Thermal Addition Reaction of Aroylketene with 1-Aryl-1-trimethylsilyloxyethylenes: Aromatic Substituent Effects of Aroylketene and Aryltrimethylsilyloxyethylene on Their Reactivity

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The thermal addition reaction of various aroylketenes (C) generated by the thermolysis of 5-aryldioxofurans (A) to 1-aryl-1-trimethylsilyloxyethylenes gave 1,5-diarylpentane-1,3,5-triones (D) and 2,6-diaryl-4*H*-pyran-4-ones (E). The introduction of electron withdrawing substituents in the aroylketene and of electron donating substituents facilitated the addition reaction. The observed substituent effects and the reaction mechanism are interpreted in terms of molecular orbital analyses.

Key words aroylketene; aryltrimethylsilyloxyethylene; thermal addition reaction; 4-pyrone; molecular orbital

Acylketenes[1] readily react with a variety of heteroolefins, including imine[2] cyanide,[3,4] diimine,[4] ketone,[5,6] thioamide,[7] and isocyanate,[3,5,8] as a heterodiene in the [4+2] cycloaddition reaction. Furthermore, it has been demonstrated that acylketenes undergo [4+2] cycloaddition to electron-rich olefins such as enol ethers[9,10] and ketene acetals,[9,11] which provide a versatile synthetic method of producing 2-alkoxy-2,3-dihydro-4*H*-pyran-4-one and of 4*H*-pyran-4-one. We reported in a preliminary paper[12] that 1-aroylketenes generated by thermoloysis of 5-aryl-2,3-dihydro-2,3-dioxofurans react with 1-aryl-1-trimethylsilyloxyethylenes in a regioselective manner to give 2,6-diaryl-4*H*-pyran-4-ones and/or 1,5-diarylpentane-1,3,5-triones. In the report we demonstrated that either the introduction of a nitro group in the benzene ring of aroylketene or the introduction of electron donating groups in the benzene ring of 1-aryl-1-trimethylsilyloxyethylene facilitated the addition reaction and improved the yields of the adducts.

In this paper we describe in detail the reaction of various aroylketenes with 1-aryl-1-trimethylsilyloxyethylenes having substituents of different electronic properties in the aromatic part, which may provide the detailed information concerning the reactivity of aroylketene for various olefins. The reaction at the same time may provide a convenient synthetic method of producing various 1,5-diarylpentane-1,3,5-trione and 2,6-diaryl-4*H*-pyran-4-ones.

Results and Discussion

Acylketenes has been known to be generated by thermal decomposition of 2,3-dihydro-2,3-dioxofurans (dioxofuran)[13] and of 4*H*-1,3-dioxin-4-ones,[14] and by photolysis of α-diazo-β-dicarbonylcompounds.[15] We chose the thermolysis of dioxofuran as the method of aroylketene generation since the preparation of dioxofurans with various substituted phenyl or heteroaromatic groups is readily accessible from the corresponding aryl methyl ketones. 5-(4-Substitued phenyl)- (**3**) and 5-(2-substituted phenyl)dioxofuran (**6**) were prepared by the condensation of 1-(4-substituted phenyl)- (**2**) and 1-(2-substituted phenyl)-1-trimethylsilyloxyethylene (**5**) with oxalylchloride in good yields, respectively. As heteroaromatic derivatives, 5-(furan-2-yl)- (**9**) and 5-(thiophen-2-yl)dioxofurans (**12**) were also prepared by the condensation of the corresponding trimethylsilyloxyethylelenes **8** and **11** with oxalylchloride.

Reaction of 5-(4-Substituted aryl)dioxofurans with 1-Aryl-1-trimethylsilyloxyethylenes In order to investigate the effect of the aryl moiety for the addition reaction of aroylketene to 1-aryl-1-trimethylsilyloxyethylene, we carried out the reaction of aroylketenes having various aromatic rings with electronically and sterically different properties. As the aroylketenes of **13**, **14**, **15**, **16**, benzoylketene (**13a**), *p*- and *o*-methoxybenzoylketenes (**13c**, **14c**), *p*- and *o*-chlorobenzoylketenes (**13f**, **14f**), *p*- and *o*-nitrobenzoylketenes (**13g**, **14g**), and *o*-allyloxybenzoylketene (**14h**), furoyl- (**15**) and thenoylketenes (**16**) were generated *in situ* from the corresponding 5-aryldioxofurans **3**, **6**, **9**, and **12**, respectively. As 1-aryl-1-trimethylsilyloxyethylenes **2**, phenyl (**a**: X=H), *p*-tolyl (**b**: X=Me), *p*-methoxyphenyl (**c**: X=OMe), *p*-trimethylsilyloxyphenyl (**d**: X=OTMS), *p*-fluorophenyl (**e**: X=F), *p*-chlorophenyl (**f**: X=Cl), and *p*-nitrophenyl (**g**: X=NO_2) derivatives were used for this reaction.

The reactions were performed simply by heating a mixture of the dioxofurans **3**, **6**, **9**, and **12** and the trimethylsilyloxyolefins **2a**—**g**, of a two molar excess, in dry toluene at 100 °C for 1 h in a sealed tube. The reaction mixture was purified by silica gel column chromatography to afford 1,5-diarylpentane-1,3,5-trione (triketone) (D) and/or 2,6-diaryl-4*H*-pyran-4-one (4-pyrone) (E). In some cases, the ketene dimers (F) were isolated from the reaction mixture. Cyclization of the triketone (D) to the 4-pyrone (E) did not proceed under the reaction conditions described above (heating in toluene for 24 h).

The structures of the products were confirmed by their elementary analyses, Mass, IR, UV, ^{1}H-, and ^{13}C-NMR spectral data (see Experimental). Treatment of the triketone (D) with sulfuric acid gave the corresponding 4-pyrone (E) in good yield, as shown in the experimental section. The triketones (D) existed as keto–enol tautomers, as shown in the ^{1}H-NMR spectra. The results are shown in Table 1.

p-Cl-, *p*-NO_2-, *o*-Cl-, and *o*-NO_2-benzoylketenes showed

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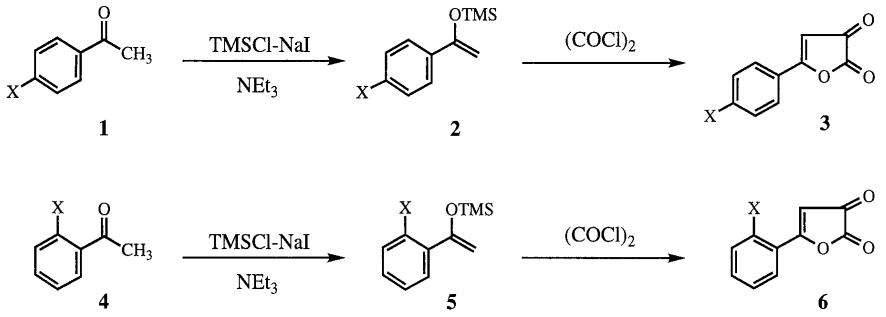
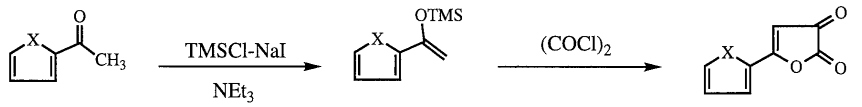


For Compounds **1 - 6**

a : X= H, **b**: X=Me, **c**: X=OMe, **d**: X=OTMS, **e**: X= F, **f**: X=Cl, **g**: X=NO_2, **h**: X=$OCH_2CH{=}CH_2$



7 : X=O
10 : X=S

8 : X=O
11 : X=S

9 : X=O
12 : X=S

Chart 1

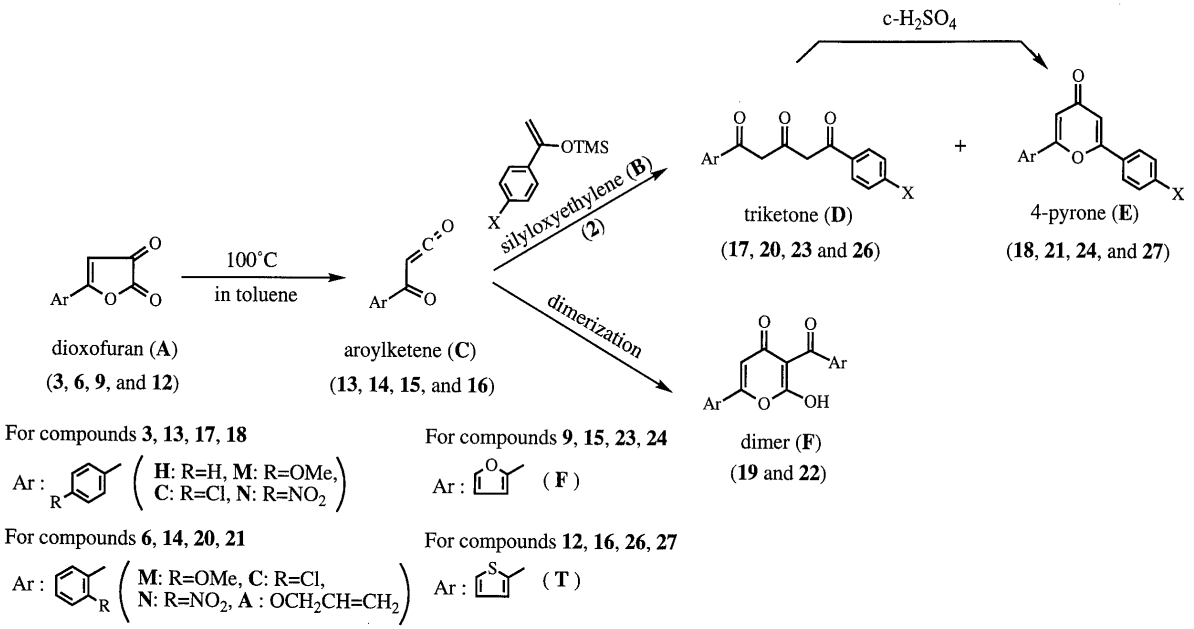


Chart 2

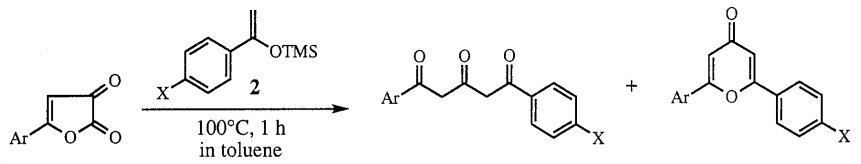
fairly good reactivities for this addition reaction. However, the yields of the products **17**C, **17**N, **20**C, **20**N, **18**C, **18**N, **21**C, and **21**N greatly depended on the olefin used. Thus, the *p*-OMe-phenyl derivative **2c** gave the adducts in good yields (54—73%). The phenyl **2a**, *p*-Me-phenyl **2b**, *p*-OTMS-phenyl **2d**, and *p*-F-phenyl derivatives **2e** gave the products in moderate yields (30—56%, 36—70%, 23—63%, and 34—55% respectively). The *p*-Cl-phenyl derivative **2f** gave the adducts in a lesser yield (18—36%) and the *p*-NO_2-phenyl derivative **2g** in a poor yield (0—26%).

Furoyl- and thenoylketenes on reaction with **2c** gave the adducts in good yields of 64% and 57%, respectively, although on reactions with the other olefins they gave the adducts in moderate or poor yields.

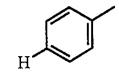
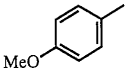
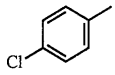
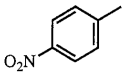
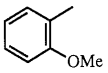
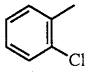
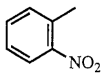
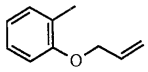
o-OMe-, *p*-OMe-, *o*-O-allyl-, and non-substituent benzoylketenes on reaction with **2c** gave the adducts in moderate yields of 45%, 21%, 48%, and 27%, respectively. However, on reaction with the other olefins they gave only poor results.

In order to estimate the reactivity of aroylketenes and 1-aryl-1-trimethylsilyloxyethylenes we used the sum of the yields as the reactivity index. The sums are given in Table 2. Thus, *o*-Cl-benzoyl- (348), *p*-Cl-benzoyl- (242), *p*-NO_2-benzoyl- (288) and *o*-NO_2-benzoyl- (234) ketenes showed a good reactivity. Thus, aroylketenes with electron withdrawing groups either in the *para* or *ortho* position are proved to be far more reactive than the non-substituted benzoylketene (132). The furoyl- (177) and thenoyl- (179) ketenes belong to the next reactive group. Although the

Table 1. Reaction of 5-Aryldioxofuran **3**, **6**, **9** and **12** with 1-Aryl-1-trimethylsilyloxyethylene **2**



A (**3**, **6**, **9**, **12**) **D** (**17**, **20**, **23**, **26**) **E** (**18**, **21**, **24**, **27**)

Entry	Starting material (A)	Ar	Product (%) (D and E)	Yields (%) with olefin **2** (X)						
				2a (H)	**2b** (Me)	**2c** (OMe)	**2d**[a] (OTMS)	**2e** (F)	**2f** (Cl)	**2g** (NO_2)
1	**3a**		17H	5	2	8	—	8	23	3
			18H	27	—	19	37	—	—	—
2	**3c**		17M	16	14	trace	18	12	12	—
			18M	1	3	21	3	1	4	—
3	**3f**		17C	26	38	53	51	32	16	7[b]
			18C	4	2	2	—	9	2	—
4	**3g**		17N	5	10	5	—	37	20	3
			18N	51	26	61	63	—	7	—
5	**6c**		20M	5	32	44	25	5	13	—[c]
			21M	3	3	1	2	9	7	—
6	**6f**		20C	51	63	63	43	49	11	19
			21C	4	7	10	6	6	9	7
7	**6g**		20N	18	9	37	—	—	11	—
			21N	32	28	17	23	34	25	—
8	**6h**		20A	3	16	36	33	4	14	3[d]
			21A	2	12	12	—	—	7	—
9	**9**		23F	—	44	60	—	21	24	—
			24F	11	4	4	5	3	1	—
10	**12**		26T	1	39	56	24	19	12	8
			27T	5	5	1	—	6	3	—

a) The compound was isolated as a phenol derivative (X=OH). *b*) Yield of dimer **19C** was 38%. *c*) Yield of dimer **22M** was 10%. *d*) Yield of dimer **22A** was 5%.

aroylketenes carrying electron donating groups belong to the least reactive group, the *o*-OMe-benzoyl- (149) and *o*-allyloxybenzoyl- (142) ketenes are slightly more reactive than the benzoylketene (132). The *p*-OMe-benzoylketene is least reactive (103).

Regarding the trimethylsilyloxyethylenes, the 1-*p*-OMe-phenyl derivative **2c** is proved to be far more reactive (510) than the other olefins examined. The *p*-Me- **2b** (357) and *p*-OTMS- **2d** (333) derivatives belong to the next reactive group. These olefins with electron donating groups are more reactive than the non-substituted olefin **2a** (270). Although the *p*-F- **2e** (255) and *p*-Cl- **2f** (221) are less reactive than the non-substituted olefin **2a**, they still keep some reactivity for the aroylketenes having electron attractive substituents. The *p*-NO_2-derivative **2g** is inactive (50) and gave practically no adducts (0—7%), with one exception (26% for *o*-Cl-benzoylketene).

The formation of such products can be rationalized by two mechanisms. One is a stepwise mechanism *via* a zwitterionic intermediate which is formed by nucleophilic attack of the trimethylsilyloxyethylene to the aroylketene generated by pyrolytic decarbonylation of 5-aryl-dioxofuran. The other is a mechanism of concerted [4+2] cycloaddition. This cycloaddition is an inverse electron-demand Diels–Alder reaction,[16] where the aroylketene behaves as an electron-deficient diene and 1-aryl-1-trimethylsilyloxyethylene as an electron-rich olefin.

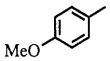
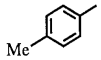
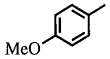
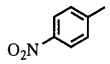
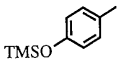
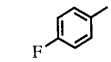
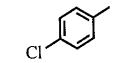
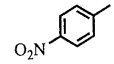
In the ionic mechanism (a) the triketone is formed by desilylation of the zwitterion, while the 4-pyrone is formed by intramolecular cyclization followed by desilyloxylation. In the [4+2] cycloaddition mechanism (b) the reaction directly gives the 4-pyrone as an intermediate, which then undergoes either pyrolytic desilyloxylation or ring opening with concomitant desilylation to yield the 4-pyrone or the triketone, respectively.

Orbital Analysis for the Addition Reaction of Aroylketene to 1-Aryl-1-trimethylsilyloxyethylene The addition reaction described above seems to be a suitable example for orbital analysis since the reaction proceeds in nonpolar and aprotic solvent merely by heating a mixture of the addends as in a typical Diels–Alder reaction. Therefore,

the analysis is expected to clarify the reactivities of these reactants and then the reaction mechanism. The experimental results clearly demonstrated that the aroylketene acts as an electrophile and that the 1-aryl-1-trimethylsilyloxyethylene acts as a nucleophile. Thus, we obtained molecular orbital (MO) energies and eigenvectors of the unoccupied molecular orbitals (UMO) for aroylketene and of the occupied molecular orbitals (OMO) for 1-aryl-1-trimethylsilyloxyethylene.[17] The data are listed in Table 3.

Inspection of the molecular orbitals demonstrated that the HOMO orbital of 1-aryl-1-trimethylsilyloxyethylene should act as a frontier orbital (FO) for this reaction since the large bonding orbital is spread over the ethylene moiety. The order of MO energy is *p*-OTMS- (−8.076 eV) > *p*-OMe- (−8.390 eV) > *p*-Me- (−8.512 eV) > H- (−8.609 eV) > *p*-Cl- (−8.630 eV) > *p*-F- (−8.728 eV) > *p*-NO_2- (−9.225 eV) derivatives. This is very consistent with the experimental results in which electron donating substituents facilitate the reaction while electron withdrawing substituents retard the reaction.

Table 2. Sum of Yields (%) of Adducts (Reactivity Index)

Ar	Aroylketene	Ar'	Siloxyethylene
	132		270
	103		357
	242		510
	288		333
	149		255
	348		221
	234		50
	142		
	177		
	179		

On the other hand, the UMOs of aroylketenes are fairly complex. This makes it difficult to assign unequivocally the FO of this reaction. In the LUMO of *o*-chlorobenzoylketene the lobes develop not only in the aroylketene part but also in the aryl part, as shown in Fig. 1. The figure demonstrated that this orbital is unable to participate in the concerted reaction (mechanism b) since the orbital of aroylketene moiety, with its lack of a the lobe at C3, does not accommodate the requirement necessary for the concerted reaction.

In this LUMO the lobes of the aroylketene moiety are relatively small when compared with those of the aryl moiety, suggesting that the reactivity of ketene for a nucleophile is decreased by a conjugation effect of the aroyl group. The LUMOs of *p*-chlorobenzoyl-, benzoyl-, furoyl-, *p*-methoxybenzoyl-, and *o*-methoxybenzoylketenes also have characteristics similar to the LUMO of *o*-chlorobenzoylketene. It can be concluded that the LUMOs may play a significant role in this reaction only when the orbital energy is very low. This is the case with *p*-chlorobenzoyl (MO: −0.698 eV, *Pz* at C_2: 0.25383) and *o*-chlorobenzoylketene (MO: −0.602 eV, *Pz* at C_2: 0.25962), which have a relatively large eigenvector at the electrophilic center. On the other hand, the reactions of nitrobenzoylketenes and thenoylketene should not be controlled by their LUMOs, in spite of their low orbital energies (−1.588 eV for *p*-NO_2, −0.632 eV for *o*-NO_2, and −0.898 eV for thenoyl), since the lobes of the electrophilic center are very small (0.14431 for *p*-NO_2, 0.12199 for *o*-NO_2, and 0.20203 for thenoyl).

The LUMO+1 of *o*-chlorobenzoylketene (Fig. 1) and those of other aroylketenes (in the case of *p*-nitrobenzoylketene the LUMO+2 corresponds to this type of orbital) have large lobes at the ketene carbonyl group (*Py* at

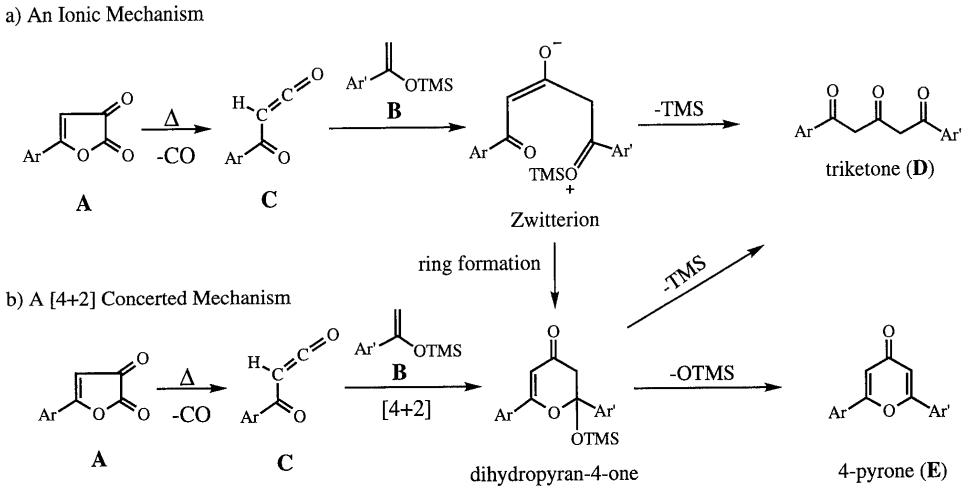
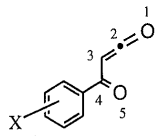


Chart 3

Table 3. Unoccupied Molecular Orbitals of Aroylketenes



X	MO	Energy (eV)		Eigenvectors				
				O-1	C-2	C-3	C-4	O-5
H	LUMO	−0.4726	*Pz*	−0.16711	0.29888	−0.06171	−0.38151	0.34243
	LUMO+1	−0.1076	*Py*	−0.52636	0.77641	0.04893	0.14363	−0.04397
	LUMO+2	0.1816	*Pz*	0.01618	−0.03090	0.01561	0.01420	−0.01312
	LUMO+3	0.5209	*Pz*	0.31506	−0.61323	0.36310	0.23808	−0.18009
p-NO_2	LUMO	−1.5880	*Pz*	0.08711	−0.14431	−0.01206	0.23748	−0.24326
	LUMO+1	−0.5474	*Pz*	0.00385	−0.00671	0.01510	0.01510	−0.01134
	LUMO+2	−0.4955	*Py*	−0.52696	0.77427	0.05546	0.14258	−0.04312
	LUMO+3	−0.1940	*Pz*	0.30592	−0.57287	0.25743	0.40980	−0.32383
o-NO_2	LUMO	−0.9698	*Pz*	−0.05483	0.07361	0.03938	0.05276	0.00768
	LUMO+1	−0.6320	*Pz*	−0.08699	0.12199	0.03695	0.06751	−0.00324
	LUMO+2	−0.3434	*Py*	−0.49865	0.74148	0.03600	0.09776	−0.02768
	LUMO+3	−0.2200	*Pz*	−0.32725	0.59307	−0.20675	−0.47608	0.37890
p-MeO	LUMO	−0.4098	*Pz*	0.16731	−0.30049	0.06629	0.37919	−0.33796
	LUMO+1	−0.0740	*Py*	0.52709	−0.77743	−0.04881	−0.14300	0.04365
	LUMO+2	0.1504	*Pz*	−0.00867	0.01667	−0.00883	−0.00482	0.00548
	LUMO+3	0.5559	*Pz*	−0.31433	0.61262	−0.36374	−0.23699	0.18046
o-MeO	LUMO	−0.1477	*Pz*	0.30105	−0.57183	−0.06419	−0.14259	0.02450
	LUMO+1	0.0344	*Py*	−0.32757	0.49284	−0.00907	0.03311	−0.03208
	LUMO+2	0.0706	*Pz*	−0.09042	0.13809	−0.00824	0.00377	−0.00386
	LUMO+3	0.2224	*Pz*	0.31946	−0.60126	0.27048	0.43339	−0.34773
p-Cl	LUMO	−0.6888	*Pz*	−0.14400	0.25383	−0.03822	−0.34674	0.31825
	LUMO+1	−0.18308	*Py*	0.52679	−0.77625	−0.05052	−0.14327	0.04358
	LUMO+2	−0.02158	*Pz*	−0.01015	0.01926	−0.00928	−0.00790	0.00816
	LUMO+3	0.37195	*Pz*	0.32291	−0.62328	0.34927	0.29081	−0.22213
o-Cl	LUMO	−0.6021	*Pz*	0.14684	−0.25962	0.04191	0.35302	−0.32714
	LUMO+1	−0.1238	*Py*	−0.52342	0.77222	0.05137	0.14687	−0.04347
	LUMO+2	−0.0599	*Pz*	−0.01210	0.02217	−0.00683	−0.02983	0.02098
	LUMO+3	0.4581	*Pz*	−0.32344	0.62637	−0.35856	−0.27435	0.20999
o-Allyl	LUMO	−0.0916	*Pz*	−0.43535	0.06934	0.06091	0.14255	−0.02558
	LUMO+1	0.1081	*Py*	0.28212	−0.42347	0.01186	−0.03320	0.04301
	LUMO+2	0.1884	*Pz*	0.04343	−0.08323	0.03739	0.07598	−0.06354
	LUMO+3	0.2571	*Pz*	−0.32489	0.61457	−0.28022	−0.45185	0.36656
Furyl	LUMO	−0.4634	*Pz*	0.20194	−0.36368	0.08901	0.43047	−0.38191
	LUMO+1	−0.2138	*Py*	0.48986	−0.72581	−0.05154	−0.15127	0.04810
	LUMO+2	0.5539	*Pz*	−0.29043	0.56913	−0.36137	−0.15041	0.11143
	LUMO+3	1.1865	*Pz*	−0.12272	0.25416	−0.23219	0.16042	−0.10885
Thienyl	LUMO	−0.8983	*Pz*	−0.11675	0.20203	−0.01432	−0.30171	0.28606
	LUMO+1	−0.2499	*Py*	0.34092	−0.51476	−0.05499	−0.12209	0.03172
	LUMO+2	0.2299	*Py*	−0.18078	0.26071	−0.03564	0.09537	−0.04301
	LUMO+3	0.3096	*Pz*	0.31814	−0.61075	0.32467	0.33511	−0.26077

$C_2 > 0.7$). Obviously, this orbital should be a major contributor to this reaction of all aroylketenes. Therefore, the reaction is facilitated when the orbital energies are low. This is the case with *p*-nitro- (−0.496 eV) and *o*-nitrobenzoylketene (−0.343 eV), and with thenoyl- (−0.250 eV) and furoylketene (−0.214 eV), *p*-chloro- (−0.183 eV) and *o*-chlorobenzoylketenes (−0.123 eV). If this orbital plays a role as the FO, the reaction should proceed in a stepwise manner (mechanism a).

The LUMO+2s of all aroylketenes (LUMO+1 for *p*-nitrobenzoylketene) are unable to be attributed to the reaction since the orbitals are spread over only the aromatic ring, such as the LUMO+2 of *o*-chlorobenzoylketene, as shown in the Fig 1.

The LUMO+3s have orbitals which are spread over the aroylketene, just like the LUMO of butadiene, and therefore may contribute to this reaction when the orbital energy is low. The orbital should operate as part of the concerted mechanism (b). This is the case with *p*-nitro- (−0.194 eV) and *o*-nitrobenzoylketene (−0.220 eV). This type of MO energy in the other aroylketenes is high (Table 3), so that these orbitals have no significance for this reaction.

It seems to be difficult to correlate this orbital analysis to the experimental results in a quantitative manner. However, in a qualitative sense this provides some interesting aspects regarding the reactivity of aroylketenes. The reactions of *p*-chloro- and *o*-chlorobenzoylketenes, which belong to the most reactive group, are controlled by the LUMO+1 and facilitated by the aid of the respective LUMO because of low MO energies. The reactions of *p*-nitro- and *o*-nitrobenzoylketenes, which also belong to the most reactive group, are facilitated by the participation of the LUMO+2 and the LUMO+3. The

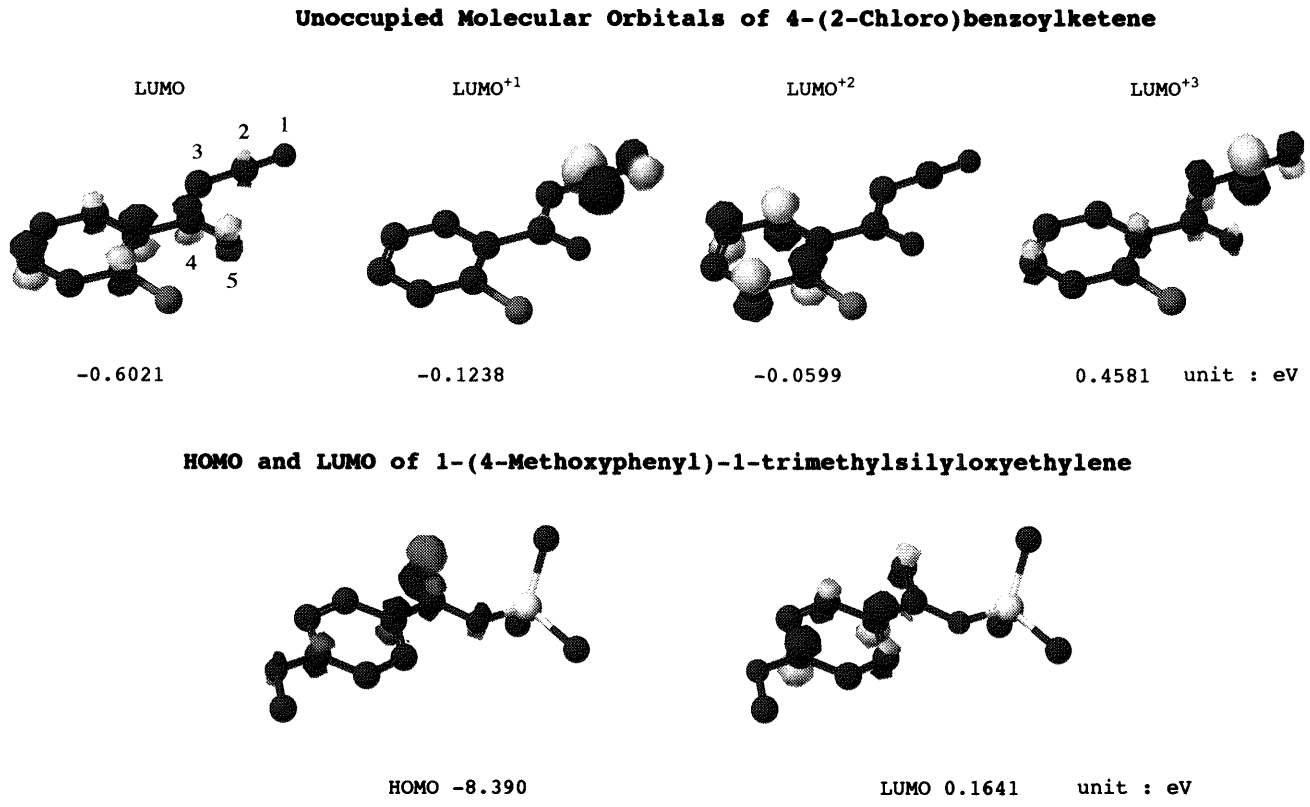


Fig. 1. Unoccupied Molecular Orbitals of 4-(2-Chloro)benzoylketene

reactions of furoylketene and thenoylketene of the second reactive group are governed by the LUMO+1s of relatively low orbital energies. The reactions of benzoyl-, *p*-methoxybenzoyl-, and *o*-methoxybenzoylketenes, which belong to the least reactive group, are controlled only by their respective LUMO since the MO energies of their LUMO+1s, most important for this reaction, are higher than those of the more reactive groups (Table 3). This probably decreases the reactivity of these aroylketenes.

Conclusions

The reactions of *p*-chlorobenzoyl-, *o*-chlorobenzoyl-, furoyl-, thenoyl-, benzoyl- and *p*-methoxybenzoyl, and *o*-methoxybenzoylketenes proceed exclusively in the ionic mechanism (a) and those of the nitrobenzoylketenes occur both in the ionic mechanism (a) and the concerted mechanism (b), in favor of the former. If mechanism a is operating, the major product should be a triketone, while if mechanism b operates, it should be the 4-pyrone. The observed fact that the nitrobenzoylketenes have a tendency to give the 4-pyrones as a major product, while the other aroylketenes have the tendency to give the triketones as a major product, suggests that the LUMO+3 participates to a considerable extent in the reaction of the nitrobenzoylketenes.

Besides the mechanistic interest, the thermal reaction of 5-aryl-2,3-dioxofuran with 1-aryl-1-trimethylsilyloxyethylene provides a simple synthetic method of preparing 1,5-diaryl-pentane-1,3,5-trione with various substituents in the aryl group. Particularly, the reaction between the aroylketene with electron withdrawing groups and the aryltrimethylsilyloxyethylene with electron donating groups is significant in the preparation of these compounds. This approach also provides a potentially versatile synthetic method of preparing various 2,6-diaryl-4*H*-pyran-4-ones since the 4-pyrone (E) is obtainable from the triketone (D) by acid catalyzed ring closure.[18]

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points (mp) were determined using a Yanaco MP-S1 melting point apparatus and are uncorrected. Infrared (IR) spectra were measured with a JASCO FT/IR-5000 Fourier transform infrared spectrometer using KBr and are given as cm^{-1}. Ultraviolet (UV) spectra were recorded on a Hitachi U-3200 spectrophotometer and are given as nm (ε). ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a JEOL JNM-EX90 (^{1}H; 90 MHz, ^{13}C; 22.5 MHz), JNM-FX100 (^{1}H; 100 MHz, ^{13}C; 25 MHz), JNM-GX270 (^{1}H; 270 MHz, ^{13}C; 67.5 MHz), or JNM-α500 (^{1}H; 500 MHz, ^{13}C; 125 MHz) Fourier transform spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard, unless otherwise noted. Chemical shifts (δ) were given in ppm from TMS. The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, ddd=double double doublet, t=triplet, q=quartet, m=multiplet. High-resolution (HR-MS) and low-resolution mass spectra (LR-MS) were obtained using JEOL JMS-D300 or JMS-HX110A or JEOL AX-505H spectrometers at 30 eV by the direct inlet system. Chemical ionization mass spectra (CI-MS) were obtained on a JEOL JMS-D300 spectrometer. Elemental analysis was recorded on a Yanaco CHN Corder MT-3. All organic extracts were washed with water or brine, and dried over Na_2SO_4 or $MgSO_4$ before concentration.

Materials Pre-coated silica gel glass plates [Merck Silica gel, Art 5715 (0.25 mm thickness)] were used for analytical thin layer chromatography (TLC), and Merck Art 13794 (0.5 mm thickness) or 13792 (1.0 mm thickness) for preparative thin layer chromatography (PTLC). Wakogel C-200 was used for column chromatography. Wakogel C-300 or Merck Silicagel 60 were used for flash column chromatography. Medium-pressure liquid chromatography (MPLC) was performed with Kusano CIG pre-packed silica gel columns, and peaks were detected with a Shodex SE-12 RI detector. The solvents used for all the reactions was a dried one.

Preparations of 1-Aryl-1-trimethylsilyloxyethylene 2 Triethylamine

(2 mol eq to ketone) and chlorotrimethylsilane (1.5 mol eq to ketone) were successively introduced into a stirred solution of acetophenone (1 mol eq 10—20 g) in CH_3CN at room temperature under an argon (Ar) atmosphere. A solution of NaI (1.5 mol eq to ketone) in CH_3CN (100—200 ml) was added dropwise to the above mixture over a period of 15 min. The resulting mixture was stirred at room temperature for 1—2 h. The reaction mixture was filtered, and the filter cake was washed with pentane or hexane. All filtrates were combined and concentrated *in vacuo*. If an inorganic salt was precipitated, the filtration–concentration process was done repeatedly. The residual oil was passed through a short column of SiO_2 eluted with hexane to give 1-aryl-1-trimethylsilyloxyethylene **2**, **5**, **8**, or **11** (yield >90%).

The data of compounds **2a**, **2b**, **2c**, **2d**, **2f**, and **2g** were reported in a preliminary paper.[12]

2e: ^{1}H-NMR: 0.27 (9H, s), 4.39 (1H, d, J=2 Hz), 4.83 (1H, d, J=2 Hz), 6.9—7.6 (4H, m).

5c: ^{1}H-NMR: 0.22 (9H, s), 3.85 (3H, s), 4.64 (1H, d, J=2 Hz), 5.01 (1H, d, J=2 Hz), 6.8—7.5 (4H, m).

5f: ^{1}H-NMR: 0.17 (9H, s), 4.55 (1H, d, J=1 Hz), 4.59 (1H, d, J=1 Hz), 7.1—7.3 (4H, m).

5g: ^{1}H-NMR: 0.22 (9H, s), 4.50 (1H, d, J=2 Hz), 4.67 (1H, d, J=2 Hz), 7.2—7.8 (4H, m).

5h: ^{1}H-NMR: 0.22 (9H, s), 4.6—4.7 (2H, m), 4.65 (1H, d, J=1 Hz), 5.07 (1H, d, J=1 Hz), 5.2—5.5 (2H, m), 5.9—6.2 (1H, m), 6.8—7.6 (4H, m).

8: ^{1}H-NMR: 0.26 (9H, s), 4.37 (1H, d, J=1 Hz), 4.88 (1H, d, J=1 Hz), 6.39 (2H, s,), 7.3—7.4 (1H, m).

11: ^{1}H-NMR: 0.31 (9H, s), 4.32 (1H, d, J=2 Hz), 4.80 (1H, d, J=2 Hz), 6.9—7.0 (1H, m), 7.2—7.3 (2H, m).

Preparations of Dioxofuran 3, 6, 9, and 12 (General Procedure) Oxalyl chloride (0.5 mol eq) was added dropwise to a solution of 1-aryl-1-trimethylsilyloxyethylene **2**, **5**, **8**, or **11** in ether (100—200 ml) at room temperature over a period of 1 h with stirring. The mixture was stirred for 5 h under the same conditions (in the case of **2g**, **5g** was heated under reflux). During the reaction, dioxofuran **3**, **6**, **9**, or **12** was precipitated as crystals. After cooling, the crystals were filtered and washed with ether. The filtrate was concentrated *in vacuo* to give a second crop. The crystals were combined and purified by recrystallization from CH_2Cl_2 to give dioxofuran **3**, **6**, **9**, or **12**.

3c: mp 133—135 °C. IR: 1818, 1715. UV: 373 (15300). ^{1}H-NMR: 3.94 (3H, s), 6.29 (1H, s), 7.0—7.2 (2H, m), 7.8—8.0 (2H, m). LR-MS m/z: 204 (M^+).

3f: mp 144—145 °C. IR: 1827, 1717. UV: 351 (13400). ^{1}H-NMR: 6.42 (1H, s), 7.48—7.74 (2H, m), 7.9—8.0 (2H, m). LR-MS m/z: 208 (M^+).

6c: mp 138—145 °C. IR: 1715, 1816. ^{1}H-NMR: 2.39 (3H, s), 5.09 (1H, s), 5.4—6.4 (4H, m).

6f: mp 1236—125 °C. IR: 1821, 1721, 1578, 1557. UV: 342 (10000), 236 (9100). HR-MS m/z (M^+): Calcd for $C_{10}H_6ClO_3$: 208.9983. Found: 209.0003.

6g: mp 94—104 °C. IR: 1734, 1829. UV: ^{1}H-NMR: 6.26 (1H, s), 7.8—8.2 (4H, m). CI-MS m/z: 220 (MH^+).

6h: mp 95—100 °C. IR: 1814, 1714, 1605, 1565. UV: 243 (9400), 268 (4500), 373 (11700). ^{1}H-NMR: 4.7—4.8 (2H, m), 5.3—5.6 (2H, m), 5.9—6.3 (1H, m), 6.77 (1H, s), 7.0—8.0 (4H, m). HR-MS m/z (M^+): Calcd for $C_{13}H_{10}O_4$: 230.0580, Found: 230.0616.

5-(2-Furyl)-2,3-dioxofuran (**9**): Yellow prisms, mp 133—136 °C. IR: 1843, 1823, 1715, 1607, 1516. UV: 239 (5700), 282 (4900), 365 (17100). ^{1}H-NMR: 6.25 (1H, s, C_4-H), 6.76 (1H, dd, J=2, 4 Hz, $C_{4'}$-H), 7.24 (1H, d, J=4 Hz, $C_{3'}$-H), 7.88 (1H, dd, J=2 Hz, C_5-H). ^{13}C-NMR: 100.0 (d, C_4), 114.0 (d, $C_{4'}$), 120. 1 (d, $C_{3'}$), 142.8 (s, C_5), 150.7 (d, $C_{5'}$), 154.8 (s, $C_{2'}$), 168.4 (s, C_3), 176.9 (s, C_2). HR-MS m/z (M^+): Calcd for $C_8H_4O_4$: 164.0110. Found: 164.0112.

5-(2-Thienyl)-2,3-dioxofuran (**12**): Yellow prisms, mp 190 °C. IR: 1827, 1711, 1572. UV: 261 (5500), 281 (5200), 373 (1500). ^{1}H-NMR: 6.23 (1H, s, C_4-H), 7.33 (1H, dd, J=4, 5 Hz, $C_{4'}$-H), 7.92 (1H, dd, J=1, 5 Hz, $C_{3'}$-H), 7.95 (1H, dd, J=1, 4 Hz, $C_{5'}$-H). ^{13}C-NMR: 100.3 (d, C_4), 129.8 (d, $C_{4'}$), 133.8 (s, $C_{5'}$), 136.5 (d, $C_{3'}$), 1136.6 (d, C_5), 155.0 (s, $C_{2'}$), 173.3 (s, C_3), 177.1 (s, C_2). HR-MS m/z (M^+): Calcd for $C_8H_4O_3S$: 179.9880. Found: 179.9880.

Reaction of Dioxofuran 3, 6, 9, or 12 with 1-Aryl-1-trimethylsilyloxyethylene 2 (General Procedure) A mixture of dioxofuran **3**, **6**, **9**, or **12** (500 mg) and 1-aryl-1-trimethylsilyloxyethylene **2** (2 mol eq) in toluene (10 ml) was stirred at 100 °C for 1 h. After concentration *in vacuo*, the residue was purified by column chromatography, flash chromatography, MPLC and/or PTLC followed by recrystallization to afford 1,5-diarylpentane-1,3,5-trione **17H**, **17M**, **17C**, **17N**, **20M**, **20C**, **20N**, **20A**, **23F**, **26T** and 2,6-diaryl-4*H*-pyran-4-one **18H**, **18M**, **18C**, **18N**, **21M**, **21C**, **21N**, **21A**, **24F**, **27T**, and/or 5-aroyl-2-aryl-6-hydroxy-4*H*-pyran-4-one **19C**, **22M**, **22A**.

17H-a, **17H-b**, **17H-c** (=**17M-a**), **17H-f**, **17H-g** (=**17N-a**), **17C-g** (=**7N-f**), **17N-a** (=**17H-g**), **17N-b**, **17N-c** (=**17M-g**), **17N-e**, **17N-g**, **18H-a**, **18H-c** (=**18M-a**), **18H-d**, **18N-a** (=**18H-g**), **18N-b**, **18N-c** (=**18M-g**), **18N-d**, and **18N-f** (=**18C-g**) were reported in a preliminary paper.[12]

1-(4-Fluorophenyl)-5-phenylpentane-1,3,5-trione (**17H-e**): Yellow needles from CH_2Cl_2–ether, mp 72—74 °C. IR: 1607, 1570. UV: 244 (844), 382 (2440). LR-MS m/z: 284 (M^+).

1-(4-Methoxyphenyl)-5-(4-tolyl)pentane-1,3,5-trione (**17M-b**): Eluting solvent for column chromatography: benzene–hexane (1:1). Yellow prisms from AcOEt–ether, mp 102—103 °C. IR: 1593, 1562. UV: 224 (10400), 260 (9100), 322 (11400), 394 (27100). LR-MS m/z: 330 (M^+).

1-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**17M-d**): Eluting solvent for column chromatography: CH_2Cl_2. Then for MPLC: AcOEt–benzene (1:2). Yellow oil. IR: 1605, 1512. UV: 217 (17000), 271 (18800), 326 (7700), 398 (4700). LR-MS m/z: 294 (M^+).

1-(4-Fluorophenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**17M-e**): Eluting solvent for flash chromatography: benzene. Yellow prisms from CH_2Cl_2–ether, mp 145—146 °C. IR: 1605, 1589, 1576, 1508. UV: 392 (24400). LR-MS m/z: 314 (M^+).

1-(4-Chlorophenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**17M-f**): Eluting solvent for column chromatography: benzene–hexane (1:1). Yellow prisms from CH_2Cl_2–ether, mp 140—141 °C. IR: 1610, 1594, 1560, 1508. UV: 238 (11300), 260 (10400), 323 (12100), 395 (32100). LR-MS m/z: 331 (M^+).

1-(4-Chlorophenyl)-5-(4-tolyl)pentane-1,3,5-trione (**17C-b**): Eluting solvent for column chromatography: benzene–hexane (2:1). Yellow prisms from CH_2Cl_2–ether, mp 135—137 °C. IR: 1604, 1568, 1510. UV: 237 (7900), 257 (8500), 321 (7300), 389 (23600). LR-MS m/z: 314 (M^+).

1-(4-Chlorophenyl)-5-(4-hydroxyphenyl)pentane-1,3,5-trione (**17C-d**): Eluting solvent for column chromatography: CH_2Cl_2. Yellow prisms from ether, mp 87—89 °C. IR: 1598, 1564. UV: 259 (9600), 322 (10000), 394 (27400). HR-MS m/z (M^+): Calcd for $C_{17}H_{13}O_4Cl$: 316.0499. Found 316.0486.

1-(4-Chlorophenyl)-5-(4-fluorophenyl)pentane-1,3,5-trione (**17C-e**): Eluting solvent for column chromatography: benzene–hexane (2:1). Yellow prisms from CH_2Cl_2, mp 112—114 °C. IR: 1618, 1598, 1564, 1504. UV: 236 (11200), 253 (11200), 386 (31000). LR-MS m/z: 318 (M^+).

1,5-Di-(4-chlorophenyl)pentane-1,3,5-trione (**17C-f**): Eluting solvent for column chromatography: benzene–hexane (2:3). Yellow prisms from ether–hexane, mp 146—149 °C. IR: 1600, 1564. UV: 236 (11800), 257 (12500), 386 (34300).

1-(2-Methoxyphenyl)-5-phenylpentane-1,3,5-trione (**20M-a**): Eluting solvent for MPLC: AcOEt. After MPLC, the resulting residue was extracted with CH_2Cl_2 and 5% sodium hydroxide. The aqueous layer was acidified with 5% hydrochloric acid. The whole was extracted with CH_2Cl_2. The organic extract gave yellow prisms. mp 108—113 °C. IR: 1586. UV: 388 (28537). LR-MS m/z: 296 (M^+).

1-(2-Methoxyphenyl)-5-(tolyl)pentane-1,3,5-trione (**20M-b**): Pale yellow needles from CH_2Cl_2, mp 110—112 °C. IR: 1586. UV: 388 (29233). LR-MS m/z: 310 (M^+).

1-(2-Methoxyphenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**20M-c**): Eluting solvent for column chromatography: benzene. Yellow plates from CH_2Cl_2, mp 100—106 °C. IR: 1605. UV: 397 (42368). LR-MS m/z: 326 (M^+).

1-(4-Hydroxyphenyl)-5-(2-methoxyphenyl)pentane-1,3,5-trione (**20M-d**): Dark brown plates from CH_2Cl_2, mp 137—143 °C. IR: 1605. UV: 397 (26043). LR-MS m/z: 312 (M^+).

1-(4-Fluorophenyl)-5-(2-methoxyphenyl)pentane-1,3,5-trione (**20M-e**): Yellow plates from CH_2Cl_2, mp 118—120 °C. IR: 1603. UV: 388 (27304). LR-MS m/z: 314 (M^+).

1-(4-Clorophenyl)-5-(2-methoxyphenyl)pentane-1,3,5-trione (**20M-f**): Yellow needles from CH_2Cl_2, mp 129—132 °C. IR: 1601. UV: 391 (29757). LR-MS m/z: 330 (M^+).

1-(2-Chlorophenyl)-5-phenylpentane-1,3,5-trione (**20C-a**): Eluting solvent for column chromatography: benzene–hexane (2:3). Yellow prisms from ether–hexane, mp 75 °C. IR: 1598, 1588, 1574, 1558. UV: 272 (4800), 291 (8700), 372 (29400). LR-MS m/z: 300 (M^+).

1-(2-Chlorophenyl)-5-(4-tolyl)pentane-1,3,5-trione (**20C-b**): Eluting solvent for column chromatography: benzene–hexane (2 : 3). Yellow prisms from CH_2Cl_2–ether, mp 64—66 °C. IR: 1610, 1600, 1580, 1558. UV: 234 (8400), 375 (28700). LR-MS *m/z*: 314 (M^+).

1-(2-Chlorophenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**20C-c**): Eluting solvent for column chromatography: benzene–hexane (1 : 1). Yellow prisms from ether–hexane, mp 85—88 °C. IR: 1604, 1560, 1510. UV: 292 (8600), 384 (30500). LR-MS *m/z*: 330 (M^+).

1-(2-Chlorophenyl)-5-(4-hydroxyphenyl)pentane-1,3,5-trione (**20C-d**): Eluting solvent for flash column chromatography: CH_2Cl_2. Yellow prisms from CH_2Cl_2–ether, mp 68—70 °C. IR: 1600, 1574, 1560, 1508. UV: 293 (8600), 386 (24600). LR-MS *m/z*: 316 (M^+).

1-(2-Chlorophenyl)-5-(4-fluorophenyl)pentane-1,3,5-trione (**20C-e**): Eluting solvent for flash column chromatography: benzene–hexane (2 : 1). Yellow prisms from ether–hexane, mp 85—88 °C. IR: 1600, 1574, 1560, 1508. UV: 234 (8700), 371 (26100). LR-MS *m/z*: 318 (M^+).

1-(2-Chlorophenyl)-5-(4-chlorophenyl)pentane-1,3,5-trione (**20C-f**): Eluting solvent for flash column chromatography: benzene–hexane (1 : 2). Yellow prisms from ether–hexane, mp 88—91 °C. IR: 1600, 1584, 1560. UV: 238 (8800), 251 (8800), 374 (25600). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{12}Cl_2O_3$: 334.0127. Found: 334.0162.

1-(2-Chlorophenyl)-5-(4-nitrophenyl)pentane-1,3,5-trione (**20C-g**): Eluting solvent for flash column chromatography: benzene–hexane (1 : 1). Yellow prisms from CH_2Cl_2–ether, mp 146—149 °C. IR: 1610, 1588, 1558, 1520. UV: 263 (32900), 380 (12300). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{12}ClNO_5$: 345.0424. Found: 345.0422.

1-(2-Nitrophenyl)-5-phenylpentane-1,3,5-trione (**20N-a**): Eluting solvent for column chromatography: benzene–hexane (1 : 1). Yellow plates from CH_2Cl_2, mp 103—107 °C. IR: 1528, 1568, 1593. UV: 366 (16200). CI-MS *m/z*: 312 (MH^+).

1-(4-Tolyl)-5-(2-nitrophenyl)pentane-1,3,5-trione (**20N-b**): Eluting solvent for column chromatography: benzene–hexane (1 : 3). Yellow plates from CH_2Cl_2–ether, mp 105—108 °C. IR: 1535, 1560, 1580, 1605 UV: 373 (12800), 258 (14200). LR-MS *m/z*: 325 (M^+).

1-(4-Methoxyphenyl)-5-(2-nitrophenyl)pentane-1,3,5-trione (**20N-c**): Eluting solvent for column chromatography: benzene–hexane. Yellow plates from CH_2Cl_2–ether, mp 98—108 °C. IR: 1539, 1603. UV: 381 (17200). LR-MS *m/z*: 341 (M^+)

1-(4-Chlorophenyl)-5-(2-nitrophenyl)pentane-1,3,5-trione (**20N-f**): Eluting solvent for column chromatography: benzene. Yellow needles from CH_2Cl_2–ether, mp 122—125 °C. IR: 1522, 1562, 1586. UV: 371 (20000), 250 (13300). LR-MS *m/z*: 345 (M^+).

1-(2-Allyloxyphenyl)-5-phenylpentane-1,3,5-trione (**20A-a**): Eluting solvent for column chromatography: benzene–hexane (1 : 1). Developing solvent for PTLC: benzene. Yellow oil. IR: 1607, 1557. UV: 388 (16600). HR-MS *m/z* (M^+): Calcd for $C_{20}H_{18}O_4$: 322.1203. Found 322.1201.

1-(2-Allyloxyphenyl)-5-(4-tolyl)pentane-1,3,5-trione (**20A-b**): Eluting solvent for column chromatography: benzene–hexane (1 : 1). Developing solvent for PTLC: CH_2Cl_2–benzene (1 : 3). Yellow oil. IR: 1562, 1589, 1603. UV: 326 (9500), 390 (19500). HR-MS *m/z* (M^+): Calcd for $C_{21}H_{20}O_4$: 336.1361. Found: 336.1383.

1-(2-Allyloxyphenyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**20A-c**): Eluting solvent for column chromatography: benzene. Yellow oil. IR: 1564, 1604. UV: 330 (12400), 395 (24900). HR-MS *m/z* (M^+): Calcd for $C_{21}H_{20}O_5$: 352.1311. Found: 352.1314.

1-(2-Allyloxyphenyl)-5-(4-hydroxyphenyl)pentane-1,3,5-trione (**20A-d**): Eluting solvent for flash column chromatography: AcOEt–hexane (1 : 2). For further purification, column chromatography was carried out by elution with AcOEt–benzene (1 : 20). Yellow oil. IR: 1562, 1603. UV: 330 (14000), 396 (25900).

1-(2-Allyloxyphenyl)-5-(4-fluorophenyl)pentane-1,3,5-trione (**20A-e**): Eluting solvent for column chromatography: benzene–hexane (3 : 2). solvent for PTLC: benzene. Yellow oil. IR: 1568, 1605. UV: 273 (16200), 339 (7700). HR-MS *m/z* (M^+): Calcd for $C_{20}H_{17}O_4$: 340.1111. Found: 340.1114.

1-(2-Allyloxyphenyl)-5-(4-chlorophenyl)pentane-1,3,5-trione (**20A-f**): Eluting solvent for flash column chromatography: benzene. For further purification, column chromatography was carried out by elution with CH_2Cl_2–hexane (1 : 3). Yellow needles from ether, mp 65—67 °C. IR: 1547. UV: 213 (16900), 249 (8800), 328 (10500), 391 (25100). CI-MS: *m/z*: 357 (MH^+).

1-(2-Allyloxyphenyl)-5-(4-nitrophenyl)pentane-1,3,5-trione (**20A-g**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 3). For further purification, column chromatography was carried out by elution with benzene–hexane (1 : 1). Yellow needles from CH_2Cl_2–ether, mp 113—115 °C. IR: 1568, 1586, 1605. UV: 254 (11900), 326 (11700), 339 (11700), 401 (36200). CI-MS *m/z*: 368 (MH^+).

1-(2-Furyl)-5-(4-tolyl)pentane-1,3,5-trione (**23F-b**): Eluting solvent for column chromatography: acetone–hexane (1 : 20). Yellow prisms from CH_2Cl_2–ether, mp 95—96 °C. IR: 1599, 1543, 1510, UV: 262 (9000), 323 (10700), 393 (25000), LR-MS *m/z*: 270 (M^+).

1-(2-Furyl)-5-(4-methoxyphenyl)pentane-1,3,5-trione (**23F-c**): Eluting solvent for column chromatography: acetone–hexane (1 : 10). Yellow needles from CH_2Cl_2–ether, mp 105—106 °C. IR: 1613, 1551, 1514. UV: 272 (10300), 328 (12900), 399 (25900). *Anal.* Calcd for $C_{16}H_{14}O_5$: C, 67.12; H, 4.93. Found: C, 67.33; H, 5.02. HR-MS *m/z* (M^+): Calcd for $C_{16}H_{14}O_5$: 286.0838. Found: 286.0823.

1-(2-Furyl)-5-(4-fluorophenyl)pentane-1,3,5-trione (**23F-e**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 20). Yellow needles from CH_2Cl_2–ether, mp 105—106 °C. IR: 1615, 1591, 1549, 1512. UV: 321 (10800), 391 (26600). CI-MS *m/z*: 275 (MH^+).

1-(2-Furyl)-5-(4-chlorophenyl)pentane-1,3,5-trione (**23F-f**): Eluting solvent for column chromatography: AcOEt–hexane (2 : 1). Yellow needles from CH_2Cl_2–ether, mp 135—136 °C. IR: 1607, 1549, 1493. UV: 235 (8200), 260 (9900), 325 (10900), 394 (30500). HR-MS *m/z* (M^+): Calcd for $C_{15}H_{11}ClO_4$: 290.0343. Found: 290.0318.

1-Phenyl-5-(2-thienyl)pentane-1,3,5-trione (**26T-a**): Eluting solvent for column chromatography: benzene–acetone (10 : 1). Yellow needles from CH_2Cl_2–ether, mp 78—79 °C. IR: 1593, 1574. UV: 253 (15500), 313 (19700), 397 (33400). *Anal.* Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.35; H, 4.55.

1-(4-Tolyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-b**): Eluting solvent for column chromatography: benzene–acetone (15 : 1). Yellow prisms from CH_2Cl_2–ether, mp 66—68 °C. IR: 1593, 1570, 1512. UV: 259 (11900), 322 (13200), 399 (19600). HR-MS *m/z* (M^+): Calcd for $C_{17}H_{14}O_3S$: 286.0661. Found: 286.0613.

1-(4-Methoxyphenyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-c**): Eluting solvent for column chromatography: AcOEt–hexane (10 : 1). Yellow plates from CH_2Cl_2–ether, mp 94—95 °C. IR: 1597, 1514. UV: 270 (1100), 330 (14000), 404 (16700). HR-MS *m/z* (M^+): Calcd for $C_{16}H_{14}O_4S$: 302.0610. Found: 302.0584.

1-(4-Hydroxyphenyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-d**): Eluting solvent for column chromatography: AcOEt–hexane (4 : 1) and benzene–acetone (4 : 1). Yellow plates from CH_2Cl_2–ether, mp 164—167 °C (dec.). IR: 1586, 1508. UV: 266 (17300), 329 (9100), 405 (9300).

1-(4-Fluorophenyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-e**): Eluting solvent for column chromatography: acetone–hexane (1 : 100). Yellow needles from CH_2Cl_2–ether, mp 88—89 °C. IR: 1605, 1589, 1510. UV: 254 (4800), 312 (8300), 397 (9100). HR-MS *m/z* (M^+): Calcd for $C_{15}H_{11}FSO_3$: 290.0413. Found: 290.0451.

1-(4-Chlorophenyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-f**): Eluting solvent for column chromatography: acetone–hexane (1 : 15). Yellow needles from CH_2Cl_2–ether, mp 102—103 °C. IR: 1611, 1491, 1404. UV: 260 (11300), 315 (12300), 399 (20800). CI-MS *m/z*: 307 (MH^+).

1-(4-Nitrophenyl)-5-(2-thienyl)pentane-1,3,5-trione (**26T-g**): Eluting solvent for column chromatography: acetone–hexane (1 : 15). Yellow prisms from CH_2Cl_2–ether, mp 145—146 °C. IR: 1622, 1580, 1531. UV: 252 (9500), 390 (31200), LR-MS *m/z*: 317 (M^+).

2-(4-Methoxyphenyl)-6-(4-tolyl)-4*H*-pyran-4-one (**18M-b**): Eluting solvent for column chromatography: AcOEt–hexane (3 : 1). Colorless prisms from CH_2Cl_2–ether, mp 138—140 °C. IR: 1659, 1611, 1510. UV: 269 (25100), 298 (25400). ^{1}H-NMR: 2.44 (3H, s), 3.89 (3H, s), 6.71 (1H, d, J=2 Hz), 6.75 (1H, d, J=2 Hz), 7.03 (2H, d, J=9 Hz), 7.32 (2H, d, J=9 Hz), 7.74 (2H, d, J=8 Hz), 7.81 (2H, d, J=8 Hz). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{16}O_3$: 292.1097. Found: 292.1087.

2,6-Di-(4-methoxyphenyl)-4*H*-pyran-4-one (**18M-c**): Colorless prisms from benzene, mp 115—118 °C. IR: 1650, 1604, 1594, 1504. UV: 283 (28900), 303 (29700). ^{1}H-NMR: 3.89 (6H, s × 2), 6.69 (2H, s × 2), 7.0—7.1 (4H, m), 7.8—7.9 (4H, m). ^{13}C-NMR: 55.5 (q × 2), 109.8 (d × 2), 114.6 (d × 4), 124.0 (s × 2), 127.6 (d × 4), 162.1 (s × 2), 163.2 (s × 2), 180.3 (s). LR-MS *m/z*: 308 (M^+).

2-(4-Hydroxyphenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**18M-d**): Eluting solvent for column chromatography: acetone. Colorless prisms from CH_2Cl_2–ether, mp 274—275 °C. IR: 1640, 1611, 1562, 1510. UV: 274 (20300), 284 (20300), 303 (19600). LR-MS *m/z*: 294 (M^+).

2-(4-Fluorophenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**18M-e**): Eluting solvent for flash chromatography: acetone. Colorless prisms from

CH_2Cl_2–ether, mp 144—148 °C. IR: 1659, 1605, 1574, 1510. UV: 265 (18000), 296 (18000). ^{1}H-NMR: 3.82 (3H, s), 6.66 (1H, s×2), 6.9—7.2 (4H, m), 7.7—7.9 (4H, m). ^{13}C-NMR: 55.5 (q), 109.9 (d), 111.1 (d), 114.6 (d×2), 116.4 (d×2, J=22 Hz, –C*–C–F), 123.7 (s), 127.6 (d×2), 127.8 (s), 128.1 (d×2, J=10 Hz, –C*–C–C–F), 162.3 (s), 163.5 (s), 164.6 (d, J=253 Hz, –C*–F), 180.0 (s). LR-MS m/z: 296 (M^+).

2-(4-Chlorophenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**18**M-**f**=**18**C-**c**): Eluting solvent for column chromatography: AcOEt–hexane (2:1). Colorless prisms from CH_2Cl_2–ether, mp 170—173 °C. IR: 1654, 1598. UV: 260 (26100), 285 (30700).^{1}H-NMR: 3.90 (3H, s), 6.71, 6.75 (each 1H, d, J=2 Hz), 7.0—7.1 (2H, m), 7.4—7.5 (2H, m), 7.7—7.8 (4H, m). ^{13}C-NMR: 55.5 (q), 110.1 (d), 111.4 (d), 114.6 (d×2), 123.6 (s), 127.2 (d×2), 127.6 (d×2), 129.5 (d×2), 130.1 (s), 137.6 (s), 162.0 (s), 162.3 (s), 163.5 (s), 180.1 (s).

2-(4-Chlorophenyl)-6-phenyl-4*H*-pyran-4-one (**18**C-**a**=**18**H-**f**). Eluting solvent for column chromatography: AcOEt–hexane (1:1). Colorless prisms, mp 158—160 °C. IR: 1682, 1600, 1570. UV: 254 (29200). ^{1}H-NMR: 6.48, 6.71 (each 1H, d, J=2 Hz), 7.3—7.7 (4H, m), 7.8—7.9 (2H, m). HR-MS m/z (M^+): Calcd for $C_{17}H_{11}ClO_2$: 282.0447. Found: 282.0457.

2-(4-Chlorophenyl)-6-(4-tolyl)-4*H*-pyran-4-one (**18**C-**b**): Colorless prisms from CH_2Cl_2–ether, mp 194—195 °C. IR: 1644, 1608, 1594, 1560, 1508. UV: 264 (26000), 288 (33000). ^{1}H-NMR: 2.32 (3H, d, J=1 Hz), 6.14 (1H, dd, J=2, 1 Hz), 6.63 (1H, d, J=2 Hz), 7.3—7.4, 7.6—7.7 (each 2H, m). ^{13}C-NMR: 21.5 (q), 110.9 (d), 111.5 (d), 125.9 (d×2), 127.2 (d×2), 128.5 (s), 129.5 (d×2), 129.9 (d×2), 130.0 (s), 137.6 (s), 142.2 (s), 162.1 (s), 163.6 (s), 180.1 (s). HR-MS m/z (M^+): Calcd for $C_{18}H_{13}ClO_2$: 296.0604. Found: 296.0611.

2-(4-Chlorophenyl)-6-(4-fluorophenyl)-4*H*-pyran-4-one (**18**C-**e**): Eluting solvent for column chromatography: MeOH. Developing solvent for PTLC: AcOEt–hexane (3:2). Colorless prisms from CH_2Cl_2–MeOH, mp 155—158 °C. IR: 1658, 1604, 1558, 1540, 1510. UV: 259 (16400), 285 (18600). ^{1}H-NMR: 6.78, 6.75 (each 1H, d, J=2 Hz), 7.1—7.3, 7.5—7.6 (each 2H, m), 7.7—7.9 (4H, m). ^{13}C-NMR: 111.0 (d), 111.3 (d), 116.6 (d×2, J=21 Hz, –C*–C–F), 127.4 (d×2, s), 128.4 (d×2, J=9 Hz, –C*–C–C–F), 129.7 (d×2, s), 138.1 (d), 163.2 (s), 164.9 (d, J=253 Hz, –C*–F). 180,7 (s). LR-MS m/z: 300 (M^+).

2,6-Di-(4-chlorophenyl)-4*H*-pyran-4-one (**18**C-**f**): Eluting solvent for column chromatography: CH_2Cl_2. Colorless prisms from CH_2Cl_2–ether, mp 215—218 °C. IR: 1714, 1648, 1580, 1560. UV: 248 (17600), 262 (17300), 286 (19000). ^{1}H-NMR: 6.83 (1H, s×2), 7.3—8.1 (8H, m). ^{13}C-NMR: 111.6 (d×2) 127.2 (d×2), 128.9 (d×2), 129.6 (d×2), 129.8 (s×2), 131.6 (d×2), 137.9 (s×2), 162.5 (s×2), 180.0 (s). LR-MS m/z: 317 (M^+).

2-(2-Methoxyphenyl)-6-phenyl-4*H*-pyran-4-one (**21**M-**a**): Eluting solvent for MPLC: AcOEt. Pale yellow needles from CH_2Cl_2, mp 123—128 °C. IR: 1657. UV: 296 (16511). ^{1}H-NMR: 3.90 (3H, s), 6.80 (1H, d, J=2 Hz), 7.10 (1H, d, J=2 Hz), 7.4—7.9 (9H, m). ^{13}C-NMR: 55.7 (q), 111.8 (d), 116.3 (d×2), 120.5 (s), 120.8 (d), 125.9 (d×2), 129.0 (d×2), 129.1 (d×2), 131.8 (s), 132.3 (d), 157.8 (s), 160.9 (s), 163.5 (s), 180.8 (s). LR-MS m/z: 278 (M^+).

2-(2-Methoxyphenyl)-6-(4-tolyl)-4*H*-pyran-4-one (**21**M-**b**): Eluting solvent for column chromatography: AcOEt. Colorless needles from CH_2Cl_2, mp 125—137 °C. IR: 1659. UV: 294 (17691). ^{1}H-NMR: 2.43 (3H, s), 3.94 (3H, s), 6.76 (1H, d, J=2 Hz), 7.08 (1H, d, J=2 Hz), 7.2—7.9 (8H, m). ^{13}C-NMR: 21.5 (q), 55.6 (q), 110.4 (d), 111.8 (d), 116.2 (d), 120.6 (s), 120.8 (d), 125.9 (d×2), 129.0 (d), 129.8 (d×3), 132.2 (d), 141.8 (s), 157.8 (s), 160.7 (s), 163.7 (s), 180.8 (s). LR-MS m/z: 292 (M^+).

2-(2-Methoxyphenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**21**M-**c**): Eluting solvent for column chromatography: CH_2Cl_2. Pale yellow plates from CH_2Cl_2, mp 115—118 °C. IR: 1644. UV: 297 (19619). ^{1}H-NMR: 3.88 (3H, s), 3.94 (3H, S), 6.73 (1H, d, J=2 Hz), 7.93 (1H, d, J=2 Hz), 7.0—7.8 (8H, m). ^{13}C-NMR: 55.5 (q), 55.7 (q), 111.8 (d), 113.7 (d), 114.5 (d×2), 116.1 (d), 120.6 (s), 120.8 (d), 124.1 (s), 127.6 (d×2), 129.0 (d), 132.2 (d), 157.8 (s), 160.7 (s), 162.1 (s), 163.7 (s), 180.9 (s). LR-MS m/z: 308 (M^+).

2-(4-Hydroxyphenyl)-6-(2-methoxyphenyl)-4*H*-pyran-4-one (**21**M-**d**): Eluting solvent for column chromatography: AcOEt. Yellow needles from CH_2Cl_2, mp 190—200 °C. IR: 1638. UV: 263 (8896). ^{1}H-NMR: 3.91 (3H, s), 6.74 (1H, d, J=2 Hz), 7.12 (1H, d, J=2 Hz), 6.9—7.8 (8H, m), 10.22 (1H, br s). ^{13}C-NMR: 55.6 (q), 111.8 (d), 115.7 (d), 116.3 (d×3), 120.3 (d), 120.9 (d), 123.3 (s), 127.9 (d×2), 129.0 (d), 132.4 (d), 152.8 (s), 161.2 (s×2), 164.4 (s), 181.5 (s). LR-MS m/z: 294 (M^+).

2-(4-Fluorophenyl)-6-(2-methoxyphenyl)-4*H*-pyran-4-one (**21**M-**e**): Eluting solvent for column chromatography: CH_2Cl_2. Dark brown plates from CH_2Cl_2, mp 141—148 °C. IR: 1651. UV: 275 (16967). ^{1}H-NMR: 3.94 (3H, s), 6.74 (1H, d, J=2 Hz), 7.28 (1H, d, J=2 Hz), 7.0—7.9 (8H, m). ^{13}C-NMR: 55.9 (q), 110.6 (d), 111.7 (d), 115.9 (d×2, J=8 Hz, –C*–C–C–F), 116.7 (d), 120.2 (s), 120.7 (d), 127.6 (s), 127.9 (s), 128.1 (d), 128.3 (d×2, J=23 Hz, –C*–C–F), 132.3 (d), 160.8 (s), 162.4 (s), 164.4 (d, J=253 Hz, –C*–F), 180.5 (s). LR-MS m/z: 296 (M^+).

2-(4-Chlorophenyl)-6-(2-methoxyphenyl)-4*H*-pyran-4-one (**21**M-**f**): Eluting solvent for column chromatography: AcOEt. Pale yellow plates from CH_2Cl_2, mp 165—170 °C. IR: 1644. UV: 248 (17266). ^{1}H-NMR ($CDCl_3$–CD_3OD): 3.68 (3H, s), 6.83 (1H, d, J=2 Hz), 7.11 (1H, d, J=2 Hz), 7.8—8.0 (8H, m). ^{13}C-NMR: 55.5 (q), 110.4 (d), 11.8 (d), 115.6 (d), 119.8 (s), 120.8 (d), 127.2 (d×2), 128.9 (d), 129.3 (d×2), 129.7 (s), 132.6 (d), 137.6 (s), 157.7 (s), 161.8 (s), 163.0 (s), 181.3 (s). LR-MS m/z: 312 (M^+).

2-(2-Chlorophenyl)-6-phenyl-4*H*-pyran-4-one (**21**C-**a**): Eluting solvent for column chromatography: CH_2Cl_2, and for PTLC: AcOEt–hexane (2:3). Colorless prisms from CH_2Cl_2–ether, mp 122—124 °C. IR: 1650, 1600, 1580. UV: 273 (16500). ^{1}H-NMR: 6.66, 6.85 (each 1H, d, J=2 Hz), 7.4—7.7 (6H, m), 7.8—7.9 (2H, m). ^{13}C-NMR: 111.5 (d), 116.7 (d), 126.1 (d×2), 127.3 (d), 129.1 (d×2), 130.8 (d), 130.9 (d), 131.1 (s), 131.7 (d), 132.0 (d), 132.8 (s), 162.9 (s), 164.4 (s), 180.4 (s). HR-MS m/z (M^+): Calcd for $C_{17}H_{11}ClO_2$: 282.0448. Found 282.0459.

2-(2-Chlorophenyl)-6-(4-tolyl)-4*H*-pyran-4-one (**21**C-**b**): Eluting solvent for column chromatography: CH_2Cl_2. Developing solvent for PTLC: AcOEt–hexane (3:2). Colorless prisms from CH_2Cl_2–ether, mp 95—98 °C. IR: 1654, 1604, 1508. UV: 278 (20300). ^{1}H-NMR: 2.42 (3H, s), 6.64, 6.81 (each 1H, d, J=2 Hz), 7.2—7.8 (8H, m). ^{13}C-NMR: 21.5 (q), 110.5 (d), 116.7 (d), 125.9 (d×2), 127.2 (d), 128.4 (s), 129.8 (d×2), 130.7 (d), 130.8 (d), 131.5 (s), 131.8 (d), 132.8 (s), 142.1 (s), 162.4 (s), 164.2 (s), 180.0 (s). LR-MS m/z: 296.

2-(2-Chlorophenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**21**C-**c**): Eluting solvent for column chromatography: CH_2Cl_2. Colorless prisms from CH_2Cl_2–ether, mp 143—145 °C. IR: 1684, 1600, 1574, 1514. UV: 253 (34600). ^{1}H-NMR: 3.87 (3H, s), 6.62, 6.75 (each 1H, s), 6.9—7.0 (2H, m), 7.4—7.6 (4H, m), 7.7—7.8 (2H, m). ^{13}C-NMR: 55.5 (q), 109.7 (d), 114.5 (d×2), 116.6 (d), 123.5 (s), 127.2 (d), 127.7 (d×2), 130.7 (d), 130.9 (d), 131.6 (s), 131.8 (d), 132.8 (s), 162.3 (s×2), 164.1 (s), 180.0 (s). CI-MS m/z: 313 (MH^+).

2-(2-Chlorophenyl)-6-(4-hydroxyphenyl)-4*H*-pyran-4-one (**21**C-**d**): Eluting solvent for flash column chromatography: CH_2Cl_2. Colorless prisms from CH_2Cl_2–ether, mp 241—244 °C. IR: 1648, 1614, 1594, 1558, 1514. UV: 260 (15300), 297 (18600).^{1}H-NMR: 6.64, 6.76 (each 1H, d, J=2 Hz), 6.92 (2H, dt, J=2, 2, 8 Hz), 7.4—7.8 (6H, m). ^{13}C-NMR: 108.6 (d), 115.9 (d), 116.0 (d×2), 121.9 (s), 127.2 (d), 127.9 (d×2), 130.7 (d), 130.8 (d), 131.2 (s), 131.9 (d), 132.6 (s), 160.5 (s), 162.7 (s), 165.1 (s), 180.8 (s). LR-MS m/z: 298 (M^+).

2-(2-Chlorophenyl)-6-(4-fluorophenyl)-4*H*-pyran-4-one (**21**C-**e**): Eluting solvent for flash column chromatography: CH_2Cl_2. Colorless prisms from CH_2Cl_2–ether, mp 147—148 °C. IR: 1704, 1644, 1600, 1594, 1570, 1510. UV: 273 (16500). ^{1}H-NMR: 6.70, 6.87 (each 1H, d, J=2 Hz), 7.0—7.3, 7.4—7.7, 7.8—7.9, 8.0—8.2 (each 2H, m). ^{13}C-NMR: 111.0 (d), 116.4 (d×2, J=21 Hz, –C*–C–F), 116.8 (d), 127.3 (d), 127.5 (s), 128.2 (d×2, J=9 Hz, –C*–C–C–F), 130.7 (d), 130.9 (d), 131.4 (s), 131.9 (d), 132.8 (s), 162.6 (s), 163.1 (s), 164.7 (d, J=252 Hz, –C*–F), 179.8 (s). LR-MS m/z: 300 (M^+).

2-(2-Chlorophenyl)-6-(4-chlorophenyl)-4*H*-pyran-4-one (**21**C-**f**): Eluting solvent for flash column chromatography: CH_2Cl_2. Colorless prisms from CH_2Cl_2–ether, mp 173—176 °C. IR: 1710, 1640, 1594, 1580, 1560. UV: 241 (19000), 277 (15200). ^{1}H-NMR: 6.68, 6.86 (each 1H, d, J=2 Hz), 7.4—7.6 (5H, m), 7.7—7.9 (2H, m), 8.0—8.1 (1H, m). ^{13}C-NMR: 111.3 (d), 116.8 (d), 127.3 (d×2), 128.8 (d), 129.4 (d), 129.6 (s), 130.7 (d), 130.9 (d), 131.2 (s), 131.5 (d), 132.0 (d), 132.8 (s), 137.8 (s), 162.8 (s), 163.0 (s), 179.9 (s). HR-MS m/z (M^+): Calcd for $C_{17}H_{10}Cl_2O_2$: 316.0093. Found: 316.0058.

2-(2-Chlorophenyl)-6-(4-nitrophenyl)-4*H*-pyran-4-one (**21**C-**g**): Eluting solvent for flash column chromatography: AcOEt–hexane (1:1). Yellow prisms from CH_2Cl_2–ether, mp 211—214 °C. IR: 1654, 1608, 1528. UV: 295 (18200). ^{1}H-NMR: 6.69, 6.94 (each 1H, d, J=2 Hz), 7.4—7.7 (4H, m), 8.0—8.1, 8.3—8.4 (each 2H, m). ^{13}C-NMR: 113.4 (d), 117.2 (d), 124.3 (d×2), 126.9 (d×2), 127.4 (d×2), 130.8 (d), 131.0 (s, d), 132.3 (d×2), 132.8 (s), 137.0 (s), 149.4 (s), 161.3 (s), 163.1 (s), 179.3 (s). HR-MS m/z (M^+): Calcd for $C_{17}H_{10}ClNO_4$: 327.0284. Found: 327.0296.

2-(2-Nitrophenyl)-6-phenyl-4*H*-pyran-4-one (**21**N-**a**): Colorless plates from CH_2Cl_2–ether, mp 144—147 °C, IR: 1526, 1622, 1659. UV: 259 (23100). ^{1}H-NMR: 6.63 (1H, d, J=2 Hz), 6.82 (1H, d, J=2 Hz), 7.3—8.2 (9H, m). ^{13}C-NMR: 111.5 (d), 115.2 (d), 124.9 (d), 125.8 (d × 2), 127.2 (s), 129.0 (d × 2), 130.7 (s), 131.1 (d), 131.5 (d), 131.8 (d), 133.4 (d), 147.9 (s), 161.8 (s), 164.1 (s), 179.5 (s). LR-MS m/z: 293 (M^+)

2-(4-Tolyl)-6-(2-nitrophenyl)-4*H*-pyran-4-one (**21**N-**b**): Colorless plates from CH_2Cl_2–ether, mp 181—191 °C. IR: 1526, 1657, UV: 263 (17800). ^{1}H-NMR: 2.40 (3H, s), 6.71 (1H, d, J=2 Hz), 6.88 (1H, d, J=2 Hz), 7.2—8.1 (8H, m). ^{13}C-NMR: 21.5 (q), 110.7 (d), 115.0 (d), 125.1 (d), 125.9 (d × 2), 127.2 (s), 127.8 (s), 129.9 (d × 2), 131.2 (d), 131.9 (d), 133.5 (d), 142.5 (s), 162.2 (s), 162.8 (s), 165.0 (s), 180.4 (s). LR-MS m/z: 307 (M^+).

2-(4-Methoxyphenyl)-6-(2-nitrophenyl)-4*H*-pyran-4-one (**21**N-**c**): Colorless plates from CH_2Cl_2–ether, mp 189—191 °C. IR: 1526, 1659. UV: 295 (23200). ^{1}H-NMR: 3.86 (3H, s), 6.59 (1H, d, J=2 Hz), 6.72 (1H, d, J=2 Hz), 6.9—8.1 (8H, m). ^{13}C-NMR: 55.4 (q), 110.1 (d), 114.5 (d × 2), 115.1 (d), 123.1 (s), 124.9 (d), 127.4 (s), 127.5 (d × 2), 131.0 (d), 131.8 (d), 133.4 (d), 148.1 (s), 161.5 (s), 162.3 (s), 164.1 (s), 179.6 (s). LR-MS m/z: 323 (M^+).

2-(4-Hydroxyphenyl)-6-(2-nitrophenyl)-4*H*-pyran-4-one (**21**N-**d**): Eluting solvent for column chromatography: AcOEt–hexane (2 : 1). Colorless plates from CH_2Cl_2–ether, mp 178—180 °C, IR: 1570, 1657. UV: 276 (19400), ^{1}H-NMR: 6.71, 6.84 (each 1H, d, J=2 Hz), 6.9—7.0 (2H, m), 7.5—8.3 (6H, m), 10.22 (1H, br s). ^{13}C-NMR: 108.8 (d), 114.6 (d), 115.9 (d), 120.9 (S), 124.8 (d), 126.1 (s), 127.5 (d × 2), 131.4 (d), 132.4 (d), 133.9 (d), 147.6 (s), 160.6 (s), 160.7 (s), 163.3 (s), 178.3 (s). LR-MS m/z: 309 (M^+).

2-(4-Fluorophenyl)-6-(2-nitrophenyl)-4*H*-pyran-4-one (**21**N-**e**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 2). Colorless prisms from CH_2Cl_2–ether, mp 178—180 °C. IR: 1526, 1665. UV: 260 (14600). ^{1}H-NMR: 6.62, 6.76 (each 1H, d, J=2 Hz), 7.1—7.3 (2H, m), 7.6—7.8 (5H, m), 8.0—8.1 (1H, m). ^{13}C-NMR: 114.5 (d), 115.3 (d), 116.2 (d × 2, J=22 Hz, –C*–C–F), 125.0 (d), 1270 (s), 127.2 (s), 128.1 (d × 2, J=10 Hz, –C*–C–C–F), 131.4 (d), 131.9 (d), 133.5 (d), 148.1 (s), 161.8 (s), 163.2 (s), 164.7 (d, J=254 Hz, –C*–F), 179.4 (s). LR-MS m/z: 311 (M^+).

2-(4-Chlorophenyl)-6-(2-nitrophenyl)-4*H*-pyran-4-one (**21**N-**f**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 2). Colorless needles from CH_2Cl_2–ether, mp 175—178 °C. IR: 1524, 1657. UV: 264 (22500). ^{1}H-NMR: 6.62, 6.68 (each 1H, d, J=2 Hz), 7.3—8.1 (8H, m, Ar). ^{13}C-NMR: 111.8 (d), 115.4 (d), 125.1 (d), 127.2 (d × 2), 129.3 (s), 129.5 (d × 2), 131.1 (d), 131.5 (s), 132.0 (d), 133.5 (d), 138.0 (s), 148.1 (s), 161.9 (s), 163.1 (s), 179.4 (s). LR-MS m/z: 327 (M^+).

2-(2-Allyloxyphenyl)-6-phenyl-4*H*-pyran-4-one (**21**A-**a**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 1). Colorless plates from CH_2Cl_2–ether, mp 100—103 °C. IR: 1597, 1640. UV: 256 (16000), 275 (17000). ^{1}H-NMR: 4.69 (2H, dt, J=1, 5 Hz), 5.2—5.3 (2H, m), 5.43 (1H, d, J=1 Hz), 5.9—6.3 (1H, m), 6.80 (1H, d, J=2 Hz), 6.8—7.9 (8H, m). ^{13}C-NMR: 69.5 (t), 111.0 (d), 113.0 (d), 116.4 (d), 118.4 (t), 120.9 (d), 121.0 (d), 126.0 (d), 129.0 (d), 131.2 (d), 131.7 (s), 132.2 (d), 132.4 (d), 156.7 (s), 161.2 (s), 180.7 (s). HR-MS m/z (M^+): Calcd for $C_{20}H_{16}O_3$: 304.1100. Found: 304.1105.

2-(2-Allyloxyphenyl)-6-(4-tolyl)-4*H*-pyran-4-one (**21**A-**b**): Eluting solvent for column chromatography: benzene–acetone, which was further purified by PTLC elution with AcOEt–hexane (2 : 1). Colorless plates from CH_2Cl_2–ether, mp 100—103 °C. IR: 1607, 1647. UV: 257 (18600), 283 (22100). ^{1}H-NMR: 2.43 (3H, s), 4.6—4.7 (2H, m), 5.2—5.5 (2H, m), 5.9—6.2 (1H, m), 6.77 (1H, d, J=2 Hz), 7.06 (1H, d, J= 2 Hz), 7.0—7.8 (8H, m). ^{13}C-NMR: 21.5 (q), 69.4 (t), 110.3 (t), 113.1 (d), 116.3 (d), 18.3 (d), 120.9 (s), 125.8 (d × 2), 128.8 (d), 129.2 (d), 129.7 (d × 2), 132.1 (d), 132.4 (d), 141.7 (s), 156.6 (s), 161.0 (s), 163.6 (s), 180.6 (s). HR-MS m/z (M^+): Calcd for $C_{21}H_{18}O_3$: 318.1256. Found: 318.1282.

2-(2-Allyloxyphenyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**21**A-**c**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 1). Yellow plates from CH_2Cl_2–ether, mp 112 °C. IR: 1597, 1647. UV: 261 (19400), 296 (23900). ^{1}H-NMR: 3.86 (3H, s), 4.86 (2H, dt, J=5, 1 Hz), 5.2—5.3 (1H, m), 5.43 (1H, q, J=2 Hz), 5.9—6.2 (1H, m), 6.72 (1H, d, J=3 Hz), 7.02 (1H, d, J=3 Hz), 6.9—7.9 (8H, m). ^{13}C-NMR: 55.4 (q), 69.4 (t), 109.4 (d), 113.0 (d), 114.4 (d × 2), 116.1 (d), 118.2 (t), 120.9 (d), 132.3 (d), 156.6 (s), 160.8 (s), 162.0 (s), 163.5 (s), 180.7 (s). HR-MS m/z (M^+): Calcd for $C_{21}H_{18}O_4$: 334.1204. Found: 334.1209

2-(2-Allyloxyphenyl)-6-(4-chlorophenyl)-4*H*-pyran-4-one (**21**A-**f**): Eluting solvent for flash column chromatography: AcOEt–benzene (1 : 10). For further purification, column chromatography was carried out by elution with AcOEt–hexane (1 : 2) , then benzene–acetone (10 : 1). Colorless plates from CH_2Cl_2–ether, mp 120—121 °C. IR: 1609, 1644. UV: 257 (20300), 282 (23400). ^{1}H-NMR: 4.6—4.8 (2H, m), 5.2—5.6 (2H, m), 5.9—6.3 (1H, m), 7.04 (1H, d, J=2 Hz), 6.8—7.9 (9H, m). ^{13}C-NMR: 69.5 (t), 111.2 (d), 113.1 (d × 2), 115.6 (d), 116.4 (d), 118.4 (t), 120.8 (s), 127.2 (d), 129.2 (d × 2), 129.4 (d), 130.2 (d), 132.4 (d), 137.5 (s), 147.7 (s), 156.7 (s), 161.3 (s), 180.4 (s). HR-MS m/z (M^+): Calcd for $C_{20}H_{15}ClO_3$: 38.0708. Found: 338.0706.

2-(2-Furyl)-6-phenyl-4*H*-pyran-4-one (**24**F-**a**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 2). Pale brown prisms from CH_2Cl_2–ether, mp 122—125 °C. IR: 1657, 1630. UV: 266 (17200), 297 (16400), 380 (2100). ^{1}H-NMR: 6.60 (1H, dd, J=2, 4 Hz), 6.71, 6.75 (each 1H, d, J=2 Hz), 7.07 (1H, dd, J=1, 4 Hz), 7.5—7.6 (3H, m), 7.62 (1H, dd, J=1, 2 Hz), 7.8—7.9 (2H, m). ^{13}C-NMR: 109.1 (d), 111.5 (d), 112.3 (d), 112.4 (d), 125.9 (d × 2), 129.2 (d × 2), 131.2 (s), 131.5 (d), 145.6 (d), 146.0 (d), 155.4 (s), 162.7 (s), 179.7 (s). Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.78; H, 4.45. HR-MS m/z (M^+): Calcd for $C_{15}H_{10}O_3$: 238.0630. Found: 238.0658.

2-(2-Furyl)-6-(4-tolyl)-4*H*-pyran-4-one (**24**F-**b**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 1). Pale brown prisms from CH_2Cl_2–ether, mp 185 °C, IR: 1657, 1620, 1595, 1547, 1512, UV: 268 (20300), 301 (19900). ^{1}H-NMR: 2.44 (3H, s), 6.60 (1H, dd, J=2, 4 Hz), 6.70 (2H, s), 7.05 (1H, dd, J=1, 4 Hz), 7.3—7.4 (2H, m), 7.61 (1H, dd, J=1, 2 Hz), 7.7—7.8 (2H, m). ^{13}C-NMR: 21.5 (q), 109.0 (d), 110.7 (d), 112.4 (d × 2), 125.9 (d × 2), 128.4 (s), 129.5 (d × 2), 142.2 (s), 145.6 (d), 146.1 (s), 155.5 (s), 163.2 (s), 179.6 (s). HR-MS m/z (M^+): Calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0821.

2-(2-Furyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**24**F-**c**): Eluting solvent for column chromatography: benzene–acetone (3 : 1). Pale yellow needles from CH_2Cl_2–ether, mp 180 °C. IR: 1667, 1628, 1611, 1595. UV: 219 (16900), 274 (27900), 306 (2600). ^{1}H-NMR: 3.89 (3H, s), 6.60 (1H, dd, J=2, 4 Hz), 6.65, 6.68 (each 1H, d, J=2 Hz), 7.0—7.1 (3H, m), 7.61 (1H, dd, J=1, 2 Hz), 7.77 (2H, d, J=9 Hz). ^{13}C-NMR: 55.5 (q), 108.9 (d), 109.9 (d), 112.1 (d), 112.4 (d), 114.6 (d × 2), 123.5 (s), 127.6 (d × 2), 145.5 (d), 146.1 (s), 155.2 (s), 162.3 (s), 162.9 (s), 179.7 (s). *Anal.* Calcd for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.70. H, 4.66. HR-MS m/z (M^+): Calcd for $C_{16}H_{12}O_4$: 268.0733. Found: 268.0730.

2-(2-Furyl)-6-(4-hydroxyphenyl)-4*H*-pyran-4-one (**24**F-**d**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 2). Colorless prisms from CH_2Cl_2–ether, mp 250—252 °C. IR: 1653, 1586, 1543, 1510. UV: 218 (12900), 273 (21400), 304 (19500). ^{1}H-NMR: 6.7 (3H, m), 7.0 (2H, m), 7.2 (1H, m), 7.7—7.8 (3H, m). ^{13}C-NMR: 108.5 (d), 109.2 (d), 113.9 (d), 114.4 (d), 117.2 (d × 2), 122.8 (s), 129.2 (d × 2), 147.0 (s), 147.7 (d), 157.5 (s), 162.7 (s), 166.0 (s), 182.4 (s). HR-MS m/z (M^+): Calcd for $C_{15}H_{10}O_4$: 254.0577. Found: 254.0565.

2-(2-Furyl)-6-(4-fluorophenyl)-4*H*-pyran-4-one (**24**F-**e**): Eluting solvent for column chromatography: benzene–acetone (15 : 1). Colorless needles from CH_2Cl_2–ether, mp 212—213 °C. IR: 1671, 1632, 1611, 1510, 1423. UV: 265 (22700), 297 (22300). ^{1}H-NMR: 6.61 (1H, dd, J=2, 4 Hz), 6.70 (2H, s), 7.05 (1H, dd, J=1, 4 Hz), 7.1—7.3 (2H, m), 7.62 (1H, dd, J=1, 2 Hz), 7.7—7.9 (2H, m). ^{13}C-NMR: 109.1 (d), 111.3 (d), 112.3 (d), 112.4 (d), 116.4 (d × 2, J=22 Hz, –C*–C–F), 127.5 (s, J=3 Hz, –C*–C–C–C–F), 128.0 (d × 2, J=8 Hz, –C*–C–C–F), 145.6 (d), 145.9 (s), 155.3 (s), 161.7 (s), 164.6 (d, J=252 Hz, –C*–F), 179.5 (s), HR-MS m/z (M^+): Calcd for $C_{15}H_9FO_3$: 256.0536. Found: 256.0556.

2-(2-Furyl)-6-(4-chlorophenyl)-4*H*-pyran-4-one (**24**F-**f**): Developing solvent for PTLC: AcOEt–hexane (4 : 5). Colorless prisms from CH2Cl_2–ether, mp 254—257 °C. IR: 1667, 1630, 1493, 1419. UV: 273 (12200), 306 (17100). ^{1}H-NMR: 6.16 (1H, dd, J=2, 4 Hz), 6.72 (2H, s), 7.05 (1H, dd, J=1, 4 Hz), 7.50 (2H, d, J=9 Hz), 7.63 (1H, dd, J=1, 2 Hz), 7.76 (2H, d, J=9 Hz). ^{13}C-NMR: 109.2 (d), 111.7 (d), 112.3 (d), 112.4 (d), 127.1 (d × 2), 129.5 (d × 2), 129.7 (s), 137.8 (s), 145.7 (d), 145.8 (s), 155.3 (s), 161.6 (s), 179.4 (s). HR-MS m/z (M^+): Calcd for $C_{15}H_9ClO_3$: 272.0241. Found: 272.0262.

2-Phenyl-6-(2-thienyl)-4*H*-pyran-4-one (**27**T-**a**): Eluting solvent for column chromatography: AcOEt–hexane (1 : 1). Colorless prisms from CH_2Cl_2–ether, mp 196—197 °C. IR: 1640, 1609. UV: 267 (19000), 302 (16000). ^{1}H-NMR: 6.68, 6.77 (each 1H, d, J=2 Hz), 7.18 (1H, dd, J=4, 5 Hz), 7.5—7.6 (4H, m), 7.66 (1H, dd, J=1, 4 Hz), 7.8—7.9 (2H, m). ^{13}C-NMR: 109.7 (d), 111.2 (d), 125.8 (d × 2), 127.7 (d), 128.4 (d), 129.1 (d × 2), 129.7 (d), 131.1 (s), 131.4 (d), 134.6 (s), 158.9 (s), 162.7 (s), 179.7 (s), HR-MS m/z (M^+): Calcd for $C_{15}H_{10}O_2S$ 254.0402, Found: 254.0444.

2-(4-Methoxyphenyl)-6-(2-thienyl)-4*H*-pyran-4-one (**27**T-**b**): Eluting

solvent for column chromatography: AcOEt–hexane (20 : 1). Colorless prisms from CH_2Cl_2–ether, mp 134—137 °C. IR: 1644, 1609, 1510. UV: 270 (22700), 304 (20000). ^{1}H-NMR: 2.44 (3H, s,), 6.65, 6.73 (each 1H, d, J=2 Hz), 7.18 (1H, dd, J=4, 5 Hz), 7.31 (2H, d, J=8 Hz), 7.56 (1H, dd, J=1, 5 Hz), 7.64 (1H, dd, J=1, 4 Hz), 7.73 (2H, d, J=8 Hz). ^{13}C-NMR: 21.5 (q), 109.7 (d), 110.6 (d), 125.8 (d × 2), 127.7 (d), 128.4 (s), 128.5 (d), 129.7 (d), 129.9 (d × 2), 134.8 (s), 142.1 (s), 158.9 (s), 163.0 (s), 179.9 (s). HR-MS m/z (M^+): Calcd for $C_{16}H_{12}O_2S$: 268.0559. Found: 268.0624.

2-(4-Methoxyphenyl)-6-(2-thienyl)-4*H*-pyran-4-one (**27T-c**): Eluting solvent for column chromatography: benzene–acetone (10 : 1). Colorless needles from CH_2Cl_2–ether, mp 145—146 °C. IR: 1651, 1609, 1514. UV: 280 (27200), 308 (23800). ^{1}H-NMR: 3.89 (3H, s), 6.65, 6.68 (each 1H, d, J=2 Hz), 7.03 (2H, d, J=9 Hz), 7.18 (1H, dd, J=4, 5 Hz), 7.56 (1H, dd, J=1, 5 Hz), 7.64 (1H, dd, J=1, 4 Hz), 7.79 (2H, d, J=9 Hz). ^{13}C-NMR: 55.5 (q), 109.5 (d), 109.7 (d), 114.6 (d × 2), 123.4 (s), 127.5 (d × 2), 127.6 (d), 128.4 (d), 129.6 (d), 134.8 (s), 158.7 (s), 162.3 (s), 162.8 (s), 179.7 (s). HR-MS m/z (M^+): Calcd for $C_{16}H_{12}O_3S$: 284.0508, Found: 284.0540.

2-(4-Fluorophenyl)-6-(2-thienyl)-4*H*-pyran-4-one (**27T-e**): Eluting solvent for column chromatography: benzene–acetone (20 : 1). Colorless prisms from CH_2Cl_2–ether, mp 176—178 °C. IR: 1642, 1609. UV: 267 (20600), 302 (17400). ^{1}H-NMR: 6.60, 6.64 (each 1H, d, J=2 Hz), 7.0—7.2 (3H, m), 7.49 (1H, dd, J=1, 5 Hz), 7.57 (1H, dd, J=1, 4 Hz), 7.7—7.8 (2H, m). ^{13}C-NMR: 108.7 (d), 110.1 (d), 115.4 (d × 2, J=22 Hz, –C*–C–F), 126.4 (d, J=3 Hz, –C*–C–C–C–F), 126.8 (d), 127.0 (d × 2, J=10 Hz, –C*–C–C–F), 127.5 (d), 128.8 (d), 133.5 (s), 157.9 (s), 160.8 (s), 169.3 (d, J=253 Hz, –C*–F), 178.5 (s), HR-MS m/z (M^+): Calcd for $C_{15}H_9FO_2S$: 272.0308. Found: 272.0330.

2-(4-Chlorophenyl)-6-(2-thienyl)-4*H*-pyran-4-one (**27T-f**): Eluting solvent for column chromatography: benzene–acetone (15 : 1). Colorless prisms from CH_2Cl_2–ether, mp 203—205 °C. IR: 1663, 1586, 1493, 1410. UV: 271 (23200), 304 (19400). ^{1}H-NMR: 6.68, 6.74 (each 1H, d, J=2 Hz), 7.19 (1H, dd, J=4, 5 Hz), 7.5—7.8 (6H, m). ^{13}C-NMR: 109.8 (d), 111.4 (d), 127.1 (d × 2), 127.9 (d), 128.6 (d), 129.5 (d × 2), 129.6 (s), 129.9 (d), 134.4 (s), 137.8 (s), 159.1 (s), 161.7 (s), 179.5 (s). HR-MS m/z (M^+): Calcd for $C_{15}H_9ClO_2S$: 288.0009. Found: 287.9977.

2-(4-Chlorophenyl)-5-(4-chlorobenzoyl)-6-hydroxy-4*H*-pyran-4-one (**19C**): Yellow prisms from $CHCl_3$, mp 185—189 °C. IR: 1740, 1618, 1590, 1564, 1540, 1518. UV: 256 (12800), 304 (9000), 386 (26000). LR-MS m/z: 360 (M^+).

2-Hydroxy-3-(2-methoxybenzoyl)-6-(2-methoxyphenyl)-4*H*-pyran-4-one (**22M**): Eluting solvent for column chromatography: CH_2Cl_2. Yellow prisms from CH_2Cl_2, mp 213—216 °C. IR: 1557, 1622, 1723. UV: 370 (26317). ^{1}H-NMR ($CDCl_3$–CD_3OD): 3.81 (3H, s), 3.97 (3H, s), 6.9—8.0 (1H, m), 6.9—8.0 (3H, m). ^{13}C-NMR: 55.4 (qx2), 101.5 (s), 102.9 (d), 110.7 (d), 111.6 (d), 118.6 (s), 120.3 (d), 120.8 (d), 127.6 (d), 129.4 (d × 2), 131.9 (d), 133.4 (d), 156.8 (s), 158.5 (s), 160.2 (s), 162.3 (s), 179.4 (s), 199.3 (s). LR-MS m/z: 370 (M^+).

2-(2-Allyloxyphenyl)-5-(2-allyloxybenzoyl)-6-hydroxy-4*H*-pyran-4-one (**22A**): Developing solvent for PTLC: CH_2Cl_2–benzene (1 : 10). Pale yellow plates from CH_2Cl_2, mp 119—121 °C. IR: 1618, 1734. UV: 270 (1600), 370 (25400). ^{1}H-NMR: 4.56 (2H, dt, J=5, 2, 2 Hz), 4.66 (2H, dt, J=5, 1, 1 Hz), 5.1—5.6 (4H, m), 5.8—6.3 (2H, m), 6.9—7.6 (10H, m). ^{13}C-NMR: 69.4 (t), 69.6 (t), 102.1 (t), 103.2 (d), 112.1 (d), 112.9 (d), 116.9 (t), 118.6 (t), 119.4 (s), 120.8 (d), 121.1 (d), 128.1 (d), 129.6 (s), 129.8 (d), 132.1 (d), 132.9 (d), 133.1 (d × 2), 156.2 (s), 157.5 (s), 159.9 (s), 162.3 (s), 179.8 (s), 219.3 (s). HR-MS m/z (M^+): Calcd for $C_{24}H_{20}O_6$: 4047.1261. Found 404.1294.

References and Notes

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