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Ring Opening of [1,2,3]Triazolo[1,5-*a*]pyrazinium Salts: Synthesis and Some Transformations of a Novel Type of 2-Aza-1,3-butadienes.[1]

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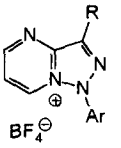
Abstract: The synthesis of 1,3-disubstituted [1,2,3]triazolo[1,5-*a*]pyrazinium salts **6** and subsequent ring opening induced by the reaction with pyrrolidine provides a facile access to 4-(1-pyrrolidino)-1-([1,2,3]triazol-5-yl)-2-aza-1,3-butadienes **7**, a new type of 2-aza-1,3-butadienes. Compounds **7** proved to be suitable starting materials for further ring formation reactions. © 1997 Elsevier Science Ltd.

We have reported[2,3] that the treatment of 2-azinyl ketone hydrazones with *N*-bromosuccinimide (NBS) or tribromophenol bromine (TBB) proved to be a general method for the synthesis of fused [1,2,3]triazolo-azinium salts. Three of the conceivable [1,2,3]triazolodiazinium salts, *i.e.* [1,2,3]triazolo[1,5-*a*] pyrimidinium **1**[2], [1,2,3]triazolo[1,5-*c*]pyrimidinium **2**[2], and [1,2,3]triazolo[1,5-*b*]pyridazinium tetrafluoroborates **3**[3] have been prepared recently.



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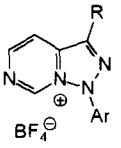

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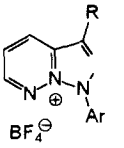
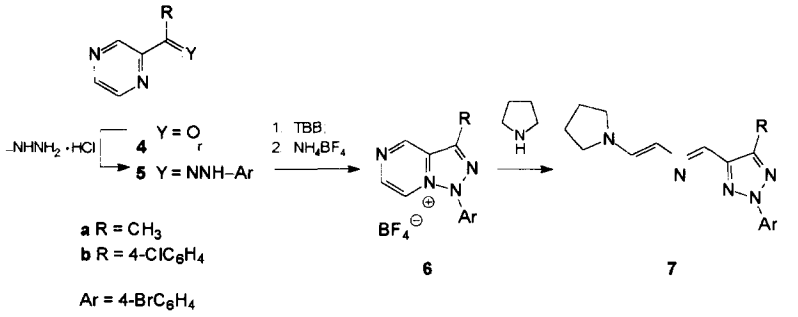


3

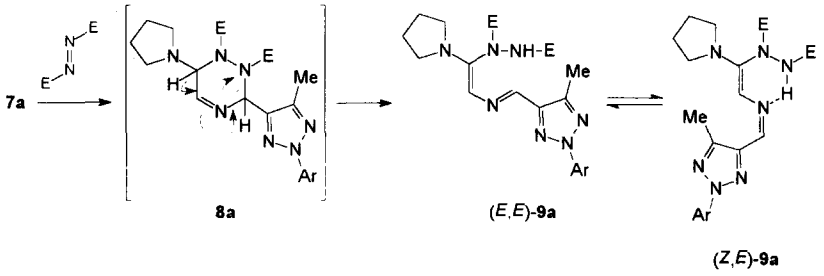
We wish to report now the synthesis of the fourth isomeric system, the [1,2,3]triazolo[1,5-*a*]pyrazinium tetrafluoroborate **6**. Its ring opening reaction leads to a new class of 2-aza-1,3-butadienes **7** which proved to be valuable starting materials for further conversions. In order to accomplish the ring closure to the target triazolium salts **6**, 2-pyrazinyl ketones **4a,b** were first converted into the 4-bromophenylhydrazones **5**. The reaction of the hydrazones **5a** and **5b** with TBB followed by the treatment with ammonium tetrafluoroborate afforded the expected new 3-substituted 1-(4-bromophenyl)-[1,2,3]triazolo[1,5-*a*]pyrazinium tetrafluoroborates **6a** and **6b** as colorless crystals. Both the 3-alkyl (**6a**) and 3-aryl (**6b**) substituted products proved to be

reactive towards nucleophiles: similar to analogous systems[2] pyrrolidine induced a smooth ring opening of the pyrazinium moiety at room temperature affording 4-(1-pyrrolidinyl)-1-([1,2,3]triazol-5-yl)-2-aza-1,3-butadienes **7** (Scheme 1).



Scheme 1.

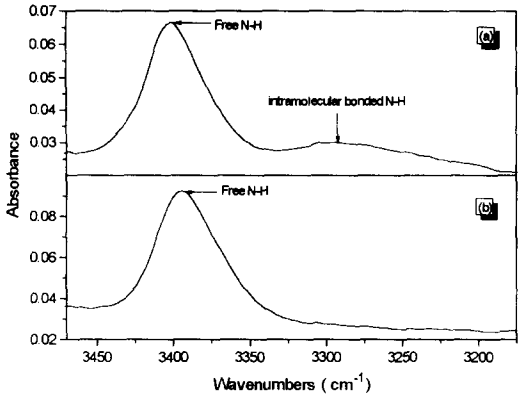
Owing to their synthetic utility in various cycloaddition reactions[4-9] considerable attention has been focused on 2-aza-1,3-butadienes and, hence, the study of the reactivity of the new triazolyl-2-aza-1,3-butadienes **7** seemed of particular interest. Based upon previous experience with related azole-substituted butadienes,[10, 11] four transformations of **7** have been selected and will be discussed.

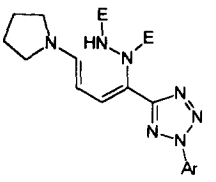


Scheme 2.

The reaction of triazolyl-2-aza-1,3-butadiene **7a** with diethyl azodicarboxylate gave a crystalline product **9a** in good yield. A possible rationalisation of this reaction anticipates a [4+2] cycloaddition reaction giving rise to the intermediate **8a**[11] followed by ring opening to furnish the isolated product **9a** (Scheme 2).

The NMR spectrum of this product **9a** revealed an equilibrium mixture of two compounds, (*E*,*E*)-**9a**, and possibly the chelate form (*Z*,*E*)-**9a**. Since no decision with respect to the structure of the two components could be reached by NMR, a detailed IR study was carried out. For this purpose, the spectrum of the analogous tetrazolylbutadiene derivative **10**[10] lacking the possibility to form an intramolecular hydrogen bridge has been compared with that of the new product **9a**.





(*E*,*E*)-**10**

Figure 1. IR spectra of **9a** (a) and **10** (b) in chloroform solutions.

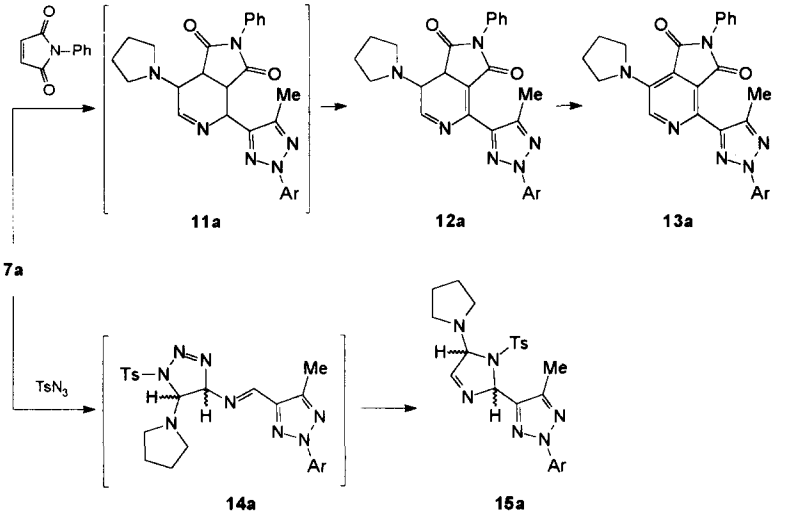
Comparison of the IR spectra of **9a** and (*E*,*E*)-**10** in dilute chloroform solutions (Figure 1) revealed, in accordance with the NMR spectra, mixture of two components in the solution of **9a** both differing mainly in the appearance of the NH signals. Furthermore, the IR spectrum of the major component of **9a** is similar to that of the reference compound (*E*,*E*)-**10** (Fig. 1,b): Only the absorption of the free $\nu_{N\text{-}H}$ occurs at 3394 cm^{-1}, whereas the IR spectrum of **9a** (Fig 1,a) exhibits two $\nu_{N\text{-}H}$ absorption bands, one at 3401 cm^{-1} characteristic for the free N-H form and attributed to (*E*,*E*)-**9a**; the other one at 3294 cm^{-1} is assigned to the intramolecularly bound N-H form (*Z*,*E*)-**9a**. The ratio of the integrated intensities of both $\nu_{N\text{-}H}$ absorptions is nearly 2:1 in favour to the free form (*E*,*E*)-**9a**.

It is interesting to note that besides the difference concerning the hydrogen bond formation ability between the derivatives 2-aza-butadiene **9a** and butadiene **10** there is another major difference between these derivatives: in **9a**, the hydrazino goup is attached to C-1 of the azadiene chain, whereas in **10** this substituent is in position C-4 which is possibly due to the activating effect of the chain-nitrogen atom in the intermediate **8a** exerted to the C-1atom.

A Diels Alder reaction took place when **7a** was reacted with *N*-phenylmaleinimide (Scheme 3). The analysis of the complex reaction mixture revealed the presence of two products: the dihydropyridine **12a** and the fully aromatic pyridine derivative **13a**. Contrary to analogous cases[10] the expected elimination of pyrrolidine from the cycloadduct **11a** did not occur[11]. Instead, oxidation of the tetrahydropyridine ring of the presumed cycloadduct **11a** afforded both the pyridine derivative **13a** and its 3,4-dihydro precursor **12a**. Bubbling air through the primary reaction mixture led to complete oxidation and provided **13a** as the only the product.

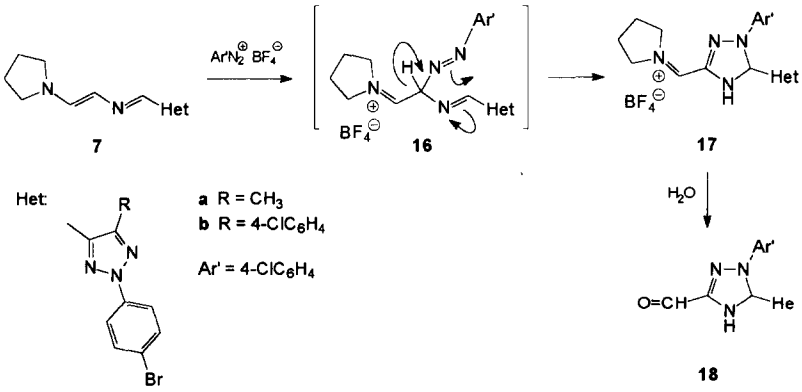
When 1-triazolyl-2-aza-1,3-butadiene **7a** reacted with tosylazide a crystalline product was obtained in good yield; its analysis (NOE and HETCOR experiments) proved structure **15a**. The expected [3+2] cycloadduct **14a** is the presumed precursor; nitrogen elimination and subsequent ring-closure (attachment of the tosyl

nitrogen atom to 1-C of the former 2-aza-1,3-butadiene moiety of **7a)** results in the formation of the 2,5-dihydro-1*H*-imidazole ring of **15a** (Scheme 3).



Scheme 3.

The reaction of **7** with 4-chlorobenzenediazonium fluoroborate follows a different course as compared to the analogous carbon chain systems[12]. Electrophilic attack at C-3 is expected to yield the azo compound **16** (Scheme 4). However, the isolated red crystals have structure **17** (presumably formed after tautomerisation to the hydrazone and its subsequent 1,5-electrocyclization). Compounds **17** proved to be sensitive towards water and were easily hydrolyzed yielding the [1,2,4]triazol-3-ylaldehydes **18** as yellow crystalline solids.



Scheme 4.

These reactions serve as examples for the usefulness of the easily accessible 2-aza-1,3-butadienes **7** as starting materials for the synthesis of various novel polyheteroaromatic derivatives (*e.g.* triazolylpyridyl, imidazolyl, or [1,2,4]triazolyl). Further studies on the synthetic use of 2-aza-butadienes **7** are in progress.

EXPERIMENTAL

M. P.s were determined by a Büchi apparatus. The IR spectra were recorded with a Nicolet Magna 750 FT-IR spectrometer; 4.10^{-4} M $CHCl_3$ solution were monitored between 4000 and 400 cm^{-1}; KBr pellets with 0.016 cm thickness were used for measurements below 400 cm^{-1}; the curve analysis was performed using the PCCAP program developed in the Optical Spectroscopy Group of the Central Research Institute for Chemsitry.

2-Acetylpyrazine 4-bromophenylhydrazone, 5a: To a solution of **4a** (9.7 g, 79.4 mmol) in chloroform (100 ml) was added at r.t. a mixture of 4-bromophenylhydrazine hydrochloride (21.3 g, 95.3 mmol) and sodium acetate (7.8 g, 95.3 mmol) in ethanol (170 ml). After stirring for 12 h, water was added, and the mixture was extracted with chloroform. The residue after evaporation of the solvent was triturated with hot methanol, and the yellow precipitate was filtered off to give **5a** (21.3 g, 93.5 %): m.p. 175-177°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.41 (d, J = 2 Hz, 1H), 8.47 (dd, J = 3 Hz, 2 Hz, 1H), 8.43 (d, J = 3 Hz, 1H), 7.66 (s, 1H), 7.42-7.11 (AA'BB', 4H), 2.25 (s, 3H). Anal. Calcd for $C_{12}H_{11}BrN_4$: C, 49.50; H, 3.81; N, 19.24. Found: C, 49.75; H, 3.51; N, 19.22.

2-(4-Chlorobenzoyl)pyrazine 4-bromophenylhydrazone, 5b: Prepared like **5a**. Yield: 94 %; m.p. 155-157°C; ^{1}H NMR ($CDCl_3$, 400 MHz) (*E*)-**5b**: δ 9.42 (d, J = 2 Hz, 1H), 8.41 (d, J = 3 Hz, 1H), 8.38 (dd, J = 3 Hz, 2 Hz, 1H), 7.83 (s, 1H), 7.58-7.02 (AA'BB', 4H), 7.38-7.32 (AA'BB', 4H). Anal. Calcd for $C_{17}H_{12}BrClN_4$: C, 52.67; H,3.12; N, 14.45. Found: C, 52.54; H, 2.83; N, 14.33.

1-(4-Bromophenyl)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyrazinium tetrafluoroborate, 6a: To a stirred solution of **5a** (4 g, 13.7 mmol) in dichloromethane (100 ml) was added tribromophenol bromine (8.4 g, 20.6 mmol) in portions at 0°C. Stirring was continued for 1 h, ether was added, and the precipitate was filtered off. The yellow crystals were suspended in nitromethane (20 ml), cyclohexene (1.6 ml) was added, and the mixture was stirred at r.t. for 30 minutes. Ether was added again, and the colorless precipitate was filtered off. For the conversion of the bromide salt into the tetrafluoroborate salt a solution of NH_4BF_4 (4 g) in water was added to a hot solution of the bromide salt in aqueous methanol. The precipitate was filtered off and recrystallized from acetonitrile/ether to give **6a** (4.1 g, 81 %): m.p. 226-229°C; ^{1}H NMR (CD_3CN, 400 MHz): δ 9.91 (d, J = 1.4 Hz, 1H), 8.93 (dd, J = 1.4 Hz, 5 Hz, 1H), 8.85 (d, J = 5 Hz, 1H), 7.98-7.68 (AA'BB', 4H), 2.91 (s, 3H). Anal. Calcd for $C_{12}H_{10}BBrF_4N_4$: C, 38.24; H, 2.67; N, 14.86. Found: C, 38.43; H, 2.44; N, 14.87.

1-(4-Bromophenyl)-3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]pyrazinium tetrafluoroborate, 6b: Prepared as **6a.** Yield: 55 %; m.p. 243°C; ^{1}H NMR (CD_3CN, 400 MHz): δ 10.15 (d, J = 1.4 Hz, 1H), 9.02

(dd, J = 1.4 Hz, 5 Hz, 1H), 8.95 (d, J = 5 Hz, 1H), 8.14-7.78 (AA'BB', 4H), 8.02-7.74 (AA'BB' 4H). Anal. Calcd for $C_{17}H_{11}BBrClF_4N_4$: C, 43.13; H, 2.34; N, 11.83, Found: C, 43.39; H, 2.16; N, 11.81.

1-[2-(4-Bromophenyl)-4-methyl-[1,2,3]triazol-5-yl]-4-(1-pyrrolidino)-2-aza-1,3-butadiene,7a: Pyrrolidine (1.6 ml) was added dropwise to a suspension of **6a** (1 g, 2.7 mmol) in absolute methanol (7 ml) at 0°C under argon atmosphere. The mixture was stirred for 1 h, then the yellow precipitate was filtered off and washed with a little methanol to give **7a** (0.82 g, 84 %): m.p. 133-139°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, 1H), 7.91-7.55 (AA'BB', 4H), 7.16 (d, J = 11 Hz, 1H), 6.28 (d, J = 11 Hz, 1H), 3.25 (m, 4H) 2.60 (s, 3H), 1.90 (m, 4H). Anal. Calcd for $C_{16}H_{18}BrN_5$: C, 53.34; H, 5.04; N, 19.43. Found: C, 53.57; H, 4.82; N, 19.41.

1-[2-(4-Bromophenyl)-4-(4-chlorophenyl)-[1,2,3]triazol-5-yl]-4-(1-pyrrolidino)-2-aza-1,3-butadiene, 7b: Prepared as **7a.** Yield: 77 %; m.p. 132-137°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, 1H), 8.06-7.35 (AA'BB' 4H), 7.89-7.60 (AA'BB', 4H), 7.17 (d, J = 11 Hz, 1H), 6.31 (d, J = 11 Hz, 1H), 3.25 (m, 4H), 1.90 (m, 4H). Anal. Calcd for $C_{21}H_{19}BrClN_5$: C, 55.22; H, 4.19; N, 15.33. Found: C, 55.19; H, 4.00; N, 15.19.

Reaction of 7a with diethyl azodicarboxylate: (*E*,*E*)-1-[2-(4-Bromophenyl)-4-methyl-[1,2,3]triazol-5-yl]-4-(1-pyrrolidino)-4-[1,2-bis(ethoxycarbonylhydrazino)]-2-aza-1,3-butadiene, (*E*,*E*)-9a: To a solution of **7a** (0.50 mg, 1.4 mmol) in absolute dichloromethane (8ml) was added diethyl azodicarboxylate (0.25 g, 1.43 mmol) at r.t. under argon. The mixture was stirred for 2 h, the solvent was removed *in vacuo*, and the residue was triturated with ethanol. The yellow precipitate was filtered off and recrystallized from dichloromethane/ethanol to give **9a** (0.45 g, 61 %); m.p. 187-189°C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.87-7.52 (AA'BB', 4H), 7.68 (s, 1H),7.38 (s, 1H), 6.81 (s, 1H), 4.21 (m, 4H), 3.7 (m, 4H), 2.61 (s, 3H), 1.9 (m, 4H), 1.3 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 156.81, 156.19, 145.98, 144.50, 138.50, 136.81, [137.28], 132.52, 132.18, 130.96, 120.10, 119.64, 61.91, 61.82, 51.68, 25.43, 14.57, 14.42, 12.29. Anal. Calcd for $C_{22}H_{28}BrN_7O_4$: C, 49.45; H, 5.28; N, 18.35. Found: C, 49.60; H, 5.08; N, 18.20.

Transformation of 7a with *N*-phenylmaleinimide: 1-[2-(4-Bromophenyl)-5,7-dihydro-4-methyl-[1,2,3]triazol-5-yl]-6-phenyl-4-(1-pyrrolidino)-pyrrolo[3,4-*c*]pyridine-5,7-dione, 13a: To a solution of **7a** (180 mg, 0.5 mmol) in absolute dichloromethane (5 ml) was added *N*-phenylmaleinimide (112 mg, 0.65 mmol) at r.t. under argon. The mixture was stirred for 2 h, the solvent was removed *in vacuo*, and the residue was triturated with acetonitrile. The precipitate was filtered off to give of yellow crystals (130 mg). This crude product was dissolved in dichloromethane (20 ml), alumina (0.5 g) was added, and air was bubbled through the solution for 2 days. The alumina was filtered off and washed with dichloromethane, the solvent was removed *in vacuo* to give the pure product **13a** as orange crystals (30 mg, 11%); m.p. 243-245°C; ^{1}H NMR ($CDCl_3$, 400

MHz): δ 8.6 (s, 1H), 8.0-7.55 (AA'BB', 4H), 7.5-7.35 (m, 5H), 3.8 (m, 4H), 2.4 (s, 3H), 2.08 (m,4H). MS *m/z* 530 (M^+)

Flash chromatography of the yellow crude product **13a** on alumina (n-hexane/ethyl acetate 1:1) permitted the separation of the main component, 1-[2-(4-Bromophenyl)-4,4a,5,7-tetrahydro-4-methyl-[1,2,3]triazol-5-yl]-6-phenyl-4-(1-pyrrolidino)-pyrrolo[3,4-*c*]pyridine-5,7-dione, **12a:** Although all efforts to purify this product **12a** for analytical purposes failed, the structure is supported by ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.36 (d, *J* = 2 Hz, 1H), 7.69-7.44 (AA'BB', 4H), 7.38-7.23 (m, 5H), 5.75 (dd, *J* = 2Hz, 7Hz, 1H), 4.02 (d, *J* = 7 Hz, 1H), 4.12 (m, 2H), 3.68 (m, 2H), 2.46 (s, 3H), 2.1 (m, 2H), 1.9 (m, 2H).

Transformation of 7a with tosyl azide: 2-(4-Bromophenyl)-5-methyl-4-[2,5-dihydro-5-(1-pyrrolidino)-1-(4-methylbenzenesulfonyl)-1*H*-imidazol-2-yl]-[1,2,3]triazol (15a): To a solution of **7a** (540 mg, 1.5 mmol) in absolute dichloromethane (10 ml) was added tosyl azide (300 mg, 1.5 mmol) at r.t. under argon. After stirring for 2 h the solvent was removed *in vacuo*, and the residue was triturated with acetonitrile to give a crude product (600 mg, 75%) which was filtered off. Purification for analytical purposes (recrystallization from dichloromethane/methanol) gave colourless crystals **15a**, m.p. 167-168°C: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.55 (AA'BB', 4H), 7.68-7.22 (AA'BB', 4H), 7.50 (d, *J* = 3 Hz, 1H), 6.65 (dd, *J* = 2 Hz, 3 Hz, 1H), 5.95 (d, *J* = 2 Hz, 1H), 2.88 (m, 4H), 2.53 (s, 3H), 2.36 (s, 3H), 1.75 (m, 4H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 163.08, 144.53, 144.39, 144.12, 138.51, 135.35, 132.16, 129.63, 127.46, 120.51, 119.76, 85.51, 82.96, 47.99, 24.01, 21.48, 10.47. Anal. Calcd for $C_{23}H_{25}BrN_6O_2S$: C, 52.18; H, 4.76; N, 15.87. Found: C, 52.10; H, 4.56; N, 15.68.

Transformation of 7 with 4-chlorobenzenediazonium tetrafluoroborate: 1-[5-[2-(4-bromophenyl)-4-methyl-2*H*-[1,2,3]triazol-5-yl]-1-(4-chlorophenyl)-4,5-dihydro-1*H*-[1,2,4]triazol-3-yl]methenopyrrolidin ium tetrafluoroborate, 17a: To a solution of 4-chlorobenzenediazonium tetrafluoroborate (250 mg, 1.1 mmol) in dry dichloromethane was added dropwise a solution of **7a** (360 mg, 1.0 mmol) in the same solvent. After stirring at r.t. for 3 h the resulting red crystals **17a** were filtered off and dried (336 mg, 57%). m.p. 189-191 °C; IR (KBr) 1100 cm^{-1} (BF_4 anion); MS: 500 (M-BF_4); ^{1}H NMR (CD_3CN, 400 MHz): δ 8,22 (s, 1H), 7.88-7.17 (m, 8H), 7,23 (d, *J* = 4 Hz, 1H), 6,36 (d, *J* = 4 Hz, 1H), 4,16 (m, 4H), 2,26 (s, 3H), 2,1-2,2 (m, 4H), Anal. Calcd for $C_{22}H_{22}BBrClF_4N_7$: C, 45.04; H, 3.78; N, 16.71. Found: C, 44.89; H, 3.60; N 16.56.

1-[5-[2-(4-bromophenyl)-4-(4-chlorophenyl)-2*H*-[1,2,3]triazol-5-yl]-1-(4-chlorophenyl)-4,5-dihydro-1*H*-[1,2,4]triazol-3-yl]methenopyrrolidinium tetrafluoroborate, 17b: Prepared from **7b** as **17a**. Yield 50%; m.p. 200-202°C; IR (KBr) 1100 cm^{-1} (BF_4^-); ^{1}H NMR (CD_3CN, 400 MHz): δ 8.17 (s, 1H), 7.95-

7.02 (m, 12H), 7.32 (d, J = 5 Hz, 1H), 6.47 (d, J = 5 Hz, 1H), 3.98-4.14 (m, 4H), 2.1-2.2 (m, 4H). MS *m/z* 596 ($[M\text{-}BF_4]^+$).

1-[5-[2-(4-bromophenyl)-4-methyl-2*H*-[1,2,3]triazol-5-yl]-1-(4-chlorophenyl)-4,5-dihydro-1*H*-[1,2,4]triazole-3-carboxaldehyde (18a): A solution of **17a** (340 mg, 0.57 mmol) in aqueous acetonitrile was stirred at r.t. until the red color disappeared, and a yellow solution was formed. After extraction with dichloromethane, the organic solvent was removed under reduced pressure to give yellow crystals **18a** (240 mg, 96%), m.p. 163-168°C; IR (KBr) 1651 cm^{-1} (CH=O); MS: m/z 445 ($M^{+\cdot}$); ^1H NMR (CD_3CN, 400 MHz): δ 9.48 (s, 1H), 7.05-7.90 (m, 8H), 6.94 (d, 1H, J = 3 Hz), 6.18 (d, J = 3 Hz, 1H), 2.2 (s, 3H). Anal. Calcd for $C_{18}H_{14}BrClN_6O$: C, 48.50; H, 3.16; N, 18.85. Found: C, 48.26; H, 3.11; N, 18.58.

Acknowledgment

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