Synthesis of 4-Amino-2(5*H*)-furanones through Intra- and Intermolecular Nitrile Addition of Ester Enolates. Construction of Carbon Framework of an Antitumor Antibiotic Basidalin

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(Received December 9, 1986)

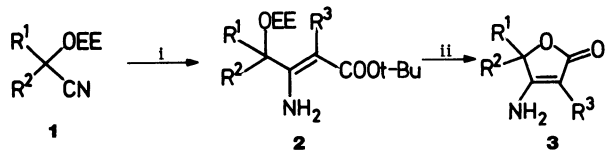
Two new routes to 4-amino-2(5*H*)-furanones are disclosed. The one is based on the reaction of a magnesium enolate of *t*-butyl acetate or propionate with *O*-protected cyanohydrins followed by acid-treatment which effects hydrolysis of the ester group, deprotection, olefin isomerization and lactonization all in a single operation. The other is base-induced ringclosure of α-acyloxy nitriles. The two methods are applied to construction of the carbon framework of an antitumor antibiotic basidalin.

Nitrile addition of an ester enolate is proved to be a promising alternative to 3-amino-2-alkenoates[1] which are versatile synthetic intermediates.[2] The addition is particularly facilitated to nitriles having α-alkoxy groups.[3] Though the (Z)-configuration of the produced 3-amino-2-alkenoates predominates due to intramolecular hydrogen bonding, Z to E isomerization takes place readily under various conditions.[2] Thus, protected cyanohydrins, after coupling with an ester enolate, isomerization of C=C bond of the adduct followed by appropriate functional group manipulations, are expected to give rise to 4-amino-2(5*H*)-furanones[4] which are precursors of defoliant, plant growth retardants,[5] and anti-hypertensive agents.[6]

An alternative approach to 4-amino-2(5*H*)-furanones emerges which employes intramolecular nitrile addition of an ester enolate, i.e., cyclization of α-alkanoyloxy nitriles.[7] Reported herein are details of the two synthetic approaches based on the inter- and intramolecular nitrile addition of ester enolates as well as their application to the construction of the carbon framework of an antibiotic basidalin.[8]

Results and Discussion

Synthesis of 4-Amino-2(5*H*)-furanones through Intermolecular Nitrile-Ester Enolate Addition. Cyanohydrins protected by 1-ethoxyethyl (=EE) ether **1** were allowed to react with the magnesium enolate of *t*-butyl acetate or propionate (Scheme 1). The resulting adduct, *t*-butyl 4-(1-ethoxyethoxy)-3-amino-2-alkenoates **2**, were treated with various acids in order to effect hydrolysis of the ester group, deprotection, (Z)→(E) isomerization, and lactonization all in a single operation without the enamine moiety affected.

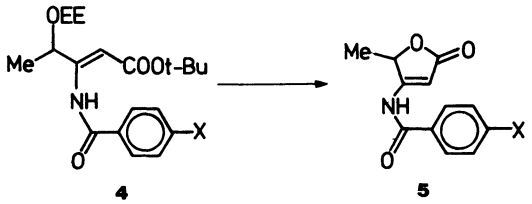


i) $R^3CH{=}C(Ot\text{-}Bu)OMgX$, Et_2O, 0 °C
ii) HX, PhH (or PhMe), 0 °C to r.t.

Scheme 1.

Organic acids like *p*-toluenesulfonic acid and trifluoroacetic acid gave intractable material. The best conditions we found were those which involve treatment of **2** with hydrogen halide gas in anhydrous nonpolar solvents like benzene and toluene, and the desired 4-amino-2(5*H*)-furanones (**3**) precipitated from the reaction medium. Purification by preparative TLC or column chromatography allowed us to isolate pure material. Typical results are summarized in Table 1. As the *N*-acyl derivatives of **2** are stable to acid and some of these derivatives are shown to exhibit biological activity, we prepared *N*-aroyl derivatives **4**, which underwent cyclization to give rise to 4-aroylamino-5-methyl-2(5*H*)-furanones **5**.[4] These results also are summarized in Table 1.

We also intended to prepare the *N*-ureido derivatives (vide infra) of **3** by the acid-catalyzed cyclization of the *N*-ureido derivatives of **2**. Actually, **2a** was converted into the corresponding urea derivative by the reaction



4 **5**

r: X=H, **s**: X=Br, **t**: X=CN, **u**: X=F, **v**: X=NO_2, **w**: X=Me

Table 1. Acid-Catalyzed Cyclization of **2** (or **4**) to **3** (or **5**)

Substrate	HX and Condition	Product	Yield/%
2a	HCl, PhH, r.t.	**3a**	65
2a	HCl, PhMe, 0 °C	**3a**	60
2a	HBr, PhH, 0 to 5 °C	**3a**	72
2b	HBr, PhH, 0 to 5 °C	**3b**	32
2c	HBr, PhH, 0 to 5 °C	**3c**	39
2d	HCl, PhH, 0 to 5 °C	**3d**	34
2e	HCl, PhH, 0 to 5 °C	**3e**	47
4r	HCl, CH_2Cl_2, 0 °C	**5r**	14
4s	HCl, CH_2Cl_2, 0 °C	**5s**	54
4t	HCl, CH_2Cl_2, 0 °C	**5t**	30
4u	HCl, CH_2Cl_2, 0 °C	**5u**	43
4v	HCl, CH_2Cl_2, 0 °C	**5v**	72
4w	HCl, CH_2Cl_2, 0 °C	**5w**	27

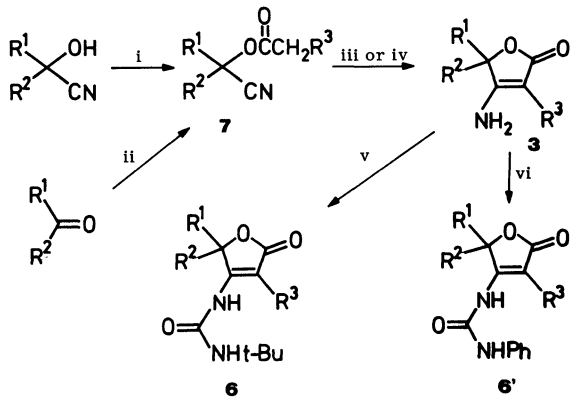
Table 2. Base-Promoted Ringclosure of **7**

Substrate	Condition	Product	Yield/%
7a	$LiN(SiMe_3)_2$, THF, −78 °C	**3a**	6
7b	$LiN(SiMe_3)_2$, THF, −78 °C	**3b**	0
7b	$LiN(SiMe_3)_2$-$Ni(acac)_2$,[a] −76 °C	**3b**	28
7d	$LiN(SiMe_3)_2$, THF, −78 °C	**3d**	82
7d	$LiN(i\text{-}Pr)_2$, THF, −78 °C	**3d**	60
7d	$Mg[N(i\text{-}Pr)_2]_2$, THF, −78 to −74 °C	**3d**	24
7e	$LiN(SiMe_3)_2$, THF, −78 °C	**3e**	74
7f	$LiN(SiMe_3)_2$, THF, −78 °C	**3f**	62
7g	$LiN(SiMe_3)_2$, THF, −78 °C	**3g**	63
7h	$LiN(SiMe_3)_2$, THF, −78 °C	**3h**	87
7i	$LiN(SiMe_3)_2$, THF, −78 °C	**3i**	96
7j	$LiN(SiMe_3)_2$, THF, −78 °C	**3j**	95
7k	$LiN(SiMe_3)_2$, THF, −78 °C	**3k**	65
7l	$LiN(SiMe_3)_2$, THF, −78 °C	**3l**	88
7m	$LiN(SiMe_3)_2$, THF, −78 °C	**3m**	16
7n	NaH, THF, reflux	**3n**	28
	Et_3N, THF, r.t.[b]	**3n**	38
7o	NaH, THF, reflux	**3o**	55
7p	NaH, THF, reflux	**3p**	22
7q	NaH, THF, reflux	**3q**	86

a) The reaction was carried out in the presence of 0.2 mol equiv of $Ni(acac)_2$. b) A mixture of 2-hydroxy-2-methylpropanenitrile (1.18 mmol), diketene (1.26 mmol), triethylamine (1.28 mmol) in THF (5 ml) was stirred at room temperature for 6 h.

with *t*-butyl isocyanate (KO*t*-Bu catalyst) in 58% yield. However, the acid-catalyzed transformation of the urea derivative to **6a** turned out futile.

Synthesis of 4-Amino-2(5*H*)-furanones through Intramolecular Nitrile-Ester Enolate Addition. Intramolecular nitrile addition of an ester enolate under ringclosure[9] is an alternative way to **3**. The requisite precursor is an α-acyloxy nitrile **7** which are derived from a cyanohydrin by acylation. In case that the cyanohydrin was commercially unavailable or thermodynamically unfavorable, the parent ketone was transformed to a cyanohydrin trimethylsilyl ether[10] which was subsequently acylated with an acid anhydride and iron(III) chloride catalyst.[11] Intramolecular nitrile addition of ester enolates were studied with **7d** as the model substrate. Ring closure was effected with KO*t*-Bu (0 °C), $Mg[N(i\text{-}Pr)_2]_2$ (−78 to −74 °C), $LiN(i\text{-}Pr)_2$ (−78 °C) or $LiN(SiMe_3)_2$ (−78 °C) all in tetrahydrofuran (THF) to afford **3d** in 4, 24, 60, or 82% yield respectively. In contrast to the intermolecular nitrile addition,[2] lithium amide was more effective than the magnesium amide. Since the use of 2.4 mol equiv of lithium hexamethyldisilazanide gave best yields, these conditions were applied to various kinds of α-acyloxy nitriles **7**, and the results are summarized in Table 2. Ringclosure of nitriles **7n—q** which have more acidic α-CH was preferably carried out with sodium hydride as the base. Desulfurization of **3p** with Raney Nickel is a byway to **3d**. It is apparent that the base-promoted cyclization proceeds highly efficiently, although **7a** and **7b** underwent competitive proton abstraction from C-H α to CN, and the expected product **3a** and **3b** were obtained in low yields. For **3b**, in particular, addition of $Ni(acac)_2$[12] improved the



i) $(R^3CH_2CO)_2O$ (or R^3CH_2COCl), Py (or Et_3N)
ii) Me_3SiCN, ZnI_2; $(R^3CH_2CO)_2O$, $FeCl_3$
iii) $LiN(SiMe_3)_2$(2.4 mol), THF, −78 °C
iv) NaH, THF, reflux
v) *t*-BuN=C=O, *t*-BuOK
vi) PhN=C=O, *t*-BuOK

	R^1	R^2	R^3		R^1	R^2	R^3
a	Me	H	H	**j**	6-MeO-2-$C_{10}H_6$	Me	H
b	Et	H	H				
c	Me	H	Me	**k**	Et	Et	H
d	Me	Me	H	**l**	Me	Me	Me
e	$-(CH_2)_5-$		H	**m**	Me	Me	Cl
f	*i*-Pr	Me	H	**n**	Me	Me	COMe
g	*n*-C_9H_{19}	Me	H	**o**	Me	Me	Ph
h	Ph	Me	H	**p**	Me	Me	SPh
i	$PhCH_2$	Me	H	**q**	Me	Me	SOPh

(Substituents for **2**, **3**, **6**, **6'**, and **7**)

Scheme 2.

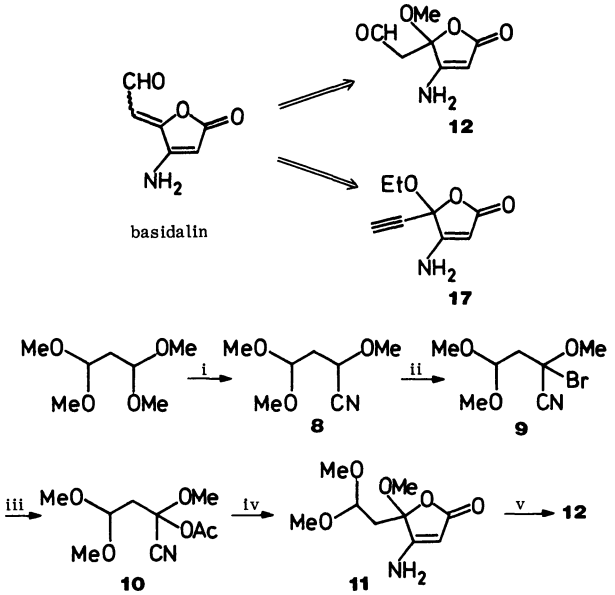
Table 3. Derivatization of **3** to Ureas **6** and

4-Amino-2(5*H*)-furanone	Isocyanate	Reaction Time	Product	Yield/%
3a	*t*-BuNCO	3 h	**6a**	47
3a	PhNCO	4 h	**6'a**	58
3b	*t*-BuNCO	1 d	**6b**	35
3d	*t*-BuNCO	2 d	**6d**	89
3d	PhNCO	2 d	**6'd**	82
3e	*t*-BuNCO	Overnight	**6e**	82
3f	*t*-BuNCO	2.5 d	**6f**	66
3g	PhNCO	Overnight	**6'g**	50
3h	*t*-BuNCO	3 d	**6h**	80
3h	PhNCO	Overnight	**6'h**	88
3i	*t*-BuNCO	Overnight	**6i**	51
3i	PhNCO	Overnight	**6'i**	62
3j	*t*-BuNCO	Overnight	**6j**	76
3j	PhNCO	Overnight	**6'j**	88
3k	*t*-BuNCO	2.5 d	**6k**	67
3l	*t*-BuNCO	2 d	**6l**	47
3q	*t*-BuNCO	2.5 d	**6q**	80

yields. Anyhow, to these substrates, the intermolecular method is applicable as disclosed before. With various kinds of 4-amino-2(5*H*)-furanones in hand, we derivatized these to the urea **6** or **6'** by the reaction to *t*-butyl isocyanate or phenyl isocyanate with potassium *t*-butoxide catalyst. In addition to the parent 4-amino-2(5*H*)-furanones (**3**), these as well as the *N*-aroyl analogs **5** were subjected to biological screening test. Although any of **5** did not show remarkable pharmacological activity, **6d**, **6'd**, and **3j** exhibited herbicidal activity against broad leaf weeds such as *Amaranthus retroflexus* at the level of 200 g/10 a by foliage application.

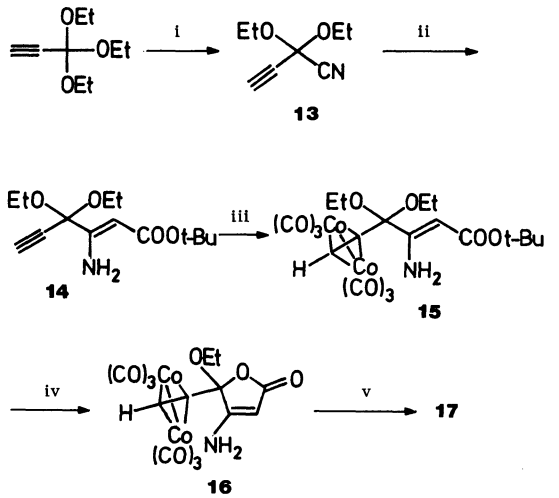
Synthetic Approach to Basidalin. With the two methods in hand, we undertook synthesis of basidalin. Basidalin is an antibiotic[8] which has an antibacterial activity and antitumor activity against L1210 mouse leukemia and possesses a 4-amino-2(5*H*)-furanone structure as well as formylmethylene substituent at C(5). We planned two synthetic routes to basidalin: Key intermediates we considered were 4-amino-2(5*H*)-furanones **12** and **17**, which were synthesized according to Schemes 3 and 4.

Cyanation of commercially available 1,1,3,3-tetramethoxypropane with trimethylsilyl cyanide and boron trifluoride etherate catalyst[13] induced substitution of one MeO group with CN to give **8** in 99% yield. The required introduction of acetoxyl group was achieved as follows. Bromination of **8** under radical conditions selectively took place at CN-substituted carbon to afford a labile bromide **9** which was immediately subjected to substitution reaction with silver acetate to give the key compound **10** needed for the intramolecular nitrile addition strategy in 74% overall yield. The success of regioselective radical bromination is ascribed to the stabilization of the intermediary radical species by "capto-dative" substituents CN and MeO.[14] The α-acetoxy nitrile **10** was treated with various bases such as lithium diisopropylamide, magnesium bis(diisopropylamide) and diethylaluminium diisopropylamide in 1.0 to 4.0 mol equiv to afford 4-amino-2(5*H*)-furanone **11** in 2 to 7% yields only. The yield of **11** was improved to 76% by use of 10 mol equiv of $Et_2AlN(i\text{-}Pr)_2$ at −78 to −60 °C for 1.7 h. Hydrolysis of the acetal moiety with a standard reagent trimethylsilyl iodide or boron tribromide turned out to induce total decomposition solely. However, combination of the Lewis acid with an amine base effectively converted **11** into **12**. Best combination was BBr_3 (3 mol) and $HN(SiMe_3)_2$ (3 mol) and thus **12** was obtained in 56% yield.



i) Me_3SiCN, $BF_3 \cdot OEt_2$(cat), 99%
ii) NBS, AIBN(cat), 94%
iii) AcOAg, 79%
iv) $Et_2AlN(i\text{-}Pr)_2$(10 equiv), 76%
v) $BBr_3 \cdot HN(SiMe_3)_2$(3 equiv), 56%

Scheme 3.



i) Me_3SiCN, $SnCl_2$, 71%
ii) CH_2=C(O*t*-Bu)OMgX, Et_2O, 85%
iii) $Co_2(CO)_8$, pentane, 81%
iv) CF_3COOH, 77%
v) $(NH_4)_2Ce(NO_3)_6$, 83%

Scheme 4.

The final step, elimination of methanol from **12**, grew to be extremely tough. Under various possible basic, acidic, or even neutral conditions, only decomposition resulted possibly via competitive ring opening of the lactone moiety of **12** by elimination and/or loss of the amino group.

We switched to the intermolecular strategy which required a nitrile whose α-carbon is a protected form of ketone carbonyl. For the candidate, we chose **13** which was derived from 3,3,3-triethoxypropyne[15] by a tin(II) chloride-catalyzed cyanation[13] in good yields. Reaction of **13** with *t*-butyl acetate through the magnesium enolate afforded **14** in 85% yield. Direct cyclization of **14** with various kinds of acids[4] failed to give the expected product **17**. However, protection of the C≡C bond of **14** with $Co_2(CO)_8$ followed by treatment with trifluoroacetic acid induced the desired ringformation to afford **16** in 77% yield. Complexation of the acetylene moiety with cobalt rendered us following advantages:[16] (a) Protection of the acetylenic triple bond and (2) stabilization of the cationic species involved in this transformation. Oxidative deprotection under the standard conditions gave **17**. Final transformation to basidalin unfortunately turned out fruitless in spite of numerous experiments including hydrometallation/oxidation.

Although total synthesis was unsuccessful, we could construct the basic carbon framework of basidalin and thus subjected the synthetic intermediates to in vitro test for cell growth inhibition of L1210 and P388. Of these, **15** exhibited IC_{50} (μmol ml^{-1}) 8.5×10^{-3} for L1210 and 3.1×10^{-3} for P388 comparable to the cytotoxicity of prostaglandin A_2 (2.6×10^{-3} and 2.8×10^{-3} for L1210 and P388 respectively).[17]

In conclusion, inter- and intramolecular nitrile-addition of ester enolates is found to be a facile and promising route to a biologically important 4-amino-2(5*H*)-furanone structure. As the structural feature is closely related to tetronic acids,[18] the new synthetic methods will provide us with an additional way to physiologically important tetronic acids and their derivatives.

Experimental

Experimental apparatus and instrumental facilities are the same as those of the preceding paper.[2] Additionally, FT ^{1}H NMR spectra were recorded on a Hitachi R-90H spectrometer. Trimethylsilyl cyanide and hexamethyldisilazane were purchased from Petrach Systems Inc. and distilled before use. *t*-Butyl 3-amino-4-(1-ethoxyethoxy)-2-alkenoates **2a—e** were prepared according to the procedure described in the preceding paper.[2] The yields and spectral properties are as follows. The compounds **2b** and **2d** were oily substance and labile to thin layer, column or gas chromatographic purification. Thus, these were characterized only spectrometrically.

***t*-Butyl 3-Amino-4-(1-ethoxyethoxy)-2-hexenoate (2b):** 65% yield. Bp 100—120 °C (bath temperature)/0.1 Torr.† ^{1}H NMR ($CDCl_3$) δ=0.92 and 0.95 (2t, J=6.5 Hz, 3H), 1.17 and 1.19 (2t, J=6.5 Hz, 3H), 1.30 (d, J=6.0 Hz, 3H), 1.47 (s, 9H), 1.63 (q, J=6.5 Hz, 2H), 3.30—3.78 (m, 2H), 3.84 (q, J=6.0 Hz, 1H), 4.43 and 4.47 (2s, totally 1H), 4.63 and 4.70 (2q, J=6.0 Hz, 1H), 5.5—6.7 (br, 2H). IR (neat) 3500, 3350, 2990, 2940, 1665, 1620, 1555, 1280, 1250, 1080, 1045, 795 cm^{-1}. MS m/z 201 (M^+ $-CH_2$=CHOEt).

***t*-Butyl 3-Amino-4-(1-ethoxyethoxy)-2-methyl-2-pentenoate (2c):** 47% yield. Bp 110—150 °C (bath temperature)/0.2 Torr. ^{1}H NMR ($CDCl_3$) δ=0.90—2.0 (m+2s (δ=1.50 and 1.67), 21 H), 3.25—3.90 (m, 2H), 4.40—4.90 (m, 2H), 6.2—6.8 (br, 2H). IR (neat) 3540, 3360, 3020, 2960, 1670, 1610, 1530, 1460, 1400, 1375, 1275, 1255, 1180, 1125, 1085, 970, 855, 790 cm^{-1}. MS m/z (rel intensity) 273 (M^+, 6), 172 (8), 171 (7), 156 (9), 145 (42), 129 (19), 128 (49), 127 (12), 110 (12), 99 (19), 82 (7), 73 (100), 72 (4), 57 (18), 56 (5), 55 (6), 54 (4), 45 (74). Found: m/z 273.1941. Calcd for $C_{14}H_{27}NO_4$: M^+ 273.1938.

***t*-Butyl 3-Amino-4-(1-ethoxyethoxy)-4-methyl-2-pentenoate (2d):** 79% yield. Bp 70—75 °C (bath temperature)/0.25 Torr. ^{1}H NMR ($CDCl_3$) δ=1.08—1.23 (t, J=13.5 Hz, 3H), 1.27 and 1.33 (2d, J=5.4 Hz, 3H), 1.43 (br s, 6H), 1.48 (s, 9H), 3.37—3.60 (q, J=6.9 Hz, 2H), 4.53 (s, 1H), 4.65—4.83 (q, J=5.4 Hz, 1H), 5.67—7.00 (br, 2H). IR (neat) 3525, 3350, 3000, 2950, 2900, 1670, 1610, 1550, 1390, 1370, 1295, 1150, 1080, 980, 800 cm^{-1}. MS m/z 227 (M^+ $-$EtOH).

***t*-Butyl 3-Amino-3-[1-(1-ethoxyethoxy)cyclohexyl]-2-propenoate (2e):** 79% yield. Bp 120—132 °C (bath temperature)/0.8 Torr. Mp 69—70 °C (hexane-ethyl acetate 3:1). ^{1}H NMR ($CDCl_3$) δ=1.13 (t, J=6 Hz, 3H), 1.30 (d, J=5 Hz, 3H), 1.47 (s, 9H), 1.40—2.20 (m, 10H), 3.47 (q, J=6 Hz, 2H), 4.60 (s, 1H), 4.63 (q, J=5 Hz, 1H), 6.0—7.0 (br, 2H). IR (KBr) 3520, 3350, 3000, 2980, 2950, 2900, 2870, 2850, 1670, 1615, 1550, 1450, 1385, 1365, 1270, 1245, 1150, 1080, 1055, 980, 790, 660 cm^{-1}. Found: C, 65.18; H, 10.14; N, 4.39%. Calcd for $C_{17}H_{31}NO_4$: C, 65.14; H, 9.97; N, 4.47%.

Synthesis of 4-Amino-5-methyl-2(5*H*)-furanone (3a). A Typical Procedure for Hydrogen Halide Induced Formation

†1 Torr=133.322 Pa.

of 4-Amino-2(5*H*)-furanones. Dry hydrogen chloride gas was bubbled into a benzene (100 ml) solution of *t*-butyl 3-amino-4-(1-ethoxyethoxy)-2-pentenoate (**2a**)[2] (100 mg, 0.39 mmol) over a period of 2 h. Colorless material precipitated after 30 min's bubbling. The precipitates were collected and washed twice with benzene. Purification by preparative TLC (silica gel, dichloromethane-methanol 10 : 1, R_f=0.19—0.29) gave colorless solid **3a**[5a,6] (29 mg, 65% yield), mp 151—152 °C (lit,[5a] 150—152 °C). ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=1.47 (d, J=6 Hz, 3H), 4.56 (s, 1H), 4.76 (q, J=6 Hz, 1H), 6.40—6.70 (br, 2H). IR (KBr) 3450, 3395, 3230, 3000, 1710, 1660, 1580, 1335, 1190, 1050, 950, 905, 785 cm^{-1}. MS m/z (rel intensity) 114 (M^++1, 7), 113 (M^+, 66), 98 (64), 70 (100), 43 (22), 42 (33), 41 (56).

Spectral properties of 4-amino-2(5*H*)-furanones prepared by the similar procedures are listed below.

4-Amino-5-ethyl-2(5*H*)-furanone (3b).[5a,b] Mp 143—143.5 °C (lit,[5a] 143—145.5 °C). ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=0.95 (t, J=6.5 Hz, 3H), 1.4—2.2 (m, 2H), 4.45—4.90 (m+s (δ=4.60), 2H), 6.0—6.6 (br, 2H). IR (neat) 3450, 3240, 2980, 2950, 2900, 1710, 1650, 1580, 1540, 1345, 1190, 1080, 980 910, 780, 720 cm^{-1}.

4-Amino-3,5-dimethyl-2(5*H*)-furanone (3c).[6] Mp 96—98 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=1.48 (d, J=6 Hz, 3H), 1.66 (s, 3H), 4.73 (q, J=6 Hz, 1H), 4.83 (br s, 2H). IR (KBr) 3480, 3370, 3250, 3025, 2950, 2900, 1720, 1670, 1620, 1430, 1340, 1122, 1105, 1060, 990, 770, 740 cm^{-1}. Found: C, 56.42; H, 7.20; N, 10.90%. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02%.

4-Amino-5,5-dimethyl-2(5*H*)-furanone (3d). Mp 205—207 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=1.48 (s, 6H), 4.48 (s, 1H), 6.4—6.7 (br, 2H). IR (KBr) 3400, 3350 (sh), 3220, 3000, 1720, 1680, 1660, 1615, 1600, 1390, 1375, 1300, 1255, 1200, 1130, 985, 945, 900, 800 cm^{-1}. MS m/z (rel intensity) 128 (M^++1, 6), 127 (M^+, 53), 112 (100), 70 (42), 66 (11), 59 (12), 43 (77). Found: C, 56.55; H, 7.14; N, 10.90%. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02%.

3′-Aminospiro[cyclohexane-1,2′(5′*H*)-furan]-5′-one (3e). Mp 194.5—195.5 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 1 : 1) δ=1.2—2.0 (m, 10H), 4.48 (s, 1H), 6.4—6.7 (br, 2H). IR (KBr) 3400, 3200, 2950, 2870, 1710, 1660, 1600, 1295, 1210, 1140, 1065, 975, 940, 860, 795 cm^{-1}. MS m/z (rel intensity) 168 (M^++1, 5), 167 (M^+, 38), 124 (27), 112 (16), 111 (100), 99 (32), 84 (65), 83 (10), 81 (27), 69 (20), 66 (77), 55 (16). Found: C, 64.56; H, 7.60; N, 8.38%. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38%.

Aroylation of 3a. Benzoyl chloride (1.37 g, 9.7 mmol) and 4-dimethylaminopyridine (0.20 g, 1.64 mmol) were added to a pyridine (20 ml) solution of **3a** (1.68 g, 6.5 mmol) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min and at 50 °C overnight. The pyridine was evaporated in vacuo and the residue was purified by column chromatography (Kieselgel 60) to give an E/Z mixture of *t*-butyl 3-(benzoylamino)-4-(1-ethoxyethoxy)-2-pentenoate (**4r**) (1.03 g, 44% yield) and a compound assigned as *t*-butyl 3-benzoylamino-4-benzoyloxy-2-pentenoate (0.20 g, 10% yield). **4r** (viscous oil, R_f=0.50 (hexane-ethyl acetate 5 : 1)) showed ^{1}H NMR ($CDCl_3$) δ=1.00—1.70 (2t+d+s (δ=1.43), 18H), 3.25—3.70 (m, 2H), 3.90—4.30 (m, 1H), 4.30 (s, 1H), 4.30—4.90 (m, 1H), 7.20—7.70 (m, 3H), 7.90—8.20 (m, 2H), 12.00—12.30 (br, 1H). IR (neat) 3500, 3230, 3080, 2950, 1700, 1660, 1635, 1490, 1370, 1300, 1265, 1250, 1150, 1070, 960, 920, 740, 710 cm^{-1}. Found: C, 66.19; H, 8.22; N, 3.71%. Calcd for $C_{20}H_{29}NO_5$: C, 66.09; H, 8.04; N, 3.85%.

The *N,O*-dibenzoate (R_f 0.40) showed mp 152—153 °C; ^{1}H NMR ($CDCl_3$) δ=1.71 (d, J=7 Hz, 3H), 1.20 (s, 9H), 5.38 (s, 1H), 6.93 (q, J=7 Hz, 1H), 7.33—7.73 (m, 6H), 7.93—8.23 (m, 4H), 11.13—11.43 (br, 1H). Found: C, 70.01; H, 6.38; N, 3.45%. Calcd for $C_{23}H_{25}NO_5$: C, 69.85; H, 6.37; N, 3.54%.

In similar manners and by using the corresponding aroyl chloride, **4s—w** were prepared.

***t*-Butyl 3-(4-Bromobenzoylamino)-4-(1-ethoxyethoxy)-2-pentenoate (4s).** Pale yellow viscous oil, R_f=0.69 (hexane-ethyl acetate 5 : 1). ^{1}H NMR ($CDCl_3$) δ=1.0—1.65 (m+s (δ=1.53), 18H), 3.35—3.90 (m, 2H), 4.73 and 4.79 (2q, 1H), 5.50—5.85 (m+2s (δ=5.32 and 5.42), 2H), 7.55—7.90 (AB q, 4H), 12.4—12.7 (br, 1H). IR (neat) 3230, 3000, 2950, 1700, 1660, 1630, 1595, 1485, 1370, 1305, 1270, 1250, 1155, 1075, 1015, 920, 825, 750, 740 cm^{-1}. Found: C, 54.11; H, 6.35; N, 3.09%. Calcd for $C_{20}H_{28}BrNO_5$: C, 54.30; H, 6.38; N, 3.17%.

***t*-Butyl 3-(4-Cyanobenzoylamino)-4-(1-ethoxyethoxy)-2-pentenoate (4t).** Colorless viscous oil, R_f=0.48 (hexane-ethyl acetate 5 : 1). ^{1}H NMR ($CDCl_3$) δ=1.00—1.60 (m+s (δ=1.53), 18H), 3.35—3.80 (m, 2H), 4.60—4.90 (2q, 1H), 5.55—5.80 (2s(δ=5.57 and 5.70)+q (δ=5.70), 2H), 7.75—8.20 (AB q, 4H), 12.3—12.6 (br 1H). IR (neat) 3500, 3350, 3200, 3100, 3000, 2950, 2230, 1700, 1660, 1630, 1490, 1370, 1300, 1270, 1240, 1150, 1080, 960, 920, 860, 760 cm^{-1}. Found: C, 64.67; H, 7.41; N, 6.93%. Calcd for $C_{21}H_{28}N_2O_5$: C, 64.93; H, 7.27; N, 7.21%.

***t*-Butyl 4-(1-Ethoxyethoxy)-3-(4-fluorobenzoylamino)-2-pentenoate (4u).** Colorless viscous oil, R_f=0.54 (hexane-ethyl acetate 5 : 1). ^{1}H NMR ($CDCl_3$) δ=1.10—1.90 (m+s (δ=1.55), 18H), 3.35—3.90 (m, 2H), 4.65—4.95 (2q, 1H), 5.50—5.90 (2s (δ=5.53 and 5.67)+q (δ=5.75, J=6 Hz), totally 2H), 7.17 (t, J=9.0 Hz, 2H), 8.03 (dd, J=9.0 and 5.0 Hz, 2H), 12.0—12.5 (br, 1H). IR (neat) 3220, 3000, 2950, 1700, 1660, 1635, 1605, 1495, 1250, 1155, 1080, 760, 740 cm^{-1}. Found: C, 63.00; H, 7.33; N, 3.58%. Calcd for $C_{20}H_{28}FNO_5$: C, 62.98; H, 7.40; N, 3.67%.

***t*-Butyl 4-(1-Ethoxyethoxy)-3-(4-nitrobenzoylamino)-2-pentenoate (4v).** Pale yellow viscous oil, R_f=0.57 (hexane-ethyl acetate 5 : 1). ^{1}H NMR ($CDCl_3$) δ=1.05—1.65 (m+s (δ=1.54), 18 H), 3.40—3.80 (m, 2H), 4.60—4.90 (2q, 1H), 5.55—5.80 (2s (δ=5.59 and 5.71) +m, totally 2H), 8.10—8.45 (AB q, 4H), 12.30—12.60 (br, 1H). IR (neat) 3210, 3140, 3000, 2950, 1700, 1660, 1640, 1605, 1535, 1485, 1350, 1300, 1265, 1250, 1155, 1080, 955, 920, 870, 850, 735, 715 cm^{-1}. Found: C, 58.70; H, 6.97; N, 6.73%. Calcd for $C_{20}H_{28}N_2O_7$: C, 58.81; H, 6.91; N, 6.86%.

***t*-Butyl 4-(1-Ethoxyethoxy)-3-(4-methylbenzoylamino)-2-pentenoate (4w).** Colorless viscous oil, R_f=0.48 (hexane-ethyl acetate 5 : 1). ^{1}H NMR ($CDCl_3$) δ=1.00—1.80 (m+s (δ=1.57), 18H), 2.43 (s, 3H), 3.30—3.80 (m, 2H), 4.55—4.90 (2q, 1H), 5.45—5.85 (2s (δ=5.48 and 5.60)+m, totally 2H), 7.10—7.95 (AB q, 4H), 12.1—12.4 (br, 1H). IR (neat) 3250, 3000, 2950, 1700, 1600, 1635, 1560, 1495, 1375, 1305, 1270, 1250, 1160, 1135, 1080, 920, 840, 750, 740 cm^{-1}. Found: C, 66.99; H, 8.37; N, 3.56%. Calcd for $C_{21}H_{31}NO_5$: C, 66.82; H, 8.28; N, 3.71%.

4-Aroylamino-5-methyl-2(5*H*)-furanones. Into a dichloromethane solution of *t*-butyl 3-aroylamino-4-(1-ethoxyethoxy)-2-pentenoate (**4r—w**) (0.27 M††), dry hydrogen chloride gas was bubbled at 0 °C for 3 h, and the reaction mixture was

††1 M=1 mol dm^{-3}.

Table 4. Physical Properties of **5**

Compound	Mp(θ_m/°C) (solvent)	IR/cm^{-1}	^{1}H NMR ($CDCl_3$) (δ)
5r[a]	Colorless needles 176—178 (Hexane-ethanol)	3325, 1730 1715, 1690 1600	1.50 (d, J=5.4 Hz, 3 H), 5.22 (q, J=5.4 Hz, 1 H), 6.15 (s, 1 H), 7.77—8.07 (m, 5 H), 11.2—11.4 (br, 1 H)
5s[b]	Colorless prisms 201—202 (Ethanol)	3345, 1730 1705, 1630 1590	1.57 (d, J=6 Hz, 3 H), 5.22 (q, J=6 Hz, 1 H), 6.22 (s, 1 H), 7.87—7.95 (AB q, 4 H), 10.3—10.5 (br, 1 H)
5t[c]	Colorless needles 203—204.5 (Ethanol)	3320, 3250 2250, 1760 1750 (sh) 1730 (sh) 1720, 1625 (sh)	1.57 (d, J=6 Hz, 3 H), 5.22 (q, J=6 Hz, 1 H), 6.23 (s, 1 H), 7.79—8.18 (AB q, 4 H), 10.9 (br, 1 H)
5u[d]	Colorless needles 206—208 (Ethanol)	3350, 3250 1745, 1730 1705, 1630	1.54 (d, J=6 Hz, 3 H), 5.20 (q, J=6 Hz, 1 H), 6.16 (s, 1 H), 7.26 (t, J=9 Hz, 2 H), 8.06 (dd, J=9 and 5 Hz, 2 H), 10.8 (br, 1 H)
5v[e]	Pale yellow prisms 244—246 (Methanol)	3350, 3250 (sh) 1730, 1710 1630, 1605 1555, 1350 1330	1.54 (d, J=7 Hz, 3 H), 5.22 (q, J=7 Hz, 1 H), 6.20 (s, 1 H), 8.15—8.40 (AB q, 4 H), 11.2 (br, 1 H)
5w[f]	Colorless needles 191—192 (Hexane-ethanol)	3350, 3250 (sh) 3150 (sh) 1745, 1730 1690, 1630	1.59 (d, J=7 Hz, 3 H), 2.43 (s, 3 H), 5.23 (q, J= 7 Hz, 1 H), 6.17 (s, 1 H), 7.20—8.05 (AB q, 4 H), 10.8 (br, 1 H)

a) MS m/z (rel intensity) 218 (M^++1, 12), 217 (M^+, 57), 174 (10), 173 (80), 172 (66), 171 (14), 129 (4), 128 (5), 105 (24), 104 (100), 103 (22), 77 (29), 76 (8), 70 (59), 69 (9), 51 (14), 43 (56). Found: m/z 217.0757. Calcd for $C_{12}H_{11}NO_3$: M^+ 217.0738. b) MS m/z (rel intensity) 297 (M^++2, 11), 295 (M^+, 11), 185 (100), 183 (100), 157 (24), 155 (25), 76 (26), 75 (20), 50 (15). Found: C, 48.63; H, 3.33; N, 4.61; Br, 26.71%. Calcd for $C_{12}H_{10}BrNO_3$: C, 48.67; H, 3.40; N, 4.73; Br, 26.98%. c) MS m/z (rel intensity) 242 (M^+, 7), 214 (10), 131 (9), 130 (100), 103 (4), 102 (39), 76 (6), 75 (9), 68 (7), 51 (6). Found: m/z 242.0709. Calcd for $C_{13}H_{10}N_2O_3$: M^+ 242.0727. d) MS m/z (rel intensity) 235 (M^+, 7), 205 (4), 124 (8), 123 (100), 95 (33), 75 (11), 68 (4). Found: C, 61.40; H, 4.17; N, 5.83%. Calcd for $C_{12}H_{10}FNO_3$: C, 61.28; H, 4.29; N, 5.95%. e) MS m/z (rel intensity) 262 (M^+, 9), 234 (10), 151 (8), 150 (100), 120 (18), 104 (29), 92 (11), 76 (19), 75 (6), 68 (6), 50 (8). Found: C, 54.94; H, 3.80; N, 10.61%. Calcd for $C_{12}H_{10}N_2O_5$: C, 54.96; H, 3.84; N, 10.68%. f) MS m/z (rel intensity) 232 (M^++1, 2), 231 (M^+, 13), 120 (27), 119 (100), 92 (7), 91 (88), 90 (7), 89 (9), 68 (5), 65 (34), 63 (7), 51 (4), 41 (5). Found: m/z 231.0898. Calcd for $C_{13}H_{13}NO_3$: M^+ 231.0895.

allowed to stand for a couple of days. The precipitated crystals were collected and recrystallized from the solvent shown in Table 4. The yields listed in Table 1 are those after recrystallization. Physical properties are summarized in Table 4.

Derivatization of 2a by the reaction with *t*-butyl isocyanate was effected by the procedure described in the derivatization of **3a**, and the resulting urea derivative showed following spectra.

***t*-Butyl 4-(1-Ethoxyethoxy)-3-(*N'*-*t*-butylureido)-2-pentenoate.** Colorless prisms, mp 114—117 °C, R_f=0.56 (hexane-ethyl acetate 5:1). ^{1}H NMR ($CDCl_3$) δ=1.07—1.43 (m, 9H), 1.33 (s, 9H), 1.48 (s, 9H), 3.37—3.67 (m, 2H), 4.50—4.80 (m, 2H), 5.20 and 5.32 (2s, 1H), 5.43—5.65 (2q, 1H), 10.1—10.5 (br, 1H). Found: C, 60.30; H, 9.78; N, 7.54%. Calcd for $C_{18}H_{34}N_2O_5$: C, 60.30; H, 9.56; N, 7.82%.

Acylation of Cyanohydrin. A typical procedure is shown for the synthesis of 2-acetoxy-2-methylpropanenitrile (**7d**). To a dichloromethane (20 ml) solution of commercially available 2-hydroxy-2-methylpropanenitrile (1.70 g, 20 mmol) were added acetic anhydride (4.0 ml) and pyridine (3.2 ml) under cooling with ice, and the reaction mixture was stirred at room temperature for 2 d. The reaction mixture was then washed 3 times with 3% hydrochloric acid and once with brine, dried over magnesium sulfate, and then concentrated. Distillation at 70—75 °C/9 Torr gave **7d** (1.28 g, 50% yield). ^{1}H NMR ($CDCl_3$) δ=1.76 (s, 6H), 2.09 (s, 3H), IR (neat) 2260 (vw), 1760, 1470, 1420, 1390, 1370, 1355, 1275, 1230, 1190, 1140 cm^{-1}.

Similarly, **7e** (36%), **7m** (81%), and **7l** (46%) were prepared. Nitriles **7a** and **7b** were finally purified by preparative GLC.

2-Acetoxypropanenitrile (7a): Bp 70—75 °C/9 Torr. ^{1}H NMR ($CDCl_3$) δ=1.63 (d, J=7.2 Hz, 3H), 2.13 (s, 3H), 5.36 (q, J=7.2 Hz, 1H).

2-Acetoxybutanenitrile (7b): Bp 75—80 °C/22 Torr. ^{1}H NMR ($CDCl_3$) δ=1.10 (t, J=6.6 Hz, 3H), 1.89 (quintet, J=6.6 Hz, 2H), 2.13 (s, 3H), 5.25 (t, J=6.6 Hz, 1H). IR (neat) 3000, 2950, 2900, 2250 (vw), 1750, 1460, 1370, 1220 cm^{-1}.

1-Cyanocyclohexyl Acetate (7e): Bp 120 °C/13 Torr, mp 48.5—49 °C, colorless prisms. ^{1}H NMR ($CDCl_3$) δ=1.15—1.95 (m, 8H), 2.10 (s, 3H), 2.18—2.42 (m, 2H). IR (KBr) 3500,

2950, 2875, 2250, 1750, 1450, 1365, 1260, 1230, 1165, 1060 cm^{-1}.

2-Chloroacetoxy-2-methylpropanenitrile (7m): Bp 70—71 °C/0.5 Torr. ^1H NMR ($CDCl_3$) δ=1.80 (s, 6H), 4.04 (s, 2H). IR (neat) 3025, 2975, 2250 (w), 1770, 1750 (sh), 1470, 1410, 1390, 1370, 1320, 1290, 1230, 1185, 1135 cm^{-1}.

2-Methyl-2-propanoylpropanenitrile (7l): Bp 50 °C/0.5 Torr. ^1H NMR ($CDCl_3$) δ=1.15 (t, J=7.5 Hz, 3H), 1.74 (s, 6H), 2.34 (q, J=7.5 Hz, 2H). IR (neat) 3000, 2950, 2250, 1775, 1470, 1420, 1390, 1370, 1355, 1225, 1190, 1140 cm^{-1}.

Synthesis of α-Acyloxy Nitriles by Silylcyanation of Ketones and Acylation with Iron(III) Chloride Catalyst. Zinc iodide (20 mg, 0.06 mmol) was added to acetophenone (1.21 g, 10 mmol) and trimethylsilyl cyanide (1.5 ml, 11 mmol) dissolved in benzene (10 ml) at 0 °C and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with benzene (30 ml) and washed with brine (50 ml), dried over magnesium sulfate, and concentrated in vacuo to give crude 2-phenyl-2-trimethylsilyloxypropanenitrile which was dissolved in acetic anhydride (5.0 ml), to which solution was added iron(III) chloride (0.10 g) at 0 °C. Stirring was continued for 1 h at 0 °C to room temperature. The color of the reaction mixture turned to green before dilution with dichloromethane (30 ml) and quenching with water (30 ml). The organic layer was separated, washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation gave **7h** (1.70 g, 90% yield). Bp 56—58 °C/0.15 Torr. ^1H NMR ($CDCl_3$) δ=2.00 (s, 3H), 2.12 (s, 3H), 7.2—7.9 (m, 5H). IR (neat) 3080, 3050, 3010, 2950, 2250, 1760, 1600, 1495, 1370, 1220, 1140, 1090, 1070, 1010, 950, 760, 695 cm^{-1}.

By this procedure following 2-acyloxy nitriles were prepared. Overall yield from the corresponding ketone or aldehyde is given.

2-Acetoxy-2,3-dimethylbutanenitrile (7f): 65%, bp 70—73 °C/16 Torr. ^1H NMR ($CDCl_3$) δ=1.08 and 1.13 (2d, J=4.5 Hz, 6H), 1.68 (s, 3H), 2.08 (s, 3H), 2.08—2.16 (m, 1H). IR (neat) 3000, 2250 (w), 1755, 1470, 1370, 1235 cm^{-1}.

2-Acetoxy-2-methylundecanenitrile (7g): 82% yield, bp 88—90 °C/0.15 Torr. ^1H NMR ($CDCl_3$) δ=0.82—0.95 (t, 3H), 1.28 (m, 14H), 1.72 (s, 3H), 1.76—2.03 (m, 2H), 2.07 (s, 3H). IR (neat) 2925, 2855, 2230 (vw), 1750, 1710, 1460, 1370, 1230 cm^{-1}.

2-Acetoxy-2-ethylpentanenitrile (7k): 66% yield, bp 95—96 °C/20 Torr. ^1H NMR ($CDCl_3$) δ=1.05 (t, J=6.9 Hz, 6H), 2.04 (q, J=6.9 Hz, 4H), 2.09 (s, 3H). IR (neat) 3000, 2950, 2245 (vw), 1750, 1460, 1370, 1230 cm^{-1}.

2-Acetoxy-2-methyl-3-phenylpropanenitrile (7i): 63% yield, bp 140—150 °C/1 Torr. ^1H NMR ($CDCl_3$) δ=1.40 (s, 3H), 2.13 (s, 3H), 3.23 (AB q, 2H), 7.36 (br s, 5H). IR (neat) 3100, 3060, 2970, 2250 (vw), 1760, 1500, 1455, 1375, 1265, 1230, 1170, 1070, 1020, 760, 700 cm^{-1}.

2-Methyl-2-[(phenylthio)acetoxy]propanenitrile (7p). To a dichloromethane (30 ml) solution of phenylthioacetyl chloride (2.40 g, 12.8 mmol) were added 2-hydroxy-2-methylpropanenitrile (1.00 g, 11.7 mmol) and then triethylamine (1.79 ml, 0.128 mmol) at 0 °C. The reaction mixture was stirred and gradually warmed to room temperature over 3 h, then washed twice with 3% hydrochloric acid (30 ml), then with brine (30 ml) and finally with aq sat. sodium hydrogencarbonate solution (30 ml), dried over magnesium sulfate, and concentrated under reduced pressure. Distillation afforded **7p** (1.20 g, 43% yield). Bp 150—160 °C (bath temperature)/0.7 Torr. ^1H NMR ($CDCl_3$) δ=1.65 (s, 6H), 3.58 (s, 2H), 7.17—7.47 (m, 5H). IR (neat) 3075, 3020, 2950, 2340, 1740, 1585, 1470, 1435, 1390, 1370, 1265, 1225, 1200, 1115, 1025, 975 cm^{-1}. MS m/z (rel intensity) 237 (M^++2, 2), 236 (M^++1, 5), 235 (M^+, 32), 168 (10), 123 (100), 109 (13), 77 (12), 65 (10), 51 (12), 45 (41), 41 (10).

Similarly, **7o** (0.64 g, 32% yield) was prepared from 2-hydroxy-2-methylpropanenitrile (0.85 g, 10 mmol), phenylacetyl chloride (1.80 g, 11.7 mmol) and triethylamine (1.60 ml, 11.5 mmol). Bp 145—150 °C/0.8 Torr. ^1H NMR ($CDCl_3$) δ=1.40 (s, 6H), 3.62 (s, 2H), 7.28 (br s, 5H). IR (neat) 3075, 3050, 3010, 2950, 2250, 1750, 1605, 1500, 1470, 1455, 1390, 1370, 1350, 1255, 1225, 1125, 970, 730, 700 cm^{-1}. MS m/z (rel intensity) 204 (M^++1, 2), 203 (M^+, 14), 119 (4), 92 (9), 91 (100), 68 (5), 65 (10), 41 (9), 39 (7).

2-Methyl-2-[(phenylsulfinyl)acetoxy]propanenitrile (7q). *m*-Chloroperoxybenzoic acid (80—85% purity, 0.19 g) was added to a dichloromethane (5 ml) solution of **7p** (0.20 g, 0.85 mmol), and the reaction mixture was stirred at room temperature overnight before dilution with dichloromethane (20 ml) and treatment with 10% sodium thiosulfate aq solution (20 ml). Extractive workup followed by preparative TLC (hexane-ethyl acetate 1 : 1, R_f=0.25) gave **7q** (0.165 g, 77% yield) as a viscous oil. ^1H NMR ($CDCl_3$) δ=1.65 (s, 3H), 1.71 (s, 3H), 3.81 and 3.71 (AB q, J=13.5 Hz, 2H), 7.45—7.80 (m, 5H). IR (neat) 3500, 3075, 3010, 2950, 2250, 1745, 1475, 1445, 1390, 1370, 1270, 1230, 1200, 1150, 1115, 1090, 1050, 975 cm^{-1}. MS m/z (rel intensity) 253 (M^++2, 1), 252 (M^++1, 3), 251 (M^+, 20), 184 (2), 167 (3), 126 (13), 125 (100), 97 (22), 77 (27), 51 (20), 41 (11).

2-Methyl-2-(3-oxobutanoyloxy)propanenitrile (7n). Diketene (1.0 g, 12 mmol) and pyridine (0.94 g, 12 mmol) were successively added to a dichloromethane (20 ml) solution of 2-hydroxy-2-methylpropanenitrile (0.85 g, 10 mmol) at 0 °C, and the reaction mixture was stirred at room temperature overnight, then poured into 5% hydrochloric acid (30 ml), extracted with dichloromethane. The organic layer was washed with brine, dried over magnesium sulfate and concentrated. Distillation gave **7n** (1.52 g, 90% yield). Bp 155—160 °C/21 Torr. ^1H NMR ($CDCl_3$) δ=1.78 (s, 6H), 2.26 (s, 3H), 3.48 (s, 2H). IR (neat) 3015, 2950, 2250, 1760, 1725, 1630, 1560, 1470, 1410, 1370, 1365, 1320, 1260, 1230, 1135, 1025, 995, 970 cm^{-1}. MS m/z (rel intensity) 168 (M^+−1, 3), 126 (2), 100 (2), 85 (12), 84 (14), 70 (75), 69 (15), 68 (10), 58 (6), 44 (12), 43 (100), 42 (18), 41 (16).

Synthesis of 4-Amino-5,5-dimethyl-2(5*H*)-furanone (3d). A Typical Procedure for the Preparation of 5,5-Disubstituted 4-Amino-2(5*H*)-furanones with $LiN(SiMe_3)_2$. A THF solution of **7d** (0.127 g, 1.0 mmol) was added to $LiN(SiMe_3)_2$ (2.5 mmol in 3 ml of THF) drop by drop at −78 °C under an argon atmosphere. After 2 h, sat. ammonium chloride aq solution (5 ml) was added to the reaction mixture to quench the reaction. The resulting mixture was warmed to room temperature and concentrated under reduced pressure. The residue was extracted with methanol. The methanolic extract was concentrated and the residual oil was purified by preparative TLC (silica gel, dichloromethane-methanol 10 : 1) to give **3d** (0.104 g, 82% yield).

In a similar manner, following amino furanones were prepared. Physical properties of these are listed below.

4-Amino-5-isopropyl-5-methyl-2(5*H*)-furanone (3f). Mp 171—172 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 10 : 1) δ=0.86 and

1.05 (2d, J=6.6 Hz, 6H), 1.42 (s, 3H), 1.93 (heptet, J=6.6 Hz, 1H), 4.54 (s, 1H), 6.23 (br s, 2H). IR (KBr) 3380, 3205, 3000, 1730 (sh), 1700, 1665, 1610, 1590, 1580, 1415, 1290, 1230 cm^{-1}. MS m/z (rel intensity) 156 (M^++1, 2), 155 (M^+, 8), 113 (11), 112 (100), 70 (23), 43 (35), 41 (12). Found: C, 61.90; H, 8.56; N, 8.97%. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03%.

4-Amino-5-methyl-5-nonyl-2(5*H*)-furanone (3g). Mp 104—107 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 20:1) δ=0.87 (t, J=6.0 Hz, 3H), 1.0—1.4 (br s, 14H), 1.44 (s, 3H), 1.55—1.90 (m, 2H), 4.65 (s, 1H), 5.58 (br s, 2H). IR (KBr) 3440, 3350, 3225, 2925, 2870, 1735, 1710, 1660, 1585 cm^{-1}. MS m/z (rel intensity) 240 (M^++1, 3), 239 (M^+, 5), 211 (6), 154 (11), 140 (12), 127 (21), 113 (59), 112 (100), 85 (24), 70 (29), 43 (44). Found: m/z 239.1868. Calcd for $C_{14}H_{25}NO_2$: M^+ 239.1883.

4-Amino-5-methyl-5-phenyl-2(5*H*)-furanone (3h). Mp 69—71 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.90 (s, 3H), 4.68 (s, 1H), 6.31 (br s, 2H), 7.3—7.6 (m, 5H). IR (KBr) 3400, 3205, 1700, 1665 (sh), 1585, 1445, 1405, 1290, 1285, 1230, 1075, 965 cm^{-1}. MS m/z (rel intensity) 191 (M^++2, 1), 190 (M^++1, 11), 189 (M^+, 83), 175 (13), 174 (100), 146 (22), 121 (33), 112 (30), 105 (67), 103 (20), 77 (38), 70 (14), 69 (17), 68 (14), 51 (20), 43 (72), 41 (42). Found: C, 66.54; H, 6.24; N, 6.99%. Calcd for $C_{11}H_{11}NO_2 \cdot 0.5\ H_2O$: C,66.65; H, 6.10; N, 7.07%. Found: m/z 189.0776. Calcd for $C_{11}H_{11}NO_2$: M^+ 189.0788.

4-Amino-5-benzyl-5-methyl-2(5*H*)-furanone (3i). Mp 158—161 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.50 (s, 3H), 3.37 (s, 2H), 4.43 (s, 1H), 6.15 (br s, 2H), 7.20 (br s, 5H). IR (KBr) 3420, 3225, 1715, 1700, 1665, 1605, 1590, 1450, 1415, 1300, 1255, 1170, 970 cm^{-1}. MS m/z (rel intensity) 203 (M^+, 6), 112 (100), 91 (7), 84 (33), 70 (15), 66 (40), 43 (19). Found: C, 70.75; H, 6.36; N, 6.76%. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%.

4-Amino-5-(6-methoxy-2-naphthyl)-5-methyl-2(5*H*)-furanone (3j). Mp 206—208 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 4:1) δ=1.97 (s, 3H), 3.90 (s, 3H), 4.73 (s, 1H), 6.25 (br s, 2H), 7.0—7.9 (m, 6H). IR (KBr) 3450, 3350, 3240, 1730 (sh), 1725, 1645, 1595, 1440, 1390, 1370, 1270, 1220, 1200, 1165, 1140, 1020, 950 cm^{-1}. MS m/z (rel intensity) 271 (M^++2, 2), 270 (M^++1, 15), 269 (M^+, 79), 255 (18), 254 (100), 226 (10), 201 (10), 185 (40), 157 (18). Found: C, 71.23; H, 5.49; N, 5.13%. Calcd for $C_{16}H_{25}NO_3$: C, 71.36; H, 5.61; N, 5.20%.

4-Amino-5,5-diethyl-2(5*H*)-furanone (3k). Mp 162—164 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 3:1) δ=0.83 (t, J=7 Hz, 6H), 1.54—1.89 (m, 4H), 4.67 (s, 1H), 5.94 (br s, 2H). IR (KBr) 3425, 3375, 3200, 3000, 1715, 1665, 1650, 1605, 1590 cm^{-1}. MS m/z (rel intensity) 156 (M^++1, 1), 155 (M^+, 9), 127 (18), 126 (100), 84 (10), 70 (14), 57 (53), 41 (12). Found: C, 61.81; H, 8.40; N, 8.95%. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03%.

4-Amino-3,5,5-trimethyl-2(5*H*)-furanone (3l). Mp 205—208 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 3:1) δ=1.43 (s, 6H), 1.61 (s, 3H), 5.69 (br s, 2H). IR (KBr) 3400, 3230, 3000, 2950, 1710, 1665, 1600, 1475, 1430, 1345, 1215, 1195, 1100, 1000 cm^{-1}. MS m/z (rel intensity) 142 (M^++1, 16), 141 (M^+, 71), 126 (100), 98 (23), 70 (16), 56 (19), 55 (32), 54 (15), 43 (38). Found; m/z 141.0770. Calcd for $C_7H_{11}NO_2$: M^+ 141.0790.

4-Amino-3-chloro-5,5-dimethyl-2(5*H*)-furanone (3m). Mp 170—172 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 1:1) δ=1.48 (s, 6H), 6.88 (br s, 2H). IR (KBr) 3450 (sh), 3375, 3220, 3000, 1720, 1670, 1650, 1600, 1300, 1225, 1140, 1040 cm^{-1}. MS m/z (rel intensity) 164 (M^++3, 3), 163 (M^++2, 18), 162 (M^+1, 8), 161 (M^+, 54), 148 (33), 146 (100), 118 (36), 104 (39), 82 (11), 76 (13), 75 (17), 70 (24), 68 (21), 43 (60). Found: m/z 161.0209. Calcd for $C_6H_8ClNO_2$: M^+ 161.0242.

4-Amino-5,5-dimethyl-3-phenylsulfinyl-2(5*H*)-furanone (3q). A Typical Procedure for the Synthesis of 3 Having Electron-Withdrawing Substituent at C(3). A THF (3 ml) solution of **7q** (50 mg, 0.20 mmol) was added drop by drop to sodium hydride (50% in oil, 20 mg, 0.40 mmol) suspended in THF (30 ml) under reflux, and the reaction mixture was heated to reflux for 2 h until all the starting material was consumed. Excess hydride was carefully quenched with sat. ammonium chloride aq solution and worked up. Isolation by column chromatography (dichloromethane-methanol 10:1) gave **3q** (43 mg, 86% yield). Mp 137—138 °C. ^1H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.41 (s, 3H), 1.53 (s, 3H), 6.9—7.3 (br, 2H), 7.33—7.57 (m, 3H), 7.57—7.90 (m, 2H). IR (KBr) 3350, 3200, 3000, 1715, 1665, 1590, 1580 (sh), 1480, 1460, 1410, 1370, 1280, 1225, 1220, 1160, 1080, 1045 (sh), 1025 cm^{-1}. MS m/z (rel intensity) 251 (M^+, 3) 235 (5), 204 (15), 203 (100), 188 (32), 160 (42), 158 (11), 126 (9), 86 (27), 78 (25), 77 (17), 68 (18), 51 (18), 43 (23), 39 (10). Found: C, 57.27; H, 5.11; N, 5.48; S, 12.94%. Calcd for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57; S, 12.76%.

By the similar procedure, **3n**, **3o**, and **3p** were prepared and their physical data are listed below.

3-Acetyl-4-amino-5,5-dimethyl-2(5*H*)-furanone (3n). Mp 188—189 °C. ^1H NMR ($CDCl_3$-DMSO-d_6) δ=1.56 (s, 6H), 2.46 (s, 3H), 8.43 and 8.82 (br 2s, 2H). IR (KBr) 3370, 1710, 1650, 1540, 1360, 1320, 1025 cm^{-1} MS m/z (rel intensity) 169 (M^+, 11), 154 (12), 112 (8), 87 (67), 86 (67), 66 (100), 48 (14), 46 (24), 43 (19). Found: C, 56.77; H, 6.65; N, 8.02%. Calcd for $C_8H_{11}NO_3$: C, 56.80; H, 6.55; N, 8.28%.

4-Amino-5,5-dimethyl-3-phenyl-2(5*H*)-furanone (3o). Mp 148—150 °C (hexane-ethyl acetate). ^1H NMR ($CDCl_3$-DMSO-d_6 1:1) δ=1.57 (s, 6H), 6.40 (br s, 2H), 7.15—7.65 (m, 5H). IR (KBr) 3400, 3330, 3000, 1700, 1640, 1615, 1595, 1500, 1470, 1425, 1370, 1330, 1245, 1200, 1155, 1120, 1010, 970, 920 cm^{-1}. MS m/z (rel intensity) 205 (M^++2, 1), 204 (M^++1, 15), 203 (M^+, 100), 188 (49), 160 (55), 158 (11), 132 (22), 118 (33), 117 (63), 115 (14), 91 (14), 89 (24), 77 (6), 43 (55). Found: C, 70.91; H, 6.49; N, 6.85%. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%.

4-Amino-5,5-dimethyl-3-phenylthio-2(5*H*)-furanone (3p). Mp 154.5—156.5 °C. ^1H NMR ($CDCl_3$) δ=1.55 (s, 6H), 6.66 (br s, 2H), 7.00—7.33 (m, 5H). IR (KBr) 3460, 3325, 3270, 3200, 1710, 1640, 1585, 1480, 1410, 1290, 1035, 740 cm^{-1}. MS m/z (rel intensity) 237 (M^++2, 6), 236 (M^++1, 16), 235 (M^+, 100), 220 (8), 192 (7), 176 (5), 151 (10), 150 (28), 149 (12), 142 (43), 141 (12), 123 (10), 121 (24), 114 (22), 113 (15), 110 (6), 109 (8), 105 (11), 86 (14), 77 (16), 68 (15), 65 (10), 51 (19), 45 (11), 43 (65), 42 (12), 39 (15). Found: m/z 235.0646. Calcd for $C_{12}H_{13}NO_2S$: M^+ 235.0665.

Desulfurization of 3p. A mixture of **3p** (15 mg, 0.064 mmol), Raney Nickel (W-2) (0.06 g) and ethanol (3 ml) was heated to reflux for 3 h. Filtration, concentration and purification by preparative TLC (dichloromethane-methanol 10:1) gave **3d** (10 mg, quantitative yield) which showed identical chromatographic and spectrometric data to those of the sample prepared before.

Derivatization of 3d to 6d. A Typical Procedure for the Synthesis of Urea 6 and 6′. To a THF (50 ml) solution of **3d** (1.27 g, 10 mmol) was added *t*-butyl isocyanate (1.50 g, 15 mmol) at room temperature and the mixture was cooled with ice bath. Potassium *t*-butoxide (1.68 g, 15 mmol) was then added, and the whole was warmed to room temperature

and stirred for 2 d. Neutralization with sat. ammonium chloride aq solution, dilution with brine (30 ml), extraction with ethyl acetate (30 ml), drying the organic extract over magnesium sulfate followed by careful evaporation of the organic solvents to ca. 5 ml afforded 4-(*N'-t*-butylureido)-5,5-dimethyl-2(5*H*)-furanone (**6d**) as colorless crystals (1.53 g) which were filtered. From the filtrate, another portion (0.5 g) of **6d** was obtained. Total yield was 89%. Mp 247.5—248 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 3:1) δ=1.37 (s, 9H), 1.48 (s, 6H), 5.85 (s, 1H), 6.25 (br s, 1H), 8.56 (br s, 1H). IR (KBr) 3390, 3005, 2955, 1745, 1730, 1700, 1625, 1540 (sh), 1450, 1395, 1370, 1320, 1280, 1255, 1200, 1180, 1170, 1005, 975, 950, 820, 775, 740, 710, 700 cm^{-1}. MS *m/z* (rel intensity) 227 (M^++1, 0.6), 226 (M^+, 1), 138 (9), 128 (10), 127 (88), 112 (100), 84 (15), 70 (11), 58 (38), 57 (77), 43 (25), 42 (16), 41 (38), 39 (11), 29 (20). Found: C, 58.30; H, 8.19; N, 12.25%. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38%.

Similarly, other urea derivatives listed in Table 3 were prepared and exhibited following characteristics.

4-(*N'-t*-Butylureido)-5-methyl-2(5*H*)-furanone (6a).[5] Mp 197—201 °C (decomp); lit,[5a,b] 204—206 °C (decomp). ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=1.37 (s, 9H), 1.50 (d, *J*=6 Hz, 3H), 4.98 (q, *J*=6 Hz, 1H), 5.86 (s, 1H), 5.97 (s, 1H), 8.70 (s, 1H). IR (KBr) 3425, 3325, 3175, 3080, 3000, 1710, 1625, 1550, 1510, 1255, 1195, 1170, 1085, 1050, 1005, 950, 905, 815, 700 cm^{-1}. MS *m/z* (rel intensity) 213 (M^++1, 2), 212 (M^+, 2), 181 (2), 173 (9), 155 (2), 154 (3), 140 (2), 139 (1), 115 (3), 114 (13), 113 (100), 112 (6), 101 (6), 98 (44), 84 (10), 70 (42), 58 (61), 57 (100).

5-Methyl-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'a).[6] ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ=1.54 (d, *J*=6 Hz, 3H), 5.02 (q, *J*=6 Hz, 1H), 5.90 (s, 1H), 7.50 (s, 5H), 8.41 (br, 1H), 8.96 (br, 1H). IR (KBr) 3380 (sh), 3350, 3150, 3075, 2990, 1715, 1630, 1605, 1550, 1500, 1440, 1330, 1295, 1230, 1190, 1170, 1095, 1050, 820, 755, 695, 685 cm^{-1} MS *m/z* (rel intensity) 233 (M^++1, 3), 232 (M^+, 14), 213 (2), 212 (10), 204 (4), 188 (2), 149 (2), 139 (2), 124 (4), 121 (1), 120 (16), 119 (100), 113 (35), 98 (29), 93 (100), 91 (31), 77 (24), 70 (35), 63 (9), 64 (20).

4-(*N'-t*-Butylureido)-5-ethyl-2(5*H*)-furanone (6b).[6] Mp 140—144 °C (decomp); lit,[5a] 142—144 °C. ^{1}H NMR ($CDCl_3$) δ=0.95 (t, *J*=7 Hz, 3H), 1.37 (s, 9H), 1.5—2.3 (m, 2H), 4.87 (dd, *J*=3 and 6 Hz, 1H), 3.90 (s, 1H), 3.95 (br s, 1H), 8.62 (br s, 1H). IR (neat) 3420, 3300, 3000, 1700, 1620, 1520, 1460, 1350, 1250, 1190, 1160, 1010, 980, 820, 695, 655 cm^{-1}. MS *m/z* (rel intensity) 227 (M^++1, 5), 226 (M^+, 3), 128 (21), 127 (64), 100 (17), 99 (84), 98 (99), 84 (9), 72 (4), 71 (7), 70 (16), 58 (40), 57 (100).

5,5-Dimethyl-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'd). Mp 239—240 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 3:1) δ=1.53 (s, 6H), 6.01 (s, 1H), 7.04—7.53 (m, 5H), 8.49 (br s, 1H), 8.85 (br s, 1H). IR (KBr) 3400, 3230, 3160, 3070, 1750 (sh), 1730 (sh), 1705, 1625, 1600, 1565 (sh), 1555 (sh), 1530, 1435, 1330, 1295, 1285, 1215, 1195, 1175, 1115, 1010, 975, 905, 860, 830, 760, 740, 695 cm^{-1}. MS *m/z* (rel intensity) 247 (M^++1, 2), 246 (M^+, 13), 138 (29), 127 (43), 120 (15), 119 (100), 112 (82), 93 (60), 92 (16), 91 (32), 77 (20), 70 (22), 68 (10), 67 (10), 66 (21), 65 (20), 64 (23), 63 (11), 51 (14), 43 (72), 41 (33). Found: C, 63.31; H, 5.82; N, 11.29%. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38%.

3'-(*N'-t*-Butylureido)spiro[cyclohexane-1,2'(5'*H*)-furan]-5'-one (6e). Mp 249.5—250 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.37 (s, 9H), 1.5—2.1 (m, 10H), 5.92 (s, 1H), 6.14 (br s, 1H), 8.61 (br s, 1H). IR (KBr) 3390, 3350, 2960, 1740, 1720 (sh), 1695, 1625, 1540, 1430, 1395, 1370, 1295, 1280, 1255, 1195, 1135, 1100, 1010, 980, 960, 940, 910, 855, 830, 760, 750, 700 cm^{-1}. MS *m/z* (rel intensity) 266 (M^+, 2), 168 (11), 167 (77), 124 (18), 112 (17), 111 (100), 68 (11), 58 (33), 57 (60), 42 (12), 41 (34), 29 (16). Found: C, 63.15; H, 8.28; N, 10.47%. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52%.

5-(*N'-t*-Butylureido)-5-isopropyl-5-methyl-2(5*H*)-furanone (6f). Mp 182—183 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 5:1) δ=0.78 and 1.08 (2d, *J*=6.6 Hz, 6H), 1.35 (s, 9H), 1.43 (s, 3H), 1.5—2.0 (m, 1H), 5.90 (s, 1H), 6.13 (br s, 1H), 8.24 (br s, 1H). IR (KBr) 3410, 3300, 3240, 3170, 3070, 3000, 1730, 1710, 1690, 1615, 1550 (sh), 1535, 1455, 1395, 1370, 1365, 1340, 1280, 1255, 1190, 1145, 1110, 1040, 1000, 975, 820, 775, 750, 710 cm^{-1}. MS *m/z* (rel intensity) 255 (M^++1, 0.4), 254 (M^+, 1), 155 (20), 113 (20), 112 (100), 58 (14), 57 (30), 43 (26), 41 (17), 29 (11). Found: C, 61.42; H, 8.52; N, 10.98%. Calcd for $C_{13}H_{22}N_2O_3$; C, 61.39; H, 8.72; N, 11.02%

4-(*N'-t*-Butylureido)-5-methyl-5-nonyl-2(5*H*)-furanone (6g). Mp 120—120.5 °C. ^{1}H NMR ($CDCl_3$) δ=0.87 (t, 3H), 1.1—2.1 (m+2s (δ=1.37 and 1.48), totally 28H), 6.00 (s, 1H), 6.12 (br s, 1H), 8.62 (br s, 1H). IR (KBr) 3430, 3320, 3240, 3175, 3080, 2980, 2950, 2875, 1735, 1625, 1555, 1515, 1460, 1395, 1390, 1370, 1340, 1255, 1090, 1050, 1005, 965, 820, 745, 720 cm^{-1}. MS *m/z* (rel intensity) 339 (M^++1, 1), 338 (M^+, 3), 239 (11), 222 (9), 211 (14), 180 (11), 154 (20), 141 (15), 140 (20), 139 (21), 138 (34), 127 (41), 113 (100), 112 (95), 85 (29), 84 (85), 83 (13), 70 (31), 68 (22), 58 (94), 57 (87), 56 (31), 51 (26), 43 (63), 42 (29), 41 (87), 40 (10). Found: C, 67.46; H, 10.04; N, 8.30%. Calcd for $C_{19}H_{34}N_2O_3$: C, 67.42; H, 10.13; N, 8.28%.

5-Methyl-5-nonyl-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'g). Mp 114—115 °C. ^{1}H NMR ($CDCl_3$) δ=0.75—0.90 (m, 3H), 1.22 (br s, 14H), 1.56 (s, 3H), 1.73—1.93 (m, 2H), 6.21 (s, 1H), 7.07—7.53 (m, 5H), 8.27 (br s, 1H), 8.98 (br s, 1H). IR (KBr) 3400, 3320, 3260, 3170, 3080, 2980, 2940, 2880, 1745, 1710 (sh), 1695, 1625, 1605, 1540, 1475, 1440, 1325, 1295, 1225 (sh), 1190, 1135, 1085, 1070, 1055, 1010, 975, 910, 885, 875, 870, 830, 755, 725, 695 cm^{-1}. MS *m/z* (rel inensity) 359 (M^++1, 1), 358 (M^+, 4), 232 (9), 222 (10), 154 (12), 140 (11), 139 (27), 138 (44), 127 (19), 119 (58), 113 (54), 112 (100), 94 (11), 93 (84), 92 (11), 91 (37), 77 (11), 70 (29), 68 (15), 66 (18), 65 (16), 64 (24), 63 (11), 57 (14), 55 (20), 43 (72), 42 (18), 41 (55). Found: C, 70.25; H, 8.39; N, 7.74%. Calcd for $C_{21}H_{30}N_2O_3$: C, 70.36; H, 8.44; N, 7.82%.

4-(*N'-t*-Butylureido)-5-methyl-5-phenyl-2(5*H*)-furanone (6h). Mp 207—208 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 3:1) δ=1.32 (s, 9H), 1.88 (s, 3H), 6.08 (s, 1H), 6.25 (br s, 1H), 7.40 (s, 5H), 8.23 (br s, 1H). IR (KBr) 3370, 2990, 1740 (sh), 1700, 1620, 1530, 1450, 1390, 1365, 1310, 1280, 1255, 1200, 1100, 1070, 1000, 970, 950, 820, 770, 740, 700 cm^{-1}. MS *m/z* (rel intensity) 289 (M^++1, 1), 288 (M^+, 1) 200 (17), 190 (14), 189 (88), 175 (12), 174 (100), 146 (17), 144 (12), 143 (10), 121 (21), 112 (12), 105 (33), 84 (16), 77 (25), 69 (10), 68 (15), 58 (41), 57 (87), 51 (13), 43 (39). Found: C, 66.78; H, 7.00; N, 9.74%. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.64; H, 6.99; N, 9.72%.

5-Methyl-5-phenyl-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'h). Mp 234—235 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 3:1) δ= 1.95 (s, 3H), 6.25 (s, 1H), 7.2—7.6 (m, 10H), 8.56 (br s, 2H). IR (KBr) 3360, 3325, 3175, 3075, 1755, 1730 (sh), 1710, 1640, 1605, 1555, 1545, 1505, 1445, 1385, 1330, 1300, 1280, 1255, 1245, 1215, 1185, 1100, 1085, 1075, 1030, 1010, 995, 970, 935, 920, 905, 890, 860, 820, 780, 755, 705 cm^{-1}. MS *m/z* (rel intensity) 309 (M^++1, 4), 308 (M^+, 25), 215 (10), 200 (59), 189 (58), 175 (11), 174 (92), 172 (17), 146 (20), 121 (25), 120 (14), 119 (100), 112 (20), 105 (82), 103 (15), 93 (76), 92 (17), 91 (50),

78 (11), 77 (67), 70 (11), 69 (12), 68 (16), 67 (13), 66 (28), 65 (25), 64 (31), 63 (18), 52 (12), 51 (40), 50 (17), 41 (68). Found: C, 70.00; H, 5.25; N, 9.07%. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09%.

4-(*N'-t*-Butylureido)-5-benzyl-5-methyl-2(5*H*)-furanone (6i). Mp 241—243 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 20:1) δ= 1.35 (s, 9H), 1.46 (s, 3H), 3.01 (AB, 2H), 5.76 (s, 1H), 6.20 (br s, 1 H), 7.21 (br s, 5H), 8.64 (br s, 1H). IR (KBr) 3420, 3310, 3170, 3075, 3000, 2975, 1735, 1710 (sh), 1700, 1625, 1555, 1510, 1460, 1395, 1385, 1370, 1310, 1255, 1190, 1170, 1130, 1090, 1065, 1050, 1005, 965, 885, 820, 765, 745, 725, 700 cm^{-1}. MS *m/z* (rel intensity) 303 (M^++1, 1), 302, (M^+, 5), 211 (15), 155 (13), 112 (100), 91 (29), 58 (17), 57 (32), 43 (21), 41 (16). Found: C, 67.47; H, 7.45; N, 9.20%. Calcd for $C_{17}H_{22}N_2O_3$: C, 67.52; H, 7.33; N, 9.27%.

5-Benzyl-5-methyl-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'i). Mp 206.5 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 20:1) δ=1.55 (s, 3H), 3.07 (AB, 2H), 6.00 (s, 1H), 7.10—7.55 (m+s (δ=7.18), 10H), 8.34 (br s, 1H), 8.96 (br s, 1H). IR (KBr) 3380 (sh), 3350, 3300, 3270, 3080, 2930, 1745, 1705, 1640, 1605, 1550, 1500, 1445, 1385, 1325, 1300, 1235, 1210, 1185, 1090, 1005, 980, 870, 815, 780, 750, 700 cm^{-1}. MS *m/z* (rel intensity) 323 (M^++1, 2), 322 (M^+, 9), 231 (40), 138 (12), 119 (18), 112 (100), 93 (26), 92 (14), 91 (86), 77 (13), 70 (22), 66 (12), 65 (23), 64 (10), 51 (10), 43 (55). Found: C, 70.75; H, 5.63; N, 8.66%. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69%.

4-(*N'-t*-Butylureido)-5-(6-methoxy-2-naphthyl)-5-methyl-2(5*H*)-furanone (6j). Mp 234—235 °C ^{1}H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.30 (s, 9H), 1.98 (s, 3H), 3.91 (s, 3H), 6.16 (br s, 1H), 6.18 (s, 1H), 7.1—7.9 (m, 6H), 8.18 (br s, 1H). IR (KBr) 3390, 3350, 3020, 2970, 1740, 1710, 1635, 1615, 1550, 1530, 1495, 1460, 1400, 1380, 1370, 1320, 1280, 1260, 1210, 1170, 1130, 1100, 1075, 1040, 1010, 970, 950, 930, 890, 855, 830, 820, 750, 725 cm^{-1}. MS *m/z* (rel intensity) 370 (M^++2, 1), 369 (M^++1, 7), 368 (M^+, 30), 296 (15), 295 (79), 281 (19), 280 (100), 269 (40), 255 (11), 254 (60), 252 (16), 201 (12), 186 (11), 185 (75), 157 (37), 142 (19), 128 (10), 127 (10), 115 (11), 114 (27), 84 (18), 67 (10), 63 (10), 58 (97), 57 (36), 43 (62). Found: C, 68.38; H, 6.77; N, 7.45%. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60%.

5-(6-Methoxy-2-naphthyl)-4-(*N'*-phenylureido)-2(5*H*)-furanone (6'j). Mp 221—222 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=2.02 (s, 3H), 3.90 (s, 3H), 6.30 (s, 1H), 6.9—7.9 (m, 11 H), 8.56 (br s, 2H). IR (KBr) 3350, 3300 (sh), 1745, 1730 (sh), 1705, 1630, 1555, 1540, 1500, 1445, 1395, 1325, 1290, 1270, 1205, 1185, 1090, 1075, 1030, 1005, 970, 960, 920, 885, 855, 845, 820, 755, 750, 695 cm^{-1}. MS *m/z* (rel intensity 388 (M^+, 1), 311 (9), 269 (42), 255 (12), 254 (66), 212 (10), 201 (11), 185 (47), 157 (21), 142 (11), 119 (40), 114 (14), 93 (100), 92 (14), 91 (31), 77 (13), 66 (21), 65 (20), 64 (25), 63 (16), 57 (11), 51 (14), 43 (57). Found: C, 70.98; H, 5.24; N, 7.16%. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21%.

4-(*N'-t*-Butylureido)-3,5,5-trimethyl-2(5*H*)-furanone (6l). Mp 200.5—201 °C. ^{1}H NMR ($CDCl_3$-DMSO-$d_6$1:1) δ=1.35 (s, 9H), 1.54 (s, 6H), 1.81 (s, 3H), 6.28 (br s, 1H), 7.85 (br s, 1H). IR (KBr) 3400, 3325, 3210, 3080, 3020, 2960, 1775, 1765, 1720, 1610, 1595, 1500, 1470, 1450, 1410, 1370, 1330, 1295, 1190, 1115, 1085, 890, 865, 845, 780, 740, 710 cm^{-1}. MS *m/z* (rel intensity) 241 (M^++1, 1), 240 (M^+, 2), 142 (9), 141 (100), 126 (80), 123 (10), 98 (23), 84 (10), 58 (28), 57 (74), 55 (12), 43 (20), 42 (12), 41 (33). Found: C, 59.99; H, 8.38; N, 11.43%. Calcd for $C_{12}H_{20}N_2O_3$: C, 59.98; H, 8.39; N, 11.66%.

4-(*N'-t*-Butylureido)-5,5-dimethyl-3-phenyl-2(5*H*)-furanone (6o). Mp 201—201.5 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 5:1) δ=1.27 (s, 9H), 1.78 (s, 6H), 6.58 (br s, 1H), 7.23—7.53 (m, 5H), 8.28 (br s, 1H). IR (KBr) 3400, 3230, 3140, 3000, 1745, 1730, 1680, 1645, 1605, 1535, 1515, 1455, 1395, 1370, 1350, 1320, 1290, 1230, 1210, 1195, 1150, 1080, 1035, 1015, 970, 960, 930, 790, 780, 750, 705 cm^{-1}. MS *m/z* (rel intensity) 303 (M^++1, 1), 302 (M^+, 3), 229 (10), 204 (15), 203 (100), 188 (27), 186 (12), 160 (41), 158 (15), 130 (11), 117 (13), 115 (14), 89 (22), 77 (5), 58 (30), 57 (39), 43 (49). Found: C, 67.42; H, 7.40; N, 9.16%. Calcd for $C_{17}H_{22}N_2O_3$: C, 67.52; H, 7.33; H, 9.27%.

4-(*N'-t*-Butylureido)-5,5-dimethyl-3-phenylsulfinyl-2(5*H*)-furanone (6q). Mp 179.5—180 °C. ^{1}H NMR ($CDCl_3$-DMSO-d_6 10:1) δ=1.36 (s, 9H), 1.74 and 1.78 (2s, 6H), 6.19 (br s, 1H), 7.47—7.60 (m, 3H), 7.76-7.93 (m, 2H), 9.95 (br s, 1H). IR (KBr) 3330, 3250, 3120, 3070, 3000, 2950, 1750 (sh), 1725, 1615, 1540, 1480, 1445, 1395, 1365, 1275, 1220, 1155, 1040, 995, 930, 920, 790, 770, 760, 695 cm^{-1}. MS *m/z* (rel intensity) 351 (M^++1, 0.2), 350 (M^+, 0.4), 229 (17), 203 (66), 188 (13), 186 (15), 160 (20), 125 (14), 109 (15), 95 (11), 94 (12), 86 (12), 84 (36), 78 (23), 77 (40), 68 (14), 65 (14), 58 (100), 57 (38), 56 (15), 53 (12), 52 (12), 51 (48), 50 (15), 45 (48), 43 (94). Found: C, 58.29; H, 6.38; N, 7.96; S, 8.96%. Calcd for $C_{17}H_{22}N_2O_4S$: C, 58.27; H, 6.33; N, 7.99; S, 9.15%.

2,4,4-Trimethoxybutanenitrile (8). Boron trifluoride etherate (0.15 ml, 1.2 mmol) was added to a mixture of 1,1,3,3-tetramethoxypropane (1.65 g, 10 mmol) and trimethylsilyl cyanide (1.35 ml, 10 mmol) at 0 °C and the mixture was stirred at 0 °C for 3 h. GLC assay (PEG 20 M, 10%, 3 m, 180 °C) showed a single new peak. Dilution with dichloromethane, treatment with sat. sodium hydrogencarbonate aq solution, extraction with dichloromethane (4 times), drying over magnesium sulfate, followed by concentration gave **8** (1.63 g, 99% yield) as a colorless oil. Bp 70—73 °C/15 Torr. ^{1}H NMR ($CDCl_3$) δ=2.10 (t, *J*=6 Hz, 2H), 3.34 (s, 6H), 3.47 (s, 3H), 4.15 (t, *J*=6 Hz, 1 H), 4.54 (t, *J*=6 Hz, 1H). IR (neat) 3400, 2950, 2850, 2250, 1460, 1390, 1370, 1335, 1190, 1120, 1065, 1020, 980, 920, 900, 800, 605 cm^{-1}. MS *m/z* (rel intensity) 158 (M^+−1, 1), 128 (M^+−OMe, 37), 98 (11), 96 (27), 75 (100), 71 (5), 70 (89), 47 (17), 45 (17). Found: C, 52.52; H, 8.12; N, 8.85%. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80%.

2-Acetoxy-2,4,4-trimethoxybutanenitrile (10). A mixture of **8** (0.62 g, 3.9 mmol), *N*-bromosuccinimide (NBS) (0.76 g, 4.3 mmol), azobis(isobutyronitrile) (7 mg, 0.043 mmol) and benzene (15 ml) was heated gradually over 10 min to 90 °C and stirred for 30 min at 90 °C. The reaction mixture was diluted with hexane, and the insoluble material was filtered off through a Celite pad. Concentration gave **9** (0.87 g, 93% yield) as a pale yellow oil which exhibited ^{1}H NMR ($CDCl_3$) δ=2.76 (d, *J*=5.6 Hz, 2H), 3.40 (s, 3H), 3.41 (s, 3H), 3.70 (s, 3H), 4.73 (t, *J*=5.6 Hz, 1H), and IR (neat) 2250 cm^{-1}.

Without purification, this was employed for the next reaction. Silver acetate (0.60 g, 3.6 mmol) was added to an acetonitrile (13 ml) solution of **9** (0.87 g, 3.6 mmol) at 0 °C, and the mixture was stirred at 0 °C for 40 min. Filtration through a Celite pad followed by concentration and distillation gave **10** (0.62 g, 79% yield) as a colorless oil. Bp 110—114 °C/0.65 Torr. ^{1}H NMR ($CDCl_3$) δ=2.12 (s, 3H), 2.53 (d, *J*=6 Hz, 2H), 3.33 (s, 3H), 3.35 (s, 3H), 3.62 (s, 3H), 4.68 (t, *J*=6 Hz, 1H). IR (neat) 3025, 2975, 2860, 2260, 1760, 1735 (sh), 1450, 1375, 1235, 1200, 1120, 1075, 1015, 950, 840 cm^{-1}. MS *m/z* (rel intensity) 186 (M^+−OMe, 2), 142 (3), 126 (38), 117 (4), 112 (7), 103 (4), 100 (6), 85 (5), 75 (99), 70 (9), 58 (5), 47 (12), 43 (100). Found: C, 49.09; H, 6.87; N, 6.28%. Calcd for

$C_9H_{15}NO_5$: C, 49.09; H, 6.96; N, 6.34%.

4-Amino-5-(2,2-dimethoxyethyl)-5-methoxy-2(5*H*)-furanone (11). Lithium diisopropylamide (4.6 mmol in THF (2 ml) and hexane (2.8 ml)) was added to a mixture of diethylaluminium chloride (2.2 M hexane solution, 2.2 ml, 4.7 mmol) and THF (1 ml) at 0 °C, and the resulting solution was stirred for 1 h then cooled to −78 °C. To this base solution was added **10** (0.100 g, 0.46 mmol) dissolved in THF (1.5 ml) over 5 min. After 1.2 h, the starting material was all consumed. Quenching was effected by addition of sat. ammonium chloride aq solution (0.2 ml) at −78 °C. The mixture was warmed to room temperature, dried over magnesium sulfate, charged on the top of a short silica-gel column (Wakogel C-100, 1 cm) and eluted with methanol-dichloromethane (1:10). Concentration followed by prepartive TLC (dichloromethane-methanol 10:1) gave **12** (68 mg, 68% yield). R_f= 0.48 (CH_2Cl_2-MeOH 10:1). Mp 109—111 °C (colorless plates). ^{1}H NMR ($CDCl_3$) δ=2.28 (d, J=5.7 Hz, 2H), 3.23 (s, 3H), 3.32 (s, 3H), 3.37 (s, 3H), 4.63 (t, J=5.5 Hz, 1H), 4.88 (s, 1H), 5.27 (br, 2H). IR (neat) 3370, 3220, 2950, 2850, 1735, 1660, 1610, 1440, 1410, 1390, 1370, 1290, 1210, 1190, 1165, 1115, 1070, 1000, 915, 795, 730 cm^{-1}. MS m/z (rel intensity) 217 (M^+, 2), 185 (28), 155 (22), 154 (23), 128 (63), 100 (49), 75 (100). Found: m/z 217.0968. Calcd for $C_9H_{15}NO_5$: M^+ 217.0950.

4-Amino-5-methoxy-5-(2-oxoethyl)-2(5*H*)-furanone (12). Hexamethyldisilazane (0.29 ml, 1.39 mmol) and then boron tribromide (1.0 M dichloromethane solution, 1.38 ml, 1.38 mmol) were added successively to a dichloromethane (12 ml) solution of **11** (0.100 g, 0.46 mmol) at −23 °C (CCl_4-Dry Ice bath). The mixture was stirred at −23 °C for 2 h and neutralized with sat. sodium hydrogencarbonate aq solution (1 ml) at −23 °C. Concentration under reduced pressure gave a solid material which was charged on TLC plate with the aid of a solvent mixture of dichloromethane-methanol (10:1). Development with the same solvent mixture afforded **12** (45 mg, 56% yield). R_f=0.27 (CH_2Cl_2-MeOH 10:1). ^{1}H NMR ($CDCl_3$) δ=2.92 (dd, J=1.97 and 5.27 Hz, 2H), 3.21 (s, 3H), 4.87 (s, 1H), 5.28 (br, 2H), 9.67 (t, J=2.0 Hz, 1H). MS m/z (rel intensity) 171 (M^+, 8), 143 (9), 140 (M^+—OMe, 12), 129 (19), 128 (35), 115 (30), 112 (27), 111 (20), 101 (37), 100 (47), 83 (7), 71 (10), 70 (16), 69 (31), 68 (57), 59 (6), 58 (4), 57 (9), 55 (5), 44 (6), 43 (42). Found: m/z 171.0552. Calcd for $C_7H_9NO_4$: M^+ 171.0530.

2,2-Diethoxy-3-butynenitrile (13). Tin(II) chloride (0.162 g, 0.85 mmol) was added to a mixture of 3,3,3-triethoxypropyne (1.72 g, 10 mmol) and trimethylsilyl cyanide (1.50 ml, 11.2 mmol) at 0 °C under a nitrogen atmosphere, and the whole was stirred at room temperature for 30 min before dilution with ether (20 ml). The mixture was washed with brine, dried over magnesium sulfate and concentrated. Distillation gave **13** (1.08 g, 71% yield). Bp 75—80 °C (bath temperature)/5 Torr. ^{1}H NMR ($CDCl_3$) δ=1.30 (t, J=7.5 Hz, 6H), 2.80 (s, 1H), 3.80 (q, J=7.5 Hz, 4H). IR (neat) 3300, 3000, 2960, 2920, 2250, 2140, 1485, 1445, 1400, 1180, 1120, 1105, 1085, 1050, 885, 680 cm^{-1}. MS m/z (rel intensity) 108 (M^+—OEt, 72), 80 (100), 53 (65), 45 (15). Found: C, 62.41; H, 7.29; N, 9.06%. Calcd for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.14%.

***t*-Butyl 3-Amino-4,4-diethoxy-2-hexen-5-ynoate (14).** Magnesium amide base was prepared by addition of ethylmagnesium bromide (2.0 M ethereal solution, 10 ml, 20 mmol) to diisopropylamine (5.6 ml, 40 mmol) in ether (15 ml) and aged at 0 °C for 1.5 h. To this base solution *t*-butyl acetate (1.30 ml, 20 mmol) was added drop by drop over 5 min, and the mixture was stirred at 0 °C for 30 min. An ethereal solution (15 ml) of **13** (0.77 g, 5.0 mmol) was added over a period of 5 min, and the reaction mixture was stirred for 30 min. Quenching with sat. ammonium chloride aq solution (20 ml), extraction with ether (30 ml×3), washing the ethereal extract with brine, drying over magnesium sulfate, concentration, followed by distillation, gave **14** (1.14 g, 85% yield) as a pale yellow oil. Bp 115—120 °C (bath temperature)/0.15 Torr. ^{1}H NMR ($CDCl_3$) δ=1.23 (t, J=7.5 Hz, 6H), 1.48 (s, 9H), 2.60 (s, 1H), 3.63 (q, J=7.5 Hz, 4H), 5.05 (s, 1H), 6.45 (br, 2H, NH_2). IR (neat) 3525, 3360, 3300, 3000, 2950, 2910, 2130, 1675, 1625, 1555, 1455, 1395, 1370, 1290, 1255, 1155, 1130, 1100, 1080, 1050, 980, 805, 670 cm^{-1}. MS m/z (rel intensity) 269 (M^+, 3), 225 (19), 224 (23), 196 (15), 170 (11), 169 (100), 168 (27), 140 (43), 127 (34), 53 (26), 51 (16), 44 (19), 43 (17), 41 (37). Found: m/z 269.1616. Calcd for $C_{14}H_{23}NO_4$: M^+ 269.1625.

Hexacarbonyl(*t*-butyl 3-amino-4,4-diethoxy-2-hexen-5-ynoate)dicobalt (15). A pentane (50 ml) solution of **14** (0.84 g, 3.1 mmol) was added to a pentane (20 ml) solution of octacarbonyldicobalt(0) (1.06 g, 3.1 mmol) at 0 °C. The reaction mixture was warmed to room temperature over a period of 1 h, and the solvent was evaporated at ambient temperature by passing nitrogen gas. The residue was purified by column chromatography on silica gel to give **15** (1.33 g, 81% yield) as a red viscous oil. R_f=0.47 (hexane-ethyl acetate 5:1). ^{1}H NMR ($CDCl_3$) δ=1.21 (t, J=7.5 Hz, 6H), 1.45 (s, 9H), 3.63 (q, J=7.5 Hz, 4H), 4.88 (s, 1H), 6.13 (s, 1H). IR (neat) 3525, 3350, 3100, 3000, 2950, 2900, 2110, 2070, 2040, 1670, 1620, 1545, 1500, 1455, 1390, 1365, 1285, 1255, 1155, 1120, 1090, 1050, 980, 920, 805, 635, 580, 520, 500, 450 cm^{-1}. MS m/z (rel intensity) 527 (M^+—CO, 2), 499 (3), 471 (4), 443 (3), 415 (6), 387 (6), 359 (2), 343 (3), 331 (4), 225 (4), 224 (3), 169 (29), 149 (26), 140 (28) 122 (40), 59 (100). Found: C, 42.98; H, 4.29; N, 2.47%. Calcd for $C_{20}H_{23}NO_{10}Co_2$: C, 43.28; H, 4.40; N, 2.66%.

Hexacarbonyl(4-amino-5-ethoxy-5-ethynyl-2(5*H*)-furanone)-dicobalt (16). Trifluoroacetic acid (3.0 ml) was added to **15** (0.187 g, 0.34 mmol) at 0 °C and stirred for 30 min at 0 °C before evaporation of the trifluoroacetic acid in vacuo. Preparative TLC of the residue (hexane-ethyl acetate 1:1) gave **16** as red viscous oil (0.110 g, 77% yield). R_f=0.44 (hexane-ethyl acetate 1:1). ^{1}H NMR ($CDCl_3$) δ=1.20 (t, J=7.5 Hz, 3H), 3.40—3.80 (m, 2H), 4.90 (s, 1H), 5.00 (br, 2H), 6.08 (s, 1H). IR (neat) 3500, 3425 (sh), 3360, 3300 (sh), 3250 (sh), 3220, 3000, 2960, 2920, 2120, 2075, 2040, 1740, 1650, 1610, 1530, 1395, 1280, 1210, 1130, 1035, 985, 925, 800, 750, 630, 610, 520, 500, 450 cm^{-1}. MS m/z (rel intensity) 425 (M^+—CO, 2), 397 (4), 369 (3), 341 (7), 313 (5), 286 (6), 167 (8), 149 (7), 125 (6), 103 (5), 96 (5), 75 (4), 73 (5), 70 (5), 69 (6), 61 (6), 46 (21), 45 (51), 44 (11), 43 (23), 31 (58), 28 (100). Found: C, 37.18; H, 2.03; N, 2.89%. Calcd for $C_{14}H_9O_9Co_2N$: C, 37.10; H, 2.00; N, 3.09%.

4-Amino-5-ethoxy-5-ethynyl-2(5*H*)-furanone (17). Cerium-(IV) ammonium nitrate (0.68 g) was added portionwise to an acetone (5.0 ml) solution of **16** (47 mg, 0.11 mmol) at −78 °C under an argon atmosphere, and the reaction mixture was stirred at −78 °C for 2 h. The solvent was evaporated in vacuo, and the residue was treated with ethyl acetate (30 ml) and water (30 ml). Separation of the organic extract, drying the organic layer over sodium sulfate, concentration, followed by preparative TLC (hexane-ethyl acetate 1:1) gave

17 (15 mg, 83% yield). Mp 113—114 °C. R_f=0.30 (hexane-ethyl acetate 1 : 1) gave **17** (15 mg, 83% yield). Mp 113—114 °C, R_f=0.30 (hexane-ethyl acetate 1 : 1). ^{1}H NMR ($CDCl_3$) δ=1.27 (t, J=7.5 Hz, 3 H), 2.73 (s, 1H), 3.65—4.05 (m, 2H), 4.85 (s, 1H), 4.95 (br, 2H, NH_2). IR (KBr) 3420, 3350, 3300, 3275, 3220, 3000, 2925, 2130, 1735, 1660, 1610, 1490, 1410, 1400, 1280, 1210, 1130, 1100, 1040, 980, 920, 890, 790, 700, 610, 590 cm^{-1}. MS m/z (rel intensity) 167 (M^+, 13), 123 (28), 122 (98), 95 (15), 94 (12), 71 (17), 69 (58), 68 (21), 53 (38), 51 (24), 44 (26), 41 (75). Found: m/z 167.0580. Calcd for $C_8H_9NO_3$: M^+ 167.0581.

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17) The in vitro test was carried out by Ms. Kaoru Yamada of our Institute. We are indebted to her greatly.

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