c) Crystal structure of $[Cu(2\text{-}AET)_2(PA)_2]$. Selected bond lengths [Å]: Cu1–O1 1.9220(16), Cu1–O2 2.3728(19), Cu1–N7 1.9951(18); Selected bond angles [°]: O1–Cu1–O2 78.71(7), O1–Cu1–N7 90.22(7), O2–Cu1–N7 90.32(7); Symmetry codes: (i) $-x, -y, 1-z$. (d) Crystal structure of $[Cu(2\text{-}AET)_2(HTNO)_2]$. Cu1–O1 1.9272(13), Cu1–O2 2.423(2), Cu1–N7 2.0007(19); Selected bond angles [°]: O1–Cu1–O2 75.24(6), O1–Cu1–N7 92.41(7), O2–Cu1–N7 90.75(7); Symmetry codes: (i) $1-x, 1-y, -z$.

perchlorate ECC of 1-(2-azidoethyl)-1,2,4-triazole (AE124Tri) does not show a ratio of 1:6 between copper and ligand [30]. Instead, the ligands occupy the *xy*-plane, leaving the elongated z^2-axis open for coordination by two perchlorate anions.

3 | CONCLUSION

This work documents the successful synthesis and characterization of 1-(2-azidoethyl)-pyrazole (5), −imidazole (6), −1,2,3-triazole (7), −1,2,4-triazole (8), and -tetrazole (9) as well as 2-(2-azidoethyl)-tetrazole (10) through a uniform reaction protocol using the transfer reagents 2-azidoethyl-4-methylbenzenesulfonate (2), 2-azidoethyl-methanesulfonate (3), and 1-azido-2-chloroethane (4), in moderate to very good yields. A reaction protocol was established that can be applied to any azole and that will result in a successful alkylation. For this, the reaction parameters were screened and it was concluded that the use of DMF as solvent, potassium carbonate as base, and 90°C as reaction temperature showed the best overall results. Triazole and tetrazole derivatives were further used as ligands in ECCs, where they showed promising properties as potential primary explosives. Three of the ECCs, which were put to test, initiated PETN in the setup used. Another set of three ECCs was successfully used in laser initiation experiments and brought to detonation by

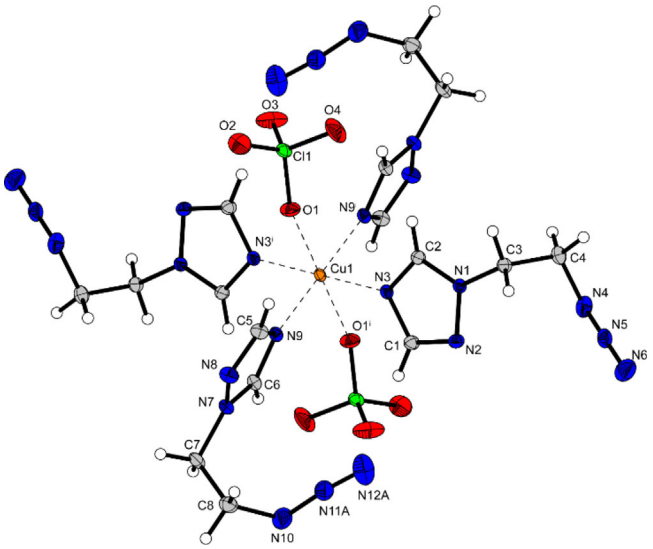


FIGURE 8 Crystal structure of $[Cu(2\text{-}AE124Tri)_4(ClO_4)_2]$. Selected bond lengths [Å]: Cu1–O1 2.4406(12), Cu1–N3 2.0027(12), Cu1–N9 2.0251(14); Selected bond angles [°]: O1–Cu1–N3 87.40(5), O1–Cu1–N9 87.11(5), N3–Cu1–N9 89.26(5); Symmetry codes: (i) $1-x, 1-y, 1-z$.

single-pulse irradiation. Furthermore, the established reaction protocol can be extended to various functionalized heterocycles as substrates, to obtain more previously uncharacterized azidoethyl-containing compounds in a fast, safe, and reliable way.

4 | EXPERIMENTAL SECTION

Caution! Some of the described compounds may be energetic with sensitivities toward impact, friction, heat, or electrostatic discharge. No major hazards occurred during the preparation. Wearing additional safety equipment (Kevlar® gloves, earplugs, face shield, leather coat, as well as earthed shoes and equipment) is recommended.

Solvents for the reaction were bought from different suppliers and were used without further purification. As far as not specifically explained, all reactions were performed under standard conditions. NMR spectra were recorded using a Bruker 400, JEOL Eclipse 400, at ambient temperature. The chemical shifts were determined to external standards: Me_4Si (^1H 399.8/400.2 MHz; ^{13}C 100.5/100.6 MHz). Infrared spectra were measured using a PerkinElmer Spectrum One spectrometer equipped with a Smiths DuraSamplIR ATR device. All spectra were recorded at ambient temperature under standard atmosphere. Analysis of C/H/N/S/Cl contents were performed using an Elementar vario El or Elementar vario micro.

4.1 | 2-Azidoethan-1-ol (1)

2-Chloroethanol (36.3 g, 30.0 mL, 0.451 mol, 1.0 eq.) was dissolved in H_2O (160 mL) and the mixture was cooled down to 0°C. NaN_3 (29.4 g, 0.452 mol, 1.0 eq.) was added in portions and the solution was allowed to warm up to ambient temperature and was stirred for 10 min. More NaN_3 (19.6 g, 0.301 mol, 0.67 eq.) was added and the solution was heated up to 80°C and left stirring for 16 h. The solution was extracted with Et_2O (3 × 100 mL) and the organic phase was washed with brine (50 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure to yield 2-azidoethan-1-ol (**1**) (37.7 g, 0.433 mol, 96%) as a colorless liquid. **^{1}H NMR (400.2 MHz, DMSO-d_6)**: δ (ppm) = 5.00 (t, 1H), 3.57 (m, 2H), 3.26 (m, 2H). **^{13}C NMR (100.6 MHz, DMSO-d_6)**: δ (ppm) = 60.2, 52.9. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 2979 (m), 2097 (vs), 1736 (m), 1598 (m), 1443 (m), 1366 (s), 1350 (m), 1293 (m), 1241 (s), 1190 (s), 1176 (vs), 1097 (s), 1047 (s), 1020 (m), 915 (s), 816 (m), 771 (m). **MS** (ESI+) *m/z*: $[C_2H_6N_3O_3]$ calc.: 88.0511 $[M + H]^+$; found: 88.0506.

4.2 | 2-Azidoethyl-4-methylbenzenesulfonate (2)

2-Azidoethan-1-ol (**1**) (20.0 g, 0.230 mol, 1.0 eq.) was dissolved in MeCN (200 mL) and the solution was cooled down to 0°C. NEt_3 (34.8 g, 48.0 mL, 0.345 mol, 1.5 eq.) was added dropwise and the reaction mixture was left stirring for 15 min at −10°C. Tosyl chloride (44.1 g, 0.230 mol, 1.0 eq.) dissolved in MeCN (200 mL) was added dropwise and the solution was allowed to warm up to ambient temperature. The resulting white precipitate was filtered off and the clear colorless solution was left stirring for 16 h at ambient temperature. The solvent was removed under reduced pressure and H_2O (100 mL) was added. The aqueous phase was extracted with EtOAc (3 × 100 mL) and the combined organic layers were washed with HCl (2 M, 100 mL), $NaHCO_3$ (saturated, 100 mL), and brine (100 mL). After drying the organic layer over anhydrous $MgSO_4$, the solvent was removed under reduced pressure to yield 2-azidoethyl-4-methylbenzenesulfonate (**2**) (41.0 g, 0.170 mol, 73%) as a slightly orange liquid that was used without further purification. **^{1}H NMR (400.1 MHz, DMSO-d_6)**: δ (ppm) = 7.80 (d, 2H), 7.50 (d, 2H) 4.16 (t, 2H), 3.54 (t, 2H), 2.43 (s, 2H). **^{13}C NMR (100.6 MHz, DMSO-d_6)**: δ (ppm) = 145.7, 132.5, 130.7, 128.1, 69.8, 49.5, 21.6. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 2109 (m), 1597 (w), 1441 (w), 1361 (s), 1305 (m), 1295 (m), 1189 (s), 1172 (vs), 1096 (m), 1018 (m), 911 (s), 814 (s), 767 (s), 661 (s), 655 (s), 571 (s), 552 (vs), 529 (s), 487 (m), 447 (m).

4.3 | 2-Azidoethyl-methylsulfonate (3)

2-Azidoethan-1-ol (**1**) (20.3 g, 0.233 mol, 1.0 eq.) was dissolved in MeCN (200 mL) and the solution was cooled down to 0°C. NEt_3 (35.4 g, 48.7 mL, 0.350 mol, 1.5 eq.) was added dropwise and the reaction mixture was left stirring for 15 min at −10°C. Methanesulfonyl chloride (26.7 g, 0.233 mol, 1.0 eq.) dissolved in MeCN (200 mL) was added dropwise and the solution was allowed to warm up to ambient temperature. The resulting white precipitate was filtered off and the clear colorless solution was left stirring for 16 h at ambient temperature. The solvent was removed under reduced pressure and H_2O (100 mL) was added. The aqueous phase was extracted with EtOAc (3 × 100 mL) and the combined organic layers were washed with HCl (2 M, 100 mL), $NaHCO_3$ (saturated, 100 mL), and brine (100 mL). After drying the organic layer over anhydrous $MgSO_4$, the solvent was removed under reduced pressure to yield 2-azidoethyl-methylsulfonate (**3**) (32.4 g, 0.170 mol, 84%) as a slightly yellow liquid, that was used without further purification. **^{1}H NMR (400.1 MHz, $CDCl_3$)**: δ (ppm) = 4.34 (t, 2H), 3.59 (t, 2H), 3.08 (s, 3H). **^{13}C NMR (100.6 MHz, $CDCl_3$)**: δ (ppm) = 67.6, 50.0, 37.9. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 3031.00 (vw), 2941.00 (vw), 2109.00 (vs), 2099.00 (s), 1442.00 (w), 1347.00 (s), 1301.00 (m), 1226.00 (w), 1169.00 (vs), 1016.00 (m), 967.00 (s), 911.00 (vs), 845.00 (w), 798.00 (s), 749.00 (w), 732.00 (m), 638.00 (w), 554.00 (w), 524.00 (vs), 492.00 (m), 441.00 (s), 420.00 (w). **Elem. Anal. Calcd**. for $C_3H_7N_3O_3S$: C, 21.82; N, 25.44; H, 4.27; S, 19.41. Found: C, 21.69; N, 25.26; H, 4.18, S, 19.73. **HR-MS** (ESI+) *m/z*: [$C_3H_7N_3O_3S$] calc.: 166.0286 $[M + H]^+$; found: 165.9928.

4.4 | 1-Azido-2-chloroethane (4)

1-Bromo-2-chloroethane (40.0 g, 0.279 mol, 1.0 eq) was dissolved in DMF (100 mL) and sodium azide (18.1 g, 0.279 mol, 1.0 eq) was added in portions over 2 h. The solution was stirred for 16 h at ambient temperature. Water (500 mL) was added and the reaction mixture was extracted with Et_2O (3 × 300 mL) and washed with LiCl solution (1 × 100 mL) and brine (1 × 100 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to yield 1-azido-2-chloroethane (**4**) (27.43 g, 260.0 mmol, 93%) as yellow liquid that was used without further purification. **^{1}H NMR (400.1 MHz, DMSO-d_6)**: δ (ppm) = 3.58 (m, 2H), 3.41 (m, 2H). **^{13}C NMR (100.6 MHz, DMSO-d_6)**: δ (ppm) = 52.6, 42.7. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 2929.00 (w), 2168.00 (w), 2102.00 (vs), 2045.00 (w), 1672.00 (vs), 1594.00 (w), 1571.00 (w), 1503.00 (w), 1441.00 (m), 1407.00 (w), 1387.00 (m), 1345.00 (m), 1313.00 (s), 1285.00 (s), 1260.00 (s), 1186.00 (w), 1091.00 (m), 1063.00 (w), 1022.00 (w), 994.00 (w), 972.00 (w), 918.00 (w), 828.00 (w), 758.00 (w), 749.00 (w), 660.00 (s), 637.00 (m), 553.00 (m), 481.00 (w), 450.00 (s).

4.5 | General procedure for the azidoethyl transfer

The azole (2.00 g, 1.0 eq) was dissolved in DMF (10 mL) and potassium carbonate (1.5 eq) and the azidoethyl transfer reagent (1.0 eq) were added under stirring and the mixture was heated to 90°C for 16 h. After cooling down to room temperature, water (100 mL) was added and the aqueous phase was extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with LiCl (aq. 10%, 3 × 50 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography (*i*-hexane:ethyl acetate). The azidoethyl azoles **3–8** were obtained as liquids.

1-(2-Azidoethyl)-pyrazole (**5**) was purified by column chromatography (*i*-hexane:ethyl acetate 30:70, $R_f = 0.62$) to yield a yellowish liquid (76%). **^{1}H NMR (400.2 MHz, $CDCl_3$)**: δ (ppm) = 7.56 (s, 1H), 7. 45 (s, 1H), 6.29 (t, 1H), 4.27 (t, 2H), 3.71 (t, 2H). **^{13}C NMR (100.6 MHz, $CDCl_3$)**: δ (ppm) = 140.4, 130.2, 106.1, 51.3, 51.2. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 2930 (w), 2858 (w), 2098 (vs), 1727 (w), 1515 (m), 1441 (m), 1397 (m), 1352 (m), 1283 (s), 1215 (m), 1172 (w), 1091 (m), 1066 (w), 1042 (m), 966 (m). **Elem. Anal. Calcd**. for $C_5H_7N_5$: C, 43.79; N, 51.07; H, 5.14. Found: C, 43.43; N, 49.08; H, 5.22, **HR-MS** (ESI+) *m/z*: [$C_5H_8N_5$] calc.: 138.0780 $[M + H]^+$; found: 138.0773.

1-(2-Azidoethyl)-imidazole (**6**) was purified by column chromatography (methanol: ethyl acetate 5:95, $R_f = 0.11$) to yield a yellowish liquid (36%). **^{1}H NMR (400.2 MHz, $CDCl_3$)**: δ (ppm) = 7.56 (dd, 1H), 7.09 (dd, 1H), 6.97 (dd, 1H), 4.09 (t, 2H), 3.62 (t, 2H). **^{13}C NMR (100.6 MHz, $CDCl_3$)**: δ (ppm) = 137.4, 130.0, 119.1, 51.9, 46.3. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 2984 (w), 2936 (w), 2102 (m), 1733 (s), 1510 (w), 1445 (m), 1373 (m), 1239 (vs), 1190 (m), 1178 (m), 1120 (w), 1108 (m), 1095 (m), 1084 (m), 1044 (s), 1011 (m). **Elem. Anal. Calcd.** for $C_5H_7N_5$: C, 43.79; N, 48.05; H, 5.14. Found: C, 43.89; N, 48.05; H, 5.22, **HR-MS** (ESI+) *m/z*: [$C_5H_8N_5$] calc.: 138.0780 $[M + H]^+$; found: 138.0775.

1-(2-Azidoethyl)-1,2,3-triazole (**7**) was purified by column chromatography (*i*-hexane:ethyl acetate 30:70, $R_f = 0.30$) to yield a yellowish liquid (68%). **^{1}H NMR (400.2 MHz, $CDCl_3$)**: δ (ppm) = 7.66 (s, 1H), 7.65 (s, 1H), 4.53 (t, 2H), 3.82 (t, 2H). **^{13}C NMR (100.6 MHz, $CDCl_3$)**: δ (ppm) = 133.9, 124.4, 50.7, 49.1. **IR (rel. int.)**:

$\tilde{\nu}$ (cm^{-1}) = 3146 (w), 3127 (w), 2959 (vw), 2941 (vw), 2098 (vs), 1438 (w), 1352 (m), 1283 (s), 1217 (s), 1076 (m), 1032 (m), 788 (s). **Elem. Anal. Calcd.** for $C_4H_6N_6$: C, 34.78; N, 60.84; H, 4.38. Found: C, 35.12; N, 59.87; H, 4.29, **HR-MS** (ESI+) *m/z*: [$C_4H_7N_6$] calc.: 139.0732 [M + H]$^+$; found: 139.0726.

1-(2-Azidoethyl)-1,2,4-triazole (**8**) was purified by column chromatography (*i*-hexane:ethyl acetate 10:90, R_f = 0.33) to yield a yellowish liquid (69%). **^{1}H NMR (400.2 MHz, $CDCl_3$)**: δ (ppm) = 8.11 (s, 1H), 7.94 (s, 1H), 4.26 (t, 2H), 3.72 (t, 2H). **^{13}C NMR (100.6 MHz, $CDCl_3$)**: δ (ppm) = 152.4, 144.0, 50.1, 48.9. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 3121 (w), 2946 (w), 2098 (vs), 1508 (s), 1439 (m), 1351 (m), 1274 (vs), 1208 (m), 1179 (w), 1138 (s), 1067 (w), 1010 (m), 958 (m). **Elem. Anal. Calcd.** for $C_4H_6N_6$: C, 34.78; N, 60.84; H, 4.38. Found: C, 34.74; N, 58.98; H, 4.14, **HR-MS** (ESI+) *m/z*: [$C_4H_7N_6$] calc.: 139.0732 [M + H]$^+$; found: 139.0725.

1-(2-Azidoethyl)-tetrazole (**9**) was purified by column chromatography (*i*-hexane:ethyl acetate 40:60, R_f = 0.46) to yield a yellowish liquid (39%). **^{1}H NMR (400.1 MHz, $CDCl_3$)**: δ (ppm) = 8.74 (s, 1H), 4.59 (t, 2H), 3.88 (t, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 143.3, 50.1, 47.6. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 3262 (m), 3145 (m), 3137 (m), 2956 (m), 2924 (m), 2853 (m), 2102 (vs), 1741 (w), 1484 (m), 1439 (m), 1352 (m), 1287 (s), 1258 (m), 1227 (m), 1171 (s), 1103 (vs), 965 (m), 874 (w), 677 (m), 657 (m), 554 (m), 486 (m). **Elem. Anal. Calcd**. for $C_3H_5N_7$: C, 25.90; N, 70.48; H, 3.62. Found: C, 26.13; N, 69.40; H, 4.01. **HR-MS** (ESI+) *m/z*: [$C_3H_5N_7$] calc.: 140.0685 [M + H]$^+$; found: not found.

2-(2-Azidoethyl)-tetrazole (**10**) was purified by column chromatography (*i*-hexane:ethyl acetate 40:60, R_f = 0.70) to yield a yellowish liquid (20%). **^{1}H NMR (400.1 MHz, $CDCl_3$)**: δ (ppm) = 8.56 (s, 1H), 4.81 (t, 2H), 3.93 (t, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 153.4, 52.1, 49.6. **IR (rel. int.)**: $\tilde{\nu}$ (cm^{-1}) = 3145 (m), 2100 (vs), 1443 (m), 1367 (m), 1350 (m), 1282 (s), 1234 (m), 1189 (m), 1152 (m), 1132 (m), 1027 (s), 1008 (m), 884 (w), 710 (m), 697 (m), 666 (m), 552 (m), 489 (m). **Elem. Anal. Calcd.** for $C_3H_5N_7$: C, 25.90; N, 70.48; H, 3.62. Found: C, 26.03; N, 69.10; H, 3.97. **HR-MS** (ESI+) *m/z*: [$C_3H_6N_7$] calc.: 140.0685 [M + H]$^+$; found: 140.0680.

ACKNOWLEDGMENTS

For financial support of this work the Ludwig Maximilian University (LMU), EMTO GmbH, the Office of Naval Research (ONR) under grant no. ONR N00014-19-1-2078, and the Strategic Environmental Research and Development Program (SERDP) under contract no. W912HQ19C0033 are gratefully acknowledged. For graphical and computational assistance, we would like to thank Dr. Jasmin Lechner and Dr. Christian Riedelsheimer. The synthetic work of Lennart Kirchhoff, Aleyna Memet Oglou, and Victoria Hauptmann is gratefully acknowledged. Open Access funding enabled and organized by Projekt DEAL.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in Klapoetke at https://www.hedm.cup.uni-muenchen.de/index.html.

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How to cite this article: L. Bauer, S. M. J. Endraß, T. M. Klapötke, J. Stierstorfer, N. Zeitlmeir, *J. Heterocycl. Chem.* **2024**, 1. https://doi.org/10.1002/jhet.4803