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Application of *N*-(ω-bromoalkyl)tetrazoles for the preparation of bitopic ligands containing pyridylazole chelators or azole rings as building blocks for iron(II) spin crossover polymeric materials

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ABSTRACT

1-(3-Bromopropyl)tetrazole, 2-(3-bromopropyl)tetrazole, 1-(4-bromobutyl)tetrazole, and 2-(4-bromobutyl)tetrazole were synthesized with the aim to prepare flexible bitopic ligands contaning 1- or 2-substituted tetrazole ring linked through 1,3-propylene or 1,4-butylene spacer with pyridylazole or azole unit. Twenty-six novel ligands i.e., α-(pyridylazolyl)-ω-(tetrazolyl)alkanes, α-(tetrazolyl)-ω-(1,2,3-triazolyl)alkanes, and α-(tetrazol-1-yl)-ω-(tetrazol-2-yl)alkanes were prepared by an alkylation of sodium salts of 5-(2-pyridyl)tetrazole, 3-(2-pyridyl)-1,2,4-triazole, 3-(2-pyridyl)pyrazole, 1,2,3-triazole, and 1,2,3,4-tetrazole with *N*-(ω-bromoalkyl)tetrazoles. An alkylation of 5-(2-pyridyl)tetrazole, 1,2,3,4-tetrazole, and 1,2,3-triazole afforded both *N*1- and *N*2-regioisomer whereas in the case of 3-(2-pyridyl)-1,2,4-triazole and 3-(2-pyridyl)pyrazole only *N*1 isomers were isolated. The positions of alkylation were confirmed by X-ray diffraction studies of 1-(5-(2-pyridyl)tetrazol-2-yl)-4-(tetrazol-1-yl)butane, 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-2-yl)butane, 1-(3-(2-pyridyl)pyrazol-1-yl)-4-(tetrazol-1-yl)butane, and 1-(tetrazol-1-yl)-4-(1,2,3-triazol-1-yl)butane. Preliminary investigations of magnetic properties of iron(II) complex with 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-1-yl)butane revealed that obtained product exhibit thermally induced spin transition accompanied by the thermochromic effect.

1. Introduction

In recent years, a great deal of attention has been devoted toward the synthesis of functional compounds containing five-membered polyazole rings. Among them, tetrazole and their derivatives have drawn widespread attention, due to their practical applications.[1,2] The large number of tetrazoles exhibits biological activity and they are investigated for applications in agriculture and in medicinal chemistry.[3] Tetrazole derivatives have found therapeutic applications as antihypertensive agents,[4] antibiotics,[5] and drugs for tuberculosis[6] and AIDS treatment.[7] Tetrazoles represent an important class of compounds utilized in materials chemistry as well. They have been used in photography, as MRI agents, for information recording systems and as explosives.[1,2,8]

Tetrazoles are also studied in the field of coordination chemistry.[9] Tetrazole[10] and its 5-substituted derivatives[11] usually act as di- and polydentate ligands exhibiting a versatility of coordination modes. This type of donors, similar to 4-substituted-1,2,4-triazoles,[12] often forms bridges between metal ions, which leads to coordination polymers. In contrast to 5-substituted tetrazoles, the *N*-substituted regioisomers usually coordinate monodentately through the N4 nitrogen atom of the ring. Mono 1- and 2-substituted tetrazoles are also utilized for construction of coordination networks, however, for such purposes an application of di- and polypodal ligands containing two or more *N*-substituted tetrazole rings is requisite.[13,14]

1-Substituted tetrazoles[13,15] and their 2-substituted regioisomers[16] form iron(II) complexes showing spin crossover (SCO) phenomenon.[17] The SCO complexes represent an important class of materials regarded for potential applications as molecular switches, data displays, memory devices, and intelligent contrast agents.[18] An application of such materials requires complexes exhibiting abrupt spin transition accompanied by the hysteresis loop.[19] Presently, polymeric iron(II) SCO complexes are investigated also in order to explain the nature of the cooperative behavior of the SCO transition in solid state.

Continuing our research concerning azole-based ligands we have designed ligand systems potentially applicable for construction of iron(II) SCO coordination polymers. We have focused on donor groups, which are usually utilized in the preparation of monomeric iron(II) SCO complexes.[20] Within the framework of these investigations we have prepared flexible bitopic ligands, containing an *N*-substituted tetrazole ring tethered via alkyl spacer with pyridylazole or azole (tetrazole, 1,2,3-triazole) unit. In this paper, syntheses of 1- and 2-(ω-bromoalkyl)tetrazole and an

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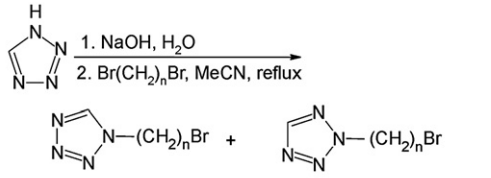
application of such derivatives for alkylation of 5-(2-pyridyl)tetrazole, 3-(2-pyridyl)-1,2,4-triazole, 3-(2-pyridyl)pyrazole, tetrazole, and 1,2,3-triazole are presented. Preliminary results of investigations of temperature dependence of the magnetic susceptibility of the reactions' product of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-1-yl)butane with iron(II) perchlorate are also presented.

2. Results and discussion

Several methods of synthesis of mono 1-substituted tetrazoles, including the reaction of primary amines with NaN_3 and triethyl orthoformate in acetic acid,[21] the [2+3] cycloaddition of isocyanides to hydrazoic acid[22] or to trimethylsilylazide[23] are known. Contrary to the 1-substituted tetrazoles, the preparation of 2-substituted regioisomers is more troublesome because of a lack of a regioselective method for their synthesis. Only a few syntheses led exclusively to formation of mono 2-substituted tetrazoles.[24] Therefore, the alkylation of tetrazole still remains the most general method. Presented in this work 1- and 2-(ω-bromoalkyl)tetrazole were prepared by an alkylation of tetrazole with α,ω-dibromoalkanes (Scheme 1).

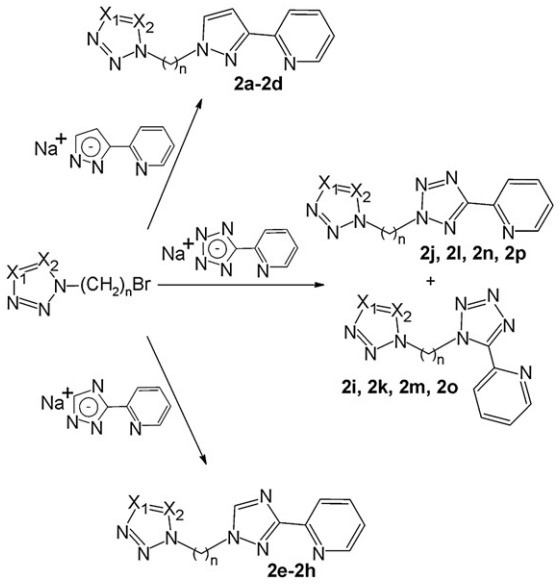


1a(14%, n=3), **1c**(15%, n=4) **1b**(24%, n=3), **1d**(26%, n=4)

Scheme 1. Preparation of 1- and 2-(ω-bromoalkyl)tetrazoles (n=3, 4).

The alkylation proceeded in the heterogenic conditions because of insolubility of the sodium salt of tetrazole in acetonitrile. An excess of the alkylating agent was used in order to reduce the formation of undesirable by-products, namely 1,ω-di(tetrazolyl)alkanes, which make isolation and further purification of the *N*-(ω-bromoalkyl)tetrazoles difficult. A similar strategy was successfully applied during the preparation of bis(bromoalkytetrazolyl)benzenes.[25] Large differences in polarities of both regioisomers (the dipole moments of mono 2-substituted tetrazoles are in the range of 2–2.5 D whereas 1-substituted regioisomers adopt greater values of ca. 5–5.5 D[2]) were utilized for the separation of the products. The 2-substituted regioisomers were extracted with pentane whereas $CCl_4/CHCl_3$ 1:1 (v/v) mixture was used for isolation of the 1-substituted derivatives. Finally, the *N*-(ω-bromoalkyl)tetrazoles were purified chromatografically on silica gel. According to the applied procedure, 1- and 2-(3-bromopropyl)tetrazole (**1a** and **1b**, respectively), as well as 1- and 2-(4-bromobutyl)tetrazole (**1c** and **1d**, respectively) were obtained. It is worth mentioning that the 1-substituted isomers exhibit a greater retention on silica gel. It is known that both electronic and steric effects influence the N2/N1 alkylation ratio.[26] A kind of solvent has also influence on an alkylation position. For example, methylation of tetrazole performed in CH_2Cl_2, CH_3CN, and CH_3OH leads to both regioisomers with a predominance of the *N*1 substituted derivative.[27] In our case, the molar ratio of the isolated regioisomers N2/N1 is equal to approx. 1.8:1 for both **1b**/**1a** and **1d**/**1c**. In an endeavor to obtain the 1-(3-bromopropyl)tetrazole, the procedure depending on reaction of 3-bromopropylamine with sodium azide and triethyl orthoformate was utilized as well. In this way, the 1-(3-bromopropyl)tetrazole was obtained in 29% yield.

Freshly prepared *N*-(ω-bromoalkyl)tetrazoles **1a**–**1d** were applied for an alkylation of pyridylazoles resulting in the formation of α-(pyridylazolyl)-ω-(tetrazolyl)alkanes (Scheme 2).

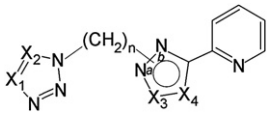


Scheme 2. Isolated products of an alkylation of pyridylazoles with **1a**–**1d**; X_1=N, X_2=C for 1-substituted isomers of tetrazole and X_1=C, X_2=N for 2-substituted ones (n=3, 4).

The sodium salts of 3-(2-pyridyl)pyrazole, 3-(2-pyridyl)-1,2,4-triazole, and 5-(2-pyridyl)tetrazole were obtained by the reactions of the appropriate pyridylazoles with sodium methanolate. Contrary to free forms of the pyridylazoles their sodium salts are insoluble in acetonitrile and the alkylations were carried out in heterogenic conditions. The syntheses of the compounds **2a**–**2p** were carried out with a 1:1 stoichiometry of the suitable *N*-(ω-bromoalkyl)tetrazole and sodium salts of pyridylazole. In the case of alkylation of sodium 3-(2-pyridyl)pyrazolate, products at the less sterically hindered nitrogen atom N1 of the pyrazole ring were isolated (compounds **2a**–**2d**, Table 1).

The position of alkylation was confirmed by X-ray diffraction study of **2d**. The molecular structure of **2d** is presented in the Figure 1a. The same direction of alkylation of 3-(2-pyridyl)pyrazole was also noticed in the case of preparation of α,ω-di(3-(2-pyridyl)pyrazol-1-yl)alkanes.[28] However, products of alkylation at the *endo* positioned nitrogen atom are known too.[28d]

Table 1
Isolated products of alkylations of 5-(2-pyridyl)tetrazole, 3-(2-pyridyl)-1,2,4-triazole, and 3-(2-pyridyl)pyrazole with *N*-(ω-bromoalkyl)tetrazoles **1a**–**1d**



Compound	X_1	X_2	X_3	X_4	Alkyl chain	n	Yield [%]	N2/N1 ratio[a]
2a	N	C	C	C	a	3	47	
2b	C	N	C	C	a	3	68	
2c	N	C	C	C	a	4	51	
2d	C	N	C	C	a	4	63	
2e	N	C	C	N	a	3	45	
2f	C	N	C	N	a	3	52	
2g	N	C	C	N	a	4	49	
2h	C	N	C	N	a	4	50	
2i	N	C	N	N	b	3	22	2.2:1
2j	N	C	N	N	a	3	45	
2k	C	N	N	N	b	3	22	2.4:1
2l	C	N	N	N	a	3	50	
2m	N	C	N	N	b	4	18	2.2:1
2n	N	C	N	N	a	4	40	
2o	C	N	N	N	b	4	20	1.5:1
2p	C	N	N	N	a	4	32	

[a] N2/N1 molar ratios based on isolated amounts of regioisomers.

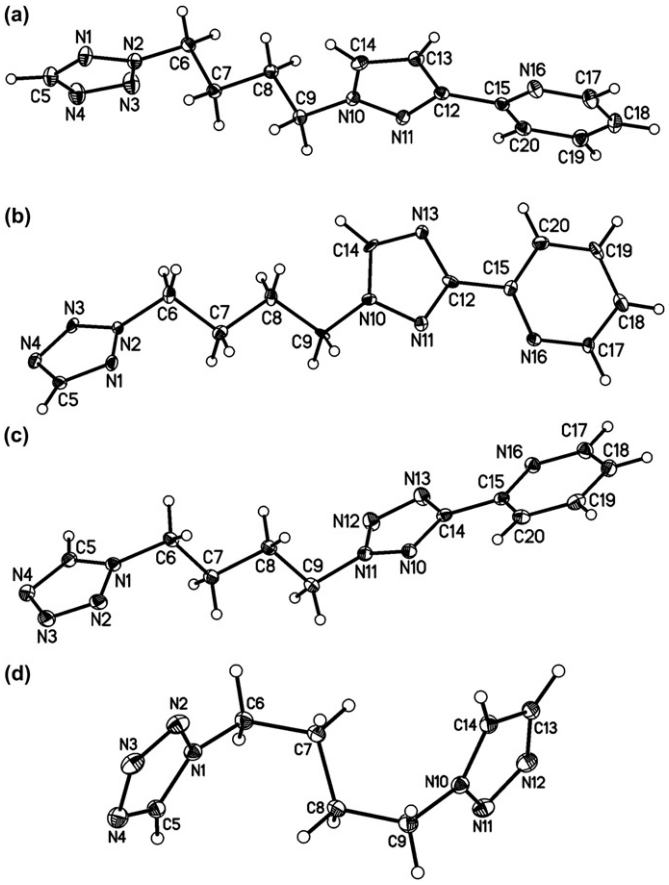


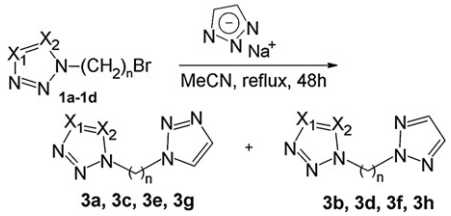
Figure 1. The molecular structures of **2d** (a), **2h** (b), **2n** (c), and **3f** (d).

An alkylation of unsubstituted 1,2,4-triazole proceeds usually at atoms N1 or N4 in the ratio of approx. 10:1.[27,29] However, in 3-(2-pyridyl)-1,2,4-triazole there are three nitrogen atoms accesible for alkylation but only the products of substitution at atom N1 were isolated (compounds **2e**–**2h**, Table 1). X-ray diffraction study of **2h** confirmed the localization of the alkyl substituent at the N1 nitrogen atom of the 1,2,4-triazole ring (see Fig. 1b).

In contrast to the above described alkylations of 3-(2-pyridyl)pyrazole and 3-(2-pyridyl)-1,2,4-triazole, reactions performed between 5-(2-pyridyl)tetrazole and *N*-(ω-bromoalkyl)tetrazoles **1a**–**1d** afforded both the 2,5- (compounds **2j**, **2l**, **2n**, and **2p**) and the 1,5-disubstituted tetrazoles (compounds **2i**, **2k**, **2m**, and **2o**) and a predominance of the 2,5-regioisomers was noticed (see Table 1). These results are in agreement with other alkylations performed on tetrazole derivatives containing a sterically bulky substituent at carbon atom of the ring.[30]

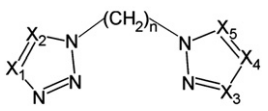
The molecular structure of **2n** showing the localization of the substituent at the N2 atom of the tetrazole ring is presented in Figure 1c. The regioisomers were separated chromatographically. In contrast to the 1- and 2-(ω-bromoalkyl)tetrazoles, the 1,5-disubstituted tetrazoles exhibit a greater mobility on the silica gel compared to their 2,5-disubstituted isomers.

Besides the ligands presented above containing pyridylazole chelators, our intention was also to design and prepare bitopic ligands containing monodentately coordinating azoles. Recently, bitopic ligands based on 4-substituted-1,2,4-triazole were reported.[31] It is known that ligands based on 4-substituted-1,2,4-triazole are involved usually in the formation of μ(N1,N2) azole bridges.[12] We have focused on ligand systems containing mono 1- or 2-substituted tetrazoles and *N*-substituted-1,2,3-triazole in order to avoid a formation of coordination networks containing μ(N1,N2) bridges. The 1-(tetrazolyl)-ω-(1,2,3-triazolyl)alkanes were prepared according to the above mentioned procedure, i.e., the reactions of *N*-(ω-bromoalkyl)tetrazoles **1a**–**1d** with sodium 1,2,3-triazolate (Scheme 3). The syntheses were performed in the heterogenic conditions between equimolar amounts of the reagents. All of the alkylations of 1,2,3-triazole afforded mixtures containing comparable amounts of 1- and 2-substituted regioisomers **3a**–**3h** (Table 2). The regioisomers were separated and purified chromatographically; 2-substituted derivatives of 1,2,3-triazole exhibit a greater movement on silica gel than 1-substituted ones. The molecular structure of **3f** was confirmed crystallographically (see Fig. 1d).



Scheme 3. Syntheses of 1-(tetrazolyl)-ω-(1,2,3-triazolyl)alkanes; X_1=N, X_2=C for 1-substituted isomers of tetrazole and X_1=C, X_2=N for 2-substituted ones (n=3, 4).

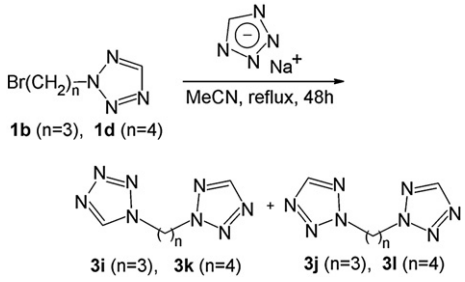
Table 2
Isolated products of alkylation of sodium 1,2,3-triazolate and tetrazolate with *N*-(ω-bromoalkyl)tetrazoles **1a**–**1d**



Compound	X_1	X_2	X_3	X_4	X_5	n	Yield [%]	N2/N1 ratio[a]
3a	N	C	C	C	N	3	30	1.2:1
3b	N	C	N	C	C	3	24	
3c	C	N	C	C	N	3	32	1.2:1
3d	C	N	N	C	C	3	26	
3e	N	C	C	C	N	4	30	1.1:1
3f	N	C	N	C	C	4	28	
3g	C	N	C	C	N	4	43	1.1:1
3h	C	N	N	C	C	4	38	
3i	C	N	N	N	C	3	17	1.6:1
3j	C	N	N	C	N	3	28	
3k	C	N	N	N	C	4	23	1.4:1
3l	C	N	N	C	N	4	33	

[a] N2/N1 molar ratios based on isolated amounts of regioisomers.

An application of sodium tetrazolate instead of the 1,2,3-triazolate salt afforded products of alkylation at N2 and N1 atoms of the tetrazole ring in the molar ratio of ca. 1.5:1 (Scheme 4, Table 2). As well as compounds **3i** and **3k**, monotopic ligands, i.e., bis(tetrazol-2-yl)alkanes (**3j**, **3l**) arised too.



Scheme 4. Alkylations of tetrazole with 2-(ω-bromoalkyl)tetrazoles.

(2-Pyridyl)azoles (paz) are a well known class of chelating ligands, which can form complexes of compositions $[M(paz)_3]^{n+}$

with six coordinating metal ions.[21] On the other hand, two (2-pyridyl)azole moieties tethered by a spacer reveal a greater diversity in reaction with metal ions forming mononuclear complexes,[28c,d,30,32] high nuclearity species,[28a,b] as well as coordination polymers.[33] In contrast to bis(2-pyridylazole)alkane ligands, the α,ω-di(tetrazol-1-yl)alkanes and α,ω-di(tetrazol-2-yl)alkanes form with metal ions only coordination polymers.[13,14] Hence, in order to increase the ability of ligands based on (2-pyridyl)azole moieties to form coordination networks we have synthesized novel bitopic ligands that contain the (2-pyridyl)azole unit and *N*-substituted tetrazole ring tethered by an alkyl spacer. Moreover, 3-(2-pyridyl)pyrazoles, 3-(2-pyridyl)-1,2,4-triazoles, 1,2,3-triazoles, and *N*-substituted tetrazoles form iron(II) ions complexes exhibiting the thermally induced spin transition (SCO). In order to investigate the usability of the synthesized ligands for the preparation of SCO complexes we have performed preliminary studies of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-1-yl)butane (**2g**) in the reaction with iron(II) perchlorate hexahydrate. It was noticed that the cooling of the sample of the obtained complex **4** is accompanied by a pronounced change of color from orange to dark red, which indicates the HS→LS transition. This observation was confirmed by the temperature dependence of the magnetic susceptibility measurement (Fig. 2).

It was noticed that a lowering of the temperature from 300 to 75 K involves the change of the $\chi_M T$ value from ca. 2.4 $cm^3\,K\,mol^{-1}$ to ca. 1.1 $cm^3\,K\,mol^{-1}$, respectively. Detailed investigations of the coordination properties of the obtained ligands are in progress.

3. Summary

Four *N*-(ω-bromoalkyl)tetrazoles: 1-(3-bromopropyl)tetrazole, 2-(3-bromopropyl)tetrazole, 1-(4-bromobutyl)tetrazole, and 2-(4-bromobutyl)tetrazole were synthesized from the reactions of sodium tetrazolate with 1,3-dibromopropane or 1,4-dibromobutane. The obtained *N*-(ω-bromoalkyl)tetrazoles were utilized for the alkylation of three pyridylazoles: 3-(2-pyridyl)pyrazole, 3-(2-pyridyl)-1,2,4-triazole, and 5-(2-pyridyl)tetrazole. In the case of 3-(2-pyridyl)pyrazole and 3-(2-pyridyl)-1,2,4-triazole the products of alkylation at position N1 of the azole rings were isolated whereas alkylation of 5-(2-pyridyl)tetrazole afforded both *N*1 and *N*2 substituted regioisomers. In this way sixteen bitopic ligands built up from (2-pyridyl)azole unit and *N*-substituted tetrazole ring tethered by an alkyl spacer were prepared. *N*-(ω-bromoalkyl)tetrazoles were also successfully utilized for the alkylation of 1,2,3-triazole and tetrazole. In both cases, the formation of *N*1- and *N*2-regioisomer was noticed. Eight 1-(tetrazolyl)-ω-(1,2,3-triazolyl)alkanes and two 1-(tetrazol-1-yl)-ω-(tetrazol-2-yl)alkanes were prepared. The molecular structures of alkylation products were confirmed by X-ray diffraction studies of **2d**, **2h**, **2n**, and **3f**.

A preliminary investigation of the coordination properties of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-1-yl)butane (**2g**) was carried out in the reaction with iron(II) perchlorate. The results of temperature dependence of magnetic susceptibility measurements showed that the obtained complex exhibits the thermally induced spin transition. The spin transition is accompanied by the thermochromic effect.

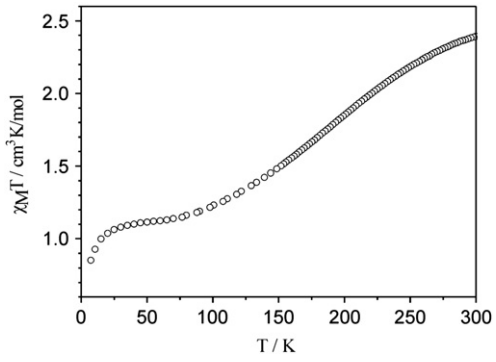


Figure 2. The $\chi_M T$ versus T plot for **4** in cooling mode.

4. Experimental section

4.1. General

Infrared spectra were recorded with a Bruker 113v FTIR spectrometer in the range 400–4000 cm^{-1} as KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on AMX Bruker NMR 300 MHz spectrometer and on Avance Bruker NMR 500 MHz spectrometer at room temperature in CD_3CN solutions. Mass spectra were recorded using Bruker MicrOTOF operating in ESI mode. HR mass spectra were recorded using Apex-Qe instrument (Bruker) equipped with APOLLOTM II ESI–MALDI Dual Source. Elemental analyses for carbon, hydrogen, and nitrogen were performed on Perkin Elmer 240C analyser. Temperature measurements of the magnetic susceptibility were carried out with a Quantum Design SQUID magnetometer in the 5–300 K temperature range operating at 1 T. Magnetic data were corrected for the diamagnetic contributions, which were estimated from Pascal's constants. Methanol and acetonitrile were dried by standard methods. Other common solvents (dichloromethane, isopropanole) were distilled before use. 1,3-Dibromopropane, 1,4-dibromobutane, and iron(II) perchlorate hexahydrate were purchased from Aldrich and used as delivered. For preparative column chromatography, silica gel Kieselgel 60 (0.063–0.1 mesh, Merck) and neutral alumina (POCh) were used. Other commercially available reagents were used without further purification. 1,2,3-Triazole,[34] tetrazole,[21] 5-(2-pyridyl)tetrazole,[35] 3-(2-pyridyl)-1,2,4-triazole,[36] and 3-(2-pyridyl)pyrazole[37] were prepared according to the known procedures. Synthesis of iron(II) complex was carried out under an nitrogen atmosphere using the standard Schlenk technique. *Caution*! Complexes containing perchlorates are potentially explosive and should be synthesized in milligram scale and handled with care.

4.2. X-ray data collection and structure determination

The crystals of **2d**, **2h**, and **2n** suitable for X-ray measurements were obtained by recrystallization of products from diethyl ether. Single crystals of **3f** were obtained by crystallization from acetonitrile. Crystals were coated by a layer of inert oil and transferred to the cold stream of nitrogen of the diffractometer. The measurements of compounds were performed at 100 K. All measurements of crystals were performed using Oxford Cryosystem device on Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp. z o.o. (formerly Kuma Diffraction Wroclaw, Poland) programs. The structures were solved by direct methods (program SHELXS97[38]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97[39] program. Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 686562–686565). Copies can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

4.3. Synthesis of 1-(3-bromopropyl)tetrazole (1a) and 2-(3-bromopropyl)tetrazole (1b)

General procedure. Solution of sodium hydroxide (0.5 mol, 20.0 g) in water (50 mL) was poured to tetrazole (0.50 mol, 35.0 g) dissolved in water (100 mL). The water was evaporated under

vacuum and the rest of water was removed by azeotropic distillation with absolute ethanole (rotary evaporator) giving a solid sodium tetrazolate. The whole amount of the obtained sodium salt was suspended in acetonitrile (200 mL) and 1,3-dibromopropane (2.5 mol, 255 mL) was added. The obtained reaction mixture was stirred and refluxed for 2 days. Then, NaBr was filtered off and acetonitrile and excess of 1,3-dibromopropane were evaporated under reduced pressure. The resulted yellow liquid was added to water (200 mL) and the obtained mixture was extracted with pentane (20×200 mL), carbon tetrachloride (200 mL), and finally with a mixture of $CCl_4/CHCl_3$ 1:1 (v/v, 15×200 mL). Pentane and $CCl_4/CHCl_3$ phases were dried over sodium sulfate. The crude products **1a** and **1b** were isolated after removal under reduced pressure of pentane or CCl_4 and $CHCl_3$, respectively. Both products were purified by column chromatography on silica gel eluting **1b** with CH_2Cl_2 and next **1a** with the mixture of CH_2Cl_2/CH_3CN 10:1 (v/v). Compounds **1a** and **1b** were isolated as colorless liquids with yields 13.0 g (14%) and 22.9 g (24%), respectively. Data for **1a**. R_f (CH_2Cl_2/CH_3CN 10:1) 0.54. δ_H (300 MHz, CD_3CN, 298 K) 8.85 (1H, s), 4.55 (2H, t, *J* 6.7 Hz), 3.43 (2H, t, *J* 6.3 Hz), 2.41 (2H, pseudo-quintet) ppm. δ_C (300 MHz, CD_3CN, 298 K) 144.3, 47.2, 32.9, 30.8 ppm. ν_{max} 3132, 2963 m, 1485 s, 1443 s, 1362 w, 1281 m, 1257 m, 1225 m, 1171 s, 1103 s, 1027 w, 966 m, 867 m, 788 w, 683 w, 661 m, 564 m cm^{-1}. HRMS (ESI) *m*/*z* found 190.9938 $[M+H]^+$, $C_4H_8N_4^{79}Br$ requires 190.9927; 192.9917 $[M+H]^+$, $C_4H_8N_4^{81}Br$ requires 192. 9906. Data for **1b**. R_f (CH_2Cl_2/CH_3CN 10:1) 0.78. δ_H (500 MHz, CD_3CN, 298 K) 8.59 (s, 1H), 4.79 (t, 2H, *J* 6.7 Hz), 3.45 (t, 2H, *J* 6.4 Hz), 2.50 (pseudo-quintet, 2H). δ_C (500 MHz, CD_3CN, 298 K) 154.0, 52.0, 32.7, 30.7. ν_{max} 3140 w, 2967 w, 1442 s, 1363 m, 1282 s, 1236 m, 1182 m, 1134 m, 1117 m, 1028 s, 1007 m, 974 w, 959 w, 882 m, 794 w, 709 m, 698 m, 665 w, 566 m, 411 w cm^{-1}. HRMS (ESI) *m*/*z* found 190.9938 $[M+H]^+$, $C_4H_8N_4^{79}Br$ requires 190.9927; 192.9918 $[M+H]^+$, $C_4H_8N_4^{81}Br$ requires 192.9906.

4.4. Synthesis of 1-(4-bromobutyl)tetrazole (1c) and 2-(4-bromobutyl)tetrazole (1d)

Following the procedure described in Section 4.3, the synthesis of **1c** and **1d** was carried out using 296 mL (2.5 mol) of 1,4-dibrombutane instead of 1,3-dibrompropane. Data for compound **1c**. Colorless liquid. Yield 15.1 g (15%). R_f (CH_2Cl_2/CH_3CN 10:1) 0.57. δ_H (300 MHz, CD_3CN, 298 K) 8.84 (1H, s), 4.43 (2H, t, *J* 7.0 Hz), 3.45 (2H, t, *J* 6.5 Hz), 1.9–2.1 (2H, m), 1.7–1.9 (2H, m). δ_C (300 MHz, CD_3CN, 298 K) 144.3, 48.1, 34.1, 30.2, 29.0 ppm. ν_{max} 3131 m, 3087 m, 2955 s, 2867 m, 1486 m, 1443 s, 1361 m, 1304 w, 1282 m, 1250 s, 1217 w, 1170 s, 1103 s, 1027 w, 967 m, 878 w, 772 w, 747 w, 663 m, 646 m, 560 m cm^{-1}. HRMS (ESI) *m*/*z* found 205.0094 $[M+H]^+$, $C_5H_{10}N_4^{79}Br$ requires 205.0083, 207.0074 $[M+H]^+$; $C_5H_{10}N_4^{81}Br$ requires 207.0063. Data for compound **1d**. Colorless liquid. Yield 27.1 g (26%). R_f (CH_2Cl_2/CH_3CN 10:1) 0.78. δ_H (500 MHz, CD_3CN, 298 K) 8.56 (1H, s), 4.68 (2H, t, *J* 7.0 Hz), 3.47 (2H, t, *J* 6.6 Hz), 2.0–2.15 (2H, m), 1.75–1.90 (2H, m). δ_C (500 MHz, CD_3CN, 298 K) 153.8, 52.9, 34.0, 30.2, 28.5, ν_{max} 3140 m, 2963 s, 2873 w, 1446 s, 1360 s, 1283 s, 1256 s, 1222 m, 1178 m, 1135 s, 1107 w, 1027 s, 1008 m, 974 w, 882 m, 776 m, 758 w, 710 m, 696 m, 662 w, 561 m cm^{-1}. HRMS (ESI) *m*/*z* found 205.0094 $[M+H]^+$; $C_5H_{10}N_4^{79}Br$ requires 205.0083, 207.0074 $[M+H]^+$; $C_5H_{10}N_4^{81}Br$ requires 207.0063.

4.5. Second synthesis method of 1a

Glacial acetic acid (200 mL) was added to a mixture of bromopropylamine hydrobromide (0.20 mol, 43.8 g), sodium azide (0.24 mol, 15.6 g), and triethyl orthoformate (54.0 mL). The obtained suspension was stirred and refluxed for 24 h. After this time, 12 M solution of HCl (5 mL) was added and the reaction mixture was filtered. The filtrate was concentrated under reduced pressure. Water (200 mL) was added to the obtained orange oil and the mixture was extracted with $CHCl_3$ (10×200 mL). The organic phase was dried over sodium sulfate. Next $CHCl_3$ was removed on rotary evaporator and the obtained crude product was purified by column chromatography on silica gel (CH_2Cl_2/CH_3OH 10:1 (v/v)). Yield 11.1 g (29%). Results of analytical investigations were in agreement with that ones given in Section 4.3 for **1a**.

4.6. Synthesis of 1-(3-(2-pyridyl)pyrazol-1-yl)-3-(tetrazol-1-yl)propane (2a)

General procedure. Sodium 3-(2-pyridyl)pyrazolate was obtained in the reaction of 3-(2-pyridyl)pyrazole (7.0 mmol, 1.016 g) dissolved in methanole (10 mL) with solution of sodium methanolate (7.0 mmol, 0.378 g) in methanol (10 mL). The methanol was removed on rotary evaporator. The obtained sodium salt was suspended in acetonitrile (10 mL) and a solution of **1a** (7.0 mmol, 1.337 g) in acetonitrile (10 mL) was added. The obtained reaction mixture was stirred and refluxed for 2 days. Then, NaBr was filtered off and acetonitrile was evaporated under reduced pressure giving the oily residue. Compound **2a** was isolated as yellowish oil (0.84 g, 47%) by column chromatography on alumina (R_f=0.38, TLC) using $CH_2Cl_2/(CH_3)_2CHOH$ 10:0.2 (v/v) mixture as eluent. δ_H (500 MHz, CD_3CN, 298 K) 8.88 (1H, s), 8.56 (1H, ddd, *J* 4.8, 1.7, 1.0 Hz, H6-pyridine), 7.95 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.77 (1H, td, *J* 7.7, 1.7 Hz, H4-pyridine), 7.60 (1H, d, *J* 2.3 Hz, H5-pyrazole), 7.24 (1H, ddd, *J* 7.5, 4.8, 1.2 Hz, H5-pyridine), 6.84 (1H, d, *J* 2.3 Hz, H4-pyrazole), 4.46 (2H, t, *J* 6.9 Hz), 4.22 (2H, t, *J* 6.5 Hz), 2.49 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 153.3, 152.8, 150.4, 144.7, 137.7, 132.6, 123.5, 120.5, 105.1, 49.6, 46.4, 31.0 ppm. ν_{max} 3147 w, 3098 s, 2967 w, 2958 m, 2948 m, 2929 m, 1592 s, 1566 m, 1492 s, 1486 s, 1465 s, 1442 s, 1428 m, 1403 m, 1363 m, 1348 m, 1330 m, 1280 m, 1254 w, 1225 s, 1181 w, 1169 s, 1155 m, 1113 s, 1094 w, 1053 m, 1040 m, 992 m, 965 m, 965 m, 908 w, 839 m, 795 m, 768 s, 754 s, 718 m, 699 m, 667 m, 636 w, 622 w, 462 w cm^{-1}. MS (ESI) *m*/*z* found 294.4 $[M+K]^+$. Anal. Calcd for $C_{12}H_{13}N_7$ (255.28) C, 56.5; H, 5.1; N, 38.4. Found: C, 56.6; H, 5.0; N, 38.5.

4.7. Synthesis of 1-(3-(2-pyridyl)pyrazol-1-yl)-3-(tetrazol-2-yl)propane (2b)

3-(2-Pyridyl)pyrazole (7.0 mmol, 1.016 g) and **1b** (7.0 mmol, 1.337 g) were used. Product was isolated (1.21 g, 68%) as colorless solid by chromatography on silica gel ($CH_2Cl_2/CH_3CN/CH_3OH$ 10:2:0.4 (v/v)). R_f=0.41 (TLC). δ_H (500 MHz, CD_3CN, 298 K) 8.60 (1H, s), 8.56 (1H, ddd, *J* 4.8, 1.7, 1.0 Hz, H6-pyridine), 7.94 (1H, dt, *J* 7.9, 1.1 Hz, H3-pyridine), 7.77 (1H, td, *J* 7.7, 1.8 Hz, H4-pyridine), 7.59 (1H, d, *J* 2.3 Hz, H5-pyrazole), 7.24 (1H, ddd, *J* 7.4, 4.8, 1.2 Hz, H5-pyridine), 6.83 (1H, d, *J* 2.3 Hz, H4-pyrazole), 4.70 (2H, t, *J* 6.8 Hz), 4.24 (2H, t, *J* 6.8 Hz), 2.60 (2H, quintet, *J* 6.8 Hz). δ_C (300 MHz, CD_3CN, 298 K) 153.3, 152.9, 150.3, 137.6, 132.7, 123.4, 120.4, 104.9, 51.2, 49.7, 30.5 ppm. ν_{max} 3145 w, 3091 m, 2967 w, 2862 w, 1635 w, 1596 s, 1568 m, 1497 s, 1463 s, 1406 m, 1355 m, 1333 m, 1285 m, 1279 m, 1245 m, 1234 m, 1178 m, 1150 m, 1133 w, 1109 w, 1094 w, 1051 m, 1032 m, 1007 m, 999 w, 992 w, 956 w, 922 w, 801 w, 768 s, 730 w, 710 w, 640 m, 628 m, 484 w cm^{-1}. MS (ESI) *m*/*z* found 278.1 $[M+Na]^+$, 294.1 $[M+K]^+$. Anal. Calcd for $C_{12}H_{13}N_7$ (255.28) C, 56.5; H, 5.1; N, 38.4. Found: C, 56.5; H, 5.2; N, 38.5.

4.8. Synthesis of 1-(3-(2-pyridyl)pyrazol-1-yl)-3-(tetrazol-1-yl)butane (2c)

3-(2-Pyridyl)pyrazole (7.0 mmol, 1.016 g) and **1c** (7.0 mmol, 1.435 g) were used. Product was isolated (0.96 g, 51%) as colorless (slowly solidifying) oil by chromatography on alumina ($CH_2Cl_2/(CH_3)_2CHOH$ 10:0.2 (v/v)). R_f=0.37. δ_H (500 MHz, CD_3CN, 298 K)

8.82 (1H, s), 8.55 (1H, ddd, *J* 4.8, 1.7, 1.0 Hz, H6-pyridine), 7.91 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.76 (1H, td, *J* 7.7, 1.8 Hz, H4-pyridine), 7.57 (1H, d, *J* 2.3 Hz, H5-pyrazole), 7.23 (1H, ddd, *J* 7.4, 4.8, 1.2 Hz, H5-pyridine), 6.82 (1H, d, *J* 2.3 Hz, H4-pyrazole), 4.42 (2H, t, *J* 6.7 Hz), 4.19 (2H, t, *J* 6.5 Hz), 1.82–1.94 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 153.4, 152.5, 150.3, 144.4, 137.7, 132.3, 123.4, 120.4, 104.9, 52.1, 48.4, 27.9, 27.5 ppm. ν_{max} 3129 m, 2950 m, 2872 w, 1594 s, 1567 m, 1493 s, 1460 s, 1443 s, 1431 s, 1404 s, 1359 s, 1331 m, 1278 m, 1232 s, 1170 s, 1151 m, 1106 s, 1051 m, 993 m, 967 m, 957 m, 874 w, 770 s, 716 m, 696 m, 664 m, 621 m cm^{-1}. HRMS (ESI) *m*/*z* found 292.1290 $[M+Na]^+$; $C_{13}H_{15}N_7Na$ requires 292.1281.

4.9. Synthesis of 1-(3-(2-pyridyl)pyrazol-1-yl)-4-(tetrazol-2-yl)butane (2d)

3-(2-Pyridyl)pyrazole (7.0 mmol, 1.016 g) and **1d** (7.0 mmol, 1.435 g) were used. Product was isolated (1.18 g, 63%) as colorless solid by chromatography on silica gel ($CH_2Cl_2/CH_3CN/CH_3OH$ 10:2:0.3 (v/v)). R_f=0.35 (TLC). δ_H (500 MHz, CD_3CN, 298 K) 8.57 (1H, s), 8.55 (1H, ddd, *J* 4.8, 1.8, 0.9 Hz, H6-pyridine), 7.91 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.76 (1H, td, *J* 7.7, 1.8 Hz, H4-pyridine), 7.56 (1H, d, *J* 2.3 Hz, H5-pyrazole), 7.23 (1H, ddd, *J* 7.5, 4.9, 1.2 Hz, H5-pyridine), 6.82 (1H, d, *J* 2.3 Hz, H4-pyrazole), 4.67 (2H, t, *J* 6.9 Hz), 4.20 (2H, t, *J* 6.7 Hz), 1.80–2.05 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 153.9, 153.5, 152.5, 150.3, 137.6, 132.2, 123.4, 120.4, 104.9, 53.3, 52.1, 28.0, 27.1 ppm. ν_{max} 3134 w, 2944 m, 2872 w, 1593 s, 1567 m, 1494 s, 1469 s, 1462 s, 1447 m, 1435 m, 1400 m, 1389 w, 1379 w, 1359 s, 1338 m, 1284 s, 1271 w, 1246 m, 1231 m, 1222 m, 1178 m, 1147 w, 1128 m, 1113 w, 1094 w, 1074 w, 1045 m, 1036 m, 1030 m, 1023 m, 1010 w, 993 m, 956 w, 914 w, 890 w, 886 w, 777 s, 762 m, 750 m, 708 m, 700 w, 687 m, 630 m, 621 w, 438 w, 407 w cm^{-1}. MS (ESI) *m*/*z* found 292.1 $[M+Na]^+$. Anal. Calcd for $C_{13}H_{15}N_7$ (269.30) C, 58.0; H, 5.6; N, 36.4. Found: C, 58.2; H, 5.5; N, 36.5. Crystal data: colorless plate, crystal dimensions 0.35×0.25×0.10 mm, monoclinic, space group $P2_1/c$, a=11.478(2), b=8.139(2), c=29.490(8) Å, β=103.45(3)°, V=2679.4(11) $Å^3$, Z=8, D_c=1.335 Mg m^{-3}, μ(Mo Kα)=0.09 mm^{-1}, T=100 K, R=0.040, wR=0.079 (3339 reflections with $I>2\sigma(I)$) for 361 variables.

4.10. Synthesis of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-3-(tetrazol-1-yl)propane (2e)

3-(2-Pyridyl)-1,2,4-triazole (7.0 mmol, 1.023 g) and **1a** (7.0 mmol, 1.337 g) were used. Product was isolated (0.81 g, 45%) as white solid by chromatography on alumina (CH_2Cl_2/CH_3OH 10:0.2 (v/v)). R_f=0.17 (TLC). δ_H (300 MHz, CD_3CN, 298 K) 8.89 (1H, s), 8.64 (1H, ddd, *J* 4.8, 1.6, 0.9 Hz, H6-pyridine), 8.26 (1H, s), 8.08 (1H, dt, *J* 8.0, 1.0 Hz, H3-pyridine), 7.82 (1H, td, *J* 7.8, 1.8 Hz, H4-pyridine), 7.35 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.48 (2H, t, *J* 6.9 Hz), 4.27 (2H, t, *J* 6.7 Hz), 2.50 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 163.1, 151.1, 150.7, 146.1, 144.7, 137.9, 124.9, 122.7, 47.3, 46.2, 30.4 ppm. ν_{max} 3084 s, 2959 w, 1590 s, 1518 m, 1498 s, 1482 m, 1444 m, 1410 s, 1351 w, 1332 s, 1272 w, 1266 w, 1254 w, 1221 s, 1184 m, 1170 s, 1144 m, 1104 s, 1088 m, 1048 m, 1018 w, 994 m, 967 m, 904 w, 889 w, 876 w, 824 w, 803 m, 751 m, 743 m, 728 s, 702 w, 663 m, 646 m, 619 w, 407 w cm^{-1}. MS (ESI) *m*/*z* found 279.1 $[M+Na]^+$. Anal. Calcd for $C_{11}H_{12}N_8$ (256.26) C, 51.6; H, 4.7; N, 43.7. Found: C, 51.6; H, 4.7; N, 43.9.

4.11. Synthesis of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-3-(tetrazol-2-yl)propane (2f)

3-(2-Pyridyl)-1,2,4-triazole (7.0 mmol, 1.023 g) and **1b** (7.0 mmol, 1.337 g) were used. Product was isolated (0.94 g, 52%) as colorless liquid by chromatography on silica gel (CH_2Cl_2/CH_3OH 10:1.1 (v/v)). R_f=0.62 (TLC). δ_H (500 MHz, CD_3CN, 298 K) 8.66 (1H, ddd, *J* 4.7, 1.7, 0.9 Hz, H6-pyridine), 8.61 (1H, s), 8.26 (1H, s), 8.10 (1H, dt, *J* 7.9, 1.1 Hz, H3-pyridine), 7.85 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.38 (1H, ddd, *J* 7.6, 4.7, 1.2 Hz, H5-pyridine), 4.74 (2H, t, *J* 6.7 Hz), 4.32 (2H, t, *J* 6.7 Hz), 2.62 (2H, quintet, *J* 6.7 Hz). δ_C (300 MHz, CD_3CN, 298 K) 163.0, 154.0, 151.0, 150.6, 146.2, 137.8, 124.8, 122.6, 51.0, 47.3, 29.8 ppm. ν_{max} 3112 m, 2959 m, 1592 s, 1570 m, 1516 m, 1493 s, 1448 m, 1413 s, 1361 m, 1331 s, 1283 s, 1247 w, 1208 s, 1183 m, 1129 s, 1088 w, 1048 m, 1028 s, 1008 m, 996 m, 979 m, 878 m, 804 s, 748 s, 731 s, 708 m, 683 w, 645 m, 621 m, 470 w, 404 m cm^{-1}. HRMS (ESI) *m*/*z* found 279.1085 $[M+Na]^+$; $C_{11}H_{12}N_8Na$ requires 279.1077.

4.12. Synthesis of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-1-yl)butane (2g)

3-(2-Pyridyl)-1,2,4-triazole (7.0 mmol, 1.023 g) and **1c** (7.0 mmol, 1.435 g) were used. Product was isolated (0.92 g, 49%) as colorless oil by chromatography on alumina (CH_2Cl_2/CH_3OH 10:0.2 (v/v)). R_f=0.25 (TLC). δ_H (500 MHz, CD_3CN, 298 K) 8.88 (1H, s), 8.62 (1H, ddd, *J* 4.8, 1.8, 0.9 Hz, H6-pyridine), 8.24 (1H, s), 8.05 (1H, dt, *J* 8.0, 1.0 Hz, H3-pyridine), 7.80 (1H, td, *J* 7.7, 1.8 Hz, H4-pyridine), 7.32 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.42 (2H, t, *J* 6.7 Hz), 4.23 (2H, t, *J* 6.4 Hz), 1.75–2.00 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 161.9, 150.1, 149.6, 144.8, 143.4, 136.8, 123.8, 121.6, 48.7, 47.3, 26.4, 26.3 ppm. ν_{max} 3109 m, 2952 m, 2871 w, 1592 s, 1570 m, 1515 m, 1492 s, 1443 s, 1413 s, 1365 m, 1333 s, 1277 w, 1247 w, 1208 s, 1170 s, 1150 m, 1128 m, 1106 s, 1088 w, 1048 w, 1034 m, 995 m, 979 w, 967 w, 874 w, 804 m, 749 s, 731 s, 665 w, 646 m, 621 w, 404 m cm^{-1}. HRMS (ESI) *m*/*z* found 271.1423 $[M+H]^+$; $C_{12}H_{15}N_8$ requires 271.1414, 293.1242 $[M+Na]^+$; $C_{12}H_{14}N_8Na$ requires 293.1234.

4.13. Synthesis of 1-(3-(2-pyridyl)-1,2,4-triazol-1-yl)-4-(tetrazol-2-yl)butane (2h)

3-(2-Pyridyl)-1,2,4-triazole (7.0 mmol, 1.023 g) and **1d** (7.0 mmol, 1.435 g) were used. Product was isolated (0.95 g, 50%) as colorless solid by chromatography on silica gel (CH_2Cl_2/CH_3OH 10:1.1 (v/v)). R_f=0.64 (TLC). δ_H (500 MHz, CD_3CN, 298 K) 8.65 (1H, ddd, *J* 4.7, 1.7, 0.9 Hz, H6-pyridine), 8.58 (1H, s), 8.25 (1H, s), 8.08 (1H, dt, *J* 7.9, 1.1 Hz, H3-pyridine), 7.83 (1H, td, *J* 7.8, 1.8 Hz, H4-pyridine), 7.35 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.69 (2H, t, *J* 6.9 Hz), 4.26 (2H, t, *J* 6.8 Hz), 1.85–2.05 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 162.8, 153.9, 151.1, 150.6, 145.8, 137.8, 124.8, 122.6, 53.2, 49.7, 27.4, 26.9 ppm. ν_{max} 3124 m, 3083 s, 3029 w, 2988 w, 2955 m, 2875 w, 1666 w, 1592 s, 1571 m, 1520 m, 1503 m, 1473 m, 1465 m, 1450 w, 1427 w, 1415 s, 1378 m, 1359 m, 1336 s, 1328 s, 1304 w, 1280 s, 1245 w, 1228 s, 1181 m, 1150 m, 1139 s, 1087 m, 1068 m, 1040 s, 1027 s, 1015 m, 1005 m, 998 m, 925 w, 905 m, 803 m, 766 s, 747 s, 731 s, 709 m, 687 m, 654 m, 620 m, 568 w, 515 w, 490 w, 457 m cm^{-1}. MS (ESI) *m*/*z* found 271.1 $[M+H]^+$, 293.1 $[M+Na]^+$. Anal. Calcd for $C_{12}H_{14}N_8$ (270.29) C, 53.3; H, 5.2; N, 41.5. Found: C, 53.1; H, 5.0; N, 41.3. Crystal data: colorless block, crystal dimensions 0.10×0.08×0.07 mm, triclinic, space group P-1, a=7.026(3), b=9.861(4), c=10.218(5) Å, α=113.75(3), β=93.16(3), γ=92.04(3)°, V=645.7(5) $Å^3$, Z=2, D_c=1.390 Mg m^{-3}, μ(Mo Kα)=0.09 mm^{-1}, T=100 K, R=0.133, wR=0.170 (1379 reflections with $I>2\sigma(I)$) for 181 variables.

4.14. Synthesis of 1-(5-(2-pyridyl)tetrazol-1-yl)-3-(tetrazol-1-yl)propane (2i) and 1-(5-(2-pyridyl)tetrazol-2-yl)-3-(tetrazol-1-yl)propane (2j)

5-(2-Pyridyl)tetrazole (7.0 mmol, 1.030 g) and **1a** (7.0 mmol, 1.337 g) were used. Products **2i** (colorless solid, R_f=0.46, TLC) and **2j** (colorless solid, R_f=0.31, TLC) were isolated by chromatography on alumina ($CH_2Cl_2/(CH_3)_2CHOH$ 10:0.15 (v/v)) with yields 0.39 g (22%) and 0.81 g (45%), respectively. Data for **2i**. δ_H (500 MHz, CD_3CN, 298 K) 8.86 (1H, s), 8.61 (1H, ddd, *J* 4.8, 1.6, 0.9 Hz, H6-pyridine), 8.26

(1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.98 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.52 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.98 (2H, t, *J* 7.0 Hz), 4.56 (2H, t, *J* 6.8 Hz), 2.62 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 153.0, 150.7, 145.7, 144.6, 138.9, 126.7, 125.2, 47.5, 46.2, 30.3 ppm. ν_{max} 3114 s, 3039 w, 3017 w, 2971 m, 2938 m, 1591 s, 1570 w, 1530 m, 1487 m, 1474 s, 1443 s, 1435 s, 1401 m, 1359 w, 1337 w, 1323 w, 1287 m, 1254 m, 1232 w, 1177 s, 1157 m, 1125 s, 1121 s, 1106 s, 1098 m, 1068 m, 1037 s, 1003 m, 995 m, 984 m, 966 m, 909 w, 895 m, 875 w, 805 s, 786 s, 763 m, 746 s, 729 s, 714 m, 702 m, 678 s, 650 m, 625 m, 521 w, 471 w, 404 w cm^{-1}. MS (ESI) *m*/*z* found 258.1 $[M+H]^+$, 280.1 $[M+Na]^+$. Anal. Calcd for $C_{10}H_{11}N_9$ (257.25) C, 46.7; H, 4.3; N, 49.0. Found: C, 46.7; H, 4.0; N, 48.8. Data for **2j**. δ_H (500 MHz, CD_3CN, 298 K) 8.88 (1H, s), 8.73 (1H, ddd, *J* 4.7, 1.7, 1.0 Hz, H6-pyridine), 8.16 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.93 (1H, td, *J* 7.8, 1.8 Hz, H4-pyridine), 7.47 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.80 (2H, t, *J* 6.6 Hz), 4.56 (2H, t, *J* 6.9 Hz), 2.68 (2H, pseudo- quintet). δ_C (300 MHz, CD_3CN, 298 K) 165.8, 151.2, 147.8, 144.7, 138.3, 126.0, 123.5, 51.2, 46.1, 29.7 ppm. ν_{max} 3128 s, 3069 w, 2977 m, 2947 w, 1595 m, 1571 m, 1522 w, 1488 m, 1466 m, 1449 s, 1423 s, 1393 m, 1381 m, 1360 m, 1327 m, 1296 w, 1248 w, 1209 m, 1166 s, 1123 m, 1107 s, 1089 w, 1045 s, 1034 w, 1015 w, 992 w, 971 m, 900 m, 871 w, 803 m, 786 m, 740 s, 727 m, 696 w, 662 m, 620 w, 514 w, 494 w, 462 w cm^{-1}. MS (ESI) *m*/*z* found 258.1 $[M+H]^+$, 280.1 $[M+Na]^+$. Anal. Calcd for $C_{10}H_{11}N_9$ (257.25) C, 46.7; H, 4.3; N, 49.0. Found: C, 46.7; H, 4.0; N, 48.7.

4.15. Synthesis of 1-(5-(2-pyridyl)tetrazol-1-yl)-3-(tetrazol-2-yl)propane (2k) and 1-(5-(2-pyridyl)tetrazol-2-yl)-3-(tetrazol-2-yl)propane (2l)

5-(2-Pyridyl)tetrazole (7.0 mmol, 1.030 g) and **1b** (7.0 mmol, 1.337 g) were used. Products **2k** (colorless solid, R_f=0.63, TLC) and **2l** (colorless solid, R_f=0.31, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/CH_3OH 10:1:0.2 (v/v)) with yields 0.39 g (22%) and 0.91 g (50%), respectively. Data for **2k**. δ_H (500 MHz, CD_3CN, 298 K) 8.55–8.65 (2H, m, H6-pyridine and H-tetrazolyl), 8.25 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.98 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.51 (1H, ddd, *J* 7.7, 4.8, 1.2 Hz, H5-pyridine), 5.00 (2H, t, *J* 7.0 Hz), 4.79 (2H, t, *J* 6.6 Hz), 2.69 (2H, quintet, *J* 6.8 Hz). δ_C (300 MHz, CD_3CN, 298 K) 154.0, 153.0, 150.6, 145.7, 138.9, 126.6, 125.2, 51.1, 47.6, 29.8 ppm. ν_{max} 3146 m, 3093 w, 3018 w, 2971 m, 2941 m, 1588 m, 1570 w, 1531 m, 1471 s, 1432 s, 1402 w, 1388 w, 1365 m, 1356 w, 1286 s, 1232 w, 1189 m, 1165 w, 1148 w, 1137 m, 1123 s, 1093 w, 1069 w, 1056 w, 1035 s, 1028 s, 1004 m, 994 m, 983 m, 901 m, 869 w, 805 s, 789 m, 759 m, 748 m, 730 m, 715 m, 701 s, 658 w, 623 w, 527 w, 487 w, 471 m, 411 w cm^{-1}. MS (ESI) *m*/*z* found 280.1 $[M+Na]^+$. Anal. Calcd for $C_{10}H_{11}N_9$ (257.25) C, 46.7; H, 4.3; N, 49.0. Found C, 46.8; H, 3.8; N, 48.9. Data for **2l**. δ_H (500 MHz, CD_3CN, 298 K) 8.73 (1H, ddd, *J* 4.8, 1.7, 0.9 Hz, H6-pyridine), 8.60 (1H, s), 8.25 (1H, s), 8.14 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.92 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.46 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.82 (2H, t, *J* 6.7 Hz), 4.81 (2H, t, *J* 6.7 Hz), 2.77 (2H, quintet, *J* 6.7 Hz). δ_C (300 MHz, CD_3CN, 298 K) 165.8, 154.1, 151.2, 147.9, 138.3, 126.0, 123.5, 51.3, 50.9, 29.2 ppm. ν_{max} 3130 m, 3070 w, 3048 w, 3009 w, 2959 w, 1596 m, 1572 m, 1526 w, 1466 m, 1441 m, 1423 s, 1382 s, 1364 m, 1327 w, 1298 w, 1283 s, 1263 w, 1216 w, 1195 m, 1174 w, 1156 m, 1136 m, 1109 w, 1090 w, 1072 w, 1042 s, 1030 s, 1006 w, 992 m, 896 m, 890 m, 872 w, 803 s, 757 m, 740 s, 729 m, 708 m, 696 w, 686 m, 665 w, 620 w, 514 w, 498 w, 460 w cm^{-1}. MS (ESI) *m*/*z* found 280.1 $[M+Na]^+$. Anal. Calcd for $C_{10}H_{11}N_9$ (257.25) C, 46.7; H, 4.3; N, 49.0. Found: C, 46.6; H, 4.0; N, 49.0.

4.16. Synthesis of 1-(5-(2-pyridyl)tetrazol-1-yl)-4-(tetrazol-1-yl)butane (2m) and 1-(5-(2-pyridyl)tetrazol-2-yl)-4-(tetrazol-1-yl)butane (2n)

5-(2-Pyridyl)tetrazole (7.0 mmol, 1.030 g) and **1c** (7.0 mmol, 1.435 g) were used. Products **2m** (colorless solid, R_f=0.46, TLC) and **2n** (colorless solid, R_f=0.34, TLC) were isolated by chromatography on alumina (CH_2Cl_2/$(CH_3)_2CHOH$ 10:0.15 (v/v)) with yields 0.34 g (18%) and 0.77 g (40%), respectively. Data for **2m**. δ_H (500 MHz, CD_3CN, 298 K) 8.80 (1H, s), 8.74 (1H, ddd, *J* 4.8, 1.7, 0.9 Hz, H6-pyridine), 8.27 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.99 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.54 (1H, ddd, *J* 7.6, 4.9, 1.2 Hz, H5-pyridine), 4.9–5.0 (2H, m), 4.4–4.5 (2H, m), 1.9–2.0 (4H, m) ppm. δ_C (300 MHz, CD_3CN, 298 K) 153.1, 150.8, 146.0, 144.4, 138.9, 126.7, 125.3, 49.6, 48.4, 27.3, 27.2 ppm. ν_{max} 3126 s, 2973 m, 2924 m, 2855 w, 1589 m, 1572 w, 1528 w, 1486 m, 1473 s, 1445 s, 1434 s, 1411 m, 1402 m, 1364 w, 1296 w, 1245 m, 1235 w, 1200 w, 1173 s, 1150 w, 1124 m, 1099 s, 1041 w, 1022 w, 1001 m, 965 m, 879 w, 804 m, 792 s, 749 m, 732 m, 718 m, 677 m, 661 w, 643 m, 623 w, 506 w, 424 w cm^{-1}. MS (ESI) *m*/*z* found 294.1 $[M+Na]^+$. Anal. Calcd for $C_{11}H_{13}N_9$ (271.28) C, 48.7; H, 4.8; N, 46.5. Found: C, 49.0; H, 4.7; N, 46.3. Data for **2n**. δ_H (500 MHz, CD_3CN, 298 K) 8.84 (1H, s), 8.73 (1H, ddd, *J* 4.8, 1.6, 0.9 Hz, H6-pyridine), 8.16 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.93 (1H, td, *J* 7.8, 1.8 Hz, H4-pyridine), 7.47 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.74 (2H, t, *J* 6.7 Hz), 4.47 (2H, t, *J* 6.9 Hz), 1.9–2.1 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 165.8, 151.2, 148.0, 144.4, 138.3, 126.0, 123.4, 53.5, 48.3, 27.3, 26.8 ppm. ν_{max} 3062 s, 3004 m, 2953 m, 2884 m, 1595 s, 1571 m, 1424 w, 1484 m, 1473 m, 1454 s, 1432 s, 1385 m, 1355 m, 1332 m, 1285 m, 1248 m, 1210 w, 1194 m, 1179 s, 1154 m, 1148 m, 1120 m, 1101 m, 1070 w, 1057 m, 1045 m, 1017 m, 1012 m, 995 m, 966 m, 917 w, 895 w, 803 s, 768 s, 746 s, 735 s, 715 w, 692 m, 670 s, 621 m, 514 w, 449 w, 407 m cm^{-1}. MS (ESI) *m*/*z* found 294.1 $[M+Na]^+$. Anal. Calcd for $C_{11}H_{13}N_9$ (271.28) C, 48.7; H, 4.8; N, 46.5. Found: C, 48.9; H, 5.1; N, 46.6. Crystal data for **2n**: colorless plate, crystal dimensions 0.55×0.40×0.20 mm, monoclinic, space group $P2_1/c$, a=5.492(2), b=12.032(3), c=19.653(4) Å, β=101.35(3)°, V=1273.3(6) $Å^3$, Z=4, D_c=1.415 Mg m^{-3}, μ(Mo Kα)=0.10 mm^{-1}, T=100 K, R=0.035, wR=0.089 (2178 reflections with $I>2\sigma(I)$) for 181 variables.

4.17. Synthesis of 1-(5-(2-pyridyl)tetrazol-1-yl)-4-(tetrazol-2-yl)butane (2o) and 1-(5-(2-pyridyl)tetrazol-2-yl)-4-(tetrazol-2-yl)butane (2p)

5-(2-Pyridyl)tetrazole (7.0 mmol, 1.030 g) and **1d** (7.0 mmol, 1.435 g) were used. Products **2o** (colorless solid, R_f=0.70, TLC) and **2p** (colorless solid, R_f=0.48, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/CH_3OH 10:1:0.2 (v/v)) with yields 0.38 g (20%) and 0.60 g (32%), respectively. Data for **2o**. δ_H (500 MHz, CD_3CN, 298 K) 8.73 (1H, ddd, *J* 4.8, 1.7, 0.9 Hz, H6-pyridine), 8.55 (1H, s), 8.26 (1H, dt, *J* 7.9, 1.0 Hz, H3-pyridine), 7.99 (1H, td, *J* 7.8, 1.7 Hz, H4-pyridine), 7.53 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.95 (2H, t, *J* 6.9 Hz), 4.69 (2H, t, *J* 6.7 Hz), 1.9–2.1 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 153.9, 153.0, 150.8, 145.9, 138.8, 126.6, 125.3, 53.2, 49.6, 27.3, 26.8 ppm. ν_{max} 3128 m, 3078 w, 3056 w, 3027 w, 3008 w, 2962 w, 2875 w, 1588 m, 1571 m, 1527 w, 1480 s, 1469 m, 1451 w, 1429 s, 1411 m, 1378 m, 1360 m, 1345 w, 1276 s, 1241 w, 1186 m, 1134 m, 1118 m, 1090 m, 1043 m, 1024 s, 1009 m, 903 w, 803 s, 767 m, 746 m, 729 m, 712 m, 699 m, 690 m, 626 m, 499 w, 423 w cm^{-1}. MS (ESI) *m*/*z* found 294.1 $[M+Na]^+$. Anal. Calcd for $C_{11}H_{13}N_9$ (271.28) C, 48.7; H, 4.8; N, 46.5. Found: C, 48.7; H, 4.6; N, 46.4. Data for **2p**. δ_H (500 MHz, CD_3CN, 298 K) 8.73 (1H, ddd, *J* 4.8, 1.7, 0.9 Hz, H6-pyridine), 8.58 (1H, s), 8.16 (1H, dt 7.9 Hz, 1.0 Hz, H3-pyridine), 7.93 (1H, td, *J* 7.7, 1.7 Hz, H4-pyridine), 7.47 (1H, ddd, *J* 7.6, 4.8, 1.2 Hz, H5-pyridine), 4.65–4.80 (4H, m), 2.06 (4H, m) ppm. δ_C (300 MHz, CD_3CN, 298 K) 165.8, 154.0, 151.2, 148.0, 138.3, 126.0, 123.4, 53.5, 53.1, 26.92, 26.90. ν_{max} 3135 m, 3060 m, 2967 m, 2951 m, 2894 w, 2872 m, 1595 s, 1571 m, 1524 m, 1461 s, 1437 w, 1418 s, 1389 m, 1354 s, 1323 w, 1283 s, 1250 w, 1214 w, 1199 m, 1176 m, 1158 m, 1141 m, 1110 w, 1094 m, 1070 w, 1048 s, 1033 s, 1022 m, 1010 m, 990 m, 912 w, 883 m, 804 m, 792 w, 773 s, 764 m, 753 s, 737 s, 708 m, 688 m, 619 w, 518 w, 455 w, 407 w cm^{-1}. MS (ESI) *m*/*z* found

294.1 $[M+Na]^+$. Calcd for $C_{11}H_{13}N_9$ (271.28) C, 48.7; H, 4.8; N, 46.5. Found: C, 48.8; H, 4.7; N, 46.3.

4.18. Synthesis of 1-(tetrazol-1-yl)-3-(1,2,3-triazol-2-yl)propane (3a) and 1-(tetrazol-1-yl)-3-(1,2,3-triazol-1-yl)propane (3b)

General procedure. Synthesis was performed according to the procedure described for **2a**–**2p** using 7.0 mmol (1.337 g) **1a** as alkylating agent and 7.0 mmol (0.484 g) 1,2,3-triazole instead of (2-pyridyl)azole. Products **3a** (colorless solid, R_f=0.55, TLC) and **3b** (colorless solid, R_f=0.38, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/CH_3OH 10:2:0.5 (v/v)) with yields 0.41 g (30%) and 0.32 g (24%), respectively. Data for **3a**. δ_H (500 MHz, CD_3CN, 298 K) 8.81(1H, s), 7.63 (2H, s), 4.45 (2H, t, *J* 6.5 Hz), 4.40 (2H, t, *J* 7.0 Hz), 2.51 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 144.7, 135.4, 52.2, 46.3, 30.2 ppm. ν_{max} 3141 s, 3126 s, 3117 s, 3006 w, 2963 m, 2886 w, 1483 m, 1464 m, 1457 m, 1444 s, 1424 s, 1388 m, 1367 m, 1357 s, 1288 w, 1258 m, 1227 w, 1197 m, 1170 s, 1123 s, 1102 s, 1083 w, 1064 m, 1055 m, 1038 w, 1031 m, 980 m, 967 s, 883 m, 837 s, 792 m, 764 m, 725 m, 708 m, 664 s, 458 m cm^{-1}. MS (ESI) *m*/*z* found 180.1 $[M+H]^+$, 202.1 $[M+Na]^+$. Anal. Calcd for $C_6H_9N_7$ (179.18) C, 40.2; H, 5.1; N, 54.7. Found: C, 40.3; H, 5.0; N, 54.8. Data for **3b**. δ_H (500 MHz, CD_3CN, 298 K) 8.84 (1H, s), 7.80 (1H, s), 7.66 (1H, s), 4.44 (4H, t, *J* 6.9 Hz), 2.51 (2H, quintet, *J* 6.9 Hz). δ_C (300 MHz, CD_3CN, 298 K) 144.6, 134.5, 125.5, 47.5, 46.2, 30.8 ppm. ν_{max} 3144 m, 3131 s, 3121 s, 3013 w, 2971 m, 2944 m, 2880 w, 1483 m, 1460 s, 1449 s, 1428 m, 1386 m, 1365 w, 1297 s, 1279 s, 1248 s, 1220 s, 1160 s, 1126 s, 1119 m, 1101 s, 1072 s, 1062 s, 1042 m, 1033 m, 970 m, 952 m, 907 m, 873 w, 800 s, 772 m, 766 m, 724 w, 693 w, 667 s, 646 w, 458 w cm^{-1}. MS (ESI) *m*/*z* found 180.1 $[M+H]^+$, 202.1 $[M+Na]^+$. Anal. Calcd for $C_6H_9N_7$ (179.18) C, 40.2; H, 5.1; N, 54.7. Found: C, 40.3; H, 5.1; N, 54.9.

4.19. Synthesis of 1-(tetrazol-2-yl)-3-(1,2,3-triazol-2-yl)propane (3c) and 1-(tetrazol-2-yl)-3-(1,2,3-triazol-1-yl)propane (3d)

Compound **1b** (7.0 mmol, 1.337 g) as alkylating agent was used. Products **3c** (colorless liquid, R_f=0.80, TLC) and **3d** (colorless oil, R_f=0.40, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/CH_3OH 10:1:0.1 (v/v)) with yields 0.40 g (32%) and 0.32 g (26%), respectively. Data for **3c**. δ_H (500 MHz, CD_3CN, 298 K) 8.59 (1H, s), 7.65 (2H, s), 4.69 (2H, t, *J* 6.8 Hz), 4.51 (2H, t, *J* 6.6 Hz), 2.62 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 154.0, 135.4, 52.3, 51.1, 29.7 ppm. ν_{max} 3139 m, 2960 w, 1449 m, 1419 s, 1362 s, 1284 s, 1189 m, 1168 w, 1135 m, 1051 m, 1028 s, 1008 m, 963 s, 881 w, 823 s, 758 w, 708 m, 686 w, 474 w cm^{-1}. HRMS (ESI) *m*/*z* found 202.0822 $[M+Na]^+$; $C_6H_9N_7Na$ requires 202. 0812. Data for **3d**. δ_H (500 MHz, CD_3CN, 298 K) 8.61 (1H, s), 7.79 (1H, s), 7.65 (1H, s), 4.68 (2H, t, *J* 6.7 Hz), 4.53 (2H, t, *J* 6.9 Hz), 2.59 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 154.0, 134.4, 125.6, 50.9, 47.6, 30.3 ppm. ν_{max} 3143 s, 3128 s, 3011 m, 2986 m, 2970 m, 1482 m, 1473 m, 1459 m, 1441 m, 1394 m, 1375 m, 1359 m, 1327 w, 1302 m, 1285 s, 1222 s, 1180 m, 1134 s, 1115 s, 1077 s, 1053 m, 1030 s, 1008 s, 949 m, 909 w, 804 s, 794 s, 748 m, 720 w, 710 s, 699 m, 685 m, 641 w, 468 m cm^{-1}. MS (ESI) *m*/*z* found 180.1 $[M+H]^+$, 202.1 $[M+Na]^+$. Anal. Calcd for $C_6H_9N_7$ (179.18) C, 40.2; H, 5.1; N, 54.7. Found: C, 40.3; H, 4.9; N, 54.5.

4.20. Synthesis of 1-(tetrazol-1-yl)-4-(1,2,3-triazol-2-yl)butane (3e) and 1-(tetrazol-1-yl)-4-(1,2,3-triazol-1-yl)butane (3f)

Compound **1c** (7.0 mmol, 1.435 g) as alkylating agent was used. Products **3e** (colorless solid, R_f=0.64, TLC) and **3f** (colorless solid, R_f=0.38, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/CH_3OH 10:2:0.5 (v/v)) with yields 0.41 g (30%) and 0.38 g (28%), respectively. Data for **3e**. δ_H (500 MHz, CD_3CN, 298 K) 8.80 (1H, s), 7.63 (2H, s), 4.45 (2H, t, *J* 6.6 Hz), 4.42 (2H, t, *J* 6.8 Hz), 1.8–1.95 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 144.4, 135.1, 54.6, 48.3, 27.4, 27.2 ppm. ν_{max} 3135 m, 3122 s, 2953 m, 2934 m, 2867 m, 1479 m, 1464 s, 1431 m, 1423 s, 1378 m, 1362 s, 1348 m, 1310 w, 1299 w, 1271 w, 1244 w, 1190 m, 1164 s, 1111 m, 1100 s, 1069 m, 1022 m, 978 m, 971 m, 962 s, 906 m, 840 s, 763 m, 743 m, 738 m, 721 m, 672 s, 444 w cm^{-1}. MS (ESI) *m*/*z* found 194.1 $[M+H]^+$, 216.1 $[M+Na]^+$. Anal. Calcd for $C_7H_{11}N_7$ (193.21) C, 43.5; H, 5.7; N, 50.8. Found: C, 43.7; H, 5.8; N, 50.9. Data for **3f**. δ_H (500 MHz, CD_3CN, 298 K) 8.80 (1H, s), 7.74 (1H, s), 7.63 (1H, s), 4.3–4.5 (4H, m), 1.75–1.95 (4H, m). δ_C (500 MHz, CD_3CN, 298 K) 144.4, 134.4, 125.2, 50.0, 48.3, 27.9, 27.4 ppm. ν_{max} 3130 s, 3112 s, 3088 s, 2957 m, 2870 w, 1488 s, 1469 w, 1454 m, 1441 m, 1428 m, 1372 m, 1341 w, 1321 m, 1250 w, 1228 m, 1216 s, 1194 m, 1173 s, 1131 m, 1120 s, 1111 m, 1094 s, 1064 w, 1042 w, 1004 w, 971 m, 954 m, 913 w, 812 m, 799 s, 722 w, 705 w, 680 m, 662 w, 646 m, 432 w cm^{-1}. MS (ESI) *m*/*z* found 194.1 $[M+H]^+$, 216.1 $[M+Na]^+$. Calcd for $C_7H_{11}N_7$ (193.21) C, 43.5; H, 5.7; N, 50.8. Found: C, 43.6; H, 5.9; N, 50.7. Crystal data for **3f**. Colorless plate, crystal dimensions 0.50×0.45×0.20 mm, triclinic, space group *P*-1, *a*=7.179(2), *b*=7.422(2), *c*=9.231(3) Å, α=74.26(3), β=82.41(3), γ=76.00(2)°, *V*=458.2(2) $Å^3$, *Z*=2, D_c=1.401 Mg m^{-3}, μ(Mo Kα)=0.10 mm^{-1}, *T*=100 K, *R*=0.043, *wR*=0.109 (1971 reflections with $I>2\sigma(I)$) for 127 variables.

4.21. Synthesis of 1-(tetrazol-2-yl)-4-(1,2,3-triazol-2-yl)butane (3g) and 1-(tetrazol-2-yl)-4-(1,2,3-triazol-1-yl)butane (3h)

Compound **1d** (7.0 mmol, 1.435 g) as alkylating agent was used. Products **3g** (colorless solid, R_f=0.84, TLC) and **3h** (colorless solid, R_f=0.37, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN 8:2 (v/v)) with yields 0.58 g (43%) and 0.51 g (38%), respectively. Data for **3g**. δ_H (500 MHz, CD_3CN, 298 K) 8.57(1H, s), 7.62 (2H, s), 4.66 (2H, t, *J* 6.6 Hz), 4.45 (2H, t, *J* 6.4 Hz), 1.92 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 153.9, 135.1, 54.6, 53.2, 27.3, 27.0 ppm. ν_{max} 3125 m, 2998 w, 2960 m, 2871 w, 1464 s, 1440 m, 1420 s, 1375 s, 1360 s, 1280 s, 1222 w, 1174 s, 1134 m, 1102 s, 1063 w, 1031 s, 1020 m, 1008 m, 977 m, 934 s, 912 m, 886 w, 830 s, 762 s, 736 m, 710 s, 690 m, 677 w, 445 m cm^{-1}. MS (ESI) *m*/*z* found 194.1 $[M+H]^+$, 216.1 $[M+Na]^+$. Anal. Calcd for $C_7H_{11}N_7$ (193.21) C, 43.5; H, 5.7; N, 50.8. Found: C, 43.6; H, 5.7; N, 51.0. Data for **3h**. δ_H (500 MHz, CD_3CN, 298 K) 8.58(1H, s), 7.74 (1H, s), 7.63 (1H, s), 4.67 (2H, t, *J* 6.8 Hz), 4.40 (2H, t, *J* 6.7 Hz), 1.8–2.0 (4H, m). δ_C (500 MHz, CD_3CN, 298 K) 153.9, 134.3, 125.1, 53.1, 49.8, 27.8, 26.9 ppm. ν_{max} 3127 s, 3112 s, 2962 s, 2943 m, 2876 m, 1487 m, 1472 m, 1458 s, 1444 s, 1372 s, 1362 m, 1341 m, 1303 m, 1287 s, 1274 s, 1218 s, 1201 m, 1177 m, 1150 s, 1123 s, 1145 s, 1094 s, 1084 s, 1031 s, 1010 m, 1001 m, 987 w, 951 m, 926 w, 913 m, 803 s, 711 m, 703 m, 697 m, 662 m, 643 w, 435 m cm^{-1}. MS (ESI) *m*/*z* found 194.1 $[M+H]^+$, 216.1 $[M+Na]^+$. Anal. Calcd for $C_7H_{11}N_7$ (193.21) C, 43.5; H, 5.7; N, 50.8. Found: C, 43.8; H, 5.7; N, 50.9.

4.22. Synthesis of 1-(tetrazol-1-yl)-3-(tetrazol-2-yl) propane (3i)

Synthesis of **3i** was performed according to the procedure described for **3a** using 7.0 mmol (1.337 g) **1a** as alkylating agent and 7.0 mmol (0.484 g) tetrazole instead of 1,2,3-triazole. Products **3i** (colorless solid, R_f=0.13, TLC) and **3j** (colorless oil, R_f=0.44, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/hexane 5:2:5 (v/v)) with yields 0.22 g (17%) and 0.35 g (28%), respectively. Data for **3i**. δ_H (300 MHz, CD_3CN, 298 K) 8.84(1H, s), 8.59 (1H, s), 4.71 (2H, t, *J* 6.7 Hz), 4.85 (2H, t, *J* 7.0 Hz), 2.59 (2H, pseudo-quintet). δ_C (300 MHz, CD_3CN, 298 K) 154.0, 144.6, 50.8, 46.0, 29.6 ppm. ν_{max} 3136 s, 2965 w, 1486 s, 1448 s, 1362 m, 1284 s, 1172 s, 1134 m, 1104 s, 1055 w, 1028 s, 1009 m, 988 w, 965 m, 882 m, 799 w,

708 m, 682 w, 661 m, 473 w cm^{-1}. MS (ESI) *m*/*z* found 203.1 $[M+Na]^+$. Anal. Calcd for $C_5H_8N_8$ (180.17) C, 33.3; H, 4.5; N, 62.2. Found: C, 33.5; H, 4.2; N, 62.1. Compound **3j** was identified as 1,3-di(tetrazol-2-yl)propane and results of analytical characteristics were consistent with the earlier reported.[14c]

4.23. Synthesis of 1-(tetrazol-1-yl)-4-(tetrazol-2-yl) butane (3k)

Synthesis of **3k** was performed according to the procedure described for **3i** using 7.0 mmol (1.435 g) **1c** as alkylating agent. Products **3k** (colorless solid, R_f=0.14, TLC) and **3l** (colorless solid, R_f=0.47, TLC) were isolated by chromatography on silica gel (CH_2Cl_2/CH_3CN/hexane 5:2:5 (v/v)) with yields 0.31 g (23%) and 0.44 g (33%), respectively. Data for **3k**. δ_H (300 MHz, CD_3CN, 298 K) 8.80(1H, s), 8.56 (1H, s), 4.85 (2H, t, *J* 6.7 Hz), 4.66 (2H, t, *J* 6.7 Hz), 1.80–2.05 (4H, m). δ_C (300 MHz, CD_3CN, 298 K) 154.0, 144.4, 53.1, 48.2, 27.3, 26.8 ppm. ν_{max} 3156 m, 3144 m, 3119 s, 2970 m, 2941 w, 2872 w, 1491 m, 1445 s, 1429 w, 1372 m, 1361 m, 1332 w, 1288 s, 1247 w, 1223 m, 1198 m, 1169 s, 1144 s, 1123 m, 1108 s, 1063 m, 1035 s, 1008 m, 970 m, 888 m, 798 m, 712 w, 695 s, 677 w, 661 m, 647 m, 433 w cm^{-1}. MS (ESI) *m*/*z* found 217.1 $[M+Na]^+$. Anal. Calcd for $C_6H_{10}N_8$ (194.19) C, 37.1; H, 5.2; N, 57.7%. Found: C, 36.9; H, 5.0; N, 57.8%. Compound **3l** was identified as 1,4-di(tetrazol-2-yl)butane and results of analytical characteristics stay in agreement with the earlier reported.[14b]

4.24. Synthesis of $[Fe(2g)_2](ClO_4)_2$ (4)

A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.060 mmol, 22.0 mg) in absolute ethanol (5.0 mL) was added to the solution of **2g** (0.12 mmol, 32.7 mg) in ethanol (5.0 mL) resulting in precipitation of the complex. Precipitate was filtered off and dried in nitrogen atmosphere. Yield: 29 mg of light orange solid. Anal. Calcd for $FeC_{24}H_{28}N_{16}Cl_2O_8$ (795.32) C, 36.2; H, 3.6; N, 28.2. Found C, 36.4; H, 3.7; N, 27.7. The proposed formula of the product was established only on the basis of elementary analysis results.

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