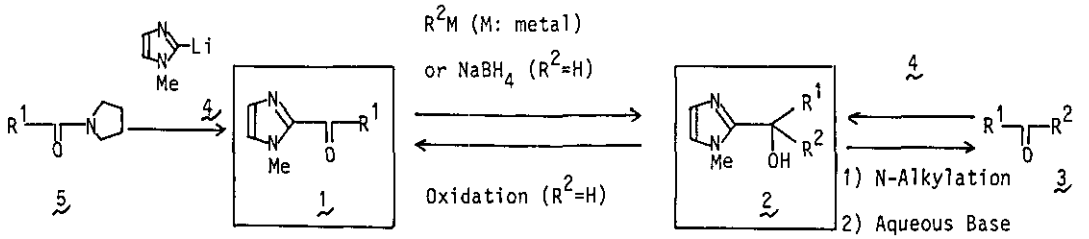
SYNTHESES OF α,β-UNSATURATED KETONES STARTING FROM VINYLIC AND ALLYLIC GRIGNARD REAGENTS VIA 2-IMIDAZOLYLMETHANOL INTERMEDIATES

Satoshi Hayakawa, Tohru Michiue, Masao Okamoto,*
Shoko Hatakeyama, and Shunsaku Ohta
Kyoto Pharmaceutical University,
Misasagi Nakauchi-cho 5, Yamashina-ku, Kyoto 607, Japan

Abstract ——— Various α,β-unsaturated ketones (9, 12 and 16) were prepared from 2-alkanol-1-methyl-1H-imidazoles (6, 10 and 13, respectively), which were obtained by treatment of 2-acyl-1-methyl-1H-imidazoles (1) with vinylic Grignard reagents, a lithium acetylide and allylic Grignard reagents, respectively. dl-(ar)-Turmerone (16i) was also synthesized as an application of the present methodology.

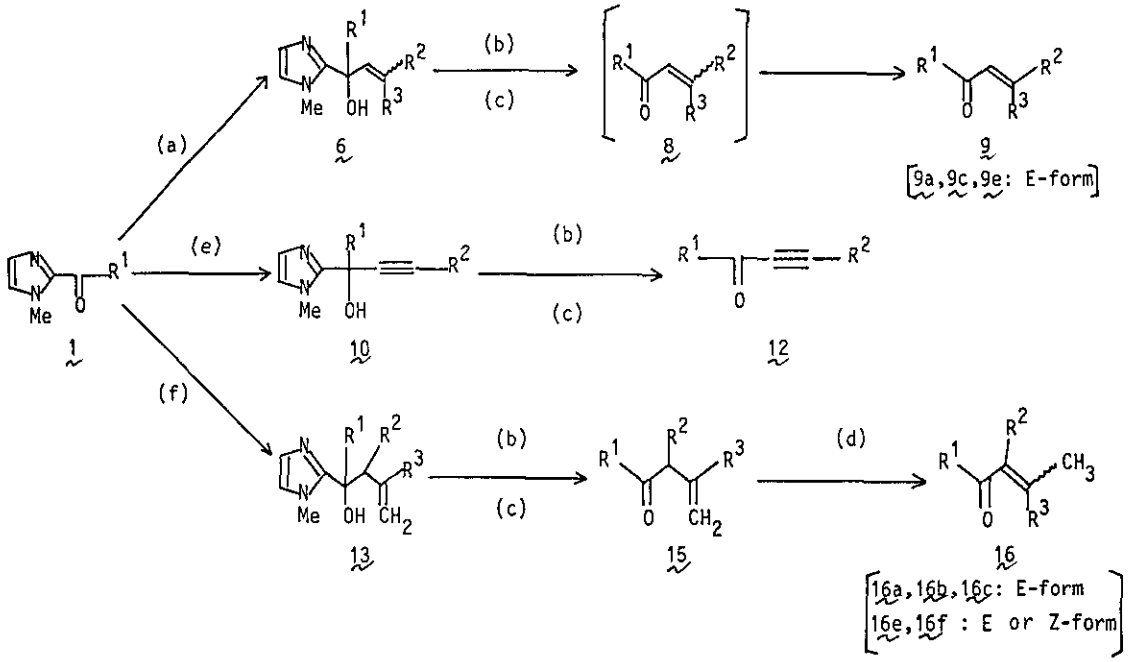
In recent years, we have studied syntheses and synthetic applications of 2-acyl-1-methyl-1H-imidazoles (1) and 2-alkanol-1-methyl-1H-imidazoles (2) as briefly illustrated in Chart 1.[1,2] The 2-acyl-1-methyl-1H-imidazoles (1), easily obtained by treating various pyrrolidine amides (5) with 2-lithio-1-methyl-1H-imidazole (4)[1], can be converted into various carbonyl compounds (3) via the corresponding 2-alkanol-1-methyl-1H-imidazoles (2).[1,2,3] The 2-alkanolimidazole (2) and the 2-acylimidazole (1) are very stable to several severe conditions, therefore, the 2-acylimidazole (1) can be utilized as a convenient synthon of the carbonyl compound



(Chart 1)

(3), while the 2-alkanolimidazole (2) can be regarded as a characteristic protected form of the carbonyl compound (3). In this paper, we would like to report preparations of various α,β-unsaturated ketones (9, 12 and 16) and synthesis of a natural perfume ingredient dl-(ar)-Turmerone (16i) as an applications of the methodology.

First, a reaction of the 2-acyl-1-methyl-1H-imidazoles (1) with vinylic magnesium halides was examined. Thus 2-benzoyl-1-methyl-1H-imidazole [1a ($R^1=C_6H_5$)] was treated with an excess amount of an ethereal solution of a mixture of cis- and trans-styrylmagnesium bromide [prepared from 7a ($R^2=C_6H_5$, $R^3=H$)] at 0 ℃ to give successfully the corresponding crystalline adduct, 2-(1,3-diphenyl-1-hydroxy-2-propenyl)-1-methyl-1H-imidazole [6a ($R^1=R^2=C_6H_5$, $R^3=H$)], in 93.1 % yield, which was probably formed in an inseparable geometrically isomeric mixture on the base of its proton nuclear magnetic resonance spectrum (^{1}H-nmr). A solution of the product (6a) in ethyl acetate was refluxed in the presence of a slight excess of dimethyl sulfate



(a) $R^2(R^3)C{=}CHBr$ (7) / Mg / Et_2O / 0 °C

(b) $(CH_3)_2SO_4$ / AcOEt / reflux

(c) 10% K_2CO_3 / benzene / 80 °C

(d) p-TsOH (cat. amt.) / benzene / reflux

(e) $R^2C{\equiv}CH$ (11) / n-BuLi / THF / -80 °C

(f) $R^2CH{=}C(R^3)CH_2Cl$ (14) / Mg / THF / 0 °C

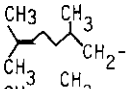
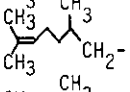
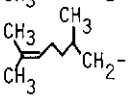
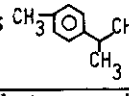
(Chart 2)

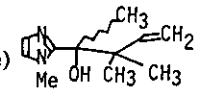
followed by treatment of the resultant quaternary salt with aqueous 10% K_2CO_3 at 80 ℃ in the presence of a small amount of hydroquinone as an anti-polymerizing agent to afford sole trans-benzylideneacetophenone (9a; Chalcone). Satisfactory results were obtained in all examples as shown in Table 1.

On the other hand, a reaction of the 2-cyclohexyl-1-methyl-1H-imidazole [1e (R^1=c-hexyl)] with lithium 2-phenylacetylide, which was prepared by treatment of phenylacetylene (11a) with n-butyllithium at -78 ℃ in THF, was also successfully afforded the corresponding 2-alkanolimidazole [10a (R^1=c-hexyl, R^2=C_6H_5)] in 99.7 % yield. The 2-alkanolimidazole (10a) could be transformed in the similar manner as described in the reaction of 6a to 9a to the α,β-alkynylalkylketone [12a (R^1=c-hexyl, R^2=C_6H_5): ir ($CHCl_3$); 2190 cm^{-1} (C≡C)] in quantitative yield (Chart 2). The result, only one instance, indicates that the preparation of such α,β-alkynylketone (12) is possible by the present method (Table 1).

Generally speaking, the reaction of the vinylic halides (7) with magnesium metal in an ethereal solution relatively slowly proceeds or sometimes results in failure even by utilizing a technique of high level or some devices for complete formation of the corresponding Grignard reagent. On the other hand, a reaction of allylic halides (14) with magnesium metal commonly proceeds more easily comparing with that of the vinylic halides (7). So we planned to examine a reaction of 2-acylimidazole (1) with allylic magnesium halide because migration of the double bond of the formed β,γ-unsaturated ketone (15) seems to be easy. Thus 2-benzoyl-1-methyl-1H-imidazole (1a) was treated with an excess amount of an ethereal solution of allylmagnesium bromide [prepared from 14a (R^2=H, R^3=H)] at 0 ℃ to give the corresponding 2-alkanolimidazole [13a (R^1=C_6H_5, R^2=R^3=H)] in 87.0 % yield. The product (13a) was subjected to the reaction condition as used in the conversion of 6a to 9a to produce initially crude 1-phenyl-1-oxo-3-butene [15a (R^1=C_6H_5, R^2=R^3=H)], which was contaminated with a considerable amount of trans-1-phenyl-1-oxo-2-butene [16a (R^1=C_6H_5; R^2=R^3=H)] on the basis of glc analysis. The mixture was treated without purification with a catalytic amount of p-toluenesulfonic acid (p-TsOH) in refluxing benzene for several hours to form almost solely 16a* in 88.3 % (calculated on the basis of 13a). When the reaction of 2-heptanoyl-1-methyl-1H-imidazole [1f (R^1=n-hexyl)] with crotylmagnesium chloride [prepared from 14d (R^2=CH_3, R^3=H)] gave a viscous material [13f (R^1=n-hexyl,

Table 1. Formation of α,β-Unsaturated Ketone (9, 12, and 16) from 2-Acyl-1-methyl-1H-imidazole (1) and Alkyl metal via 2-Alkanol-1-methyl-1H-imidazole (6, 10, and 13)

Entry	Substrate (1) R¹	Halide (7 and 14) or Acetylene (11)	Product (6[b], 10, and 13) mp(℃) (Recryst. Solv.) Isolated yield (%)	Time (15→16) (hour)	Product (9, 12, and 16[d]) bp(℃/mmHg) or mp(℃) Isolated yield (%)
1	1a; 	14a; R²=H R³=H	13a; 134.5-136.5 (CCl_4) 87.0	2.0	16a; bp_3 113.0-125.0 [$bp_{0.5}$ 84.0-85.0][4] 88.3
2	1a; 	7a; R²=Ph R³=H	6a; 178.0-180.0 (AcOEt) 93.1	——	9a; mp 56.0-57.0 [mp 57.0-58.0][5] 86.9
3	1b; 	14a; R²=H R³=H	13b; 164.5-166.0 (CCl_4) 95.8	easily[c]	16b; viscous material 73.7
4	1b; 	7b; R²=H R³=H	6b; 180.0-180.5 (benzene) 78.3	——	9b; viscous material 36.3
5	1c; 	14a; R²=H R³=H	13c; viscous material[a] 89.1	3.0	9c; bp_5 149.0-151.0 87.4
6	1c; 	7c; R²=CH_3 R³=H	6c; viscous material quant.	——	9c; bp_5 149.0-151.0 89.6
7	1c; 	7d; R²=CH_3 R³=CH_3	6d; viscous material 64.5	——	9d; $bp_{4.5}$ 105.0-113.0 81.3
8	1d; $Cl(CH_2)_4$-	14b; R²=H R³=CH_3	13d; 74.0-75.0 (n-hexane) 85.1	3.0	16d; bp_3 85.0-95.0 94.5
9	1e; 	14c; R²=Ph R³=H	13e; 172.0-173.0 (AcOEt)[a] 67.8	3.5	16e; viscous material quant.
10	1e; 	11a; R²=Ph	10a; 141.0-142.0 (n-hexane-CH_2Cl_2) 99.7	——	12a; bp_5 135.0 quant.
11	1f; $CH_3(CH_2)_5$-	14d; R²=CH_3 R³=H	13f; viscous material 76.5	3.5	16f; bp_3 80.0-88.0 91.1
12	1f; $CH_3(CH_2)_5$-	14e; 	13g; 138.0-138.5[e] (AcOEt-n-hexane) 87.1	——	15g; bp_3 65.0-80.0[f] quant.
13	1f; $CH_3(CH_2)_5$-	7c; R²=CH_3 R³=H	6e; 110.0-113.0 (n-hexane) 92.5	——	9e; bp_{10} 75.0-87.0 86.9
14	1i; 	14b; R²=H R³=CH_3	13i; viscous material[a] 83.7	3.0	16i; bp_5 117.0 [bp_7 156.0-158.0][7] 93.3

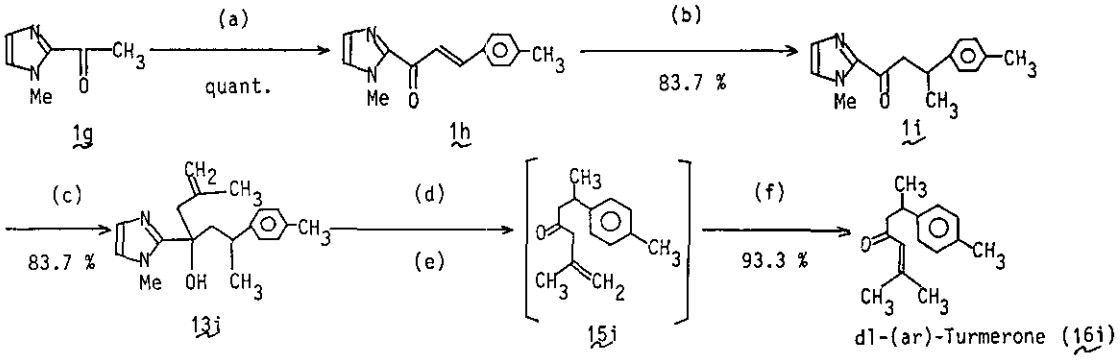
a) The product was a diastereomeric mixture. b) The product was a diastereomeric mixture except for 6b. c) The migration of the double bond to the α,β- from the β,γ- position easily proceeded even in the absence of p-toluenesulfonic acid.
d) The structures of 16a-c were assigned as E form on the basis of ^{1}H-nmr, but the stereochemistries of 16e and 16f were ambiguous. e)  13g
f) The migration of olefinic bond of 15g is structurally impossible.

$R^2=CH_3$, $R^3=H$)] in 76.5 % yield, which was presumed to be produced in a diastereomeric mixture. Literatures state that in general, the Grignard reaction of crotylmagnesium halide and its analogues gives a mixture of 1- and 2-butene derivatives in a predominant formation of the former.[8] ^{1}H-Nmr of the product (13f) showed two double doublets at 4.96 (1.6 H) and 4.78 ppm (0.4H), assigned as the terminal methylene protons of the respective diastereoisomers. This indicates that the Grignard reaction was occurred exclusively at the γ-site of the reagent to produce the diastereomeric mixture. In other cases in Table 1, the similar Grignard reactions [entry 9 and 12] of the 2-acyl-1-methyl-1H-imidazole [1e (R^1=c-hexyl) and 1f (R^1=n-hexyl), respectively] also afforded surprisingly only the γ-adducts in each cases as crystalline products [13e (67.8 %; R^1=c-hexyl, $R^2=C_6H_5$, R^3=H) and 13g (87.1%; see footnote in Table 1), respectively] rather than the α-adduct. The literatures also state that γ-adduct is generally obtained almost exclusively in the cases of hindered ketones such as diisopropylketone and t-butylketone.[8] The present high regiochemical selectivity of the Grignard reaction of the 2-acyl-1-methyl-1H-imidazole (1) is presumed to be concerned with a strong chelating effect of the lone pair electron of the imidazole 3-position nitrogen atom to the magnesium atom and steric interference of the 1-methyl group of the imidazole ring. Further examples are now under investigations and the results will be reported elsewhere. The 2-alkanolimidazoles (13e and 13f) were converted in the usual manner to the corresponding α,β-unsaturated ketones [16e (R^1=c-hexyl, $R^2=C_6H_5$, R^3=H) and 16f (R^1=n-hexyl, $R^2=CH_3$, R^3=H), respectively] in quantitative and 91.1% yield, respectively. Glc and ^{1}H-nmr spectra of the product (16f and 16e) indicate almost no presence of the corresponding regiochemical isomer, but the stereochemistries of 16e and 16f were not confirmed.[9]

Finally, we wished to apply the present methodology to a total synthesis of dl-(ar)-Turmerone (16i), which is a natural perfume ingredient isolated from Curcuma longa Linn. (Zingiberaceae).[6] 2-Acetyl-1H-imidazole[1] (1g) was treated with lithium diisopropylamide (LDA) at -78 ℃ followed by addition of 4-methylacetophenone to give a complex mixture, from which 2-acetyl-1-methyl-4(or 5)-[1-hydroxy-1(4-methylphenyl)-1-ethyl]-1H-imidazole (17) was isolated by the preparative thin-layer chromatography (ptlc) on silica gel in 30.1 % yield. The structure (17) was

estimated from its ^{1}H-nmr, which showed signals of acetyl protons at 2.66 ppm (s, 3H), a imidazole ring proton of the 4- or 5-position at 7.15 ppm (s, 1H). Anyway we can not use this procedure for synthesis of 16i. Next, an aldol condensation at room temperature in the presence of alkali between 2-acety-1-methyl-1H-imidazole (1g) and p-tolualdehyde was examined. The reaction was successfully proceeded in methanol in the presence of an equimolar amount of sodium hydroxide to give 1-methyl-2-[3-(4-methylphenyl)acryroyl]-1H-imidazole (1h) in quantitative yield. Structure of the product (1h) was confirmed by ^{1}H-nmr, which showed singnals of the two protons of the imidazole ring and two olefinic protons. It is noteworthy that the product (1h) could be easily separated in an almost pure state from neutral substances such as tolualdehyde by a simple extraction of the crude reaction product with a diluted hydrochloric acid, and that is one of the virtues of the 2-imidazole chemistry. The olefinic ketone (1h) was treated with an ethereal solution of lithium dimethylcuprate[10] at room temperature to afford smoothly the corresponding 1,4-adduct (1i) in 83.7 % yield. The structure of the oily 2-acylimidazol (1i) was confirmed by the presence of a doublet signal (3H, J = 7Hz at 1.29 ppm) of the introduced methyl group and the absence of signal of vinylic protons in its ^{1}H-nmr. A Grignard reaction of the ketonic imidazole (1i) with $CH_2=C(CH_3)CH_2MgCl$ (prepared from 14b) was furnished a viscous material of the corresponding 2-alkanolimidazole (13i) in 83.7 % yield, which was purified by ptlc on silica gel. The 2-alkanolimidazole (13i) was converted to the corresponding ketone (15i) in the usual manner followed by refluxing a solution of the crude intermediate in benzene in the presence of a catalytic amount of p-TsOH to give dl-(ar)-Turmerone (16i) in 93.3 % (calculated on the basis of 13i). The product (16i) was identified by inspections of its high-resolution mass spectrum and comparison of its spectral data with the reported.[7]

The present method for the preparation of the α,β-unsaturated ketone may be characterized by no use of transition metal, and such type of synthetic route for the α,β-unsaturated ketones has been hitherto scarecely appeared as preparative procedure. Importance of the α,β-unsaturated ketone is increasing in the field of organic synthesis, therefore, the present procedure may provide a new strategy for synthesis of various compounds.



(a) p-tolualdehyde/ NaOH/ MeOH/ r.t.
(b) $(CH_3)_2CuLi$/ Et_2O/ 0 °C
(c) methallyl chloride/ Mg/ Et_2O
(d) $(CH_3)_2SO_4$/ AcOEt/ reflux
(e) 10% K_2CO_3/ benzene/ 80 °C
(f) p-TsOH/ benzene/ reflux

(Chart 3)

EXPERIMENTAL

General Procedure for Reactions of 2-Acyl-1-methyl-1H-imidazoles (1) with Vinylic Halide (7) [Preparation of 2-(1,3-Diphenyl-1-hydroxy-2-propenyl)-1-methyl-1H-imidazole (6a) as an Example] ----- An ethereal solution of styrylmagnesium bromide, prepared from β-bromostyrene (7a) (1.83 g, 10 mmol; a mixture of cis- and trans-isomers), magnesium metal (486 mg, 20 mgatom) and Et_2O (10 ml) according to the usual manner, was added to a solution of 2-benzoyl-1-methyl-1H-imidazole (1a) (465 mg, 2.5 mmol) in Et_2O (2.5 ml) at 0 ℃ under nitrogen atmosphere. The mixture was stirred for 45 min, and then ether and 10 % HCl were added to the resulting mixture at 0 ℃. The organic layer was extracted with 10 % HCl again. The combined aqueous layer was washed with ether and basified with solid K_2CO_3. A separated viscous material was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The obtained crystalline residue was purified by recrystallization from ethyl acetate. Colorless needles. Yield, 675 mg (93.1 %). mp 178.0 - 180.0 ℃. Ir ($CHCl_3$): 3580 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 3.31 and 3.39 (s each, total 3H, $-NCH_3$), 3.70 (br, 1H, OH), 6.30 - 7.60 (m, 14H, vinylic H, imidazole H and benzene H). The nmr spectrum indicates that the compound was produced in a diastereomeric mixture.

2-[1-Hydroxy-1-(3,4-methylenedioxyphenyl)-2-propenyl]-1-methyl-1H-imidazole (6b) --- Recrystallized from benzene. Colorless needles. Yield, 78.3 %. mp 180.0 - 180.5 ℃.

Ir ($CHCl_3$): 3600 (OH), 3050 - 3550cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 3.35 (s, 3H, NCH_3), 3.45 - 3.90 (br, 1H, -OH), 5.00 - 5.40 (m, 2H, $-CH=CH_2$), 5.94 (s, 2H, $-OCH_2O-$), 6.45 - 7.35 (m, 6H, imidazole H, benzene H and $-CH=CH_2$). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 64.99; H, 5.43; N, 10.84.

2-(6,10-Dimethyl-4-hydroxy-2,9-undecadien-4-yl)-1-methyl-1H-imidazole (6c) ----- Viscous material. Yield, quant. Ir ($CHCl_3$): 3000 - 3500 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 0.50 - 2.30 (m, 8H, $C(OH)CH_2CH(CH_3)(CH_2)_2-$ and -OH), 0.65 (d, 3H, CH_3CH-, J = 6 Hz), 1.34 (d, 3H, $CH_3CH=CH-$, J = 6 Hz), 1.57 and 1.65 (s each, 3H each, $(CH_3)_2CH=CH-$), 3.61 and 3.65 (s each, total 3H, $-NCH_3$), 4.80 - 5.20 (m, 1H, $-CH=C(CH_3)_2$), 5.50 - 5.85 (m, 2H, $-CH=CH-$), 6.85 - 6.95 (m, 2H, imidazole H). The nmr spectrum indicates that the compound was produced in a diastereomeric mixture.

2-(4-Hydroxy-2,6,10-trimethyl-2,9-undecadien-4-yl)-1-methyl-1H-imidazole (6d) ----- Viscous material. Yield, 64.5 %. Ir ($CHCl_3$): 3450 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 0.57 (d, 3H, CH_3CH-, J = 6 Hz), 1.33 1.59, 1.67 and 1.73 (s each, total 12H, $(CH_3)_2C=CHCCH_2-$ and $(CH_3)_2C=CHC(OH)-$), 1.00 - 2.25 (m, 8H, $-CH_2CH(CH_3)(CH_2)_2-$ and -OH), 3.56 (s, 3H, $-NCH_3$), 5.05 (m, 1H, $-CH_2CH=C-$), 5.56 (br, 1H, $C(OH)CH=C-$), 6.79 and 6.90 (d each, 1H each, imidazole H, J = 1 Hz each). The nmr spectrum indicates that the compound was produced in a diastereomeric mixture.

2-(4-Hydroxy-2-decen-4-yl)-1-methyl-1H-imidazole (6e) ----- Recrystallized from n-hexane. Colorless needles. Yield, 92.5 %. mp 111.0 - 113.0 ℃. Ir ($CHCl_3$): 3600 (OH), 3550 - 3020 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 0.85 (t, 3H, CH_3CH_2-, J = 7 Hz), 1.00 - 2.25 (m, 13H, $CH_3(CH_2)_5-$ and $CH_3CH=CH-$), 2.33 (br, 1H, -OH), 3.67 and 3.82 (s each, total 3H, $-NCH_3$), 5.50 - 5.70 (m, 2H, vinylic H), 6.65 - 6.95 (m, 2H, imidazole H). The nmr spectrum indicates that the compound was produced in a diastereomeric mixture.

Preparation of 2-(1-Cyclohexyl-1-hydroxy-3-phenyl-2-propynyl)-1-methyl-1H-imidazole (10a) ----- A THF solution (10 ml) of phenylacetylene (11a) (510 mg, 5 mmol) was cooled to -78 ℃ and 1.55M n-BuLi solution in n-hexane (3.2 ml, 5 mmol) was added. The mixture was stirred for 15 min at -78 ℃, and then 2-cyclohexylcarbonyl-1-methyl-1H-imidazole (1e) (960 mg, 5 mmol) was added to the mixture. The whole was stirred for 30 min with removal of the cooling bath. Ether (10 ml) and 10 % HCl (10

ml) were added to the mixture. The combined aqueous layer was washed with ether and then basified by addition of solid K_2CO_3 to separate crystalline precipitates, which was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The obtained crude crystalline material was purified by recrystallization from n-hexane - methylene chloride. Colorless neeles. Yield, 1.46 g (99.7 %). mp 141.0 - 142.0 ℃. Ir ($CHCl_3$): 3400 (OH), 2250 cm^{-1} (C≡C). ^{1}H-Nmr ($CDCl_3$) δ ppm: 1.00 - 2.55 (m, 11H, cyclohexyl H), 3.86 (s, 3H, -NC<u>H</u>$_3$), 4.64 (s, 1H, -O<u>H</u>), 6.87 and 6.95 (d each, 1H each, imidazole H, J = 1 Hz each). 7.05 - 7.55 (m, 5H, benzene H). Anal. Calcd for $C_{18}H_{22}N_2O$: C, 76.99; H, 8.16; N, 9.45. Found: C, 77.43; H. 7.69; N, 9.57.

<u>General Procedure for Syntheses of α,β-Unsaturated Ketones (9) from 2-(1-Alkyl-1-hydroxy-2-alkenoyl)-1-methyl-1H-imidazoles (6) [Synthesis of Benzylideneacetophenone (9a) as an example]</u> ----- A solution of 2-(1,3-diphenyl-1-hydroxy-2-propenyl)-1-methyl-1H-imidazole (<u>6a</u>) (580 mg, 2 mmol) in ethyl acetate (10 ml) was refluxed for 2 h in the presence of dimethyl sulfate (277 mg, 2.2 mmol) followed by evaporation of the solvent. Benzene (4 ml) and 10 % K_2CO_3 (10 ml) were added to the viscous residue and the mixture was heated at 80 ℃ under a vigorous stirring and nitrogen atmosphere for 2 h. The resulting mixture was extracted several times with ethyl acetate. The organic layer was washed with water and 10 % HCl. A small amount of hydroquinone and drying reagent Na_2SO_4 were added and the solution was kept standing overnight. Evaporation of the solution gave a crystalline residue, which was purified by recrystallization from petroleum ether. Colorless needles. Yield, 368 mg (86.9 %). mp 56.0 - 57.0 ℃ [Lit. mp 57.0 - 58.0 ℃]. Ir (nujol): 1675 (C=C), 1615 cm^{-1} (C=O). [Lit. Ir (nujol): 1675, 1615 cm^{-1}].[5] ^{1}H-Nmr ($CDCl_3$) δ ppm: 7.00 - 8.20 (m, 12H, all protons). [Lit. ^{1}H-nmr ($CDCl_3$) δ ppm: 7.00 - 8.20 (m, 12H)].[5]

<u>3-(3,4-Methylenedioxyphenyl)-3-oxopropene (9b)</u> ----- In this case, the prepared imidazolium salt was stirred overnight in a two-layer mixture of 10 % K_2CO_3 and benzene at room temperature to yield <u>13b</u>, which was purified with column chromatography on silica gel (eluting solvent: Et_2O). Yield, 36.3 %. Colorless viscous material. Ir ($CHCl_3$): 1600 (C=C), 1670 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 5.87 (dd, 1H, -CH=(H)<u>H</u>, J = 12 Hz and 2 Hz), 6.39 (dd, 1H, -CH=C(H)<u>H</u>, J = 12 Hz and 2

Hz), 6.04 (s, 2H, -OCH$_2$O-), 6.75 - 7.60 (m, 4H, benzene H and -CH=CH$_2$). High-resolution ms: Calcd for $C_{10}H_8O_3$ = 176.0473. Found = 176.0495.

6,10-Dimethyl-4-oxo-2,9-undecadiene (9c) ----- Yield, 89.6 %. Cololess oil. bp_5 149.0 - 151.0 ℃. Ir ($CHCl_3$): 1623 (C=C), 1664 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.91 (d, 3H, CH$_3$CH-, J = 9 Hz), 1.00-1.50 (m, 3H, -CHCH$_2$CH$_2$CH=), 1.59 and 1.67 (s each, 3H each, (CH$_3$)$_2$C=), 1.89 (dd, 3H, CH$_3$CH=, J = 9 Hz and 1 Hz), 1.80-2.20 (m, 2H, -CH$_2$CH=), 2.41 (t, 2H, -CH$_2$CO-, J = 7 Hz), 5.09 (t, 1H, (CH$_3$)$_2$C=CH-, J = 6 Hz), 5.90 - 6.30 (m, 1H, -COCH=), 6.50 - 7.00 (m, 1H, CH$_3$CH=). High-resolution ms: Calcd for $C_{13}H_{22}O$ = 194.1669. Found = 194.1648.

2,6,10-Dimethyl-4-oxo-2,9-undecadiene (9d) ----- Yield, 81.3 %. Cololess oil. $bp_{4.5}$ 105.0 - 113.0 ℃. Ir ($CHCl_3$): 1620 (C=C), 1680cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.93 (d, 3H, CH$_3$CH-, J = 6 Hz), 1.05 - 1.45 (m, 3H, -CH(CH$_3$)CH$_2$CH$_2$CH=), 1.60 and 1.68 (s each, 3H each, (CH$_3$)$_2$C=), 1.88 and 2.14 (s each, 3H each, (CH$_3$)$_2$CH=), 1.27 - 2.50 (m, 4H, -CH$_2$CO- and -CH$_2$C=), 5.09 (t, 1H, (CH$_3$)$_2$CH=, J = 6 Hz), 6.06 (s, 1H, -COCH=). High-resolution ms: Calcd for $C_{14}H_{24}O$ = 208.1826. Found = 208.1844.

4-Oxo-2-decene (9e) ----- Colorless oil. Yield, 86.9 %. bp_{10} 75.0 - 87.0 ℃. Ir ($CHCl_3$): 1635 (C=C), 1670 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.87 (t, 3H, CH$_3$CH$_2$-, J = 6 Hz), 1.00 - 2.10 (m, 8H, CH$_3$(CH$_2$)$_4$-), 1.89 (dd, total 3H, CH$_3$CH=, J = 9 Hz and 1Hz), 2.51 (t, 2H, -CH$_2$CO-, J = 7 Hz), 5.80 - 6.45 (m, 1H, -COCH=), 6.50 - 7.05 (m, 1H, -COCH=CH-). High-resolution ms: Calcd for $C_{10}H_{18}O$ = 154.1357. Found = 154.1358.

3-Phenyl-1-cyclohexyl-1-oxo-2-propyne (12a) ----- Colorless oil. Yield, quant. bp_5 135.0 ℃. Ir ($CHCl_3$): 1660 (C≡C), 1705 (C=O), 2190 cm^{-1} (C≡C). ^{1}H-Nmr ($CDCl_3$) δ : 1.00 - 2.25 (m, 10H, -(CH$_2$)$_5$-), 2.25 - 2.70 (m, 1H, -CH-), 7.15 - 7.70 (m, 5H, benzene H). High-resolution ms: Calcd for $C_{15}H_{18}O$ = 212.1200. Found = 212.1177.

General Procedure for Preparations of 2-(1-Alkyl-1-hydroxy-3-alkenyl)-1-methyl-1H-imidazoles (13) from 2-Acyl-1-methyl-1H-imidazoles (1) and Allylic Halide (14)

[Preparation of 2-(1-Hydroxy-1-phenyl-3-butenyl)-1-methyl-1H-imidazole (13a) as an Example] ----- Iodine (trace) was added to a mixture (5 ml) containing magnesium metal (486 mg, 20 mgatom) and allyl chloride (14a) (70 μl) and THF (5 ml) under nitrogen atmosphere at 0 ℃. As soon as the color of iodine of the solution was disappeared, a THF solution (10 ml) of 2-benzoyl-1-methyl-1H-imidazole (1a) (930 mg,

5 mmol) and allyl chloride (14a) (765 mg, 10 mmol) was dropped slowly to the mixture at 0 ℃. The reaction mixture was stirred for 30 min at 0 ℃ followed by addition of water (2 ml). Ether and 10% HCl were added to the mixture. The ether layer was again extracted with 10% HCl. The combined aqueous layer was basified with solid K_2CO_3, and separated crystalline material was extracted with AcOEt. Evaporation of the solvent gave a crude crystalline residue. The product was purified by recrystallization from carbon tetrachloride. Colorless needles. Yield, 992 mg (87.0 %). mp 134.5 - 136.5 ℃. Ir ($CHCl_3$): 1638 (C=C), 3450 - 3100, 3530 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 2.84 (dd, 2H, $-\underline{CH_2}CH=CH_2$, J = 18 Hz and 8 Hz), 3.15 (br, 1H, OH), 3.32 (s, 3H, $-NCH_3$), 5.00 - 5.40 (m, 2H, $-CH=\underline{CH_2}$), 5.60 - 6.20 (m, 1H, $-\underline{CH}=CH_2$), 6.76 and 6.95 (d each, 1H each, imidazole H, J = 1 Hz each), 7.10 - 7.45 (m, 5H, benzene H). Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.18; H, 6.85; N, 12.26.

2-[1-Hydroxy-1-(3,4-methylenedioxyphenyl)-3-butenyl]-1-methyl-1H-imidazole (13b)---- Recrystallized from carbon tetrachloride. Colorless needles. Yield, 95.8 %. mp 164.5 - 166.0 ℃. Ir ($CHCl_3$): 1638 (C=C), 3020 - 3450, 3540 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 2.80 (d each, 2H, $-\underline{CH_2}CH=CH_2$, J = 18 Hz and 8 Hz), 3.13 (s, 1H, OH), 3.37 (s, 3H, $-NCH_3$), 5.00 - 5.35 (m, 2H, $-CH=\underline{CH_2}$), 5.60 - 6.20 (m, 1H, $-\underline{CH}=CH_2$), 5.93 (s, 2H, $-OCH_2O-$), 6.50 - 6.70 (m, 3H, benzene H), 6.82 and 6.93 (d each, 1H each, imidazole H, J = 1 Hz each). Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29. Found: C, 65.89; H, 5.82; N, 10.45.

2-(4-Hydroxy-6,10-dimethyl-1,9-undecen-4-yl)-1-methyl-1H-imidazole (13c) ----- Colorless viscous material. Yield, 89.1 %. Ir ($CHCl_3$): 1642 (C=C), 3050 - 3670 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 0.70 (d, 3H, $\underline{CH_3}CH-$, J = 6Hz), 0.85 - 1.45 (m, 3H, $-\underline{CH}(CH_3)\underline{CH_2}CH_2-$), 1.56 and 1.65 (s each, 3H each, $(\underline{CH_3})_2C=CH-$), 1.45 - 2.05 (m, 4H, $CH_2=CH\underline{CH_2}-$, $(CH_3)_2C=CH\underline{CH_2}-$, and $-\underline{OH}$), 2.30 - 3.10 (m, 2H, $-CH(CH_3)\underline{CH_2}C(OH)-$), 3.75 (s, 3H, $-NCH_3$), 4.80 - 5.25 (m, 3H, $\underline{CH_2}=CH-$ and $(CH_3)_2C=\underline{CH}-$), 5.50 - 6.10 (m, 1H, $CH_2=\underline{CH}-$), 6.77 and 6.99 (d each, 1H each, imidazole H, J = 1 Hz each). The nmr indicates that the product was formed in a diastereomeric mixture.

2-(8-Chloro-4-hydroxy-2-methyl-1-nonen-4-yl)-1-methyl-1H-imidazole (13d) ----- Recrystallization from n-hexane. Colorless needles. mp 74.0 - 75.0 ℃. Yield, 85.1 %. Ir ($CHCl_3$): 1622 (C=C), 3000 - 3600 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 1.49 (s, 3H,

$CH_3C(=CH_2)-$), 1.00 - 2.05 (m, 7H, $ClCH_2(CH_2)_3-$ and -OH), 2.35-3.85 (m, 2H, $-CH_2C(CH_3)=CH_2$), 3.48 (t, 2H, $ClCH_2-$, J = 7 Hz), 3.76 (s, 3H, $-NCH_3$), 4.50 - 4.85 (m, 2H, $-C=CH_2$), 6.76 and 6.89 (d each, 1H each, imidazole H, J = 1 Hz each). Anal. Calcd for $C_{13}H_{21}ClN_2O$: C, 60.81; H, 8.24; N, 10.91. Found: C, 60.94; H, 8.32; N, 11.01.

2-(1-Cyclohexyl-1-hydroxy-2-phenyl-3-butenyl)-1-methyl-1H-imidazole (13e) ----- Recrystallized from ethyl acetate. Colorless needles. Yield, 67.8 %. mp 172.0 - 173.0 ℃. Ir ($CHCl_3$): 1600 (C=C), 3010-3500, 3550 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 1.00 - 2.00 (m, 10H, $-(CH_2)_5-$), 2.50 - 3.25 (m, 2H, $-CHC(OH)CH-$), 3.34 (s, 1H, OH), 3.75 (s, 3H, $-NCH_3$), 5.80 - 6.60 (m, 3H, $-CH=CH_2$), 6.74 and 6.91 (d each, 1H each, imidazole H, J = 1 Hz each), 7.00 - 7.35 (m, 5H, benzene H). The nmr indicates that the product was formed in a diastereomeric mixture.

2-(4-Hydroxy-3-methyl-1-decen-4-yl)-1-methyl-1H-imidazole (13f) ----- Colorless viscous material. Yield, 76.5 %. Ir ($CHCl_3$): 1640 (C=C), 3450 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 0.50 - 1.50 (m, 14H, CH_3CH- and $CH_3(CH_2)_4-$), 1.60 - 2.00 (m, 2H, $-CH_2C(OH)-$), 2.40 - 2.90 (m, 1H, $CH_2=CHCH-$), 3.71 (s, 3H, $-NCH_3$), 3.98 (s, 1H, OH), 4.70 - 5.20 (m, 2H, $CH_2=CH-$), 5.45 - 6.20 (m, 1H, $CH_2=CH-$), 6.60 - 6.90 (m, 2H, imidazole H). The nmr indicates that the product was formed in a diastereomeric mixture.

2-(4-Hydroxy-3,3-dimethyl-1-decen-4-yl)-1-methyl-1H-imidazole (13g) ----- Recrystallized from ethyl acetate-n-hexane. Colorless needles. Yield, 87.1 %. mp 138.0 - 138.5 ℃. Ir ($CHCl_3$): 1635 (C=C), 3020 - 3650 cm^{-1} (OH). ^{1}H-nmr ($CDCl_3$) δ : 0.83 (t, 3H, $CH_3(CH_2)_7-$, J = 7 Hz), 1.07 and 1.03 (s each, 3H each, $(CH_3)_2C-$), 1.00 - 1.90 (m, 8H, $CH_3(CH_2)_4-$), 1.90 - 2.50 (m, 2H, $-CH_2C(OH)-$), 3.20 (br, 1H, OH), 3.76 (s, 3H, $-NCH_3$), 4.85-5.20 (m, 2H, $CH_2=CH-$), 5.25 - 6.20 (m, 1H, $CH_2=CH-$), 6.73 and 6.95 (d each, 1H each, imidazole H, J = 1 Hz each). Anal. Calcd for $C_{18}H_{28}N_2O$: C, 72.68; H, 10.67; N, 10.60. Found: C, 72.71; H, 10.96; N, 10.52.

General Procedure for Syntheses of α,β-Unsaturated Ketones (16) from 2-(1-Alkyl-1-hydroxy-3-alkenyl)-1-methyl-1H-imidazoles (13) via β,γ-Unsaturated Ketones (15) [Synthesis of 1-Phenyl-1-oxo-2-butene (16a) as an Example] ----- A solution of 2-(1-hydroxy-1-phenyl-3-butenyl)-1-methyl-1H-imidazole (13a) (456 mg, 2 mmol) in ethyl acetate (10 ml) was refluxed for 2 h in the presence of dimethyl sulfate (277 mg, 2.2 mmol) followed by evaporation of the solvent. Benzene (4 ml) and 10 % K_2CO_3 (10

ml) were added to the viscous residue, and the mixture was heated at 80 ℃ under a vigorous stirring and nitrogen atmosphere for 2 h. The reaction mixture was extracted several times with ethyl acetate. The organic layer was washed with water and 10 % HCl. The solvent was evaporated and the residual crude product (15a) was refluxed in benzene (10 ml) in the presence of a catalytic amount of p-TsOH under nitrogen atmosphere for 2 h. The solvent was evaporated after the reaction mixture was washed with water and dried over anhydrous Na_2SO_4. A crude product was purified by distillation under a reduced pressure. Yield, 258 mg (88.3 %). Colorless oil. bp_3 113.0-125.0 ℃. Ir ($CHCl_3$): 1622 (C=C), 1670cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 2.00 (d, 3H, CH_3CH=CH-, J = 5 Hz), 6.70 - 8.10 (m, 7H, -COCH=CH- and benzene H). The ^{1}H-nmr values were almost consistent with the reported values.[4]

1-(3,4-Methylenedioxyphenyl)-1-oxo-2-butene (16b) ----- The migration of the double bond of 13b easily proceeded without p-TsOH. The crude product was purified by a column chromatography on silica gel (eluting solvent: Et_2O). Colorless viscous material. Yield 73.7 %. Ir ($CHCl_3$): 1625 (C=C), 1670cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 1.97 (d, 3H, CH_3CH=CH-, J = 5 Hz), 6.03 (s, 3H, -OCH_2O-), 6.60 - 7.60 (m, 5H, -COCH=CH- and benzene H). High-resolution ms: Calcd for $C_{11}H_{10}O_3$ = 190.0629. Found = 190.0631.

6,10-Dimethyl-2,9-undecadien-4-one (9c) ----- Yield, 87.4 %. Cololess oil. bp_5 149.0 - 151.0 ℃. Ir ($CHCl_3$): 1623 (C=C), 1664 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.91 (d, 3H, CH_3CH-, J = 9 Hz), 1.00-1.50 (m, 3H, -CHCH_2CH_2CH=), 1.59 and 1.67 (s each, 3H each, $(CH_3)_2$C=), 1.84 and 1.93 (d each, 3H, CH_3CH=, J = 1 Hz each), 1.80-2.20 (m, 2H, -CH_2C=), 2.41 (t, 2H, -CH_2CO-, J = 7 Hz), 5.09 (t, 1H, $(CH_3)_2$C=CH-, J=6Hz), 5.90 - 6.30 (m, 1H, -COCH=), 6.50 - 7.00 (m, 1H, CH_3CH=). High-resolution ms: Calcd for $C_{13}H_{22}O$ = 194.1669. Found = 194.1648.

8-Chloro-2-methyl-4-oxo-2-octene (16d) ----- Yield, 94.5 %. Colorless oil. bp_3 85.0 - 95.0 ℃. Ir ($CHCl_3$): 1620 (C=C), 1682 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 1.50 - 2.00 (m, 4H, $ClCH_2(CH_2)_2$-), 1.89 and 2.15 (s each, 3H each, $(CH_3)_2$C=C-), 2.44 (t, 2H, -$COCH_2$-, J = 6 Hz), 3.54 (t, 2H, $ClCH_2$-, J = 6 Hz), 5.95 - 6.10 (m, 1H, -COCH=C-). High-resolution ms: Calcd for $C_9H_{15}ClO$ = 174.0809. Found = 174.0805.

1-Cyclohexyl-2-phenyl-1-oxo-2-butene (16e) ----- Purified by column chromatography on silica gel (eluting solvent: Et_2O : n-hexane = 1 : 9). Colorless viscous

material. Yield, quant. Ir ($CHCl_3$): 1620 (C=C), 1680 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 1.00 - 2.00 (m, 10H, methylene of cyclohexyl group), 1.73 (d, 3H, $\underline{CH_3}CH$=C-, J = 7 Hz), 2.75 (br, 1H, -COC$\underline{H}$-), 6.89 (q, 1H, $CH_3C\underline{H}$=C-, J = 7 Hz), 6.95-7.45 (m, 5H, benzene H). High-resolution ms: Calcd for $C_{16}H_{20}O$ = 228.1513. Found = 228.1518.

3-Methyl-4-oxo-2-decene (16f) ----- Colorless oil. Yield, 91.1 %. bp_3 80.0 - 88.0 ℃. Ir ($CHCl_3$): 1660 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.88 (t, 3H, $\underline{CH_3}CH_2$-, J = 5 Hz), 1.00 - 2.00 (m, 14H, $CH_3(\underline{CH_2})_4$- and -C($\underline{CH_3}$)C=CH($\underline{CH_3}$)), 2.63 (t, 2H, -$\underline{COCH_2}$-, J = 7 Hz), 6.50-6.85 (m, 1H, C$\underline{H}$(CH_3)=C(CH_3)-). High-resolution ms: Calcd for $C_{11}H_{20}O$ = 168.1512. Found = 168.1493.

3,3-Dimethyl-4-oxo-1-decene (15g) ----- Colorless oil. Yield, quant. bp_3 65.0 - 80.0 ℃. Ir ($CHCl_3$): 1638 (C=C), 1708 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 0.87 (t, 3H, $\underline{CH_3}CH_2$-, J = 7 Hz), 1.00-1.75 (m, 8H, $CH_3(\underline{CH_2})_4$-), 1.21 (s, 6H, $(\underline{CH_3})_2$C-), 2.44 (t, 2H, -$\underline{COCH_2}$-, J = 7 Hz), 4.95-5.25 (m, 2H, -CH=C$\underline{H_2}$), 5.65-6.10 (m, 1H, -C$\underline{H}$=CH_2). High-resolution ms: Calcd for $C_{12}H_{22}O$ = 182.1668. Found = 182.1668.

1-Cyclohexyl-1-hydroxy-2-phenyl-2-butene (18) ----- A solution of 1-cyclohexyl-2-phenyl-1-oxo-butene (16e) (134 mg, 0.58 mmol) in THF (12 ml) was slowly dropped to a THF containing of $LiAlH_4$ (10 mg, 0.25 mmol) at 0 ℃ under nitrogen atmosphere. The mixture was stirred for 1 h, and then water (1 ml), 10 % HCl and Et_2O were added. The separated organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified with ptlc on silica gel (eluting solv.: ethyl acetate: n-hexane = 1:3). Yield 131 mg (97.0 %). Viscous material. Ir ($CHCl_3$): 3640 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ ppm: 1.55 (d, 3H, CH_3CH=, J = 8 Hz), 0.50 - 2.00 (m, 12H, cyclohexyl and -O$\underline{H}$), 3.95 (br, 1H, -C$\underline{H}$(OH)-), 5.72 (q, 1H, -C$\underline{H}$=C-, J = 7 Hz), 7.00 - 7.50 (m, 5H, benzene). High-resolution ms: Calcd for $C_{18}H_{22}O$ = 230.1670. Found = 230.1700.

2-Acetyl-1-methyl-4(or 5)-[1-hydroxy-1-(4-methylphenyl)-1-ethyl]-1H-imidazole (17) ----- 2-Acetyl-1-methyl-1H-imidazole (1g) (3.10 g, 25 mmol) was dropped to a lithium diisopropylamide (LDA) solution in THF (60 ml), prepared from n-BuLi (19.2 ml, 30 mmol), diisopropylamine (4.20 ml, 30 mmol) according to the usual manner. The reaction mixture was stirred for 20 min, and 4-methylacetophenone (2.68 g, 20 mmol) was

added. The mixture was stirred for 1 h, and then ether and 10% HCl were added to the reaction mixture at 0 ℃. The organic layer was extracted with 10 % HCl. The combined aqueous layer was washed with ether and basified with solid K_2CO_3. A separated viscous material was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated in vacuo. The obtained crystalline residue was purified by recrystallization from ethyl acetate. Colorless needles. Yield, 1.94 g (30.1 %). mp 194.0 - 195.0 ℃. Ir ($CHCl_3$): 3580 cm^{-1}, 3510 - 3080 cm^{-1} (OH), 1670 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ ppm: 1.92 (s, 3H, $C\underline{H}_3C(OH)$-), 2.33 (s, 3H, $C\underline{H}_3C_6H_4$-), 2.66 (s, 3H, $C\underline{H}_3CO$-), 2.93 (s, 1H, -O<u>H</u>), 3.62 (s, 3H, -$NC\underline{H}_3$), 7.15 (s like, 5H, benzene and imidazole H). High-resolution ms: Calcd for $C_{15}H_{18}N_2O_2$ = 258.1367. Found = 258.1377.

<u>2-[3-(4-Methylphenyl)-2-acryroyl]-1-methyl-1H-imidazole (1h)</u> ----- A methanolic (20 ml) solution consisting of 2-acetyl-1-methyl-1H-imdazole (1g) (2.48 g, 20 mmol), p-tolualdehyde (2.40 g, 20 mmol) and sodium hydroxide (800 mg, 20 mmol) was stirred overnight under nitrogen atmosphere at room temperature. Ethyl acetate was added to the residue after evaporation of methanol. The solution was washed with water several times, dried over anhydrous Na_2SO_4, and evaporated under a reduced pressure. The obtained crystalline residue was recrystallized from n-hexane. Colorless needles. Yield, 4.52 g (quant.). mp 85.5 - 86.5 ℃. Ir ($CHCl_3$): 1661 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 2.37 (s, 3H, $C\underline{H}_3Ph$-), 4.08 (s, 3H, -NCH_3), 6.95 - 7.98 (m, 8H, imidazole H, benzene H and vinylic proton). Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.28; H, 6.18; N, 12.39.

<u>2-[3-(4-Methylphenyl)butanoyl]-1-methyl-1H-imidazole (1i)</u> ----- 1.5M MeLi (13.3 ml, 20 mmol) was added to a slurry of copper(I) iodide (2.10 g, 11 mmol) in ether (20 ml) under nitrogen atmosphere at 0 ℃.[10] The mixture was stirred until a homogeneous solution was obtained. The ethereal Me_2CuLi solution was slowly dropped into an ethereal solution (20 ml) of 2-[3-(4-methylphenyl)acryroyl]-1-methyl-1H-imidazole (1h) (1.13 g, 5 mmol) at 0 ℃, and the reaction mixture was stirred for 30 min. The mixture was quenched with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford an oily

residue. The product was purified by column chromatography on silica gel (eluting solvent: ethyl acetate), and the obtained oily product was distilled under a reduced pressure. Colorless oil. Yield, 1.01 g (83.7 %). bp_3 187.0 - 192.0 ℃. Ir ($CHCl_3$): 1680 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 1.29 (d, 3H, $C\underline{H}_3CH$(tolyl)CH_2-, J = 7 Hz), 2.28 (s, 3H, $C\underline{H}_3C_6H_5$-), 3.20 - 3.60 (m, 3H, -$COC\underline{H}_2C\underline{H}(CH_3)$-), 3.98 (s, 3H, -$NC\underline{H}_3$), 6.80 - 7.30 (m, 6H, imidazole H and benzene H). High-resolution ms: Calcd for $C_{15}H_{18}N_2O$ = 242.1428. Found = 242.1432.

2-[4-Hydroxy-6-methy-2-(4-methylphenyl)-6-hepten-4-yl]-1-methyl-1H-imidazole (13i) ---- A THF solution (4 ml) of 2-[3-(4-methylphenyl)butanoyl]-1-methyl-1H-imidazole (1i) (968mg, 4mmol) and methally chloride (14b) (398mg, 4.4mmol) was added to a mixture of magnesium metal (194 mg, 8 mgatom) and methallyl chloride (14b) (40 μl) and THF (4 ml) according to the procedure as described in the preparation of 2-(1-hydroxy-1-phenyl-3-butenyl)-1-methyl-1H-imidazole (15a). Colorless viscous material was obtained by a column chromatography on silica gel of the crude product (eluting solvent: $CHCl_3$: MeOH = 20 : 1). Yield, 998 mg (83.7 %). Ir ($CHCl_3$): 3560 cm^{-1} (OH). ^{1}H-Nmr ($CDCl_3$) δ : 0.90 - 1.60 (m, 6H, $C\underline{H}_3CH$(tolyl)- and $C\underline{H}_3C(=CH_2)$-), 1.95 - 3.10 (m, 9H, $C\underline{H}_3C_6H_5$-, $CH_3C\underline{H}$(tolyl)-, -$C\underline{H}_2C(OH)C\underline{H}_2$-, and and OH), 3.23 and 3.63 (s each, total 3H, -$NC\underline{H}_3$), 4.50 - 4.90 (m, 2H, $CH_3C(=C\underline{H}_2)$-), 6.35 - 7.30 (m, 6H, benzene H and imidazole H). The nmr spectrum indicates that the product was formed in a diastereomeric mixture.

dl-(ar)-Turmerone (16i) ----- The ketone (16i) was obtained starting from 2-[4-hydroxy-6-methyl-2-(4-methylphenyl)-6-hepten-4-yl]-1-methyl-1H-imidazole (13i) (894 mg, 3 mmol) by the similar procedure as used for the preparation of 1-phenyl-1-oxo-2-propene (16a). Colorless oil. Yield, 605 mg (93.3 %). bp_5 117.0 ℃. Ir ($CHCl_3$): 1620 (C=C), 1688 cm^{-1} (C=O). ^{1}H-Nmr ($CDCl_3$) δ : 1.24 (d, 3H, $C\underline{H}_3CH$(tolyl)-, J = 7 Hz), 1.84 and 2.10 (d each, 3H each, $(C\underline{H}_3)_2C$=CH-, J = 1 Hz each), 2.30 (s, 3H, -$C\underline{H}_3C_6H_5$-), 2.50 - 2.70 (m, 2H, -$COC\underline{H}_2$-), 3.00 - 3.50 (m, 1H, -$C\underline{H}$(tolyl)-), 5.85 - 6.05 (m, 1H, -$COC\underline{H}$=C-), 7.09 (br, 4H, benzene H). The nmr date is almost consistent with the reported.[7] High-resolution ms: Calcd for $C_{15}H_{20}O$ = 216.1513. Found = 216.1527.

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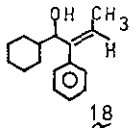
9 The stereochemistry of 16e is presumed to be Z-form because ^{1}H-nmr of the corresponding alcohol 18 (prepared by reduction of 16e with $LiAlH_4$; see experimental section) shows signals of the vinylic proton at 5.72 ppm. The chemical sift is nearly equal to the expected value (5.73 ppm), which is caluculated on the basis of the Pascual equation [C. Pascual, J. Meier, W. Simon, Helv. Chim. Acta, 49, 64 (1966)]. The caluculated value for E-18 is 5.36 ppm.



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