PERKIN 1

Reactions of 2-[(2-arylimino-2-cyano-1,1-dimethylethyl)arylamino]-3-methylbut-2-enenitrile with copper(II) acetate: synthesis of 2-(2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitriles

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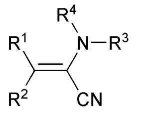
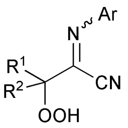
Treatment of 2-[(2-arylimino-2-cyano-1,1-dimethylethyl)arylamino]-3-methylbut-2-enenitrile **15**, prepared by reactions of *N*-aryl α-cyanoenamines **3** with $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.) in the presence of pyridine (2 equiv.) in EtOH at reflux, and with $Cu(OAc)_2{\cdot}H_2O$ (1 equiv.) in HOAc at reflux gave 2-(2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitriles **11** in moderate to good yields.

Introduction

N-Alkyl-α-cyanoenamines **1** and *N*-methyl-*N*-phenyl-α-cyanoenamines **2** have received considerable attention as starting materials for the preparation of a variety of organic compounds.[1] Nevertheless, no radical reactions of **1** and **2** have been reported. Recently we found that, unlike α-cyanoenamines **1** and **2**,[2] *N*-aryl α-cyanoenamines **3** were slowly autoxidized to α-hydroperoxy-*N*-arylimidoyl cyanides **4** in either crystalline or solution state in air.[1] The mechanism for the formation of hydroperoxides **4** is uncertain. A coupling between triplet oxygen and a radical **5** formed by oxidation of **3**[3] may be envisaged as a possible route leading to **4**. We were interested in the generation of **5** and **6** since the coupling product formed from **5** and **6** could be utilized as a new precursor for the preparation of 1,2-dihydroindol-3-one derivatives which are useful synthetic intermediates for the synthesis of biologically active compounds.[4]





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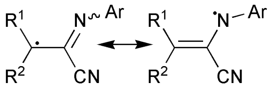


5 **6**

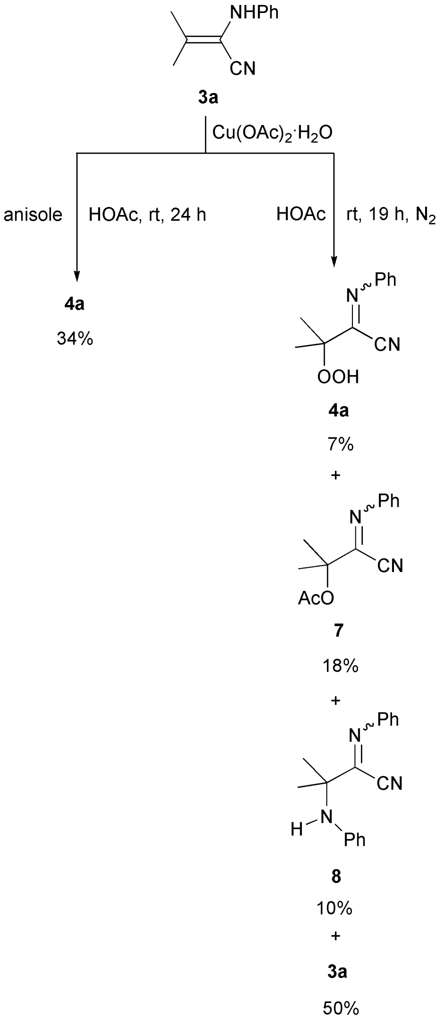
1, R^1, R^2, R^3: alkyl; R^4: H
2, R^1, R^2: alkyl; R^3: Me; R^4: Ph
3, R^1, R^2: alkyl; R^3: H; R^4: Ar

With this in mind, we examined the reactivity of **3** toward Cu(II) acetate which is known as a good single electron oxidant[5] under various reaction conditions. The results are described herein.

Results and discussion

(i) In acetic acid at room temperature

Treatment of α-cyanoenamine **3a** ($R^1 = R^2 = Me$, $R^3 = H$, $R^4 = Ph$) with $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.) in HOAc for 19 h at rt under a nitrogen atmosphere gave α-hydroperoxyimidoyl cyanide **4a** (7%), α-acetoxyimidoyl cyanide **7** (18%), α-anilinoimidoyl cyanide **8** (10%), along with unreacted **3a** (50%) (Scheme 1). In order to trap any cationic intermediate which might cause the formation of **7** and/or **8**, the same reaction was carried out in the presence of anisole[6] in air. However, no anisole-derived product was detected. Instead, hydroperoxide **4a** (34%) which was the only identifiable product, was obtained, together with complex mixtures.



Scheme 1

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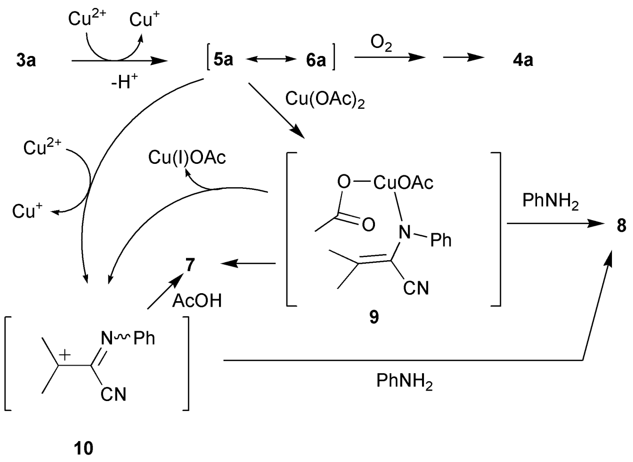
The formation of hydroperoxide **4a** in different yields under a nitrogen atmosphere and in air indicates the involvement of oxygen. A single electron transfer from **3a** by either self-oxidation (*vide infra*) or from $Cu(OAc)_2{\cdot}H_2O$, followed by deprotonation would give radicals **5a** ($R^1 = R^2 =$ Me, Ar = Ph) and **6a** ($R^1 = R^2 =$ Me, Ar = Ph), which would react with oxygen to give **4a**.

The formation of **7** and **8** may be rationalized by assuming an intermediate **9** in which copper(II) acetate makes a complex on the nitrogen radical center of **5a** to give a Cu(III) intermediate **9**[7] (Scheme 2). As a result the C=C double bond may be activated to give the acetoxy compound **7** *via* a pericyclic transition state. On the other hand the reaction of the intermediate **9** with aniline would give anilino compound **8**. Alternatively nucleophilic attack of acetic acid and aniline on a cation **10**,[8] generated *via* oxidation of **5a** and/or **6a** by copper(II) acetate might give **7** and/or **8**, respectively.



Scheme 2

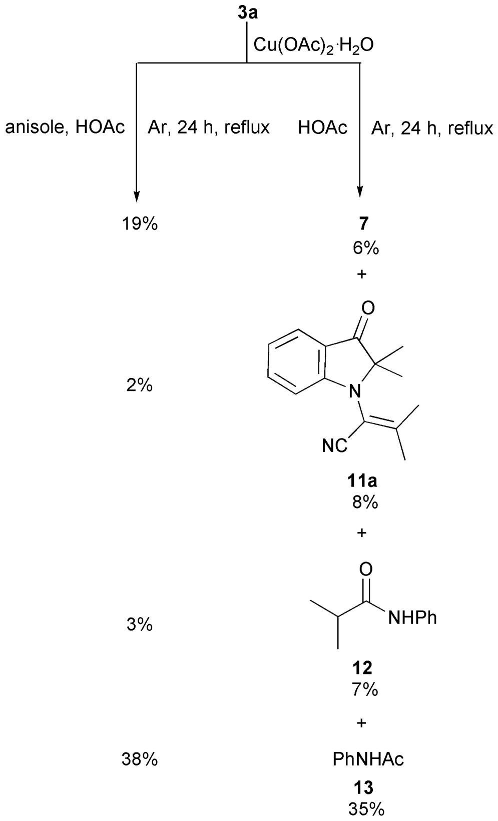
It is uncertain whether the intermediate cation **10** is directly formed from either **5a** or **6a**, or *via* Cu(III) intermediate **9**.

(ii) In acetic acid at reflux

The foregoing reaction was carried out at reflux in expectation of a shorter reaction time. The reaction was allowed to proceed until no spot corresponding to **3a** was observed on TLC. Contrary to expectation, the reaction was not completed in a shorter time. From the reactions having no anisole as a cation trapping agent, were obtained **7** (6%), 2,3-dihydro-1*H*-indole derivative **11a** (8%), isobutyramide **12** (7%), acetanilide **13** (35%), and complex mixtures which were unidentifiable (Scheme 3). Similarly, **7** (19%), **11a** (2%), **12** (3%), **13** (38%), and unidentifiable complex mixtures were obtained from the reaction where anisole was added.

Amide **12** is envisaged to be formed by hydrolysis of **3a**, which is analogous to the formation of an amide by treatment of 2-alkylaminoalk-2-enenitrile with anhydrous HCl in EtOH.[9] The formation of **13** may be explained by the reaction of aniline with $Cu(OAc)_2{\cdot}H_2O$[10] at reflux. The structure of 1,2-dihydroindol-3-one **11a** was determined based on spectroscopic (^1H and ^{13}C NMR, IR, MS) and analytical data. An examination of the structure **11a** suggested that the coupling of radicals **5a** and **6a**, followed by an intramolecular cyclization, was involved. From the reaction carried out in the presence of anisole under the same conditions were obtained the same products, **7**, **11a**, **12**, and **13**. However, no anisole-incorporating product was detected.

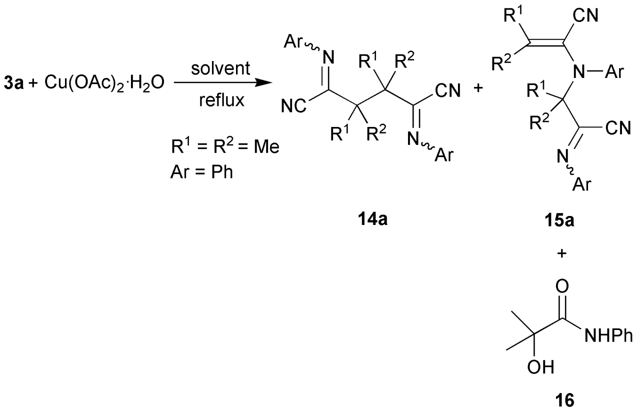
The formation of **11a**, albeit in low yield at reflux temperature may be due to an increase in the concentrations of **5a** and **6a** because it is expected that oxidation by $Cu(OAc)_2{\cdot}H_2O$ at an elevated temperature is more favorable than at rt as a result of an increase in the solubility of $Cu(OAc)_2{\cdot}H_2O$.[11] Therefore, it was desirable to find better conditions giving rise to radicals **5a** and **6a** in order to obtain **11a** in a higher yield.



Scheme 3

(iii) Solvent effects

For higher concentrations of **5** and **6**, we chose non-acidic polar solvents such as absolute EtOH, DMF, and DMSO wherein $Cu(OAc)_2{\cdot}H_2O$ was more soluble than in HOAc. From the reaction of **3a** with $Cu(OAc)_2{\cdot}H_2O$ in such solvents were isolated the head-to-head dimer **14a**, head-to-tail dimer **15a**, and *N*-phenyl-2-hydroxy-2-methylpropionamide **16** (Scheme 4).



Scheme 4

The quantities of **3a** and $Cu(OAc)_2{\cdot}H_2O$, solvent, temperature, reaction times, and yields of **14a**, **15a**, and **16** are summarized in Table 1.

Table 1 shows that compound **16** is formed in DMSO and in wet or dried DMF. An independent experiment showed that *N*-phenyl-2-methylpropionamide was inert to $Cu(OAc)_2{\cdot}H_2O$ in DMF at 120 °C. However, Compound **3a** underwent self-oxidation in DMF at 120 °C to give **4a**[1] (Scheme 5), which was monitored by TLC and GC–MS. Addition of $Cu(OAc)_2{\cdot}H_2O$

Table 1 Reactions of **3a** with $Cu(OAc)_2{\cdot}H_2O$ in various solvents

Entry	**3a**/mmol	$Cu(OAc)_2{\cdot}H_2O$/mmol	Solvent	*T*/°C	*t*/h	Yield[a] (%) **14a**	**15a**	**16**
1	1.05	2.10	EtOH	Reflux/Ar	48	36	25	0
2	1.08	2.16	DMF	120	24	41	15	27
3	0.77	1.69	Dried DMF	120/Ar	24	19	12	32
4	1.29	2.84	DMSO	120	24	37	0	28

[a] Isolated yields.

Table 2 Reactions of **3a** with different concentrations of $Cu(OAc)_2{\cdot}H_2O$ in EtOH

Entry	**3a**/mmol	$Cu(OAc)_2{\cdot}H_2O$/mmol	Additive	*t*/h	Yield[a] (%) **14a**	**15a**	**17a**
1	1.05	2.10		48	36	25[b]	
2	0.72	4.43		48	22	21	
3	0.99	1.98	Styrene	48	30	20	
4	0.78	1.72	Hex-1-ene	48	11	10	
5	3.31	6.62	Pyridine	48	44	34	7[c]
6	5.01	15.03	Pyridine	96	26	30	20
7	1.47	3.23[d]		48	27	22	

[a] Isolated yields. [b] Unreacted **3a** was recovered in 24% yield. [c] Unreacted **3a** was recovered in 13% yield. [d] $Mn(OAc)_3$ was used as an oxidant.

$$\mathbf{3a} \xrightarrow[120^\circ C,\ 18\ h]{DMF} \mathbf{4a} \xrightarrow{Cu(OAc)_2{\cdot}H_2O} \mathbf{16}$$

Scheme 5

(2 equiv. based on **3a**) to the mixture produced by self-oxidation gave **16** in 47% yield.

Conversion of **4a** into **16** may be explained by assuming a complex formed by interaction between the imino nitrogen of **4a** and $Cu(OAc)_2{\cdot}H_2O$ acting as a Lewis acid,[12] followed by hydrolysis of the imidoyl cyanide complex to give an α-hydroperoxyamide in which the O–O bond is readily cleaved by the action of $Cu(OAc)_2{\cdot}H_2O$ to give **16**. An analogous cleavage of the O–O bond has been reported.[7]

(iv) Concentrations of $Cu(OAc)_2{\cdot}H_2O$

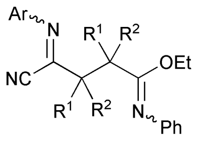
Since ethanol was found to be a better solvent than any of the other solvents tried for **15a**, dependence of the yield of **15a** with respect to the concentrations of $Cu(OAc)_2$ was examined in EtOH. The results are summarized in Table 2. When the concentration of $Cu(OAc)_2{\cdot}H_2O$ increased from 2 equiv. (entry 1) to 6 equiv. (entry 2), yields of both **14a** and **15a** decreased somewhat. Addition of either styrene (entry 3) or hex-1-ene (entry 4) to the solution of **3a** containing $Cu(OAc)_2{\cdot}H_2O$ (2 equiv.), did not lead to the formation of a radical-incorporating product. Yields of **14a** and **15a** increased to 44% and 34%, respectively, when the reaction was carried out in the presence of pyridine (2 equiv.), which was reported to increase the oxidation potential of Cu(II)[5a] under the foregoing conditions. Interestingly, compound **17a**, which is envisaged to be formed by the substitution of one of the cyano groups of **14a** by an ethoxy group, was formed in 7% yield (entry 5). The yield of **17a** (20%) increased significantly at the expense of the yields of **14a** and **15a** when a higher concentration of $Cu(OAc)_2{\cdot}H_2O$ (3 equiv.) and a longer reaction time (96 h) was allowed (entry 6). Use of $Mn(OAc)_3$[13] in place of $Cu(OAc)_2{\cdot}H_2O$ as an oxidant caused a decrease in the yields of **14a** and **15a** (entry 7). We chose the conditions represented by entry 5 for other reactions of cyanoenamines. Reaction times and yields of **14**, **15**, and **17** are summarized in Table 3.

Table 3 shows that the reactions of **3** bearing an electron-donating group on the Ar group, *i.e.*, 3-Me (24 h), 4-Me (22 h), and 2-Me (24 h) have shorter reaction times compared with those with an electron-withdrawing group on the Ar, *i.e.*, 4-Cl (60 h), and 4-Br (48 h). Moreover, in the case of the Ar having an electron-withdrawing group, compounds **17b**,**c** were formed in comparable yields to those of **14b**,**c**, respectively. The result indicates that the yields of **17** increase with the reaction times. In addition, it is noteworthy that when $R^1 = R^2 = Et$, no head-to-head product **14j** is formed. This must be due to the severe steric hindrance arising from two ethyl groups of **5** ($R^1 = R^2 = Et$). In contrast, no head-to-tail product **15g** was detected. This might be due to the instability of radicals **5g** ($R^1 = R^2 = Me$, Ar $= 4\text{-}MeOC_6H_4$) and **6g** ($R^1 = R^2 = Me$, Ar $= 4\text{-}MeOC_6H_4$) and/or dimers **14g** and **15g**, which have an electron-donating group, in view of the relatively short reaction time (12 h) and a lower yield of **14g** compared with those of other head-to-head dimers.

Table 3 Reactions of **3** with $Cu(OAc)_2{\cdot}H_2O$ in the presence of pyridine

Compound	R^1	R^2	Ar	*t*/h	Yield[a] (%) **14**	**15**	**17**
3a	Me	Me	Ph	48	**a** 44	**a** 34	**a** 7
3b	Me	Me	$4\text{-}ClC_6H_4$	60	**b** 21	**b** 34	**b** 24
3c	Me	Me	$4\text{-}BrC_6H_4$	48	**c** 24	**c** 35	**c** 18
3d	Me	Me	$2\text{-}MeC_6H_4$	24	**d** 34	**d** 8	
3e	Me	Me	$3\text{-}MeC_6H_4$	24	**e** 37	**e** 31	
3f	Me	Me	$4\text{-}MeC_6H_4$	22	**f** 37	**f** 33	
3g	Me	Me	$4\text{-}MeOC_6H_4$	12	**g** 15	**g** 0	
3h[b]	Me	Et	$4\text{-}MeC_6H_4$	22	**h** 25	**h** 17	
3i	$–(CH_2)_5–$		Ph	48	**i** 20	**i** 29	
3j	Et	Et	Ph	48	**j** 0	**j** 41	

[a] Isolated yields. [b] A mixture of (*E*)-and (*Z*)-**3h** (1.2:1) was used.

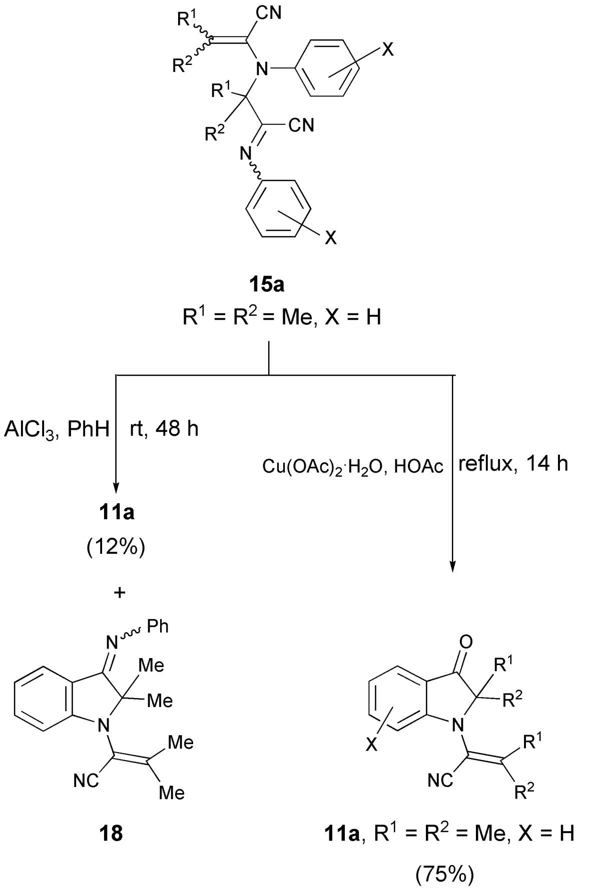


17a, Ar = Ph, $R^1 = R^2 = Me$

Attempts to separate a mixture of stereoisomers **3h** (E:Z = 1.2:1) were unsuccessful. Their reaction afforded a mixture of diastereomers **14h** and **15h**, respectively, which were inseparable by column chromatography. However, the structures of diastereomeric mixtures of **14h** and **15h** together with the ratios of diastereomers **14h** and **15h**, were determined based on ^{1}H NMR and high resolution mass spectroscopy (*vide infra*).

(v) Cyclization of head-to-tail dimers 15

Compound **11a** was obtained from the reaction of **3a** with $Cu(OAc)_2{\cdot}H_2O$ in HOAc at reflux under an argon atmosphere. In order to gain information about the mechanistic pathway, compounds **14a** and **15a** were subjected to the same reaction conditions. Interestingly, treatment of **14a** with $Cu(OAc)_2{\cdot}H_2O$ (1.1 equiv.) in HOAc at reflux gave inseparable unknown mixtures, whereas compound **15a** under the same conditions as for **14a** afforded 2-(2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitrile **11a** in 75% yield. The same reaction in the presence of $AlCl_3$ (2.0 equiv.) instead of $Cu(OAc)_2{\cdot}H_2O$ in benzene at rt afforded **11a** and imino compound **18** in 12% and 35% yields, respectively (Scheme 6).



Scheme 6

In order to ascertain the generality of the transformation of **15** into **11**, compound **15** was subjected to the conditions under which compound **11a** was obtained (Scheme 6). In contrast to the reactions of **14**, which gave rise to complex mixtures, reactions of compounds **15b–j** under the same conditions afforded 3-alkyl-2-(2,2-dialkyl-2,3-dihydro-3-oxo-1*H*-indol-1-yl)alk-2-enenitriles **11b–j** in good yields except for **15j** ($R^1 = R^2$ = Et). Quantities of reactants, reaction times, and yields of **11** are summarized in Table 4.

The reactions of compound **15a** in the presence (1.1–1.8 equiv.) and in the absence of $Cu(OAc)_2{\cdot}H_2O$ gave **11a** in 75% and 56% yields, respectively. The higher yield of **11a** in the presence of $Cu(OAc)_2{\cdot}H_2O$ indicates the importance of $Cu(OAc)_2{\cdot}H_2O$ as a Lewis acid catalyst. When the aryl group has a 3-Me group on it, regioisomers **11e(I)** and **11e(II)** were obtained in 14% and 58% yields, respectively. The predominant formation of **11e(II)** rather than **11e(I)** may be due to the lesser steric interaction in the course of the cyclization. When one of the R groups is an ethyl group (R^2 = Et), a longer reaction time was required than with R^2 = Me, presumably due to the steric hinderance. It took 48 h for the reaction of **15j** which has two ethyl groups. This indicates the significance of the steric hindrance.

To the best of our knowledge, this type of compound **11** has never been reported although several methods of synthesizing 1,2-dihydroindol-3-ones are known.[14] 1,2-Dihydroindol-3-ones are an important class of organic compound because not only have they been utilized as intermediates for the synthesis of various biologically active compounds such as indomethacin,[15] tryptamin,[16] ellipticine,[17] but also some natural products, *i.e.*, austamide[18] and brevianamide[19] consist of this skeleton. There have been numerous methods for the synthesis of 1,2-dihydroindol-3-ones which comprise mainly the cyclization of alkyl *o*-azidoaryl ketones under the basic conditions,[20] the reaction of 2-phenylindol-3-one with a Grignard reagent,[21] and MCPBA mediated oxidation of 1-substituted 3-formyl-1*H*-indoles.[22] In summary, it has been found that the title compound **8** undergoes an intramolecular cyclization, analogous to a Friedel–Craft acylation, in the presence of copper(II) acetate in HOAc at reflux to give 1,2-dihydro-2,2-dimethylindol-3-ones having an α-cyanoisobutenyl group at N-1 of the indol-3-ones. It would appear worthwhile to explore further the synthetic utility of 1,2-dihydroindol-3-ones, and such research is currently in progress.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, for samples in $CDCl_3$ solution containing tetramethylsilane as internal standard: J-values are given in Hz. IR spectra were recorded for KBr discs or thin-film samples on KBr plates. Mass spectra were obtained by electron impact at 70 eV, unless otherwise specified. Elemental analyses were determined by the National Center for Inter-University Research Facilities, Seoul National University. Column chromatography was performed using silica gel (Merck, 70–230 mesh ASTM). Mps were determined on a Fisher-Johns melting-point apparatus and are uncorrected. α-Chloroalkylaldehydes[23] and α-chloroaldimines[24] were prepared according to literature precedures.

General procedure for the synthesis of 3-alkyl-2-arylaminoalk-2-enenitriles 3

To a solution of α-chloroaldehyde (38–84 mmol) in CCl_4 (20 cm^3) were added aniline derivatives (38–84 mmol) and potassium carbonate (23–91 mmol). The mixture was stirred for 12 h at rt and then heated for 1 h at reflux. The cooled reaction mixture was filtered to remove the solid which was washed with CH_2Cl_2 (50 × 3 cm^3). The filtrate was concentrated, followed by addition of CH_3CN (120–150 cm^3). Potassium cyanide (115–224 mmol) was added to the solution, which was heated for 8–13 h at reflux. The cooled reaction mixture was filtered and then washed with CH_2Cl_2. Removal of the solvent *in vacuo* gave a brown liquid, which was chromatographed on a silica gel column (2 × 20 cm) using a mixture of *n*-hexane and EtOAc (5:1) to give the title compound.

3-Methyl-2-phenylaminobut-2-enenitrile 3a. 2-Chloro-2-methylpropionaldehyde (6.38 g, 59.3 mmol) was treated with aniline (5.52 g, 59.3 mmol) in the presence of K_2CO_3 (9.84 g, 71.2 mmol) in CCl_4, followed by addition of KCN (7.73 g, 118.6

Table 4 Quantities of reactants, reaction times, and yields of **11**

Compound	R^1	R^2	X	mmol	$Cu(OAc)_2{\cdot}H_2O$/mmol	*t*/h	Compound	**11** Yield[a] (%)
15a	Me	Me	H	0.48	0.53	14	**a** (X = H)	75
15a	Me	Me	H	0.80	0	30	**a**(X = H)	56
15c	Me	Me	4-Br	0.17	0.20	28	**b** (X = 5-Br)	45
15b	Me	Me	4-Cl	0.36	0.65	14	**c**(X = 5-Cl)	86
15d	Me	Me	2-Me	0.19	0.23	14	**d** (X = 7-Me)	68
15e	Me	Me	3-Me	0.69	0.83	6	**e (I)** (X = 4-Me)	14
							e (II)(X = 6-Me)	58
15f	Me	Me	4-Me	0.38	0.46	4	**f** (X = 5-Me)	92
15h	Me	Et	4-Me	0.20	0.24	30	**h** (X = 5-Me)	60[b]
15j	Et	Et	H	0.33	0.40	480	**j** (X = H)	15

[a] Isolated yields. [b] A mixture of (*E*)- and (*Z*)-stereoisomers.

mmol) in CH_3CN (150 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3a** (5.62 g, 55%).

2-(4-Chlorophenylamino)-3-methylbut-2-enenitrile 3b. 2-Chloro-2-methylpropionaldehyde (6.65 g, 61.8 mmol) was treated with 4-chloroaniline (7.89 g, 61.8 mmol) in the presence of K_2CO_3 (10.26 g, 74.2 mmol) in CCl_4, followed by addition of KCN (8.05 g, 123.6 mmol) in CH_3CN (180 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3b** (5.62 g, 50%).

2-(4-Bromophenylamino)-3-methylbut-2-enenitrile 3c. 2-Chloro-2-methylpropionaldehyde (8.37 g, 77.8 mmol) was treated with 4-bromoaniline (13.39 g, 77.8 mmol) in the presence of K_2CO_3 (6.45 g, 46.7 mmol) in CCl_4, followed by addition of KCN (15.20 g, 223.5 mmol) in CH_3CN (230 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3c** (8.21 g, 42%).

3-Methyl-2-(*o*-tolylamino)but-2-enenitrile 3d. 2-Chloro-2-methylpropionaldehyde (8.17 g, 76.0 mmol) was treated with *o*-toluidine (8.14 g, 76.0 mmol) in the presence of K_2CO_3 (6.30 g, 45.6 mmol) in CCl_4, followed by addition of KCN (9.90 g, 152.0 mmol) in CH_3CN (230 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3d** (8.06 g, 57%).

3-Methyl-2-(*m*-tolylamino)but-2-enenitrile 3e. 2-Chloro-2-methylpropionaldehyde (8.18 g, 76.1 mmol) was treated with *m*-toluidine (8.15 g, 76.1 mmol) in the presence of K_2CO_3 (12.62 g, 91.3 mmol) in CCl_4, followed by addition of KCN (9.90 g, 152.1 mmol) in CH_3CN (230 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3e** (7.51 g, 53%).

3-Methyl-2-(*p*-tolylamino)but-2-enenitrile 3f. 2-Chloro-2-methylpropionaldehyde (9.09 g, 84.5 mmol) was treated with *p*-toluidine (9.06 g, 84.5 mmol) in the presence of K_2CO_3 (7.01 g, 50.7 mmol) in CCl_4, followed by addition of KCN (11.01 g, 169.0 mmol) in CH_3CN (250 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3f** (9.13 g, 58%).

2-(4-Methoxyphenylamino)-3-methylbut-2-enenitrile 3g. 2-Chloro-2-methylpropionaldehyde (7.43 g, 69.1 mmol) was treated with *p*-anisidine (8.51 g, 69.1 mmol) in the presence of K_2CO_3 (5.73 g, 41.5 mmol) in CCl_4, followed by addition of KCN (13.49 g, 207.1 mmol) in CH_3CN (210 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3g** (7.26 g, 52%); liquid (Found: C, 71.2; H, 6.9; N, 13.9. $C_{12}H_{14}N_2O$ requires C, 71.3; H, 7.00; N 13.85%); ν_{max} (neat)/cm^{-1} 3352, 2910, 2224 and 1624; δ_H 1.87 (3H, s, CH_3), 2.11 (3H, s, CH_3), 3.74 (3H, s, OCH_3), 4.65 (1H, br s, NH), 6.67 (2H, d, *J* 8.9 Hz, ArH) and 6.83 (2H, d, *J* 8.9 Hz, ArH); δ_C 19.06, 21.99, 55.68, 110.00, 114.88, 116.19, 122.82, 137.58, 147.18 and 153.94; *m*/*z* 202 (M^+, 91%), 187 ($M^+ - CH_3$, 100).

(*E*)- and (*Z*)-3-Methyl-2-(*p*-tolylamino)pent-2-enenitrile (*E*)- and (*Z*)-3h. 2-Chloro-2-methylbutyraldehyde (4.98 g, 41.3 mmol) was treated with aniline (4.29 g, 40.0 mmol) in the presence of K_2CO_3 (3.31 g, 24.0 mmol) in CCl_4, followed by addition of KCN (8.07 g, 123.9 mmol) in CH_3CN (120 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave a mixture of *(E)*- and *(Z)*-**3h** (4.45 g, 56%); liquid (Found: C, 77.9; H, 8.1; N, 13.9. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.05; N 14.0%); ν_{max} (KBr)/cm^{-1} 3352, 2960, 2920, 2208 and 1611; (*Z*)-isomer, δ_H 0.95 (3H, t, *J* 7.6 Hz, CH_3), 2.05 (3H, d, *J* 1.2 Hz, CH_3), 2.19 (3H, s, ArC*H*$_3$), 2.26 (2H, q, *J* 7.6 Hz, CH_2), 4.56 (1H, s, NH), 6.48–6.57 (2H, m, ArH) and 6.97 (2H, d, *J* 8.2 Hz, ArH); (*E*)-isomer, 1.10 (3H, t, *J* 7.5 Hz, CH_3), 1.80 (3H, s, CH_3), 2.19 (3H, s, ArC*H*$_3$), 2.43 (2H, q, *J* 7.6 Hz, CH_2), 4.56 (1H, s, NH), 6.48–6.57 (2H, m, ArH) and 6.97 (2H, d, *J* 8.2 Hz, ArH); *m*/*z* 200 (M^+, 97%), 185 ($M^+ - CH_3$, 100).

2-Anilino-2-cyclohexylideneacetonitrile 3i. 1-Chlorocyclohexanecarbaldehyde (7.94 g, 54.2 mmol) was treated with aniline (5.04 g, 54.2 mmol) in the presence of K_2CO_3 (4.49 g, 32.5 mmol) in CCl_4, followed by addition of KCN (10.58 g, 162.5 mmol) in CH_3CN (160 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3i** (6.52 g, 57%); mp 82–84 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 79.3; H, 7.6; N, 13.1. $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%); ν_{max} (neat)/cm^{-1} 3352, 2976, 2208 and 1629; δ_H 0.85 (3H, t, *J* 7.6 Hz, CH_3), 1.02 (3H, t, *J* 7.6 Hz, CH_3), 2.15 (2H, q, *J* 7.6 Hz, CH_2), 2.35 (2H, q, *J* 7.6 Hz, CH_2), 4.68 (1H, s, NH), 6.53 (2H, d, ArH, *J* 7.5 Hz, ArH), 6.70 (1H, t, ArH, *J* 7.5 Hz, ArH) and 7.07 (2H, td, ArH, *J* 7.5, 0.9 Hz, ArH); δ_C 11.77, 12.71, 22.78, 26.15, 107.86, 114.10, 116.25, 119.59, 129.08, 143.95 and 160.37; *m*/*z* 200 (M^+, 100%), 185 ($M^+ - CH_3$, 95).

2-Anilino-3-ethylpent-2-enenitrile 3j. 2-Chloro-2-ethylbutyraldehyde (5.16 g, 38.3 mmol) was treated with aniline (3.57 g, 38.3 mmol)in the presence of K_2CO_3 (3.18 g, 23.0 mmol) in CCl_4, followed by addition of KCN (7.48 g, 114.9 mmol) in CH_3CN (120 cm^3). Work-up of the reaction mixture in accordance with the above general procedure gave **3j** (4.21 g, 54%); liquid (Found: C, 78.1; H, 8.1; N, 13.9. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.05; N, 14.0%); ν_{max} (neat)/cm^{-1} 3352, 2976, 2208 and 1629; δ_H 0.85 (3H, t, *J* 7.6 Hz, CH_3), 1.02 (3H, t, *J* 7.6 Hz, CH_3), 2.15 (2H, q, *J* 7.6 Hz, CH_2), 2.35 (2H, q, *J* 7.6 Hz, CH_2), 4.68 (1H, s, NH), 6.53 (2H, d, *J* 7.5 Hz, ArH), 6.70 (1H, t, *J* 7.5 Hz, ArH) and 7.07 (2H, td, *J* 7.5, 0.9 Hz, ArH); δ_C 11.77, 12.71, 22.78, 26.15, 107.86, 114.10, 116.25, 119.59, 129.08, 143.95 and 160.37; *m*/*z* 200 (M^+, 100%), 185 ($M^+ - CH_3$, 95).

Reaction of 3a with $Cu(OAc)_2$

(i) Under a nitrogen atmosphere at rt. To a solution of **3a** (178 mg, 1.03 mmol) in HOAc (5 cm^3) under a nitrogen atmosphere was added $Cu(OAc)_2 \cdot H_2O$ (453 mg, 2.27 mmol). The mixture was stirred for 19 h at rt, followed by addition of water (30 cm^3) and CH_2Cl_2 (30 cm^3). The mixture was neutralized with aqueous Na_2CO_3 and extracted with CH_2Cl_2 (30 × 2 cm^3). The combined extracts were dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* gave a brown liquid, which was chromatographed on a silica gel column (2 × 20 cm) using a mixture of *n*-hexane and EtOAc (10:1) to give 2-cyano-1,1-dimethyl-2-phenyliminoethyl acetate **7** (20 mg, 18%); liquid (Found: C, 67.9; H, 6.0; N, 12.1. $C_{13}H_{14}N_2O_2$ requires C, 67.8; H, 6.1; N, 12.2%); ν_{max} (neat)/cm^{-1} 2990, 2940, 2219, 1742, 1638, 1591, 1483, 1371, 1250, 1147, 1081, 1018, 781 and 699; δ_H 1.64 (6H, s, 2 × CH_3), 2.07 (3H, s, CH_3) and 6.97–7.37 (5H, m, ArH); δ_C 21.82, 24.96, 81.39, 110.37, 120.27, 127.55, 129.63, 147.54, 148.79 and 170.92; *m*/*z* 230 (M^+, 100%), 172 (58), 129 (75), 101 (42), 77 (72). Continuous elution with the same solvent mixture gave 3-anilino-3-methyl-2-phenyliminobutyronitrile **8** (12 mg, 10%): liquid (Found: C, 77.4; H, 6.4; N, 15.9. $C_{17}H_{17}N_3$ requires C, 77.5; H, 6.5; N, 16.0%); ν_{max} (neat)/cm^{-1} 2990, 2938, 2220, 1636, 1572, 1145 and 702; δ_H 1.69 (6H, s, 2 × CH_3), 4.14 (1H, br s, NH), 6.69 (2H, d, *J* 7.8 Hz, ArH), 6.79 (1H, t, *J* 7.6 Hz, ArH), 6.68–7.08 (2H, m, ArH), 7.17 (2H, t, *J* 7.5 Hz, ArH), 7.25–7.33 (1H, m, ArH) and 7.41 (2H, t, *J* 7.4 Hz, ArH); *m*/*z* 263 (M^+, 4%), 172 (3), 134 (100). Continuous elution with the same solvent mixture gave unreacted **3a** (87 mg, 50%) and 3-hydroperoxy-3-methyl-2-phenyliminobutyronitrile **4a** (14 mg, 7%): mp 53–55 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 64.9; H, 6.1; N, 13.9. $C_{11}H_{12}N_2O_2$: C, 64.7; H, 5.9; N 13.7%); ν_{max} (neat)/cm^{-1} 3250, 2990, 2224 and 1625; δ_H 1.63 (6H, s, 2 × CH_3), 7.09 (2H, d, *J* 7.5 Hz, ArH), 7.32 (1H, t, *J* 7.4 Hz, ArH), 7.44 (2H, t, *J* 7.4 Hz, ArH) and 8.86 (1H, br s, OOH); δ_C 22.17, 84.96, 110.29, 120.05, 127.61, 129.26, 147.59 and 147.70.

(ii) In the presence of anisole in air at rt. To a solution of **3a** (342 mg, 2.00 mmol) in HOAc (10 cm^3) was added anisole (238 mg, 2.20 mmol) and $Cu(OAc)_2 \cdot H_2O$ (453 mg, 2.27 mmol). The mixture was stirred for 24 h at rt. The mixture was worked up as described in (i). Chromatography of the reaction mixture using a mixture of *n*-hexane and EtOAc (5:1) gave **4a** (137 mg, 34%).

(iii) Under a nitrogen atmosphere at reflux. To a solution of **3a** (210 mg, 1.22 mmol) in HOAc (5 cm^3) under a nitrogen atmosphere was added $Cu(OAc)_2 \cdot H_2O$ (465 mg, 2.33 mmol). The mixture was heated for 24 h at reflux and then worked up as before. Chromatography (2 × 20 cm) of the reaction mixture using a mixture of *n*-hexane and EtOAc (5:1) gave **7** (17 mg, 6%), unknown mixtures (40 mg), a mixture of *N*-phenylisobutyramide **12** and 2-(2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitrile **11a** (45 mg). Elution with the same solvent mixture (2:1) gave acetanilide **13** (58 mg, 35%). Rechromatography (2 × 20 cm) of the mixture of **11a** and **12** using a mixture of *n*-hexane and CH_2Cl_2 (2:1) gave **12** (14 mg, 7%) and **11a** (23 mg, 8%): mp 60–62 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 75.0; H, 6.7; N, 11.7. $C_{15}H_{16}N_2O$ requires C, 75.0; H, 6.7; N, 11.7%); ν_{max} (neat)/cm^{-1} 2210, 1707 and 1611; δ_H 1.22 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.82 (3H, s, CH_3), 2.22 (3H, s, CH_3), 6.56 (1H, d, *J* 8.2 Hz, ArH), 6.82 (1H, t, *J* 7.4 Hz, ArH), 7.44 (1H, t, *J* 7.2 Hz, ArH) and 7.61 (1H, d, *J* 7.6 Hz, ArH); δ_C 20.54, 22.10, 22.54, 22.56, 69, 89, 105.91, 110.23, 116.44, 119.35, 119.70, 125.29, 137.61, 156.85, 159.99 and 202.74; *m*/*z* 240 (M^+).

(iv) In the presence of anisole under a nitrogen atmosphere at reflux. To a solution of **3a** (200 mg, 1.16 mmol) in HOAc (5 cm^3) under a nitrogen atmosphere was added anisole (275 mg, 2.55 mmol) and $Cu(OAc)_2 \cdot H_2O$ (463 mg, 2.55 mmol). The mixture was heated for 24 h at reflux and then worked up as before. Chromatography of the reaction mixture using a mixture of *n*-hexane and EtOAc (5:1) gave **7** (51 mg, 19%), unknown mixtures (32 mg), and a mixture of **11a** and **12** (14 mg). Elution with the same solvent mixture (2:1) gave **13** (59 mg, 38%). Rechromatography (2 × 20 cm) of the mixture of **11a** and **12** using a mixture of *n*-hexane and EtOAc (2:1) gave **12** (7 mg, 3%) and **11a** (5 mg, 2%).

Reaction of 3a with $Cu(OAc)_2 \cdot H_2O$ in different solvents

(i) In EtOH. To a solution of **3a** (180 mg, 1.05 mmol) in EtOH (5 cm^3) was added $Cu(OAc)_2 \cdot H_2O$ (381 mg, 2.10 mmol) under an argon atmosphere. The mixture was heated for 48 h at reflux, followed by work-up as before. Chromatography (2 × 20 cm) of the reaction mixture using a mixture of *n*-hexane and EtOAc (10:1) as the eluent gave 3,3,4,4-tetramethyl-2,5-bis(phenylimino)adiponitrile **14a** (47 mg, 36%), 2-(2-cyano-*N*-phenyl-2-phenylimino-1,1-dimethylethylamino)-3-methylbut-2-enenitrile **15a** (33 mg, 25%), and unreacted **3a** (43 mg, 24%). **14a**: mp 110–112 °C (from MeOH–H_2O) (Found: C, 77.0; H 6.4; N, 16.2. $C_{22}H_{22}N_4$ requires C, 77.2; H, 6.50; N, 16.4%); ν_{max} (KBr)/cm^{-1} 2211 and 1616; δ_H 1.49(12H, s, 4 × CH_3) and 6.92–7.34 (10H, m, 2 × ArH); δ_C 23.38, 48.60, 111.60, 120.09, 127.46, 129.68, 149.13 and 149.99; *m*/*z* 342 (M^+, 47%), 341 (22), 327 (13), 250 (32), 213 (55), 172 (77), 171 (100).**15a**: liquid (Found: C, 77.1; H, 6.4; N, 16.3. $C_{22}H_{22}N_4$ requires C, 77.2; H, 6.5; N, 16.4%); ν_{max} (neat)/cm^{-1} 2207, 1632 and 1592; δ_H 1.68 (6H, s, 2 × CH_3), 2.05 (3H, s, CH_3), 2.12 (3H, s, CH_3) and 6.89–7.35 (10H, m, 2 × ArH); δ_C 22.85, 22.68, 23.91, 65.75, 111.93, 112.44, 118.57, 119.93, 122.12, 123.81, 126.30, 127.60, 129.75, 129.85, 145.19, 148.75, 150.33 and 158.77; *m*/*z* 342 (M^+, 30%), 341 (26), 327 (9), 250 (11), 213 (14), 172 (41), 171 (51), 155 (30), 144 (53), 77 (100).

(ii) In DMF. To a solution of **3a** (186 mg, 1.08 mmol) in DMF (10 cm^3) was added $Cu(OAc)_2 \cdot H_2O$ (381 mg, 2.16 mmol) at rt. The mixture was heated for 24 h at 120 °C. Water (50 cm^3) was added to the cooled reaction mixture, which was then extracted with CH_2Cl_2 (50 cm^3 × 3) and EtOAc (50 cm^3) in a series. The combined organic layer was dried and worked up as usual. Chromatography (2 × 20 cm) of the residue using a mixture of *n*-hexane and EtOAc (10:1) gave **14a** (74 mg, 41%) and **15a** (26 mg, 15%). Subsequent elution with the same solvent mixture (3:1) gave 2-hydroxy-2-methyl-*N*-phenylpropionamide **16** (52 mg, 27%): liquid (Found: C, 67.1; H, 7.1; N, 7.7. $C_{10}H_{13}NO_2$ requires C, 67.0; H, 7.3; N, 7.8%); ν_{max} (neat)/cm^{-1} 3263, 2974, 1653, 1441, 1185 and 1152; δ_H 1.47 (6H, s, 2 × CH_3), 2.73 (1H, br s, OH), 7.04 (1H, t, *J* 7.4 Hz, ArH), 7.25 (2H, t, *J* 7.6 Hz, ArH), 7.49 (2H, d, *J* 7.6 Hz, ArH) and 8.67 (1H, br s, NH); *m*/*z* 179 (M^+, 29%), 121 (45), 93 (100). The same reaction of **3a** (133 mg, 0.77 mmol) with $Cu(OAc)_2 \cdot H_2O$ (34 mg, 1.69 mmol) in dried DMF under an argon atmosphere gave **14a** (34 mg, 19%), **15a** (21 mg, 12%), and **16** (62 mg, 32%).

(iii) In DMSO. From the reaction of **3a** (222 mg, 1.29 mmol) with $Cu(OAc)_2 \cdot H_2O$ (516 mg, 2.84 mmol) in DMSO (10 cm^3) at 120 °C were obtained **14a** (83 mg, 37%) and **15a** (64 mg, 28%).

Reaction of 4a with $Cu(OAc)_2 \cdot H_2O$

A solution of **3a** (186 mg, 1.05 mmol) in DMF (10 cm^3) was heated for 24 h at 120 °C by which time **3a** was completely converted into 3-hydroperoxy-3-methyl-2-phenyliminobutyronitrile **4a**. $Cu(OAc)_2 \cdot H_2O$ (500 mg, 2.60 mmol) was added to the mixture, which was then stirred for 18 h at 120 °C. Work-up of the reaction mixture as described in (ii) gave **16** (101 mg, 47%).

General procedure for the reactions of 3 with $Cu(OAc)_2{\cdot}H_2O$ in the presence of pyridine

To a solution of **3** (1.72–5.36 mmol) in absolute EtOH (15–52 cm^3) was added $Cu(OAc)_2{\cdot}H_2O$ (6.62–10.34 mmol) and pyridine (6.62–10.34 mmol). The mixture was heated for an appropriate time at reflux. Water (50 cm^3) was added to the cooled reaction mixture, which was then extracted with CH_2Cl_2 (50 cm^3) and dimethyl ether (50 cm^3 × 3). The combined organic layers were dried ($MgSO_4$). Removal of the solvent gave a residue, which was chromatographed on silica gel (2 × 20 cm) using a mixture of *n*-hexane and EtOAc (10:1) to give **14**, **15**, and **17**.

Reaction of 3a. Reaction of **3a** (570 mg, 3.31 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (1.02 g, 6.62 mmol) in the presence of pyridine (523 mg, 6.62 mmol) in EtOH (30 cm^3) for 48 h gave **14a** (217 mg, 44%), **15a** (164 mg, 34%), 4-cyano-2,2,3,3-tetramethyl-*N*-phenyl-4-phenyliminobutyrimidic acid ethyl ester **17a** (41 mg, 7%), and unreacted **3a** (75 mg, 13%).

17a: sticky solid (Found: C, 76.2; H, 7.4; N, 11.7. $C_{23}H_{27}N_3O$ requires C, 76.4; H, 7.5; N, 11.6%); ν_{max} (KBr)/cm^{-1} 1637 and 1581; δ_H 0.52 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 1.20 (6H, s, 2 × CH_3), 1.29 (6H, s, 2 × CH_3), 3.57 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 6.53 (2H, d, *J* 7.6 Hz, ArH), 6.80 (2H, d, *J* 7.1 Hz, ArH) and 6.85–6.98 (2H, m, ArH), 7.05–7.21 (m, 4H, ArH); δ_C 12.94, 21.05, 22.29, 46.99, 47.39, 62.90, 118.23, 123.07, 127.96, 128.20, 148.51, 150.50, 157.58, 161.54 and 164.04.

Reaction of 2-(4-chlorophenylamino)-3-methylbut-2-enenitrile 3b. The reaction of **3b** (971 mg, 4.70 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (1.88 g, 10.34 mmol) in the presence of pyridine (818 mg, 10.34 mmol) in EtOH (50 cm^3) for 60 h gave 2,5-bis(4-chlorophenylimino)-3,3,4,4-tetramethyladiponitrile **14b** (201 mg, 21%), 2-[*N*-(4-chlorophenyl)-2-(4-chlorophenylimino)-2-cyano-1,1-dimethylethylamino]-3-methylbut-2-enenitrile **15b** (331 mg, 34%), and *N*-(4-chlorophenyl)-4-(4-chlorophenylimino)-4-cyano-2,2,3,3-tetramethylbutyrimidic acid ethyl ester **17b** (237 mg, 24%).

14b: mp 187–188 °C (from *n*-hexane) (Found: C, 64.3; H, 5.0; N, 13.5. $C_{22}H_{20}Cl_2N_4$ requires C, 64.2; H, 4.90; N, 13.6%); ν_{max} (KBr)/cm^{-1} 2213 and 1617; δ_H 1.54 (12H, s, 4 × CH_3), 6.94 (4H, d, *J* 6.7 Hz, 2 × ArH) and 7.36 (4H, d, *J* 6.7 Hz, 2 × ArH); δ_C 22.82, 48.31, 110.93, 121.14, 129.44, 132.82, 146.84 and 150.12.

15b: mp 74–75 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 64.3; H, 5.15; N, 13.7. $C_{22}H_{20}Cl_2N_4$ requires C, 64.2; H, 4.9; N, 13.6%; δ_H 1.65 (6H, s, 2 × CH_3), 2.02 (3H, s, $ArCH_3$), 2.11 (3H, s, CH_3), 6.87 (2H, d, *J* 7.8 Hz, ArH), 6.90 (2H, d, *J* 8.6 Hz, ArH), 7.18 (2H, d, *J* 8.6 Hz, ArH) and 7.20 (1H, d, *J* 7.8 Hz, ArH); δ_C 20.36, 22.23, 23.42, 65.44, 111.17, 111.63, 117.72, 121.06, 122.81, 128.78, 129.40, 129.50, 133.09, 143.22, 146.32, 149.78 and 158.78.

17b: mp 88–89 °C (from *n*-hexane–EtOAc (10:1) (Found: C, 66.5; H, 5.9; N, 10.2. $C_{23}H_{25}N_3Cl_2O$ requires C, 66.7; H, 6.1; N, 10.1%); ν_{max} (KBr)/cm^{-1} 1637 and 1581; δ_H 0.69 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 1.25 (6H, s, 2 × CH_3), 1.33 (6H, s, 2 × CH_3), 3.69 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 6.55 (2H, d, *J* 8.6 Hz, ArH), 6.79 (2H, d, *J* 8.6 Hz, ArH) and 7.20 (1H, d, *J* 8.6 Hz, ArH); δ_C 12.94, 21.05, 22.29, 46.99, 47.39, 62.90, 118.23, 123.07, 127.96, 128.20, 148.51, 150.50, 157.58, 161.54 and 164.04.

Reaction of 2-(4-bromophenylamino)-3-methylbut-2-enenitrile 3c. The reaction of **3c** (432 mg, 1.72 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (687 mg, 3.78 mmol) in the presence of pyridine (299 mg, 3.78 mmol) for 48 h in EtOH gave 2,5-bis(4-bromophenylimino)-3,3,4,4-tetramethyladiponitrile **14c** (100 mg, 24%), 2-[*N*-(4-bromophenyl)-2-(4-bromophenylimino)-2-cyano-1,1-dimethylethylamino]-3-methylbut-2-enenitrile **15c** (149 mg, 35%), and *N*-(4-bromophenyl)-4-(4-bromophenylimino)-4-cyano-2,2,3,3-tetramethylbutyrimidic acid ethyl ester **17c** (81 mg, 18%).

14c: mp 193–194 °C (from *n*-hexane) (Found: C, 53.0; H, 4.3; N, 11.0. $C_{22}H_{20}Br_2N_4$ requires C, 52.8; H, 4.0; N, 11.2%); ν_{max} (KBr)/cm^{-1} 2213 and 1617; δ_H 1.47 (12H, s, 4 × CH_3), 6.80 (4H, d, *J* 8.7 Hz, 2 × ArH) and 7.44 (4H, d, *J* 8.7 Hz, 2 × ArH); δ_C 22.83, 48.33, 110.90, 120.74, 121.40, 132.41, 147.34 and 150.15.

15c: mp 132–133 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 52.8; H, 4.0; N, 11.0. $C_{22}H_{20}Br_2N_4$ requires C, 52.8; H, 4.0; N, 11.2%); ν_{max} (neat)/cm^{-1} 2200 and 1626; δ_H 1.66 (6H, s, 2 × CH_3), 2.03 (3H, s, $ArCH_3$), 2.13 (3H, s, CH_3), 6.81 (2H, d, *J* 8.7 Hz, ArH), 6.84 (2H, d, *J* 9.1 Hz, ArH), 7.32 (2H, d, *J* 9.1 Hz, ArH) and 7.49 (1H, d, *J* 8.7 Hz, ArH); δ_C 20.33, 22.22, 23.38, 65.39, 111.07, 111.33, 116.07, 117.58, 120.96, 121.29, 122.59, 131.81, 132.43, 143.64, 146.74, 149.84 and 158.94.

17c: sticky solid (Found: C, 53.1; H, 4.7; N, 7.9. $C_{23}H_{25}N_3Br_2O$ requires C, 53.2; H, 4.85; N, 8.1%); ν_{max} (KBr)/cm^{-1} 1626 and 1584; δ_H 0.72 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 1.26 (6H, s, 2 × CH_3), 1.35 (6H, s, 2 × CH_3), 3.71 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 6.56 (2H, d, *J* 8.6 Hz, ArH), 6.81 (2H, d, *J* 8.6 Hz, ArH) and 7.18 (1H, d, *J* 8.6 Hz, ArH).

Reaction of 3-methyl-2-(*o*-tolylamino)but-2-enenitrile 3d. The reaction of **3d** (947 mg, 5.30 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (2.03 g, 11.2 mmol) in the presence of pyridine (876 mg, 11.2 mmol) in EtOH (50 cm^3) for 24 h gave 3,3,4,4-tetramethyl-2,5-bis(*o*-tolylimino)adiponitrile **14d** (324 mg, 34%) and 2-[2-cyano-1,1-dimethyl-*N*-(*o*-tolyl)-2-(*o*-tolylimino)ethylamino]-3-methylbut-2-enenitrile **15d** (72 mg, 8%).

14d: mp 132–133 °C (from *n*-hexane–EtOAc) (Found: C, 77.6; H 6.8; N, 15.2. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (KBr)/cm^{-1} 2200 and 1603; δ_H 1.51 (12H, s, 4 × CH_3), 2.10 (6H, s, 2 × $ArCH_3$), 6.72–6.78 (2H, m, 2 × ArH) and 7.02–7.18 (6H, m, 2 × ArH); δ_C 17.85, 23.04, 48.21, 111.15, 117.75, 125.79, 126.62, 127.06, 129.49, 130.56, 147.45 and 149.15; *m*/*z* 370 (M$^+$, 26%), 355 (M$^+$ – Me, 44), 185 (100).

15d: sticky solid (Found: C, 77.6; H, 7.0; N, 15.0. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (neat)/cm^{-1} 2912 and 1622; δ_H 1.67 (6H, s, 2 × CH_3), 1.94 (3H, s, $ArCH_3$), 2.00 (3H, s, $ArCH_3$), 2.03 (3H, s, CH_3), 2.36 (3H, s, CH_3), 6.57–6.64 (1H, m, ArH), 7.01–7.17 (6H, m, ArH) and 7.47–7.54 (1H, m, ArH); δ_C 17.51, 20.42, 21.62, 23.04, 24.82, 67.34, 11.13, 114.22, 117.40, 118.76, 126.27, 126.51, 126.58, 127.07, 129.35, 129.90, 130.51, 132.04, 137.39, 143.22, 146.92, 147.19 and 154.35; *m*/*z* 370 (M$^+$, 31%), 355 (M$^+$ – CH_3, 60), 185 (100).

Reaction of 3-methyl-2-(*m*-tolylamino)but-2-enenitrile 3e. The reaction of **3e** (998 mg, 5.36 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (2.14 g, 11.8 mmol) in the presence of pyridine (933 mg, 11.8 mmol) in EtOH (50 cm^3) for 24 h gave 3,3,4,4-tetramethyl-2,5-bis(*m*-tolylimino)adiponitrile **14e** (371 mg, 37%) and 2-[2-cyano-1,1-dimethyl-*N*-(*m*-tolyl)-2-(*m*-tolylimino)ethylamino]-3-methylbut-2-enenitrile **15e** (310 mg, 31%).

14e: mp 62–64 °C (from *n*-hexane) (Found: C, 77.85; H 6.8; N, 15.3. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (KBr)/cm^{-1} 2216 and 1599; δ_H 1.45 (12H, s, 4 × CH_3), 2.23 (6H, s, 2 × $ArCH_3$), 6.67–6.76 (4H, m, 2 × ArH), 6.95 (2H, d, *J* 7.7 Hz, 2 × ArH) and 7.16 (2H, t, *J* 8.0 Hz, 2 × ArH); δ_C 21.21, 22.83, 48.01, 111.07, 116.45, 120.22, 127.64, 128.94, 138.99, 148.61 and 149.15.

15e: mp 74–75 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 77.7; H 7.3; N, 15.25. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (neat)/cm^{-1} 2209 and 1633; δ_H 1.64 (6H, s, 2 × CH_3), 2.02 (3H, s, $ArCH_3$), 2.09 (3H, s, $ArCH_3$), 2.23 (3H, s, CH_3), 2.28 (3H, s, CH_3), 6.64–6.73 (2H, m, ArH), 6.75–6.84 (3H, m, ArH), 6.95–7.02 (1H, m, ArH), 7.04–7.12 (1H, m, ArH) and 7.16–7.24 (1H, m, ArH); δ_C 20.29, 21.26, 21.67, 22.11, 23.27, 65.14, 111.41, 111.94, 116.11, 118.10, 118.79, 119.92, 122.27, 124.12, 127.70, 129.03, 129.08, 138.98, 139.13, 144.67, 148.37, 149.77 and 158.0.

Reaction of 3-methyl-2-(*p*-tolylamino)but-2-enenitrile 3f. The reaction of **3f** (998 mg, 5.30 mmol) with $Cu(OAc)_2\cdot H_2O$ (2.12 g, 11.7 mmol) in the presence of pyridine (922 mg, 11.7 mmol) in EtOH (50 cm^3) for 22 h gave 3,3,4,4-tetramethyl-2,5-bis(*p*-tolylimino)adiponitrile **14f** (360 mg, 37%), 2-[2-cyano-1,1-dimethyl-*N*-(*p*-tolyl)-2-(*p*-tolylimino)ethylamino]-3-methylbut-2-enenitrile **15f** (325 mg, 33%).

14f: mp 116–117 °C (from *n*-hexane) (Found: C, 78.0; H, 7.15; N, 15.0. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (KBr)/cm^{-1} 2208 and 1604; δ_H 1.42 (12H, s, 4 × CH_3), 2.21 (6H, s, 2 × ArCH_3), 6.84 (4H, d, *J* 7.8 Hz, 2 × ArH) and 7.06 (4H, d, *J* 7.8 Hz, 2 × ArH); δ_C 20.92, 22.73, 47.97, 111.27, 119.75, 129.61, 136.89, 146.00 and 148.51.

15f: mp 74–75 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 77.7; H 7.3; N, 15.25. $C_{24}H_{26}N_4$ requires C, 77.8; H, 7.1; N, 15.1%); ν_{max} (neat)/cm^{-1} 2209 and 1633; δ_H 1.64 (6H, s, 2 × CH_3), 2.02 (3H, s, ArCH_3), 2.09 (3H, s, ArCH_3), 2.23 (3H, s, CH_3), 2.28 (3H, s, CH_3), 6.64–6.73 (2H, m, ArH), 6.75–6.84 (3H, m, ArH), 6.95–7.02 (1H, m, ArH), 7.04–7.12 (1H, m, ArH) and 7.16–7.24 (1H, m, ArH); δ_C 20.29, 21.26, 21.67, 22.11, 23.27, 65.14, 111.41, 111.94, 116.11, 118.10, 118.79, 119.92, 122.27, 124.12, 127.70, 129.03, 129.08, 138.98, 139.13, 144.67, 148.37, 149.77 and 158.0.

Reaction of 2-(4-methoxyphenylamino)-3-methylbut-2-enenitrile 3g. The reaction of **3g** (889 mg, 4.40 mmol) with $Cu(OAc)_2\cdot H_2O$ (1.60 g, 8.80 mmol) in the presence of pyridine (696 mg, 8.80 mmol) in EtOH (44 cm^3) for 12 h gave 2,5-bis-(4-methoxyphenylimino)-3,3,4,4-tetramethyladiponitrile **14g** (127 mg, 15%); mp 140–142 °C (from *n*-hexane) (Found: C, 71.4; H 6.4; N, 13.8. $C_{24}H_{26}N_4O_2$ requires C, 71.6; H, 6.5; N, 13.9%); ν_{max} (KBr)/cm^{-1} 2206 and 1608; δ_H 1.45 (12H, s, 4 × CH_3), 3.73 (6H, s, 2 × CH_3O), 6.83 (4H, d, *J* 8.9 Hz, 2 × ArH) and 7.02 (4H, d, *J* 8.9 Hz, 2 × ArH); δ_C 22.83, 48.20, 55.40, 111.80, 114.26, 122.15, 141.32, 146.95 and 158.98.

Reaction of (*E*)- and (*Z*)-3-methyl-2-(*p*-tolylamino)pent-2-enenitrile (*E*)- and (*Z*)-3h. The reaction of a mixture of *(E)*- and *(Z)*-**3h** (757 mg, 3.78 mmol) with $Cu(OAc)_2\cdot H_2O$ (1.51 g, 8.32 mmol) in the presence of pyridine (658 mg, 8.32 mmol) in EtOH (38 cm^3) for 22 h gave a diastereomeric mixture of 3,4-diethyl-3,4-dimethyl-2,5-bis(*p*-tolylimino)adiponitrile **14h** (191 mg, 25%) and a diastereomeric mixture of 2-{1-[cyano-(*p*-tolylimino)methyl]-1-methyl-*N*-(*p*-tolyl)propylamino}-3-methylpent-2-enenitrile **15h** (132 mg, 17%).

14h: sticky solid; δ_H 0.80–0.92 (6H, m, 2 × CH_3), 1.36–1.44 (6H, m, 2 × CH_3), 1.63–1.87 (2H, m, CH_2), 2.27 (6H, s, 2 × ArCH_3), 2.24–2.42 (2H, m, CH_2), 6.81–6.92 (4H, m, 2 × ArH), 7.05–7.16 (4H, m, 2 × ArH).

15h: sticky solid; δ_H 0.80–0.91 (4.5H, m, CH_3), 1.05 (1.5H, t, *J* 7.5 Hz, CH_3), 1.57–1.63 (3H, m, CH_3), 1.97–2.03 (3H, m, CH_3), 2.04 (2H, q, *J* 7.5 Hz, CH_2), 2.22 (3H, s, ArCH_3), 2.29 (3H, s, ArCH_3), 2.39 (1H, qd, *J* 7.6, 2.0 Hz, CH_2), 2.56 (1H, d, *J* 7.6 Hz, CH_2), 6.77–6.83 (2H, m, ArH), 6.94–7.10 (4H, m, ArH) and 7.10–7.16 (2H, m, ArH); *m*/*z* 398 (M^+, 10%), 369 ($M^+ - CH_2CH_3$, 5), 342 (9), 292 (11), 255 (100). *m*/*z* HRMS (EI) Calc. for $C_{26}H_{30}N_4$: [M + H]; 398.2470. Found: *m*/*z*, 398.2472.

Reaction of 1,1′-cyclohexylidene-1-phenylaminoacetonitrile 3i. The reaction of **3i** (998 mg, 4.70 mmol) with $Cu(OAc)_2\cdot H_2O$ (1.88 g, 10.3 mmol) in the presence of pyridine (818 mg, 10.3 mmol) in EtOH (50 cm^3) for 48 h gave {1′-[cyano(phenylimino)methyl]bicyclohexan-1-yl}phenyliminoacetonitrile **14i** (198 mg, 20%) and {1-[cyano(phenylimino)methyl]-*N*-phenylcyclohexylamino}cyclohexylidenacetonitrile **15i** (312 mg, 31%).

14i: mp 224–225 °C (from *n*-hexane–EtOAc) (Found: C, 79.7; H 7.2; N, 13.3. $C_{28}H_{30}N_4$ requires C, 79.6; H, 7.2; N, 13.3%); ν_{max} (KBr)/cm^{-1} 2200 and 1621; δ_H 1.14–1.41 (6H, m, 3 × CH_2), 1.56–1.81 (10H, m, 5 × CH_2), 2.44 (4H, d, *J* 12.3 Hz, 2 × CH_2), 6.93 (4H, d, *J* 7.9 Hz, 2 × ArH), 7.17 (2H, t, *J* 7.9 Hz, 2 × ArH) and 7.30 (4H, t, *J* 7.9 Hz, 2 × ArH); δ_C 22.88, 25.46, 29.51, 53.47, 111.66, 119.62, 126.94, 129.18, 147.88 and 149.16.

15i: sticky solid (Found: C, 79.4; H, 7.1; N, 13.3. $C_{28}H_{30}N_4$ requires C, 79.6; H, 7.2; N, 13.3%); ν_{max} (neat)/cm^{-1} 2208 and 1626; δ_H 1.15–1.86 (12H, m, 4 × CH_3), 1.88–2.10 (2H, m, CH_3), 2.39–2.53 (4H, m, CH_3), 2.53–2.68 (2H, m, CH_3), 6.80 (2H, d, *J* 7.5 Hz, ArH) and 7.04–7.41 (8H, m, 2 × ArH); δ_C 23.12, 25.08, 25.79, 26.87, 27.65, 29.92, 32.13, 32.82, 66.83, 109.70, 111.19, 118.85, 119.20, 119.52, 125.84, 126.84, 127.87, 129.03, 129.09, 144.79, 146.14, 148.54 and 163.74.

Reaction of 3-ethyl-2-phenylaminopent-2-enenitrile 3j. The reaction of **3j** (1.06 g, 5.24 mmol) with $Cu(OAc)_2\cdot H_2O$ (2.09 g, 11.5 mmol) in the presence of pyridine (912 mg, 11.5 mmol) in EtOH (52 cm^3) for 48 h gave 2-{1-[cyano(phenylimino)methyl]-1-ethyl-*N*-phenylpropylamino}-3-ethylpent-2-enenitrile **15j** (434 mg, 41%); sticky solid (Found: C, 78.5; H, 7.5; N, 14.0. $C_{26}H_{30}N_4$ requires C, 78.35; H, 7.6; N, 14.1%); ν_{max} (neat)/cm^{-1} 2209 and 1633; δ_H 0.67 (3H, t, *J* 7.5 Hz, CH_3), 0.98 (6H, t, *J* 7.5 Hz, 2 × CH_3), 1.11 (3H, t, *J* 7.5 Hz, CH_3), 2.10 (2H, sextet, *J* 7.3Hz, CH_2), 2.29–2.52 (6H, m, 3 × CH_2), 6.95–7.12 (3H, m, ArH), 7.13–7.34 (5H, m, ArH) and 7.36–7.51 (2H, m, ArH); δ_C 8.27, 10.36, 12.39, 23.83, 24.86, 25.93, 70.09, 111.56, 113.13, 119.40, 119.58, 123.88, 124.39, 127.07, 128.92, 129.34, 146.62, 148.60, 149.29 and 166.39; *m*/*z* 398 (M^+, 14%), 369 ($M^+ - CH_2CH_3$, 14), 342 (29), 306 (15), 269 (100). *m*/*z* HRMS (EI) Calc. for $C_{26}H_{30}N_4$: [M + H]; 398.2470. Found: *m*/*z*, 398.2472.

Reaction of 15a with $AlCl_3$

To a solution of **15a** (89 mg, 0.26 mmol) in benzene (3 cm^3) was added anhydrous $AlCl_3$ (69 mg, 0.52 mmol). The mixture was stirred for 48 h at rt. Water (30 cm^3) was added into the mixture and then the mixture was extracted with CH_2Cl_2 (30 cm^3 × 2). The combined extract was dried ($MgSO_4$). Removal of the solvent, followed by chromatography (2 × 20 cm) of the residue using a mixture of *n*-hexane and EtOAc (5:1) gave 2-(2,3-dihydro-2,2-dimethyl-3-phenylimino-1*H*-indol-1-yl)-3-methylbut-2-enenitrile **18** (29 mg, 35%) and **11a** (7 mg, 12%).

18: sticky solid (Found: C, 81.0; H, 6.9; N, 13.1. $C_{21}H_{21}N_3$ requires C, 80.0; H, 6.7; N, 13.3%); ν_{max} (neat)/cm^{-1} 2209, 1660 and 1598; δ_H 1.39 (3H, s, CH_3), 1.56 (3H, s, CH_3), 1.87 (3H, s, CH_3), 2.22 (3H, s, CH_3), 6.56 (1H, t, *J* 8.2 Hz, ArH), 6.82 (1H, d, *J* 7.6 Hz, ArH), 7.44 (1H, t, *J* 8.2 Hz, 3 × ArH), 7.61 (1H, d, *J* 7.6 Hz, ArH); *m*/*z* 315 (M^+, 36%), 300 (29), 235 (100).

General procedure for the synthesis of 1,2-dihydroindol-3-ones 11

A mixture of compound **15** and $Cu(OAc)_2\cdot H_2O$ in HOAc (3 cm^3) was heated for an appropriate length of time at reflux. The reaction mixture was cooled to rt, followed by addition of water (50 cm^3), and CH_2Cl_2 (30 cm^3), and then neutralized with aqueous Na_2CO_3. The mixture was extracted with CH_2Cl_2 (30 cm^3 × 2). The combined extract was dried ($MgSO_4$). Evaporation of the solvent gave a brown liquid, which was chromatographed on a silica gel column (2 × 20 cm^3) using a mixture of *n*-hexane and EtOAc (5:1) as the eluent.

2-(2,3-Dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11a. The reaction of **15a** (164 mg, 0.48 mmol) with $Cu(OAc)_2\cdot H_2O$ (96 mg, 0.53 mmol) in HOAc (10 cm^3) for 14 h gave **11a** (86 mg, 75%). From the reaction of **15a** (273 mg, 0.80 mmol) in HOAc (20 cm^3) for 30 h was obtained **11a** (108 mg, 56%).

2-(5-Chloro-2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11b. The reaction of **15b** (149 mg, 0.36 mmol) with $Cu(OAc)_2\cdot H_2O$ (78 mg, 0.43 mmol) in HOAc

(8 cm^3) for 96 h gave **11b** (85 mg, 86%): mp 91–92 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 65.4; H 5.6; N, 10.1. $C_{15}H_{15}ClN_2O$ requires C, 65.6; H, 5.6; N, 10.1%); ν_{max} (neat)/cm^{-1} 2960, 2209, 1717 and 1607; δ_H 1.22 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.81 (3H, s, CH_3), 2.22 (3H, s, CH_3), 6.53 (1H, dd, *J* 8.7, 2.2 Hz, ArH), 7.39 (1H, d, *J* 8.7 Hz, ArH) and 7.57 (1H, d, *J* 2.2 Hz, ArH); δ_C 20.49, 22.01, 22.45, 22.53, 70.59, 105.49, 111.45, 116.10, 120.37, 124.52, 125.00, 137.38, 155.14, 160.38 and 201.41; *m*/*z* 276 (M$^+$ + 2, 29%), 274 (M$^+$, 89), 259 (44), 231 (100), 152 (51).

2-(5-Bromo-2,3-dihydro-2,2-dimethyl-3-oxo-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11c. The reaction of **15c** (85 mg, 0.17 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (36 mg, 0.20 mmol) in HOAc (4 cm^3) for 28 h gave **15c** (30 mg, 35%) and **11c** (15 mg, 45%); sticky solid (Found: C, 56.6; H, 4.9; N, 9.0. $C_{15}H_{15}BrN_2O$ requires C, 56.4; H, 4.7; N, 8.8%); ν_{max} (neat)/cm^{-1} 2990, 2208 and 1698; δ_H 1.29 (3H, s, CH_3), 1.47 (3H, s, CH_3), 1.88 (3H, s, CH_3), 2.29 (3H, s, CH_3), 6.55 (1H, d, *J* 8.7 Hz, ArH), 7.60 (1H, dd, *J* 8.7, 2.1 Hz, ArH) and 7.81 (1H, d, *J* 2.1 Hz, ArH); δ_C 20.55, 22.01, 22.51, 22.61, 70.49, 105.41, 111.85, 111.92, 116.12, 120.93, 127.72, 140.03, 155.45, 160.46 and 201.27; *m*/*z* 320 (M$^+$ + 2, 97%), 318 (M$^+$, 100), 305 (M$^+$ + 2 – CH_3, 44), 303 (M$^+$ – CH_3, 45), 277 (81), 275 (83).

2-(2,3-Dihydro-3-oxo-2,2,7-trimethyl-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11d. The reaction of **15d** (70 mg, 0.19 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (42 mg, 0.23 mmol) in HOAc (2 cm^3) for 18 h gave **11d** (32 mg, 68%): sticky solid; ν_{max} (neat)/cm^{-1} 2208, 1698 and 1613; δ_H 1.20 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.86 (3H, s, CH_3), 2.16 (3H, s, CH_3), 2.17 (3H, s, CH_3), 6.79 (1H, t, *J* 7.5 Hz, ArH), 7.24 (1H, d, *J* 7.2 Hz, ArH) and 7.61 (1H, d, *J* 7.5 Hz, ArH); δ_C 18.21, 20.77, 22.22, 22.62, 22.74, 70.15, 109.65, 117.04, 120.47, 120.89, 122.45, 123.00, 140.77, 155.94, 157.18 and 203.35; *m*/*z* 254 (M$^+$, 98%), 239 (73), 211 (100), 198 (21). *m*/*z* HRMS (EI) Calc. for $C_{16}H_{18}N_2O$: [M + H]; 254.1419. Found: *m*/*z*, 254.1407.

2-(2,3-Dihydro-3-oxo-2,2,4-trimethyl-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11e(I) and 2-(2,3-dihydro-3-oxo-2,2,6-trimethyl-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11e(II). The reaction of **15e** (254 mg, 0.69 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (151 mg, 0.83 mmol) in HOAc (14 cm^3) for 6 h gave **11e(I)** (26 mg, 14%): mp 84–86 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 75.7; H 7.0; N, 11.0. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%); ν_{max} (neat)/cm^{-1} 2209, 1699 and 1598; δ_H 1.19 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.80 (3H, s, CH_3), 2.20 (3H, s, CH_3), 2.53 (3H, s, CH_3), 6.36 (1H, d, *J* 8.1 Hz, ArH), 6.58 (1H, d, *J* 7.4 Hz, ArH) and 7.29 (1H, t, *J* 7.8 Hz, ArH); δ_C 18.31, 20.48, 22.29, 22.47, 22.68, 69.54, 106.13, 107.40, 116.49, 117.33, 121.27, 136.78, 140.82, 157.35, 159.69 and 203.32; *m*/*z* 254 (M$^+$, 98%), 239 (100), 211 (84), 132 (25); and **11e(II)** mp 81–82 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 75.3; H 7.35; N, 11.1. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%); ν_{max} (neat)/cm^{-1} 2208, 1704 and 1613; δ_H 1.19 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.81 (3H, s, CH_3), 2.21 (3H, s, CH_3), 2.30 (3H, s, CH_3), 6.35 (1H, s, ArH), 6.65 (1H, d, *J* 7.9 Hz, ArH) and 7.49 (1H, d, *J* 7.9 Hz, ArH); δ_C 20.35, 22.03, 22.41 (3 overlapped peaks), 69.99, 105.75, 110.15, 116.34, 116.97, 121.29, 124.79, 149.32, 157.20, 159.99 and 201.86; *m*/*z* 254 (M$^+$, 100%), 239 (75), 211 (84), 174 (20), 132 (30).

2-(2,3-Dihydro-3-oxo-2,2,5-trimethyl-1*H*-indol-1-yl)-3-methylbut-2-enenitrile 11f. The reaction of **15f** (142 mg, 0.38 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (84 mg, 0.46 mmol) in HOAc (8 cm^3) for 4 h gave **11f** (90 mg, 92%): mp 96–97 °C (from *n*-hexane–CH_2Cl_2) (Found: C, 75.6; H 7.4; N, 11.1. $C_{16}H_{18}N_2O$ requires C, 75.6; H, 7.1; N, 11.0%); ν_{max} (neat)/cm^{-1} 2200, 1698 and 1613; δ_H 1.19 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.80 (3H, s, CH_3), 2.19 (3H, s, CH_3), 2.23 (3H, s, CH_3), 6.49 (1H, d, *J* 8.3 Hz, ArH), 7.27 (1H, d, *J* 8.3 Hz, ArH) and 7.39 (1H, s, ArH); δ_C 13.99, 20.29, 21.32, 22.07, 22.32, 69.96, 106.02, 110.11, 116.34, 119.25, 124.45, 129.11, 138.76, 155.16, 159.55 and 202.57; *m*/*z* 254 (M$^+$, 100%), 239 (57), 211 (98), 132 (43).

2-(2,3-Dihydro-2,5-dimethyl-2-ethyl-3-oxo-1*H*-indol-1-yl)-3-methylpent-2-enenitrile 11h. The reaction of **15h** (81 mg, 0.20 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (44 mg, 0.24 mmol) in HOAc (1 cm^3) for 480 h gave **11h** (35 mg, 60%); sticky solid; ν_{max} (neat)/cm^{-1} 2968, 2208, 1692 and 1606; δ_H 0.77–0.83 (3H, m), 1.02 (2H, m), 1.23–1.44 (4H, m), 1.45 (2H, m), 1.75 (1H, m), 1.97 (1H, m), 2.27–2.34 (5H, m), 2.61 (1H, m), 6.47–6.64 (1H, m, ArH), 7.31–7.39 (1H, m, ArH) and 7.47 (1H, m, ArH); *m*/*z* of isomer-1 282 (M$^+$, 50%), 267 (M$^+$ – CH_3, 10), 253 (M$^+$ – CH_2CH_3, 100); *m*/*z* of isomer-2 282 (M$^+$, 53%), 267 (M$^+$ – CH_3, 10), 253 (M$^+$ – CH_2CH_3, 100). *m*/*z* HRMS (EI) Calc. for $C_{18}H_{22}N_2O$: [M + H]; 282.1732. Found: *m*/*z*, 282.1743.

2-(2,2-Diethyl-2,3-dihydro-3-oxo-1*H*-indol-1-yl)-3-ethylpent-2-enenitrile 11j. The reaction of **15j** (133 mg, 0.33 mmol) with $Cu(OAc)_2{\cdot}H_2O$ (77 mg, 0.40 mmol) in HOAc (4 cm^3) for 480 h gave **11j** (15 mg, 15%): sticky solid (Found: C, 77.2; H 8.3; N, 9.6. $C_{19}H_{24}N_2O$ requires C, 77.0; H, 8.2; N, 9.45%); ν_{max} (neat)/cm^{-1} 2968, 2200, 1698 and 1606; δ_H 0.71 (3H, t, *J* 7.4 Hz, CH_3), 0.78 (3H, t, *J* 7.4 Hz, CH_3), 0.96 (3H, t, *J* 7.5 Hz, CH_3), 1.20 (3H, t, *J* 7.5 Hz, CH_3), 1.56 (1H, q, *J* 7.5 Hz, CH_2), 1.71 (1H, q, *J* 7.5 Hz, CH_2), 1.89 (1H, q, *J* 7.5 Hz, CH_2), 2.01 (1H, q, *J* 7.5 Hz, CH_2), 2.16 (2H, q, *J* 7.5 Hz, CH_2), 2.58 (2H, octet, *J* 7.5 Hz, CH_2), 6.49 (1H, d, *J* 8.3 Hz, ArH), 6.79 (1H, t, *J* 7.5 Hz, ArH), 7.42 (1H, t, *J* 8.3 Hz, ArH), 7.58 (1H, d, *J* 7.9 Hz, ArH); *m*/*z* 296 (M$^+$, 22%), 267 (100).

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11 $Cu(OAc)_2 \cdot H_2O$ (450 mg) was treated with HOAc (10 cm^3) at rt and reflux temperatures for 24 h, respectively, followed by filtration of the undissolved copper acetate. From the filtrate were obtained 280 mg (62%) and 367 mg (82%) of copper acetate, respectively.

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