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Chemical reactivity of [1,2,3]triazolo[1,5-*a*]- and [1,5-*c*]-pyrimidinium salts☆

Sándor Bátori,[a,b,*] Eszter Gács-Baitz,[b] Sándor Bokotey[a] and András Messmer[b]

[a]*Chinoin Pharmaceutical and Chemical Works Co, Ltd., P.O. Box 110, H-1325 Budapest, Hungary*
[b]*Chemical Research Center, Institute of Chemistry, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary*

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Abstract—The chemical reactivity of the [1,2,3]triazolo[1,5-*a*]- and [1,5-*c*]-pyrimidinium salts towards morpholine, water and sodium methoxide have been studied. Among others, new 1-aza and 2-azabutadienes substituted by a [1,2,3]-triazole ring were obtained in the course of the opening of the positively charged pyrimidine ring.

1. Introduction

Recently, we reported the synthesis of new [1,2,3]triazolo[1,5-*a*]- and [1,5-*c*]pyrimidinium salts via oxidation (i.e. cyclodehydrogenation) of the appropriate pyrimidyl ketone arylhydrazones using 'TBB' (2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one) as reagent.[2]

Here we report on the results of the investigation of the chemical reactivity of these new 1,2,3-triazolopyrimidinium salts.

Earlier, Sutherland and Tennant[3–6] investigated the synthesis and chemical reactivity of the neutral [1,2,3]triazolo[1,5-*a*]pyrimidines. They found that in acidic conditions (acetic acid, trifluoroacetic acid) the triazole ring would be opened and decomposed to give 2-substituted pyrimidine derivatives. They explained the reactions found by a Dimroth-type rearrangement in which a diazoalkylideneamine–1,2,3-triazole tautomerism was proved a feature similar to the azidoazomethine–tetrazole equilibrium. Tsuiguk and Medik described[7] that although the attempted reaction of 5,7-dimethyl-2,3-diphenyl-[1,2,3]triazolo[1,5-*a*]pyrimidinium perchlorate with an alcoholic solution of ammonia resulted in no change of the molecule, its reaction with sodium hydroxide, however, led to the opening of the pyrimidine ring to form a substituted 4-amino-1,2,3-triazole derivative.

The other possible pyrimidine derivative, the [1,2,3]triazolo[1,5-*c*]pyrimidine, first described by Maury et al.[8] was found to undergo ring opening at the pyrimidine ring on influence of water to give a 4-[2-(*N*-formyl)amino]vinyl-1*H*-triazole derivative. A short review of the reactions of this ring system was published recently by Abarca et al.[9] (see references therein).

2. Results and discussion

The positively charged new compounds **1a–c** and **5ab**, prepared by us[2] recently under mild and strictly water-free conditions, are highly reactive towards different nucleophiles (e.g. morpholine, water and sodium methoxide).

The reaction of the [1,2,3]triazolo[1,5-*a*]pyrimidinium salts **1a–c** with morpholine, even at room temperature, gave the 4-morpholino-1-azadienes **3a–c** in good yield (80–85%). These new yellow crystalline compounds belong to the family of the vinamidines.[10]

The ring opening can be rationalized by a similar reaction pattern that was reported for other triazolo- and tetrazoloazinium salts:[11–16] the salt is attacked by the nucleophile (e.g. morpholine) at one of the α-positions adjacent to the positively charged bridgehead nitrogen (C-7) to form the pseudobase **2a–c** (see Scheme 1). After electrocyclic ring opening, the dienes **3a–c** were formed. (Under the conditions applied, usually the all-*trans* dienes are formed; see Ref. 17.) Besides **3b**, a small amount (~4%) of the 4-amino-1,2,3-triazole derivative **4** was isolated too (starting from **1b**).

The reaction of the [1,2,3]triazolo[1,5-*c*]pyrimidinium salt **5b** with morpholine gave yellow crystals of 1-[2-(4-

☆ Fused azolium salts, part 21. For part 20, see Ref. 1.

Keywords: 1-azadienes; 2-azadienes; vinamidines; ring opening; reactivity of pyrimidinium salts.

* Corresponding author. Tel.: +36-1396-0900; fax: +36-1370-5412; e-mail: sandor.batori@sanofi-synthelabo.com

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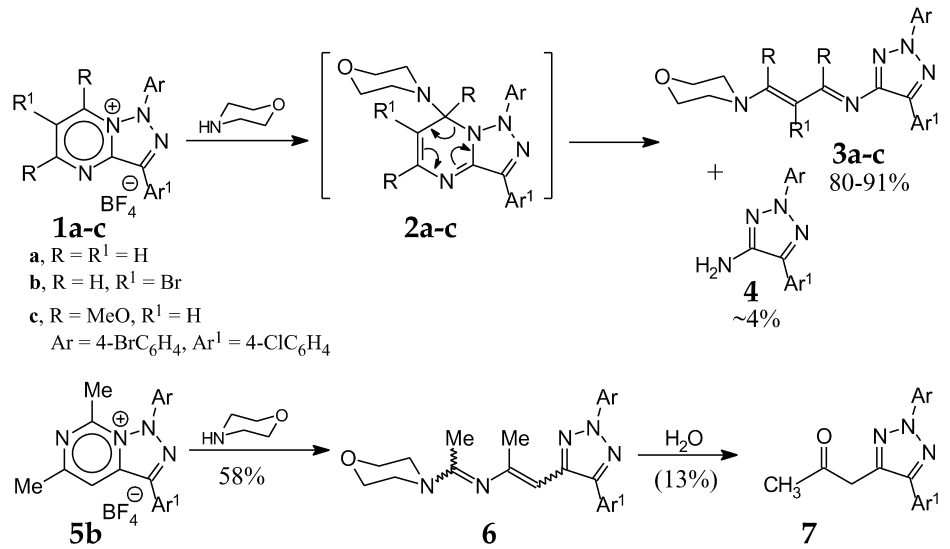
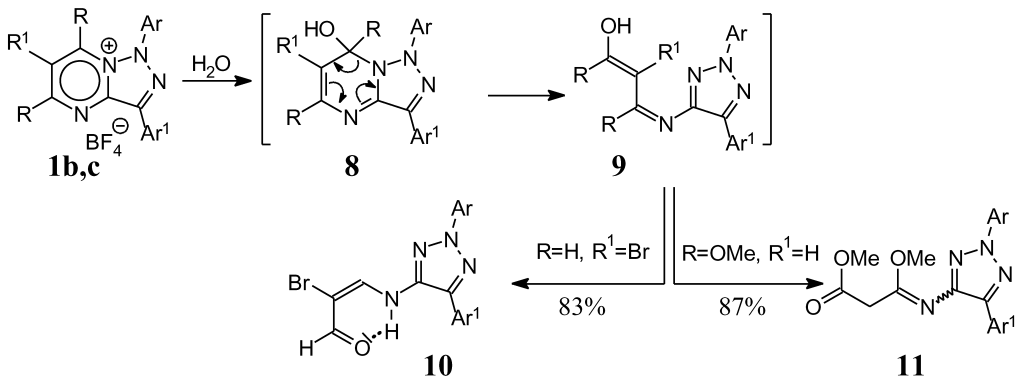


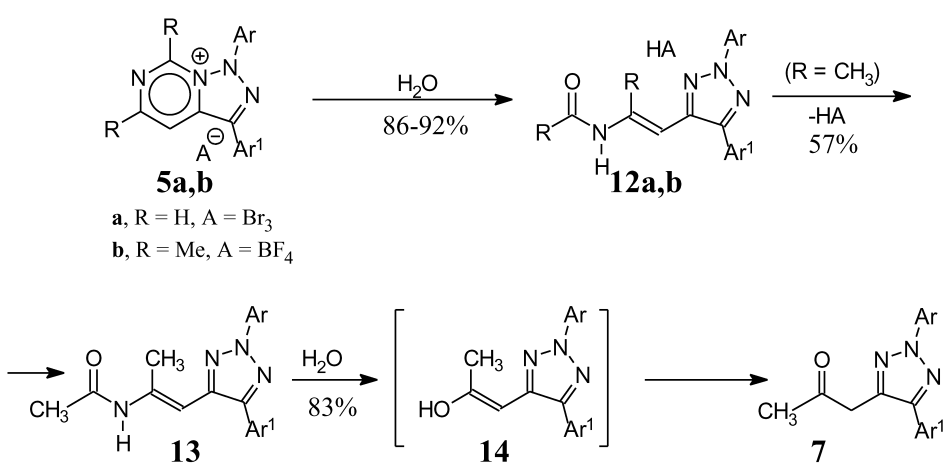
Scheme 1.



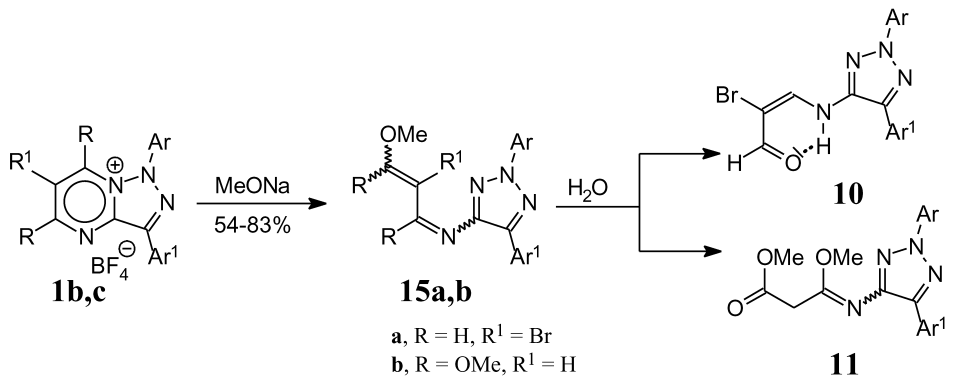
Scheme 2.

bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]-*N*-[1-(4-morpholinyl)ethylidene]-1-propen-2-amine (**6**) in moderate yield (57%). This 3-azadiene is less stable than the 1-azadienes (e.g. **3a**) and can be hydrolyzed easily (even on influence of traces of water in the solvent). This is the reason why the product of the side reaction, the acetonyl-triazole derivative **7**, was also isolated (13%).

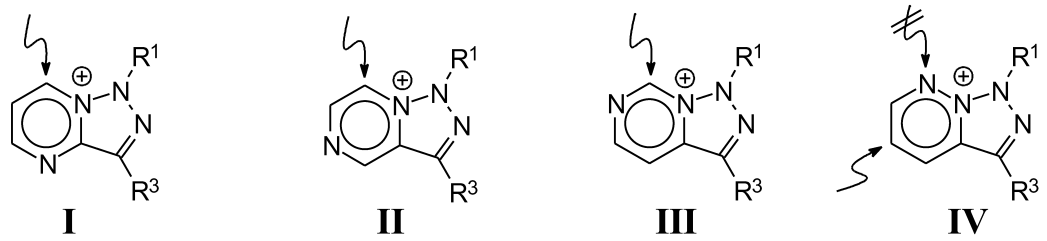
The [1,2,3]triazolo[1,5-*a*]pyrimidinium salts **1b**,**c** react with the following nucleophile, water—with a similar mechanism as proposed for morpholine—through the formation of intermediates **8** and **9** (Scheme 2). While the 6-bromo derivative **1b** gave the derivative **10** (in 83% yield, stabilized by a strong intramolecular H-bond: ^{1}H NMR (DMSO-d_6), δ 9.69 ppm), the reaction product of the



Scheme 3.



Scheme 4.



Scheme 5.

5,7-dimethoxy derivative **1c** was isolated as the methyl ester of the iminomalonic acid derivative **11** similarly in good (87%) yield.

The reaction of 1-(4-bromophenyl)-3-(4-chlorophenyl)[1,2,3]triazolo[1,5-*c*]pyrimidinium perbromide **5a** with water resulted in, according to our expectations, (*E*)-2-[2-(4-bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]vinylformamide hydrobromide **12a** in good yield (86%). The coupling constant between the protons H-1 and H-2 (11.5 Hz) makes probable that the double bond between the atoms C-1 and C-2 is *trans* (Scheme 3).

In a similar reaction with water, the 5,7-dimethyl derivative **5b** gave the enamine **12b** (in excellent, 92% yield). During its recrystallization from acetonitrile a deprotonation took place to give the free base **13**. This latter was further hydrolyzed with water resulting in the acetonyltriazole derivative **7**.

The third type of nucleophiles used, the methoxide ion reacted with the [1,2,3]triazolo[1,5-*a*]-pyrimidinium system similarly to morpholine or water: the salts **1b**,**c** gave the 1-azadiene ethers **15a**,**b** in moderate to good yields (Scheme 4).

These azadiene ethers **15a**,**b** are more reactive compounds than azadiene amines and react with water smoothly to give **10** or **11**. For a detailed study of similar systems see Ref. 17.

On the basis of our studies we found significant differences in the reactivity of the four possible [1,2,3]triazolodiazinium salts (**I**–**IV**)[18,19] (see Scheme 5).

The [1,2,3]triazolo[1,5-*b*]pyridazinium system (**IV**) has a unique and different reactivity because in this case there is a N-atom at the α-position to the positively charged, bridgehead nitrogen, hence a nucleophilic attack at this position can be excluded. The reactivity of the pyrazinium-(**II**) and the two pyrimidinium system (**I** and **III**) is similar to each other (electrocyclic ring opening) and they give, taking the triazole ring as a common substituent, 1-aza-, 2-aza- and 3-azabutadiens.

From the reactivity point of view, the most stable system is the [1,2,3]triazolo[1,5-*b*]-pyridazinium (**IV**), which is followed by the [1,2,3]triazolo[1,5-*a*]pyrazinium (**II**) and the [1,2,3]triazolo[1,5-*a*]pyrimidinium (**I**) system. The [1,2,3]triazolo[1,5-*c*]pyrimidinium salts (**III**) proved to be the most unstable derivatives.

3. Experimental

3.1. General

Melting points were determined by a Büchi apparatus. IR spectra (KBr pellet) were recorded on Specord IR-75 and Bruker IFS-28 equipments. The ^{1}H NMR spectra were measured on Varian XL-100 (100 MHz) and Varian VXR-400 and Bruker DRX-400 instruments (400 MHz) at ambient temperature using TMS as internal standard. ^{13}C NMR spectra were recorded on a Bruker DRX-400 instrument. The yields of the reactions were not optimized.

3.1.1. 2-(4-Bromophenyl)-5-(4-chlorophenyl)-*N*-[(1*E*,2*E*)-3-morpholin-4-ylprop-2-enylidene]-2*H*-1,2,3-triazol-4-amine (3a). Morpholine (2.4 g, 2.4 mL, 28 mmol) was added to a stirred solution of the fluoroborate salt **1a** (2.34 g, 5 mmol) in dry acetonitrile (25 mL), and the mixture was stirred at room temperature for 10 min. The crystals which separated were filtered off and washed with

acetonitrile to give 2.15 g (91%) of pale yellow prisms, mp 205–207°C; ν_{max} (KBr): 3063, 2962, 2925, 2900, 2850, 1624, 1570, 1517, 1487, 1475, 1440, 1379 cm^{-1}; δ_H ($CDCl_3$): 8.61 (d, 1H, J=9.6 Hz, H-2), 8.18 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.95 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.58 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.40 (m, 2H, H-3′,5′(4-Cl-phenyl)), 6.90 (d, 1H, J=13.2 Hz, H-3), 5.65 (dd, 1H, J=9.6, 13.2 Hz, H-4), 3.77 (m, 4H, morpholine), 3.33 (m, 4H, morpholine). Found: C, 53.41; H, 4.13; N, 14.71%. Calcd for $C_{21}H_{19}BrClN_5O$: C, 53.35; H, 4.05; N, 14.81%.

3.1.2. *N*-[(1*E*,2*Z*)-2-Bromo-3-morpholin-4-ylprop-2-enylidene]-2-(4-bromophenyl)-5-(4-chloro-phenyl)-2*H*-1,2,3-triazol-4-amine (3b). A solution of morpholine (0.18 g, 2 mmol) in dry acetonitrile (3 mL) was added to an ice-cooled, stirred solution of **1b** (0.55 g, 1 mmol) in dry acetonitrile (13 mL) and stirred for 2 h. The crystals were filtered off, washed with acetonitrile and recrystallized from acetonitrile–benzene to give 0.46 g (84%) of yellow prisms, mp 132–134°C; ν_{max} (KBr): 3000, 2900, 2800, 1625, 1565, 1520, 1440 cm^{-1}; δ_H ($CDCl_3$): 8.43 (s, 1H, H-2), 8.34 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.95 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.57 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.42 (m, 2H, H-3′,5′(4-Cl-phenyl)), 7.04 (s, 1H, H-4), 3.78 (m, 8H, morpholine); δ_C (DMSO-d_6): 161.65, 154.06, 151.23, 138.99, 138.36, 133.02, 132.24, 129.02, 128.62, 119.50, 89.47, 66.13, 50.86. Found: C, 45.95; H, 3.32; N, 12.50%. Calcd for $C_{21}H_{18}Br_2ClN_5O$: C, 45.72; H, 3.29; N, 12.70%. The chromatography of the mother liquor gave white needles of 2-(4-bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-amine (**4**, 14 mg, 4%), mp 179–180°C; ν_{max} (KBr): 3397, 3310, 3216, 3107, 1622, 1592, 1571, 1529, 1488, 1474, 1412, 1387, 1340 cm^{-1}; δ_H ($CDCl_3$): 7.86 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.75 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.56 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.46 (m, 2H, H-3′,5′(4-Cl-phenyl)), 4.04 (s, 2H, NH_2). Found: C, 47.95; H, 2.88; N, 15.84%. Calcd for $C_{14}H_{10}BrClN_4$: C, 48.09; H, 2.89; N, 16.03%.

3.1.3. Methyl (*Z*)-*N*-[2-(4-bromophenyl)-5-(4-chloro-phenyl)-2*H*-1,2,3-triazol-4-yl]-3-methoxy-3-(4-morpholinyl)-2-propenimidoate (3c). A solution of morpholine (98 mg, 1.18 mmol) in dry acetonitrile (1 mL) was added to a stirred solution of **1c** (0.3 g, 0.56 mmol) in dry acetonitrile (6 mL) and stirred at room temperature for 4 h. The crystals were filtered off, washed with acetonitrile and recrystallized from ethyl acetate to give 0.24 g (80%) of pale yellow prisms, mp 204–206°C; ν_{max} (KBr): 3010, 2900, 2830, 2795, 1660 cm^{-1}; δ_H ($CDCl_3$): 8.05 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.89 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.60 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.42 (m, 2H, H-3′,5′(4-Cl-phenyl)), 6.36 (s, 1H, H-3), 4.00 (s, 3H, CH_3O), 3.78 (s, 3H, CH_3O), 3.62 (m, 8H, morpholine). Found: C, 52.07; H, 4.59; N, 12.97; Hal_{Cl}, 13.59%. Calcd for $C_{23}H_{23}BrClN_5O_3$: C, 51.84; H, 4.35; N, 13.14; Hal_{Cl}, 13.31%.

3.1.4. 1-[2-(4-Bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]-*N*-[1-(4-morpholinyl)-ethylidene]-1-propen-2-amine (6). An ice-cooled solution of **5b** (0.5 g, 1 mmol) in dry acetonitrile (1 mL) was stirred with a solution of morpholine (0.174 g, 2 mmol) in dry acetonitrile (2 mL) for 2 h. The crystals were filtered off, washed with acetonitrile and recrystallized from benzene–ethyl acetate to give 0.29 g (58%) of yellow prisms, mp 166–168°C; ν_{max} (KBr): 3000, 2920, 2860, 2800, 1620 cm^{-1}; δ_H ($CDCl_3$): 8.02 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.75 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.54 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.36 (m, 2H, H-3′,5′(4-Cl-phenyl)), 5.66 (s, 1H, H-1), 3.60 (m, 4H, morpholine), 3.30 (m, 4H, morpholine), 1.96 (s, 3H, H-5), 1.80 (s, 3H, CH_3). Found: C, 55.31; H, 4.58; N, 13.82; Hal_{Cl}, 14.35%. Calcd for $C_{23}H_{23}BrClN_5O$: C, 55.16; H, 4.63; N, 13.96; Hal_{Cl}, 14.16%. The work up of the mother liquors by column chromatography (Silica gel) gave 50 mg (13%) of white needles of 1-[2-(4-bromophenyl)-5-(4-chlorophenyl)-2H-1,2,3-triazol-4-yl]acetone (**7**), mp 155–157°C; ν_{max} (KBr): 3020, 2920, 2850, 1705, 1590, 1495, 1420 cm^{-1}; δ_H (tetrachloroethylene): 8.07 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.73 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.58 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.40 (m, 2H, H-3′,5′(4-Cl-phenyl)), 3.92 (s, 2H, CH_2), 2.20 (s, 3H, CH_3). Found: C, 52.45; H, 3.45; N, 10.53%. Calcd for $C_{17}H_{12}BrClN_3O$: C, 52.26; H, 3.35; N, 10.73%.

3.1.5. (2*E*)-2-Bromo-3-{[2-(4-bromophenyl)-5-(4-chloro-phenyl)-2*H*-1,2,3-triazol-4-yl]amino}acrylaldehyde (10). A solution of the fluoroborate salt **1b** (275 mg, 0.5 mmol) in DMSO (20 mL) was stirred with water (3 mL) at room temperature for 3 h. After addition of water (30 mL), the precipitated crystals were filtered off, washed with water and recrystallized from ethyl acetate to give 200 mg (83%) of white crystals, mp 191–192°C; ν_{max} (KBr): 3150, 3000, 1660, 1620, 1545, 1515, 1490, 1415 cm^{-1}; δ_H ($CDCl_3$): 9.26 (s, 1H, H-1), 8.26 (d, J=12.6 Hz, 1H, H-3), 7.97 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.65 (m, 4H, H-2′,3′,5′,6′(4-Br-phenyl)), 7.55 (m, 2H, H-3′,5′(4-Cl-phenyl)), 7.46 (d, J=12.6 Hz, 1H, NH) ppm; ^{1}H NMR (DMSO-d_6): δ 9.69 (s, 1H, NH), 9.16 (s, 1H, H-1), 8.35 (s, 1H, H-3), 7.99 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.87 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.76 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.60 (m, 2H, H-3′,5′(4-Cl-phenyl)). Found: C, 42.29; H, 2.49; N, 11.83; Hal_{Cl}, 22.29. Calcd for $C_{17}H_{11}Br_2ClN_4O$: C, 42.31; H, 2.30; N, 11.61; Hal_{Cl}, 22.04%.

3.1.6. Methyl 3-{[2-(4-bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]imino}-3-methoxypropanoate (11). A solution of **1c** (270 mg, 0.5 mmol) in acetonitrile (10 mL) was stirred with a solution of K_2CO_3 (70 mg, 0.5 mmol) in water (6 mL) at room temperature for 0.5 h. After addition of water (30 mL) the precipitated crystals were filtered off, washed with water and recrystallized from ethanol–water to give 200 mg (87%) of white crystals, mp 141–143°C; ν_{max} (KBr): 3060, 3020, 2970, 2890, 2830, 1740, 1650, 1580, 1490, 1430 cm^{-1}; δ_H ($CDCl_3$): 8.10 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.93 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.55 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.36 (m, 2H, H-3′,5′(4-Cl-phenyl)), 4.00 (s, 3H, OCH_3), 3.70 (s, 2H, CH_2), 3.66 (s, 3H, OCH_3). Found: C, 49.43; H, 3.61; N, 11.94; Hal_{Cl}, 15.42%. Calcd for $C_{19}H_{16}BrClN_4O_3$: C, 49.21; H, 3.48; N, 12.08; Hal_{Cl}, 15.29%.

3.1.7. (*E*)-2-[2-(4-Bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]vinylformamide hydrobromide (12a, HA=HBr). The perbromide salt **5a** (150 mg, 0.24 mmol) was stirred in acetonitrile (3 mL) with water (1 mL) and acetone (0.5 mL) at room temperature for 5 h. The precipitated crystals were filtered off washed with water to

give the product (100 mg, 86.5%), mp 120–122°C; ν_{max} (KBr): 3250, 3030, 1660, 1580, 1480, 1400 cm^{-1}; δ_H (DMSO-d_6): 8.53 (s, 1H, H-formyl), 8.30 (d, 1H, J=11.5 Hz, H-2), 8.10 (d, 1H, J=11.5 Hz, H-1), 8.0–7.5 (m, 9H, NH and diaryl). Found: C, 42.30; H, 2.81; N, 11.30%. Calcd for $C_{17}H_{13}Br_2ClN_4O$: C, 42.13; H, 2.70; 11.56%.

3.1.8. *N*-{(*E*)-2-[2-(4-bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]-1-methylvinyl}acetamide (12b and 13). *Fluoroborate salt* **12b**. The fluoroborate salt **5b** (200 mg, 0.4 mmol) was stirred in acetonitrile (2 mL) with water (3 mL) at room temperature for 2 h. Water (10 mL) was then added and the precipitated crystals were filtered off, washed with water to give the product (190 mg, 92%), mp 296–298°C; δ_H (DMSO-d_6): 8.70 (s, 1H, NH), 8.45 (s, 1H, H-1), 8.2–7.5 (m, 8H, H-aryls), 7.05 (s, 1H, NH), 2.82 (s, 3H, CH_3-acetyl), 2.57 (s, 3H, CH_3). Found: C, 44.14; H, 3.55; N, 10.52%. Calcd for $C_{19}H_{17}BBrClF_4N_4O$: C, 43.92; H, 3.30; N, 10.78%.

Free base **13**. 140 mg of the salt obtained above was recrystallized from acetonitrile to give 80 mg (57%) of white needles, mp 182–184°C; ν_{max} (KBr): 3310, 3050, 2920, 1670, 1630, 1530, 1490, 1400 cm^{-1}. Found: C, 53.09; H, 3.92; N, 12.96; Hal_{Cl}, 16.22%. Calcd for $C_{19}H_{16}BrClN_4O$: C, 52.86; H, 3.74; N, 12.98; Hal_{Cl}, 16.43%.

3.1.9. 1-[2-(4-Bromophenyl)-5-(4-chlorophenyl)-2*H*-1,2,3-triazol-4-yl]acetone (7). Compound **13** (200 mg, 0.46 mmol) was stirred in DMSO (4 mL) with water (1 mL) at room temperature for 12 h. The solution was mixed with water (15 mL) and the precipitated crystals were filtered off, washed with water to give 150 mg (83%) of cotton-like fine needles, mp 155–157°C. The compound was identical with that obtained earlier.

3.1.10. *N*-(2-Bromo-3-methoxyprop-2-enylidene)-2-(4-bromophenyl)-5-(4-chloro-phenyl)-2*H*-1,2,3-triazol-4-amine (15a). Fluoroborate salt **1b** (0.55 g, 1 mmol) was added to a solution of sodium methoxide (54 mg, 1 mmol) in dry acetonitrile (5 mL) and dry methanol (10 mL) at −20°C and stirred for 1 h. The reaction mixture was evaporated to half of its volume, the precipitate was filtered off, washed with methanol and recrystallized from dichloromethane–ether to give 0.27 g (54%) of pale yellow needles, mp 174–176°C; ν_{max} (KBr): 3020, 2930, 1625, 1595, 1520, 1490, 1440 cm^{-1}; δ_H ($CDCl_3$): 8.55 (s, 1H, H-2), 8.30 (m, 2H, H-2′,6′(4-Cl-phenyl)), 7.97 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.55 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.40 (m, 2H, H-3′,5′(4-Cl-phenyl)), 7.30 (s, 1H, H-4), 4.03 (s, 3H, OCH_3). Found: C, 43.71; H, 2.82; N, 11.04; Hal_{Cl}, 21.68%. Calcd for $C_{18}H_{13}Br_2ClN_4O$: C, 43.53; H, 2.64; N, 11.28; Hal_{Cl}, 21.42%.

3.1.11. Methyl *N*-[2-(4-bromophenyl)-5-(4-chloro-phenyl)-2*H*-1,2,3-triazol-4-yl]-3,3-dimethoxyprop-2-enimidoate (15b). Fluoroborate salt **1c** (0.27 g, 0.5 mmol) was added to a solution of sodium methoxide (27 mg, 0.5 mmol) in dry acetonitrile (5 mL) and dry methanol (10 mL) at −20°C and stirred for 1 h. The reaction mixture was evaporated to half of its volume, the precipitate was filtered off and recrystallized from acetonitrile to give 0.19 g (83%) of pale yellow crystals, mp 136–138°C; ν_{max} (KBr): 3070, 3010, 2970, 2840, 1620, 1580, 1520, 1430 cm^{-1}; δ_H ($CDCl_3$): 8.10 (m, 2H, H-2′,6′(4-Cl-phenyl)), 8.00 (m, 2H, H-2′,6′(4-Br-phenyl)), 7.60 (m, 2H, H-3′,5′(4-Br-phenyl)), 7.39 (m, 2H, H-3′,5′(4-Cl-phenyl)), 4.73 (s, 1H, H-3), 4.02 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3). Found: C, 50.30; H, 3.78; N, 11.90; Hal_{Cl}, 15.32%. Calcd for $C_{20}H_{18}Br_2ClN_4O_3$: C, 50.28; H, 3.80; N, 11.73; Hal_{Cl}, 15.23%.

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