

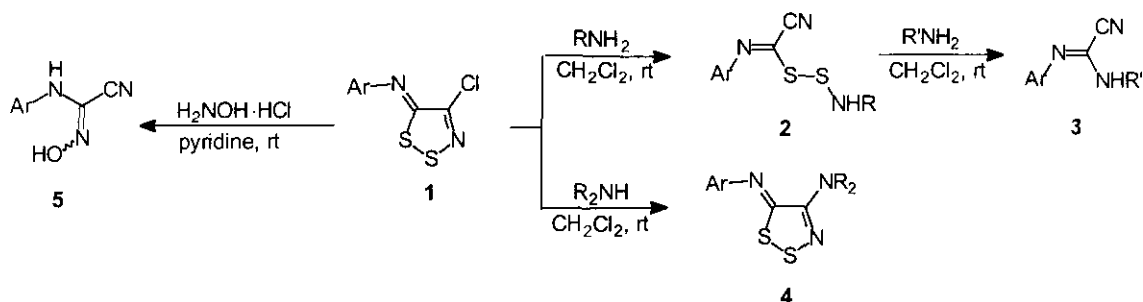
A FACILE SYNTHESIS OF *N*-ARYLCYANOFORMAMIDOXIMES, 4-ARYL-3-CYANO-1,2,4-OXADIAZIN-5(6*H*)-ONES, 2-CYANOQUINAZOLINE-3-OXIDES, AND 2-CYANOQUINAZOLINES VIA 5-ARYLIMINO-4-CHLORO-5*H*-1,2,3-DITHIAZOLES

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Abstract - The reaction of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles with hydroxylamine hydrochloride in pyridine at room temperature gave *N*-arylcyanoforamidoximes, which were utilized as starting materials for the synthesis of 4-alkyl- (or aryl)-2-cyanoquinazolines and 4-aryl-3-cyano-1,2,4-oxadiazin-5(6*H*)-ones.

Recently much attention has been focused on exploring the synthetic utility of 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles (**1**)¹ which can be readily prepared from primary arylamines and 4,5-dichloro-5*H*-1,2,3-dithiazolium chloride (Appel's salt) in the presence of tertiary amine, mostly pyridine, in CH₂Cl₂ at room temperature.² Compounds (**1**) are attacked by primary and simple secondary alkylamines to give *N*-aryl-*N'*-alkylcyanoforamidines (**3**) via amino disulfides (**2**),³ whereas treatment with bulky secondary alkylamines gave 5-arylimino-4-dialkylamino-5*H*-1,2,3-dithiazoles (**4**)⁴ (Scheme 1).



Scheme 1

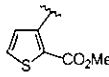
In a continuation of our ongoing project to develop the chemistry of **1**, compounds (**1**) were treated with hydroxylamine hydrochloride in pyridine at room temperature. The reactions proceeded smoothly to give

N-arylcyanoforamidoximes (**5**), which have received little attention in spite of extensive study on the synthesis and properties of amidoximes and related compounds.⁵

N-Phenylcyanoforamidoxime (**5a**) was reported to be prepared by treatment of chloroglyoxime with SOCl₂ in dry ether.⁶ Later base catalyzed 1,2-migration of *N*-nitroso-areneaminoacetonitrile in MeOH was reported to give **5**.⁷ However, the applicability of **5** has seldom been reported. Cyanoforamidoxime derivatives such as cyanoforamidoxime *O*-carbamate have been of biological interest because some of them have had significant use as acaracides, neumatocides, soil fungicides, and insecticides.⁸

Table 1 shows yields and melting points of **5** prepared and reaction times.

Table 1. Reaction times and yields and melting points of *N*-arylcyanoforamidoximes **5** and 4-aryl-3-cyano-1,2,4-oxadiazin-5(6*H*)-ones (**12**)

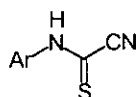
Ar	Time h	Yield ^a (E/Z) %	mp (decomp) °C	Time min	Yield ^a %	mp °C
1a Ph	3	5a 28 (1 : 10)	144-145 ^b	10	12a 74	109-110 ^b
1b 4-BrC ₆ H ₄	15	5b 30 (1 : 7)	144-146 ^b	10	12b 84	146-148 ^b
1c 4-ClC ₆ H ₄	3	5c 26 (1 : 7)	157-158 ^b	10	12c 77 ^f	124-125 ^b
1d 2-MeO ₂ CC ₆ H ₄	18	5d 84	184-186 ^c	10	12d 73	85-86 ^b
1e 4-O ₂ NC ₆ H ₄	3	5e 54 (1 : 3)	168-170 ^c	10	12e 59, 65 ^g	158-159 ^d
1f 2-O ₂ NC ₆ H ₄	6	5f 47 (1 : 20)	121-122 ^b	10	12f 70	99-100 ^b
1g 3-O ₂ NC ₆ H ₄	20	5g 54 (1 : 4)	143-144 ^b	10	12g 61 ^h	153-154 ^b
1h 2-Me-4-O ₂ NC ₆ H ₃	7	5h 79 (1 : 7)	156-158 ^b	10	12h 56	Sticky
1i 2-Cl-5-O ₂ NC ₆ H ₃	7	5i 40 (1 : 7)	126-128 ^b	10	12i 67 ⁱ	118-119 ^b
1j 	4	5j 83	176-177 ^b	60	12j 10 ^j	156-158 ^b
1k 4-MeC ₆ H ₄ SO ₂	24	5k 69 (1 : 3)	170-172 ^e			

^aIsolated yields. ^bRecrystallized from a mixture of CH₂Cl₂ and *n*-hexane. ^cRecrystallized from CHCl₃. ^dRecrystallized from EtOH.

^eRecrystallized from CH₂Cl₂. ^fChloroacetic anhydride was used. ^gTriisopropylamine was used instead of TEA. ^hCompound (**5g**) was

recovered in 35% yield. ⁱCompound (**5i**) was recovered in 12% yield. ^jCompound (**5j**) was recovered in 72% yield.

In addition to compounds (**5**), small amounts of sulfur and unknown mixtures were obtained. In the cases of the reactions of **1a**, **1b**, and **1c**, *N*-arylcyanothioformamides (**6a**) (5%), (**6b**) (36%), and (**6c**) (26%) were isolated.⁹ No *N*-arylcyanothioformamide was isolated from the reactions with other dithiazoles (**1**)



6a, Ar = Ph
6b, Ar = 4-BrC₆H₄
6c, Ar = 4-ClC₆H₄

6d, Ar = 2-NCC₆H₄
6e, Ar = 4-MeOC₆H₄

6f, Ar = 4-Me-C(=O)-C₆H₄

listed in Table 1. Interestingly, the reaction with **11** (Ar = 2-NCC₆H₄) under the same conditions gave a complex mixture from which only **6d** (27%) was isolated.

It has been found that the reactions of **1** bearing an electron-donating group did not give **5**. For instance, the reaction of **1** having a 4-MeO group afforded the corresponding cyanothioformamide (**6e**) (33%),⁹ and those of **1** having 2-HO and 2-Me groups gave sulfur and unknown mixtures without **6**. It has been observed that amidoximes are configurationally labile and amidoximes which are monosubstituted on the amide nitrogen generally form oximes with the *Z* configurations.¹⁰ However, the stereochemistry around the C=N double bond of **5** is uncertain. A single crystal of **5** has not yet been obtained for X-Ray crystallography. The ¹H NMR spectra of **5a-k** indicate that compounds (**5**) exist in a single stereoisomer in CDCl₃, whereas **5a-c**, **5e-i** and **5k** exist in a mixture of *E*- and *Z*-isomers in DMSO-d₆. The assignment of the stereochemistry of **5** was made based on the relationship between the reported ¹H NMR spectral data observed from *E*- and *Z*-amidoximes.¹¹ That is, the N-H protons of *Z*-isomers appeared upfield compared with those of *E*-isomers, whereas the chemical shifts of the O-H protons of *E*- and *Z*-amidoximes showed an opposite tendency, probably due to hydrogen-bonding effects between the amino hydrogen and the oximino oxygen atoms. Based on this result, the *E/Z* ratios of **5** in DMSO-d₆ were determined. The results are summarized in parentheses in Table 1.

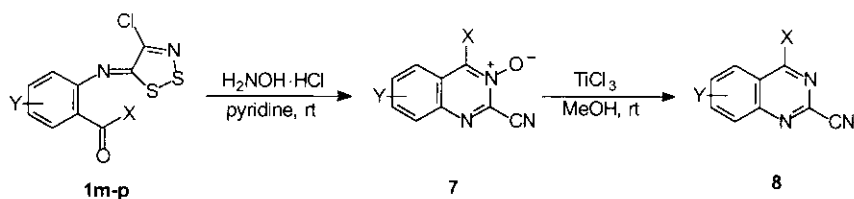
It is envisaged that the polarity of DMSO-d₆ causes the hydrogen bonding of *Z*-stereoisomer to break so that *E*-stereoisomer tends to be formed. In contrast, CDCl₃ which is nonpolar would not significantly influence the strength of the hydrogen-bond of *Z*-isomer. Consequently, only single isomer exists in CDCl₃.

When the aryl group of **1** has an acetyl or a benzoyl group at its *ortho* position, 2-cyanoquinazoline-3-oxides (**7**) were formed under the same conditions. Treatment of **7** with TiCl₃ according to the documented procedure gave 4-alkyl- and 4-aryl-2-cyanoquinazolines (**8**)¹² (Scheme 2). The results are summarized in Table 2.

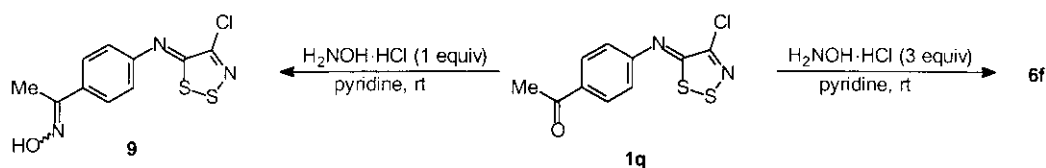
Table 2. Reaction times, and yields of 2-cyanoquinazoline-3-oxides (**7**) and 2-cyanoquinazolines (**8**)

Compound	X	Y	Time	Yield ^a		mp (decomp)	Time	Yield ^a		mp
			h	%	°C	min	%	°C		
1m	Me	H	72	7a	92	210-214 ^b	40	8a	69	148-149 ^b (lit., ¹³ 145 - 147)
1n	Ph	H	24	7b	62	223-225 ^c	60	8b	51	124-125 ^c (lit., ¹³ 127 - 129)
1o	Ph	5-Me	48	7c	41	190-192 ^b	5	8c	51	156-158 ^b
1p	Ph	4-Cl	72	7d	62	194-196 ^b	5	8d	75	178-180 ^d

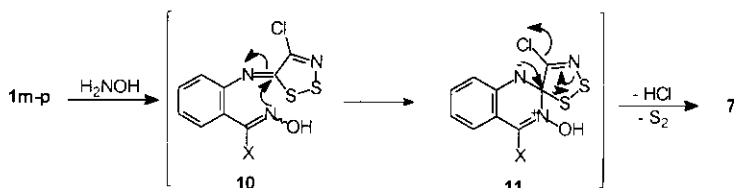
^aIsolated yields. ^bRecrystallized from a mixture of CH₂Cl₂ and *n*-hexane. ^cRecrystallized from EtOH. ^dRecrystallized from MeOH.



In contrast, the reactions of compound (**1q**) (Ar = 4-MeCOC₆H₄) with 1 and 3 molar equivalents of hydroxylamine hydrochloride under the same conditions gave oxime (**9**) and cyanothioformamide (**6f**) in 82% and 36% yields, respectively (Scheme 3).

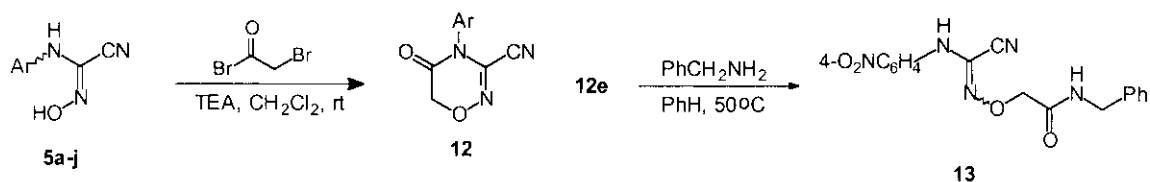


This result suggests that the non-bonding electrons on the oximino nitrogen of **10** attack C-5 of the dithiazole ring of **1** to give an intermediate (**11**), which extrudes S₂ concomitant with HCl, leading to **7** (Scheme 4).



In the meantime, compounds (**5a-j**) were found to be useful starting materials for the synthesis of 4-aryl-3-cyano-1,2,4-oxadiazin-5(6*H*)-ones (**12**), which have never been reported in the literature although various 5,6-dihydro-4*H*-1,2,4-oxadiazines¹⁴ and 3-alkyl- and 3-aryl-4*H*-1,2,4-oxadiazin-5(6*H*)-ones¹⁵ have been prepared.

Treatment of **5a-j** with bromoacetyl bromide in the presence of triethylamine at room temperature gave **12** in good yields (Scheme 5). Compound (**5k**) was recovered quantitatively under the same reaction conditions. Reaction times and yields of **12** are summarized in Table 1.

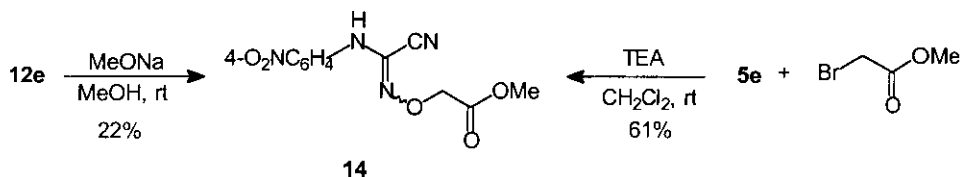


The regiochemistry of **12** was determined based on the HMBC spectrum of **12a**, coupled with the

chemical transformation of **12e**. Most of compounds (**12**) exhibited carbonyl absorptions at 1731 to 1738 cm^{-1} except for **12d** and **12j**, which showed two absorptions at 1706 and 1744 cm^{-1} . The IR spectral data are of no useful in determining the regiochemistry of **12** in view of the carbonyl absorptions at 1705 - 1725 cm^{-1} and 1750 - 1776 cm^{-1} exhibited by 3-aryl-4*H*-1,2,4-oxadiazin-5(6*H*)-one¹⁵ and 4,5-dihydro-1,2,4-oxadiazin-6(5*H*)-one,¹⁴ respectively. Similarly an indistinguishable tendency was found from the ¹H NMR spectral data. That is, the ¹H NMR spectral data of **12a-c**, **12e**, and **12g-j** exhibited a singlet at 4.72 to 4.79 ppm except for **12d** and **12f** which exhibited two singlets at 4.61 and 4.77, and 4.61 and 4.84 ppm, respectively. However, the chemical shifts exhibited by the former are close to 4.23 - 4.72 and 3.86 - 5.20 ppm, exhibited by 3-aryl-4*H*-1,2,4-oxadiazin-5(6*H*)-one and 4,5-dihydro-1,2,4-oxadiazin-6(5*H*)-one, respectively.

The HMBC spectrum of **12a** shows that the methylene protons at C-6 do not correlate with the quaternary carbon bonded to N-4. This result clearly indicates that the compound has a skeleton of 1,2,4-oxadiazin-5(6*H*)-one rather than 1,2,4-oxadiazin-6(5*H*)-one. Furthermore, treatment of **12e** with benzylamine in benzene at 50 °C gave *O*-alkylated cyanoformamidoxime (**13**) in 79% yield (Scheme 5). The ¹H NMR spectral data recorded in DMSO-*d*₆ suggest that **13** is a mixture of stereoisomers whose ratio is 1.8:1. More work has to be done for the assignment of the stereochemistry of **13**.

Similarly treatment of **12e** with MeONa in MeOH at room temperature gave *O*-alkylated cyanoformamidoxime (**14**) (22%), whose structure was identical with that obtained from the reaction of **5e** with methyl bromoacetate (Scheme 6).



Scheme 6

In conclusion, we demonstrated that 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles (**1**) are useful starting materials for the synthesis of *N*-arylcyanoforamidoximes (**5**) which can be utilized for the synthesis of 4-alkyl- (or aryl)-2-cyanoquinazolines (**8**) and 4-aryl-3-cyano-1,2,4-oxadiazin-5(6*H*)-ones (**12**).

EXPERIMENTAL

All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained on a Shimadzu IR-470 IR spectrophotometer for samples of KBr pellets or thin films. ¹H NMR spectra were determined on a Bruker 300 MHz spectrometer using tetramethylsilane as internal standard; J values are given in Hz. MS spectra were obtained by electron impact at 70 eV. Elemental analyses were determined by the Korea Basic Science Institute. Column chromatography was

performed on silica gel (Merck, 70 – 230 mesh, ASTM). 5-Arylimino-4-chloro-5*H*-1,2,3-dithiazoles (1) were prepared according to the literature procedures.²

General Procedure for the Preparation of *N*-Arylcyanoforamidoximes (5). To a solution of 1 (0.4–0.5 mmol) in pyridine (5 mL) was added H₂NOH·HCl (56 – 70 mg, 0.8 – 1.0 mmol). The mixture was stirred for an appropriate time at rt, followed by neutralization with 5% HCl. The mixture was extracted with CH₂Cl₂ (25 mL x 3), which was dried over MgSO₄. Chromatography (3 x 10 cm) of the residue with *n*-hexane gave sulfur. Elution with a mixture of *n*-hexane and EtOAc (10:1) gave unknown mixtures. Elution with the same solvent mixture whose ratios were 5:1 and 2:1 gave 6 and 5, respectively. Reaction time and yields and melting points of 5 are summarized in Table 1.

***N*-Phenylcyanoamidoximes (5a):** ¹H NMR (DMSO-*d*₆, δ, ppm) 7.08 – 7.40 (5H, m, ArH of major and minor), 9.16 (1H, s, NH of major), 9.46 (1H, s, NH of minor), 11.28 (1H, s, OH of minor), 11.82 (1H, s, OH of major); IR (KBr) (ν, cm⁻¹) 3408, 3248, 2240, 1619, 1590, 1494, 1436, 1360, 976, 928, 745, 698; MS (EI) *m/z* 161 (M⁺, 60%), 144 (100), 131 (18), 129 (12), 118 (15). *Anal.* Calcd for C₈H₇N₃O: C, 59.62; H, 4.38; N, 26.07. Found: C, 59.70; H, 4.41; N, 26.01.

***N*-(4-Bromophenyl)cyanoformamidoxime (5b):** ¹H NMR (CDCl₃, δ, ppm) 6.99 (1H, s, NH), 7.09 (2H, d, *J* = 8.8 Hz, ArH), 7.51 (2H, d, *J* = 8.8 Hz, ArH), 8.51 (1H, s, OH); ¹H NMR (DMSO-*d*₆, δ, ppm) 7.14 (2H, d, *J* = 8.7 Hz, ArH of major), 7.34 (2H, d, *J* = 8.4 Hz, ArH of minor), 7.46 (2H, d, *J* = 8.4 Hz, ArH of minor), 7.51 (2H, d, *J* = 8.8 Hz, ArH of major), 9.31 (1H, s, NH of major), 9.65 (1H, s, NH of minor), 11.41 (1H, s, OH of minor), 12.0 (1H, s, OH of major); IR (KBr) (ν, cm⁻¹) 3360, 3152, 2224, 1634, 1578, 1482, 1355, 1066, 994, 928, 826, 778; MS (EI) *m/z* 222 (M⁺ - 18, 98%), 196 (8), 170 (5), 155 (14), 143 (8), 117 (8). *Anal.* Calcd for C₈H₆N₃OBr: C, 40.03; H, 2.52; N, 17.50. Found: C, 40.06; H, 2.50; N, 17.50.

***N*-(4-Chlorophenyl)cyanoformamidoxime (5c):** ¹H NMR (CDCl₃, δ, ppm) 6.94 (1H, s, NH), 7.14 (2H, d, *J* = 8.8 Hz, ArH), 7.36 (2H, d, *J* = 8.8 Hz, ArH), 8.09 (1H, s, OH); ¹H NMR (DMSO-*d*₆, δ, ppm) 7.21 (2H, d, *J* = 8.7 Hz, ArH of major and minor), 7.39 (2H, d, *J* = 8.8 Hz, ArH of major and minor), 9.29 (1H, s, NH of major), 9.62 (1H, s, NH of minor), 11.38 (1H, s, OH of minor), 11.93 (1H, s, OH of major); IR (KBr) (ν, cm⁻¹) 3368, 3152, 2232, 1634, 1586, 1486, 1406, 1358, 1068, 992, 930, 832; MS (EI) *m/z* 195 (M⁺, 31%), 178 (100), 165 (20), 152 (34), 138 (2), 127 (20). *Anal.* Calcd for C₈H₆N₃OCl: C, 49.12; H, 3.09; N, 21.48. Found: C, 49.23; H, 3.13; N, 21.38.

***N*-(2-Methoxycarbonylphenyl)cyanoformamidoxime (5d):** ¹H NMR (DMSO-*d*₆/CDCl₃, δ, ppm) 3.90

(3H, s, CH₃), 6.94 – 7.21 (1H, m, ArH), 7.49 – 7.62 (2H, m, ArH), 7.99 (1H, d, $J = 8.0$ Hz, ArH), 10.30 (1H, s, NH), 12.25 (1H, s, OH); IR (KBr) (ν , cm⁻¹) 3216, 3168, 2232, 1685, 1621, 1502, 1254, 1080, 989, 938, 749; MS (EI) m/z 219 (M⁺, 13%), 203 (6), 187 (17), 170 (11), 157 (43), 144 (39). *Anal.* Calcd for C₁₀H₉N₃O₃: C, 54.79; H, 4.14; N, 19.17. Found: C, 54.62; H, 4.20; N, 19.02.

***N*-(4-Nitrophenyl)cyanoforamidoxime (5e)**: ¹H NMR (CDCl₃, δ , ppm) 7.32 (2H, d, $J = 9.1$ Hz, ArH), 8.02 (1H, s, NH), 8.28 (2H, d, $J = 9.1$ Hz, ArH); ¹H NMR (DMSO-d₆, δ , ppm) 7.34 (2H, d, $J = 9.2$ Hz, ArH of major), 7.58 (2H, d, $J = 9.3$ Hz, ArH of minor), 8.11 (2H, d, $J = 9.2$ Hz, ArH of minor), 8.18 (2H, d, $J = 9.1$ Hz, ArH of major), 9.21 (1H, s, NH of major), 9.84 (1H, s, NH of minor), 11.36 (1H, s, OH of minor); IR (KBr) (ν , cm⁻¹) 3320, 3200, 2232, 1627, 1587, 1501, 1328, 1296, 1106, 1006, 976, 846, 741, 702; MS (EI) m/z 190 (M⁺ - 16, 100%), 174 (3), 160 (19), 117 (29), 108 (5). *Anal.* Calcd for C₈H₆N₄O₃: C, 46.61; H, 2.93; N, 27.18. Found: C, 46.59; H, 2.89; N, 27.22.

***N*-(2-Nitrophenyl)cyanoforamidoxime (5f)**: ¹H NMR (CDCl₃, δ , ppm) 7.23 – 7.26 (1H, m, ArH), 7.71 – 7.72 (2H, m, ArH), 8.26 (1H, d, $J = 8.5$ Hz, ArH), 8.44 (1H, s, NH), 9.97 (1H, s, OH); IR (KBr) (ν , cm⁻¹) 3328, 3087, 2238, 1607, 1507, 1452, 1356, 1282, 1001, 780, 745, 675; MS (EI) m/z 206 (M⁺, 100%), 190 (20), 143 (61), 138 (29). *Anal.* Calcd for C₈H₆N₄O₃: C, 46.61; H, 2.93; N, 27.18. Found: C, 46.80; H, 2.87; N, 27.19.

***N*-(3-Nitrophenyl)cyanoforamidoxime (5g)**: ¹H NMR (DMSO-d₆, δ , ppm) 7.57 – 7.60 (2H, m, ArH of minor), 7.62 – 7.71 (2H, m, ArH of major), 7.80 – 7.82 (1H, m, ArH of minor), 7.89 – 7.93 (1H, m, ArH of major), 8.05 (1H, s, ArH of major), 8.46 (1H, s, ArH of minor), 9.67 (1H, s, NH of major), 10.06 (1H, s, NH of minor), 11.71 (1H, s, OH of minor), 12.21 (1H, s, OH of major); IR (KBr) (ν , cm⁻¹) 3328, 3184, 2240, 1690, 1622, 1523, 1341, 1011, 883, 794, 736; MS (EI) m/z 206 (M⁺, 76%), 190 (58%), 189 (22), 188 (18), 176 (100), 174 (19). *Anal.* Calcd for C₈H₆N₄O₃: C, 46.61; H, 2.93; N, 27.18. Found: C, 46.75; H, 2.99; N, 27.05.

***N*-(2-Methyl-4-nitrophenyl)cyanoforamidoxime (5h)**: ¹H NMR (CDCl₃, δ , ppm) 2.44 (3H, s, CH₃), 6.79 (1H, br s, NH), 7.51 (1H, d, $J = 9.6$ Hz, ArH), 8.17 – 8.20 (3H, m, ArH and OH); ¹H NMR (DMSO-d₆, δ , ppm) 2.35 (3H, s, CH₃ of minor), 2.37 (3H, s, CH₃ of major), 7.31 (1H, d, $J = 8.8$ Hz, ArH of major), 7.56 (1H, d, $J = 8.7$ Hz, ArH of minor), 8.05 – 8.10 (1H, m, ArH of major), 8.05 – 8.10 (2H, ArH of minor), 8.14 (1H, s, ArH of major), 8.96 (1H, s, NH of major), 9.00 (1H, s, NH of minor), 12.14 (1H, s, OH of minor), 12.25 (s, 1H, OH of major); IR (KBr) (ν , cm⁻¹) 3376, 3280, 2240, 1613, 1581, 1501, 1459, 1318, 1280, 998, 896, 822, 739. *Anal.* Calcd for C₉H₈N₄O₃: C, 49.09; H, 3.66; N, 25.44. Found: C, 49.15; H, 3.62; N, 25.52.

***N*-(2-Chloro-5-nitrophenyl)cyanoforamidoxime (5i)**: ^1H NMR (DMSO- d_6 , δ , ppm) 7.77 (1H, d, $J = 8.7$ Hz, ArH of minor), 7.85 (1H, d, $J = 8.8$ Hz, ArH of major), 8.07 (1H, d, $J = 8.8$ Hz, ArH of major and minor), 8.14 (1H, s, ArH of major), 8.56 (1H, s, ArH of minor), 9.20 (1H, s, NH of major), 9.24 (1H, s, NH of minor), 12.05 (1H, s, OH of minor), 12.19 (1H, s, OH of major); IR (KBr) (ν , cm^{-1}) 3360, 3088, 2240, 1629, 1523, 1341, 1050, 1014, 992, 883, 736; MS (EI) m/z 224 ($M^+ - 16$, 100%), 207 (10), 189 (18), 179 (46), 151 (52). *Anal.* Calcd for $\text{C}_8\text{H}_5\text{N}_4\text{O}_3\text{Cl}$: C, 39.94; H, 2.09; N, 23.29. Found: C, 39.86; H, 2.12; N, 23.20.

***N*-(2-Methoxycarbonylthiophen-3-yl)cyanoforamidoxime (5j)**: ^1H NMR (CDCl_3 , δ , ppm) 3.91 (3H, s, CH_3), 7.59 (1H, d, $J = 5.6$ Hz, =CH), 7.62 (1H, d, $J = 5.6$ Hz, =CH), 8.34 (1H, s, NH), 10.21 (1H, s, OH); IR (KBr) (ν , cm^{-1}) 3304, 3240, 1670, 1630, 1555, 1446, 1365, 1261, 1098, 979, 872, 768; MS (EI) m/z 225 (M^+ , 58%), 209 (13), 193 (45), 163 (100), 150 (37), 136 (30), 125 (17). *Anal.* Calcd for $\text{C}_8\text{H}_7\text{N}_3\text{O}_3\text{S}$: C, 42.66; H, 3.13; N, 18.66; S, 14.24. Found: C, 42.80; H, 3.14; N, 18.58; S, 14.36.

***N*-(4-Tosyl)cyanoforamidoxime (5k)**: ^1H NMR (DMSO- d_6 , δ , ppm) 2.40 (3H, s, CH_3 of major and minor), 7.45 (2H, d, $J = 8.1$ Hz, ArH of major and minor), 7.72 (2H, d, $J = 8.3$ Hz, ArH of minor), 7.78 (2H, d, $J = 8.3$ Hz, ArH of major), 12.55 (1H, br s, OH of major), 12.97 (1H, s, OH of minor); IR (KBr) (ν , cm^{-1}) 3584, 3376, 2224, 1629, 1584, 1389, 1283, 1258, 1136, 1085, 1037, 973, 870, 806, 758, 701, 666; FAB MS m/z 240 ($M^+ + 1$). *Anal.* Calcd for $\text{C}_9\text{H}_9\text{N}_3\text{O}_3\text{S}$: C, 45.18; H, 3.79; N, 17.56; S, 13.40. Found: C, 45.23; H, 3.68; N, 17.70; S, 13.28.

Reaction of 4-Chloro-5-(2-cyanophenylimino)-5*H*-1,2,3-dithiazole (11) with Hydroxylamine Hydrochloride. Hydroxylamine hydrochloride (167 mg, 2.40 mmol) was added into a solution of **11** (158 mg, 0.60 mmol) in pyridine (5 mL). The mixture was stirred at rt for 4 h and then worked up as usual. Chromatography (1.5 x 10 cm) of the reaction mixture with *n*-hexane gave sulfur (23 mg). Elution with a mixture of *n*-hexane and EtOAc (5 : 1) gave an unknown (12 mg) and *N*-(2-cyanophenyl)cyanothioformamide (**6d**) (30 mg, 27%): mp (decomp) 104 – 105 °C (CH_2Cl_2 – *n*-hexane); ^1H NMR (DMSO- d_6 , δ , ppm) 7.54 (1H, t, $J = 7.6$ Hz, ArH), 7.63 (1H, t, $J = 8.0$ Hz, ArH), 7.81 (t, 1H, $J = 7.6$ Hz, ArH), 7.97 (d, 1H, $J = 7.7$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 3184, 2992, 2240, 1360; MS (m/z) 160 ($M^+ - 27$, 100%). *Anal.* Calcd for $\text{C}_9\text{H}_5\text{N}_3\text{S}$: C, 57.74; H, 2.69; N, 22.44; S, 17.13. Found: C, 57.88; H, 2.75; N, 22.39; S, 17.25.

General Procedure for the Preparation of 2-Cyanoquinazoline-3-oxides 7. 2-Acyl- (or aroyl)phenyl-4-chloro-5*H*-1,2,3-dithiazoles (**1m-p**) (1.1–2.3 mmol) were treated with hydroxylamine hydrochloride

(174 – 229 mg, 2.5–3.3 mmol) in pyridine (5 mL) at rt according to the procedure described for the preparation of **5**. Chromatography of the reaction mixture (3 x 8 cm) with *n*-hexane gave sulfur. Subsequent elution with a mixture of *n*-hexane and EtOAc (1 : 2) gave **7**. Reaction times, yields and melting points of **7** are summarized in Table 2.

2-Cyano-4-methylquinazoline-3-oxide (7a): $^1\text{H NMR}$ (DMSO- d_6 , δ , ppm) 2.79 (3H, s, CH_3), 7.89 - 7.93 (2H, m, ArH), 8.04 - 8.07 (1H, m, ArH), 8.20 - 8.23 (1H, m, ArH); IR (KBr) (ν , cm^{-1}) 1600, 1539, 1286, 1214, 1195, 1146, 773, 762, 707, 635; MS (EI) m/z 185 (M^+ , 100), 169 (32), 168 (41), 159 (31), 141 (16), 128 (20), 116 (27). *Anal.* Calcd for $\text{C}_{10}\text{H}_7\text{N}_3\text{O}$: C, 64.86; H, 3.81; N, 22.69. Found: C, 64.77; H, 3.88; N, 22.73.

2-Cyano-4-phenylquinazoline-3-oxide (7b): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 7.65 - 7.67 (6H, m, ArH), 7.74 (1H, t, $J = 7.1$ Hz, ArH), 7.86 (1H, t, $J = 7.0$ Hz, ArH), 8.13 (1H, d, $J = 8.4$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1594, 1555, 1526, 1462, 1286, 1139, 774, 755, 694; MS (EI) m/z 247 (M^+ , 26%), 246 (48), 231 (46), 230 (46), 218 (23), 177 (10), 151 (11). *Anal.* Calcd for $\text{C}_{15}\text{H}_9\text{N}_3\text{O}$: C, 72.87; H, 3.67; N, 16.99. Found: C, 73.19; H, 3.90; N, 17.15.

2-Cyano-7-methyl-4-phenylquinazoline-3-oxide (7c): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 2.61 (3H, s, CH_3), 7.55 (2H, s, ArH), 7.64 (5H, s, ArH), 7.89 (1H, s, ArH); IR (KBr) (ν , cm^{-1}) 1606, 1523, 1315, 1274, 1037, 1014, 954, 752; MS (EI) m/z 261 (M^+ , 10%), 260 (14), 245 (56), 244 (69), 231 (19), 230 (100). *Anal.* Calcd for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}$: C, 73.55; H, 4.24; N, 16.08. Found: C, 73.68; H, 4.19; N, 15.92.

6-Chloro-2-cyano-4-phenylquinazoline-3-oxide (7d): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 7.56 - 7.69 (6H, m, ArH), 7.75 - 7.78 (1H, m, ArH), 8.07 (1H, d, $J = 8.95$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1590, 1520, 1466, 1283, 1178, 694; MS (EI) m/z 281 (M^+ , 13%), 280 (15), 265 (60), 264 (90), 237 (11), 230 (100). *Anal.* Calcd for $\text{C}_{15}\text{H}_8\text{N}_3\text{OCl}$: C, 63.96; H, 2.86; N, 14.92. Found: C, 64.02; H, 2.89; N, 14.80.

General Procedure for the Preparation of 4-Alkyl- and 4-Aryl-2-cyanoquinazolines (8). Compounds (**8**) were prepared according to the literature procedures.¹² Reaction times, yields and melting points of (**8**) are summarized in Table 2.

2-Cyano-7-methyl-4-phenylquinazoline (8c): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 2.67 (3H, s, CH_3), 7.58 - 7.67 (4H, m, ArH), 7.78 - 7.83 (2H, m, ArH), 7.98 (1H, s, ArH), 8.13 (1H, d, $J = 8.6$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1610, 1546, 1520, 1472, 1392, 1331, 1030, 768, 691; MS (EI) m/z 245 (M^+ , 53%), 244 (63), 230

(100). *Anal.* Calcd for $C_{16}H_{11}N_3$: C, 78.35; H, 4.52; N, 17.13. Found: C, 78.29; H, 4.52; N, 17.22.

6-Chloro-2-cyano-4-phenylquinazoline (8d): 1H NMR ($CDCl_3$, δ , ppm) 7.59 - 7.67 (3H, m, ArH), 7.80 - 7.83 (2H, m, ArH), 7.90 - 8.02 (1H, m, ArH), 8.16 - 8.22 (2H, m, ArH); IR (KBr) (ν , cm^{-1}) 1594, 1542, 1507, 1472, 1373, 1338, 1072, 915, 835, 694; MS (EI) m/z 265 (M^+ , 62%), 264 (85), 237 (12), 230 (100), 203 (15). *Anal.* Calcd for $C_{15}H_8N_3Cl$: C, 67.81; H, 3.03; N, 15.82. Found: C, 67.68; H, 2.98; N, 15.98.

Reaction of 5-(4-Acetylphenylimino)-4-chloro-5H-1,2,3-dithiazole (1q) with Hydroxylamine Hydrochloride. (i) To a solution of **1q** (299 mg, 1.10 mmol) in pyridine (5 mL) was added hydroxylamine hydrochloride (77 mg, 1.11 mmol). The mixture was stirred at rt for 24 h, followed by work-up as described in the general procedure for the preparation of compounds (**5**). Chromatography (3 x 15 cm) of the reaction mixture with CH_2Cl_2 as an eluent gave unreacted **1q** (32 mg, 11%). Subsequent elution with a mixture of EtOAc and *n*-hexane (1 : 1) gave 4-(4-chloro-5H-1,2,3-dithiazol-5-yl)iminoacetophenone oxime (**9**) (258 mg, 82%): mp 142 - 144 °C (CH_2Cl_2 - *n*-hexane); 1H NMR ($CDCl_3$, δ , ppm) 2.34 (3H, s, CH_3), 7.26 (2H, d, $J = 8.6$ Hz, ArH), 7.78 (2H, d, $J = 8.6$ Hz, ArH), 8.69 (1H, br s, OH); IR (KBr) (ν , cm^{-1}) 3232, 1600, 1565, 1488, 1453, 1398, 1363, 1299, 1226, 1174, 1123, 832. *Anal.* Calcd for $C_{10}H_8N_3OClS_2$: C, 42.03; H, 2.82; N, 14.70; S, 22.44. Found: C, 42.15; H, 2.75; N, 14.55; S, 22.60.

(ii) To a solution of **1q** (239 mg, 0.88 mmol) in pyridine (5 mL) was added hydroxylamine hydrochloride (184 mg, 2.65 mmol). The mixture was stirred at rt for 18 h and worked up as described in (i). Elution of the reaction mixture with a mixture of *n*-hexane and EtOAc (3 : 1) gave yellow solids, identified as *N*-(4-oximinoacetylphenyl)cyanothioformamide (**6f**): mp (decomp) 162 - 165 °C (EtOAc - *n*-hexane); 1H NMR ($DMSO-d_6$, δ , ppm) 2.16 (3H, s, CH_3), 7.77 (2H, d, $J = 8.9$ Hz, ArH), 7.94 (2H, d, $J = 8.8$ Hz, ArH), 11.39 (1H, s, NH or OH), 13.55 (1H, s, NH or OH); IR (KBr) (ν , cm^{-1}) 3280, 2224, 1594, 1535, 1504, 1376, 1094, 1002, 915, 826; MS (EI) m/z 192 ($M^+ - 27$, 67%). *Anal.* Calcd for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16; S, 14.62. Found: C, 54.63; H, 4.07; N, 19.28; S, 14.48.

General Procedure for the Preparation of 4-Aryl-3-cyano-1,2,4-oxadiazin-5(6H)-ones (12). To a solution of **5** (0.3 - 0.7 mmol) and TEA (101 - 293 mg, 1.0 - 2.9 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of bromoacetyl bromide (101 - 242 mg, 0.5 - 1.2 mmol) for 10 min. The mixture was stirred for 10 min except for the reaction with **5j** (60 min) and quenched when no spot corresponding to **5** had been observed on TLC (EtOAc : *n*-hexane = 1 : 2). The mixture was washed with 1% HCl (30 mL), followed by drying over $MgSO_4$. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (70 - 230 mesh, 3 x 5 cm). Elution with CH_2Cl_2 gave **12**. Reaction times, yields and melting points of **12**, are summarized in Table 1.

3-Cyano-4-phenyl-1,2,4-dxadiazin-5(6H)-one (12a): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.73 (2H, s, CH_2), 7.28 – 7.34 (2H, m, ArH), 7.56 – 7.59 (3H, m, ArH); IR (KBr) (ν , cm^{-1}) 1734, 1571, 1347, 1315, 899, 762; MS (EI) m/z 201 (M^+ , 67%), 173 (33), 172 (25), 116 (14), 105 (100), 91 (24). *Anal.* Calcd for $\text{C}_{10}\text{H}_7\text{N}_3\text{O}_2$: C, 59.70; H, 3.51; N, 20.89. Found: C, 59.85; H, 3.45; N, 20.80.

4-Bromophenyl-3-cyano-1,2,4-oxadiazin-5(6H)-one (12b): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.72 (2H, s, CH_2), 7.21 (2H, d, $J = 8.8$ Hz, ArH), 7.71 (2H, d, $J = 8.8$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1738, 1574, 1341, 1302, 896, 819; MS (EI) m/z 279 (M^+ , 71%), 251 (44), 223 (10), 183 (100), 171 (41). *Anal.* Calcd for $\text{C}_{10}\text{H}_6\text{N}_3\text{OBr}$: C, 42.88; H, 2.16; N, 15.00. Found: C, 42.70; H, 2.12; N, 15.13.

4-Chlorophenyl-3-cyano-1,2,4-oxadiazin-5(6H)-one (12c): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.72 (2H, s, CH_2), 7.27 (2H, d, $J = 8.8$ Hz, ArH), 7.56 (2H, d, $J = 8.8$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1734, 1571, 1334, 1302, 896, 822; MS (EI) m/z 235 (M^+ , 61%), 207 (33), 177 (16), 139 (100). *Anal.* Calcd for $\text{C}_{10}\text{H}_6\text{N}_3\text{O}_2\text{Cl}$: C, 50.97; H, 2.57; N, 17.83. Found: C, 51.09; H, 2.53; N, 17.71.

3-Cyano-4-(2-methoxycarbonylphenyl)-1,2,4-oxadiazin-5(6H)-one (12d): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 3.91 (3H, s, OCH_3), 4.61 (1H, d, $J = 15.1$ Hz, CH), 4.77 (1H, d, $J = 15.1$ Hz, CH), 7.38–7.41 (1H, m, ArH), 7.64 – 7.76 (2H, m, ArH), 8.23 – 8.26 (1H, m, ArH); IR (KBr) (ν , cm^{-1}) 1744, 1706, 1574, 1331, 1286, 1251, 1120, 896, 755; MS (EI) m/z 259 (M^+ , 29%), 228 (18), 202 (11), 178 (13), 172 (15), 170 (33), 151 (12), 148 (13), 146 (59), 144 (48), 119 (100). *Anal.* Calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_4$: C, 55.60; H, 3.50; N, 16.21. Found: C, 55.49; H, 3.57; N, 16.34.

3-Cyano-4-(4-nitrophenyl)-1,2,4-oxadiazin-5(6H)-one (12e): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.77 (2H, s, CH_2), 7.56 (2H, d, $J = 9.0$ Hz, ArH), 8.45 (2H, d, $J = 9.0$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1731, 1568, 1517, 1488, 1347, 1302, 1053, 986, 854; MS (EI) m/z 246 (M^+ , 37%), 218 (68), 217 (37), 150 (100). *Anal.* Calcd for $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_4$: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.90; H, 2.51; N, 22.62.

3-Cyano-4-(2-nitrophenyl)-1,2,4-oxadiazin-5(6H)-one (12f): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.61 (1H, d, $J = 15.4$ Hz, CH), 4.84 (1H, d, $J = 15.4$ Hz, CH), 7.52 (1H, d, $J = 7.7$ Hz, ArH), 7.80 – 7.93 (2H, m, ArH), 8.36 (1H, d, $J = 8.1$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 1744, 1584, 1475, 1344, 1293, 1201, 986, 899; MS (EI) m/z 246 (M^+ , 62%), 201 (84), 200 (99), 173 (33), 143 (85), 90 (100). *Anal.* Calcd for $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_4$: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.83; H, 2.44; N, 22.68.

3-Cyano-4-(3-nitrophenyl)-1,2,4-oxadiazin-5(6H)-one (12g): $^1\text{H NMR}$ (CDCl_3 , δ , ppm) 4.76 (2H, s,

CH₂), 7.67 (1H, d, $J = 7.2$ Hz, ArH), 7.80 (1H, t, $J = 8.3$ Hz, ArH), 8.25 (1H, s, ArH), 8.43 (1H, d, $J = 7.4$ Hz, ArH); IR (KBr) (ν , cm⁻¹) 2240, 1731, 1578, 1523, 1347, 1309, 986, 906, 678; MS (EI) m/z 246 (M⁺, 25%), 218 (54), 217 (32), 150 (100). *Anal.* Calcd for C₁₀H₆N₄O₄: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.70; H, 2.39; N, 22.77.

3-Cyano-4-(2-methyl-4-nitrophenyl)-1,2,4-oxadiazin-5(6H)-one (12h): ¹H NMR (CDCl₃, δ , ppm) 2.38 (3H, s, CH₃), 4.77 (2H, d, $J = 5.1$ Hz, CH₂), 7.47 (1H, d, $J = 8.6$ Hz, ArH), 8.26 (1H, d, $J = 8.6$ Hz, ArH), 8.31 (1H, s, ArH); IR (KBr) (ν , cm⁻¹) 2240, 1738, 1574, 1520, 1344, 1312, 989, 752; MS (EI) m/z 260 (M⁺, 50%), 232 (32), 233 (46), 230 (81), 164 (100). *Anal.* Calcd for C₁₁H₈N₄O₄: C, 50.78; H, 3.10; N, 21.53. Found: C, 50.85; H, 3.09; N, 21.61.

4-(2-Chloro-5-nitrophenyl)-3-cyano-1,2,4-oxadiazin-5(6H)-one (12i): ¹H NMR (CDCl₃, δ , ppm) 4.79 (2H, s, CH₂), 7.86 (1H, d, $J = 9.0$ Hz, ArH), 8.35 (1H, s, ArH), 8.43 (1H, d, $J = 9.0$ Hz, ArH); IR (KBr) (ν , cm⁻¹) 2240, 1741, 1597, 1574, 1523, 1341, 1312, 1293, 992, 736; MS (EI) m/z 280 (M⁺, 13%), 253 (11), 252 (28), 251 (26), 245 (43), 184 (100). *Anal.* Calcd for C₁₀H₅N₄O₄Cl: C, 42.80; H, 1.80; N, 19.96. Found: C, 42.83; H, 1.86; N, 19.92.

Methyl 3-(3-cyano-5-oxo-1,2,4-oxadiazin-4-yl)thiophenecarboxylate (12j): ¹H NMR (CDCl₃, δ , ppm) 3.92 (3H, s, OCH₃), 4.71 (2H, d, $J = 9.1$ Hz, CH₂), 7.16 (1H, d, $J = 5.3$ Hz, =CH), 7.72 (1H, d, $J = 5.3$ Hz, =CH); IR (KBr) (ν , cm⁻¹) 1747, 1696, 1581, 1530, 1434, 1306, 1267, 867, 774; MS (EI) m/z 265 (M⁺, 54%), 234 (14), 176 (35), 152 (46), 125 (100). *Anal.* Calcd for C₁₀H₇N₃O₄S: C, 45.28; H, 2.66; N, 15.84; S, 12.09. Found: C, 45.37; H, 2.60; N, 15.89; S, 12.22.

Reaction of 12e with Benzylamine. To a solution of 12e (12 mg, 0.46 mmol) in benzene (50 mL) was added benzylamine (490 mg, 4.57 mmol). The mixture was heated at 50 °C for 5 min and then cooled to rt. The solids formed (60 mg) which were identified as *N*-(4-nitrophenyl)cyanoforamidoximes (13) were filtered. Removal of the solvent from the filtrate gave a residue which was chromatographed on a silica gel column (70 – 230 mesh, 1.5 x 2.0 cm) with a mixture of *n*-hexane and EtOAc (2 : 1) as an eluent to give a mixture of stereoisomer of 13 whose ratio was 1.8 : 1. The major stereoisomer of 13: ¹H NMR (DMSO-*d*₆, δ , ppm) 4.38 (2H, d, $J = 6.1$ Hz, CH₂), 4.70 (2H, s, CH₂), 7.20 – 7.33 (5H, m, ArH), 7.45 (2H, d, $J = 9.2$ Hz, ArH), 8.26 (2H, d, $J = 9.2$ Hz, ArH), 8.51 (1H, s, NH), 10.27 (1H, br s, NH). The minor stereoisomer of 13: ¹H NMR(DMSO-*d*₆, δ , ppm) 4.35 (2H, d, $J = 6.2$ Hz, CH₂), 4.66 (2H, s, CH₂), 7.20 – 7.33 (5H, m, ArH), 7.59 (2H, d, $J = 9.3$ Hz, ArH), 8.16 (2H, d, $J = 9.3$ Hz, ArH), 10.57 (1H, br s, NH); IR (KBr) (ν , cm⁻¹) of 13: 3379, 3136, 1654, 1610, 1587, 1570, 1328, 1072, 1008, 912, 848. *Anal.* Calcd for

$C_{17}H_{15}N_5O_4$: C, 57.79; H, 4.28; N, 19.82. Found: C, 57.87; H, 4.21; N, 19.90.

Reaction of 12e with Sodium Methoxide. Compound (12e) (111 mg, 0.45 mmol) was added into the solution of NaOMe in MeOH, *in situ* prepared by treatment of Na (10 mg, 0.44 mmol) with absolute MeOH (10 mL). The color of the solution turned red. Water (20 mL) was added to the mixture when the spot corresponding to 12e had disappeared on TLC (CH_2Cl_2). The mixture was extracted with CH_2Cl_2 (25 mL x 3). Evaporation of the solvent gave *O*-methoxycarbonylmethyl-*N*-(4-nitrophenyl)cyanoforamidoxime (14) (28 mg, 22%); mp 122–123 °C (CH_2Cl_2 – *n*-hexane); 1H NMR ($CDCl_3$, δ , ppm) 3.84 (3H, s, CH_3), 4.80 (2H, s, CH_2), 7.34 (2H, d, $J = 9.1$ Hz, ArH), 7.72 (1H, s, NH), 8.28 (2H, d, $J = 9.1$ Hz, ArH); IR (KBr) (ν , cm^{-1}) 3280, 2224, 1734, 1613, 1587, 1504, 1328, 1226, 1082, 851, 592; MS (EI) m/z 278 (M^+ , 100%), 251 (13), 219 (19), 189 (44), 174 (40), 150 (37), 143 (91). *Anal.* Calcd for $C_{11}H_{10}N_4O_5$: C, 47.49; H, 3.62; N, 20.14. Found: C, 47.38; H, 3.62; N, 20.20.

The reddish aqueous layer was neutralized with 1% HCl, followed by extraction with CH_2Cl_2 (25 mL x 3). Evaporation of the solvent gave *N*-(4-nitrophenyl)cyanoforamidoximyl-*O*-acetic acid (15) (42 mg, 35%); 1H NMR ($CDCl_3$, δ , ppm) 4.85 (2H, s, CH_2), 7.34 (2H, d, $J = 9.1$ Hz, ArH), 7.50 (1H, s, NH or OH), 8.28 (2H, d, $J = 9.1$ Hz, ArH); IR (neat) (ν , cm^{-1}) 3296, 2240, 1728, 1610, 1587, 1507, 1331, 1091, 1024. *Anal.* Calcd for $C_{10}H_8N_4O_5$: C, 57.79; H, 4.28; N, 19.82. Found: C, 57.87; H, 4.21; N, 19.90.

Reaction of 5e with Methyl Bromoacetate. To a solution of 5e (125 mg, 0.61 mmol) in CH_2Cl_2 (50 mL) was added triethylamine (290 mg, 2.87 mmol), followed by addition of methyl bromoacetate (178 mg, 1.16 mmol). The mixture was stirred at rt for 24 h. After 1% HCl (50 mL) was added, the mixture was extracted with CH_2Cl_2 (30 mL x 3). The extracts were dried over $MgSO_4$. Removal of the solvent gave a residue, which was chromatographed (silica gel, 1.5 x 5 cm) with CH_2Cl_2 to give 14 (104 mg, 61%) and unreacted 5e (20 mg, 16%).

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