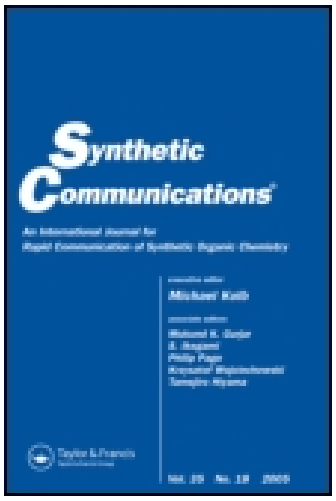

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

AN IMPROVED METHOD FOR SYNTHESIS OF 1-BENZOPYRANS FROM UNSATURATED ALCOHOLS AND PHENOLS USING A CATALYTIC AMOUNT OF ACIDS

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Published online: 09 Nov 2006.

To cite this article: Yoshio Ishino, Masatashi Mihara, Noboru Hayakawa, Tatsuya Miyata, Yoichi Kaneko & Toshiyuki Miyata (2001) AN IMPROVED METHOD FOR SYNTHESIS OF 1-BENZOPYRANS FROM UNSATURATED ALCOHOLS AND PHENOLS USING A CATALYTIC AMOUNT OF ACIDS, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:3, 439-448, DOI: 10.1081/SCC-100000537

To link to this article: http://dx.doi.org/10.1081/SCC-100000537

SYNTHETIC COMMUNICATIONS, 31(3), 439–448 (2001)

AN IMPROVED METHOD FOR SYNTHESIS OF 1-BENZOPYRANS FROM UNSATURATED ALCOHOLS AND PHENOLS USING A CATALYTIC AMOUNT OF ACIDS

Yoshio Ishino,* Masatashi Mihara, Noboru Hayakawa, Tatsuya Miyata, Yoichi Kaneko, and Toshiyuki Miyata

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ABSTRACT

1-Benzopyrans, such as chromans and chromenes, were prepared in good to excellent yields by using a catalytic amount of *p*-toluenesulfonic acid through intermolecular cyclization reaction of phenols with unsaturated alcohols in 1,2-dichlroroethane.

Recently, much attention has been paid to the development of new methods for the synthesis of heterocyclic compounds, due to their potential importance in the fields of pharmaceutical and agricultural drugs. The 1-benzopyran ring system constitutes the basic skeleton of a variety of natural compounds that show interesting biological activities (1,2). The direct synthesis of these compounds based on the reaction of phenols with unsaturated compounds, such as allylic alcohols, isoprene, dienes, and halides, are reported in the literature, including a) an

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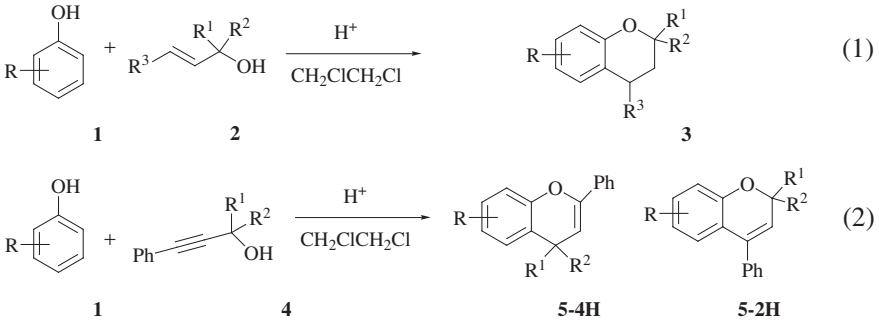
acid and base catalyzed condensation (3–7), b) metal-catalyzed ring closure (8–12), and c) comprehensive Lewis acid catalyzed methods (13–17). Many other reagents, such as isoprene, prenyl halides, 1,3-dichloro-3-methyl-butane, and so on, were also used for such a process (18–22). Although the acid catalyzed condensation and its modified versions represent a highly effective and classical method, the use of large excess of acids, their low yields, and multistep procedures have all encouraged the development of processes using a catalytic amount of acids.

In the course of our investigations on the intermolecular cycloaddition via allylic cations, we described new and convenient synthesis of benzothiopyrans and benzothiepins by the reactions of allylic alcohols and thiophenols (23–25). Now, we report here by a catalytic amount of acids, very convenient and regioselective one-pot synthesis of 2H-1-benzopyrans, such as chromans **3** (3,4-dihydro-2H-1-benzopyrans) and chromenes **5** (2H- and 4H-1-benzopyrans), through intermolecular cyclization by the reaction of allylic alcohols **2** or proparglic alcohols **4** with phenols **1**, respectively [Eqs. (1) and (2)]. Compared with the conventional methods for synthesis of **3** and **5**, this reaction involves only one step using a catalytic amount of acids in 1,2-dichlroroethane.



(1)

1 **2** **3**

(2)

1 **4** **5-4H** **5-2H**

1: R = H, Alkyl, Phenyl, or Cl
2 and **4**: $R^1 = R^2 = R^3$ = H, Alkyl, or Phenyl

RESULTS AND DISCUSSION

The reactions usually were carried out at reflex temperature for 4 h in anhydrous dichlroroethane containing a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH), phenols, and unsaturated alcohols. Detailed studies on the reaction of 2-methyl-3-buten-2-ol (**2a**) with *p*-cresol (**1b**) to 2,2-dimethyl-6-methylchroman (**3b**) showed that this catalytic intermolecular cycloaddition is considerably influenced by the solvents used, kinds of acids, and the molar ratio of acids to **1b**, as shown in Table 1.

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Table 1. Reactions of *p*-Cresol (**1b**) and 2-Methyl-3-butene-2-ol (**2a**) in the Presence of Acids

Entry	Acids (mol. eq.)	Solvents	**3b** Yield (%)[a]
1	None	$ClCH_2CH_2Cl$	0
2	*p*-TsOH (0.250)	$ClCH_2CH_2Cl$	72
3	*p*-TsOH (0.150)	$ClCH_2CH_2Cl$	73
4	*p*-TsOH (0.050)	$ClCH_2CH_2Cl$	90
5	*p*-TsOH (0.025)	$ClCH_2CH_2Cl$	81
6	*p*-TsOH (0.050)	THF	0
7	*p*-TsOH (0.050)	DMF	0
8	H_2SO_4 (0.100)	$ClCH_2CH_2Cl$	32
9	$ZnCl_2$(1.5)	$ClCH_2CH_2Cl$	22[b]
10	$AlCl_3$ (1.5)	$ClCH_2CH_2Cl$	29

[a] Isolated yield.
[b] 4-Methyl-2-prenylphenol was additionally obtained in the yield of 47%.

Noteworthy is the fact that the reaction in the absence of *p*-TsOH did not give any of **3b**, whereas the presence of a catalytic amount (0.050 mol. eq.) of *p*-TsOH caused a smooth reaction to give the intermolecular cycloadditon product **3b** in good to excellent yields. To our knowledge, the direct condensation of phenols and olefins, using a catalytic amount of acids has not been reported. The direct formation of chromans from phenols usually was carried out with large excess of acids and/or with strong acids because of the high threshold of acidity required for the benzopyran formation (3–7). As shown in Table 1, the optimum reaction condition for the formation of **3b** is attained when the molar ratio of **1a**:**2b**:*p*-TsOH is 1:30:0.05. 1,2-Dichloroethane is the best choice of solvents.

The direct condensation between phenols and allylic alcohols gave regioslectively only one type of product **3**. On the other hand, the reactions with propargylic alcohols led to regioisomeric mixtures of **5-2H** and **5-4H** chromenes. A molar ratio of **2H**- to **4H**-isomer (**2H/4H**) was determined by means of ^{1}H NMR and GLC analyses. Representative examples are given in Tables 2 and 3.

A combination of a catalytic amount of *p*-TsOH and 1,2-dichloroethane has been found to promote the catalytic transformation of various phenols with unsaturated alcohols, such as allylic alcohol (**1a**) and propargylic alcohols (**1b**), to the corresponding cyclo-condensation products, such as substituted chromans **3** and chromenes **4**, under mild reaction conditions, respectively. Several comments are worth nothing. 1) Phenols with electron-donating groups at their para-position reacted more smoothly with **1** than the phenols with electron-withdrawing groups; 2) 2,2-dimethylchroman (**3a**) was obtained as a single isomer from both of the reactions of 2-methyl-3-buten-2-ol (**2a**) and 3-methyl-2-buten-1-ol (**2b**) with

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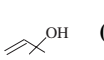
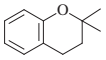
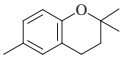
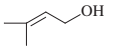
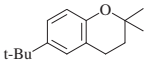
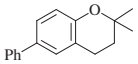
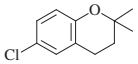
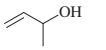
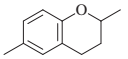
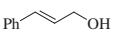
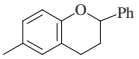
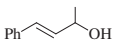
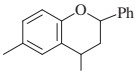
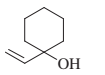
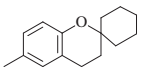
Table 2. Acid-Catalyzed Reactions of Allylic Alcohols (**2**) with Phenols (**1**)[a]

Entry	Phenols (**1**)	Allylic Alcohols (**2**)	Chromans (**3**)	Yield (%)[b]
1	C_6H_5OH (**1a**)	 **(2a)**		**3a** (48)[c]
2	*p*-MeC_6H_4OH (**1b**)	**2a**		**3b** (90)
3	**1b**	 **(2b)**		**3b** (66)
4	*p*-*tert*-BuC_6H_4OH (**1c**)	**2a**		**3c** (84)
5	*p*-PhC_6H_4OH (**1d**)	**2a**		**3d** (74)
6	*p*-ClC_6H_4OH (**1e**)	**2a**		**3e** (70)
7	**1b**	 **(2c)**		**3f** (53)
8	**1b**	 **(2d)**		**3g** (72)
9	**1b**	 **(2e)**		**3h** (61)
10	**1b**	 **(2f)**		**3i** (61)

[a] *p*-Toluenesulfonic acid (0.01 g; 0.05 eq. mol based on **1**) was used.
[b] Isolated yield.
[c] *p*-Prenylphenol was also obtained in 31% yield.

Table 3. Reaction of Alkynols and Phenols in the Presence of *p*-Toluenesulfonic Acid[a]

Run	Phenols (**1**)	R^1 and R^2 in **4**	Yield of **5** (%)[b]	Ratio of **5-2H/5-4H**
a	H C_6H_4OH (**1a**)	$R^1 = R^2 =$ Me (**4a**)	**5a** (9)[c]	0/1
b	*p*-CH_3 C_6H_4OH (**1b**)	**4a**	**5b** (76)	1/2
c	*m*-CH_3 C_6H_4OH (**1c**)	**4a**	**5c** (25)	0/1
d	*p*-MeO C_6H_4OH (**1d**)	**4a**	**5d** (65)	1/1
e	*p*-*tert*-butyl C_6H_4OH (**1e**)	**4a**	**5e** (49)	0/1
f	2-$C_{10}H_7OH$ (**1g**)	**4a**	**5g** (67)	1/0
g	**1b**	$R^1 =$ Me, $R^2 =$ Et (**4b**)	**5h** (64)	2/1
h	**1b**	$R^1 = R^2 =$ H (**4d**)	**5j** (53)	1/0

[a] *p*-Toluenesulfonic acid (0.01 g; 0.05 eq. mol based on **1**) was used as an acid catalyst.
[b] Isolated yield.
[c] *p*-Prenylphenol was also obtained in 31% yield.

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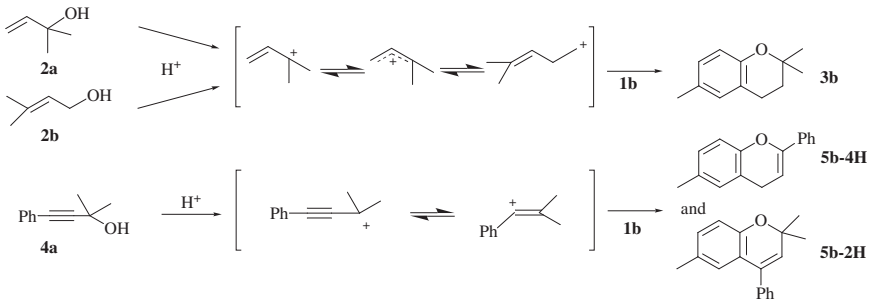
p-cresol (Table 2, runs 2 and 3); 3) 1- and 3-substituted allylic alcohols (such as **2a** and **2b**) were easily reacted with phenols to give the corresponding substituted benzopyrans (**3a–g**); on the other hand, allyl alcohol and 2-substituted allylic alcohols, such as 2-methyl-2-propen-1-ol, did not give any corresponding cycloaddition products; 4) propargyl alcohols **4** reacted smoothly with phenols under the same reaction conditions to give the corresponding chromenes (**5a–j**) as a isomeric mixtures in good yields; 5) the **4H** isomer was obtained as a major isomer.

Although the details concerning the mechanism still remain ambiguous, the reaction may proceed through cation intermediates, such as allylic or propargylic (and/or allenic) cations, which are generated from the reaction of the hydroxyl groups of allylic alcohols or propargylic alcohols with acids, respectively. These cation intermediates gave the products **3** or **5** through a subsequent cross-cyclic addition with the phenols. For analogous cycloaddition, see Ref. (26).



Scheme 1.

In conclusion, the present method of using a catalytic amount of acid and easily available unsaturated alcohols and phenols is characterized by high operational simplicity and mild reaction conditions. These reactions provide a route to prepare cyclo products with high regioselectively in good-to-moderate yields. We believe that this cross-cycloaddition offers one of the most simple and convenient methods.

EXPERIMENTAL

General. The ^{1}H and ^{13}C NMR spectra were obtained with JEOL-JNM-EX270 spectrometers in $CDCl_3$ solutions. The chemical shifts are expressed in ppm downfield from TMS in δ units. The GCMS spectra were recorded on a JEOL-JMS-DX303-HF spectrometer. The IR spectra were measured with a Shimadzu

IR-435 spectrometer in liquid film. Silica gel $60F_{254}$ (Merck) was used for TLC and Silica gel 60 (Merck) was used for column chromatography.

Materials. 1,2-Dichloroethane and DMF were freshly distilled prior to use. THF was freshly distilled from a sodium/benzophenone mixture prior to use. TMSCl was freshly distilled prior to use. Commercially available phenols, alcohols, and acids were used without further purification. Some of the alcohols were prepared from the corresponding carbonyl compounds and Grignard reagents according to the Ref. (27).

General Procedure for the Preparation of Chromans from Phenols and Allylic Alcohols in the Presence of a Catalytic Amount of *p*-Toluene Sulfuric Acid. To a mixture of 2-methyl-3-buten-2-ol (**2a**, 86 mg, 10.0 mmol) and *p*-toluenesulfonic acid (100 mg, 0.05 mmol) in dry dichloroethane (20 mL) was added dropwise a dichloroethane solution (15 mL) of *p*-cresol (**1b**, 3.24 g, 300 mmol), and the mixture was stirred under a nitrogen atmosphere for 1 h at room temperature. The reaction mixture was then stirred for an additional 4 h at reflex temperature. The reaction mixture was then poured into 200 mL of saturated aqueous ammonium chloride solution and the crude reaction products were extracted using three 100-mL portions of ether. The combined ethereal solution was washed with a 100-mL portion of water, and then dried over anhydrous magnesium sulfate. After removing the drying agent by filtration, the solvent was evaporated by distillation. Then the crude product was purified by silica-gel column chromatography to give 2,2,6-trimethylchroman (**3b**) in a yield of 90% as an oil.

General Procedure for the Preparation of Chromenes from Phenols and Propargyl Alcohols in the Presence of a Catalytic Amount of *p*-Toluene Sulfuric Acid. To a mixture of 2-methyl-4-phenyl-3-butyn-2-ol (**4a**, 80 mg, 5.0 mmol) and *p*-toluenesulfonic acid (500 mg, 3 mmol) in dry dichloroethane (20 mL) was added dropwise a dichloroethane solution (20 mL) of *p*-cresol (**1b**, 1.64 g, 150 mmol) under a nitrogen atmosphere at room temperature. The reaction mixture was then stirred for additional 4 h at reflex temperature. The reaction mixture was then poured into 200 mL of saturated aqueous ammonium chloride solution and the crude reaction products were extracted using three 100-mL portions of ether. The combined ethereal solution was washed with a 100-mL portion of water, and then dried over anhydrous magnesium sulfate. After removing the drying agent by filtration, the solvent was evaporated by distillation. The crude product was purified by the silica-gel column chromatography, to give 2-phenyl-4,4,6-trimethyl-2-chromene (**5a**) and 2,2,6-trimethyl-4-phenyl-3-chromene (**5a**) in a yield of 52 and 24%, respectively.

All new compounds, **3** and **5** prepared in this study were identified by ^{1}H and ^{13}C NMR, IR, and MASS spectroscopies.

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6-*tert*-Butyl-2,2-dimethylchroman (3c). Oil; IR (neat) 3000, 1500, 1385, 1395, 1160, 1210, 1115, 950, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (9H, s), 1.29 (6H, s), 1.78 (2H, t, $J = 9.0$ Hz), 2.73 (2H, t, $J = 9.0$ Hz), 6.92 (3H, m); HRMS calcd for $C_{15}H_{22}O$: 218.1671. Found: 218.1675.

2,2-Dimethyl-6-phenylchroman (3d). Oil; IR (neat) 2900, 1480, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (6H, s), 1.72 (2H, t, $J = 7.2$ Hz), 2.73 (2H, t, $J = 7.2$ Hz), 7.1 (3H, m); HRMS calcd for $C_{17}H_{18}O$: 238.1358. Found: 238.1353.

6-Chloro-2,2-dimethylchroman (3e). Oil; IR (neat) 3000, 1480, 1260, 1120, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (6H, s), 1.85 (2H, t, $J = 9.0$ Hz), 2.83 (2H, t, $J = 9.0$ Hz), 7.1 (3H, m); HRMS calcd for $C_{11}H_{13}ClO$: 196.0655. Found: 196.0660.

6-Acetyl-2,2-dimethylchroman (3f). Oil; IR (neat) 2900, 1670, 1260, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (6H, s), 1.80 (2H, t, $J = 7.2$ Hz), 2.49 (3H, s), 2.80 (2H, t, $J = 7.2$ Hz), 6.76 (1H, s), 7.7 (2H, m); HRMS calcd for $C_{11}H_{14}O$: 162.1045. Found: 162.1049.

6-Methyl-2-phenylchroman (3g). Oil; IR (neat) 3000, 1500, 1250, 1230, 815, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (2H, m), 2.23 (3H, s), 2.77 (2H, t $J = 7.2$ Hz), 3.73 (2H, d, $J = 3.6$ Hz), 5.00 (1H, q, $J = 7.2$ Hz), 7.0 (8H, m); HRMS calcd for $C_{16}H_{16}O$: 224.1201. Found: 224.1207.

2,6-Dimethyl-4-phenylchroman (3h). Oil; IR (neat) 2900, 1490, 1240, 1230, 815, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (3H, d, $J = 7.2$ Hz), 2.00 (2H, m), 2.27 (3H, s), 5.00 (1H, m), 5.04 (1H, m), 7.08 (8H, m); HRMS calcd for $C_{17}H_{18}O$: 238.1358. Found: 238.1364.

6-Methylchroman-2-spiro-cyclohexane (3i). Oil; IR (neat) 3000, 1500, 1240, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6 (10H, m), 2.38 (2H, t, $J = 9.0$ Hz), 2.25 (3H, s), 2.72 (2H, t, $J = 9.0$ Hz), 6.8 (3H, m); HRMS calcd for $C_{15}H_{20}O$: 216.1514. Found: 216.1510.

4,4-Dimethyl-2-phenyl-4H-chromene (5a-4H). Oil; IR 2940, 1670, 1325 cm^{-1}, 1045; ^1H NMR ($CDCl_3$) δ 1.46 (6H, s), 5.31 (1H, s), 7.4 (9H, m); HRMS calcd for $C_{11}H_{14}O$: 236.1201. Found: 236.1207.

2,2,6-Trimethyl-4-phenyl-2H-chromene (5b-2H). Oil; IR (neat) 3000, 1500, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (6H, s), 2.18 (3H, s), 5.58 (1H, s), 7.0 (8H, m); HRMS calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1351.

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4,4,6-Trimethyl-2-phenyl-4H-chromene (5b-4H). Oil; IR (neat) 2950, 1670, 1570, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (6H, s), 2.30 (3H, s), 5.29 (1H, s), 7.4 (8H, m); ^{13}C NMR ($CDCl_3$) δ 20.7, 30.5, 31.7, 33.0, 107.2, 116.0, 124.4, 126.4, 127.7, 128.8, 129.0, 132.2, 134.4, 146.2, 148.2; HRMS calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1364.

4,4,5-Trimethyl-2-phenyl-4H-chromene (5c-4H). Oil; IR (neat) 2950, 1670, 1570, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (6H, s), 2.31 (3H, s), 5.31 (1H, s), 7.4 (8H, m); HRMS calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1351.

4,4-Dimethyl-6-methoxy-2-phenyl-4H-chromene (5d-4H). Oil; IR 2930, 1665, 1295, 1045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (6H, s), 3.74 (3H, s), 5.26 (1H, s), 7.4 (8H, m); HRMS calcd for 266.1307. Found: 266.1312.

2,2-Dimethyl-6-methoxy-4-phenyl-2H-chromene (5d-2H). Oil; IR 2950, 1570, 1485, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (6H, s), 3.63 (3H, s), 5.63 (1H, s), 7.4 (8H, m); HRMS calcd for $C_{18}H_{18}O_2$: 266.1307; Found: 266.1303.

6-*tert*-Butyl-4,4-dimethyl-2-phenyl-4H-chromene (5e-4H). Oil; IR (neat) 2930, 1665, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (9H, s), 1.45 (6H, s), 5.28 (1H, s), 7.4 (8H, m); HRMS calcd for $C_{21}H_{24}O$: 292.1827. Found: 292.1832.

2,2-Dimethyl-4-phenyl-2H-naptho[2,1,-*b*]pyran (5g-2H). Oil; IR 2950, 1710, 1625, 1140, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (6H, s), 5.67 (1H, s), 7.4 (11H, m); HRMS calcd for $C_{21}H_{18}O$: 286.1358. Found: 286.1352.

4,6-Dimethyl-4-ethyl-2-phenyl-4H-chromene (5h-4H). Oil; IR 2950, 1670, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (3H, t, $J = 7.6$ Hz), 1.44 (3H, s), 1.81 (2H, q, $J = 7.6$ Hz), 2.32 (3H, s), 5.13 (1H, s), 7.4 (8H, m); HRMS calcd for $C_{19}H_{20}O$: 264.1514. Found: 264.1510.

2,6-Dimethyl-2-ethyl-4-phenyl-2H-chromene (5h-2H). Oil; IR 2950, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (3H, t, $J = 7.6$ Hz), 1.42 (3H, s), 1.76 (2H, q, $J = 7.6$ Hz), 2.17 (3H, s), 5.54 (1H, s), 7.4 (8H, m); HRMS calcd for $C_{19}H_{20}O$: 264.1514. Found: 264.1512.

6-Methyl-4-phenyl-2H-chromene (5j-2H). Oil; IR; ^1H NMR ($CDCl_3$) δ 2.25 (3H, s), 3.56 (2H, d, $J = 7.3$ Hz), 5.84 (1H, t, $J = 7.3$ Hz), 7.2 (8H, m); HRMS calcd for $C_{16}H_{14}O$: 222.1045. Found: 222.1049.

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Received in Japan March 17, 2000

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