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Ring Transformation of 4-Acylmethyl-2-chloro-4-hydroxy-2-cyclobutenone to γ-Acylmethylenetetronate by Thermal Rearrangement: New Synthetic Aspect of Squaric Acid as a C_4-Synthon

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Abstract: Title cyclobutenones prepared from the $TiCl_4$-catalyzed addition of a silyl enol ether to squaric acid dichloride and ester chloride were subjected to thermolysis (reflux in an aromatic solvent), and γ-acylmethylenetetronates were obtained stereoselectively with (*Z*)-geometry *via* an α,β-unsaturated chloroketene intermediate. The mechanism, application of this novel rearrangement to synthesis of basidalin and related photolysis were described.

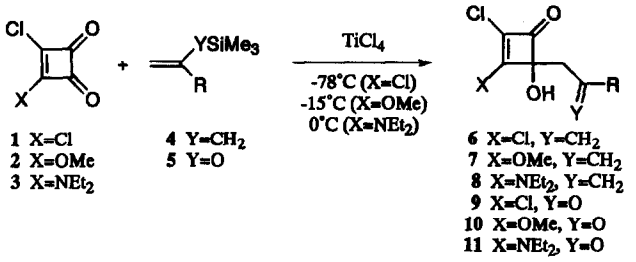
INTRODUCTION

Building block methodologies have provided a viable solution for the assembly of highly functionalized molecules that would require lengthy steps using other methods. In this respect, cyclobutenones, especially squaric acid derivatives have recently been utilized as C_4-synthon for highly substituted aromatic systems.[1] While squaric acid itself has been studied theoretically and applied as a key component of advanced materials,[2] in the synthetic point of view, it also provides a wide variety of cyclobutenediones and cyclobutenones having multiple substitution patterns by virtue of its useful multifunctionality.[3] Hopefully, the modified cyclobutenone rings have many possibilities to be transformed to other ring systems, for example, *via* an unsaturated ketene intermediate.[4] In our laboratory the new method for carbon-carbon bond formation on the cyclobutenedione ring was developed using unsaturated organosilanes.[5] The resulted derivatives were further utilized for the conversion to other cyclic compounds such as tetronates.[6] We now wish to report the detailed study along this line: first, known intramolecular [2+2]cycloaddition of squaric acid chlorides-allylsilane adducts **6**, **7**, and then, thermal rearrangement of squaric acid chlorides-silyl enol ether adducts **9**, **10** to tetronates together with related photochemical rearrangement, and finally, the total synthesis of natural product, basidalin, as an application of this novel ring transformation.

RESULTS AND DISCUSSION

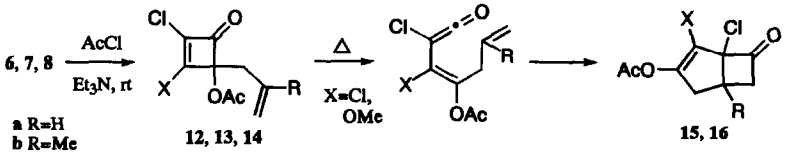
The ring transformation starts from the reaction of squaric acid families, dichloride **1** (3,4-dichloro-3-cyclobutene-1,2-dione), ester chloride **2** (3-chloro-4-methoxy-3-cyclobutene-1,2-dione), and amide chloride **3**

(3-chloro-4-diethylamino-3-cyclobutene-1,2-dione) with unsaturated organosilanes.[5a,b] Thus, $TiCl_4$-catalyzed addition of allylsilanes **4** and silyl enol ethers **5** to these chlorides **1**, **2** and **3** proceeded smoothly at -78 °C, -15 °C and 0 °C, respectively, to give 4-allyl- and 4-acylmethyl-4-hydroxycyclobutenones **6-11** (Scheme 1).



Scheme 1

Cyclobutenones undergo thermal ring-opening to α,β-unsaturated ketenes with high torquoselectivity.[7] Then the ring transformation is achieved by efficient trapping of these intermediates. When an allylic group lies at C_4 in the ring, facile intramolecular [2+2]cycloaddition gives rise to bicyclo[3.2.0]heptenones *via* the preferred inward rotation of the substituent, as demonstrated in the Moore's work.[8] In our case, the chloroketenes from squaric acid dichloride-allylsilane adducts **6a**, **b** were so reactive that the expected products were obtained more easily in higher yields than in the reported cases;[8] thermolysis of *O*-acetylated cyclobutenones **12a**, **b** in refluxing xylene for 1 h afforded the bicyclo[3.2.0]heptenones **15a**, **b** in more than 90 % yield (Scheme 2). Here, acylation of the 4-hydroxyl group was requisite since this reaction failed in an unprotected form (*i.e.*, **6**), which may cause decomposition of the product. Also protection with a trimethylsilyl group was not successful for the rearrangement. The structure of **15a** was assigned on the basis of following spectral data. In addition to the satisfactory MS measurement, the IR spectrum showed an absorption due to cyclobutanone at 1790 cm^{-1}, and the ^1H NMR spectrum indicated the presence of a couple of unequivalent methylene protons (δ 2.76 and 3.10, and 3.29 and 3.52 ppm) and a bridgehead proton (δ 3.02 ppm). The ^{13}C NMR signals were compatible with the assigned structure. In a similar fashion, the 3-methoxy-4-acetoxycyclobutenones **13a**, **b** were transformed in refluxing toluene to **16a**, **b** also in good yields. While the reaction of **13** (C_3-OMe) occurred at lower temperature than that of **12** (C_3-Cl), **14** (C_3-NEt_2) was found to be intact even at higher temperature (reflux in mesitylene) as shown in Table 1. These facts indicate that the above ring-opening reactivity depends on a C_3-substituent, although further studies are awaited for the reasonable explanation. Previously, it has been established that the electrocyclic ring opening of cyclobutene is influenced to great extent by a C_4-substituent.[7]



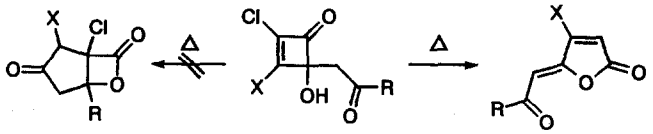
Scheme 2

Table 1. Rearrangement of 4-Allyl-4-acetoxycyclobutenones **12**, **13**, **14** to Bicyclo[3.2.0]heptenones **15**, **16**

entry	X	R	cyclobutenone (Yield %)	solvent	time (h)	bicycloheptenone (Yield %)
1	Cl	H	**12a** (61)	xylene	1	**15a** (91)
2	Cl	Me	**12b** (59)	xylene	1	**15b** (90)
3	OMe	H	**13a** (67)	toluene	1	**16a** (93)
4	OMe	Me	**13b** (85)	toluene	1	**16b** (84)
5	NEt_2	H	**14a** (67)	mesitylene	3	no reaction

In connection with the ring transformation described above, the thermal behavior of 4-acylmethyl-substituted cyclobutenones **9**-**11** next attracted our attention. As depicted in Scheme 3, a cyclopentane-fused β-lactone **17** (or its decarboxylated product)[9] was expected to be produced *via* the cycloaddition reaction similar to the transformation of **12** to **15**. In this regard, the thermal rearrangement of 4-phenacylcyclobutenone **9** occurred smoothly in refluxing benzene for 2 h, but unexpected γ-phenacylidene-2(5*H*)-furanone **18** was obtained in 37 % yield after chromatographic separation. The structure was elucidated by spectral inspections; the mass spectral and elemental analyses indicated loss of HCl from the molecule, and the IR absorptions at 1795 and 1661 cm^{-1} suggested the existence of a furanone moiety. The ^{13}C NMR signals appeared all at lower field (δ 106.3, 128.7, 129.3, 132.0, 134.3, 136.6, 138.1, 157.8, 163.4 and 189.3 ppm), showing all the carbons to be sp^2 hybridized. Particularly, the ^1H NMR spectrum revealed that two vinylic protons (δ 7.03 and 8.36 ppm) had a long-range coupling (J=0.6 Hz). The observed spectral patterns were closely related to those reported for a γ-methylenefuranone[10] and supported *Z*-stereochemistry at the acylmethylene moiety by the observed long-range coupling.[11] In the same manner the 3-methoxy-substituted analogue **10a** produced γ-phenacylidenetetronate **19a** upon heating in xylene for 2 h. Again, the spectral data of **19a** were consistent with the tetronate structure. In this case, the yield was low (15 %), probably because the liberated HCl damaged the product. To this end, the reaction was carried out in the presence of a base; pyridine was more effective than 4-diethylaminopyridine, triethylamine and *N*,*N*-diethylaniline and the yield was raised to 64 %. The other γ-acylmethylenetetronates **19b-i** were thus produced in 54-63 % yields under these conditions from the adducts **10b-i** of ester chloride **2** which were obtained from the reaction with silyl enol ethers **5b-h** of alkyl, alkenyl, aryl and trimethylsilyl ketones and a silyl ketene acetal **5i**. These results are summarized in Table 2. In contrast to the above successful results for **9** and **10**, the attempted reaction using the 3-diethylamino-substituted analogue **11** did not afford the corresponding aminofuranone but resulted in the formation of a complex mixture; disubstitution on the amino group might sterically suppress the smooth ring-opening reactivity (for an unsubstituted case, see the basidalin synthesis described below).

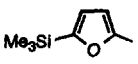
The other 4-acylmethylcyclobutenones **20** having substituents on their acylmethyl side chain showed different chemical behavior. These were prepared by the reaction of ester chloride **2** with a methyl-substituted silyl enol ether, silyl ketene acetal, and dimethyl-substituted silyl ketene acetal. When **20a-c** were heated in xylene, thermal rearrangement occurred without liberation of HCl, affording 2(3*H*)-furanones **21a-c** in good yields. Here, relatively longer reaction time was required than that for **10** (Scheme 4). The 2(3*H*)-furanone structures were determined as follows. Primarily, their mass spectral and elemental analyses indicated the



17 9 X=Cl, R=Ph 10 X=OMe 18 X=Cl, R=Ph 19 X=OMe

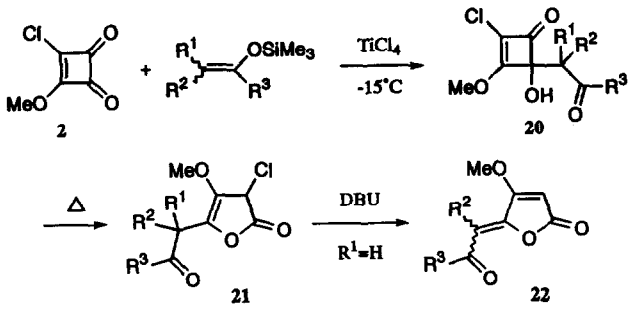
Scheme 3

Table 2. Formation of Tetronates **19** from Ester Chloride **2** and Silyl Enol Ethers **5**

entry	R	**5**	**10** (Yield %)	**19** (Yield %)	mp (°C)
1	Ph	**5a**	**10a** (80)	**19a** (64)	159-162
2	CH_3	**5b**	**10b** (72)	**19b** (56)	80-83
3	$CH_3(CH_2)_4$-	**5c**	**10c** (61)	**19c** (63)	oil
4		**5d**	**10d** (45)	**19d** (61)	74-78
5		**5e**	**10e** (73)	**19e** (61)	77-80
6		**5f**	**10f** (82)	**19f** (54)	131-133
7		**5g**	**10g** (66)	**19g** (61)	84-88
8	Me_3Si	**5h**	**10h** (80)	**19h** (60)	77-80
9	PhO	**5i**	**10i** (83)	**19i** (61)	136-139

presence of a chlorine atom. The IR spectra showed a non-conjugated carbonyl absorption near 1800 cm^{-1} and the ^1H NMR spectra of **21a, b** had two signals due to methine protons on the ring and side chain. Finally, **21a, b** were further converted to γ-acylmethylenetetronates **22a, b** by treatment with DBU in THF at ambient temperature. In these cases, corresponding tetronate **22a** was obtained as a pure *Z*-isomer in 95 % yield and **22b** as a 3:1 mixture of *Z*- and *E*-isomers in 72 % yield (Table 3). The stereochemistry was deduced from the relative chemical shifts of the methyl protons on the γ-methylene moiety in the ^1H NMR of **22b**; the methyl proton of the *E*-isomer (δ 2.21 ppm) was more deshielded by virtue of its *cis*-relationship to the butenolide oxygen than that of the *Z*-isomer (δ 2.12 ppm).[12] On the analogy of **19a** and **22b**, **22a** is believed to have *Z*-stereochemistry. The observed stereorandomness in the reaction of **21b** to **22b** was informative for the reaction pathway of the present ring transformation (*vide infra*).

Scheme 5 illustrates the plausible mechanisms for the stereoselective formation of the tetronate **19**. The 4-hydroxycyclobutenone **10** undergoes thermally allowed conrotatory electrocyclic ring-opening to generate a kinetically favored enol ketene **23** and a minor stereoisomer **24**, which are in equilibrium under thermal conditions. Although the torquoselectivity orients a hydroxyl group outwardly, the equilibrium allows the



Scheme 4

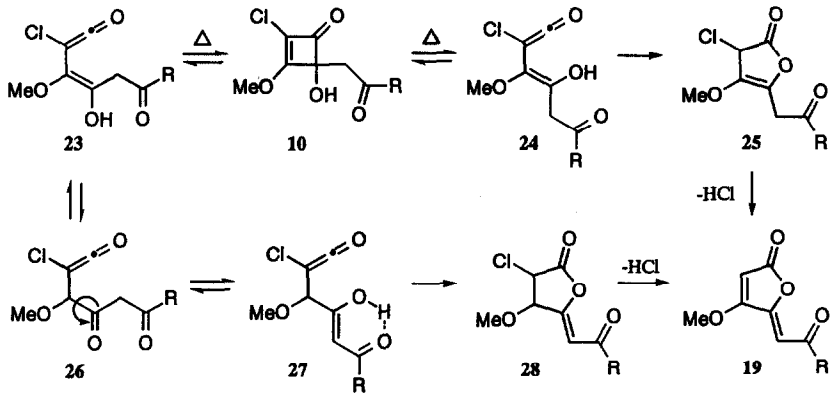
Table 3. Formation of 2(*3H*)-Furanones **21** and Tetronates **22** from Ester Chloride **2**

entry	R^1	R^2	R^3	**20** (Yield %)	reflux time (h)	**21** (Yield %)	**22** (Yield %)
1	H	Me	Ph	**20a** (49)	2	**21a** (77)	**22a** (95)
2	H	Me	OEt	**20b** (64)	6	**21b** (86)	**22b** (72)
3	Me	Me	OMe	**20c** (76)	12	**21c** (76)	-

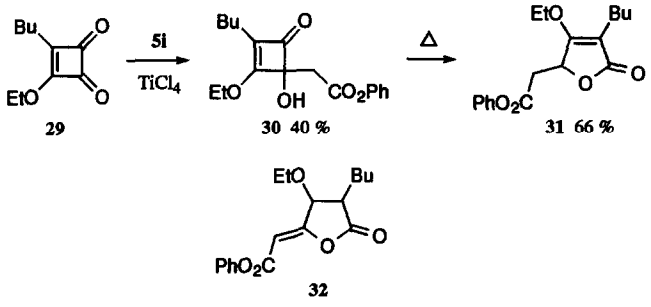
reaction to shift to 2(*3H*)-furanone **25** as a result of lactonizaton of **24**. Finally, stereoselective dehydrochlorination of **25** produces thermodynamically more stable tetronate **19**.[13] This stereoselectivity might be explained by the other mechanism. Isomerization of the enol moiety in the ketene intermediate **23** leads to **27** *via* a 1,3-diketone **26** and following recyclization gives a γ-lactone **28**.[14] Subsequent dehydrochlorination affords the tetronate **19**, in which the stereoselectivity originates from intramolecular hydrogen-bonding in **27**. However, involvement of **27** is incompatible with the formation of a *Z*- and *E*-isomeric mixture from **21b**. Furthermore, the latter mechanism was not supported by the reaction using **30** (Scheme 6). Because a chlorine atom is absent in this molecule, a primary product **32** should be formed. Actually, the product derived therefrom was 2(*5H*)-furanone **31**. Consequently, the reaction pathway *via* **24→25→19** is likely for the ring transformation of squaric acid ester chloride-silyl enol ether adducts to tetronates.

Associated with the thermolysis, photolysis of a 4-acylmethyl-substituted cyclobutenone was also undertaken (Scheme 7). The photorearrangement of cyclobutenone **10i** was carried out in THF at ambient temperature using a high-pressure mercury lamp with a quartz immersion well. The reaction was completed within 5 h to give the α-chlorotetronate **33** in 48 % yield, where 1,3-hydrogen shift took place in preference to dehydrochlorination of the 2(*3H*)-furanone intermediate **25i**. The structural determination was based on the spectral inspections: MS M^+ peak at m/z 282, IR absorption due to a conjugated carbonyl group at 1771 cm^{-1}, and ^1H NMR ABX signals at δ 2.91, 3.16 and 5.22 ppm. Thus, photolysis of **10i** provides a method for construction of chlorinated tetronate derivatives.[15]

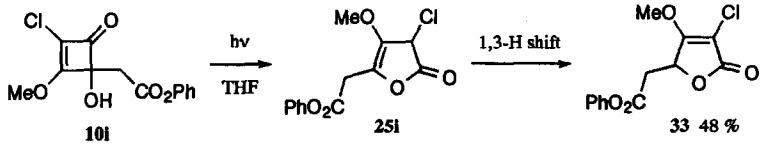
A wide variety of compounds containing the 5-ylidene-2(*5H*)-furanone structure are found in nature,[16] and some of them display useful biological properties (*e.g.* protoanemonine, fimbrolide, agglomerin and rubrolide).[17] Thus, new synthetic methods to construct this ring system have drawn considerable attention. We have now applied the present ring transformation to the total synthesis of basidalin **41**, isolated from *Leucoagaricus*



Scheme 5



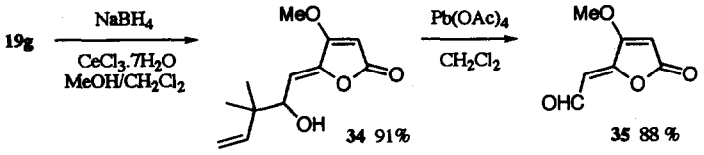
Scheme 6



Scheme 7

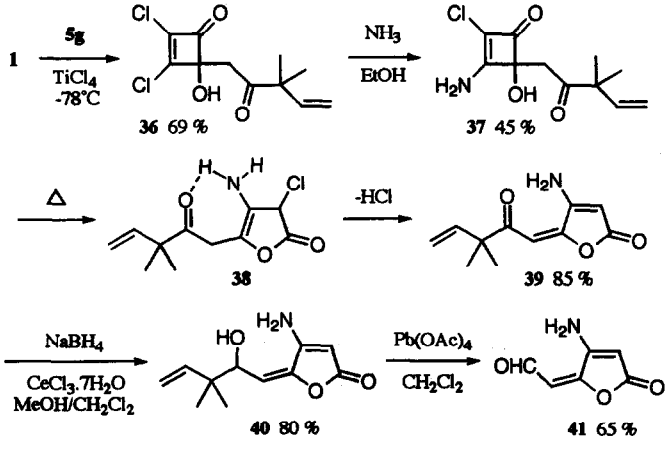
naucina, a simple enamine derivative of tetronic acid (both *E*- and *Z*-forms are known), exhibiting antibacterial and antitumor activities.[18] At the outset, synthesis of the related compound **35** (an amino group is replaced by a methoxy group) was attempted for the aim to find out an efficient method for introducing a γ-formylmethylene moiety. At first straightforward addition of a silyl enol ether of acetaldehyde to ester chloride **2** was envisaged but in vain because of polymerization of the reagent. Such polymerization was depressed by using an analogous silane **5h**, however desilylation for both products **10h** and **19h** under various conditions (*e.g.* tetrabutylammonium fluoride / aq. THF, K_2CO_3 / MeOH and tetrabutylammonium hydroxide / CH_3CN) failed. These discouragements were surmounted by employing an alternative silane **5g**. (*Z*)-γ-Acylmethylenetetronate **19g**, obtainable from **5g** as indicated in entry 7 (Table 2), was followed by reduction/oxidation procedures;[19] selective reduction of **19g** to alcohol **34** with $NaBH_4/CeCl_3$ and subsequent oxidation of **34** with $Pb(OAc)_4$

gave rise to desired **35** fruitfully. The structure of **35** was clarified by the IR absorptions at 1820 and 1674 cm^{-1}, and the ^1H NMR signals at δ 5.45 (d, *J*=0.6 Hz), 5.76 (dd, *J*=0.6, 8 Hz) and 10.17 (d, *J*=8 Hz) ppm. The coupling constant of vinyl protons (*J*=0.6 Hz) confirmed the *Z*-stereochemistry of **35** (Scheme 8).



Scheme 8

With these results in hand, the total synthesis of basidalin was carried out as outlined in Scheme 9. In the beginning, required 4-hydroxycyclobutenone **36** was obtained by the $TiCl_4$-catalyzed addition of the silane **5g** to squaric acid dichloride **1**. This was converted to amide chloride **37** with ethanolic NH_3. Thus prepared aminocyclobutenone **37** was transformed to a (*E*)-5-acylmethylene-4-amino-2(5*H*)-furanone **39** upon heating in xylene for 2 h in the presence of pyridine. The *E*-configuration of the product was indicated by the long-range coupling (*J*=1.4 Hz) in the ^1H NMR spectrum. The observed stereospecific dehydrochlorination to only *E*-isomer deserves to be mentioned; in contrast to the formation of the *Z*-isomer **19g** (*vide supra*), the *E*-isomer **39** was formed as a result of the different substitution at C3 (*i.e.*, MeO *vs* NH_2). This is ascribable to hydrogen-bonding between amino and carbonyl groups prior to 1,4-elimination as shown in the 2(3*H*)-furanone intermediate **38**. This phenomenon seems to be, in some sense, mimic to the biogenetic route of naturally occurring 5-ylidene-2(5*H*)-furanones, in which the covalent bond plays a role to fix the *E*-geometry.[20] Furthermore it is of interest that, in spite of lack of ring-opening reactivity of 3-diethylaminocyclobutenone **8** (entry 5 in Table 1), the rearrangement of **37** having an amino function was accomplished (85 % yield). Finally, **39** was subjected to the reduction/oxidation procedures as employed for **19g**, affording (*E*)-basidalin (**41**). Synthesized basidalin showed the physical and spectral properties identical with those reported for the natural product.[18]



Scheme 9

CONCLUSION

Thermal rearrangement of 4-acylmethyl-2-chloro-4-hydroxy-2-cyclobutenones prepared from squaric acid ester chloride and a silyl enol ether provided the novel entry to γ-acylmethylenetetronates in which an acyl group was introduced stereoselectively (*Z*-geometry). As for C3-substituent on the cyclobutene ring, replacement of a methoxy group with an amino group reversed the stereochemistry of the product (*E*-geometry). This merit of preparation overcomes the nonstereoselective condensation reaction of maleic anhydride with an ylide,[12] and was successfully applied to the total synthesis of (*E*)-basidalin. In contrast, photolysis of the 4-acylmethyl-2-chloro-4-hydroxycyclobutenone produced the γ-acylmethyl-α-chlorotetoronate.

EXPERIMENTAL

General. IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Varian GEMINI-200 spectrometer at 200 and 50 MHz, respectively, for samples in $CDCl_3$ or DMSO-d_6 with $SiMe_4$ as internal standard. Mass spectra were recorded on a JEOL JMS-AX 505 HA mass spectrometer. Flash chromatography was performed with a silica gel column (Fuji-Davison BW-300) eluted with mixed solvents [hexane (H), ethyl acetate (A)]. Microanalyses were performed with a Perkin-Elmer 2400S CHN elemental analyzer. THF was freshly distilled over Na and benzophenone. Benzene, toluene, xylene and mesitylene were dried over Na. Dichloromethane was dried over $CaCl_2$, distilled, and stored over 4Å molecular sieves. Squaric acid was supplied by Kyowa Hakko Kogyo Co. Ltd.. Its derivatives, dichloride **1** and methyl ester chloride **2**, were prepared by our methods[5a,b] and diethylamide chloride **3** was prepared by the established procedure.[21] The cyclobutenones **6-9** and **11** were obtained according to the methods described in the previous papers.[5a,b]

Synthesis of 4-Hydroxycyclobutenones 10. General Procedure. To a solution of **1** (0.5 mmol) and **5** (1 mmol) in dry dichlroromethane (2 mL) was added $TiCl_4$ (0.06 mL, 0.5 mmol) by syringe at -78°C under exclusion of moisture, and the solution was stirred for 10 min. The reaction mixture was poured into cold water, extracted with dichloromethane, dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue with the solvent specified gave the product. The yields are listed in Table 2. The compound **10a** was reported in the previous paper.[5b]

2-Chloro-4-hydroxy-3-methoxy-4-(2-oxopropyl)-2-cyclobutenone (10b). *oil* (Elution H-A 3:1); IR (neat) 3399, 1782, 1713, 1613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (3 H, s), 2.95 and 3.05 (each 1 H, d, *J*=17.4 Hz), 4.35 (3 H, s), 4.98 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 31.2, 44.0, 61.2, 87.5, 105.5, 182.7, 185.8, 208.4; MS (EI) m/z (rel. intensity) 204 (M^+, 43), 168 (43), 161 (100), 153 (59); Anal Calcd for $C_8H_9ClO_4$: C, 46.96; H, 4.43. Found: C, 46.83; H, 4.66.

2-Chloro-4-hydroxy-3-methoxy-4-(2-oxoheptyl)-2-cyclobutenone (10c). *oil* (Elution H-A 3:1); IR (neat) 3395, 2957, 1784, 1711, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (3 H, t, *J*=6.6 Hz), 1.22-1.59 (6 H, m), 2.52 (2 H, m), 2.90 and 3.00 (each 1 H, d, *J* =17.0 Hz), 4.35 (3 H, s), 4.98 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 23.0, 31.1, 42.9, 44.1, 61.2, 87.7, 105.0, 182.6, 185.7, 211.2; MS (EI) m/z (rel. intensity) 260 (M^+, 11), 225 (14), 203 (21), 189 (30), 168 (71), 161 (91), 153 (100); Anal Calcd for $C_{12}H_{17}ClO_4$: C, 55.28; H, 6.57. Found: C, 55.20; H, 6.64.

4-[(1-Adamantyl)carbonylmethyl]-2-chloro-4-hydroxy-3-methoxy-2-cyclobutenone (10d). *oil* (Elution H-A 3:1); IR (neat) 3399, 2908, 1786, 1700, 1616 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64-2.07 (15 H, m), 2.91 and 3.04 (each 1 H, d, *J*=17.4 Hz), 4.33 (3 H, s), 5.41 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 27.7, 36.3, 36.5, 37.6, 47.4, 61.1, 88.2, 104.8, 182.7, 185.6, 216.3; MS (EI) m/z (rel. intensity) (no molecular ion), 288 (79), 260 (91), 161 (57), 107 (100); Anal Calcd for $C_{17}H_{21}ClO_4$: C, 62.86; H, 6.52. Found: C, 62.73; H, 6.64.

2-Chloro-4-hydroxy-3-methoxy-4-(4-methyl-2-oxo-3-pentenyl)-2-cyclobutenone (10e). *oil* (Elution H-A 3:1); IR (neat) 3393, 2955, 1786, 1680, 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (3 H, d, *J*=1.2 Hz), 2.19 (3 H, d, *J*=1.0 Hz), 2.90 and 3.00 (each 1 H, d, *J* =17.0 Hz), 4.33 (3 H, s), 5.49 (1 H, br s), 6.08 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 21.4, 28.1, 43.7, 61.1, 88.3, 104.7, 123.6, 160.9, 182.9, 185.8, 199.5; MS (EI) m/z (rel. intensity) 244 (M^+, 21), 229 (43), 212 (93), 208 (63), 193 (43), 161 (100); Anal Calcd for $C_{11}H_{13}ClO_4$: C, 54.00; H, 5.36. Found: C, 53.75; H, 5.51.

2-Chloro-4-hydroxy-3-methoxy-4-[(5-trimethylsilyl-2-furoyl)methyl]-2-cyclobutenone (10f). *oil* (Elution H-A 3:1); IR (neat) 3389, 2959, 1786, 1667, 1615, 1252, 854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33 (9 H, s), 3.37 and 3.46 (each 1 H, d, *J* =16.2 Hz), 4.35 (3 H, s), 5.22 (1 H, br s), 6.74 (1 H, d, *J*=3.7 Hz); ^{13}C NMR ($CDCl_3$) δ -2.0, 39.2, 61.2, 88.1, 105.0, 119.4, 122.1, 155.7, 169.1, 182.8, 185.4, 187.5; MS (EI) m/z (rel. intensity) 328 (M^+, 52), 313 (77), 292 (65), 284 (36), 277 (46), 167 (100); Anal Calcd for $C_{14}H_{17}ClO_5Si$: C, 51.14; H, 5.21. Found: C, 51.09; H, 5.25.

2-Chloro-4-(3,3-dimethyl-2-oxo-4-pentenyl)-4-hydroxy-3-methoxy-2-cyclobutenone (10g). *oil* (Elution H-A 4:1); IR (neat) 3407, 1788, 1711, 1613 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 and 1.25 (each 3 H, s), 2.93 and 3.05 (each 1 H, d, *J* =17.6 Hz), 4.33 (3 H, s), 5.18 (1 H, br s), 5.21 (1 H, dd, *J*=17.2, 0.8 Hz), 5.23 (1 H, dd, *J*=11.0, 0.8 Hz), 5.86 (1 H, dd, *J*=17.2, 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 23.0, 23.1, 38.1, 51.7, 61.1, 88.1, 104.9, 116.2, 141.3, 182.5, 185.4, 213.6; MS (EI) m/z (rel. intensity) (no molecular ion) 243 (4), 189 (4), 161 (61), 153 (37), 147 (23), 133 (13), 119 (8), 98 (100); (CI) m/z (rel. intensity) 259 (MH^+, 100), 223 (41); Anal Calcd for $C_{12}H_{15}ClO_4$: C, 55.71; H, 5.84. Found: C, 55.85; H, 5.70.

2-Chloro-4-hydroxy-3-methoxy-4-[(trimethylsilyl)carbonylmethyl]-2-cyclobutenone (10h). *oil* (Elution H-A 4:1); IR (neat) 3397, 1784, 1613, 1252, 849 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (9 H, s), 3.04 and 3.18 (each 1 H, d, *J* =17.4 Hz), 4.33 (3 H, s), 5.02 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ -3.6, 46.8, 61.1, 88.4, 112.7, 182.6, 185.6, 250.1; MS (EI) m/z (rel. intensity) (no molecular ion) 234 (7), 211 (5), 199 (3), 183 (5), 144 (3), 73 (100); (CI) m/z (rel. intensity) 263 (MH^+, 100), 227 (48); Anal Calcd for $C_{10}H_{15}ClO_4Si$: C, 45.72; H, 5.76. Found: C, 45.78; H, 5.70.

Phenyl (3-Chloro-1-hydroxy-2-methoxy-4-oxo-2-cyclobutenyl)acetate (10i). *oil* (Elution H-A 3:1); IR (neat) 3410, 1784, 1757, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.11 and 3.18 (each 1 H, d, *J* =14.0 Hz), 4.37 (3 H, s), 4.47 (1 H, br s), 7.01-7.43 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 37.1, 61.3, 87.2, 105.4, 121.7, 126.7, 129.9, 150.4, 169.3, 182.3, 185.4; MS (EI) m/z (rel. intensity) 282 (M^+, 10), 246 (9), 189 (13), 161 (54), 153 (100); Anal Calcd for $C_{13}H_{11}ClO_5$: C, 55.24; H, 3.92. Found: C, 55.17; H, 4.08.

Synthesis of Bicyclo[3.2.0]heptenones 15 and 16. General Procedure. Acetylation of **6**, **7** and **8** was performed as follows. To a solution of 4-allyl-4-hydroxycyclobutenone (0.3 mmol) and acetyl chloride (47 mg, 0.6 mmol) in dry ether (2mL) was added triethylamine (61 mg, 0.6 mmol) by syringe. After being stirred overnight at ambient temperature, the reaction mixture was diluted with dichloromethane and washed with water. The organic layer was dried (Na_2SO_4) and evaporated to dryness. Flash chromatography of the residue (H-A 5:1) gave the product. The yields are listed in Table 1.

4-Acetoxy-2,3-dichloro-4-(2-propenyl)-2-cyclobutenone (12a). *oil* ; IR (neat) 1796, 1761, 1645, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (3 H, s), 2.72-2.79 (2 H, m), 5.13-5.26 (2 H, m), 5.58-5.80 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 20.9, 35.7, 96.3, 121.6, 129.3, 135.5, 165.3, 169.8, 182.7; MS (EI) m/z (rel. intensity) (no molecular ion), 198 (100), 164 (46), 157 (45); (CI) m/z 235 (MH^+, 100); Anal Calcd for $C_9H_8Cl_2O_3$: C, 45.99; H, 3.43. Found: C, 45.76; H, 3.56.

4-Acetoxy-2,3-dichloro-4-(2-methyl-2-propenyl)-2-cyclobutenone (12b). *oil* ; IR (neat) 1796, 1759, 1649, 1589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73, (3 H, dd, *J*=1.4, 0.8 Hz), 2.09 (3 H, s), 2.67 and 2.82 (each 1 H, dd, *J*=14.4, 0.8 Hz), 4.87 and 4.98 (each 1 H, m); ^{13}C NMR ($CDCl_3$) δ 21.0, 23.5, 39.4, 96.5, 117.9, 135.4, 138.0, 165.5, 169.7, 182.6; MS (EI) m/z (rel. intensity) (no molecular ion), 206 (36), 191 (47), 171 (100); Anal Calcd for $C_{10}H_{10}Cl_2O_3$: C, 48.22; H, 4.05. Found: C, 48.25; H, 4.02.

4-Acetoxy-2-chloro-3-methoxy-4-(2-propenyl)-2-cyclobutenone (13a). *oil* ; IR (neat) 1796, 1750,

1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (3 H, s), 2.72-2.78 (2 H, m), 4.35 (3 H, s), 5.14-5.24 (2 H, m), 5.63-5.84 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 21.0, 35.5, 61.0, 92.6, 105.6, 120.5, 130.3, 169.7, 180.0, 182.4; MS (EI) m/z (rel. intensity) (no molecular ion), 188 (100), 173 (4), 160 (4), 153 (21); (CI) m/z 231 (MH^+, 100); Anal Calcd for $C_{10}H_{11}ClO_4$: C, 52.07; H, 4.81. Found: C, 52.04; H, 4.87.

4-Acetoxy-2-chloro-3-methoxy-4-(2-methyl-2-propenyl)-2-cyclobutenone (13b). *oil* ; IR (neat) 1796, 1755, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77, (3 H, dd, *J*=1.4, 1.0 Hz), 2.06 (3 H, s), 2.67 and 2.77 (each 1 H, dd, *J*=14.0, 0.8 Hz), 4.35 (3 H, s), 4.84 and 4.94 (each 1 H, m); ^{13}C NMR ($CDCl_3$) δ 21.1, 23.2, 39.1, 61.0, 92.9, 105.7, 116.9, 138.8, 169.7, 179.8, 182.5; MS (EI) m/z (rel. intensity) (no molecular ion), 202 (100), 187 (19), 167 (10), 161 (44); (CI) m/z 245 (MH^+, 100); Anal Calcd for $C_{11}H_{13}ClO_4$: C, 54.00; H, 5.36. Found: C, 53.97; H, 5.43.

4-Acetoxy-2-chloro-3-diethylamino-4-(2-propenyl)-2-cyclobutenone (14a). *crystals*, mp 65-66°C; IR (KBr) 1782, 1763, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (3 H, t, *J*=7.2 Hz), 1.29 (3 H, t, *J*=7.2 Hz), 2.06 (3 H, s), 2.55 and 2.98 (each 1 H, ddt, *J*=14.5, 7.8, 1.0 Hz), 3.39 (2 H, q, *J*=7.2 Hz), 3.60 and 3.63 (each 1 H, dq, *J*=8.4, 7.2 Hz), 5.11-5.23 (2 H, m), 5.60-5.81 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 13.6, 14.1, 21.4, 37.3, 43.2, 45.4, 92.3, 95.3, 120.0, 130.7, 167.3, 169.5, 179.3; MS (EI) m/z (rel. intensity) 271 (M^+, 26), 229 (100), 214 (39), 194 (82); (CI) m/z 231 (MH^+, 100); Anal Calcd for $C_{13}H_{18}ClNO_3$: C, 57.46; H, 6.62; N, 5.15. Found: C, 57.32; H, 6.75; N, 5.16.

Thermal rearrangement of **12** and **13** was performed as follows. A solution of **12** (or **13**) (0.45 mmol) in dry xylene (or in dry toluene) (15 mL) was refluxed for 1 h. The obtained colorless solution was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was chromatographed (H-A 5:1) to afford the product. The yields are listed in Table 1.

3-Acetoxy-1,2-dichlorobicyclo[3.2.0]hept-2-en-7-one (15a). *oil* ; IR (neat) 1790, 1779, 1651, 1186 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.26 (3 H, s), 2.76 (1 H, d, *J*=17.4 Hz), 3.02 (1 H, m), 3.10 (1 H, dd, *J*=17.4, 6.2 Hz), 3.29 (1 H, dd, *J*=17.4, 7.0 Hz), 3.52 (1 H, dd, *J*=17.4, 9.2 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 34.6, 35.9, 50.5, 84.5, 114.4, 150.3, 167.4, 196.1; MS (EI) m/z (rel. intensity) 234 (M^+, 6), 199 (27), 192 (100); Anal Calcd for $C_9H_8Cl_2O_3$: C, 45.99; H, 3.43. Found: C, 45.90; H, 3.52.

3-Acetoxy-1,2-dichloro-5-methylbicyclo[3.2.0]hept-2-en-7-one (15b). *oil* ; IR (neat) 1796, 1784, 1655, 1173 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (3 H, s), 2.25 (3 H, s), 2.94 (2 H, s), 3.02 (1 H, d, *J*=17.8 Hz), 3.18 (1 H, d, *J*=17.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.1, 38.7, 42.8, 56.9, 87.2, 115.1, 149.8, 167.5, 196.9; MS (EI) m/z (rel. intensity) (no molecular ion) 206 (41), 164 (100), 129 (19); Anal Calcd for $C_{10}H_{10}Cl_2O_3$: C, 48.22; H, 4.05. Found: C, 48.16; H, 4.11.

3-Acetoxy-1-chloro-2-methoxybicyclo[3.2.0]hept-2-en-7-one (16a). *oil* ; IR (neat) 1792, 1769, 1682, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3 H, s), 2.55 (1 H, d, *J*=16.4 Hz), 2.80 (1 H, m), 3.11 (1 H, dd, *J*=16.4, 7.4 Hz), 3.12 (1 H, dd, *J*=18.2, 6.8 Hz), 3.46 (1 H, dd, *J*=18.2, 9.6 Hz), 3.77 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 20.7, 32.7, 33.3, 50.6, 58.6, 82.6, 131.8, 137.4, 168.4, 197.7; MS (EI) m/z (rel. intensity) 230 (M^+, 2), 187 (60), 160 (80), 146 (100); Anal Calcd for $C_{10}H_{11}ClO_4$: C, 52.07; H, 4.81. Found: C, 51.91; H, 4.97.

3-Acetoxy-1-chloro-2-methoxy-5-methylbicyclo[3.2.0]hept-2-en-7-one (16b). *oil* ; IR (neat) 1794, 1767, 1686, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (3 H, s), 2.20 (3 H, s), 2.75 (2 H, s), 2.96 (1 H, d, *J*=17.6 Hz), 3.37 (1 H, d, *J*=17.6 Hz), 3.76 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 20.6, 20.7, 35.8, 40.6, 56.8, 58.5, 85.3, 131.5, 138.0, 168.4, 198.5; MS (EI) m/z (rel. intensity) 244 (M^+, 3), 210 (8), 201 (63), 173 (38), 159 (100); Anal Calcd for $C_{11}H_{13}ClO_4$: C, 54.00; H, 5.36. Found: C, 53.99; H, 5.37.

Synthesis of (*Z*)-4-Chloro-5-phenacylidene-2(*5H*)-furanone (18). A solution of **9** (191 mg, 0.70 mmol) in dry benzene (30 mL) was refluxed for 2 h. The resulting dark brown solution was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (H-A 10:1) to afford **18** (62 mg, 37 %) as yellow crystals: mp 97-100°C; IR (KBr) 1796,

1661, 1603, 986 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03 (1 H, d, *J*=0.8 Hz), 7.48-8.00 (5 H, m), 8.36 (1 H, d, *J*=0.8 Hz); ^{13}C NMR ($CDCl_3$) δ 106.3, 128.7, 129.3, 132.0, 134.3, 136.6, 138.1, 157.8, 163.4, 189.3; MS (EI) m/z (rel. intensity) 234 (M^+, 7), 206 (8), 157 (11), 105 (100); Anal Calcd for $C_{12}H_7ClO_3$: C, 61.43 ; H, 3.01. Found: C, 61.26 ; H, 3.28.

Synthesis of γ-Acylmethylenetetronates 19. General Procedure. A solution of **10** (0.3 mmol) and pyridine (26 mg, 0.33 mmol) in dry xylene (10 mL) was refluxed for 2 h. The resulting dark brown solution was cooled to ambient temperature and the solvent was removed under reduced pressure. The residue was purified by flash chromatography [H-A 3:1 except for **19h** (H-A 4:1)] to afford the product. The yield and physical data were listed in Table 2.

(*Z*)-4-Methoxy-5-phenacylidene-2(*5H*)-furanone (19a). IR (KBr) 1803, 1680, 1624, 961, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03 (3 H, s), 5.44 (1 H, d, *J*=0.6 Hz), 6.55 (1 H, d, *J*=0.6 Hz), 7.44-8.00 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 59.9, 91.4, 100.2, 128.9, 129.0, 133.8, 138.0, 151.0, 167.6, 171.0, 188.5; MS (EI) m/z (rel. intensity) 230 (M^+, 10), 170 (36), 105 (100); Anal Calcd for $C_{13}H_{10}O_4$: C, 67.82 ; H, 4.38. Found: C, 67.57 ; H, 4.43.

(*Z*)-5-(Acetylmethylene)-4-methoxy-2(*5H*)-furanone (19b). IR (KBr) 1796, 1769, 1665, 1645, 1613, 976, 847 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.53 (3 H, s), 4.02 (3 H, s), 5.43 (1 H, d, *J*=0.6 Hz), 6.75 (1 H, d, *J*=0.6 Hz); ^{13}C NMR ($CDCl_3$) δ 31.2, 60.0, 91.0, 105.3, 150.8, 166.8, 171.4, 196.8; MS (EI) m/z (rel. intensity) 168 (M^+, 26), 153 (100), 137 (84), 125 (42), 111 (39); Anal Calcd for $C_8H_8O_4$: C, 57.14 ; H, 4.80. Found: C, 57.03 ; H, 4.91.

(*Z*)-5-(Hexanoylmethylene)-4-methoxy-2(*5H*)-furanone (19c). IR (neat) 2934, 1796, 1680, 1624, 961, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (3 H, t, *J*=6.6 Hz), 1.32-1.63 (6 H, m), 2.84 (2 H, t, *J*=7.2 Hz), 4.01 (3 H, s), 5.42 (1 H, d, *J*=0.8 Hz), 5.75 (1 H, d, *J*=0.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.5, 23.5, 31.3, 43.5, 59.9, 90.9, 104.8, 150.1, 167.0, 171.5, 199.4; MS (EI) m/z (rel. intensity) 224 (M^+, 11), 168 (79), 153 (100), 125 (84), 111 (35); Anal Calcd for $C_{12}H_{16}O_4$: C, 64.27 ; H, 7.19. Found: C, 64.26 ; H, 7.19.

(*Z*)-5-[(1-Adamantyl)carbonylmethylene]-4-methoxy-2(*5H*)-furanone (19d). IR (KBr) 2903, 1802, 1701, 1680, 1628, 959, 829 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73-2.08 (15 H, m), 4.00 (3 H, s), 5.40 (1 H, d, *J*=0.8 Hz), 6.20 (1 H, d, *J*=0.8 Hz); ^{13}C NMR ($CDCl_3$) δ 27.9, 36.5, 37.9, 46.7, 59.8, 91.3, 98.6, 150.8, 168.0, 171.0, 202.5; MS (EI) m/z (rel. intensity) 288 (M^+, 8), 260 (22), 188 (100); Anal Calcd for $C_{17}H_{20}O_4$: C, 70.81 ; H, 6.99. Found: C, 70.69 ; H, 7.10.

(*Z*)-4-Methoxy-5-[(3-methyl-2-butenoyl)methylene]-2(*5H*)-furanone (19e). IR (KBr) 1796, 1660, 1649, 1613, 974 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 and 2.20 (each 3 H, d, *J*=1.2 Hz), 4.00 (3 H, s), 5.39 (1 H, d, *J*=0.6 Hz), 5.79 (1 H, d, *J*=0.6 Hz), 6.64 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 21.4, 28.1, 59.8, 90.7, 106.9, 124.5, 148.5, 158.8, 167.4, 171.5, 188.1; MS (EI) m/z (rel. intensity) 208 (M^+, 41), 193 (25), 180 (38), 153 (100), 125 (48), 111 (73); Anal Calcd for $C_{11}H_{12}O_4$: C, 63.45 ; H, 5.81. Found: C, 63.20 ; H, 6.01.

(*Z*)-4-Methoxy-5-[(5-trimethylsilyl-2-furoyl)methylene]-2(*5H*)-furanone (19f). IR (KBr) 1794, 1678, 1618, 972, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (9 H, s), 4.03 (3 H, s), 5.43 (1 H, d, *J*=0.6 Hz), 6.51 (1 H, d, *J*=0.6 Hz), 6.72 (1 H, d, *J*=3.6 Hz), 7.24 (1 H, d, *J*=3.6 Hz); ^{13}C NMR ($CDCl_3$) δ −1.9, 59.7, 91.3, 99.6, 118.3, 122.1, 151.2, 157.5, 167.7, 167.8, 171.1, 175.8; MS (EI) m/z (rel. intensity) 292 (M^+, 57), 277 (70), 264 (22), 193 (26), 164 (100); Anal Calcd for $C_{14}H_{16}O_5Si$: C, 57.51 ; H, 5.52. Found: C, 57.50 ; H, 5.52.

(*Z*)-5-[(2,2-Dimethyl-3-butenoyl)methylene]-4-methoxy-2(*5H*)-furanone (19g). IR (KBr) 1802, 1701, 1626 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (6 H, s), 3.99 (3 H, s), 5.22 (1 H, dd, *J*=17.6, 0.8 Hz), 5.23 (1 H, dd, *J*=10.6, 0.8 Hz), 5.40 (1 H, d, *J*=0.6 Hz), 5.93 (1 H, dd, *J*=17.6, 10.6 Hz), 6.12 (1 H, d, *J*=0.6 Hz); ^{13}C NMR ($CDCl_3$) δ 23.3, 51.1, 59.8, 91.4, 99.3, 115.7, 142.2, 150.9, 167.9, 171.0, 199.5; MS (EI) m/z (rel. intensity) 222 (M^+, 1), 153 (100), 125 (9); Anal Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.97; H, 6.23.

(*Z*)-4-Methoxy-5-[(trimethylsilyl)carbonylmethylene]-2(*5H*)-furanone (19h). IR (KBr) 1792, 1657, 1613, 1584, 1250, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.29 (9 H, s), 4.00 (3 H, s), 5.39 (1 H, d, *J*=0.6 Hz), 5.79 (1 H, d, *J*=0.6 Hz); ^{13}C NMR ($CDCl_3$) δ -2.9, 59.9, 90.8, 108.2, 149.4, 167.0, 171.7, 236.4; MS (EI) m/z (rel. intensity) 226 (M^+, 11), 211 (2), 198 (16), 183 (31), 169 (7), 125 (2), 89 (38), 73 (100); Anal Calcd for $C_{10}H_{14}O_4Si$: C, 53.08; H, 6.24. Found: C, 52.97; H, 6.35.

(*Z*)-4-Methoxy-5-[(phenoxycarbonyl)methylene]-2(*5H*)-furanone (19i). IR (KBr) 1813, 1728, 1678, 1626, 961, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.01 (3 H, s), 5.44 (1 H, d, *J*=0.6 Hz), 5.83 (1 H, d, *J*=0.6 Hz), 7.14-7.45 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 60.0, 91.6, 95.8, 121.8, 126.4, 129.8, 150.8, 153.4, 162.0, 167.0, 170.6; MS (EI) m/z (rel. intensity) 246 (M^+, 9), 153 (100), 125 (37); Anal Calcd for $C_{13}H_{10}O_5$: C, 63.42 ; H, 4.09. Found: C, 63.20 ; H, 4.09.

Synthesis of 2(*3H*)-furanones 21. General Procedure. The cyclobutenones **20a** and **20c** were reported in the previous paper.[5b] The cyclobutenone **20b** was prepared as a *ca.* 1:2 diastereomeric mixture following the same procedures as described in the first part. The yields are listed in Table 3.

Ethyl 2-(3-Chloro-1-hydroxy-2-methoxy-4-oxo-2-cyclobutenyl)propanoate (20b). *oil* (Elution H-A 3:1); IR (neat) 3422, 1786, 1732, 1613 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, t, *J*=7.2 Hz), 1.29 and 1.34 (2 H and 1 H, respectively, t, *J*=7.4 Hz), 2.96 and 2.97 (2/3 H and 1/3 H, respectively, q, *J*=7.4 Hz), 4.23 (2 H, q, *J*=7.2 Hz), 4.35 and 4.36 (2 H and 1 H, respectively, s), 4.65 (1 H, br s); ^{13}C NMR ($CDCl_3$) pairing signals due to a diastereomeric mixture: δ 12.8 and 12.6, 14.0, 41.9 and 41.6, 61.8 and 61.2, 90.2 and 90.5, 105.1 and 105.2, 174.4, 181.9 and 181.6, 184.7 and 185.3; MS (EI) m/z (rel. intensity) 248 (M^+, 21), 212 (23), 189 (19), 174 (100); Anal Calcd for $C_{10}H_{13}ClO_5$: C, 48.30; H, 5.27. Found: C, 48.14; H, 5.43.

The thermal rearrangement of **20** was carried out by refluxing **20** (0.39 mmol) in dry xylene (15 mL) for the specified time in Table 3. The work-up as above and flash chromatography (H-A 3:1) afforded the product. The yields are listed in Table 3.

5-[(1-Benzoyl)ethyl]-3-chloro-4-methoxy-2(*3H*)-furanone (21a). *oil* (*ca.* 7:1 mixture of diastereomers); IR (neat) 1798, 1775, 1684, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 and 1.46 (21/8 H and 3/8 H, respectively, d, *J*=7.2 Hz), 3.75 and 4.04 (21/8 H and 3/8 H, respectively, s), 4.21 and 4.47 (7/8 H and 1/8 H, respectively, q, *J*=7.2 Hz), 5.16 and 5.31 (7/8 H and 1/8 H, respectively, s), 7.45-7.96 (5 H, m); ^{13}C NMR ($CDCl_3$) pairing signals due to a diastereomeric mixture: δ 13.2 and 14.2, 47.6 and 49.4, 60.1 and 60.4, 89.3 and 88.9, 98.3, 128.6 and 128.8, 129.2 and 129.4, 134.1 and 134.2, 135.9 and 136.2, 168.3 and 169.5, 179.7 and 181.5, 197.8 and 198.2; MS (EI) m/z (rel. intensity) 280 (M^+, 1), 244 (8), 216 (1), 140 (27), 105 (100); Anal Calcd for $C_{14}H_{13}ClO_4$: C, 59.90 ; H, 4.67. Found: C, 59.75 ; H, 4.82.

3-Chloro-5-[1-(ethoxycarbonyl)ethyl]-4-methoxy-2(*3H*)-furanone (21b). *oil* (*ca.* 5:1 mixture of diastereomers) IR (neat) 1800, 1778, 1738, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 and 1.28 (15/6 H and 3/6 H, respectively, t, *J*=7.2 Hz), 1.58 and 1.35 (15/6 H and 3/6 H, rspectively, d, *J*=7.2 Hz), 3.22 and 3.32 (5/6 H and 1/6 H, respectively, q, *J*=7.2 Hz), 4.00 and 4.01 (15/6 H and 3/6 H, respectively, s), 4.02-4.28 (2 H, m), 5.16 and 5.21 (5/6 H and 1/6 H, respectively, s); ^{13}C NMR ($CDCl_3$) pairing signals due to a diastereomeric mixture: δ 12.1 and 13.2, 14.0 and 14.1, 47.5 and 49.1, 60.3 and 60.4, 61.6 and 61.4, 88.4 and 89.2, 97.8 and 97.0, 168.5 and 168.4, 169.7 and 169.6, 180.8 and 180.3; MS (EI) m/z (rel. intensity) 248 (M^+, 11), 213 (100), 203 (22), 174 (26), 167 (20), 147 (56), 141 (100), 119 (65); Anal Calcd for $C_{10}H_{13}ClO_5$: C, 48.30 ; H, 5.27. Found: C, 48.31 ; H, 5.25.

3-Chloro-4-methoxy-5-[1-(methoxycarbonyl)-1-methylethyl]-2(*3H*)-furanone (21c). *oil*; IR (neat) 1798, 1736, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 and 1.52 (each 3 H, s), 3.67 (3 H, s), 4.00 (3 H, s), 5.16 (1 H, s); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.4, 52.1, 52.6, 60.3, 88.4, 101.0, 168.3, 172.9, 182.1; MS (EI) m/z (rel. intensity) 248 (M^+, 10), 213 (100), 188 (15), 169 (13), 147 (61), 119 (46); Anal Calcd for $C_{10}H_{13}ClO_5$: C, 48.30 ; H, 5.27. Found: C, 48.13 ; H, 5.44.

Conversion of 2(*3H*)-Furanones 21 to γ-Acylmethylenetetronates 22. General Procedure. To a

solution of **21** (0.14 mmol) in THF (2 mL) was added diazabicyclo[5.4.0]undec-7-ene (23 mg, 0.15 mmol), and the solution was stirred for 1 h at ambient temperature. The reaction mixture was diluted with dichloromethane, washed with water, and dried over Na_2SO_4. After evaporation of the solvent, the residue was subjected to chromatography (H-A 3:1) to afford the product. The yields are listed in Table 3.

(*Z*)-5-(1-Benzoylethylidene)-4-methoxy-2(*5H*)-furanone (22a). *crystals*, mp 125-127 °C; IR (KBr) 1771, 1738, 1672, 1610, 903 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.19 (3 H, s), 3.60 (3 H, s), 5.25 (1 H, s), 7.46-7.94 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 16.0, 59.5, 90.7, 120.6, 129.2, 129.4, 134.3, 136.1, 141.6, 168.1, 169.4, 195.5; MS (EI) m/z (rel. intensity) 244 (M^+, 99), 229 (1), 222 (15), 216 (18), 184 (87), 167 (11), 105 (100); Anal Calcd for $C_{14}H_{12}O_4$: C, 68.85 ; H, 4.95. Found: C, 68.75 ; H, 5.04.

5-[(1-Ethoxycarbonyl)ethylidene]-4-methoxy-2(*5H*)-furanone (22b). *crystals* (*ca.* 3:1 mixture of *Z*- and *E*-isomers), mp 75-77 °C; IR (KBr) 1780, 1721, 1690, 1613, 887 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 and 1.35 (9/4 H and 3/4 H, respectively, t, *J*=7.2 Hz), 2.12 and 2.21 (9/4 H and 3/4 H, respectively, s), 3.90 and 3.98 (9/4 H and 3/4 H, respectively, s), 4.27 and 4.31 (6/4 H and 2/4 H, respectively, q, *J*=7.2 Hz), 5.31 and 5.40 (3/4 H and 1/4 H, respectively, s); ^{13}C NMR ($CDCl_3$) paring signals due to a *Z*- and *E*-isomeric mixture δ 14.1, 15.0 and 13.0, 59.6 and 59.8, 61.8, 91.1 and 92.4, 114.6 and 113.5, 143.0 and 144.6, 167.7 and 167.3, 167.8 and 166.9, 169.4 and 172.1; MS (EI) m/z (rel. intensity) 212 (M^+, 99), 184 (10), 167 (100), 138 (22); Anal Calcd for $C_{10}H_{12}O_5$: C, 61.22 ; H, 6.16. Found: C, 61.09 ; H, 6.28.

Thermal Rearrangement of 4-Hydroxycyclobutenone 30. The cyclobutenone **30** was prepared as follows. To a solution of **29**[3b] (69 mg, 0.38 mmol) and **5i** (158 mg, 0.76 mmol) was added $TiCl_4$ (0.042 mL, 0.38 mmol) by syringe at 0°C under exclusion of moisture, and the solution was stirred for 1 h. The reaction was allowed to warm to ambient temperature and the solution was stirred for further 1 h. The work-up as described in the first part and flash chromatography (H-A 1:1) afforded **30** (52 mg, 42%) as a yellow oil, IR (neat) 3355, 1757, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (3 H, t, *J*=7.2 Hz), 1.23-1.59 (4 H, m), 1.46 (3 H, t, *J*=7.0 Hz), 2.14 (2 H, t, *J*=7.2 Hz), 3.06 and 3.17 (each 1 H, d, *J* =15.2 Hz), 4.44 and 4.52 (each 1 H, dq, *J*=9.6, 7.0 Hz), 4.48 (1 H, br s), 7.06-7.43 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 13.7, 15.0, 22.4, 22.6, 29.8, 38.2, 69.1, 88.3, 121.7, 126.5, 127.8, 129.8, 150.7, 169.6, 181.6, 191.2; MS (EI) m/z (rel. intensity) 318 (M^+, 5), 225 (7), 207 (36), 197 (100), 179 (24), 169 (17), 154 (16), 125 (30); Anal Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.96. Found: C, 67.71; H, 7.15.

Thermal rearrangement of **30** was performed by refluxing a solution of **30** (61 mg, 0.19 mmol) in dry mesitylene (10 mL) for 3 h followed by the same work-up as employed for preparation of **19**. The residue was purified by flash chromatography (H-A 3:1) to afford the tetronate **31** (40 mg, 66%) as a pale-yellow oil, IR (neat) 1759, 1661, 1593 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3 H, t, *J*=7.0 Hz), 1.27-1.57 (4 H, m), 1.41 (3 H, t, *J*=7.0 Hz), 2.37 (2 H, t, *J*=7.0 Hz), 2.81 (1 H, dd, *J*=16.0, 8.0 Hz), 3.10 (1 H, dd, *J*=16.0, 4.4 Hz), 4.37 and 4.43 (each 1 H, dq, *J*=9.4, 7.0 Hz), 5.12 (1 H, dd, *J*=8.0, 4.4 Hz), 7.07-7.43 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 13.8, 15.3, 22.6, 23.2, 32.3, 37.8, 67.7, 73.9, 103.2, 121.8, 126.4, 129.8, 150.8, 168.2, 171.5, 174.5; MS (EI) m/z (rel. intensity) 318 (M^+, 25), 272 (2), 225 (100), 197 (34), 183 (57), 179 (90), 155 (26); Anal Calcd for $C_{18}H_{22}O_5$: C, 67.91 ; H, 6.96. Found: C, 67.81 ; H, 7.05.

Photolysis of 4-Hydroxycyclobutenone 10i. A solution of **10i** (85 mg, 0.30 mmol) in dry THF (10 mL) was irradiated with high-pressure Hg lamp (100 W Ushio UM-102) through a quartz filter under an atomosphere of nitrogen for 5 h. The solvent was evaporated, and the residue was purified by flash chromatography (H-A 3:1) to afford the tetronate **33** (42 mg, 48%) as a pale-yellow oil, IR (neat) 1771, 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.91 (1 H, dd, *J*=16.4, 7.6 Hz), 3.16 (1 H, dd, *J*=16.4, 4.2 Hz), 4.37 (3 H, s), 5.22 (1 H, dd, *J*=7.6, 4.2 Hz), 7.06-7.44 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 37.0, 60.2, 73.3, 94.2, 121.6, 126.6, 129.9, 137.6, 150.6, 167.4, 169.6; MS (EI) m/z (rel. intensity) 282 (M^+, 69), 247 (37), 189 (70), 161 (74), 147 (100), 121 (66), 119 (33); Anal Calcd for $C_{13}H_{11}ClO_5$: C, 55.24 ; H, 3.92. Found: C, 55.11 ; H, 4.04.

Synthesis of (*Z*)-5-(Formylmethylene)-4-methoxy-2(5*H*)-furanone (35). A solution of **19g** (310 mg, 1.39 mmol) and $CeCl_3 \cdot 7H_2O$ (673 mg, 1,81 mmol) in 1:1 methanol-dichloromethane (6 mL) was cooled to -70°C and treated with a solution of $NaBH_4$ (79 mg, 2.09 mmol) in 1:1 methanol-dichloromethane (2 mL). The reaction mixture was allowed to warm slowly to -30°C during 1 h and then quenched with saturated aq. $NaHCO_3$ (5 mL). After filtration of precipitates, the organic layer was separated, washed with water and dried (Na_2SO_4). After evaporation of the solvent the residue was purified by flash chromatography (H-A 4:1) to afford the alcohol **34** (284 mg, 91%) as a colorless oil.

To a solution of $Pb(OAc)_4$ (164 mg, 0.37 mmol) in dry dichloromethane (6 mL) was added a solution of **34** (77 mg, 0.34 mmol) in dry dichloromethane (2 mL) at -78°C under an atomosphere of nitrogen, and the solution was stirred for 2 h and for additional 1.5 h at ambient temperature. The work-up as above and flash chromatography (H-A 3:1) afforded the tetronate **35** (46 mg, 88%) as yellow crystals.

Spectral Data for (*Z*)-5-(2-Hydroxy-3,3-dimethyl-4-pentenylidene)-4-methoxy-2(5*H*)-furanone (34). IR (neat) 3453, 1782, 1765, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 and 1.07 (each 3 H, s), 2.27 (1 H, br s), 3.94 (3 H, s), 4.45 (1 H, d, *J*=9.4 Hz), 5.10 (1 H, dd, *J*=17.4, 1.4 Hz), 5.15 (1 H, dd, *J*=11.0, 1.4 Hz), 5.25 (1 H, d, *J*=0.6 Hz), 5.45 (1 H, dd, *J*=9.4, 0.6 Hz), 5.90 (1 H, dd, *J*=17.4, 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7, 23.5, 42.2, 59.4, 72.8, 89.7, 109.2, 114.5, 144.3, 144.8, 168.7, 170.3; MS (EI) m/z (rel. intensity) 155 (100), 127 (38); (CI) m/z (rel. intensity) 225 (MH^+, 84), 207 (100); Anal Calcd for $C_{12}H_{16}O_4$: C, 64.27 ; H, 7.19. Found: C, 64.58 ; H, 6.88.

Spectral Data for (*Z*)-5-(Formylmethylene)-4-methoxy-2(5*H*)-furanone (35). mp 134-138 °C; IR (neat) 1819, 1674, 1661, 1616 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.04 (3 H, s), 5.45 (1 H, d, *J*=0.6 Hz), 5.76 (1 H, dd, *J*=8.0, 0.6 Hz), 10.17 (1 H, d, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 60.1, 91.4, 104.6, 156.5, 166.3, 170.6, 189.0; MS (EI) m/z (rel. intensity) 154 (M^+, 33), 126 (100); Anal Calcd for $C_7H_6O_4$: C, 54.55 ; H, 3.92. Found: C, 54.54; H, 3.93.

Synthesis of (*E*)-Basidalin (41). To a solution of **1** (1.132 g, 7.5 mmol) and **5g** (2.765 g, 15 mmol) in dry dichloromethane (12 mL) was added $TiCl_4$ (0.83 mL, 7.5 mmol) at -78°C under exclusion of moisture, and the solution was stirred for 1 h. After the same work-up as described in the first part, the residue was purified by flash chromatography (H-A 8:1) to afford **36** (1.367 g, 69%) as a yellow-green oil.

To a solution of **36** (695 mg, 2.6 mmol) in ether (5 mL) was added a 7.0 M solution of NH_3 in ethanol (1.1 mL, 7.8 mmol) at -30°C, and the solution was stirred for 1 h. The reaction mixture was washed with water, extracted with dichloromethane, dried (Na_2SO_4) and evaporated to dryness. The residue was purified by recrystallization from hot acetone to give the amide **37** (288 mg, 45%) as colorless needles.

A solution of **37** (210 mg, 0.86 mmol) and pyridine (75 mg, 0.95 mmol) was refluxed in dry xylene (100 mL) for 2 h. The work-up as described for the synthesis of **19** and flash chlomatography (H-A 5:1) afforded the aminofuranone **39** (151 mg, 85%) as yellow crystals.

Following the same procedures for the conversion of **19g** to **35**, **39** (126 mg, 0.61 mmol) was reduced and chromatographed (H-A 1:1) to give **40** (102 mg, 80%) as white crystals, and further, **40** (81 mg, 0.39 mmol) was oxidized and chromatographed (H-A 3:1) to give (*E*)-basidalin (**41**) (35 mg, 65%) as yellow crystals.

Spectral Data for 2,3-Dichloro-4-(3,3-dimethyl-2-oxo-4-pentenyl)-4-hydroxy-2-cyclobutenone (36). IR (neat) 3422, 1786, 1709, 1636, 1586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (6 H, s), 2.93 and 3.10 (each 1 H, d, *J* =17.8 Hz), 5.23 (1 H, dd, *J*=17.2, 0.6 Hz), 5.25 (1 H, dd, *J*=11.0, 0.6 Hz), 5.28 (1 H, br s), 5.86 (1 H, dd, *J*=17.2, 11.0 Hz); ^{13}C NMR ($CDCl_3$) δ 23.0, 23.1, 37.8, 51.8, 92.5, 116.7, 134.4, 141.1, 169.5, 185.7, 213.5; MS (EI) m/z (rel. intensity) 247 (5), 230 (2), 212 (1), 193 (4), 179 (5), 165 (57), 151 (22), 137 (15), 112 (100); (CI) m/z (rel. intensity) 263 (MH^+, 100); Anal Calcd for $C_{11}H_{12}Cl_2O_3$: C, 50.21; H, 4.60. Found: C, 50.15; H, 4.66.

Spectral Data for 3-Amino-2-chloro-4-(3,3-dimethyl-2-oxo-4-pentenyl)-4-hydroxy-2-cyclo-

butenone (37). mp 198-200°C; IR (KBr) 2800-3600 (broad), 1771, 1709, 1622, 1543 cm^{-1}; ^1H NMR (DMSO-d6) δ 1.13 (6 H, s), 2.70 and 3.17 (each 1 H, d, *J* =17.4 Hz), 5.14 (1 H, dd, *J*=10.6, 1.2 Hz), 5.15 (1 H, dd, *J*=17.6, 1.2 Hz), 5.93 (1 H, dd, *J*=17.6, 10.6 Hz), 5.99 (1 H, br s), 7.77 and 8.35 (each 1 H, br s); ^{13}C NMR (DMSO-d6) δ 23.1, 40.2, 50.8, 86.2, 92.9, 114.8, 142.5, 174.7, 184.2, 210.3; MS (EI) m/z (rel. intensity) 243 (M^+, 4), 228 (1), 208 (2), 174 (2), 156 (1), 146 (100), 132 (7), 128 (7), 111 (3), 98 (14), 69 (19); Anal Calcd for $C_{11}H_{14}ClNO_3$: C, 54.22; H, 5.79; N, 5.74. Found: C, 54.09; H, 5.87; N, 5.80.

Spectral Data for (*E*)-4-Amino-5-(3,3-dimethyl-2-oxo-4-pentenylidene)-2(5*H*)-furanone (39). mp 135-137°C; IR (KBr) 3349, 1777, 1748, 1678, 1628, 1599 cm^{-1}; ^1H NMR (DMSO-d6) δ 1.23 (6 H, s), 5.00 (1 H, d, *J* =1.4 Hz), 5.22 (1 H, dd, *J*=10.4, 1.0 Hz), 5.23 (1 H, dd, *J*=17.4, 1.0 Hz), 6.01 (1 H, dd, *J*=17.4, 10.4 Hz), 6.63 (1 H, d, *J*=1.4 Hz), 8.25 and 8.65 (each 1 H, br s); ^{13}C NMR (DMSO-d6) δ 23.3, 51.0, 83.4, 105.9, 116.0, 142.0, 158.3, 158.5, 168.8, 204.2; MS (EI) m/z (rel. intensity) 207 (M^+, 11), 138 (100), 110 (10), 69 (14); Anal Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 64.02; H, 6.28; N, 6.53.

Spectral Data for (*E*)-4-Amino-5-(2-hydroxy-3,3-dimethyl-4-pentenylidene)-2(5*H*)-furanone (40). mp 136-137°C; IR (KBr) 3360, 1721, 1699, 1636, 1574 cm^{-1}; ^1H NMR (DMSO-d6) δ 0.99 (6 H, s), 4.23 (1 H, t, *J*=6.6 Hz), 4.80 (1 H, d, *J* =1.4 Hz), 5.01 (1 H, dd, *J*=18.0, 1.4 Hz), 5.02 (1 H, dd, *J*=10.4, 1.4 Hz), 5.62 (1 H, dd, *J*=6.6, 1.4 Hz), 5.91 (1 H, dd, *J*=18.0, 10.4 Hz), 6.04 (1 H, d, *J*=6.6 Hz), 7.43 (2 H, br s); ^{13}C NMR (DMSO-d6) δ 21.9, 23.3, 42.4, 72.3, 84.2, 113.2, 113.7, 144.9, 146.7, 159.0, 167.0; MS (EI) m/z (rel. intensity) 209 (M^+, 1), 140 (100), 112 (79), 69 (9); Anal Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.43; H, 7.19; N, 6.43.

Spectral Data for (*E*)-Basidalin (41). mp. 115-120°C [lit. mp. 116-124 °C][18]; IR (KBr) 3347, 3185, 1748, 1684, 1655, 1579 cm^{-1}; ^1H NMR (DMSO-d6) δ 5.10 (1 H, d, *J* =1.4 Hz), 6.33 (1 H, dd, *J*=4.8, 1.4 Hz), 8.10 (2 H, br s), 9.78 (1 H, d, *J*=4.8 Hz); ^{13}C NMR (DMSO-d6) δ 84.7, 108.8, 158.5, 158.8, 168.6, 191.7; MS (EI) m/z (rel. intensity) 139 (M^+, 49), 111 (100).

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