

Synthesis and Biological Activities of Novel Triazole Compounds Containing 1,3-Dioxolane Rings

Liang-Zhong Xu, Shu-Sheng Zhang*, Shu-Yan Niu, Yong-Qi Qin, Xue-Mei Li and Kui Jiao

College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R. China

* Author to whom correspondence should be addressed; E-mail: zhangshush@public.qd.sd.cn; Tel: (+86)-532-4022750; Fax: (+86)-532-4023927

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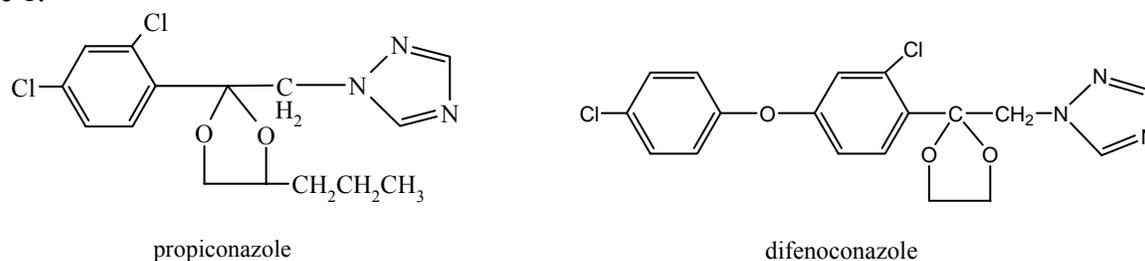
Abstract: Thirteen new triazoles containing 1,3-dioxolane rings were synthesized and their identities confirmed by means of IR, NMR, MS, elemental analysis and X-ray crystallography. The results of preliminary biological tests show that all of these compounds possess some fungicidal and plant growth regulant activities.

Keywords: 1,2,4-Triazole; 1,3-Dioxolane; Biological activities; Fungicide; Plant growth regulant.

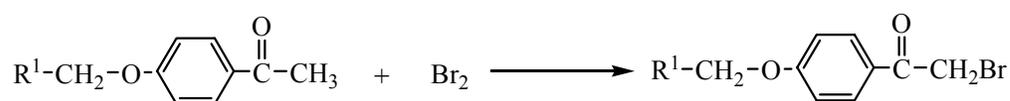
Introduction

Many triazole compounds have good fungicidal and plant growth regulating activities [1-5]. In particular, triazole compounds containing 1,3-dioxolanes have been shown to have remarkable preventative and control activities for a variety of plant diseases [6]. Propiconazole and difenoconazole are two important representatives of this class, especially the latter, which has been used as the most efficient triazole fungicide in the control of some common plant diseases. The key intermediates for its synthesis, however, are not easily obtained, which makes the costs of production and application too high. Following the concept of bioisosterism [7-8], we have now synthesized ten novel 1,2,4-triazole compounds containing 1,3-dioxolane rings, **3a~3j**, using difenoconazole as the lead compound. In addition, according to empirical data [9], the presence of an exposed triazole ring is conducive to

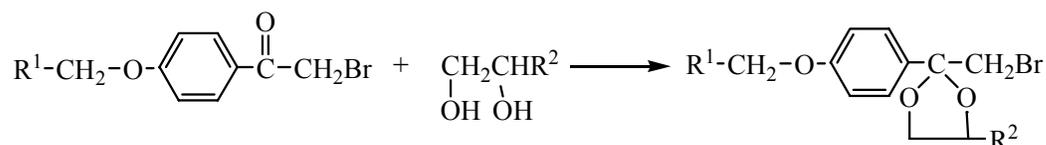
improvements of the biological activity. To explore this idea three new compounds **5a~5c** containing 1,2,4-triazole-substituted 1,3-dioxolanes were also synthesized. The synthetic routes used are shown in Scheme 1.



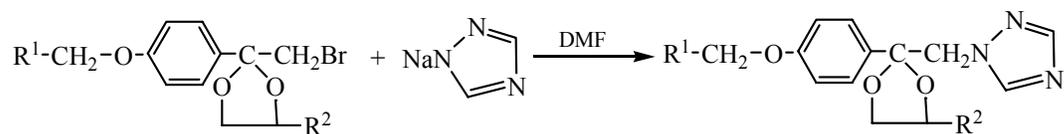
Scheme 1



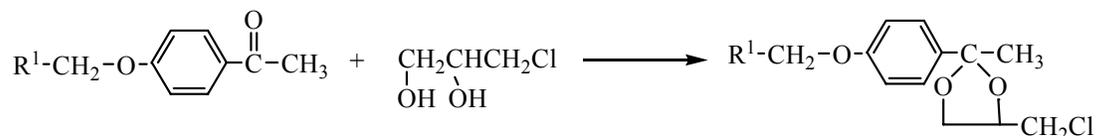
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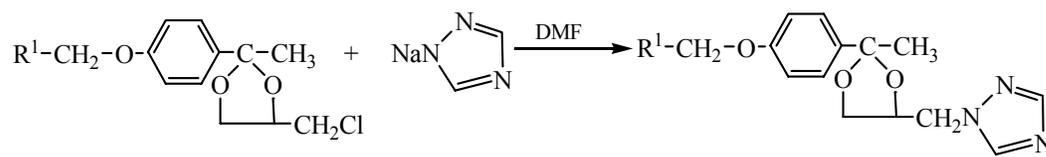
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3



4



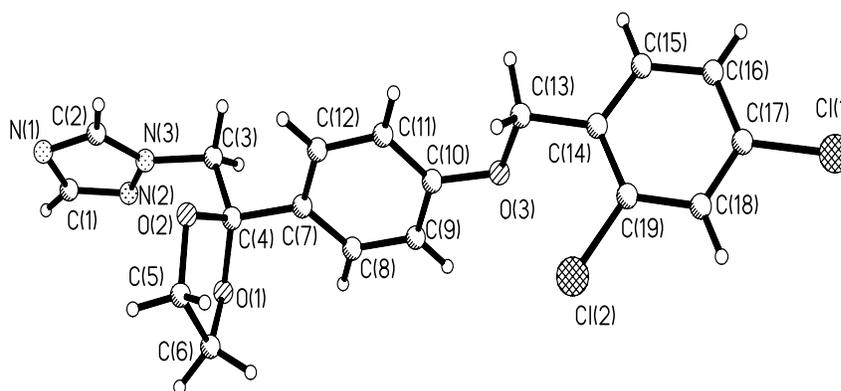
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Results and Discussion

Characterization of the target compounds

Compounds **3a~3j** and **5a~5c** were identified by their CHN analysis, IR, $^1\text{H-NMR}$, EA and MS fragmentation pattern data. The measured values in the elemental analyses were consistent with the corresponding calculated ones. The IR spectra display medium or weak absorption bands for the benzene and triazole rings at around 3100 cm^{-1} ($\nu_{\text{C-H}}$), while the two C-O-C ether bonds give relatively strong absorption bands at around 1170 cm^{-1} and 1140 cm^{-1} . The absorption for the $\text{PhCH}_2\text{-O-Ph}$ ether bond appears at around 1240 cm^{-1} . In the $^1\text{H-NMR}$ spectra of compounds **5a~5c** the signals of the two protons of the CH_2 group connecting the triazoles with the 1,3-dioxolane appear as a multiplet at around 3.8 ppm. It is believed that this is due to the fact they are attached to an asymmetrical carbon atom, which makes the magnetic environments of the two CH_2 group protons different. When R^2 is CH_3 , the protons of the CH_3 group and triazole ring are all split into two sets of peaks. The molecular ion peaks of the title compounds examined by mass spectrometry are very weak, but all of the key fragment ion peaks appear. Additional proof for the proposed structures was provided by single crystal X-ray diffraction of a representative compound (Figure 1) [10].

Figure 1. Molecular structure of compound **3g** with the atomic numbering scheme.



Biological evaluation

The antifungal activities of the synthesized compounds against *Gibberella zeae*, *Alternaria solani*, *Phoma asparagi*, *Physalospora pircola* and *Cercospora arachidicola* were determined by the “contained poison in the medium” method [11]. Plant-growth regulatory activities of the target compounds on wheat coleoptile elongation, cucumber cotyledon rooting, rape hypocotyls inhibition and growth of cucumber cotyledon were tested by the methods mentioned in the literature [12~15].

The data in Table 1 show that most of the target compounds have some fungicidal activity. Overall they exhibit better efficiency against *P. Pircolae*, particularly **3a**, **3i** and **3j**, with inhibition rates at 50mg/L reaching 77.8%, 84.1% and 84.1%, respectively. As far as the relationships between structure and the activity are concerned, when the R¹ group is 2-chlorophenyl, the compounds have more comprehensive fungus-inhibiting properties. All thirteen target compounds have plant-growth regulatory activity. They show inhibiting activity towards wheat coleoptile elongation, with rates ranging from 3.1%~22.5%. Most of them have promoting effects towards rooting of cucumber cotyledon, with promoting rates reaching 3.1%~69.3%. All the compounds displayed much less promoting activity towards growth of cucumber cotyledon. The highest promoting rate was 9.4%.

Table 1. The fungicidal and plant growth regulatory activities of compounds **3** and **5**

Compound No.	Fungicidal activities (50mg/L, inhibition %)					Plant-growth regulatory activities (%) at 10mg/L			
	<i>Gibberella zeae</i>	<i>Alternaria solani</i>	<i>Phomaas paragi</i>	<i>Physalospora pircola</i>	<i>Cercosporaa rachidicola</i>	Wheat coleoptile elongation	Cucumber Cotyledon rooting	Rape hypocotyls inhibition	Cucumber cotyledon growth
3a	50.0	71.0	90.9	77.8	43.8	-22.5	61.2	-29.7	-6.3
3b	40.0	67.7	88.9	71.4	43.8	-20.2	53.2	-24.9	0
3c	5.0	25.8	11.8	28.9	28.6	-5.4	2.1	-19.7	3.1
3d	25.0	38.7	41.2	57.8	28.6	-3.1	-8.6	-16.3	-1.6
3e	20.0	41.9	17.6	40.0	14.3	-13.2	69.3	-24.5	1.6
3f	26.9	0	0	44.6	22.2	-7.4	-39.7	-24.9	3.1
3g	7.7	19.0	7.7	24.6	0	-6.2	50.5	-7.1	-1.6
3h	23.1	0	0	35.4	0	-5.4	37.0	-2.8	-1.6
3i	50.0	80.6	87.8	84.1	59.1	-10.9	66.6	-20.2	4.7
3j	45.0	64.5	87.8	84.1	92.0	-13.2	53.2	-38.8	3.1
5a	0	0	0	35.4	0	-3.9	31.7	-19.3	6.3
5b	42.3	38.7	30.8	73.0	33.3	-3.9	31.7	-10.2	7.8
5c	7.7	0	0	30.8	0	-10.1	69.3	-8.9	9.4
Ref.	99.0	100	100	99.9	100	-7.6	62.6	-12.8	8.6

Ref. = difenconazole

Conclusions

Thirteen novel triazole analogs of difenoconazole containing 1,3-dioxolane rings have been synthesized. Their structures have been verified by $^1\text{H-NMR}$, IR, MS and x-ray diffraction data and elemental analysis. Some of them display levels of plant-growth regulatory activity similar to those of a difenoconazole standard, but compared to the commercial agent their antifungal activities were not encouraging. It is possible that the existence of the methylene on the phenyl group destroys the conjugated system of the molecule, thus causing the lower fungicidal activities observed.

Acknowledgements

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Experimental

General

IR spectra (KBr disks) were recorded on a Shimadzu-IR-435 Spectrophotometer. $^1\text{H-NMR}$ spectra were recorded with a JEOL-ECP600 NMR Spectrometer (CDCl_3 as solvent, TMS as internal standard). Mass spectra were taken on a HP-5988A Spectrometer. Elemental analyses were determined on a Yanaco-CHNCORDER MT-3 automatic elemental analyzer. All agents were analytical grade and were used without further purification.

Preparation of intermediates 1.

The intermediates **1** were prepared according to a literature procedure [16]. The substituted acetophenones were reacted with bromine in anhydrous ether in the presence of 1,4-dioxane. Five intermediates **1** were prepared in this manner: $\text{R}^1 = \text{C}_6\text{H}_5$, 83.1%, 88~90°C; $\text{Me}_3\text{CC}_6\text{H}_4$, 83.7%, 74~76°C; 4- ClC_6H_4 , 81.5%; 104~106°C; 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$, 75.3%, 91~93°C; 2- ClC_6H_4 , 76.7%, 83~84°C.

Preparation of intermediates 2 and 4.

The intermediates **2a~2j** and **4a~4c** are prepared according to the literature method [17]. Their melting point data is listed in Table 2.

Table 2. The melting points and yields of intermediates **2** and **4**

Intermediate No.	R ¹	R ²	mp / °C
2a	Ph	H	110~112
2b	Ph	CH ₃	76~78
2c	<i>t</i> -Bu-Ph	H	79~81
2d	<i>t</i> -Bu-Ph	CH ₃	96~98
2e	<i>p</i> -Cl-Ph	H	106~108
2f	<i>p</i> -Cl-Ph	CH ₃	88~90
2g	2,4-Cl ₂ -Ph	H	92~94
2h	2,4-Cl ₂ -Ph	CH ₃	83~85
2i	<i>o</i> -Cl-Ph	H	141~143
2j	<i>o</i> -Cl-Ph	CH ₃	67~69
4a	<i>p</i> -Cl-Ph	—	77~79
4b	2,4-Cl ₂ -Ph	—	89~91
4c	<i>o</i> -Cl-Ph	—	97~99

General procedure for the synthesis of compounds **3a~3j** and **5a~5c** (with the preparation of **3a** given as an example).

DMF (25 g) and 1H-1,2,4-triazole (15 mmol) were placed in a 100 mL flask. After the latter was completely dissolved through stirring, sodium methoxide in methanol (15 mmol, prepared with 15 mmol sodium and 10 mL anhydrous methanol) was added dropwise. The mixture was maintained at room temperature (18°C) for 0.5 h and the methanol was then distilled off till the temperature of the mixture rose to 140°C. After the mixture was cooled below 60 °C, intermediate **2a** (15 mmol) and dry KI (0.1 g) were added. The mixture was stirred under reflux for 3 h, and then it was poured into water (50 mL) under vigorous stirring to give 4.3 g of crude precipitate that was collected by filtration and further purified by column chromatography (silica gel, using 3:1 v/v ethyl acetate-cyclohexane as the eluent) to afford 3.16 g (62.5%) of the target product *1-((2-(4-(benzyloxy)phenyl)-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole (3a)*, as white crystals with mp 105~107°C; IR cm⁻¹: 1174, 1136 (C-O-C), 1249 (CH₂-O-Ph); ¹H-NMR δ: 8.12 (s, 1H, Tr-H), 7.90 (s, 1H, Tr-H), 6.89~7.43 (m, 9H, J=8.4Hz, Ar-H), 5.05 (s, 2H, PhCH₂-O), 4.47 (s, 2H, CH₂Tr), 3.76 (m, 4H, O-CH₂-CH₂-O); Anal. Calc. for C₁₉H₁₉N₃O₃ (337.38) C 67.64, H 5.68, N 12.45; Found: C 67.60, H 5.77, N 12.70. The thirteen title compounds, which include the ten compounds **3a~3j** and the three compounds **5a~5c** were synthesized in the same manner.

1-((2-(4-(benzyloxy)phenyl)-4-methyl-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3b): Yield 58.7%; mp 111~113°C; IR cm^{-1} : 1171, 1136 (C-O-C), 1239 (CH₂-O-Ph); ¹H-NMR δ : 9.16 (s, 1H, Tr-H), 8.90 (s, 1H, Tr-H), 7.90~8.47 (m, 9H, J=8.7Hz, Ar-H), 6.06 (s, 2H, PhCH₂), 5.43 (d, 2H, CH₂Tr), 4.87~5.06 (m, 1H, O-CH-C-O), 4.22~4.88 (m, 2H, O-CH₂-C-O), 1.00~1.09 (s, 3H, CH₃); Anal. Calc. for C₂₀H₂₁N₃O₃ (351.41) C 68.36, H 6.02, N 11.96; Found: C 68.47, H 5.95, N 12.18.

*1-((2-(4-(4-*t*-butylbenzyloxy) phenyl)-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3c)*: Yield 63.7%; mp 112~114°C; IR cm^{-1} : 1171, 1136 (C-O-C), 1236 (CH₂-O-Ph); ¹H-NMR δ : 8.11 (s, 1H, Tr-H), 7.89 (s, 1H, Tr-H), 6.90~7.44 (m, 8H, J=8.5Hz, Ar-H), 5.01 (s, 2H, PhCH₂-O), 4.48 (s, 2H, CH₂Tr), 3.76~3.78 (m, 4H, O-CH₂-CH₂-O), 1.32 (s, 9H, 3CH₃); MS (EI): m/z 394 [M⁺]; Anal. Calc. for C₂₃H₂₇N₃O₃ (393.49) C 70.21, H 7.18, N 10.31; Found: C 70.53, H 6.85, N 10.82.

*1-((2-(4-(4-*t*-butylbenzyloxy)phenyl)-4-methyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole (3d)*: Yield 62.6%; mp 83~85°C; IR cm^{-1} : 1174, 1173 (C-O-C), 1245 (CH₂-O-Ph); ¹H-NMR δ : 8.12~8.16 (d, 1H, Tr-H), 7.90 (s, 1H, Tr-H), 6.90~7.47 (m, 8H, J=8.6Hz, Ar-H), 5.02 (s, 2H, PhCH₂O), 4.43~4.45 (d, 2H, TrCH₂), 3.87~3.96 (m, 1H, O-CH-C-O), 3.03~3.84 (m, 2H, O-CH₂-C-O), 1.33(s, 9H, 3CH₃), 1.05~1.33 (d, 3H, J=5.6Hz,CH₃); Anal. Calc. for C₂₄H₂₉N₃O₃ (407.22) C 70.72, H 7.18, N 10.32; Found: C 70.68, H 7.10, N 10.18.

1-((2-(4-(4-chlorobenzyloxy)phenyl)-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3e): Yield 66.7%; mp 137~139°C; IR cm^{-1} : 1170, 1133 (C-O-C), 1232 (CH₂-O-Ph); ¹H-NMR δ : 8.12 (s, 1H, Tr-H), 7.91 (s, 1H, Tr-H), 6.93~7.40 (m, 8H, J=8.8Hz,Ar-H), 5.03 (s, 2H, PhCH₂O), 4.48 (s, 2H, TrCH₂), 3.76~3.78 (m, 4H, J=7.0Hz, A₂B₂, O-CH₂-CH₂-O); Anal. Calc. for C₁₉H₁₈ClN₃O₃ (371.1) C 61.44, H 4.89, N 11.32; Found C 61.50, H 4.85, N 11.28.

1-((2-(4-(4-chlorobenzyloxy)phenyl)-4-methyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole (3f): Yield 52.3%; mp 115~117°C; IR cm^{-1} : 1172, 1134 (C-O-C); 1229 (CH₂-O-Ph); ¹H-NMR δ : 8.13~8.18 (d, 1H, Tr-H), 7.91~7.92 (d, 1H, Tr-H), 6.93~7.42 (m, 8H, J=8.6Hz, Ar-H), 5.03 (s, 2H, PhCH₂), 4.20~4.59 (m, 2H, CH₂Tr), 3.82~3.97 (m, 1H, O-CH-C-O), 3.11~3.80 (m, 2H, O-CH₂-C-O), 1.09~1.42 (d, 3H, J=5.8Hz, CH₃); Anal. Calc. for C₂₀H₂₀ClN₃O₃ (385.85) C 62.32, H 5.23, N 10.91; Found C 62.29, H 5.27, N 10.84.

1-((2-(4-(2,4-dichlorobenzyloxy)phenyl)-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole (3g): Yield 62.1%; mp 136~138°C; IR cm^{-1} : 1182, 1144 (C-O-C); 1235 (CH₂-O-Ph); ¹H-NMR δ : 8.13 (s, 1H, Tr-H), 7.91 (s, 1H, Tr-H), 6.95~7.43 (m, 7H, J=8.4Hz, J=6.6Hz, Ar-H), 5.12 (s, 2H, PhCH₂O), 4.49 (s, 2H, TrCH₂), 3.77~3.80 (m, 4H, J=7.0Hz, A₂B₂, O-CH₂-CH₂-O); MS (EI): m/z 406 [M⁺]; Anal. Calc. for C₁₉H₁₇Cl₂N₃O₃ (406.27) C 56.17, H 4.22, N 10.34; Found C 56.21, H 4.28, N 10.24.

1-((2-(4-(2,4-dichlorobenzoyloxy)phenyl)-4-methyl-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3h): Yield 53.6%; mp 110~112°C; IR cm^{-1} : 1176, 1141 (C-O-C), 1233 (CH₂-O-Ph); ¹H-NMR δ : 8.13~8.18 (d, 1H, Tr-H), 7.91~7.92 (d, 1H, Tr-H), 6.95~7.46 (m, 7H, J=8.4Hz, J=6.6Hz, Ar-H), 5.12 (s, 2H, PhCH₂O), 4.43~4.46 (m, 2H, CH₂Tr), 3.82~3.98(m, 1H, O-CH-C-O), 3.11~3.98 (m, 2H, O-CH₂-C-O), 1.09~1.14 (m, 3H, J=5.9 Hz, CH₃); Anal. Calc. for C₂₀H₁₉Cl₂N₃O₃ (420.30) C 57.16, H 4.56, N 10.00; Found C 57.20, H 4.49, N 10.10.

1-((2-(4-(2-chlorobenzoyloxy)phenyl)-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3i): Yield 52.4%; mp 113~115°C; IR cm^{-1} : 1193, 1159 (C-O-C), 1236 (CH₂-O-Ph); ¹H-NMR δ : 8.14 (s, 1H, Tr-H), 7.92 (s, 1H, Tr-H), 6.97~7.42 (m, 8H, J=8.4Hz, J=5.5Hz, Ar-H), 5.17 (s, 2H, PhCH₂O), 4.92 (s, 2H, TrCH₂), 3.75~3.80 (m, 4H, J=7.0Hz, A₂B₂, O-CH₂-CH₂-O); Anal. Calc. for C₁₉H₁₈ClN₃O₃ (371.82) C 61.38, H 4.88, N 11.30; Found C 61.32, H 4.90, N 11.38.

1-((2-(4-(2-chlorobenzoyloxy)phenyl)-4-methyl-1,3-dioxolan-2-yl) methyl)-1H-1,2,4-triazole (3j): Yield 35.8%; mp 108~110°C; IR cm^{-1} : 1176, 1138 (C-O-C), 1235 (CH₂-O-Ph); ¹H-NMR δ : 8.14~8.19 (s, 1H, Tr-H), 7.91 (s, 1H, Tr-H), 6.98~7.44 (m, 8H, J=8.4Hz, J=6.2Hz, Ar-H), 5.17 (s, 2H, PhCH₂O), 4.43~4.47 (m, 2H, CH₂Tr), 3.09~4.07 (m, 2H, O-CH₂-C-O), 3.98~4.07 (m, 1H, O-CH-C-O), 1.08~1.14 (d, 3H, J=6.2Hz, CH₃); MS (EI) 386 [M⁺], 388 [M+2]; Anal Calc. for C₂₀H₂₀ClN₃O₃ (385.85) C 62.26, H 5.22, N 10.89; Found C 62.29, H 5.27, N 10.84.

1-((2-(4-(4-chlorobenzoyloxy)phenyl)-2-methyl-1,3-dioxolan-4-yl) methyl)-1H-1,2,4-triazole (5a): Yield 45.7%; mp 132~134°C; IR cm^{-1} : 1176, 1136 (C-O-C), 1242 (CH₂-O-Ph); ¹H-NMR δ : 8.24 (s, 1H, Tr-H), 7.96 (s, 1H, Tr-H), 6.89~7.35 (m, 8H, J=8.7Hz, Ar-H), 5.02 (s, 2H, PhCH₂O), 4.35~4.37 (m, 2H, CH₂Tr), 3.81~4.31 (m, 3H, J=8.8Hz, -CH₂CH-), 1.61 (s, 3H, CH₃); MS (EI) 386 [M⁺], 388 [M+2]; Anal Calc. for C₂₀H₂₀ClN₃O₃ (385.85) C 62.26, H 5.22, N 10.89; Found C 62.20, H 5.18, N 10.92.

1-((2-(4-(2,4-dichlorobenzoyloxy)phenyl)-2-methyl-1,3-dioxolan-4-yl) methyl)-1H-1,2,4-triazole (5b): Yield 53.8%; mp 109~111°C; IR cm^{-1} : 1174, 1140 (C-O-C), 1230 (CH₂-O-Ph); ¹H-NMR δ : 8.24 (s, 1H, Tr-H), 7.91 (s, 1H, Tr-H), 6.90~7.42 (m, 7H, J=8.6Hz, Ar-H), 5.10 (s, 2H, PhCH₂O), 4.35~4.63 (m, 2H, CH₂Tr), 3.81~4.37 (m, 3H, -CH₂CH-), 1.60 (s, 3H, CH₃); Anal Calc. for C₂₀H₁₉Cl₂N₃O₃ (420.30) C 57.16, H 4.56, N 10.00; Found C 57.19, H 4.50, N 10.12.

1-((2-(4-(2-chlorobenzoyloxy) phenyl)-2-methyl-1, 3-dioxolan-4-yl) methyl)-1H-1, 2,4-triazole (5c): Yield 25.3%; mp 130~132°C; IR cm^{-1} : 1176, 1138 (C-O-C), 1235 (CH₂-O-Ph); ¹H NMR δ : 8.24 (s, 1H, Tr-H), 7.96 (s, 1H, Tr-H), 6.93~7.39 (m, 8H, J=8.8Hz, Ar-H), 5.15 (s, 2H, PhCH₂O), 4.35~4.38 (m, 2H, CH₂Tr), 3.82~3.88 (m, 3H, -CH₂CH-), 1.60 (s, 3H, CH₃); Anal. Calc. for C₂₀H₂₀ClN₃O₃ (385.85) C 62.32, H 5.23, N 10.91; Found C 62.28, H 5.20, N 10.93

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