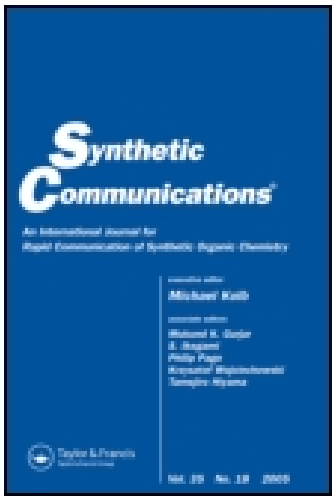

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SYNTHESIS OF 5-IMINO-1,2,4-OXADIAZOLIDIN-3-ONE

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SYNTHESIS OF 5-IMINO-1,2,4-OXADIAZOLIDIN-3-ONE

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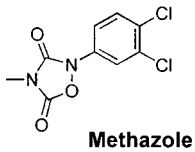
ABSTRACT

N-Aryl-*N*-cyanocarbamoyl chloride and *N*-aryl-*N*-carbomethoxy-cyanamide were reacted with *N*-alkylhydroxylamines to afford selectively 2-alkyl-4-aryl-5-imino-1,2,4-oxazolidin-3-one and 2-alkyl-4-aryl-3-imino-1,2,4-oxadiazolidin-5-one, respectively.

Those compounds with frameworks of 1,2,4-oxadiazolidine or its analogues have diverse biological activities.[1] For example, 1,2,4-oxadiazolidine-3,5-dione, embodies the backbone of herbicides such as methazole and BAS-3820. Relating to the structural modification of 1,2,4-oxadiazolidine-3,5-dione, the carbonyl group at C-3 or C-5 can be modified to an imino group. Several methods on the syntheses of 3-alkyl- (or aryl) imino-1,2,4-oxadiazolidin-5-one have been reported.[2–5] Nonetheless, the synthesis of 1,2,4-oxadiazolidin-5-one with free imino at 3-position has not yet been disclosed.

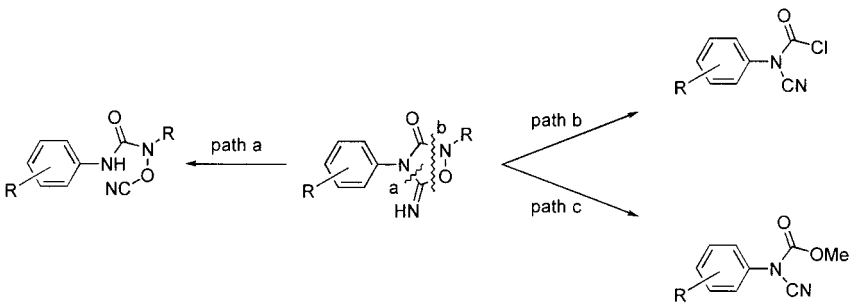
*Corresponding author.



Methazole

BAS-3820

We report herein the first synthesis of 5-imino-1,2,4-oxadiazolidin-3-ones as well as 3-imino-1,2,4-oxadiazolidin-5-ones. In our initial synthetic plan for the synthesis of 5-imino-1,2,4-oxadiazolidin-3-ones, carbodiimide was excluded as a starting material utilizing 1,3-dipolar cycloaddition, because it cannot produce the free imino group and besides, it is rather difficult to prepare unsymmetrical carbodiimides. Careful examination of structure of the desired product infers to the reaction routes shown in the Scheme 1. Cleavage at the bond-a of the product discloses the construction of framework from the cyclization reaction of *N*-cyanourea which can be built upon *N*-hydroxy-*N*-alkyl-*N*′-arylurea (path a). Alternatively, the cleavage at the bond-b of the product indicates the synthesis of the product from the *N*-cyano-*N*-arylcarbamoyl chloride (path b) or its equivalent, i.e., an ester of *N*-cyano-*N*-arylcarbamate (path c).



Scheme 1.

The reaction of aniline and cyanogen bromide generated in situ in an aqueous solution provided *N*-phenylcyanamide as a semihydrate, which was subjected to the treatment with excess of phosgene to obtain *N*-cyano-*N*-phenylcarbamoyl chloride (**1a**).[6] Subsequent reaction of this carbamoyl chloride with *N*-methylhydroxylamine in anhydrous acetonitrile in the presence of organic base such as triethylamine or pyridine led to a mixture of desired product (**6a**) and its isomers (**7a**). However, the reaction of this

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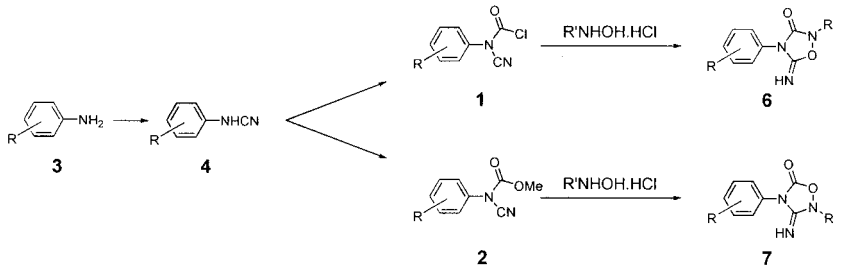
carbamoyl chloride (**1a**) with *N*-isopropylhydroxylamine[7,8] in anhydrous methanol in the presence of inorganic base such as sodium bicarbonate at low temperature gave selectively the desired 5-imino-2-isopropyl-4-phenyl-1,2,4-oxadiazolidin-3-one (**6e**) in almost quantitative yield (Scheme 2). The synthetic methodology employing the inorganic base circumvented the generation of the isomeric product and seems to be usually applicable to prepare 2-alkyl-4-aryl-5-imino-1,2,4-oxadiazolidin-3-ones (**6a–h**).



Scheme 2.

As a supplementary route to the previous reaction of carbamoyl derivatives, from the reaction of *N*-phenylcyanamide semihydrate with methyl chloroformate, *N*-carbomethoxy-*N*-phenylcyanamide (**2a**) was obtained. When this compound was allowed to react with equimolar amount of *N*-isopropyl-hydroxylamine in refluxing ether, a mixture of the desired product (**6e**) and its isomeric product (**7f**) in the ratio of 54 : 46 was obtained. As it was the case of 5-imino-1,2,4-oxadiazolidin-3-one, we hoped that the use of inorganic base would differentiate the reactivities between *N*-cyano group and carbamate group. Indeed, the utilization of sodium bicarbonate furnished solely the isomeric product (**7f**) in 72% yield. The structure of this isomer was determined as 3-imino-1,2,4-oxadiazolidin-5-one deduced from the spectroscopic data. A fragmental pattern of its mass spectrum showing the expulsion of carbon dioxide from the molecular ion implied the presence of cyclic carbamate. ^{1}H NMR spectrum of the isomeric product showed a singlet at δ 10.1 ppm, which is analogous to that of the guanidine, indicative of the presence of 3-imino group, while characteristic 5-imino group of the desired product at δ 6.07 ppm was comparable to that of the imino ester. The absorption peak of infrared spectroscopic data showed the difference between 3-imino-1,2,4-oxadiazolidin-5-one (**7**) and 5-imino-1,2,4-oxadiazolidin-3-one (**6**). Compound **6** showed C=O stretching frequency at 1786 cm^{-1} and C=N stretching frequency for the above isomer at 1668 cm^{-1}, whereas **7** showed absorptions at 1738 and 1625 cm^{-1} for C=O and C=N

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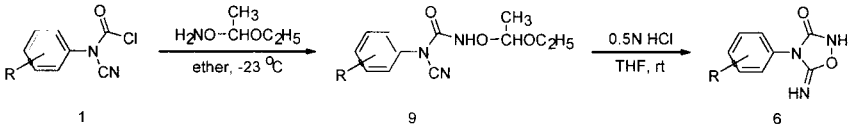
stretchings, respectively. Especially, the feature revealing marked difference between C=N stretchings for the above isomer was found to be consistent for other analogous compounds we prepared. This process allowed easy access to *ortho*-substituted 5-imino-1,2,4-oxadiazolidin-3-one (**6**). Judging from the experimental evidence in the presence of inorganic base the reactivity toward nucleophilic agents decreases in the order of carbamoyl > *N*-cyanide > carbamate. According to substrates, carbamoyl chloride (**1**) or carbomethoxycyanamide (**2**), and the reaction condition, 5-imino-1,2,4-oxadiazolidin-3-one (**6**) and 3-imino-1,2,4-oxadiazolidin-5-one (**7**) could be obtained as a sole product. The results are summarized in Table 1.

After the successful synthesis of 3-imino and 5-imino-1,2,4-oxazolidin-5(3)-ones with unsubstituted phenyl group, we undertook the preparation of *ortho*-substituted phenyl derivatives from the reaction of *N*-*ortho*-substituted phenyl-*N*-carbomethoxycyanamide (**2**) and *N*-alkylhydroxylamine. However, in contrast to the *N*-alkylhydroxylamines, we could only obtain the reaction intermediates of 2-hydroxyguanidine from the reaction of *N*-aryl-*N*-carbomethoxycyanamide with hydroxylamine hydrochloride. These intermediates were found to be defying the cyclization conditions. It seems that this difficulty is originated from the steric hindrance caused by the ortho substituents.

In addition to 2-alkyl substituted derivatives, we employed *o*-protected hydroxylamine in other to provide the free form at 2-position of 4-aryl-5-imino-1,2,4-oxadiazolidin-3-one. In the course of our synthesis, hydroxylamine was protected as ethoxyethyloxyamine and was allowed to react with carbamoyl chloride. The resulting reaction intermediate was simultaneously deprotected and eventually cyclized to the desired product under the acidic condition as shown in Scheme 3. This reaction was found to be achievable so far only *ortho*-methyl derivative perhaps because of acid lability of ethoxyethyloxy group in general and unexpected explosive nature of the reaction.



Scheme 3.

It is noteworthy that there are existing discrepancy between our physical and spectral data for 5-imino-2-methyl-4-phenyl-1,2,4-oxadiazolidin-3-one (**6a**) and 3-imino-2-methyl-4-phenyl-1,2,4-oxadiazolidin-5-one (**7a**)

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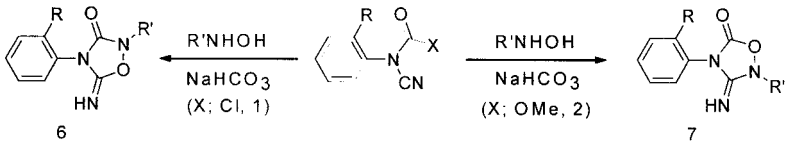
Table 1. Reaction of *N*-Cyano-*N*-arylcarbamoyl Chloride (1a–d) and *N*-Aryl-*N*-carbomethoxycyanamide (2a–e) with *N*-Alkylhydroxylamine (5)



Substrate	X	R	R'	Product	Yield(%) [a]
1a	Cl	H	Me	6a	98
1b	Cl	Me	Me	6b	98
1c	Cl	OMe	Me	6c	98
1d	Cl	Cl	Me	6d	98
1a	Cl	H	$(Me)_2CH$	6e	93
1b	Cl	Me	$(Me)_2CH$	6f	94
1c	Cl	OMe	$(Me)_2CH$	6g	95
1d	Cl	Cl	$(Me)_2CH$	6h	97
2a	OMe	H	Me	7a	75
2b	OMe	Me	Me	7b	58
2c	OMe	OMe	Me	7c	72
2d	OMe	Cl	Me	7d	58
2e	OMe	NO_2	Me	7e	92
2a	OMe	H	$(Me)_2CH$	7f	72
2b	OMe	Me	$(Me)_2CH$	7g	86
2c	OMe	OMe	$(Me)_2CH$	7h	80
2d	OMe	Cl	$(Me)_2CH$	7i	78
2e	OMe	NO_2	$(Me)_2CH$	7j	87
2e	OMe	H	H	7k	93

[a] Isolated yield.

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and those reported previously in the literature. It seems that our structural assignment is correct because of our consistency in the synthesis.

EXPERIMENTAL SECTION

General: Melting points were measured in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz, unless otherwise specified, in $CDCl_3$ solution using tetramethylsilane as internal standard. Analytical thin-layer chromatography was performed on precoated silica gel plates (0.25-mm 60 F-254 E. Merck). THF was dried over sodium benzophenone prior to use.

General procedure for 2-alkyl-4-aryl-5-imino-1,2,4-oxadiazolidin-3-one (6a–h): A slurry of *N*-alkyl or hydroxylamine hydrochloride (5.0 mmol), anhydrous $NaHCO_3$ (30.0 mmol) in dry methanol (20 ml) was stirred for 20 min at room temperature and then the temperature was lowered to −78°C. *N*-Cyano-*N*-arylcarbamoyl chloride (**1**) (5.0 mmol) in THF (5 ml) was added dropwise for 10 min. The stirring was continued for 30 min at −78°C and the reaction temperature was allowed to rise slowly to room temperature and the reaction mixture was stirred for 1.5 h. The reaction mixture was combined with EtOAc (100 ml), washed with saturated brine, and dried over $MgSO_4$. After evaporation of solvent under the reduced pressure, the residue was column chromatographied on silica gel by eluting with CH_2Cl_2/EtOAc (3/1) to afford **6** as white solids.

2-Methyl-4-phenyl-5-imino-1,2,4-oxadiazolidin-3-one (6a): Yield 98%; m.p. 102.5–103°C; ^{1}H NMR (300 MHz) δ 7.30 (br, s, 5H, Ph), 5.80 (br, s, 1H, NH), 3.20 (s, 3H, CH_3); IR (KBr) 3232 (NH), 1756 (CO), 1681 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 192 ($M^+ + 1$, 19.0), 191 (M^+, 10.5), 134 (100), 118 (53.1), 91 (98.5), 90 (87.1), 64 (57.5). Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.75; N, 21.98. Found: C, 56.61; H, 4.73; N, 22.01.

2-Methyl-4-(2-methylphenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6b): Yield 98%; m.p. 84.5–85°C; ^{1}H NMR (300 MHz) δ 7.00–7.50 (m, 4H, aromatic), 5.60 (br, s, 1H, NH), 3.22 (s, 3H, CH_3), 2.17 (s, 3H, CH_3); IR (KBr) 3313 (NH), 1771 (CO), 1700 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 205 (M^+, 10.6), 160 (42.2), 104 (100), 78 (45.2). Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.59; H, 5.28; N, 20.50.

2-Methyl-4-(2-methoxyphenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6c): Yield 98%; m.p. 135–136°C; ^{1}H NMR (300 MHz) δ 6.80–7.60 (m, 4H, aromatic), 5.55 (br, s, 1H, NH), 3.77 (s, 3H, OCH_3), 3.30 (s, 3H, CH_3); IR (KBr) 3291 (NH), 1760 (CO), 1694 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 222 ($M^+ + 1$, 11.2), 221 (M^+, 56.1), 220 (36.5), 133 (61.1), 120 (100), 78 (48.8),

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51 (52.7). Anal. Calcd for $C_{10}H_{11}N_3O_3$: C, 54.30; H, 5.01; N, 19.00. Found: C, 54.41; H, 5.00; N, 19.08.

2-Methyl-4-(2-chlorophenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6d): Yield 98%; ^{1}H NMR (300 MHz) δ 7.00–7.70 (m, 4H, aromatic), 5.95 (br, s, 1H, NH), 3.30 (s, 3H, CH_3); IR (KBr) 3281 (NH), 1759 (CO), 1680 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 226 (M^+, 11.0), 190 (28.3), 120 (100), 78 (48.8), 51 (52.7). Anal. Calcd for $C_9H_8ClN_3O_2$: C, 47.91; H, 3.57; N, 18.62. Found: C, 47.89; H, 3.65; N, 18.65.

2-Isopropyl-4-phenyl-5-imino-1,2,4-oxadiazolidin-3-one (6e): Yield 93%; m.p. 64–64.5°C; ^{1}H NMR (300 MHz) δ 7.40 (br, s, 5H, aromatic), 6.07 (br, s, 1H, NH), 4.20 (m, 1H, CH), 1.25 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3302 (NH), 1786 (CO), 1668 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 220 ($M^+ + 1$, 32.2), 219 (M^+, 7.1), 175 (97.5), 91 (40.2), 77 (40.3), 43 (100), 41 (54.3). Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.23; H, 6.05; N, 19.18.

2-Isopropyl-4-(2-methylphenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6f): Yield 94%; m.p. 64–64.5°C; ^{1}H NMR (300 MHz) δ 6.90–7.50 (m, 4H, aromatic), 5.71 (br, s, 1H, NH), 4.20 (m, 1H, CH), 2.22 (s, 3H, CH_3), 1.35 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3298 (NH), 1788 (CO), 1669 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 234 ($M^+ + 1$, 7.2), 233 (M^+, 12.5), 146 (100), 104 (44.6), 43 (47.0). Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.69; H, 6.49; N, 17.96.

2-Isopropyl-4-(2-methylphenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6g): Yield 95%; m.p. 88.5–89°C; ^{1}H NMR (300 MHz) δ 6.80–7.70 (m, 4H, aromatic), 5.70 (br, s, 1H, NH), 4.25 (m, 1H, CH), 3.77 (s, 3H, OCH_3), 1.35 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3297 (NH), 1784 (CO), 1674 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 250 ($M^+ + 1$, 29.1), 249 (M^+, 12.5), 218 (39.2), 149 (53.4), 120 (71.3), 78 (38.1), 43 (100), 41 (61.6). Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.89; H, 6.04; N, 16.79.

2-Isopropyl-4-(2-chlorophenyl)-5-imino-1,2,4-oxadiazolidin-3-one (6h): Yield 97%; m.p. 82–83°C; ^{1}H NMR (300 MHz) δ 7.20–7.70 (m, 4H, aromatic), 5.85 (br, s, 1H, NH), 4.20 (m, 1H, CH), 1.42 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3297 (NH), 1785 (CO), 1670 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 254 (M^+, 22.6), 253 (17.9), 211 (55.5), 210 (44.1), 132 (32.9), 43 (100), 41 (54.1). Anal. Calcd for $C_{11}H_{12}ClN_3O_2$: C, 52.08; H, 4.77; N, 16.56. Found: C, 52.21; H, 4.76; N, 16.60.

General procedure for 2-alkyl-4-aryl-3-imino-1,2,4-oxadiazolidin-5-one (7a–k): A mixture of *N*-carbomethoxy-*N*-arylcyanamide (5.0 mmol), *N*-alkyl or hydroxylamine hydrochloride (5.0 mmol), and anhydrous $NaHCO_3$ (20.0 mmol) in dry THF (20 ml) was stirred 1.5 h at room temperature under nitrogen atmosphere. The insoluble solids were filtered off

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and the filtrate was concentrated under the reduced pressure to afford crude product, which was purified on the silica gel column eluted with CH_2Cl_2/THF (10/1) to furnish the product as white solids. For analytical sample, the product was recrystallized from isopropyl alcohol.

3-Imino-2-methyl-4-phenyl-1,2,4-oxadiazolidin-5-one (7a): Yield 75%: m.p. 205–205.5°C; ^{1}H NMR (300 MHz) δ 9.50 (br, s, 1H, NH), 680–7.50 (m, 5H, aromatic), 3.35 (s, 3H, NCH_3); IR (KBr) 3141 (NH), 1773 (CO), 1615 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 191 (M^+, 23.5), 165 (45.5), 146 (100), 98 (60.0). Anal. Calcd for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.41; H, 4.80; N, 21.91.

3-Imino-2-methyl-4-(2-methylphenyl)-1,2,4-oxadiazolidin-5-one (7b): Yield 58%: m.p. 144.5–145°C; ^{1}H NMR (300 MHz) δ 9.30 (br, s, 1H, NH), 6.80–7.50 (m, 4H, aromatic), 3.35 (s, 3H, NCH_3), 2.20 (s, 3H, CH_3); IR (KBr) 3151 (NH), 1774 (CO), 1611 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 205 (M^+, 53.8), 162 (24.5), 159 (100), 118 (66.7). Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.51; H, 5.49; N, 20.55.

3-Imino-2-methyl-4-(2-methoxyphenyl)-1,2,4-oxadiazolidin-5-one (7c): Yield 72%: m.p. 119.5–120°C; ^{1}H NMR (300 MHz) δ 9.00 (br, s, 1H, NH), 6.50–7.90 (m, 4H, aromatic), 3.71 (s, 3H, OCH_3), 3.37 (s, 3H, NCH_3); IR (KBr) 3247 (NH), 1723 (CO), 1604 (C = N) cm^{-1}; MS *m/e* (rel. intensity) 222 ($M^+ + 1$, 20.6), 221 (M^+, 97.7), 175 (100), 56 (88.1). Anal. Calcd for $C_{10}H_{11}N_3O_3$: C, 54.30; H, 5.01; N, 19.00. Found: C, 54.38; H, 5.02; N, 18.91.

3-Imino-2-methyl-4-(2-chlorophenyl)-1,2,4-oxadiazolidin-5-one (7d): Yield 58%: m.p. 144–144.4°C; ^{1}H NMR (300 MHz) δ 9.25 (br, s, 1H, NH), 6.85–7.75 (m, 4H, aromatic), 3.49 (s, 3H, NCH_3); IR (KBr) 3205 (NH), 1730 (CO), 1598 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 227 ($M^+ + 1$, 14.7), 226 (M^+, 23.9), 179 (100), 83 (80.1). Anal. Calcd for $C_9H_8ClN_3O_2$: C, 47.91; H, 3.57; N, 18.62. Found: C, 48.01; H, 3.56; N, 18.65.

3-Imino-2-methyl-4-(2-nitrophenyl)-1,2,4-oxadiazolidin-5-one (7e): Yield 92%: m.p. 153.5–154.5°C; ^{1}H NMR (300 MHz) δ 10.1 (br, s, 1H, NH), 7.10–8.20 (m, 4H, aromatic), 3.47 (s, 3H, NCH_3); IR (KBr) 3198 (NH), 1776 (CO), 1603 (C=N) cm^{-1}. Anal. Calcd for $C_9H_8N_4O_4$: C, 45.77; H, 3.41; N, 23.72. Found: C, 45.88; H, 3.40; N, 23.64.

2-Isopropyl-3-imino-4-phenyl-1,2,4-oxadiazolidin-5-one (7f): Yield 72%: m.p. 137.5–138.5°C; ^{1}H NMR (300 MHz) δ 10.01 (br, s, 1H, NH), 6.80–7.77 (m, 4H, aromatic), 4.48 (m, 1H, CH), 1.20 (d, $J = 7.0$ Hz, 6H, $2CH_3$); IR (KBr) 3247 (NH), 1738 (CO), 1625 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 220 ($M^+ + 1$, 35.6), 219 (M^+, 41.1), 145 (100), 77 (62.2). Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.44; H, 5.96; N, 19.15.

2-Isopropyl-3-imino-4-(2-methylphenyl)-1,2,4-oxadiazolidin-5-one (7g): Yield 86%: m.p. 174–175°C; ^{1}H NMR (300 MHz) δ 9.60 (br, s, 1H, NH),

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6.90–7.30 (m, 4H, aromatic), 4.31 (m, 1H, CH), 2.20 (s, 3H, CH_3), 1.18 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3160 (NH), 1768 (CO), 1610 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 234 (M^+, 24.4), 146 (100), 118 (48.3). Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.85; H, 6.50; N, 17.96.

2-Isopropyl-3-imino-4-(2-methoxyphenyl)-1,2,4-oxadiazolidin-5-one (7h): Yield 80%: m.p. 172–173°C; ^{1}H NMR (300 MHz) δ 9.60 (br, s, 1H, NH), 6.60–7.60 (m, 4H, aromatic), 4.37 (m, 1H, CH), 3.74 (s, 3H, OCH_3), 1.20 (d, $J = 6.0$ Hz, 6H, $2CH_3$); IR (KBr) 3152 (NH), 1771 (CO), 1613 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 250 ($M^+ + 1$, 50.4), 249 (M^+, 61.1), 175 (100), 56 (55.9). Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.89; H, 6.05; N, 16.80.

2-Isopropyl-3-imino-4-(2-chlorophenyl)-1,2,4-oxadiazolidin-5-one (7i): Yield 78%: m.p. 157.5–158.5°C; ^{1}H NMR (300 MHz) δ 9.90 (br, s, 1H, NH), 6.90–7.70 (m, 4H, aromatic), 4.41 (m, 1H, CH), 1.24 (d, $J = 7.0$ Hz, 6H, $2CH_3$); IR (KBr) 3178 (NH), 1736 (CO), 1602 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 255 ($M^+ + 1$, 19.8), 254 (M^+, 35.7), 179 (94.4), 43 (100). Anal. Calcd for $C_{11}H_{12}ClN_3O_2$: C, 52.08; H, 4.77; N, 16.56. Found: C, 52.11; H, 4.71; N, 16.63.

2-Isopropyl-3-imino-4-(2-nitrophenyl)-1,2,4-oxadiazolidin-5-one (7j): Yield 87%: m.p. 160–161°C; ^{1}H NMR (300 MHz) δ 10.35 (br, s, 1H, NH), 7.00–8.30 (m, 4H, aromatic), 4.47 (m, 1H, CH), 1.38 (d, $J = 7.0$ Hz, 6H, $2CH_3$); IR (KBr) 3262 (NH), 1759 (CO), 1593 (C=N) cm^{-1}; MS *m/e* (rel. intensity) 265 ($M^+ + 1$, 13.1), 264 (M^+, 10.0), 70 (100), 43 (44.8). Anal. Calcd for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.90; H, 4.56; N, 21.19.

3-Imino-4-phenyl-1,2,4-oxadiazolidin-5-one (7k): Yield 93%; ^{1}H NMR (300 MHz) δ 7.05–7.73 (m, 5H, Ph), 6.02 (br, s, 2H, 2NH); IR (KBr) 3347 (NH), 1748 (CO), 1638 (C = N) cm^{-1}; MS *m/e* (rel. intensity) 178 ($M^+ + 1$, 50.2), 177 (M^+, 80.2), 91 (64.3), 77 (100), 64 (40.0). Anal. Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.72. Found: C, 54.41; H, 4.01; N, 54.32.

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