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RELATIVE STABILITIES OF 1- AND 2-SUBSTITUTED 1,2,3-TRIAZOLES

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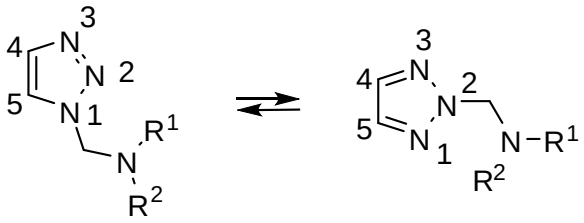
Abstract - *N*-(α-Aminoalkyl)-1,2,3-triazoles are potentially tautomeric between the 1- and 2-substituted forms. They exist in solution predominantly as 2-isomers as shown by ^{1}H and ^{13}C NMR; electron attracting substituents on the amino nitrogen increase the proportion of the 1-isomer in the equilibrium mixture.



INTRODUCTION

The relative stabilities of 1- **1A** and 2-substituted benzotriazoles **1B** have been studied intensively.[1-7] When the N-substituent is hydrogen (X = H in 1A, 1B) there is rapid tautomeric exchange between **1A** and **1B** (Figure 1),[8] and this equilibrium is overwhelmingly on the side of the 1-*H* benzotriazole **1A** in the crystalline state, but significant amounts of 2-*H* benzotriazole **1B** are found in gas and solution phases.[2,9] Rapidly equilibrating *N*-(dialkylaminomethyl)benzotriazoles are shown by ^{1}H, ^{13}C NMR and X-ray analysis to exist solely in the 1-substituted form in the crystalline phase but as mixtures of benzotriazole-1-yl and 2-yl isomers in solution and vapor phases.[2] These results are explained by (i) the greater aromaticity of 1-substituted benzotriazoles and (ii) the fact that in media of low dielectric constant the much higher dipole moment of a 1-substituted benzotriazole compared to its 2-substituted isomer displaces the equilibrium towards the 2-substituted form (e.g. 1-methylbenzotriazole: 4.65D, 2-methylbenzotriazole: 0.77D).[10]

This paper is dedicated to Prof. Dr. Albert Eschenmoser on the occasion of his 85th birthday.

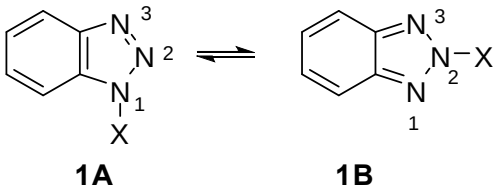


Figure 1. 1- and 2-substituted benzotriazoles.

Far less is known about the corresponding 1- and 2-substituted monocyclic 1,2,3-triazoles (Figure 2). When the N-substituent is simply a hydrogen atom, 2*H*-tautomer **2B** is calculated to be about 4.5 kcal mol^{-1} more stable than 1*H* tautomer **2B** in the gas phase and this is supported by experiment.[3,11,12] In solution, the more polar 1*H* isomer with the higher dipole moment (4.38 D) exists alongside the 2*H* tautomer.[3,11] Low temperature ^{1}H NMR studies of the parent 1,2,3-triazole by Lunazzi et al. indicated tautomeric equilibrium in CD_2Cl_2 and toluene: at -98 ^{o}C in CD_2Cl_2 the 1*H* form **2A** is predominant, while at 27 ^{o}C the 2*H* form **2B** is observed to the extent of 80% in CD_2Cl_2 and 97% in toluene.[13] Similar results were obtained by Begtrup.[14] Based on circumstantial arguments (basicity and partitioning) Albert and Taylor concluded that in aqueous solution the 2*H* form of 1,2,3-triazole is favored over the 1*H* tautomer by a factor of about two.[15]

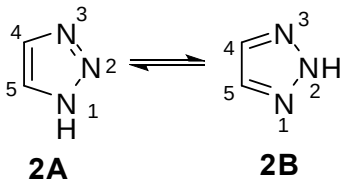


Figure 2. 1- and 2-substituted triazoles.

Quantum chemical calculations indicate that the 2*H* form of 4-Me-1,2,3-triazole is more stable than the 1-isomer even in aqueous solution, despite the smaller dipole moment of this former.[11,16] *Ab initio* calculations for C-substituted 1,2,3-triazoles suggest that 2*H* tautomers predominate in the gas phase, while both 1*H* and 2*H* tautomers are present in aqueous solution.[17]

The two tautomers of 1,2,3-triazole allow three different complexes connected by two hydrogen bonds, i,e, 1:1, 1:2 and 2:2 (Figure 3). According to CCSD(T)/[aug]-cc-pVDZ calculations reported by Rauhut[18] the 2:2 complex is the most stable complex in the gas phase.

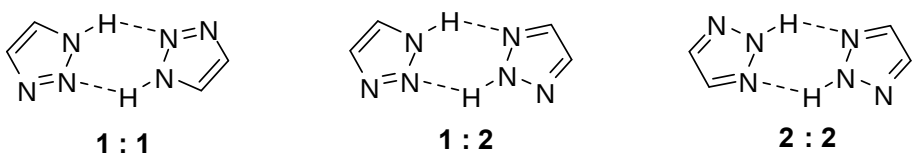


Figure 3. Complexes of 1,2,3-triazole.[18]

N-(*α*-Aminoalkyl)benzotriazoles and *N*-(*α*-aminoalkyl)-1,2,3-triazoles dissociate into stabilized ion pairs of benzotriazole or triazole anions and an immonium cation (Figure 4), which enables rapid isomerization between the 1-substituted **3A, 4A** and the 2-substituted **3B, 4B** isomers. We have now examined a series of N-substituted 1,2,3-triazoles in order to provide further information about their tautomeric equilibria.

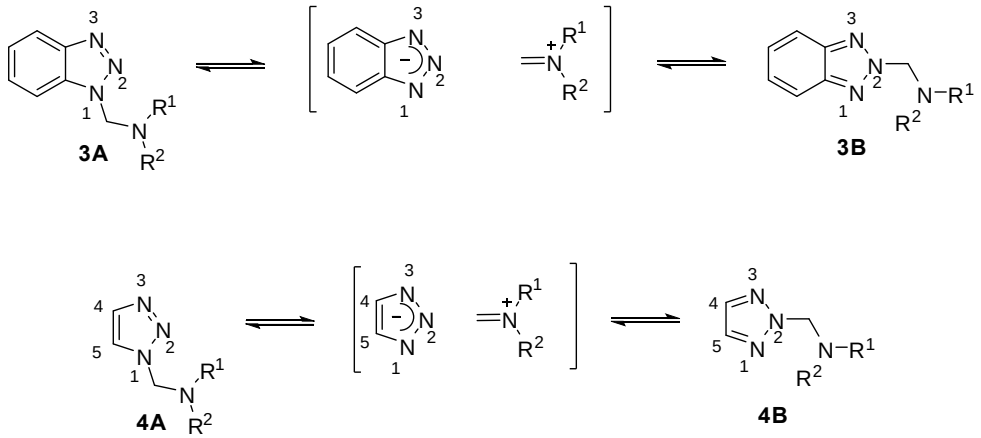
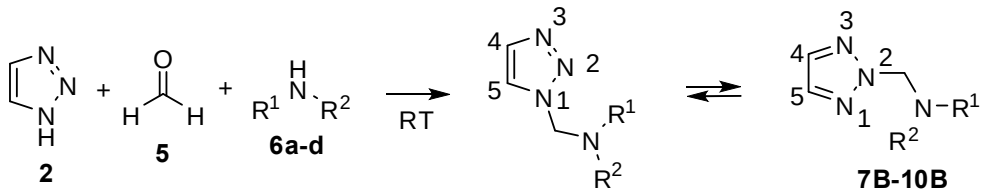


Figure 4

RESULTS AND DISCUSSION

Preparation of *N*-(*α*-aminoalkyl)-1,2,3-triazoles

As an addition to existing literature procedures,[19-21] novel N-substituted 1,2,3-triazoles **7-10** (Table 1) were prepared following procedures similar to our published method for the analogous benzotriazoles.[4,22] The reaction of 1,2,3-triazole, with an aldehyde and amine or sulfonamide in water or acetonitrile afforded compounds **7-10** in 54-95% yields (Scheme1).



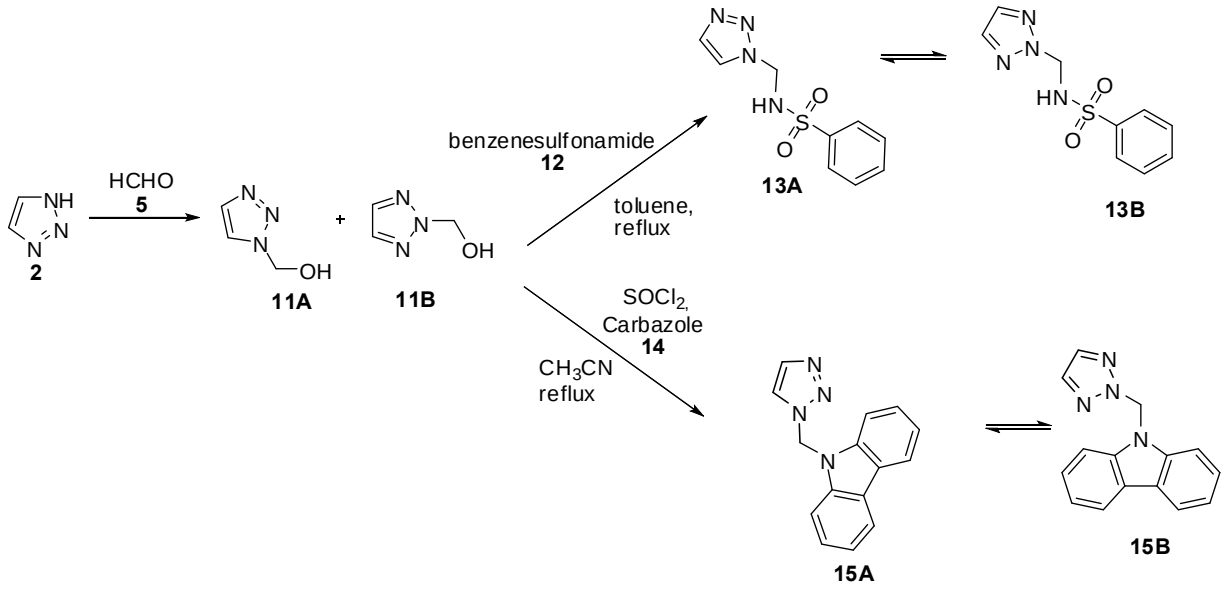
6a: morpholine
6b: 1-methylpiperazine
6c: aniline
6d: pyrrolidine

(for designation of R^1 and R^2 see Table 1)

Scheme 1. Preparation of N-substituted 1,2,3-triazoles **7-10**

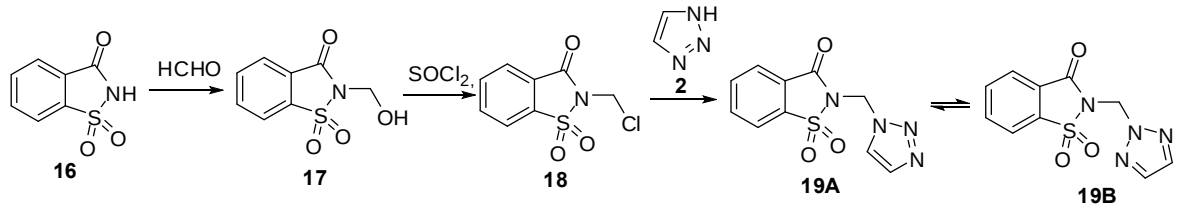
Compound **13** was prepared by the reaction of (1,2,3-triazol-2-yl)methanol **11** with benzenesulfonamide **12** in 95% yield.

Deprotonation of carbazole with NaOH under reflux and nucleophilic substitution of 1-chloromethyl-1,2,3-triazole hydrochloride leads to compound **15** in 60% yield.



Scheme 2. Preparation of N-substituted 1,2,3-triazoles **13, 15**

The reaction of saccharin **16** with paraformaldehyde and subsequent treatment with $SOCl_2$ resulted in the formation of **18** which was then reacted with triazole to give **19** in 78% yield.



Scheme 3. Preparation of *N*-(triazol-1-yl)methylsaccharin **19**

Table 1. Preparation of N-substituted 1,2,3-triazoles **7-10**, **13**,**15** and **19**

Product	R^1	R^2	% of N^2-isomer			Yield (%)	Mp (^oC)
			$CDCl_3$	DMSO-d_6	D_2O		
7	$(CH_2)_2$-O-$(CH_2)_2$		>95	85	66	80	74-76
8	$(CH_2)_2$-NCH_3-$(CH_2)_2$		>95	76	50	54	78-80
9	H	C_6H_5	>95	>95	NS	95	97-99
10	$(CH_2)_4$		90	67	NS	82	62-64
13	H	$SO_2C_6H_5$	>95	75	NS	81	141-142
15	oC_6H_4- oC_6H_4		<5	<5	NS	60	198-199
19	CO-$o(C_6H_4)_2$- SO_2		NS	<5	NS	78	168-170

Characterization of compounds 7-10, 13, 15 and 19

The isomer ratios of triazoles **7-10**, **13**, **15**, and **19** in $CDCl_3$, DMSO-d_6 or D_2O as determined by ^{1}H-NMR are shown in Table 1. The ^{13}C spectral data for the same series of compounds in $CDCl_3$ and DMSO-d_6 are shown in Tables 2 and 3. The ^{13}C spectral data for **7** and **8** in D_2O are shown in Table 4. In deutoriochloroform, compounds **7-8** and **13** exist solely in the 2-substituted form, while compound **10** exists as a mixture of the 1- and 2-substituted derivatives as confirmed by the existence of two sets of signals; three signals were observed in the aromatic region at 123.9, 133.4 and 133.9 ppm corresponding to C4 and C5 carbons and two signals in the aliphatic region at 67.1 and 70.7 ppm corresponding to N*CH*$_2$N.

Table 2. Carbon-13 chemical shifts in $CDCl_3$[a]

Prod	R^1	R^2	N^1-isomer				N^2-isomer		
			C-4	C-5	NCH_2N	C-R^1R^2	C-4,5	NCH_2N	C-R^1R^2
7	$(CH_2)_2$-O-$(CH_2)_2$		Not detectable				134.0	74.8	66.5; 49.8
8	$(CH_2)_2$-NCH_3-$(CH_2)_2$		Not detectable				134.0	54.8	49.5; 45.9
9	H	C_6H_5	Not detectable				134.3	62.7	144.7; 129.2; 119.4; 113.7
10	$(CH_2)_4$		123.9	133.4	67.1	49.7; 23.8	133.9	70.7	49.4; 23.9
13	H	$SO_2C_6H_5$	Not detectable				134.8	60.8	132.6; 128.7; 126.9
15	*o*C_6H_4- *o*C_6H_4		123.8	139.4	56.2	134.6; 126.6; 122.4; 121.0; 120.7; 108.6	Not detectable		
19	CO-*o*$(C_6H_4)_2$-SO_2		Not soluble						

[a] Compound **19** was insoluble

The change from $CDCl_3$ to the more polar DMSO for **7-8, 10** and **13** resulted in increased amounts of the 1-substituted isomers, but only the 2-isomer of **9** was detected in both solvents.

Incorporation of electron attracting substituents such as carbazole or saccharine on the nitrogen of the amino group shifted the equilibrium toward the 1*H*-isomer. According to ^{1}H and ^{13}C NMR compounds **15** and **19** exist solely in 1*H* form in both solvents $CDCl_3$ and DMSO-d_6.

Table 3. Carbon-13 chemical shifts in DMSO-d_6

Prod	R^1	R^2	N^1-isomer				N^2-isomer		
			C-4	C-5	NCH_2N	C-R^1R^2	C-4,5	NCH_2N	C-R^1R^2
7	$(CH_2)_2$-O-$(CH_2)_2$		132.8	125.6	69.9	65.9; 49.4	134.3	74.4	66.0; 49.5
8	$(CH_2)_2$-NCH_3-$(CH_2)_2$		132.7	125.5	69.8	54.4; 48.9; 45.7	134.1	74.3	54.5; 49.0; 45.7
9	H	C_6H_5	Not detectable				134.2	62.1	146.1; 128.9; 117.7; 112.9
10	$(CH_2)_4$		125.5	132.7	65.7	48.9; 23.4	134.1	70.0	48.7; 23.5
13	H	$SO_2C_6H_5$	132.6	133.4	56.1	141.1; 129.1; 124.3	134.7	60.5	132.2; 128.7; 126.0
15	*o*C_6H_4- *o*C_6H_4		122.8	139.3	55.0	133.5; 126.2; 125.0; 120.4; 120.4; 110.1	Not detectable		
19	CO-*o*$(C_6H_4)_2$-SO_2		121.8	133.8	50.2	158.1; 136.6; 136.5; 135.6; 125.8; 125.7; 125.6	Not detectable		

Table 4. Carbon-13 chemical shifts in D_2O

Prod	R^1	R^2	N^1-isomer				N^2-isomer		
			C-4	C-5	NCH_2N	C-R^1R^2	C-4,5	NCH_2N	C-R^1R^2
7	$(CH_2)_2$-O-$(CH_2)_2$		133.2	126.2	69.4	65.4; 48.7	134.6	73.2	65.5; 48.9
8	$(CH_2)_2$-NCH_3-$(CH_2)_2$		133.2	126.2	69.1	52.5; 48.1; 43.7	134.5	72.9	52.7; 48.3; 43.7

CONCLUSIONS

A series of novel *N*-(*α*-aminoalkyl)-1,2,3-triazoles has been synthesized and the relative stabilities of their 1-and 2-isomers studied by ^{1}H and ^{13}C NMR. They exist solely as the 2-isomer in $CDCl_3$ but as a mixture of the 1- and 2- isomers in more polar solvents in agreement with literature reports. Electron attracting groups on the exocyclic nitrogen shift the equilibrium towards the 1-isomer.

EXPERIMENTAL

Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. The NMR spectra were recorded in $CDCl_3$, DMSO-d_6 or D_2O with TMS for ^{1}H (300 MHz) and ^{13}C (75 MHz) as an internal reference.

General procedure for preparation of 7, 8 and 10

1,2,3-1*H*-Triazole (5.0 mmol, 1 equiv.) and amine (5.0 mmol, 1 equiv.) were mixed in water (10 mL) for 5 min. Paraformaldehyde 96% (5.0 mmol, 1 equiv) was added to the reaction mixture and kept under vigorous stirring for 4 h. The aqueous phase was extracted with ether and the organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure to give the final products **7**, **8** and **10**.

4-((1*H*-1,2,3-Triazol-1-yl)methyl)morpholine (7A) and 4-((2*H*-1,2,3-triazol-2-yl)methyl)morpholine (7B). Colorless microcrystals (from toluene) (80%), mp 74-76 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 5.25 (d, *J*=1.1 Hz, 2H), 3.69 (t, *J*=4.8 Hz, 4H), 2.64 (t, *J*=4.8 Hz 4H); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.13 (br s, 0.15H from 7A), 7.83 (d, *J*=2.0, 1.7H from 7B), 7.77 (br s, 0.15H from 7A), 5.26-5.24 (m, 2H from 7B and 7A), 3.55-3.52 (m, 4H from 7B and 7A), 2.51-2.44 (m, 4H from 7B and 7A). ^{1}H NMR (300 MHz, D_2O) δ 7.93 (br s, 0.34H from 7A), 7.71 (br s, 0.34H from 7A), 7.70 (s, 1.3H from 7B), 5.16 (s, 0.7H from 7A), 5.12 (s, 1.3H from 7B), 3.66-3.57 (m, 4H from 7B and 7A), 2.53-2.48 (m, 4H from 7B and 7A); Anal. Calcd for $C_7H_{12}N_4O$: C, 49.99; H, 7.19; N, 33.31. Found: C, 50.35; H, 7.26; N, 33.04.

1-((1*H*-1,2,3-Triazol-1-yl)methyl)-4-methylpiperazine (8A) and 1-((2*H*-1,2,3-triazol-2-yl)methyl)-4-methylpiperazine (8B). Colorless microcrystals (from toluene) (54%), mp 78-80 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 2H), 5.28 (s, 2H), 2.69 (brs, 4H), 2.43 (brs, 4H), 2.25 (s, 3H); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.10 (br s, 0.24H from 8A), 7.81 (1.5H from 8B), 7.75 (br s, 0.24H from 8A), 5.24 (s, 0.5H from 8A), 5.23 (s, 1.5H from 8B), 2.51-2.40 (m, 6H from 8B and 8A), 2.27 (br s, 4H from 8B and 8A), 2.11-2.09 (m, 4H from 8B and 8A); ^{1}H NMR (300 MHz, D_2O) δ 7.91 (br s, 0.5H from 8A), 7.68-7.66 (m, 1.5H from 8B and 8A), 5.15 (s, 1H from 8A), 5.11 (s, 1H from 8B), 2.56-2.38 (m, 4H from 8B and 8A), 2.06 (s, 3H from 8B and 8A); Anal. Calcd for $C_8H_{15}N_5$: C, 53.02; H, 8.34; N, 38.64. Found: C, 53.37; H, 8.66; N, 38.82.

1-(Pyrrolidin-1-ylmethyl)-1*H*-1,2,3-triazole (10A) and 2-(pyrrolidin-1-ylmethyl)-2*H*-1,2,3-triazole (10B). Colorless needles (from CH_2Cl_2/hexane) (82%), mp 62-64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (br s, 0.1H from 10A), 7.62 (br s, 1.8H from 10B and 0.1H from 10A), 5.39 (s, 1.8 from 10B), 5.33 (s, 0.2H from 10A), 2.79-2.69 (m, 4H from 10B and 10A), 1.77-1.65 (m, 4H from 10B and 10A); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.13 (s, 0.3H from 10A), 7.79 (s, 1.4H from 10B), 7.72 (s, 0.3H from 10A), 5.34 (s, 1.4H from 10B), 5.32 (s, 0.6H from 10A), 2.66-2.62 (m, 2.8H from 10B) 2.60-2.54 (m, 1.2H from 10A), 1.60-1.55 (m, 4H from 10B and 10A); Anal. Calcd for $C_7H_{12}N_4$: C, 55.24; H, 7.95; N, 36.81. Found: C, 55.38; H, 8.44; N, 36.83.

Preparation of 9

1,2,3-1*H*-Triazole (0.35 g, 5.0 mmol) and aniline (0.46 mL, 5.0 mmol) were mixed in water (10 mL) for 5 min. Paraformaldehyde 96% (0.16 g, 5.0 mmol) was added to the reaction mixture and it was stirred vigorously for 4 h. The precipitate formed was filtered off and washed with ether to give **9**.

***N*-((2*H*-1,2,3-Triazol-2-yl)methyl)aniline (9).** Colorless prisms (from toluene) (95%), mp 97-99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.18 (td, *J*=7.6, 0.8, 2H), 6.84 (dd, *J*=7.8, 0.7, 2H), 6.79 (td, J=7.4, 0.8, 1H), 5.79 (d, *J*=7.8, 2H), 5.18-5.16 (m, 1H); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.77 (s, 2H), 7.19 (t, *J*=7.3 Hz, 1H), 7.09 (t, *J*=7.9 Hz, 2H), 6.82 (d, *J*=7.9 Hz, 2H), 6.61 (t, *J*=7.3 Hz, 1H), 5.73 (d, *J*=7.4, Hz 2H); Anal. Calcd for $C_9H_{10}N_4$: C, 62.05; H, 5.79; N, 32.16. Found: C, 62.39; H, 5.79; N, 32.25.

Preparation of chloromethyl-1,2,3-triazole hydrochloride

(2*H*-1,2,3-Triazol-2-yl)methanol (0.25 g, 2.5 mmol) in $SOCl_2$ (1.25 mL, 17.0 mmol) was left for 5 min and then evaporated to dryness under reduced pressure at a temperature below 25 °C. The resulting crude solid was used immediately without purification.

Preparation of 13

(2*H*-1,2,3-Triazol-2-yl)methanol (4.0 mmol, 1 equiv.) and benzensulfonamide (4.0 mmol, 1 equiv.) in toluene (10 mL) were stirred under reflux. The water resulting from the reaction was removed using a Dean-Stark apparatus. The reaction was considered finished when the exact volume of water (4.0 mmol, 1 equiv.) was collected. The solvent was removed under reduced pressure and the solid products were recrystallized from EtOH.

***N*-((1*H*-1,2,3-Triazol-1-yl)methyl)benzenesulfonamide (13A) and *N*-((2*H*-1,2,3-triazol-2-yl)methyl)-benzenesulfonamide(13B).** Colorless microcrystals (EtOH) (95%), mp 141-142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 2H), 7.45-7.27 (m, 5H), 6.24 (br s, 1H), 7.73 (d, *J*=7.0 Hz, 2H), ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.42 (br s, 0.5H from 16A), 7.65 (d, *J*=0.8 Hz, 0.25H from 16A), 7.69-7.62 (m, 0.25H from

16A), 7.60-7.52 (m, 4H from 16B and 16A), 7.51-7.49 (m, 1H from 16B and 16A), 7.47-7.38 (m, 2H from 16B and 16A), 5.63 (br s, 0.5H from 16A), 5.60 (d, *J*=5.4 Hz, 1.5H from 16B). Anal. Calcd for $C_9H_{10}N_4O_2S$: C, 45.37; H, 4.23; N, 23.51. Found: C, 45.77; H, 4.01; N, 23.02.

Preparation procedure for 15

To a solution of carbazole (0.42 g, 2.5 mmol) in MeCN (20 mL), NaOH powder (0.4g, 10.0 mmol) was added slowly and the mixture was heated under reflux for 2 h. To the reaction mixture freshly prepared chloromethyl-1,2,3-triazole hydrochloride in 5 mL MeCN was added and kept under reflux for an additional 4 h. The precipitate was filtered off and the filtrate was concentrated under reduced pressure to give crude product as a brown solid that was washed 3 times with cold EtOH to give 15 (0.37 g, 60%) as a white solid.

9-((2*H*-1,2,3-Triazol-2-yl)methyl)-9*H*-carbazole (15). White needles (60%), mp 198-199 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J*=7.6, 2H), 7.64 (d, *J*=7.3, 3H), 7.56-7.49 (m, 3H), 7.37-7.27 (m, 2H), 6.85 (s, 2H); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.37 (d, *J*=0.8, 1H), 8.15 (d, *J*=7.7, 2H), 7.99 (d, *J*=8.2, 2H), 7.69 (d, *J*=0.8, 1H), 7.52 (tripletoidd, *J*=7.0, 8.4, 1.1, 2H), 7.27 (t, *J*=7.1, 2H), 7.12 (s, 2H); Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.39; H, 4.82; N, 22.60.

Preparation of 17

A mixture of saccharin (1.83 g, 10.0 mmol) and formalin 37% (2.43 mL, 30.0 mmol) in water (20 mL) was heated under reflux for 30 min. After storing at 5 °C overnight, the solid was filtered off and dried to produce *N*-hydroxymethyl saccharin (2.08 g, 98%) as a white pure solid.

***N*-Hydroxymethylsaccharin (17).** White solid (98%), mp 124-126 °C (lit.,[23] mp 136-137 °C) ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.30 (d, *J*=7.3 Hz, 1H), 8.14 (d, *J*=7.0 Hz, 1H), 8.07 (td, *J*=7.4, 1.4 Hz, 1H), 8.00 (td, *J*=7.4, 1.1 Hz, 1H), 5.17 (s, 2H); ^{1}H NMR (75 MHz, DMSO-d_6) δ 158.5, 137.2, 136.1, 135.2, 126.1, 125.3, 121.5, 62.8; Anal. Calcd for $C_8H_7NO_4S$: C, 45.07; H, 3.31; N, 6.57. Found: C, 45.12; H, 3.39; N, 6.44.

Preparation of 18

A mixture of *N*-hydroxymethylsaccharin (1.00 g, 4.7 mmol) and thionyl chloride (3.00 mL, mmol) was heated under reflux and under anhydrous conditions. After 10 minutes, the residual oil was evaporated free of excess thionyl chloride and dried overnight to obtain *N*-chloromethylsaccharin (1.06 g, 98%) as a yellow pure solid.

***N*-Chloromethylsaccharin (18).** Yellow solid (98%) mp 137-138 °C (lit.,[23] mp 137-138 °C). ^{1}H NMR

(300 MHz, DMSO-d_6) δ 8.40 (d, J=7.6 Hz, 1H), 8.20 (d, J=7.6 Hz, 1H), 8.13 (td, J=7.6, 1.1 Hz, 1H), 8.05 (td, J=7.6, 1.1 Hz, 1H), 5.83 (s, 2H); ^{1}H NMR (75 MHz, DMSO-d_6) δ 157.5, 136.7, 136.7, 135.6, 125.7, 125.5, 121.9, 46.4. Anal. Calcd for $C_8H_7ClNO_3S$: C, 41.48; H, 2.61; N, 6.05. Found: C, 41.56; H, 2.92; N, 5.93.

Preparation of 19

A mixture of 1,2,3-1*H*-triazole (0.10 g, 1.4 mmol) and NaOH (0.06 g, 1.4 mmol) in MeCN (7 mL) was heated under reflux. After 30 minutes, the heating was stopped and *N*-chloromethylsaccharine (0.303g, 1.4 mmol) dissolved in MeCN (5 mL) was added. The reaction was cooled at room temperature and stirred for 2 h. The solid was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (15 mL), and the suspension was filtered thorough celite. The clear solution was concentrated under reduced pressure. The white solid was recrystallized from EtOH to give *N*-(triazol-1-yl)methylsaccharin (0.30 g, 78%) as colorless needles.

***N*-(Triazol-1-yl)methylsaccharin (19).** Colorless needles (78%), mp 168-170 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.36 (d, J=7.1 Hz, 1H), 8.26 (d, J=1.0 Hz, 1H), 8.18 (dd, J=7.3, 0.8 Hz, 1H), 8.09 (td, J=7.4, 1.2 Hz, 1H), 8.02 (td, J=7.4, 1.1 Hz, 1H), 7.80 (d, J=1.0 Hz, 1H), 6.43 (s, 2H); Anal. Calcd for $C_{10}H_8N_4O_3S$: C, 45.45; H, 3.05; N, 21.20. Found: C, 45.73; H, 2.95; N, 20.93.

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