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Diene-Transmissive Hetero Diels-Alder Reactions of 3-Oxo-1,4-pentadiene Equivalents Leading to Functionalized 2-Chromanones

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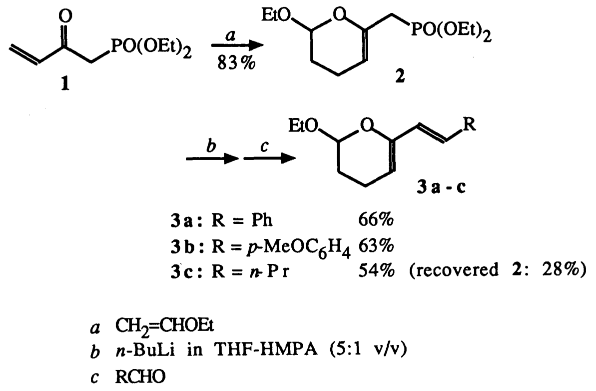
Through hetero Diels-Alder reaction with a vinyl ether and Horner-Emmons olefination, diethyl 2-oxo-3-butenylphosphonate leads to 2-ethoxy-6-(1-alkenyl)-3,4-dihydro-2*H*-pyrans which are further transformed into 2-chromanones via regioselective Diels-Alder reactions with activated acetylenes followed by hydrolysis and oxidation.

Diene-transmissive Diels-Alder reactions of cross-conjugated trienes offer a direct and stereoselective synthetic route to highly functionalized hydronaphthalene skeletons.[1] The cross type of reactions with activated trienes[2] as well as the reaction sequences with some cross-conjugated triene equivalents[3] has been also developed.

In the preceding article we have opened a new synthetic route of diethyl 2-oxo-3-alkenylphosphonates which can be successfully applied to regioselective Diels-Alder reactions with vinyl ethers to give 4-substituted 2-alkoxy-6-[(diethoxyphosphinyl)methyl]-3,4-dihydro-2*H*-pyrans.[4] As these pyrans have an allylphosphonate functionality, they should be transformed into 1,3-dienes by a Horner-Emmons olefinations.[5] Diels-Alder reactions of the resulting 6-(1-alkenyl)-3,4-dihydro-2*H*-pyrans with acetylenes would become a convenient route to highly functionalized chroman derivatives after dehydrogenation. The present article describes details of the research performed along these lines.

Results and Discussion

The Diels-Alder reaction between diethyl 2-oxo-3-butenylphosphonate (**1**) and ethoxyethene regioselectively leads to 2-ethoxy-6-[(diethoxyphosphinyl)methyl]-3,4-dihydro-2*H*-pyran (**2**) in 83% yield.[4] As Horner-Emmons olefinations of **2** as an allylphosphonate are expected to produce 1,3-dienes,[5] the reaction of **2** with benzaldehyde was examined under various conditions. Deprotonation of **2** readily took place with butyllithium in tetrahydrofuran (THF) and the resulting anion reacted with bezaldehyde at room temperature to give the expected diene **3a** (Scheme 1). Under these conditions, however, the yield of **3a** was poor (34%) and some starting phosphonate **2** was recovered unchanged (37%), indicating the participation of a competitive retro carbonyl addition which has been often observed when the phosphonate anions are not so highly stabilized.[6]



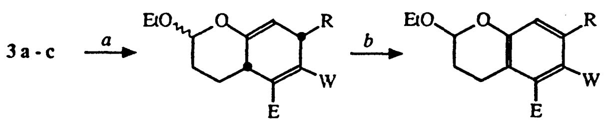
Scheme 1.

It was found that the elimination reaction was accelerated by hexamethylphosphoric triamide (HMPA), but still a temperature higher than 5 °C was needed to complete the elimination. After some efforts, the reaction was optimized as follows: The anion of **2** was generated with butyllithium (1.2 equiv) in THF containing HMPA (THF : HMPA=5 : 1 v/v) at −78 °C and benzaldehyde (1.2 equiv) was added. The reaction temperature was gradually raised to 10 °C and the reaction was continued for 6 h. Thus (*E*)-1,3-diene **3a** was obtained as the sole product in 66% yield.

Similar condensations with *p*-methoxybenzaldehyde and butanal produced (*E*)-6-(1-alkenyl)-2-ethoxy-3,4-dihydro-2*H*-pyrans **3b, c** in 63 and 54% yields, respectively (Scheme 1).

Three activated acetylene dienophiles such as dimethyl acetylenedicarboxylate (DMAD), methyl propynoate (MPR), and 3-butyn-2-one (BYO) were employed in the Diels-Alder reactions with these dienes **3a—c**. The Diels-Alder reactions were carried out in benzene in a sealed tube at 90—115 °C, and a catalytic amount of hydroquinone or 2,5-di(*t*-butyl)hydroquinone was used as an inhibitor for the homolytic polymerization of **3**.

Since the starting 1,3-dienes **3a—c** are 2-alkoxy-substituted *E*-isomers, the cycloadducts **4a—h** must be regiochemically pure and accordingly consist of only two isomers of cycloadducts, 2,4a-cis and 2,4a-trans isomers, on the basis of the high regio control by an



4a-h 5a-h

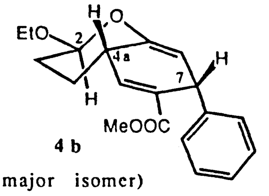
4 and 5:
a: R = Ph, E = W = COOMe
b: R = Ph, E = H, W = COOMe
c: R = Ph, E = H, W = COMe
d: R = p-MeOC$_6$H$_4$, E = W = COOMe
e: R = p-MeOC$_6$H$_4$, E = H, W = COOMe
f: R = p-MeOC$_6$H$_4$, E = H, W = COMe
g: R = n-Pr, E = W = COOMe
h: R = n-Pr, E = H, W = COOMe

a EC≡CW *b* Dehydrogenation

Scheme 2.

oxygen substituent and the stereochemical integrity of Diels-Alder cycloadditions (Scheme 2 and Table 1). Thus the Diels-Alder reactions of 1-aryl-substituted dienes **3a**, **b** with MPR and BYO afforded a clean mixture of two stereoisomers of regioselective cycloadducts **4a**, **b**. Only in the reaction of **3c** bearing a 1-alkyl substituent with MPR a trace of regioisomer **5h** (R=n-Pr, E=COOMe, W=H) was produced. In one case where the Diels-Alder reaction was carried out at such a high temperature as 155 °C for 60 h, spontaneous dehydrogenation of the cycloadduct **4b** took place.

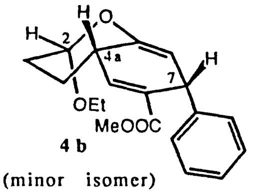
Assignment of each stereoisomer of Diels-Alder cycloadducts **4** as well as determination of the isomer ratio was not thought so important in this particular sequence directed to 2-chromanones that characterization was made only for limited cases. The stereostructures of 2,4a-cis and 2,4a-trans isomers were determined on the basis of ^{1}H NMR spectra. As for two stereoisomers of **4b**, the major isomer with lower ethoxy methyl protons (δ=1.22) was assigned to be 2,4a-trans and the minor one with higher protons (1.05) 2,4a-cis. The major isomer should have an axial 2-H, and this was confirmed by the coupling constant $J_{2\text{-}3}$ (8.8 and 2.6 Hz).[7,8] An abnormally large 1,4-long-range coupling constant was observed between 4a-H and 7-H of the major isomer of **4b** ($J_{4a\text{-}7}$=8.1 Hz). This large coupling is anticipated for the 4a,7-cis structure with two methine hydrogen in a pseudo-axial configuration.[9]



4 b

(major isomer)

$J_{2\text{-}3}$ = 8.8 and 2.6 Hz
$J_{4a\text{-}7}$ = 8.1 Hz

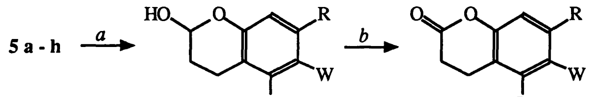


4 b

(minor isomer)

As shown in Table 1, 2,4a-trans isomers were a little more favored than 2,4a-cis isomers, indicating the preference of the sterically less hindered approach of an acetylene dienophile to **3** from the face opposite to the axial 2-ethoxy substituent.[10]

The 1,4-cyclohexadiene rings of the Diels-Alder cycloadducts **4a**—**h** were readily aromatized by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or tetrachloro-1,4-benzoquinone (p-chloranil) under reflux in benzene or toluene, respectively, to give 2-ethoxychromans **5a**—**h** (Scheme 2 and Table 1). As DDQ is stronger dehydrogenating reagent than chloranil, a less amount of DDQ and a lower reaction temperature were enough to complete the dehydrogenation. Existence of an acetyl moiety in **4** resulted in



6a-h 7a-h

(*Suffixes* a-h *designated in Scheme* 2)

a 4M-HCl in THF
b PCC (3 equiv) in CH$_2$Cl$_2$

Scheme 3.

Table 1. Diels-Alder Reactions of 6-(1-Alkenyl)-2-ethoxy-3,4-dihydro-2H-pyrans **3a**—**c** Followed by Dehydrogenation Leading to 2-Ethoxychromans **5a**—**h**

Diene	Dienophile[a]	Diels-Alder reaction[b]		Product			Dehydrogenation[c]	Product	
		Temp/°C	Time/h	4	Yield/%[d]	Isomer ratio[e]		5	Yield/%[d,f]
3a	DMAD	115	24	**4a**	70	g)	A or B	**5a**	90 (80)
3a	MPR	115	60	**4b**	87	8:3[h]	A or B	**5b**	90 (73)
3a	BYO	90	48	**4c**	69	9:5	A or B	**5c**	50 (50)
3b	DMAD	115	20	**4d**	75	3:1	B	**5d**	(80)
3b	MPR	115	60	**4e**	88	2:1	A or B	**5e**	70 (74)
3b	BYO	90	48	**4f**	79	1:1	A or B	**5f**	36 (57)
3c	DMAD	105	84	**4g**	66	g)	A	**5g**	85
3c	MPR	105	84	**4h**	72	g)	A	**5h**	80[i]

a) DMAD: dimethyl acetylenedicarboxylate. MPR: methyl propynoate. BYO: 3-butyn-2-one. b) Carried out in a sealed tube in the presece of a catalytic amount of hydroquinone or 2,5-di(t-butyl)hydroquinone. c) A: DDQ (2 equiv), reflux in benzene, 24 h. B: p-chloranil (5 equiv), reflux in toluene, 48 h. d) Yield of isolated products. e) Ratio of 2,4a-trans : 2,4a-cis isomers (^{1}H NMR). f) Yield in parenthesis from procedure B. g) No ^{1}H NMR taken. h) Contaminated by a trace of **5b** (**4b** : **5b**=12 : 1 mol/mol). i) Contaminated by a trace of m-isomer (**5h** : R=n-Pr, E=COOMe, W=H).

the low-yield formation of **5c** and **5f**; *p*-chloranil gave better yields of **5e**, **f** than DDQ in dehydrogenations of *p*-methoxyphenyl-substituted cycloadducts **4e**, **f**.

The coupling constants between 2-H and 3-Hs of **5a**—**h** are relatively small ($J_{2\text{-}3}$=2.6 to 2.9 Hz). This indicates that the benzo-fused 2-ethoxy-3,4-dihydro-2*H*-pyran ring exclusively takes one conformation, in a chloroform solution, with the 2-ethoxy substituent axial.

The acetal moiety of 2-ethoxychromans **5a**—**h** was readily hydrolyzed with 4 M hydrochloric acid (1 M=1 mol dm^{-3}) in THF at room temperature; the products **6a**—**e** excellently produced were characterized as not 3-(*o*-hydroxyaryl)propanals but as 2-chromanols (Scheme 3) on the basis of the absence of formyl proton in ^{1}H NMR spectra. However, they were smoothly oxidized into 2-chromanones **7a**—**e** with pyridinium chlorochromate (PCC) in good yields. In most cases, both steps of hydrolysis and oxidation of **5** were performed in a single procedure without trouble. Total yields of 2-chromanones **7** were as good as 68 to 78% based on **5a**—**h**, not depending upon the isolation procedure of **6** (Table 2).

In conclusion, a new entry to the synthesis of 2-chromanones has been presented here. The method starts with diethyl 2-oxo-3-butenylphosphonate (**1**) through the Diels-Alder reaction with a vinyl ether, the Horner-Emmons olefination, the Diels-Alder reaction with acetylenes, and the PCC oxidation. Through the above sequence of reactions, the phosphonate **1** can be regarded as a synthetic equivalent of 1,4-pentadien-3-ones, a hetero cross-conjugated triene. 7-Substituted 2-chromanones bearing functional groups at 5- and 6-positions were synthesized in this article, and further introduction of several substituents or functional groups would be possible at the 4- and 8-positions of 2-chromanones by a simple extension of the present method.

Table 2. Transformation of 2-Ethoxychromans **5a**—**h** into 2-Chromanones **7a**—**h** by a Sequence of Hydrolysis and Pyridinium Chlorochromate Oxidation

2-Ethoxychromans	2-Chromanols[a]		2-Chromanones[b]	
	6	Yield/%[c]	7	Yield/%[d]
5a	**6a**	90	**7a**	83 (75)
5b	**6b**	90	**7b**	81 (73)
5c	**6c**	90	**7c**	80 (72)
5d	**6d**	92	**7d**	85 (78)
5d	**6d**	e)	**7d**	(74)
5e	**6e**	90	**7e**	84 (76)
5f	**6f**	e)	**7f**	(68)
5g	**6g**	e)	**7g**	(70)
5h	**6h**	e)	**7h**	(69)

a) Obtained by hydrolysis of **5** with 4M-HCl in THF at room temperature for 15 h. b)Obtained by oxidation of **6** with PCC (3 equiv) in dichloromethane at room temperature for 24 h. c) Yield of isolated product based on **5**. d) Yield of isolated product based on **6**. Yield based on **5** in parenthesis e) Crude **6** was used in the subsequent transformation without isolation.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-720 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 (90 MHz), a JEOL FX-100 (100 MHz), or a JEOL GSX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra as well as high-resolution mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Material. Compound **2**[4)] was prepared according to the previously reported method.

General Procedure for the Horner-Emmons Olefination of 2-Ethoxy-6-[(diethoxyphosphinyl)methyl]-3,4-dihydro-2*H*-pyran (2) Leading to 6-(1-Alkenyl)-3,4-dihydro-2*H*-pyrans 3a—c. As a typical example the preparation of **3a** is described as follows: To a solution of **2** (1.7 g, 6.11 mmol) and HMPA (5 ml) in dry THF (25 ml) was added butyllithium (15% in hexane, 4.57 ml, 7.33 mmol) at −78 °C under nitrogen. After 1 h at the same temperature, benzaldehyde (0.777 g, 7.33 mmol) was added and stirring was continued at 10 °C for 6 h. The mixture was poured into saturated aqueous ammonium chloride and extracted with diethyl ether (25 ml×2). The combined extracts were dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-diethyl ether (96 : 4 v/v) as an eluent to give **3a** (0.93 g, 66%).

(*E*)-2-Ethoxy-6-(2-phenylethenyl)-3,4-dihydro-2*H*-pyran (3a): Colorless liquid; IR (neat) 1640, 1610, 1490, 1445, 1120, 1030, 955, 750, and 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.24 (3H, t, J=7.0 Hz, EtO), 1.8—1.9 (2H, m, 3-H), 2.0—2.2, 2.3—2.5 (each 1H, m, 4-H), 3.66, 3.93 (each 1H, dq, J_{gem}=9.9 and J=7.0 Hz, EtO), 5.00 (1H, t, $J_{5\text{-}4}$=4.4 Hz, 5-H), 5.18 (1H, t, $J_{2\text{-}3}$=3.3 Hz, 2-H), 6.44 (1H, d, J=15.8 Hz, 6-CH=), 6.83 (1H, d, J=15.8 Hz, =CHPh), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=15.25 (EtO), 17.80 (4-C), 26.54 (3-C), 63.81 (EtO), 97.19 (2-C), 104.47 (5-C), 124.33, 125.94, 126.46, 127.28, 128.55, 137.23, 147.77 (6-C); MS *m*/*z* (rel intensity, %) 230 (M$^+$, 30), 131 (67), 129 (37), 128 (46), 115 (46), 105 (36), 103 (71), 102 (25), 91 (37), 76 (base peak), 55 (24), and 51 (44). HRMS Found: *m*/*z* 230.1332. Calcd for $C_{15}H_{18}O_2$: M, 230.1306.

(*E*)-2-Ethoxy-6-[2-(*p*-(methoxyphenyl)ethenyl]-3,4-dihydro-2*H*-pyran (3b): Pure **3b** was obtained in 63% yield by silica-gel column chromatography of the curde product by using hexane–diethyl ether (7 : 1 v/v) as an eluent: Colorless solid (hexane); mp 62—64 °C; IR (KBr) 1640, 1595, 1500, 1440, 1245, 1175, 1110, 1040, 970, and 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.25, (3H, t, J=7.0 Hz, EtO), 1.8—2.0 (2H, m, 3-H), 2.11, 2.33 (each 1H, m, 4-H), 3.67, 3.94 (each 1H, dq, J_{gem}=9.9 and J=7.0 Hz, EtO), 3.80 (3H, s, *p*-MeO), 4.95 (1H, t, $J_{5\text{-}4}$=4.4 Hz, 5-H), 5.17 (1H, t, $J_{2\text{-}3}$=3.3 Hz, 2-H), 6.32 (1H, d, J=16.1 Hz, 6-CH=), 6.77 (1H, d, J=16.1 Hz, =CHPh), 6.85 (2H, dt, J=8.8 and 1.9 Hz, Ar), and 7.34 (2H, dt, J=8.8 and 1.9 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ=15.25 (EtO), 17.83 (4-C), 26.64 (3-C), 55.26 (*p*-MeO), 63.79 (EtO), 97.23 (2-C), 103.35 (5-C), 114.05, 122.36, 125.51, 127.66, 130.06, 147.94 (6-C), and 159.10 (Ar); MS *m/z* (rel intensity, %) 260 (M^+, 74), 178 (25), 161 (48), 136 (64), 135 (base peak), 92 (21), and 77 (33). Found: C, 74.01; H, 7.79%. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%.

(*E*)-2-Ethoxy-6-(1-pentenyl)-3,4-dihydro-2*H*-pyran (3c): Pure **3c** was obtained in 54% yield by silica-gel column chromatography of the crude product by using hexane–diethyl ether (9 : 1 v/v) as an eluent: Pale yellow liquid; IR (neat) 1660, 1625, 1440, 1370, 1120, 1035, 955, and 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7.3 Hz, *n*-Pr), 1.10 (3H, t, J=7.0 Hz, EtO), 1.37 (2H, sex, J=7.3 Hz, *n*-Pr), 1.6—1.9 (3H, m, 3- and 4-H), 2.03 (2H, q, J=7.3 Hz, *n*-Pr), 2.30 (1H, m, 4-H), 3.43, 3.88 (each 1H, J_{gem}=9.5 and J=7.0 Hz, EtO), 4.72 (1H, dd, $J_{5\text{-}4}$=5.2 and 3.6 Hz, 5-H), 4.98 (1H, dd, $J_{2\text{-}3}$=3.3 and 2.7 Hz, 2-H), 5.84 (1H, br d, J=15.4 Hz, 6-CH=), and 6.24 (1H, br dt, J=15.4 and 7.3 Hz, =CHPr-*n*); ^{13}C NMR ($CDCl_3$) δ=13.87 (*n*-Pr), 15.45 (EtO), 17.68 (4-C), 22.94 (*n*-Pr), 26.98 (3-C), 34.82 (*n*-Pr), 63.70 (EtO), 97.35 (2-C), 101.12 (5-C), 126.89, 128.23, 148.17 (6-C); MS *m/z* (rel intensity, %) 196 (M^+, 78), 153 (39), 151 (21), 150 (41), 121 (20), 109 (20), 107 (23), 97 (34), 86 (45), 79 (31), and 73 (base peak). HRMS Found: *m/z* 196.1470. Calcd for $C_{12}H_{20}O_2$: M, 196.1462.

General Procedure for the Diels-Alder Reaction and Dehydrogenation of 6-(1-Alkenyl)-2-ethoxy-3,4-dihydro-2*H*-pyrans 3a—c Leading to 2-Ethoxychromans 5a—h. As a typical example the reaction of **3a** with methyl propynoate is described as follows: A solution of **3a** (0.105 g, 0.46 mmol), methyl propynoate (0.084 g, 1 mmol), and a catalytic amount of hydroquinone in dry benzene (2 ml) was charged in a sealed tube and heated at 115 °C for 60 h. The benzene was evaporated in vacuo and the residue was chromatographed over silica gel with hexane–diethyl ether (6 : 1 to 4 : 1 v/v) to give **4b** which was contaminated by a trace of **5b** (**4b** : **5b**=12 : 1 mol/mol by ^{1}H NMR).

The product **4b** consisted of two stereoisomers (2,4a-trans : 2,4a-cis=8 : 3 by ^{1}H NMR) from which 2,4a-*trans*-**4b** was separated by crystallization. 2,4a-*trans*-**4b**: Colorless prisms (diethyl ether–hexane); mp 131—132 °C; IR (KBr) 1710, 1690, 1430, 1250, 1130, 1040, 960, 830, 740, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (3H, t, J=7.0 Hz, EtO), 1.56 (1H, dq, J_{gem}=$J_{4\text{-}3}$=$J_{4\text{-}4a}$=12.4 and $J_{4\text{-}3}$=8.8 Hz, 4(ax)-H), 1.83 (1H, dddd, J_{gem}=13.6, $J_{3\text{-}4}$=12.4, 4.8, and $J_{3\text{-}2}$=8.8 Hz, 3(ax)-H), 2.03 (1H, m, 3(eq)-H), 2.21 (1H, m, 4(ax)-H), 3.01 (1H, m, 4a-H), 3.53, 3.94 (each 1H, dq, J_{gem}=9.9 and J=7.0 Hz, EtO), 3.56 (3H, s, COOMe), 4.46 (1H, ddd, $J_{7\text{-}4a}$=8.1, $J_{7\text{-}8}$=3.7, and $J_{7\text{-}5}$=1.5 Hz, 7-H), 4.58 (1H, dd, $J_{2\text{-}3}$=8.8 and 2.6 Hz, 2-H), 5.20 (1H, dd, $J_{8\text{-}7}$=3.7 and $J_{8\text{-}4a}$=1.5 Hz, 8-H), 6.85 (1H, dd, $J_{5\text{-}4a}$=3.7 and $J_{5\text{-}7}$=1.5 Hz, 5-H), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=15.21 (EtO), 28.45 (4-C), 31.16 (3-C), 34.86 (4a-C), 42.68 (7-C), 51.52 (COOMe), 64.58 (EtO), 103.14 (2-C), 109.15 (8-C), 126.46, 128.04, 128.42 (each Ph), 131.10 (6-C), 138.15 (5-C), 143.93 (Ph), 148.61 (8a-C), and 166.73 (COOMe); MS *m/z* (rel intensity, %) 314 (M^+, 3), 165 (15), 153 (24), 152 (26), 141 (20), 115 (37), 85 (27), and 77 (28). Found: C, 72.40; H, 7.11%. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05%.

A solution of **4b** (0.47 g, 1.495 mmol) and DDQ (0.679 g, 2.99 mmol) in dry benzene (25 ml) was heated under reflux for 20 h. The solid precipitated was removed off by filtration through Celite 545 and the filtrate was again filtered through alumina by using ethyl acetate as an eluent. The eluate was evaporated in vacuo and the residue was chromatographed over silica gel with hexane–diethyl ether (5 : 1 v/v) to give **5b** (0.418 g, 90%).

In other cases, Diels-Alder cycloadducts **4a** and **4c—h** were not characterized, but the cis/trans ratio was determined by ^{1}H NMR spectrum of the unpurified mixture. The ratio between the 3,4a-trans and 3,4a-cis isomers was determined on the basis of the relative integration of the 2-ethoxy methyl protons (in parenthesis): **4b**: 8 : 3 (δ=1.22 and 1.05); **4c**: 9 : 5 (1.20 and 1.08); **4d**: 3 : 1 (1.23 and 1.05); **4e**: 2 : 1 (1.22 and 1.08); **4f**: 1 : 1 (1.20 and 1.11). The reaction conditions and results are summarized in Table 1.

Dimethyl 2-Ethoxy-7-phenylchroman-5,6-dicarboxylate (5a): Colorless viscous oil; IR (neat) 1725, 1600, 1560, 1320, 1270, 1040, 960, 880, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, t, J=7.0 Hz, EtO), 1.91, 2.08 (each 1H, m, 3-H), 2.74 (1H, ddd, J_{gem}=17.3, $J_{4\text{-}3}$=5.5, and 3.3 Hz, 4(eq)-H), 3.03 (1H, ddd, J_{gem}=17.3, $J_{4\text{-}3}$=11.4, and 5.9 Hz, 4(ax)-H), 3.53 (3H, s, 6-COOMe), 3.62, 3.86 (each 1H, dq, J_{gem}=9.9 and 7.0 Hz, EtO), 3.87 (3H, s, 5-COOMe), 5.28 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), 6.92 (1H, s, 8-H), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.97 (q, EtO), 18.25 (t, 4-C), 25.85 (t, 3-C), 51.83, 52.29 (each q, COOMe), 63.98 (t, EtO), 96.87 (d, 2-C), 120.28 (s), 120.28 (d), 127.41 (d), 128.00 (d), 133.50 (s), 140.05 (s), 140.99 (s), 153.62 (s), 168.01, and 168.48 (each s, COOMe); MS *m/z* (rel intensity, %) 370 (M^+, 26), 338 (base peak), 281 (25), 279 (27), 249 (24), 185 (21), 165 (24), and 154 (21). HRMS Found: *m/z* 370.1418. Calcd for $C_{21}H_{22}O_6$: M, 370.1415.

Methyl 2-Ethoxy-7-phenylchroman-6-carboxylate (5b): Colorless prisms (hexane); mp 46—48 °C; IR (KBr) 1700, 1610, 1550, 1480, 1440, 1290, 1155, 960, and 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.19 (3H, t, J=7.0 Hz, EtO), 1.95, 2.08 (each 1H, m, 3-H), 2.68 (1H, br ddd, J_{gem}=16.8, $J_{4\text{-}3}$=6.0, and 3.6 Hz, 4(eq)-H), 3.20 (1H, br ddd, J_{gem}=16.8, $J_{4\text{-}3}$=12.1, and 6.2 Hz, 4(ax)-H), 3.56 (3H, s, COOMe), 3.64, 3.88 (each 1H, dq, J_{gem}=9.5 and J=7.0 Hz, EtO), 5.29 (1H, t, $J_{2\text{-}3}$=2.6 Hz, 2-H), 6.80 (1H, s, 8-H), 7.2—7.5 (5H, m, Ph), and 7.65 (1H, s, 5-H); ^{13}C NMR ($CDCl_3$) δ=15.03 (EtO), 20.00 (4-C), 26.32 (3-C), 51.48 (COOMe), 63.88 (EtO), 97.28 (2-C), 119.22, 121.50, 122.44, 126.94, 127.71, 128.23, 131.86, 141.39, 142.92, 154.79 (each Ph and Ar), and 168.31 (COOMe); MS *m/z* (rel intensity, %) 312 (M^+, 28), 266 (23), 74 (30), 59 (66), 57 (28), 45 (51), 43 (51), and 31 (base peak). Found: C, 73.30; H, 6.54%. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

6-Acetyl-2-ethoxy-7-phenylchroman (5c): Colorless prisms (hexane); mp 51—53 °C; IR (KBr) 1675, 1600, 1545, 1475, 1275, 1145, 1100, 1045, 955, and 875 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, t, J=7.0 Hz, EtO), 1.96 (1H, m, one of 3-H), 1.96 (3H, s, MeCO), 2.09 (1H, m, the other of 3-H), 2.70 (1H, ddd, J_{gem}=16.2, $J_{4\text{-}3}$=6.0, and 3.6 Hz, 4(eq)-H), 3.03 (1H, ddd, J_{gem}=16.2, $J_{4\text{-}3}$=12.6, and 5.4 Hz, 4(ax)-H), 3.66, 3.90 (each 1H, dq, J_{gem}=9.5 and J=7.0 Hz, EtO), 5.30 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), 6.82 (1H, s, 8-H), and 7.2—7.5 (6H, 5-H and Ph); ^{13}C NMR (CDCl$_3$) δ=15.10 (EtO), 20.09 (4-C), 26.42 (3-C), 30.27 (MeCO), 63.96 (EtO), 97.28 (2-C), 118.67, 121.77, 127.70, 128.51, 128.76, 130.23, 133.16, 140.97, 141.15, 154.47 (each Ph and Ar), and 203.10 (MeCO); MS m/z (rel intensity, %) 296 (M$^+$, 41), 281 (57), 235 (31), 209 (21), 165 (28), 153 (27), 152 (38), and 43 (base peak). Found: C, 77.19; H, 6.85%. Calcd for $C_{19}H_{20}O_4$: C, 77.00; H, 6.80%.

Dimethyl 2-Ethoxy-7-(*p*-methoxyphenyl)chroman-5,6-dicarboxylate (5d): Colorless prisms (hexane); mp 94—95 °C; IR (KBr) 1725, 1600, 1430, 1320, 1265, 1230, 1020, 955, and 830 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.18 (3H, t, J=7.3 Hz, OEt), 1.92, 2.07 (each 1H, m, 3-H), 2.73 (1H, ddd, J_{gem}=17.3, $J_{4\text{-}3}$=5.5, and 3.3 Hz, 4(eq)-H), 3.03 (1H, ddd, J_{gem}=17.3, $J_{4\text{-}3}$=11.4, and 5.9 Hz, 4(ax)-H), 3.58 (3H, s, 6-COOMe), 3.63, 3.83 (each 1H, dq, J_{gem}=9.5 and J=7.3 Hz, OEt), 3.81 (3H, s, 5-COOMe), 3.87 (3H, s, *p*-MeO), 5.27 (1H, t, $J_{2\text{-}3}$=2.6 Hz, 2-H), 6.90 (1H, s, 8-H), 6.90 (2H, dt, J=8.8 and 2.2 Hz, Ar), and 7.22 (2H, dt, J=8.8 and 2.2 Hz, Ar); ^{13}C NMR (CDCl$_3$) δ=15.08 (EtO), 18.39 (4-C), 26.02 (3-C), 52.08, 52.44 (each COOMe), 55.23 (*p*-MeO), 64.00 (EtO), 96.97 (2-C), 113.69, 120.11, 120.38, 124.03, 129.24, 132.47, 133.42, 140.64, 153.65, 159.19 (each Ar), 168.19, and 168.86 (each COOMe); MS m/z (rel intensity, %) 400 (M$^+$, 32), 368 (43), 58 (35), and 43 (base peak). Found: C, 66.11; H, 6.02%. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%.

Methyl 2-Ethoxy-7-(*p*-methoxyphenyl)chroman-6-carboxylate (5e): Colorless viscous oil; IR (neat) 1725, 1610, 1490, 1280, 1240, 1160, 960, 880, 830, and 730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.19 (3H, t, J=7.0 Hz, EtO), 1.95, 2.08 (each 1H, m, 3-H), 2.68 (1H, ddd, J_{gem}=16.8, $J_{4\text{-}3}$=6.0, and 3.6 Hz, 4(eq)-H), 3.02 (1H, ddd, J_{gem}=16.8, $J_{4\text{-}3}$=12.1, and 6.2 Hz, 4(ax)-H), 3.63 (3H, s, COOMe), 3.65, 3.88 (each 1H, dq, J_{gem}=9.9 and J=7.0 Hz, EtO), 3.83 (3H, s, *p*-MeO), 5.29 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), 6.87 (1H, s, 8-H), 6.91 (2H, dt, J=8.8 and 2.2 Hz, Ar), 7.21 (2H, dt, J=8.8 and 2.2 Hz, Ar), and 7.62 (1H, s, 5-H); ^{13}C NMR (CDCl$_3$) δ=15.10 (EtO), 20.04 (4-C), 26.41 (3-C), 51.65 (COOMe), 55.22 (*p*-MeO), 63.96 (EtO), 97.35 (2-C), 113.33, 119.28, 121.22, 122.50, 129.44, 131.89, 133.76, 142.53, 154.77, 158.83 (each Ar), and 168.65 (COOMe); MS m/z (rel intensity, %) 342 (M$^+$, 14), 248 (27), 246 (21), 58 (26), 44 (37), and 43 (base peak). HRMS Found: m/z 342.1459. Calcd for $C_{20}H_{22}O_5$: M, 342.1466.

6-Acetyl-2-ethoxy-7-(*p*-methoxyphenyl)chroman (5f): Colorless prisms (hexane); mp 99—101 °C; IR (KBr) 1675, 1600, 1570, 1270, 1230, 1145, 1100, 1045, 870, and 825 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.20 (3H, t, J=7.0 Hz, EtO), 1.97 (3H, s, MeCO), 1.97, 2.07 (each 1H, m, 3-H), 2.68 (1H, ddd, J_{gem}=16.1, $J_{4\text{-}3}$=5.9, and 3.5 Hz, 4(eq)-H), 3.02 (1H, ddd, J_{gem}=16.1, $J_{4\text{-}3}$=12.1, and 6.2 Hz, 4(ax)-H), 3.65, 3.90 (each 1H, dq, J_{gem}=9.5 Hz, and J=7.0 Hz, EtO), 3.84 (3H, s, *p*-MeO), 5.30 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), 6.80 (1H, s, 8-H), 6.94 (2H, dt, J=8.8 and 2.2 Hz, Ar), 7.24 (2H, dt, J=8.8 and 2.2 Hz, Ar), and 7.36 (1H, s, 5-H); ^{13}C NMR (CDCl$_3$) δ=15.12 (EtO), 20.06 (4-C), 26.44 (3-C), 30.32 (MeCO), 55.29 (*p*-MeO), 63.96 (EtO), 97.33 (2-C), 114.01, 118.50, 121.44, 129.87, 130.13, 133.26, 133.29, 140.73, 154.41, 159.43 (each Ar), and 203.52 (MeCO); MS m/z (rel intensity, %) 326 (M$^+$, base peak), 311 (58), 265 (21), 247 (27), 246 (38), 245 (23), 231 (46), 221 (42), 217 (22), 123 (27), 109 (20), 108 (69), 57 (38), and 56 (20). Found: C, 73.83; H, 6.94%. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

Dimethyl 2-Ethoxy-7-propylchroman-5,6-dicarboxylate (5g): Colorless liquid; IR (neat) 1725, 1605, 1570, 1440, 1300, 1140, and 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.93 (3H, t, J=7.3 Hz, EtO), 1.18 (3H, t, J=7.0 Hz, *n*-Pr), 1.59 (2H, sex, J=7.3 Hz, *n*-Pr), 1.89, 2.04 (each 1H, m, 3-H), 2.6—2.8 (3H, m, *n*-Pr and 4(eq)-H), 2.95 (1H, ddd, J_{gem}=16.9, $J_{4\text{-}3}$=11.7, and 6.2 Hz, 4(ax)-H), 3.63, 3.81 (each 1H, dq, J_{gem}=9.9 and J=7.0 Hz, EtO), 3.82, 3.86 (each 3H, s, COOMe), 5.24 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), and 6.78 (1H, s, 8-H); ^{13}C NMR (CDCl$_3$) δ=14.00 (*n*-Pr), 15.09 (EtO), 18.36 (4-C), 24.46 (*n*-Pr), 26.09 (3-C), 35.64 (*n*-Pr), 52.12, 52.31 (each COOMe), 63.99 (EtO), 96.99 (2-C), 119.12, 120.18, 123.54, 133.66, 141.91, 155.93 (each Ar), 168.37 (COOMe), and 168.53 (COOMe); MS m/z (rel intensity, %) 336 (M$^+$, 28), 304 (base peak), 289 (40), 275 (21), 245 (18), 215 (12), 163 (14), and 43 (12). HRMS Found: m/z 336.1574. Calcd for $C_{18}H_{24}O_6$: M, 336.1571.

Methyl 2-Ethoxy-7-propylchroman-6-carboxylate (5h): This compound is contaminated by a trace of regioisomer **5h** (R=*n*-Pr, E=COOMe, W=H). Colorless viscous oil; IR (neat) 1715, 1610, 1560, 1430, 1270, 1135, 1055, 970, and 870 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.97 (3H, t, J=7.3 Hz, *n*-Pr), 1.19 (3H, t, J=7.0 Hz, EtO), 1.60 (2H, sex, J=7.3 Hz, *n*-Pr), 1.92, 2.04 (each 1H, m, 3-H), 2.62 (1H, ddd, J_{gem}=16.2, $J_{4\text{-}3}$=5.5, and 4.1 Hz, 4(eq)-H), 2.8—3.0 (3H, m, 4(ax)-H and *n*-Pr), 3.64, 3.88 (each 1H, dq, J_{gem}=9.5 and J=7.0 Hz, EtO), 3.84 (3H, s, COOMe), 5.26 (1H, t, $J_{2\text{-}3}$=2.9 Hz, 2-H), 6.69 (1H, s, 8-H), and 7.68 (1H, s, 6-H); ^{13}C NMR (CDCl$_3$) δ=14.77 (*n*-Pr), 15.12 (EtO), 20.03 (4-C), 24.69 (*n*-Pr), 26.54 (3-C), 36.40 (*n*-Pr), 51.52 (COOMe), 63.94 (EtO), 97.41 (2-C), 118.99, 119.90, 121.39, 132.64, 145.03, 155.33 (each Ar), and 167.68 (COOMe); MS m/z (rel intensity, %) 278 (M$^+$, base peak), 247 (22), 233 (29), 232 (52), and 231 (24). HRMS Found: m/z 278.1520. Calcd for $C_{16}H_{22}O_4$: 278.1517.

General Procedure for the Hydrolysis and Oxidation of 2-Ethoxychromans 5a—h Leading to 2-Chromanones 7a—h. As a typical example the sequence of hydrolysis and PCC-oxidation of **5a** is described as follows: A solution of **5a** (0.53 g, 1.43 mmol) in THF (50 ml) containing 4M hydrochloric acid (25 ml) was stirred at room temperature for 15 h. The THF was evaporated in vacuo and the residual solution was extracted with dichloromethane (25 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (1 : 1 v/v) to give **6a** (0.44 g, 90%).

6a: ^{1}H NMR (CDCl$_3$) δ=1.8—2.1 (2H, m, 3-H), 2.77 (1H, dt, J_{gem}=16.9 Hz, and $J_{4\text{-}3}$=5.5 Hz, 4(eq)-H), 3.01 (1H, ddd, J_{gem}=16.9, $J_{4\text{-}3}$=10.2, and 6.9 Hz, 4(ax)-H), 3.52 (3H, s, 6-COOMe), 3.86 (3H, s, 5-COOMe), 3.93 (1H, d, J=2.7 Hz, OH), 5.57 (1H, q, $J_{2\text{-}3}$=$J_{2\text{-OH}}$=2.7 Hz, 2-H), 6.85 (1H, s, 8-H), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR (CDCl$_3$) δ=18.32 (3-C), 26.52 (4-C), 52.12, 52.57 (each COOMe), 92.14 (2-C), 119.89, 120.41, 124.03, 127.54, 128.06, 128.19, 133.49, 140.02, 141.22, 153.73 (each Ar), 168.25, and 168.81 (each COOMe).

A mixture of this compound **6a** (0.065 g, 0.19 mmol) and PCC (0.123 g, 0.57 mmol) in dichloromethane (3 ml) was stirred at room temperature for 24 h. Diethyl ether (10 ml) was added and the ether layer was decanted. This procedure was repeated three times. The combined ether extracts were filtered through a short column packed with silica gel and the silica gel was washed with ethyl acetate. The ether and the ethyl acetate were combined and evaporated in vacuo.

The residue was again chromatographed over silica gel with hexane–diethyl ether (4 : 1 v/v) to give **7a** (0.054 g, 83%).

The eluents used for the final column chromatography are as follows: **7b**: hexane–diethyl ether (4:1 v/v); **7c**, **7d**, **7f**: hexane–ethyl acetate (1 : 1 v/v); **7e**, **7h**: hexane–ethyl acetate (3 : 1 v/v); **7g**: hexane–ethyl acetate (3 : 2 v/v). The results are summarized in Table 2.

Dimethyl 2-Oxo-7-phenylchroman-5,6-dicarboxylate (7a): Colorless needles (dichloromethane–hexane); mp 205—207 °C; IR (KBr) 1780, 1730, 1715, 1600, 1430, 1330, 1275, 1220, 1180, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.81 (2H, dd, $J_{3\text{-}4}$=7.7 and 5.9 Hz, 3-H), 3.17 (2H, dd, $J_{4\text{-}3}$=7.7 and 5.9 Hz, 4-H), 3.58 (3H, s, 6-COOMe), 3.90 (3H, s, 5-COOMe), 7.17 (1H, s, 8-H), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=21.57 (3-C), 28.41 (4-C), 52.38, 52.85 (each COOMe), 120.53, 121.22, 128.03, 128.17, 128.49, 128.59, 131.82, 138.81, 141.87, 152.94 (each Ph and Ar), 166.88, 167.08, and 168.10 (each COOMe and 2-C); MS *m/z* (rel intensity, %) 340 (M$^+$, 8), 339 (27), 309 (44), 308 (78), 281 (40), 280 (base peak), 265 (25), 249 (80), 222 (21), 221 (27), 194 (53), 166 (24), 165 (75), 153 (25), 152 (42), 151 (22), and 139 (34). Found: C, 66.80; H, 4.60%. Calcd for $C_{19}H_{16}O_6$: C, 67.05; H, 4.75%.

Methyl 2-Oxo-7-phenylchroman-6-carboxylate (7b): Colorless prisms (diethyl ether–hexane); mp 144—145 °C; IR (KBr) 1755, 1725, 1270, 1230, 1130, 1080, and 900 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.84 (2H, dd, $J_{3\text{-}4}$=7.6 and 5.5 Hz, 3-H), 3.08 (2H, dd, $J_{4\text{-}3}$=7.6 and 5.5 Hz, 4-H), 3.62 (3H, s, COOMe), 7.04 (1H, s, 8-H), 7.2—7.5 (5H, m, Ph), and 7.73 (1H, s, 5-H); ^{13}C NMR ($CDCl_3$) δ=23.33 (3-C), 29.00 (4-C), 51.99 (COOMe), 119.10, 121.45, 126.71, 127.64, 128.13, 130.22, 140.20, 143.68, 153.73 (each Ph and Ar), 167.57 (2-C), and 168.03 (COOMe); MS *m/z* (rel intensity,%) 282 (M$^+$, base peak), 251 (85), 223 (61), 181 (27), 166 (21), 165 (63), 153 (43), 152 (85), 151 (25), 139 (36), 127 (21), 115 (22), and 77 (21). Found: C, 72.05; H, 4.86%. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

6-Acetyl-2-oxo-7-phenylchroman (7c): Colorless prisms (diethyl ether–hexane); mp 134—135 °C; IR (KBr) 1755, 1675, 1610, 1470, 1350, 1275, 1135, 900, 770, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.96 (3H, s, MeCO), 2.85 (2H, dd, $J_{3\text{-}4}$=8.4 and 5.9 Hz, 3-H), 3.09 (2H, dd, $J_{4\text{-}3}$=8.4 and 5.9 Hz, 4-H), 7.06 (1H, s, 8-H), 7.3—7.4 (2H, m, Ph), and 7.4—7.5 (4H, m, 5-H and Ph); ^{13}C NMR ($CDCl_3$) δ=23.35 (3-C), 29.03 (4-C), 30.34 (MeCO), 118.47, 121.77, 128.40, 128.69, 128.87, 136.96, 139.62, 141.64, 153.36 (each Ph and Ar), 167.63 (2-C), and 203.28 (MeCO); MS *m/z* (rel intensity, %) 266 (M$^+$, 41), 251 (base peak), 223 (22), 209 (28), 165 (52), 153 (45), 152 (50), 139 (22), and 63 (25). Found: C, 76.77; H, 5.20%. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H 5.30%.

Dimethyl 7-(*p*-Methoxyphenyl)-2-oxochroman-5,6-dicarboxylate (7d): Colorless needles (diethyl ether–hexane); mp 164—165 °C; IR (KBr) 1775, 1725, 1710, 1600, 1435, 1335, 1280, 1225, 1185, and 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.80 (2H, dd, $J_{3\text{-}4}$=7.7 and 7.0 Hz, 3-H), 3.14 (2H, dd, $J_{4\text{-}3}$=7.7 and 7.0 Hz, 4-H), 3.62 (3H, s, 6-COOMe), 3.83 (3H, s, 5-COOMe), 3.89 (3H, s, *p*-MeO), 6.92 (2H, br d, *J*=8.4 Hz, Ar), 7.14 (1H, s, 8-H), and 7.22 (2H, dt, *J*=8.4 and 1.8 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ=21.59 (3-C), 28.47 (4-C), 52.44, 52.86 (each COOMe), 55.30 (*p*-MeO), 113.99, 120.53, 120.83, 128.56, 129.27, 131.11, 131.66, 141.48, 152.90, 159.65 (each Ar), 166.91, 167.17, and 168.32 (each COOMe and 2-C); MS *m/z* (rel intensity, %) 370 (M$^+$, base peak), 339 (46), 338 (70), 311 (25), 310 (98), 279 (59), 224 (33), 152 (31), and 139 (27). Found: C, 64.98; H, 4.87%. Calcd for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90%.

Methyl 7-(*p*-Methoxyphenyl)-2-oxochroman-6-carboxylate (7e): Colorless prisms (cyclohexane); mp 85—87 °C; IR (KBr) 1775, 1720, 1615, 1490, 1250, 1130, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.83 (2H, dd, $J_{3\text{-}4}$=8.1 and 5.8 Hz, 3-H), 3.05 (2H, dd, $J_{4\text{-}3}$=8.1 and 5.8 Hz, 4-H), 3.65 (3H, s, COOMe), 3.84 (3H, s, *p*-MeO), 6.93 (2H, dd, *J*=8.8 and 2.2 Hz, Ar), 7.02 (1H, s, 8-H), 7.20 (2H, dd, *J* = 8.8 and 2.2 Hz, Ar), and 7.69 (1H, s, 5-H); ^{13}C NMR ($CDCl_3$) δ=23.28 (3-C), 29.01 (4-C), 52.05 (COOMe), 55.26 (*p*-MeO), 113.63, 119.02, 121.05, 126.65, 129.37, 130.15, 132.44, 143.22, 153.67, 159.27 (each Ar), 167.64 (2-C), and 168.26 (COOMe); MS *m/z* (rel intensity, %) 312 (M$^+$, base peak), 281 (24), 239 (10), and 152 (9). Found: C, 69.03; H, 5.13%. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16%.

6-Acetyl-7-(*p*-methoxyphenyl)-2-oxochroman (7f): Colorless prisms (diethyl ether–hexane); mp 118—120 °C; IR (KBr) 1760, 1670, 1605, 1480, 1270, 1250, 1130, 900, and 830 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s, MeCO), 2.84 (2H, dd, $J_{3\text{-}4}$=7.7 and 5.5 Hz, 3-H), 3.07 (2H, dd, $J_{4\text{-}3}$=7.7 and 5.5 Hz, 4-H), 3.86 (3H, s, *p*-MeO), 6.92 (2H, dt, *J*=8.8 and 2.2 Hz, Ar), 7.04 (1H, s, 8-H), 7.23 (2H, dt, *J*=8.8 and 2.2 Hz, Ar), and 7.42 (1H, s, 5-H); ^{13}C NMR ($CDCl_3$) δ=23.31 (3-C), 29.06 (4-C), 30.32 (MeCO), 55.35 (*p*-MeO), 114.34, 118.28, 121.35, 128.30, 129.87, 131.85, 136.96, 141.25, 153.38, 159.91 (each Ar), 167.73 (2-C), and 203.68 (MeCO); MS *m/z* (rel intensity, %) 296 (M$^+$, base peak), 295 (20), 281 (76), 239 (32), and 55 (25). Found: C, 72.81; H, 5.47%. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%.

Dimethyl 2-Oxo-7-propylchroman-5,6-dicarboxylate (7g): Colorless prisms (hexane); mp 81—83 °C; IR (KBr) 1770, 1720, 1580, 1440, 1310, 1200, 1140, 990, and 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.94 (3H, t, *J* = 7.3 Hz, *n*-Pr), 1.61 (2H, sex, *J* = 7.3 Hz, *n*-Pr), 2.69 (2H, t, *J* = 7.3 Hz, *n*-Pr), 2.76 (2H, dd, $J_{3\text{-}4}$=7.7 and 5.5 Hz, 3-H), 3.10 (2H, dd, $J_{4\text{-}3}$=7.7 and 5.5 Hz, 4-H), 3.87, 3.88 (each 3H, s, COOMe), and 7.03 (1H, s, 8-H); ^{13}C NMR ($CDCl_3$) δ = 13.85 (*n*-Pr), 21.51 (3-C), 24.26 (*n*-Pr), 28.51 (4-C), 35.36 (*n*-Pr), 52.50, 52.72 (each COOMe), 120.03, 120.33, 128.38, 131.73, 142.62, 153.13 (each Ar), 167.17, 167.35, and 167.93 (each 2-C and COOMe); MS *m/z* (rel intensity,%) 306 (M+, 5), 279 (25), 274 (31), 217 (43), 201 (21), 167 (27), 149 (55), and 40 (base peak). Found: C, 62.53; H, 5.99%. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92%.

Methyl 2-Oxo-7-propylchroman-6-carboxylate (7h): Colorless prisms (hexane); mp 50—51 °C; IR (KBr) 1775, 1700, 1610, 1430, 1400, 1260, 1110, and 895 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.97 (3H, t, *J*=7.3 Hz, *n*-Pr), 1.61 (2H, sex, *J*=7.3 Hz, *n*-Pr), 2.80 (2H, dd, $J_{3\text{-}4}$=7.7 and 5.5 Hz, 3-H), 2.92 (2H, dd, *J*=7.3 Hz, *n*-Pr), 3.01 (2H, dd, $J_{4\text{-}3}$=7.7 and 5.5 Hz, 4-H), 3.89 (3H, s, COOMe), 6.92 (1H, s, 8-H), and 7.77 (1H, s, 5-H); ^{13}C NMR ($CDCl_3$) δ=14.05 (*n*-Pr), 23.23 (3-C), 24.59 (*n*-Pr), 29.14 (4-C), 36.15 (*n*-Pr), 51.96 (COOMe), 118.99, 119.79, 125.43, 130.97, 146.03, 154.19 (each Ar), 167.84 (2-C), and 168.36 (COOMe); MS *m/z* (rel intensity, %) 248 (M$^+$, 40), 217 (base peak), 201 (48), 91 (24), 57 (66), 56 (32), and 43 (27). Found: C, 67.96; H, 6.57%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

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