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A new method of synthesis of substituted 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles and their fungicidal activity

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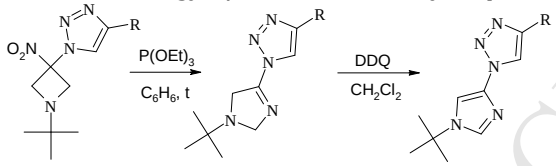

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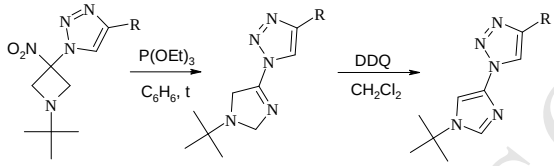

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ABSTRACT

Based on the deoxygenation reaction of 1-(1-*tert*-butyl-3-nitroazetidine-3-yl)-1*H*-1,2,3-triazoles a new method for the synthesis of substituted 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles has been developed. Fungicidal activity of these compounds has been investigated at a range of phytophatogenic fungi.

Introduction

Imidazoles are an important class of heterocycles. Their chemical and biological importance has been well investigated [1]. Many bioactive heterocyclic compounds and natural products containing this cycle show a wide spectrum of pharmacological activities such as anticancer, antiviral, antibacterial, antitubercular, anti-inflammatory and antidiabetic [2]. The imidazole ring is a frequent structural unit found innumerous natural products and biologically active compounds [3].

The 1,2,3-triazole moiety is not present in nature although synthetic molecules containing 1,2,3-triazole unit show diverse biological activities including antibacterial, herbicidal, fungicidal, antiallergic and anti-HIV [4].

Antifungal agents including imidazole and triazole rings such as bifonazole, clotrimazole, ketoconazole and fluconazole are widely used in clinical practice for fungal infection treatment (**Figure 1**) [5]. It is commonly considered that the imidazole ring could efficiently coordinate with the iron(II) ion of heme to restrain the biosynthesis of ergosterol thus inhibiting the growth of fungi [6].

We studied the structures of different antifungal drugs both in combinations with halogen-substituted aromatic residues and with each other and found out that most of the combinations contain 1*H*-imidazole as well as 1*H*-1,2,4-triazole. However there is no information about the system that contains 1,2,3-triazole in the fourth position of the imidazole ring. In this work we focused our attention on the creation of new molecules which contain 1*H*-imidazole and monosubstituted or 1,4-disubstituted 1*H*-1,2,3-triazole rings. 1,2,3-Triazole moieties are interesting molecules for this purpose. They are stable to metabolic degradation and are capable of hydrogen bonding which can be favorable in binding biomolecular targets and for solubility [6,7].

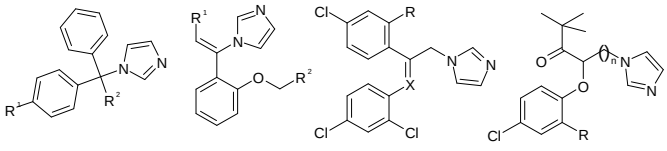
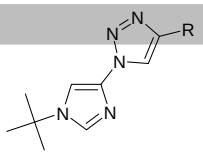


Figure 1 Some imidazole-based antifungal compounds

The number of methods and reagents that allow the direct introduction of 1*H*-1,2,3-triazole ring in the fourth position of the 1*H*-imidazole are limited by only 2- and 5- substituted imidazoles [8]. The preparation method of these molecules involves using *n*-buthyllithium or diazonium ion which is impossible in our conditions.

In the current work we developed a new and original way to synthesize 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles (**1a-k**) (**Figure 2**).



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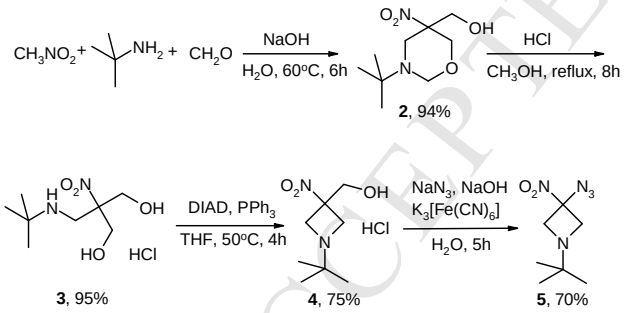
R = H (**1a**); $SiMe_3$ (**1b**); cyclo-Pr (**1c**), C_6H_5 (**1d**), 2-FC_6H_4 (**1e**), 2-ClC_6H_4 (**1f**), 3-ClC_6H_4 (**1g**), 2,4-$Cl_2C_6H_3$ (**1h**), 4-$CF_3C_6H_4$ (**1i**), 3-$CF_3C_6H_4$ (**1j**), 3-$CH_3OC_6H_4$ (**1k**)

Figure 2. Substituted1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles.

Results and Discussion

Several methods are currently known for deoxygenation of primary and secondary nitroalkanes with trivalent phosphorus compounds, leading to the formation of nitriles [9], amines [10], and derivatives of oximes [11]. Recently we have shown that substituted 1-(5-nitro-1,3-dioxan-5-yl)-1*H*-1,2,3-triazoles easily transform into a new 4,7-dihydro-1,3,5-dioxazepine heterocyclic system by heating with triethyl phosphite [12]. The positive results of this investigation did allow us to use 1-(1-*tert*-butyl-3-nitroazetidine-3-yl)-1*H*-1,2,3-triazoles **6a-k** as starting materials for the 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles **1a-k** synthesis.

3-Azido-3-nitro-azetidine **5** was used as a key intermediate for the synthesis of 1-(1-*tert*-butyl-3-nitroazetidine-3-yl)-1*H*-1,2,3-triazoles **6a-k**. The heminal nitroazide **5** was obtained by a previously developed scheme with nitromethane, formaldehyde and *tert*-butyl amine [13]. The main method of the preparation of α-nitroazides consists of oxidative coupling of the azide anion with nitroalkane salts. The reaction is performed in an alkaline medium in the excess of azide under the conditions of electrochemical and chemical oxidation [14]. In the latter case, ammonium persulfate or potassium ferricyanide are most widely used as oxidants. In the current work the nitroazetidine salt was obtained in situ using retro-Henry reaction from **4** (Sheme 1). Potassium ferricyanide was used as an oxidant.

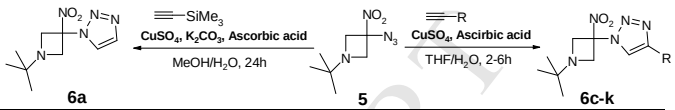


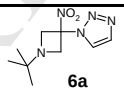
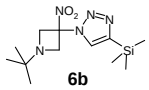
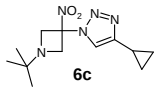
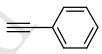
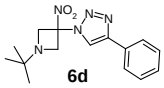
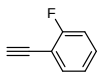
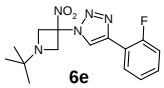
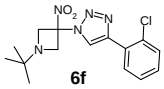
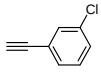
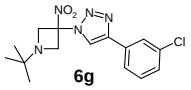
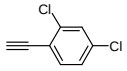
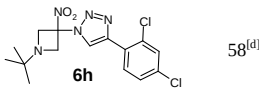
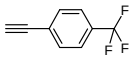
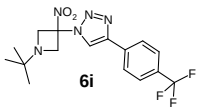
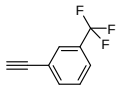
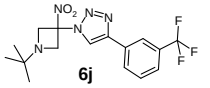
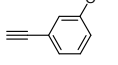
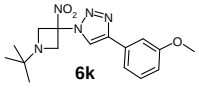
Scheme 1. The synthesis of 3-Azido-1-tert-butyl-3-nitro-azetidine.

As it was shown in our previous work [15] heterocyclic α-nitroazides are highly reactive in 1,3-dipolar cycloaddition to terminal acetylenes under thermal cyclization conditions giving a mixture of 1,4- and 1,5-triazoles regardless of the structure of the aliphatic heterocycle. Performing the cyclization in the presence of copper(I) salts resulted in a selective formation of 1,4-disubstituted triazoles.

In the current work we used both 1-substituted and 1,4-disubstituted 1,2,3-triazoles. The monosubstituted triazole **6a** was synthesized from the 3-azido-3-nitro-azetidine **5** and trimethylsilyl acetylene (TMS-acetylene). The reaction was performed at room temperature in aqueous methanolic medium in the presence of copper(II) sulfate, ascorbic acid, and potassium carbonate [16]. The process was found to be selective without formation of trimethylsilyl-substituted triazole according to NMR spectroscopy and LC-MS. The 1,4-disubstituted triazoles **6c-k** were obtained by addition of 3-azido-3-nitro-azetidine **5** to substitute acetylenes in the presence of ascorbic acid and copper(II) sulphate. 1-(1-*tert*-Butyl-3-nitroazetidine-3-yl)-4-trimethyl-silyl-1*H*-1,2,3-triazole **6b** was synthesized from 3-azido-3-nitro-azetidine **5** and TMS-acetylene without a catalyst [15] (Table 1):

Table 1. Synthesis of substituted azetidines



Entry	Acetylene	Time, [h]	Product	Yield, [%][a]
1		24	 **6a**	86[b]
2		48	 **6b**	78[c]
3		3	 **6c**	50[d]
4		2	 **6d**	74[d]
5		2	 **6e**	75[d]
6		4	 **6f**	77[d]
7		4	 **6g**	93[d]
8		3	 **6h**	58[d]
9		4	 **6i**	87[d]
10		4	 **6j**	81[d]
11		6	 **6k**	81[d]

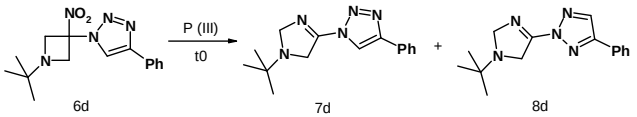
[a] Isolated yield. [b] Reaction conditions: K_2CO_3 (1.25 mmol), ascorbic acid (0.2 mmol), TMSA (1.2 mmol), $CuSO_4 \cdot 5H_2O$ (0.1 mmol), 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (1 mmol), MeOH (10 ml), H_2O (5 ml), 24h, rt. [c] Reaction conditions: 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (1 mmol), TMSA (10 mmol), CH_2Cl_2 (10 ml), reflux 48h. [d] Reaction conditions: Ascorbic acid (0.5 mmol), acetylene (1.05 mmol), $CuSO_4 \cdot 5H_2O$ (0.15 mmol), 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (1 mmol), THF (10 ml), H_2O (5 ml), 2-6h, rt.

All compounds **6a-k** are colorless, crystalline solids, with their infrared spectra contained bands of asymmetric (1564-1589 cm^{-1}) and symmetric (1333-1367 cm^{-1}) vibrations of the nitro group. All 1*H*-1,2,3-triazoles **6a-k** gave clear mass spectral signals of positively charged ions $[M+H]^+$ (100%) under the conditions of chemical ionization. Also every molecule showed partial nitrogen extrusion and an intensive $[M+H-N_2]^+$ ion signal (%), which characterizes for 1*H*-1,2,3-triazoles [17]. ^{1}H NMR spectra of these molecules are characterized by a large spin-spin doublet type coupling constant of about 9.8 Hz and untypical 4.20 and 4.37 ppm values for CH_2 protons. These are not regular values for these molecules [18]. Apparently it can be explain to the presence of an electron-withdrawing nitro group [15].

A key step of our investigation was deoxygenation of these substituted azetidines **6a-k**. In this work we studied the possibility of the nitro group transformation by the action of trivalent phosphorus compounds.

We began our research work by searching for an appropriate phosphorus agent and a solvent for the deoxygenation reaction. 1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole (**6d**) was chosen as a model compound. To find out the optimal reaction conditions a range of phosphorus reagents (triethylphosphite, triphenylphosphine, triphenylphosphite and chlorodiphenylphosphine), solvents [toluene, benzene, dioxane, 1,2-dichloroethane (DCE) and tetrahydrofuran (THF)] and amounts of the phosphorus reagents were tested (Table 2).

Table 2. Reaction of the nitro compound **6d** with various phosphorus agents.



Phosphorus reagent [P(III)]	Amount of P(III) [mmol]	Solvent	Reaction time [h]	Yield of **7d** [%][a]
$P(OEt)_3$	2	benzene	48	72
$P(OEt)_3$	4	benzene	30	83
$P(OEt)_3$	6	benzene	14	85
$P(OEt)_3$	8	benzene	10	88
$P(OEt)_3$	10	benzene	10	86
$P(OEt)_3$	8	toluene	6	70
$P(OEt)_3$	8	dioxane	10	75
$P(OEt)_3$	8	DCE	15	83
$P(OEt)_3$	8	THF	18	58
PPh_3	2	benzene	20	60
$P(OPh)_3$	2	benzene	60	trace
$PClPh_2$	2	benzene	60	trace

[a] Isolated yield. Reaction conditions: 3 ml of solvent, reflux.

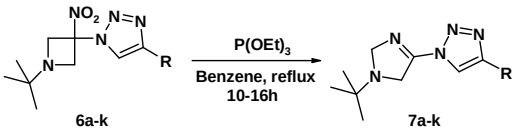
The reaction progress was monitored by LC-MS and GC-MS analysis. Besides triethylphosphite and triethylphosphate two products were found in the reaction mixture by GC-MS method with very close retention times (rt 18.35 and 18.48 min) and m/z 269. That corresponds to substituted 2,5-dihydro-1*H*-imidazoles (**7d** and **8d**). The major product **7d** (rt 18.35 min) fragmented with ejection of N_2 (m/z (I_{rel}, %) 269(5) $[M]^{\cdot+}$, 254 (40) $[M-CH_3]^{\cdot+}$, 226 (33) $[M-CH_3-N_2]^{\cdot+}$]) in the electron impact conditions. In the LC-MS of the minor product **8d** (rt 18.48 min) was found stable ion which corresponds phenyl-1,2,3-triazole (m/z (I_{rel}, %) 269(8) $[M]^{\cdot+}$; 254 (21) $[M-CH_3]^{\cdot+}$; 145 (71) $[M-123]^{\cdot+}$).

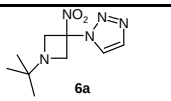
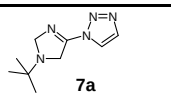
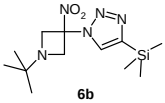
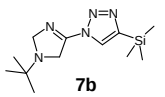
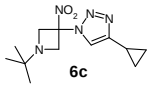
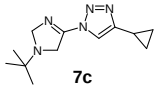
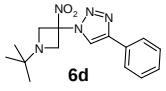
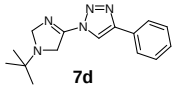
The use of $P(OPh)_3$ and $PClPh_2$ in benzene gave no reaction. We also found that the efficiency of triethylphosphite ($P(OEt)_3$) and triphenylphosphine (PPh_3) in the boiling benzene is similar, but the appropriate compound yield is lower with triphenylphosphine. The LC-MS method showed that heating the **6d** with triphenylphosphine leads to partial degradation of the final compound with formation of monosubstituted 1*H*-1,2,3-triazole. The best yield after a reasonable reaction time was achieved using $P(OEt)_3$ (8 mmol) in boiling benzene. We did not find any molecular degradation and found that the reaction selectivity was high and the second isomer was not obtained. We also tried to use lower amounts of $P(OEt)_3$, but when 2 mmol of $P(OEt)_3$ were used, the transformation proceeded much more slowly and the starting material conversion was incomplete, approximately 5 percent of azetidine did not react. Increasing the amount of $P(OEt)_3$ led us to a decrease of the reaction time from 48 to 10 hours.

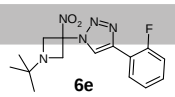
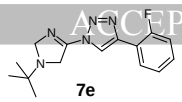
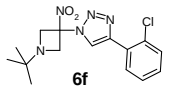
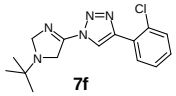
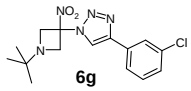
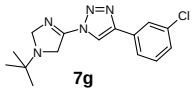
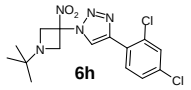
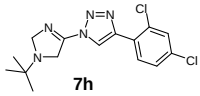
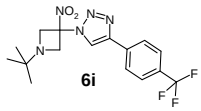
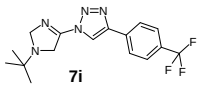
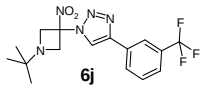
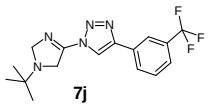
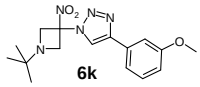
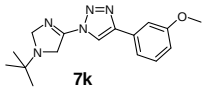
We also tested different solvents. In toluene and dioxane, the reaction finished in 6 and 10 hours respectively, but there was found the partial degradation product and the target compound (i.e. **7d**) could not be isolated in a good yield. In THF, starting material conversion was incomplete and the yield did not exceed 58 percent. Although, using DCE led us to a good yield, but we chose benzene that is the solvent the most frequently used in the deoxygenation reaction.

Thus, the reaction of azetidine **6d** with P(III) was found to produce the maximal yield with 8 mmol of $P(OEt)_3$ in boiling benzene with the reaction time of 10 hours. Having identified these optimal conditions for substance **6d** we carried out deoxygenation reactions of triethylphosphite with other azetidines **6a-k.** The reaction progress was monitored by LC-MS and GC-MS analysis. The target products were isolated by column chromatography after the removal of solvent (Table 3):

Table 3. Synthesis of substituted 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazole-4-*yl*)-1*H*-1,2,3-triazoles **7a-k**.



Entry	Starting material	Time, [h]	Product	Yield, [%][a]
1	 **6a**	14	 **7a**	71
2	 **6b**	13	 **7b**	87
3	 **6c**	12	 **7c**	95
4	 **6d**	10	 **7d**	88

5	 **6e**	10	 **7e**	62
6	 **6f**	10	 **7f**	68
7	 **6g**	11	 **7g**	66
8	 **6h**	12	 **7h**	90
9	 **6i**	10	 **7i**	72
10	 **6j**	10	 **7j**	75
11	 **6k**	11	 **7k**	61

[a] Yield isolated

Deoxygenation reactions in the studied series of compounds were apparently stepwise and occurred analogously to deoxygenation of geminal chloronitrocycloalkanes with triphenylphosphine [19]. The performed study showed that the reaction of **6a-k** with triethylphosphite ($P(OEt)_3$) occurred without noticeable heat effect or changes of color of the solution which was not specific to deoxygenation of nitroso compounds. Any attempts to detect nitroso intermediate 1-(1-*tert*-butyl-3-nitrozoazetidine-3-yl)-1*H*-1,2,3-triazoles by chromatographic methods also were not successful. With an insufficient amount and gradual addition of triethylphosphite the target 2,5-dihydroimidazoles **7a-k** were detected immediately. Thus, the most probable mechanism of azetidine ring expansion was through the stage of ion pair; this can explain the second isomer **8** and partial degradation of some molecules (Figure 3):

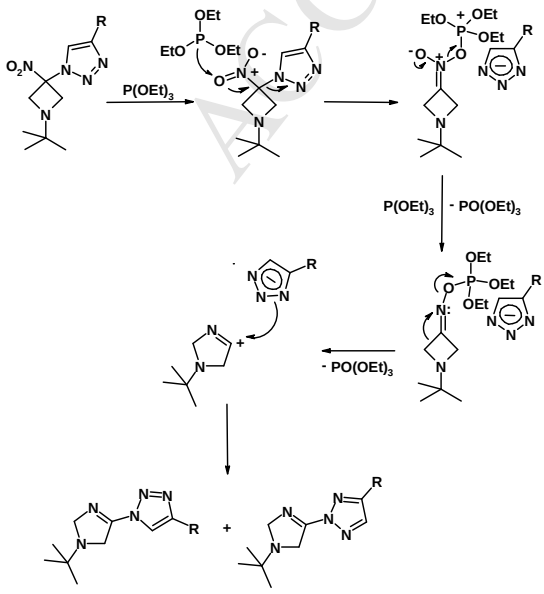


Figure 3 Deoxygenation mechanism

The 2,5-dihydroimidazoles **7a-k** are colorless, crystalline solids. The infrared spectra of these compounds lacked vibrational bands of nitro group while a strong band appeared in the region of C=N bond vibration (1691-1700 cm^{-1}). All compounds gave clear mass spectral signals of positively charged ions $[M+H]^+$ (100%) under the conditions of chemical ionization. Also every molecule showed partial nitrogen extrusion and an intensive $[M+H-N_2]^+$ ion signal (%). The downfield region of ^{13}C NMR spectrum contained resonance signals due to vicinal triazole carbon atoms (average values are 120 and 140 ppm) and another signal was found at 157 ppm. 2,5-Dihydroimidazole proton spectra should be noted as methylene protons which are characterized by a big spin-spin triplet type coupling constant of about $^4J_{H,H}$ = 4.8-5.0 Hz. The obtained results indicated the difference between hybridization of the carbon atoms adjacent to methylene groups (CH_2N) and hybridization of the carbon atom in the iminium fragment (C=N) in the structure. Finally the structure of these new heterocyclic compounds was confirmed by X-ray structural analysis using the example of 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazole-4-yl)-4-phenyl-1*H*-1,2,3-triazole **7d** (Figure 4).

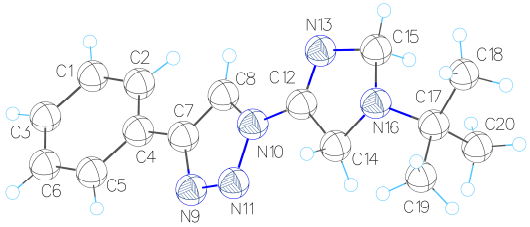
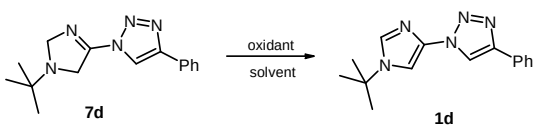


Figure 4. X-ray crystallographic structure of 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole **7d**. Atoms are represented by spheres indicating their isotropic thermal displacements (ρ = 50%). Key bond lengths (Å) and angels [°] for 2,5-dihydro-1*H*-imidazol cycle: C12-N13 1.268(5), C12-C14 1.511(5), N13-C15 1.456(5), C15-N16 1.457(5), C14-N16 1.467(5), N13-C12-C14 113.96, C12-C14-N16 98.84, C14-N16-C15 108.00, N16-C15-N13 108.87, C15-N13-C12 106.14. For details see CCDC 1554112.

The corresponding representation and important geometrical parameters are shown in **Figure 4**. The torsion angle C(15)-N(13)-C(12)-C(14) is (-16.86). It means, that the structure of 2,5-dihydro-1*H*-imidazole cycle is not planar. There is no conjugation between the C(12)=N(13) bond and the phenyltriazole ring, because the C(12)–N(10) bond is single (its length is 1.462(4) Å), while the C(12)=N(13) is a double bond (its length is 1.268(5) Å), which is typical for 4-imidazoles and *N*-imidoylbenzotriazole compounds [20, 21, 22]. A similar picture was observed for the 4,7-dihydro-1,3,5-dioxazepine heterocyclic system [12].

At the next step of our research we tried to transform 2,5-dihydro-1*H*-imidazoles **7a-k** into 1*H*-imidazoles **1a-k** under the influence of different oxidants. To screen the optimal reaction conditions for this process 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole **7d** was chosen as the model compound. Various oxidants (O_2 (air), H_2O_2, MnO_2, DDQ,) and solvents (acetonitrile, THF, CH_2Cl_2) were tested to find the optimal conditions (Table 4):

Table 4. Reaction of the 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole **7d** with various oxidant agents



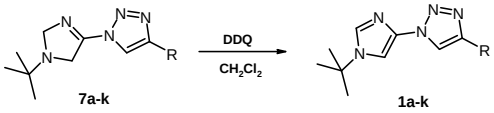
7d **1d**

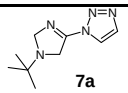
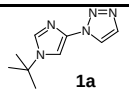
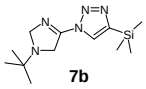
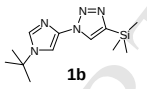
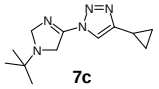
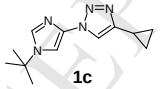
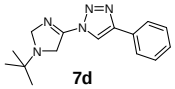
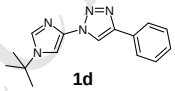
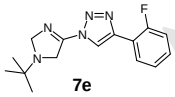
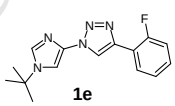
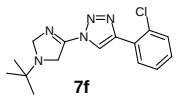
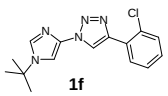
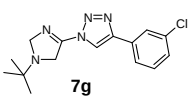
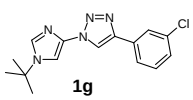
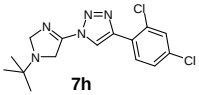
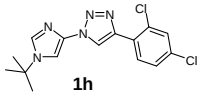
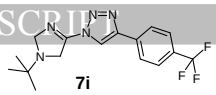
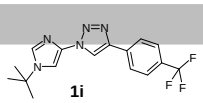
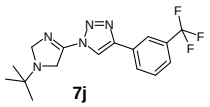
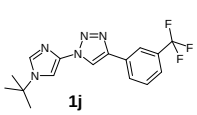
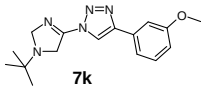
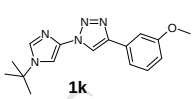
Oxidant	Amount of oxidant, mmol	Solvent	Reaction time, h	Yield, [%][a]
O_2 (air)	-	CH_3CN	10	53
H_2O_2	10	CH_3CN	24	27
MnO_2	20	THF	48	50
DDQ	2	CH_2Cl_2	1	95

[a] Yield isolated

We found that the 2,5-dihydro-1*H*-imidazoles **7a-k** are not stable in air and eventually these compounds transform into 1*H*-imidazoles. Thus, we decided to bubble air into the reaction mixture of **7d** in acetonitrile but this process gave no good results. We also used hydrogen peroxide and MnO_2 in acetonitrile and THF respectively but the final compound (i.e., **1d**) was not isolated in a good yield. The best result after 1 hour was achieved using DDQ (2 mmol) in CH_2Cl_2. Having identified these optimal conditions for substance **7d**, we obtained new series of 1-(1-*tert*-butyl-1*H*-imidazole-4-*yl*)-1*H*-1,2,3-triazoles **1a-k** (Table 5):

Table 5. Synthesis of substituted 1-(1-*tert*-butyl-1*H*-imidazole-4-*yl*)-1*H*-1,2,3-triazoles **1a-k**.



Entry	Starting material	Time, [h]	Product	Yield, [%][a]
1	 **7a**	1	 **1a**	99
2	 **7b**	1	 **1b**	99
3	 **7c**	1	 **1c**	92
4	 **7d**	1	 **1d**	95
5	 **7e**	1	 **1e**	85
6	 **7f**	1	 **1f**	92
7	 **7g**	1	 **1g**	93
8	 **7h**	1	 **1h**	95
9	 **7i**	1	 **1i**	60
10	 **7j**	1	 **1j**	74
11	 **7k**	1	 **1k**	78

[a] Isolated yield.

The 1*H*-imidazoles **1a-k** are colorless, crystalline solids. All compounds gave clear mass spectral signals of positively charged ions $[M+H]^+$ (100%) under the conditions of chemical ionization. The downfield region of ^{13}C NMR spectrum contained resonance signals due to vicinal triazole carbon atoms and carbon signals typical for 1*H*-imidazole. In the proton spectrum we registered imidazole proton signals with a typically low spin-spin coupling constant of 1.6 Hz [23]. The structure of these new heterocyclic compounds was finally confirmed by X-ray structural analysis using the example of 1-(1-*tert*-butyl-1*H*-imidazole-4-yl)-4-phenyl-1*H*-1,2,3-triazole **1d** (Figure 5).

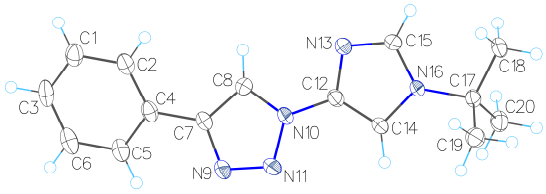
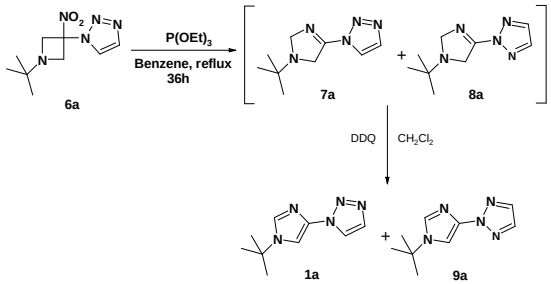


Figure 5. X-ray crystallographic structure of 1-(1-*tert*-butyl-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole **1d**. Atoms are represented by thermal displacement ellipsoids (p = 50%). Key bond lengths (Å) and angels [°] for 2,5-dihydro-1*H*-imidazol cycle: C12-N13 1.357(2), C12-C14 1.356(2), N13-C15 1.316(2), C15-N16 1.344(2), C14-N16 1.380(2), N13-C12-C14 111.82, C12-C14-N16 104.73, C14-N16-C15 106.43, N16-C15-N13 112.92, C15-N13-C12 104.10. For details see CCDC 1554111.

Corresponding representation and important geometrical parameters are shown in **Figure 5**. The structure is absolutely planar. The torsion angle C(15)-N(13)-C(12)-C(14) is (-0.1). Thus, the bond lengths and angles of the imidazole ring are the same for dimensions of imidazole [24].

The conformation of the reaction mechanism was obtained by deoxygenation of **6a** with 2 moles of $P(OEt)_3$ in boiling benzene (Scheme 2):



Scheme 2. Deoxygenation of **6a** with 2 moles of $P(OEt)_3$.

It was found by GC-MS method that besides the starting material **6a** there were only triethylphosphate, diethylphosphonate and two products with similar m/z 193, which corresponds to **7a** and

8a. It should be noted that nitroazetidine **6a** or others azetidine cycle transformation products were not found in the reaction mixture. When the reaction was completed benzene and triethylphosphate were evaporated under reduced pressure. The crude product was dissolved in CH_2Cl_2 and DDQ was added. After the reaction was completed (TLC control) the mixture of **1a** and **9a** was separated by RP-HPLC to afford **1a** (31%) as a white solid and **9a** (23 %) as a white solid.

Fungicidal activity

The 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles **1a-k** were tested *in vitro* for the fungicidal activity according to a very common conventional procedure [25] with seven phytopathogenic fungi from different taxonomic classes: R.*s.* – *Rhizoctonia solani, F.o. – Fusarium oxysporum, F.m. – Fusarium moniliforme, F.g. – Fusarium graminearum, S.s. — Sclerotinia/ sclerotiorum, V.i. – Venturia inaequalis, B.s. – Bipolaris sorokiniana* (Table 6). The effect of the tested compounds on the mycelium radial growth in the potato-saccharose agar with widely used fungicide triadimefon as a reference compound was measured in a 30 μg mL^{-1} concentration.

Table 6. Fungicidal activity of the synthesized copmpounds **1a-k**

№	Mycelium growth inhibition, % (C = 30 μg mL^{-1})						
	R.s.	F.o.	F.m.	F.g.	S.s.	V.i.	B.s.
1a	23	13	3	20	3	1	1
1b	53	14	11	20	10	3	2
1c	35	12	20	14	15	20	15
1d	55	17	48	44	66	30	45
1e	49	28	53	53	29	42	36
1f	45	29	29	57	16	45	53
1g	78	47	36	68	16	62	68
1h	88	60	65	66	27	49	70
1i	46	22	33	26	10	56	38
1j	46	11	17	14	5	25	35
1k	41	19	33	51	11	33	65
Triadimefon	43	60	79	78	47	41	44

[a] R.s. – Rhizoctonia solani, F.o. – Fusarium oxysporum, F.m. – Fusarium moniliforme, F.g. – Fusarium graminearum, S.s. — Sclerotinia/ sclerotiorum, V.i. – Venturia inaequalis, B.s. – Bipolaris sorokiniana

The first three members (**1a, 1b** and **1c**) in the sequence of the 1-(1*H*-imidazole-4-yl)-1*H*-1,2,3-triazoles **1a-k** demonstrated low fungicidal activity. Their potency is much lower than the commercial fungicide (*triadimefon*) with respect to all phytopatogens – they do not inhibit the mycelium growth in the majority of fungi at concentration 30 μg mL^{-1}. The modification of the triazole ring showed that the fungicidal activity increased in this row. The compound **1d** showed much more activity than its non-substituted or alkyl-substituted analogs. Its impact on the agricultural plant scab *R. solani* was higher than triadimefon and equivalent in activity to triadimefon towards plant pathogenic fungus *S. sclerotiorum* and *B. sorokiniana*. Further modification of the triazole ring of the halogen-substituted aromatic residues showed an increase of fungicidal activity of the final compounds. So **1e, 1f, 1i** and **1j** had equal activity against *Rhizoctonia solani*, *Venturia inaequalis* and B*ipolaris sorokiniana* fungus like triadimefon. However the **1g** and **1h** compounds showed much more activity than the triadimefon against agricultural plant scab *R. solani* and the same activity as the triadimefon against the other fungi. And finally the introduction of metoxy group in phenyl ring decreased the fungicidal activity of compound **1k**.

Conclusions

The current work first showed the possibility of deoxygenation of the nitrogroup by the action of trivalent phosphorus compounds in the 1-(1-*tert*-butyl-3-nitroazetidine-3-yl)-1*H*-1,2,3-triazole row. We found that the 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazole-4-*yl*)-1*H*-1,2,3-triazoles represent useful intermediates for the synthesis of 1-(1-*tert*-butyl-1*H*-imidazole-4-*yl*)-1*H*-1,2,3-triazoles. A series of compounds showed that some of those imidazoles demonstrated a satisfactory fungicidal activity and could be the prototypes for the synthesis of new bioactive compounds.

Experimental Section

General Remarks: IR spectra were recorded on a Thermo Nicolet 360 FTIR instrument in KBr pellets. ^1H and ^{13}C NMR spectra were obtained with Varian Mercury Plus instrument (400 and 100 MHz, respectively) in DMSO-d_6 and $CDCl_3$. The LC-MS analysis was performed on Thermo Finnigan Surveyor MSQ with gradient elution and chemical ionization at atmospheric pressure with simultaneous recording of positive and negative ions. The GS-MS was performed on Trace 1310/ISQ-LT (Thermo Scientific) using a capillary column TG-SQC (15 m, 0.25 mm, 0.25 μm). High-resolution ESI mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument. Elemental analysis was performed on a Perkin Elmer 2400 Series II CHN-analyzer. Melting points were determined on a Boetius hot stage. Durasil H silica gel (40-63 μm) was used for purification of the obtained compounds by column chromatography. Compounds **1a**, **9a** and **9d** also were purified by preparative RP-HPLC on Gilson Combinatorial Chromatography System using 100×30 00 mm 10 micron Phenomenex Gemini column and flow rate of 30 mL/minute. Separations were accomplished with a gradient of 5-40% acetonitrile in water containing ammonium acetate and ammonium water (pH=9) over 15 minutes. TLC was carried out on precoated silica plates (Sorbfil UV-254), which were visualized with UV light and/or staining with ninhydrin solution. All solvents and reagents for the reactions were used without further purification or drying. Phenylacetylenes, trimethylsilylacetylene and triethylphosphite used in this work were purchased from Sigma-Aldrich. Compounds **2**, **3**, **4**, **5** [13] and **6b** [15] were synthesized according to published procedures.

3-Azido-1-*tert*-butyl-3-nitro-azetidine (5): (1-*tert*-butyl-3-nitro-azetidin-3-yl)-methanol **4** (1.9 g 10 mmol) was added to a solution of NaOH (2.0 g, 50 mmol) in water (10 mL). The mixture was stirred at room temperature for 30 min; then treated with a solution of NaN_3 (3.25 g, 50 mmol) in water (10 mL) and poured into a vigorously stirred solution of $K_3Fe(CN)_6$ (16.46 g, 50 mmol) in water (70 mL). The reaction mixture was stirred for 5 h at room temperature and extracted with EtOAc (3×20 mL).

The combined extract was washed with water and dried over Na_2SO_4. The solvent was removed at reduced pressure, the residue was purified by flash chromatography (EtOAc/*n*-hexane, 1:1). To afford the pure **5** (1.55 g, 78%), as a light yellow oil, m.p. 3-5 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.96 (s, 9H, CH_3), 3.50 (dd, $^2J_{H,H}$=8.3 Hz, $^4J_{H,H}$=1.7 Hz, 2H, CH_2), 3.89 (dd, $^2J_{H,H}$=8.3 Hz, $^4J_{H,H}$=1.7 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.7 (C-CH_3), 55.3 (CH_2), 92.5 (C-NO_2). IR (KBr): *ν*= 1353, 1558 (NO_2), 2128 (N_3), 2968 (C-H) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 200 (100) $[M+H]^+$. $C_7H_{13}N_5O_2$: C 42.20, H 6.58, N 35.16; found C 42.11, H 6.50, N 35.06.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-1*H*-1,2,3-triazole (6a): A solution of K_2CO_3 (862 mg, 6.25 mmol) and ascorbic acid (176 mg, 1 mmol) in water (10 mL) was stirred at room temperature and treated by adding a solution of trimethylsilylacetylene (588 mg, 6 mmol) in MeOH (20 mL), followed by solution of $CuSO_4 \cdot 5H_2O$ (125 mg, 0.5 mmol) in water (10 mL) and then solution of 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (995 mg, 5 mmol) in MeOH (20 mL). The reaction mixture was stirred for 24 h at room temperature and extracted with CH_2Cl_2 (3×10 mL). The combined extract was washed with water (20 mL) and dried over Na_2SO_4. The solvent was removed at reduced pressure, and the residue was purified by flash chromatography (EtOAc/*n*-hexane, 1:1) to afford the pure **6a** (967 mg, 86%) as a white solid; m.p. 86-88°C; ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.99 (s, 9H, CH_3), 4.13 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 4.35 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 7.96 (d, $^3J_{H,H}$=1.3 Hz, 1H, H-4 triazole), 8.68 (d, $^3J_{H,H}$=1.3 Hz, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.6 (CH_2), 89.6 (C-NO_2), 126.1 (C-5 triazole), 134.0 (C-4 triazole) ppm. IR (KBr): *ν*= 1365, 1567 (NO_2), 2975 (C-H aliphatic), 3129 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 226 (100) $[M+H]^+$. HRMS (ESI): calcd. for $C_9H_{15}N_5O_2$ $[M+H]^+$ 226.1299; found 226.1305.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (6b): A mixture of a 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (995 mg, 5 mmol) and trimethylsilylacetylene (4900 mg, 50 mmol) was kept in anhydrous CH_2Cl_2 at 55ºC for 48 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/*n*-hexane, 1:1) to afford the pure **6b** (1158 mg, 78%) as a white solid; m.p. 76-78°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.32 (s, 9H, Si-CH_3), 0.99 (s, 9H, CH_3), 4.13 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 4.34 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 8.69 (s, 1H, CH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 1.4 (C-Si), 23.5 (CH_3), 51.8 (C-CH_3), 55.6 (CH_2), 89.4 (C-NO_2) 131.4 (C-5 triazole), 145.9 (C-4 triazole) ppm. IR (KBr): *ν*= 1367, 1569 (NO_2), 2974 (C-H aliphatic), 3129 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 298 (100) $[M+H]^+$. HRMS (ESI): calcd. for $C_{12}H_{23}N_5O_2Si$ $[M+H]^+$ 298.1694; found 298.1700.

General Procedure for the Synthesis of Substituted 1*H*-1,2,3-triazoles (6c-k): A solution of 3-azido-1-*tert*-butyl-3-nitro-azetidine **5** (995 mg, 5 mmol) and substituted acetylene (**c-k**) (5.25 mmol.) in THF (40 mL) was treated at room temperature by adding a solution of ascorbic acid (440 mg, 2.5 mmol) in water (20 mL), followed by a solution of $CuSO_4 \cdot 5H_2O$ (188 mg, 0.75 mmol) in water (10 mL). The reaction mixture was stirred for 2-6 h at room temperature. After the reaction was complete according to TLC, the mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (4×20 mL). The organic layer was dried over Na_2SO_4, the solvent was removed at reduced pressure, and the residue was purified by flash chromatography (EtOAc/*n*-hexane, 2:3) to give the desired products **6c-k** as colorless solids.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-cyclopropyl-1*H*-1,2,3-triazole (6c): White solid (50%), m.p. 62-64°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.83-0.77 (m, 2H, cyclopropyl), 0.98 (s, 9H, CH_3), 1.00-0.94 (m, 2H, CH_2, cyclopropyl), 2.08-1.98 (m, 1H, CH, cyclopropyl), 4.08 (d, $^2J_{H,H}$=10.2 Hz, CH_2-N), 4.29 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2-N), 8.36 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 6.4 (CH-cyclopropyl), 7.8 (CH_2-cyclopropyl), 23.6 (CH_3), 52.1 (C-CH_3), 55.6 (CH_2-N), 89.6 (C-NO_2), 121.9 (C-5 triazole), 149.9 (C-4 triazole) ppm. IR (KBr): *ν*= 1365, 1565 (NO_2), 2963 (C-H aliphatic), 3096 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 265 (100) $[M+H]^+$. $C_{12}H_{19}N_5O_2$: C 54.32, H 7.22, N 26.40; found C 54.30, H 7.20, N 26.35

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole (6d): White solid (74%), m.p. 120-121°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, CH_3), 4.19 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 4.38 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 7.40 (t, $^3J_{H,H}$=7.4 Hz, 1H, Ar), 7.51 (t, $^3J_{H,H}$=7.6 Hz, 2H, Ar), 7.92 (d, $^3J_{H,H}$=7.2 Hz, 2H, Ar), 9.12 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.5 (CH_2), 89.8 (C-NO_2), 122.3 (C-5 triazole), 125.3 (Ar), 128.3 (Ar), 128.8 (Ar), 129.5 (Ar), 147.0 (C-4 triazole) ppm. IR (KBr): *ν*= 1365, 1567 (NO_2), 2970 (C-H aliphatic), 3128 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 302 (100) $[M+H]^+$. HRMS (ESI): calcd. for $C_{15}H_{19}N_5O_2$ $[M+H]^+$ 302.1612; found 302.1621.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(2-fluoro-phenyl)-1*H*-1,2,3-triazole (6e): Light yellow solid (75%), m.p. 149-151°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.00 (s, 9H, CH_3), 4.22 (d, $^2J_{H,H}$= 9.2 Hz, 2H, CH_2), 4.38 (d, $^2J_{H,H}$= 9.2 Hz, 2H, CH_2), 7.37 (t, $^3J_{H,H}$= 8.5 Hz, 2H, Ar), 7.45-7.50 (m, 1H, Ar), 8.19 (t, $^3J_{H,H}$= 7.6 Hz, 1H, Ar), 8.99 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.7 (CH_2), 90.0 (C-NO_2), 115.9 (d, *J*= 21.2 Hz, C-F), 117.3 (d, *J*= 13.1 Hz, Ar), 124.5 (C-5 triazole), 124.9 (Ar),127.6 (Ar), 130.2 (d, *J*= 8.4 Hz, Ar), 140.6 (C-4 triazole), 157.2 (Ar), 159.7 (Ar) ppm. IR (KBr): *ν*= 1366, 1564 (NO_2), 2972 (C-H aliphatic), 3168 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 292 $[M-N_2]^+$ (17), 320 $[M+H]^+$ (100), 361 $[M+H+CH_3CN]^+$ (20). HRMS (ESI): calcd. for $C_{15}H_{18}FN_5O_2$ $[M+H]^+$ 320.1517; found 320.1518.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(2-chlorophenyl)-1*H*-1,2,3-triazole (6f): White solid (77%), m.p. 109-111°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, CH_3), 4.22 (d, $^2J_{H,H}$= 10.0 Hz, 2H, CH_2), 4.39 (d, $^2J_{H,H}$= 10.0 Hz, 2H, CH_2), 7.42-7.54 (m, 2H, Ar), 7.61 (d, $^3J_{H,H}$= 7.8 Hz, 1H, Ar), 8.07-8.13 (m, 1H, Ar), 9.17 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.7 (CH_2), 90.0 (C-NO_2), 125.2 (C-5 triazole), 127.4 (Ar), 128.1 (Ar), 129.7 (Ar), 129.9 (Ar), 130.1 (Ar), 130.6 (Ar), 143.5 (C-4 triazole) ppm. IR (KBr): *ν*= 1367, 1568 (NO_2), 2962 (C-H aliphatic), 3099 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 308 $[M-N_2]^+$ (40), 336 $[M]^+$ (100), 338 [M+2] (40), 377 $[M+H+CH_3CN]^+$ (25). HRMS (ESI): calcd. for $C_{15}H_{18}ClN_5O_2$ $[M+H]^+$ 336.1222; found 336.1216.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(3-chlorophenyl)-1*H*-1,2,3-triazole (6g): White solid (93%), m.p. 124-126°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.00 (s, 9H, CH_3), 4.18 (d, $^2J_{H,H}$= 9.8 Hz, 2H, CH_2), 4.38 (d, $^2J_{H,H}$= 9.8 Hz, 2H, CH_2), 7.46 (d, $^3J_{H,H}$= 7.7 Hz, 1H, Ar), 7.54 (t, $^3J_{H,H}$= 7.8 Hz, 1H, Ar), 7.89 (d, $^3J_{H,H}$= 7.8 Hz, 1H, Ar), 7.96 (s, 1H, Ar), 9.23 (s, 1H, H-5

triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.4 (CH_2), 89.8 (C-NO_2), 123.8 (C-5 triazole), 125.0 (Ar), 128.1 (Ar), 130.8 (Ar), 131.6 (Ar), 133.7 (Ar), 145.6 (C-4 triazole) ppm. IR (KBr): *v*= 1367, 1568 (NO_2), 2962 (C-H aliphatic), 3099 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 308 $[M-N_2]^+$ (20), 336 $[M]^+$ (100), 338 [M+2] (40), 377 $[M+H+CH_3CN]^+$ (20). HRMS (ESI): calcd. for $C_{15}H_{18}ClN_5O_2$ $[M+H]^+$ 336.1222; found 336.1216.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(2,4-dichlorophenyl)-1*H*-1,2,3-triazole (6h): White solid (58%), m.p. 137-139°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, CH_3), 4.22 (d, $^2J_{H,H}$= 10.0 Hz, 2H, CH_2), 4.38 (d, $^2J_{H,H}$=10.2 Hz, 2H, CH_2), 7.59 (dd, $^3J_{H,H}$= 8.5, $^3J_{H,H}$=2.1 Hz, 1H, Ar), 7.76 (d, $^3J_{H,H}$= 2.0 Hz, 1H), 8.15 (d, $^3J_{H,H}$= 8.5 Hz, 1H, Ar), 9.20 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.7 (CH_2), 90.0 (C-NO_2), 125.3 (C-5 triazole), 127.2 (Ar), 127.7 (Ar), 129.6 (Ar), 130.8 (Ar), 131.4 (Ar), 133.6 (Ar), 142.5 (C-4 triazole) ppm. IR (KBr): *v*= 1367, 1565 (NO_2), 2965 (C-H aliphatic), 3128 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 370 $[M]^+$ (60), 372 [M+2] (100), 374 [M+4] (10), 411 $[M+H+CH_3CN]^+$ (60). HRMS (ESI): calcd. for $C_{15}H_{17}Cl_2N_5O_2$ $[M+H]^+$ 370.0832; found 370.0822.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-[4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (6i): Light yellow solid (87%), m.p. 149-150°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, CH_3), 4.20 (d, $^2J_{H,H}$= 9.8 Hz, 2H, CH_2), 4.39 (d, $^2J_{H,H}$= 9.8 Hz, 2H, CH_2), 7.87 (d, $^3J_{H,H}$= 8.2 Hz, 2H, Ar), 8.14 (d, $^3J_{H,H}$= 8.2 Hz, 2H, Ar), 9.30 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.5 (CH_2), 89.9 (C-NO_2), 123.8 (C-5 triazole), 125.9 (Ar), 128.0 (Ar), 128.4 (Ar), 128.7 (Ar), 133.5 (Ar), 145.5 (C-4 triazole) ppm. IR (KBr): *v*= 1333, 1589 (NO_2), 2975 (C-H aliphatic), 3111 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 370 (100) $[M+H]^+$, 411 $[M+H+CH_3CN]^+$ (20). HRMS (ESI): calcd. for $C_{16}H_{18}F_3N_5O_2$ $[M+H]^+$ 370.1485; found 370.1485.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(3-trifluoromethyl-phenyl)-1*H*-1,2,3-triazole (6j): Light yellow solid (81%), m.p. 94-95°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, CH_3), 4.19 (d, $^2J_{H,H}$= 10.1 Hz, 2H, CH_2), 4.39 (d, *J* = 10.1 Hz, 2H, CH_2), 7.71-7.80 (m, 2H, Ar), 8.24 (t, $^3J_{H,H}$= 3.6 Hz, 2H, Ar) 9.33 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.5 (CH_3), 51.9 (C-CH_3), 55.4 (CH_2), 89.8 (C-NO_2), 121.7 (q, $^2J_{C,F}$= 3.9 Hz, C-CF_3) 122.5 (Ar), 123.5 (C-5 triazole), 124.8 (q, $^1J_{C,F}$= 3.8 Hz, CF_3), 125.2 (Ar), 129.0 (Ar), 130.1 (Ar), 130.6 (Ar), 145.5 (C-4 triazole) ppm. IR (KBr): *v*= 1328, 1596 (NO_2), 2978 (C-H aliphatic), 3144 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 370 (100) $[M+H]^+$, 411 $[M+H+CH_3CN]^+$ (20). HRMS (ESI): calcd. for $C_{16}H_{18}F_3N_5O_2$ $[M+H]^+$ 370.1485; found 370.1485.

1-(1-*tert*-Butyl-3-nitro-azetidin-3-yl)-4-(3-methoxyphenyl)-1*H*-1,2,3-triazole (6k): White solid (61%), m.p. 114-116°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.01 (s, 9H, C-CH_3), 3.84 (s, 3H, O-CH_3), 4.19 (d, $^2J_{H,H}$= 10.1 Hz, 2H, CH_2), 4.38 (d, $^2J_{H,H}$= 10.1 Hz, 2H, CH_2), 6.98 (dd, $^3J_{H,H}$= 8.1, $^3J_{H,H}$ = 2.1 Hz, Ar), 7.41 (t, $^3J_{H,H}$= 7.9 Hz, 1H, Ar), 7.46-7.54 (m, 2H, Ar), 9.18 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 23.7 (C-CH_3), 52.1 (C-CH_3), 55.2 (O-CH_3), 55.7 (CH_2), 89.9 (C-NO_2), 110.6 (Ar), 114.4 (Ar), 117.7 (Ar), 122.9 (C-5 triazole), 130.3 (Ar), 130.9 (Ar), 146.9 (C-4 triazole), 159.7 (Ar) ppm. IR (KBr): *v*= 1370, 1596 (NO_2), 2962 (CH aliphatic), 3115 (C-H Ar) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 332 (100) $[M+H]^+$. $C_{16}H_{21}N_5O_3$: C 57.99, H 6.39, N 21.13; found C 57.96, H 6.40, N 21.10

General Procedure for the Synthesis of Substituted 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles (7a-k): The mixture of 1-(1-*tert*-butyl-3-nitro-azetidin-3-yl)-1*H*-1,2,3-triazole **6a-k** (1 mmol) and triethyl phosphite (1328 mg, 8 mmol) in benzene (3 mL) was stirred at reflux for 10-14h. After the completion of reaction (TLC control), the solvent was removed under reduced pressure. The residue was purified by flash chromatography (EtOAc/*n*-hexane, 50:50) to give the desired products **7a-k** as colorless solids.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazole (7a): Light yellow solid (88%), m.p. 65-71°C. ^{1}H NMR (400 MHz, $CDCl_3$, 50ºC): δ= 1.15 (s, 9H, CH_3), 4.34 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.86 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 7.75 (s, 1H, H-4 triazole) 8.32 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 50ºC): δ= 26.1 (CH_3), 51.3 (CH_2-C), 52.5 (C-CH_3), 74.9 (CH_2-N=), 121.3 (C-5 triazole), 134.2 (C-4 triazole), 158.3 (-C=N) ppm. IR (KBr): *v*= 1682 (C=N) cm^{-1}. MS (APCI, 30 EV), m/z (I_{rel},%): 194 (100) $[M+H]^+$. MS (EI, 70 EV), *m/z* (I_{rel},%): 193 (5), 178 (50), 136 (10), 82 (50), 70 (40). $C_9H_{15}N_5$: C 55.94, H 7.82, N 36.24; found C 55.92, H 7.79, N 36.29.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-trimethylsilanyl-1*H*-1,2,3-triazole (7b): White solid (87%), m.p. 80-86°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.31 (s, 9H, Si-CH_3), 1.10 (s, 9H, C-CH_3), 4.24 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.79 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 8.68 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= -1.52 (Si-CH_3), 25.6 (CH_3-C), 50.9 (CH_2-C), 51.8 (C-CH_3), 74.2 (CH_2-N=), 127.7 (C-5 triazole), 146.2 (C-4 triazole), 157.3 (-C=N) ppm. IR (KBr): *v*= 1683 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 238 $[M-N_2]^+$ (40), 266 $[M+H]^+$ (100). $C_{12}H_{23}N_5Si$: C 54.30, H 8.73, N 26.38 found C 54.33, H 8.74, N 26.39.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-cyclopropyl-1*H*-1,2,3-triazole (7c): White solid (95%), m.p. 50-53°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.77-0.84 (m, 2H, cyclopropyl), 0.93-1.00 (m, 2H, cyclopropyl), 1.09 (s, 9H, CH_3), 1.99-2.03 (m, 1H, cyclopropyl), 4.20 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.77 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 8.39 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 6.1 (CH-cyclopropyl), 7.6 (CH_2-cyclopropyl), 25.7 (CH_3), 50.5 (CH_2-C), 51.8 (C-CH_3), 74.1 (CH_2-N=), 117.7 (C-5 triazole), 150.2 (C-4 triazole), 157.4 (-C=N) ppm. IR (KBr): *v*= 1672 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 206 $[M-N_2]^+$ (70), 234 $[M+H]^+$ (100). HRMS (ESI): calcd. for $C_{12}H_{19}N_5$ $[M+H]^+$ 234.1718; found 234.1715.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole (7d): White solid (88%), m.p. 83-86°C. ^{1}H NMR (400 MHz, $CDCl_3$, 50ºC): δ= 1.18 (s, 9H, CH_3), 4.38 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.90 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 7.38 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, Ar), 7.45 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, Ar), 7.86-7.93 (m, 2H, Ar), 8.52 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.8 (C-CH_3), 74.2 (CH_2-N=), 118.3 (Ar), 125.6 (C-5 triazole), 128.4 (Ar), 128.7 (Ar), 129.3 (Ar), 147.0 (C-4 triazole), 157.5 (-C=N) ppm. IR (KBr): *v*= 1683 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 270 $[M+H]^+$ (100). HRMS (ESI): calcd. for $C_{15}H_{19}N_5$ $[M+H]^+$ 270.1718; found 270.1725.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(2-fluorophenyl)-1*H*-1,2,3-triazole (7e): White solid (62%), m.p. 91-95°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.12 (s, 9H, CH_3), 4.30 (t, $^4J_{H,H}$ = 4.9 Hz, 2H, CH_2-C), 4.84 (t, $^4J_{H,H}$ = 4.9 Hz, 2H, CH_2-N=), 7.33-7.42 (m, 2H, Ar), 7.45-7.54 (m, 1H, Ar), 8.16 (m, 1H, Ar), 8.78 (d, $^5J_{H,F}$= 3.2 Hz, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C),

51.9 (C-CH_3), 74.2 (CH_2-N=), 115.8 (Ar), 116.0 (Ar), 124.8 (C-5 triazole), 127.8 (Ar), 130.3 (Ar), 130.4 (Ar), 140.7 (C-4 triazole), 157.4 (-C=N) ppm. IR (KBr): *v*= 1683 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 260 $[M-N_2]^+$ (100), 288 $[M+H]^+$ (92), 329 $[M+H+CH_3CN]^+$ (10). $C_{15}H_{18}FN_5$: C 62.70, H 6.31, N 24.34; found C 62.79, H 6.34, N 24.28.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(2-chlorophenyl)-1*H*-1,2,3-triazole (7f): White solid (68%), m.p. 101-105°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.11 (s, 9H, CH_3), 4.31 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.84 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 7.42-7.55 (m, 2H, Ar), 7.58-7.66 (m, 1H, Ar), 8.07 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 1.8 Hz, 1H, Ar), 8.99 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.9 (C-CH_3), 74.2 (CH_2-N=), 120.6 (Ar), 120.8 (Ar), 127.4 (Ar), 127.8 (C-5 triazole), 130.0 (Ar), 130.1 (Ar), 130.9 (Ar), 143.5 (C-4 triazole), 157.5 (-C=N) ppm. IR (KBr): *v*= 1682 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 276 $[M-N_2]^+$ (100), 304 $[M+H]^+$ (90), 306 [M+2] (30), 345 $[M+H+CH_3CN]^+$ (20). $C_{15}H_{18}ClN_5$: C 59.30, H 5.97, N 23.05; found C 59.35, H 6.04, N 23.02.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(3-chlorophenyl)-1*H*-1,2,3-triazole (7g): White solid (66%), m.p. 147-150°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.11 (s, 9H, CH_3), 4.28 (t, $^4J_{H,H}$ = 4.7 Hz, 2H, CH_2-C), 4.84 (t, $^4J_{H,H}$ = 4.7 Hz, 2H, CH_2-N=), 7.45 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, Ar), 7.52 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar), 7.97 (d, $^3J_{H,H}$ = 7.7 Hz, 1H, Ar), 8.06 (s, 1H, Ar), 9.30 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.9 (C-CH_3), 74.3 (CH_2-N=), 124.1 (Ar), 125.3 (C-5 triazole), 128.2 (Ar), 130.7 (Ar), 131.4 (Ar), 133.6 (Ar), 145.7 (C-4 triazole), 157.5 (-C=N) ppm. IR (KBr): *v*= 1682 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 276 $[M-N_2]^+$ (85), 304 $[M+H]^+$ (100), 306 [M+2] (30), 345 $[M+H+CH_3CN]^+$ (15). $C_{15}H_{18}ClN_5$: C 59.30, H 5.97, N 23.05; found C 59.35, H 6.04, N 23.02.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(2,4-dichloro-phenyl)-1*H*-1,2,3-triazole (7h): White solid (90%), m.p. 142-147°C, ^{1}H NMR (400 MHz, $CDCl_3$, 50ºC): δ= 1.18 (s, 9H, CH_3), 4.39 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.91 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 7.39 (dd, $^3J_{H,H}$ = 8.5, $^3J_{H,H}$ = 1.9 Hz, 1H, Ar), 7.51 (d, $^3J_{H,H}$ = 1.9 Hz, 1H, Ar), 8.24 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, Ar), 8.91 (s, 1H, H-5 triazole) ppm. IR (KBr): *v*= 1682 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 312 $[M-N_2]^+$ (10), 338 $[M]^+$ (70), 340 [M+2] (100), 342 [M+4] (10), 345 $[M+H+CH_3CN]^+$ (15). $C_{15}H_{17}Cl_2N_5$: C 53.26, H 5.07, N 20.71; found C 53.35, H 5.11, N 20.69.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(4-trifluoromethyl-phenyl)-1*H*-1,2,3-triazole (7i): Light yellow solid (72%); m.p. 127-130°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.12 (s, 9H, CH_3), 4.29 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.85 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 7.84 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 8.22 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 9.37 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.9 (C-CH_3), 74.3 (CH_2-N=), 119.8 (C-5 triazole), 122.6 (CF_3), 125.3 (Ar), 125.7 (q, $^3J_{C,F}$ = 3.5 Hz, CH-CF_3), 126.2 (Ar), 128.6 (sept, $^2J_{C,F}$ = 31.9 Hz, C-CF_3), 133.3 (Ar), 145.6 (C-4 triazole), 157.5 (-C=N) ppm. IR (KBr): *v*= 1682 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 310 $[M-N_2]^+$ (20), 338 $[M+H]^+$ (100), 345 $[M+H+CH_3CN]^+$ (15). HRMS (ESI): calcd. for $C_{16}H_{18}F_3N_5$ $[M+H]^+$ 338.1592; found 338.1597.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(3-trifluoromethyl-phenyl)-1*H*-1,2,3-triazole (7j): Light yellow solid (75%), m.p. 114-117°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.12 (s, 9H, CH_3), 4.29 (t, $^4J_{H,H}$ = 4.6 Hz, 2H, CH_2-C), 4.85 (t, $^4J_{H,H}$ = 4.6 Hz, CH_2-N=), 7.65-7.83 (m, 2H, Ar), 8.27-8.41 (m, 2H, Ar), 9.41 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.9 (C-CH_3), 74.2 (CH_2-N=), 119.6 (C-5 triazole), 122.0 (q, $^3J_{C,F}$ = 3.8 Hz, CH-CF_3), 122.5 (CF_3), 124.9 (q, $^3J_{C,F}$ = 3.8 Hz, CH-CF_3), 125.2 (CF_3), 129.4 (Ar), 129.6 (Ar), 129.9 (Ar), 130.5 (Ar), 145.6 (C-4 triazole), 157.5 (-C=N) ppm. IR (KBr): *v*= 1677 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 310 $[M-N_2]^+$ (20), 338 $[M+H]^+$ (100), 345 $[M+H+CH_3CN]^+$ (15). HRMS (ESI): calcd. for $C_{16}H_{18}F_3N_5$ $[M+H]^+$ 338.1592; found 338.1596.

1-(1-*tert*-Butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-(3-methoxy-phenyl)-1*H*-1,2,3-triazole (7k): White solid (61%), m.p. 108-111°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.12 (s, 9H, C-CH_3), 3.83 (s, 3H, O-CH_3), 4.28 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-C), 4.84 (t, $^4J_{H,H}$ = 4.8 Hz, 2H, CH_2-N=), 6.96 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 2.4 Hz, 1H, Ar), 7.39 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 7.52-7.59 (m, 2H, Ar), 9.22 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 25.7 (CH_3), 50.7 (CH_2-C), 51.9 (C-CH_3), 55.1 (O-CH_3), 74.2 (CH_2-N=), 110.9 (Ar), 114.4 (Ar), 117.9 (Ar), 118.6 (C-5 triazole), 129.9 (Ar), 130.6 (Ar), 146.9 (C-4 triazole), 157.5 (-C=N), 159.6 (Ar) ppm. IR (KBr): *v*= 1671 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 272 $[M-N_2]^+$ (100), 300 $[M+H]^+$ (92). HRMS (ESI): calcd. for $C_{16}H_{21}N_5O$ $[M+H]^+$ 300.1824; found 300.1824.

General Procedure for the Synthesis of Substituted 1-(1-*tert*-butyl-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles (1a-k):

4,5-dichloro-3,6-dioxo-cyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) (147 mg, 0.65 mmol) was added portionwise to the solution of 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles **7 a-k** (0.5 mmol) in anhydrous dichloromethane. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete according to TLC the solvent was removed at reduced pressure and the residue was purified by flash chromatography (EtOAc/*n*-hexane, 30:70) to give the desired products **1a-k** as colorless solids.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazole (1a): White solid (91%), m.p. 80-81°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.55 (s, 9H, CH_3), 7.79 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH-N), 7.82 (d, $^3J_{H,H}$ = 1.0 Hz, 1H, H-4 triazole), 7.84 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH-C), 8.39 (d, $^3J_{H,H}$ = 1.0 Hz, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ= 29.6 (CH_3), 55.7 (C-CH_3), 107.5 (C-5-imidazole), 122.5 (C-5 triazole), 133.0 (C-2-imidazole) 133.1 (C-4 triazole) 136.5 (C-4-imidazole) ppm. IR (KBr): *v*= 3133 (C-H Ar), 1592 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 192 $[M+H]^+$ (100). $C_9H_{13}N_5$: C 56.53, H 6.85, N 36.62; found C 56.60, H 6.88, N 36.52.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazole (1a) and 2-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-2*H*-1,2,3-triazole (9a): The mixture of 1-(1-*tert*-butyl-3-nitro-azetidin-3-yl)-1*H*-1,2,3-triazole **6a** (225 mg, 1 mmol) and triethyl phosphite (332 mg, 2 mmol) in benzene (3 mL) was stirred at reflux for 60h. After the completion of reaction (GC-MS control), the solvent was removed under reduced pressure. The residue was dissolved in anhydrous dichloromethane and 4,5-dichloro-3,6-dioxo-cyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) (454 mg, 2 mmol) was added portionwise to this solution. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete according to TLC the solvent was removed at reduced pressure The residue was purified by preparative RP-HPLC to afford the pure **1a** (60 mg 31%) as a white solid and **9a** (44 mg, 23 %) as a white solid, m.p. 127-130°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ=1.57 (s, 9H, C-CH_3), 7.68 (d, $^4J_{H,H}$ = 1.67

Hz, 1H, CH-N), 7.84 (d, $^4J_{H,H}$ = 1.5 Hz, 1H, CH-C), 7.94 (s, 2H, CH-triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3-C), 55.6 (C-CH_3), 107.9 (C-5-imidazole), 132.7 (C-2-imidazole), 134.9 (C-4,5 triazole) , 139.6 (C-4-imidazole) ppm. IR (KBr): *v*= 3109 (C-H Ar), 2977 (C-H aliphatic), 1587 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 192 $[M+H]^+$ (100). $C_9H_{13}N_5$: C 56.53, H 6.85, N 36.62; found C 56.60, H 6.88, N 36.52.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole (1b): White solid (76%), m.p. 132-133°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.31 (s, 9H, Si-CH_3), 1.58 (s, 9H, C-CH_3), 7.79 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.85 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.40 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= -1.3 (CH_3-Si), 29.6 (CH_3-C), 55.7 (C-CH_3), 107.6 (C-5-imidazole), 128.1 (C-5 triazole), 133.1 (C-2-imidazole), 136.3 (C-4-imidazole), 144.7 (C-4 triazole) ppm. IR (KBr): *v*= 3101 (C-H Ar), 1583 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 236 (10) $[M-N_2]^+$, 264(100) $[M+H]^+$. $C_{12}H_{21}N_5Si$: C 54.72, H 8.04, N 26.59; found C 54.80, H 8.08, N 26.52.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-cyclopropyl-1*H*-1,2,3-triazole (1c): White solid (92%), m.p. 93-95°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 0.74-0.82 (m, 2H, CH_2), 0.88-0.97 (m, 2H, CH_2), 1.55 (s, 9H, CH_3), 1.93-2.10 (m, 1H, CH), 7.81 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.86 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.16 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 6.5 (CH_2), 7.8 (CH-CH_2), 29.8 (CH_3), 55.9 (C-CH_3), 107.5 (C-5-imidazole), 118.6 (C-5 triazole), 133.2 (C-2-imidazole), 136.7 (C-4-imidazole), 149.2 (C-4 triazole) ppm. IR (KBr): *v*= 3134 (C-H Ar), 1599 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 204 (50) $[M-N_2]^+$, 232 (100) $[M+H]^+$. HRMS (ESI): calcd. for $C_{12}H_{17}N_5$ 232.1562; found 232.1560.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole (1d): White solid (95%), m.p. 99-101°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.34-7.38 (t, $^3J_{H,H}$ = 7.38 Hz, 1H, Ar), 7.45-7.49 (t, $^3J_{H,H}$ = 7.64 Hz, 2H, Ar), 7.88 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.93-8.00 (m, 2H, Ar), 7.91 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.90 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.8 (C-CH_3), 107.6 (C-5-imidazole), 118.9 (C-5 triazole), 125.2 (Ar), 127.8 (Ar), 128.6 (Ar), 130.2 (Ar), 133.2 (C-2-imidazole), 136.3 (C-4-imidazole), 146.1 (C-4 triazole) ppm. IR (KBr): *v*= 3118 (C-H Ar), 1598 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 268 $[M+H]^+$ (100). $C_{15}H_{17}N_5$: C 67.39, H 6.41, N 26.20; found C 67.45, H 6.48, N 26.07.

2-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-phenyl-2*H*-1,2,3-triazole (9d): product was obtained similarly **9a.** White solid (42%), m.p. 208-210 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.59 (s, 9H, CH_3), 7.41 (m, 1H, Ar), 7.50 (m, 2H, Ar), 7.76 (d, ^4J = 1.7 Hz, 1H, CH-C), 7.83 (d, ^4J = 1.7 Hz, 1H, CH-N), 7.93 (m, 2H, Ar), 8.42 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.62 (CH_3), 55.63 (C-CH_3) , 107.97 (C-5-imidazole), 125.58 (Ar), 128.41 (Ar), 128.74 (Ar), 129.55 (Ar), 132.12 (C-5 triazole), 132.79 (C-2-imidazole), 139.55 (C-4 triazole), 147.31(C-4-imidazole) ppm. IR (KBr): *v*= 3081 (C-H Ar), 1571 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 268 $[M+H]^+$ (100). $C_{15}H_{17}N_5$: C 67.39, H 6.41, N 26.20; found C 67.45, H 6.48, N 26.07.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(2-fluorophenyl)-1*H*-1,2,3-triazole (1e): White solid (85%), m.p. 138-140°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.32-7.40 (m, 2H, Ar), 7.41-7.49 (m, 1H, Ar), 7.91 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.93 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.17 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, Ar), 8.61 (d, $^5J_{H,F}$ = 3.5 Hz, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 107.8 (C-5-imidazole), 115.7 (d, $^4J_{C,F}$ = 21.3 Hz, C-5 triazole), 117.9 (Ar), 120.8 (d, $^2J_{C,F}$ = 10.55 Hz, C-F), 124.7 (Ar), 127.5 (Ar), 129.7 (Ar), 133.3 (C-2-imidazole), 136.1 (C-4-imidazole), 139.7 (C-4 triazole), 159.7 (Ar) ppm. IR (KBr): *v*= 3116 (C-H Ar), 1602 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 258 $[M-N_2]^+$ (10), 286 $[M+H]^+$ (100). $C_{15}H_{16}FN_5$: C 63.14, H 5.65, N 24.55; found C 63.17, H 5.60, N 24.56.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(2-chlorophenyl)-1*H*-1,2,3-triazole (1f): White solid (92%), m.p. 146-148°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.38-7.53 (m, 2H, Ar), 7.59 (d, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 7.92 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.93 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.10 (dd, $^3J_{H,H}$ = 7.7, $^3J_{H,H}$ = 1.5 Hz, 1H, Ar), 8.80 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 107.9 (C-5-imidazole), 121.4 (C-5 triazole), 127.3 (Ar), 128.7 (Ar), 129.5 (Ar), 129.6 (Ar), 130.0 (Ar), 130.5 (Ar), 133.3 (C-2-imidazole), 136.1 (C-4-imidazole), 142.6 (C-4 triazole) ppm. IR (KBr): *v*= 3126 (C-H Ar), 1596 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 274 $[M-N_2]^+$ (10), 302 $[M+H]^+$ (100), 304 [M+2] (30). $C_{15}H_{16}ClN_5$: C 59.70, H 5.34, N 23.21; found C 59.73, H 5.40, N 23.25.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(3-chlorophenyl)-1*H*-1,2,3-triazole (1g): White solid (93%), m.p. 163-165°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.40 (dd, $^3J_{H,H}$ = 7.1, $^3J_{H,H}$ = 1.9 Hz, 1H, Ar), 7.49 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 7.88 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-N), 7.91 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-C), 7.94 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar), 8.02 (t, $^3J_{H,H}$ = 1.8 Hz, 1H), 9.02 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 107.7 (C-5-imidazole), 119.7 (C-5 triazole), 123.7 (Ar), 124.8 (Ar), 127.6 (Ar), 130.6 (Ar), 132.3 (Ar), 133.3 (C-2-imidazole), 133.5 (Ar), 136.2 (C-4-imidazole), 144.8 (C-4 triazole) ppm. IR (KBr): *v*= 3122 (C-H Ar), 1604 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 274 $[M-N_2]^+$ (10), 302 $[M+H]^+$ (100), 304 [M+2] (30). $C_{15}H_{16}ClN_5$: C 59.70, H 5.34, N 23.21; found C 59.73, H 5.40, N 23.25.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(2,4-dichlorophenyl)-1*H*-1,2,3-triazole (1h): White solid (95%), m.p. 153-154°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.56 (dd, $^3J_{H,H}$ = 8.5, $^3J_{H,H}$ = 2.2 Hz, 1H, Ar), 7.75 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, Ar), 7.92 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-N), 7.94 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-C), 8.12 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, Ar), 8.84 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 108.0 (C-5-imidazole), 121.5 (C-5 triazole), 127.6 (Ar), 127.7 (Ar), 129.5 (Ar), 130.7 (Ar), 131.3 (Ar), 133.2 (C-2-imidazole), 133.4 (Ar), 136.0 (C-4-imidazole) 141.7 (C-4 triazole) ppm. IR (KBr): *v*= 3116 (C-H Ar), 1602 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 307 $[M-N_2]^+$ (36), 336 $[M]^+$ (100), 338 [M+2] (71), 340 [M+4] (31). $C_{15}H_{15}Cl_2N_5$: C 53.58, H 4.50, N 20.83; found C 53.55, H 4.40, N 20.80.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-[4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (1i): White solid (60%), m.p. 134-136°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, CH_3), 7.82 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 7.91 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-N), 7.93 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-C), 8.20 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 9.10 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 107.8 (C-5-imidazole), 120.2 (C-5 triazole), 125.6 (CF_3), 125.8 (Ar), 128.2 (Ar), 133.3 (C-2-imidazole), 134.2 (Ar), 136.1 (C-4-imidazole), 144.8 (C-4 triazole) ppm. IR (KBr): *v*= 3196 (C-H Ar), 1634 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 308

$[M-N_2]^+$ (14), 336 $[M+H]^+$ (100). HRMS (ESI): calcd. for $C_{16}H_{16}F_3N_5$ $[M+H]^+$ 336.1435; found 336.1432.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-[3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (1j): White solid (74%), m.p. 152-154°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 6H, CH_3), 7.69-7.75 (m, 2H, Ar), 7.90 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-N), 7.93 (d, $^4J_{H,H}$ = 1.7 Hz, 1H, CH-C), 8.23-8.34 (m, 2H, Ar), 9.15 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.9 (C-CH_3), 107.7 (C-5-imidazole), 119.9 (C-5 triazole), 121.5 (CF_3), 122.6 (Ar), 124.2 (Ar), 125.3 (CF_3), 129.0 (Ar), 129.5 (Ar), 129.8 (Ar), 131.3 (Ar), 133.3 (C-2-imidazole), 136.2 (C-4-imidazole), 144.7 (C-4 triazole) ppm. IR (KBr): *v*= 3144 (C-H Ar), 1596 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 308 $[M-N_2]^+$ (20), 336 $[M+H]^+$ (100). HRMS (ESI): calcd. for $C_{16}H_{16}F_3N_5$ $[M+H]^+$ 336.1435; found 336.1431.

1-(1-*tert*-Butyl-1*H*-imidazol-4-yl)-4-(3-methoxyphenyl)-1*H*-1,2,3-triazole (1k): White solid (78%), m.p. 115-117°C. ^{1}H NMR (400 MHz, DMSO-d_6, 50ºC): δ= 1.60 (s, 9H, C-CH_3), 3.84 (s, 3H, O-CH_3), 6.93 (dd, $^3J_{H,H}$ = 8.2, $^3J_{H,H}$ = 1.8 Hz, 1H, Ar), 7.37 (t, $^3J_{H,H}$ = 7.9 Hz, 1H, Ar), 7.54 (t, $^3J_{H,H}$ = 5.7 Hz, 2H, Ar), 7.87 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-N), 7.91 (d, $^4J_{H,H}$ = 1.6 Hz, 1H, CH-C), 8.94 (s, 1H, H-5 triazole) ppm. ^{13}C NMR (100 MHz, DMSO-d_6, 50ºC): δ= 29.6 (CH_3), 55.0 (CH_3-O), 55.8 (C-CH_3), 107.6 (C-5-imidazole), 110.5 (Ar), 113.8 (Ar), 117.5 (Ar), 119.2 (C-5 triazole), 129.7 (Ar), 131.5 (Ar), 133.2 (C-2-imidazole), 136.3 (C-4-imidazole), 146.0 (C-4 triazole), 159.6 (Ar) ppm. IR (KBr): *v*= 3115 (C-H Ar), 1596 (C=N) cm^{-1}. MS (APCI, 30 EV), *m/z* (I_{rel},%): 270 $[M-N_2]^+$ (30), 298 $[M+H]^+$ (100). HRMS (ESI): calcd. for $C_{16}H_{19}N_5O$ $[M+H]^+$ 298.1667; found 298.1669.

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