Synthesis and fungicidal activities of 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles

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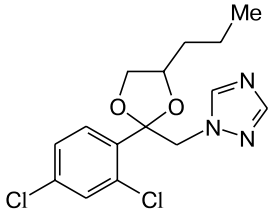
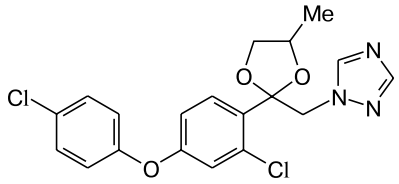
Ketalization of benzophenones with epichlorohydrin or 3-chloropropane-1,2-diol gave 2,2-diaryl-4-chloromethyl-1,3-dioxolanes, which were used to alkylate sodium salts of imidazole or 1,2,4-triazole. The resulting 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles exhibit high fungicidal activities.

Key words: imidazoles, 1,2,4-triazoles, alkylation, 1,3-dioxolanes, epichlorohydrin, 1-[(1,3-dioxolan-4-yl)methyl]-1*H*-azoles, fungicides.

A considerable part of current fungicides are 1,2,4-triazole or imidazole derivatives. Azole fungicides exhibit system properties, have low consumption rates and a broad range of action, and are slightly toxic; in this respect, they are superior to many other classes of fungicidal preparations.[1] According to their mechanism of action, 1-substituted azoles are inhibitors of the biosynthesis of steroids.[2,3] The best known and widely used dioxolane-containing azole fungicides include propiconazole and difenoconazole with an azolylmethyl group in position 2 of the dioxolane ring.



Propiconazole



Difenoconazole

With the aim to obtain novel fungicides in the series of 1-substituted azoles, we synthesized 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles and studied their fungicidal activities. The above compounds are structurally similar to propiconazole and difenoconazole but contain an azolylmethyl group in a different position (Scheme 1).

Novel substituted 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles **3** and **4** were obtained in two steps. Ketalization of benzophenones **1** with epichlorohydrin in CCl_4 in the presence of $BF_3 \cdot Et_2O$ as a catalyst[4—6] (method *A*) or with 3-chloropropane-1,2-diol with azeotropic removal of water in benzene in the presence of *p*-toluenesulfonic acid as a catalyst[7,8] (method *B*) gave 2,2-diaryl-4-chloromethyl-1,3-dioxolanes **2**, which then were used to alkylate sodium salts of 1,2,4-triazole or imidazole[9,10] (Scheme 1).

To reduce the amount of a by-product of epichlorohydrin polymerization, we employed an excess of benzophenones in the synthesis of 2,2-diaryl-4-chloromethyl-1,3-dioxolanes **2** according to method *A*. However, method *B* is preferred because the use of a double excess of comparatively inexpensive 3-chloropropane-1,2-diol allows a higher degree of conversion of the benzophenones and the diol can be easily removed by washing of the reaction mixture with water. The yields of 2,2-diaryl-4-chloromethyl-1,3-dioxolanes were 78% (**2a**, *A*), 80% (**2b**, *A*), and 93—96% (**2a**—**e**, *B*). The compounds obtained are yellowish oily liquids that are soluble in most organic solvents. The ^{1}H NMR spectra of derivatives **2** show characteristic signals for the 2,2,4-trisubstituted dioxolane: two doublets of doublets at δ 3.48—3.49 and 3.64—3.67 for the chloromethyl protons, usually two doublets of doublets at δ 4.02—4.04 and 4.11—4.12 for the methylene protons of the dioxolane ring, and a quintet at δ 4.43—4.45 for the methine proton of the dioxolane ring. The IR spectra of chloromethyldioxolanes **2** contain no signal for the carbonyl group of the starting ketone; instead, five characteristic bands of the dioxolane ring[11] appear at 1085—1250 cm^{-1}.

Alkylation of sodium salts of 1,2,4-triazole and imidazole was carried out in boiling DMF for 16—18 h.

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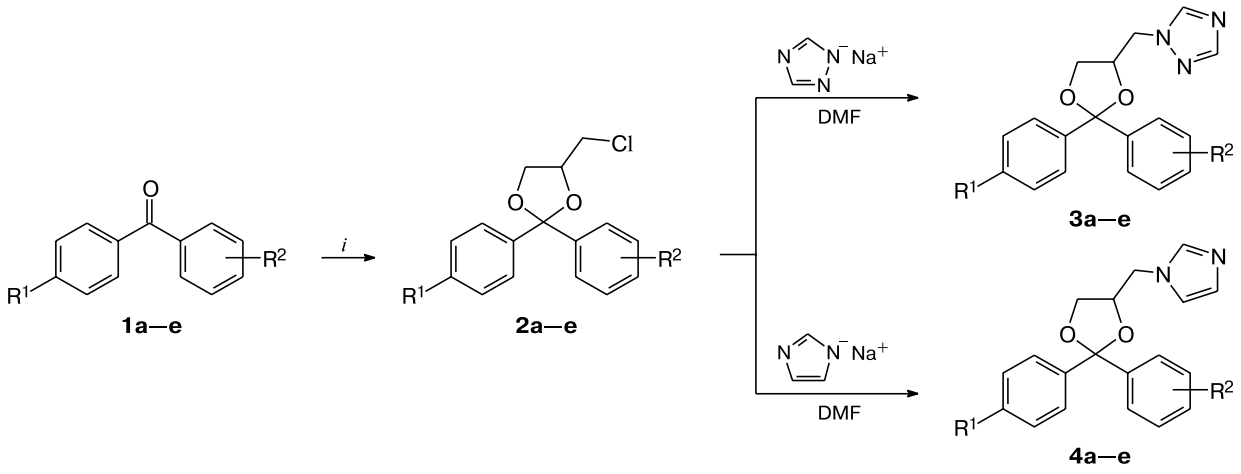
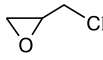
Scheme 1



i.  , $BF_3 \cdot Et_2O$, CCl_4 or $HOCH_2CH(OH)CH_2Cl$, TsOH, PhH, Δ.

	a	**b**	**c**	**d**	**e**
R^1	Bu^t	Cl	Cl	Cl	Br
R^2	4-Cl	4-Cl	2,4-Cl_2	4-Br	4-Br

In lower-boiling solvents such as acetonitrile and dioxane, the reaction did not yield the desired products. Nor were derivatives **3** and **4** obtained in an alternative way using reactions of 3-(1*H*-azol-1-yl)propane-1,2-diols with benzophenones both under azeotropic removal of water in an aromatic solvent (benzene, toluene, and *p*-xylene) in the presence of *p*-toluenesulfonic acid as a catalyst and over molecular sieves (3 Å) in dehydrated polar solvents (THF, DMSO, and EtOH) in the presence of *p*-toluenesulfonic acid or H_2SO_4 as a catalyst.

It is known that alkylation of 1,2,4-triazole with alkyl halides produces 1- and 4-substituted derivatives.[12] In the synthesis of triazoles **3**, the percentage of the 4-substituted isomer in the reaction products was 2—9% (HPLC-MS data). Individual 1-substituted 1,2,4-triazoles and imidazoles were isolated by flash chromatography as white crystals (**3d,e**) or yellowish oily liquids (**3a—c**, **4a—e**) and converted into crystalline oxalates that are stable in storage. The ^{1}H NMR spectra of 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles show quintets for the methine proton of the dioxolane ring at δ 4.54—4.59 (**3**) and 4.47—4.54 (**4**), two doublets of doublets for the methylene protons of the dioxolane ring at δ 3.87—4.16 (**3**) and 3.82—4.05 (**4**), and two doublets of doublets for the methylene protons of the azolylmethyl fragment at δ 4.33—4.44 (**3**) and 4.14—4.43 (**4**). The double set of doublet signals in the ^{1}H NMR spectra of dioxolane-containing azoles **3c** and **4c** indicates the formation of mixtures of the diastereomers in the ratios 1 : 4.56 and 1 : 3.76, respectively. The 2D ^{1}H—^{1}H NMR spectrum (NOE) of a diastereomeric pair of compound **3c** shows a cross peak due to a coupling of the H(5) proton of triazole with the H(2) and H(6) protons of the 4-chlorophenyl substituent in the major stereoisomers; therefore, they have *E*-configuration.

The compounds obtained were tested *in vitro* for fungicidal activity according to a very common procedure[13] with five phytopathogenic fungi: *Fusarium oxysporum (F.o.)*, *Fusarium moniliforme (F.m.)*, *Bipolaris sorokiniana (B.s.)*, *Rhizoctonia solani (R.s.)*, and *Venturia inaequalis (V.i.)*. We studied the effects of the test compounds (c = 30 mg L^{-1}) on the radial growth of mycelium in potato saccharose agar with the widely used fungicide triadimefon as a reference compound (Table 1). The compounds obtained proved to be mostly superior in fungicidal activity

Table 1. Growth inhibition of the mycelium of the pathogenic fungi by 1-[(2,2-diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles **3** and **4** *in vitro* (c = 30 mg L^{-1})

Compound	Mycelium growth inhibition (%)				
	V.i.	*R.s.*	*F.o.*	*F.m.*	*B.s.*
3a	30	63	54	59	66
3b	65	94	77	72	71
3c	39	99	72	70	70
3d	47	95	73	72	78
3e	47	94	62	71	75
4a	51	75	64	79	71
4b	67	81	74	60	67
4c	59	92	78	93	93
4d	74	95	73	99	85
4e	56	85	57	94	100
Triadimefon	53	54	72	90	45

to triadimefon. Imidazole derivatives **4** were more efficient than 1,2,4-triazole derivatives **3**. The best inhibitor was compound **4d** derived from imidazole and 4-bromo-4′-chlorobenzophenone.

Experimental

^{1}H NMR spectra were recorded on a Bruker AM-300 instrument (300.13 MHz). ^{13}C NMR spectra were recorded on a Bruker WM-250 instrument (62.9 MHz) with Me_4Si as the internal standard. IR spectra were recorded on a Specord M-80 instrument (thin films for liquids and Nujol for solids). The course of the reaction was monitored and the purity of the compounds was checked by TLC (Sorbfil A-UF). Substituted benzophenones were prepared according to a known procedure.[14]

2,2-Diaryl-4-chloromethyl-1,3-dioxolanes 2a,b. Method *A* (general procedure). Boron trifluoride etherate (0.28 g, 0.25 mL, 0.002 mol) was added to a stirred solution of benzophenone **1a,b** (0.1 mol) in CCl_4 (250 mL). The mixture was stirred at room temperature for 20 min. Then epichlorohydrin (7.40 g, 6.27 mL, 0.08 mol) was added at 25—30 °C and stirring was continued at room temperature for 2 h. The reaction mixture was washed with 3% NaOH (100 mL) and water (100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was fractionated *in vacuo*.

2,2-Diaryl-4-chloromethyl-1,3-dioxolanes 2a—e. Method *B* (general procedure). A mixture of benzophenone **1a—e** (0.05 mol), 3-chloropropane-1,2-diol (11.05 g, 0.1 mol), and *p*-toluenesulfonic acid monohydrate (0.48 g, 0.0025 mol) was refluxed in benzene for ~24 h with azeotropic removal of water. The reaction mixture was neutralized with 2% NaOH (100 mL) and washed with water (200 mL). The solvent was removed and the residue was fractionated *in vacuo*.

2-(4-*tert*-Butylphenyl)-4-chloromethyl-2-(4-chlorophenyl)-1,3-dioxolane (2a). The yield was 78% (method *A*) and 95% (*B*), b.p. 189—191 °C (0.5 Torr), n_D^{20} = 1.5670. Found (%): C, 65.59; H, 6.16. $C_{20}H_{22}Cl_2O_2$. Calculated (%): C, 65.76; H, 6.07. ^{1}H NMR (DMSO-d_6), δ: 1.33 (s, 9 H, C$\underline{Me}_3$); 3.49 (dd, 1 H, CH_2Cl, ^3J = 8.8 Hz, ^2J = 11.0 Hz); 3.67 (dd, 1 H, CH_2Cl, ^3J = 5.2 Hz, ^2J = 11.0 Hz); 4.02 (dd, 1 H, CH_2O, ^3J = 5.2 Hz, ^2J = 8.0 Hz); 4.11 (dd, 1 H, CH_2O, ^3J = 6.7 Hz, ^2J = 8.0 Hz); 4.44 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.18—7.54 (m, 8 H, Ar). ^{13}C NMR (DMSO-d_6), δ: 30.7 (C$\underline{Me}_3$); 34.1 (C$\underline{Me}_3$); 44.9 (CH_2Cl); 67.2 (CH_2O); 75.7 (CHO); 109.1 (OCO); 125.3, 125.4, 125.6, 125.7, 127.3, 127.6, 127.7,128.0, 128.2, 131.3, 132.8, 138.5, 141.1, 150.6, 150.7 (Ar). IR (thin film, ν/cm^{-1}): 1248, 1222, 1170, 1115, 1085 (COCOC); 735 (C—Cl).

4-Chloromethyl-2,2-bis(4-chlorophenyl)-1,3-dioxolane (2b). The yield was 80% (*A*) and 92% (*B*), b.p. 168—170 °C (0.4 Torr), n_D^{20} = 1.5953. Found (%): C, 55.65; H, 3.98. $C_{16}H_{13}Cl_3O_2$. Calculated (%): C, 55.92; H, 3.81. ^{1}H NMR (DMSO-d_6), δ: 3.49 (dd, 1 H, CH_2Cl, ^3J = 8.2 Hz, ^2J = 11.0 Hz); 3.64 (dd, 1 H, CH_2Cl, ^3J = 5.6 Hz, ^2J = 11.0 Hz); 4.03 (dd, 1 H, CH_2O, ^3J = 5.8 Hz, ^2J = 7.6 Hz); 4.12 (dd, 1 H, CH_2O, ^3J = 7.0 Hz, ^2J = 7.6 Hz); 4.45 (q, 1 H, CHO, ^3J = 5.8 Hz); 7.35, 7.46 (both d, 4 H each, Ar, ^3J = 8.8 Hz). ^{13}C NMR (DMSO-d_6), δ: 44.9 (CH_2Cl); 66.9 (CH_2O); 75.0 (CHO); 109.2 (OCO); 127.8, 128.4, 133.3, 140.5, 144.7 (Ar). IR (thin film, ν/cm^{-1}): 1250, 1225, 1170, 1115, 1087 (COCOC); 732 (C—Cl).

4-Chloromethyl-2-(4-chlorophenyl)-2-(2,4-dichlorophenyl)-1,3-dioxolane (2c). The yield was 96% (*B*), b.p. 205—207 °C (0.5 Torr), n_D^{20} = 1.5960. Found (%): C, 50.46; H, 3.34. $C_{16}H_{12}Cl_4O_2$. Calculated (%): C, 50.83; H, 3.20. A mixture of diastereomers A and B. ^{1}H NMR (DMSO-d_6), δ: 3.48 (dd, 0.43 H^B, CH_2Cl, ^3J = 8.0 Hz, ^2J = 8.8 Hz); 3.64 (dd, 0.57 H^A, CH_2Cl, ^3J = 5.8 Hz, ^2J = 8.8 Hz); 3.75—3.80 (m, 1.43 H, CH_2Cl; CH_2O); 4.02 (d, 1 H, CH_2O, ^3J = 8.8 Hz); 4.25 (dd, 0.57 H^A, CH_2O, ^3J = 6.2 Hz, ^2J = 8.8 Hz); 4.45 (q, 0.57 H^A, CHO, ^3J = 5.6 Hz); 4.55 (q, 0.43 H^B, CHO, ^3J = 5.6 Hz); 7.32—7.46 (m, 4 H, Ar); 7.51—7.69 (m, 2 H, Ar); 7.75 (d, 0.57 H^A, Ar, ^4J = 4.2 Hz); 7.81 (d, 0.43 H^B, Ar, ^4J = 4.2 Hz). ^{13}C NMR (DMSO-d_6), δ: 45.1 (CH_2Cl); 67.1 (CH_2O); 75.2 (CHO); 109.1 (OCO); 127.0, 128.0, 128.8, 129.9, 130.5, 130.7, 132.5, 132.7, 133.1, 133.3, 134.2, 134.3, 137.4, 138.4, 139.2 (Ar). IR (thin film, ν/cm^{-1}): 1248, 1225, 1175, 1117, 1085 (COCOC); 736 (C—Cl).

2-(4-Bromophenyl)-4-chloromethyl-2-(4-chlorophenyl)-1,3-dioxolane (2d). The yield was 93% (*B*), b.p. 183—185 °C (0.5 Torr), n_D^{20} = 1.5953. Found (%): C, 49.19; H, 3.47. $C_{16}H_{13}BrCl_2O_2$. Calculated (%): C, 49.52; H, 3.38. ^{1}H NMR (DMSO-d_6), δ: 3.48 (dd, 1 H, CH_2Cl, ^3J = 8.1 Hz, ^2J = 11.0 Hz); 3.66 (dd, 1 H, CH_2Cl, ^3J = 4.4 Hz, ^2J = 11.0 Hz); 4.02 (dd, 1 H, CH_2O, ^3J = 5.2 Hz, ^2J = 7.4 Hz); 4.11 (dd, 1 H, CH_2O, ^3J = 7.0 Hz, ^2J = 7.4 Hz); 4.43 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.25—7.53 (m, 8 H, Ar). ^{13}C NMR (DMSO-d_6), δ: 45.1 (CH_2Cl); 67.1 (CH_2O); 75.1 (CHO); 109.0 (OCO); 121.8, 127.9, 128.0, 128.3, 128.5, 131.2, 131.4, 133.1, 140.5, 140.9 (Ar). IR (thin film, ν/cm^{-1}): 1245, 1225, 1175, 1115, 1085 (COCOC); 736 (C—Cl); 625 (C—Br).

2,2-Bis(4-bromophenyl)-4-chloromethyl-1,3-dioxolane (2e). The yield was 95% (*B*), b.p. 194—196 °C (0.5 Torr), n_D^{20} = 1.6022. Found (%): C, 44.11; H, 3.21. $C_{16}H_{13}Br_2ClO_2$. Calculated (%): C, 44.43; H, 3.03. ^{1}H NMR (DMSO-d_6), δ: 3.46 (dd, 1 H, CH_2Cl, ^3J = 8.1 Hz, ^2J = 11.0 Hz); 3.64 (dd, 1 H, CH_2Cl, ^3J = 4.4 Hz, ^2J = 11.0 Hz); 4.04 (dd, 1 H, CH_2O, ^3J = 5.2 Hz, ^2J = 7.4 Hz); 4.12 (dd, 1 H, CH_2O, ^3J = 7.0 Hz, ^2J = 7.4 Hz); 4.45 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.34, 7.48 (both d, 4 H each, Ar, ^3J = 8.6 Hz). ^{13}C NMR (DMSO-d_6), δ: 44.9 (CH_2Cl); 66.9 (CH_2O); 75.0 (CHO); 109.1 (OCO); 121.3, 125.4, 127.7, 127.9, 139.8, 130.0, 140.5, 141.0 (Ar). IR (thin film, ν/cm^{-1}): 1245, 1225, 1175, 1115, 1085 (COCOC); 736 (C—Cl); 635 (C—Br).

1-[(2,2-Diaryl-1,3-dioxolan-4-yl)methyl]-1*H*-azoles 3a—e and 4a—e (general procedure). A mixture of a chloromethyldioxolane **2** (0.03 mol) and a sodium salt of 1,2,4-triazole or imidazole (0.03 mol) was refluxed in DMF (50 mL) for 16—20 h, filtered, and evaporated. The residue was chromatographed on silica gel in acetone—hexane with a concentration gradient of acetone from 10 to 40%. Noncrystallized products were dissolved in acetone (20 mL) and treated with an equimolar amount of oxalic acid dissolved in acetone (20 mL). The resulting crystals of oxalates of azoles **3a—c** and **4a—e** were filtered off, washed with acetone (10 mL) and hexane (50 mL), and dried in air.

1-{[2-(4-*tert*-Butylphenyl)-2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-1,2,4-triazole (3a), oxalate. The yield was 59%, m.p. 162—163 °C. Found (%): C, 59.31; H, 5.58; N, 8.40. $C_{22}H_{24}ClN_3O_2 \cdot H_2C_2O_4$. Calculated (%): C, 59.08; H, 5.37; N, 8.61. ^{1}H NMR (DMSO-d_6), δ: 1.29 (s, 9 H, C$\underline{Me}_3$); 3.94—4.18 (m, 2 H, CH_2O); 4.35 (d, 2 H, CH_2N, ^3J = 5.9 Hz); 4.59 (q, 1 H, CHO, ^3J = 5.8 Hz); 7.25—7.47 (m, 8 H, Ar); 7.97

(s, 1 H, H(3) triaz.); 8.09 (s, 1 H, H(5) triaz.). ^{13}C NMR (DMSO-d_6), δ: 30.8 (CMe_3); 34.2 ($\underline{C}Me_3$); 50.7, 50.8 (CH_2N); 66.9 (CH_2O); 74.4, 74.5 (CHO); 109.1 (OCO); 124.9, 125.0, 125.3, 125.5, 127.6, 127.7, 128.0, 128.2, 131.3, 132.8, 138.5, 138.6, 141.1 (arom.); 144.7 (C(3) triaz.); 150.7 (Ar); 151.4 (C(5) triaz.); 160.9 (oxalate). IR (Nujol, ν/cm^{-1}): 1247, 1220, 1172, 1115, 1087 (COCOC); 720 (C—Cl).

1-{[2,2-Bis(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-1,2,4-triazole (3b), oxalate. The yield was 74%, m.p. 173—174 °C. Found (%): C, 51.84; H, 3.77; N, 9.17. $C_{18}H_{15}Cl_2N_3O_2 \cdot H_2C_2O_4$. Calculated (%): C, 51.52; H, 3.67; N, 9.01. ^{1}H NMR (DMSO-d_6), δ: 3.97 (dd, 1 H, CH_2O, ^3J = 5.5 Hz, ^2J = 8.8 Hz); 4.05 (dd, 1 H, CH_2O, ^3J = 6.8 Hz, ^2J = 8.8 Hz); 4.38 (dd, 1 H, CH_2N, ^3J = 6.6 Hz, ^2J = 13.9 Hz); 4.44 (dd, 1 H, CH_2N, ^3J = 5.2 Hz, ^2J = 13.9 Hz); 4.54 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.35, 7.42 (both d, 4 H each, Ar, ^3J = 8.8 Hz); 7.98 (s, 1 H, H(3) triaz.); 8.45 (s, 1 H, H(5) triaz.). ^{13}C NMR (DMSO-d_6), δ: 50.7 (CH_2N); 67.0 (CH_2O); 74.7 (CHO); 108.6 (OCO); 127.6, 128.2, 133.1, 140.4, 144.7 (Ar); 144.7 (C(3) triaz.); 151.4 (C(5) triaz.); 160.9 (oxalate). IR (Nujol, ν/cm^{-1}): 1245, 1215, 1175, 1115, 1085 (COCOC); 725 (C—Cl).

1-{[2-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-1,2,4-triazole (3c), oxalate. The yield was 65%, m.p. 193—195 °C. Found (%): C, 48.16; H, 3.36; N, 8.18. $C_{18}H_{14}Cl_3N_3O_2 \cdot H_2C_2O_4$. Calculated (%): C, 47.97; H, 3.22; N, 8.39. A mixture of diastereomers A and B. ^{1}H NMR (DMSO-d_6), δ: 3.87 (dd, 0.18 H^B, CH_2O, ^3J = 5.6 Hz, ^2J = 8.8 Hz); 4.02 (dd, 0.82 H^A, CH_2O, ^3J = 5.6 Hz, ^2J = 8.8 Hz); 4.08 (dd, 0.82 H^A, CH_2O, ^3J = 6.8 Hz, ^2J = 8.8 Hz); 4.24 (dd, 0.18 H^B, CH_2O, ^3J = 6.8 Hz, ^2J = 8.8 Hz); 4.33 (dd, 0.18 H^B, CH_2N, ^3J = 6.6 Hz, ^2J = 14.0 Hz); 4.42—4.58 (m, 2.64 H, CH_2N + CHO); 4.54 (q, 0.18 H^B, CHO, ^3J = 5.6 Hz); 7.24, 7.47 (both d, 2 H each, Ar, ^3J = 8.0 Hz); 7.53 (d, 2 H, Ar, ^3J = 8.2 Hz); 7.79 (s, 1 H, Ar); 7.98 (s, 1 H, H(3) triaz.); 8.45 (s, 1 H, H(5) triaz.). ^{13}C NMR (DMSO-d_6), δ: 50.1, 50.6 (CH_2N); 67.0 (CH_2O); 74.6, 75.2 (CHO); 108.3 (COC); 127.0, 128.0, 128.9, 129.7, 130.5, 130.7, 132.8, 133.3, 134.3, 136.7, 138.6 (Ar); 144.7 (C(3) triaz.); 151.5 (C(5) triaz.); 161.0 (oxalate). IR (Nujol, ν/cm^{-1}): 1247, 1220, 1172, 1115, 1087 (COCOC); 727 (C—Cl).

1-{[2-(4-Bromophenyl)-2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-1,2,4-triazole (3d). The yield was 72%, m.p. 128—129 °C. Found (%): C, 51.52; H, 3.74; N, 9.83. $C_{18}H_{15}BrClN_3O_2$. Calculated (%): C, 51.39; H, 3.59; N, 9.99. ^{1}H NMR (DMSO-d_6), δ: 4.04 (dd, 1 H, CH_2O, ^3J = 5.2 Hz, ^2J = 8.8 Hz); 4.09 (dd, 1 H, CH_2O, ^3J = 6.6 Hz, ^2J = 8.8 Hz); 4.33 (d, 2 H, CH_2N, ^3J = 5.2 Hz); 4.58 (q, 1 H, CHO, ^3J = 5.2 Hz); 7.23—7.42 (m, 6 H, Ar); 7.47 (d, 2 H, Ar, J = 8.8 Hz); 7.94 (s, 1 H, H(3) triaz.); 8.01 (s, 1 H, H(5) triaz.). ^{13}C NMR (DMSO-d_6), δ: 50.6 (CH_2N); 66.9 (CH_2O); 74.6 (CHO); 108.6 (OCO); 121.7, 127.6, 127.9, 128.2, 128.4, 131.1, 131.3, 133.0, 140.4, 140.8 (Ar); 144.7 (C(3) triaz.); 151.4 (C(5) triaz.). IR (Nujol, ν/cm^{-1}): 1245, 1215, 1177, 1115, 1080 (COCOC); 715 (C—Cl); 625 (C—Br).

1-{[2,2-Bis(4-bromophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-1,2,4-triazole (3e). The yield was 67%, m.p. 116—117 °C. Found (%): C, 46.73; H, 3.33; N, 9.19. $C_{18}H_{15}Br_2N_3O_2$. Calculated (%): C, 46.48; H, 3.25; N, 9.03. ^{1}H NMR (DMSO-d_6), δ: 3.93—4.16 (m, 2 H, CH_2O); 4.33 (d, 2 H, CH_2N, ^3J = 5.4 Hz); 4.59 (q, 1 H, CHO, ^3J = 5.4 Hz); 7.31 (d, 4 H, Ar, ^3J = 8.3 Hz); 7.47 (d, 4 H, Ar, ^3J = 8.8 Hz); 7.95 (s, 1 H, H(3) triaz.); 8.02 (s, 1 H, H(5) triaz.). ^{13}C NMR (DMSO-d_6), δ: 50.6 (CH_2N); 66.9 (CH_2O); 74.5 (CHO); 108.6, 109.0 (OCO); 121.4, 125.6, 127.9, 128.1, 131.0, 131.2, 140.7, 141.2 (Ar); 144.7 (C(3) triaz.), 151.4 (C(5) triaz.). IR (Nujol, ν/cm^{-1}): 1247, 1212, 1177, 1117, 1087 (COCOC); 625 (C—Br).

1-{[2-(4-*tert*-Butylphenyl)-2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-imidazole (4a), oxalate. The yield was 63%, m.p. 177—178 °C. Found (%): C, 61.97; H, 5.69; N, 5.44. $C_{23}H_{25}ClN_2O_2 \cdot H_2C_2O_4$. Calculated (%): C, 61.66; H, 5.59; N, 5.75. ^{1}H NMR (DMSO-d_6), δ: 1.28 (s, 9 H, $C\underline{Me}_3$); 3.87 (dd, 1 H, CH_2O, ^3J = 5.6 Hz, ^2J = 8.6 Hz); 4.02 (dd, 1 H, CH_2O, ^3J = 7.2 Hz, ^2J = 8.6 Hz); 4.18 (dd, 1 H, CH_2N, ^3J = 7.0 Hz, ^2J = 14.0 Hz); 4.35 (dd, 1 H, CH_2N, ^3J = 3.5 Hz, ^2J = 14.0 Hz); 4.48 (q, 1 H, CHO, ^3J = 5.8 Hz); 7.12 (s, 1 H, H(5) imidaz.); 7.28—7.45 (m, 9 H, Ar + H(4) imidaz.); 8.17 (s, 1 H, H(2) imidaz.). ^{13}C NMR (DMSO-d_6), δ: 31.0 ($C\underline{Me}_3$); 34.2 ($\underline{C}Me_3$); 49.5 (CH_2N); 66.6 (CH_2O); 74.9 (CHO); 109.2 (OCO); 121.5, 121.9 (C(5) imidaz.); 123.3 (C(4) imidaz.); 124.9, 125.2, 125.4, 125.6, 127.5, 127.6, 127.7, 128.1, 128.3, 132.8 (Ar); 136.7 (C(2) imidaz.); 138.5, 141.0, 150.7 (Ar); 163.4 (oxalate). IR (Nujol, ν/cm^{-1}): 1247, 1220, 1172, 1115, 1087 (COCOC); 720 (C—Cl).

1-{[2,2-Bis(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-imidazole (4b), oxalate. The yield was 42%, m.p. 192—193 °C. Found (%): C, 54.54; H, 3.81; N, 6.11. $C_{19}H_{16}Cl_2N_2O_2 \cdot H_2C_2O_4$. Calculated (%): C, 54.21; H, 3.90; N, 6.02. ^{1}H NMR ($CDCl_3$), δ: 3.87 (dd, 2 H, CH_2O, ^3J = 5.4 Hz, ^2J = 8.8 Hz); 4.05 (dd, 1 H, CH_2N, ^3J = 6.8 Hz, ^2J = 13.2 Hz); 4.14 (dd, 1 H, CH_2N, ^3J = 4.8 Hz, ^2J = 13.2 Hz); 4.47 (q, 1 H, CHO, ^3J = 5.4 Hz); 6.97 (s, 1 H, H(5) imidaz.); 7.29 (s, 1 H, H(4) imidaz.); 7.34, 7.41 (both d, 4 H each, Ar, ^3J = 8.8 Hz); 7.67 (s, 1 H, H(2) imidaz.). ^{13}C NMR (DMSO-d_6), δ: 49.3 (CH_2N); 66.6 (CH_2O); 75.0 (CHO); 108.8 (OCO); 121.5 (C(5) imidaz.); 123.3 (C(4) imidaz.);127.5, 128.1, 133.0 (Ar); 136.7 (C(2) imidaz.); 140.3, 144.6 (Ar); 163.4 (oxalate). IR (Nujol, ν/cm^{-1}): 1247, 1220, 1170, 1115, 1085 (COCOC); 720 (C—Cl).

1-{[2-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-imidazole (4c), oxalate. The yield was 66%, m.p. 179—181 °C. Found (%): C, 50.76; H, 3.54; N, 5.77. $C_{19}H_{15}Cl_3N_2O_2 \cdot H_2C_2O_4$. Calculated (%): C, 50.47; H, 3.43; N, 5.61. A mixture of diastereomers A and B. ^{1}H NMR (DMSO-d_6), δ: 3.82 (dd, 0.21 H^B, CH_2O, ^3J = 5.8 Hz, ^2J = 8.6 Hz); 4.01 (d, 0.79 H, CH_2O, ^3J = 5.4 Hz); 4.12—4.32 (m, 0.21 H^B + 0.79 H^A, CH_2O); 4.40 (dd, 1 H, CH_2N, ^3J = 6.2 Hz, ^2J = 14.1 Hz); 4.43—4.50 (m, 1.79 H, CH_2N + CHO); 4.54 (q, 0.21 H^B, CHO, ^3J = 5.4 Hz); 7.07 (s, 0.21 H^B, H(5) imidaz.); 7.12 (s, 0.79 H^A, H(5) imidaz.); 7.26—7.43 (m, 4 H, Ar); 7.51 (d, 2 H, Ar, ^3J = 8.6 Hz); 7.77 (s, 1 H, Ar); 7.82 (s, 0.79 H^A, H(4) imidaz.); 7.87 (s, 0.21 H^B, H(4) imidaz.); 8.42 (s, 0.21 H^B, H(2) imidaz.); 8.45 (s, 0.79 H^A, H(2) imidaz.). ^{13}C NMR (DMSO-d_6), δ: 48.9, 49.3 (CH_2N); 66.7 (CH_2O); 74.9, 75.7 (CHO); 108.3, 108.5 (OCO); 121.4, 121.6 (C(5) imidaz.); 123.2 (C(4) imidaz.); 127.0, 128.0, 128.8, 129.9, 130.5, 130.7, 132.5, 132.7, 133.1, 133.3, 134.2, 134.3 (Ar); 136.6, 136.7 (C(2) imidaz.); 137.4, 138.4, 139.2 (Ar); 163.4 (oxalate). IR (Nujol, ν/cm^{-1}): 1247, 1220, 1172, 1115, 1087 (COCOC); 727 (C—Cl).

1-{[2-(4-Bromophenyl)-2-(4-chlorophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-imidazole (4d), oxalate. The yield was 60%, m.p. 221—222 °C. Found (%): C, 49.79; H, 3.63; N, 5.38. $C_{19}H_{16}BrClN_2O_2 \cdot H_2C_2O_4$. Calculated (%): C, 49.48; H, 3.56; N, 5.50. ^{1}H NMR (DMSO-d_6), δ: 3.89 (dd, 1 H, CH_2O, ^3J = 5.9 Hz, ^2J = 8.8 Hz); 4.04 (dd, 1 H, CH_2O, ^3J = 7.4 Hz,

^2J = 8.8 Hz); 4.20 (dd, 1 H, CH_2N, ^3J = 6.6 Hz, ^2J = 14.0 Hz); 4.37 (dd, 1 H, CH_2N, ^3J = 3.7 Hz, ^2J = 14.0 Hz); 4.51 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.17 (s, 1 H, H(5) imidaz.); 7.28—7.47 (m, 7 H, Ar + H(4) imidaz.); 7.56 (d, 2 H, Ar, ^3J = 8.1 Hz); 8.17 (s, 1 H, H(2) imidaz.). ^{13}C NMR (DMSO-d_6), δ: 49.4 (CH_2N); 66.7 (CH_2O); 75.1 (CHO); 108.8 (OCO); 119.6 (Ar); 121.5, 121.8 (C(5) imidaz.); 123.3 (C(4) imidaz.); 127.5, 127.6, 127.8, 128.0, 128.2, 128.5, 131.2, 131.4 (Ar); 136.7 (C(2) imidaz.); 140.2, 140.7 (Ar); 163.5 (oxalate). IR (Nujol, ν/cm^{-1}): 1245, 1215, 1175, 1115, 1085 (COCOC); 720 (C—Cl); 630 (C—Br).

1-{[2,2-Bis(4-bromophenyl)-1,3-dioxolan-4-yl]methyl}-1*H*-imidazole (4e), oxalate. The yield was 59%, m.p. 210—212 °C. Found (%): C, 45.82; H, 3.31; N, 5.20. $C_{19}H_{16}Br_2N_2O_2\,H_2C_2O_4$. Calculated (%): C, 45.51; H, 3.27; N, 5.05. ^{1}H NMR (DMSO-d_6), δ: 3.87 (dd, 1 H, CH_2O, ^3J = 5.9 Hz, ^2J = 8.8 Hz); 4.04 (dd, 1 H, CH_2O, ^3J = 6.6 Hz, ^2J = 8.8 Hz); 4.18 (dd, 1 H, CH_2N, ^3J = 6.6 Hz, ^2J = 13.9 Hz); 4.35 (dd, 1 H, CH_2N, ^3J = 3.7 Hz, ^2J = 13.9 Hz); 4.48 (q, 1 H, CHO, ^3J = 5.9 Hz); 7.12 (s, 1 H, H(5) imidaz.); 7.25—7.41 (m, 5 H, Ar + H(4) imidaz.); 7.48 (d, 4 H, Ar, ^3J = 8.8 Hz); 8.05 (s, 1 H, H(2) imidaz.). ^{13}C NMR (DMSO-d_6), δ: 49.3 (CH_2N); 66.6 (CH_2O); 74.9 (CHO); 108.8, 109.2 (OCO); 121.4, 121.7 (C(5) imidaz.); 123.4 (Ar); 125.5 (C(4) imidaz.); 127.8, 128.1, 131.0, 131.2, (Ar); 136.7 (C(2) imidaz.); 140.7, 141.2 (Ar), 163 (oxalate). IR (Nujol, ν/cm^{-1}): 1245, 1210, 1175, 1115, 1085 (COCOC); 625 (C—Br).

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