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Nucleophilic attack of intramolecular hydroxyl groups on electron-rich aromatics using hypervalent iodine(III) oxidation

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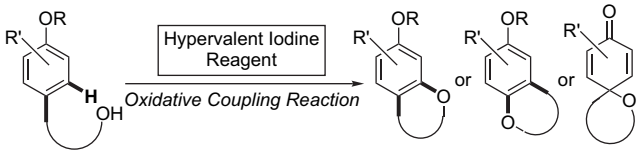
Abstract—The hypervalent iodine(III) reagent, phenyliodine bis(trifluoroacetate) (PIFA)-mediated oxidative nucleophilic substitution of electron-rich aromatics involving aromatic cation radical intermediates was utilized in the direct aromatic carbon–oxygen bond formation reaction, and a novel and simple synthetic method for chroman derivatives was developed. As an extension of this methodology, a facile access to spirodienone derivatives was also achieved.

1. Introduction

The construction of the aromatic carbon–oxygen bond is an important step in the synthesis of many pharmaceutically and agriculturally valuable compounds.[1–3] Much effort has been made in developing a methodology for this purpose, and the most predominant process in this field is the metal (palladium)-catalyzed reaction of the halogenated aromatic carbons, which generally requires selective insertion steps for preparation of the substrate.[2]

On the other hand, although the direct aromatic carbon–oxygen bond formation reaction of the unfunctionalized aromatic carbons should be a potential attractive means to assemble chroman skeletons, only a few facile approaches are known.[4,5]

Over the past 20 years, hypervalent iodine(III) reagents have received much attention due to their low toxicity, ready availability, easy handling, and reactivity similar to those of heavy metal reagents.[6] As a continuation of our research on the use of hypervalent iodine(III) reagents in organic synthesis, the direct nucleophilic substitution of electron-rich phenyl ethers involving aromatic cation radical intermediates was originally reported by us[7] and has been extensively applied for the novel synthesis of important aromatic substrates such as biaryls,[8,9] spirodienones,[9] quinone imines,[10] or sulfur-containing heterocycles.[11] We focused on the hydroxyl group as a nucleophile to produce two types of products, i.e., chromans and spirodienones (Scheme 1). Recently, we reported the novel synthesis of chromans using phenyliodine bis(trifluoroacetate) (PIFA) in 1,1,1,3,3,3-hexafluoro-2-propanol ($(CF_3)_2CHOH$).[12] Additionally, the novel use of the heteropoly acid (HPA) as an activator in the presence of PIFA caused a different reaction to afford the spirodienone derivatives, which are also important precursors of many pharmaceutical compounds.[9] In this paper, we provide a full account of our studies on the direct carbon–oxygen bond formation of unfunctionalized aromatic substrates based on the hypervalent iodine(III) reagent-mediated intramolecular oxidation via single-electron transfer processes.



Scheme 1. Intramolecular coupling reaction of phenyl ether derivatives with hydroxyl group.

2. Results and discussion

The construction of the aromatic carbon–oxygen bond was achieved through two approaches, **a** and **b** (Fig. 1). Approach **a**, a two-step synthesis involving a metal-mediated/catalyzed coupling reaction, is the general and predominant approach, and several methods for this purpose have been developed. Although some efficient syntheses were reported using the palladium-catalyzed reaction,[2] these approaches still require the introduction of a halogen or 4-(trifluoromethyl)benzenesulfonyloxy (OTf) group into the aromatic ring

Keywords: Chroman; Spirodienone; Cyclization; Hypervalent iodine(III) reagent; Heterocycle.
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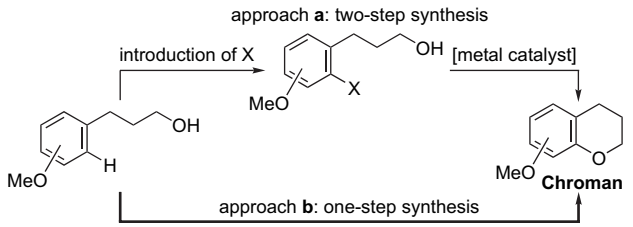
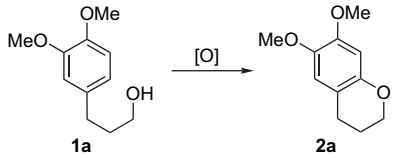


Figure 1. Aromatic C–O bond-forming reaction.

to form the carbon–oxygen bond. In contrast to approach **a**, approach **b**, the direct aromatic carbon–oxygen bond formation reaction using unfunctionalized aromatics, should be a potential attractive means to assemble the chroman skeletons, but only a few facile approaches are known.[4,5] One of them is the method using an oxygen-centered radical with the hypervalent iodine(III) reagent, but the chroman was obtained by iodination on the aromatic ring in an undesirable yield (5–64%).[5,13] We planned the one-step chroman synthesis via the cation radical intermediate using the hypervalent iodine(III) reagent.

Previously, the intramolecular aromatic carbon–oxygen bond formation reaction via the aromatic cation radical intermediate was reported using the heavy metal reagent, thallium(III) trifluoroacetate, by McKillop (Table 1, entry 1).[4] However, the yield of the coupling step was low (21%). Alternatively, other heavy metal reagent-mediated coupling reactions did not provide practical routes to the chroman derivatives, such as entries 2 and 3. Moreover, heavy metal reagents are highly toxic and must be handled with great care. In order to develop a versatile route to the chroman derivatives via the aromatic cation radical pathway, the reactivity of the PIFA-mediated cyclization of 3-(3,4-dimethoxyphenyl)propan-1-ol (**1a**) was studied under various reaction conditions. When the reaction was carried out in the presence of an acid additive, a low yield was observed (entry 4). On the other hand, a notable increase in the reaction yield occurred in poor nucleophilic polar solvents, such as $(CF_3)_2CHOH$ (entry 5), and the addition of solid acid additives, such as montmorillonite K10 (MK10), also caused an improvement in the yield (entry 6).

Table 1. Intramolecular oxidative cyclization of **1a**

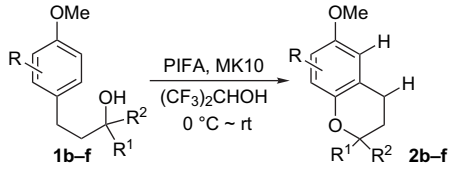


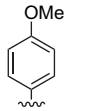
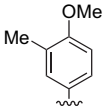
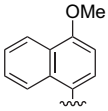
Entry	Conditions	Yield[b] (%)
1[a]	Tl_2O_3, $BF_3{\cdot}Et_2O$, CF_3CO_2H, $(CF_3CO)_2O$, CH_2Cl_2	21
2	RuO_2, $BF_3{\cdot}Et_2O$, CF_3CO_2H, $(CF_3CO)_2O$, CH_2Cl_2	nd[c]
3	VOF_3, CF_3CO_2H, $(CF_3CO)_2O$, CH_2Cl_2	nd[c]
4	PIFA, $BF_3{\cdot}Et_2O$, CH_2Cl_2	28
5	PIFA, $(CF_3)_2CHOH$	40
6	PIFA, MK10, $(CF_3)_2CHOH$	55

[a] Ref. 4.
[b] Isolated yield.
[c] nd: not detected.

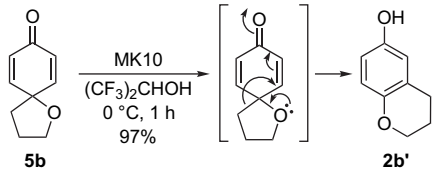
The reactions of monomethoxy precursors **1b–f** with PIFA were investigated in $(CF_3)_2CHOH$ in the presence of MK10 and these results are shown in Table 2. Primary, secondary, and tertiary alcohols had almost the same reactivity (entries 1–3). Interestingly, in all cases, no directly cyclized compound was observed at all, but only the compound in which the position of the carbon–carbon bond was changed was produced. The structures of the **2b–f** were determined by comparing the NMR spectra of the compounds synthesized according to the reported method[14] and/or the NOE experiment. The migration reaction of the spiroether **5b** was examined in $(CF_3)_2CHOH$ in the presence of MK10, and only the corresponding C-migrated chroman **2b′** was produced in quantitative yield (Scheme 2).

Table 2. Application to 4-monomethoxy derivatives



Entry	Substrate		R^1	R^2	Time (h)	Yield[a] (%)
1[b]	**1b**		H	H	0.5	43 (**2b**)
2[b]	**1c**		Me	H	4	45 (**2c**)
3[b]	**1d**		Me	Me	4	46 (**2d**)
4	**1e**		H	H	2.5	42 (**2e**)
5	**1f**		H	H	3	47 (**2f**)

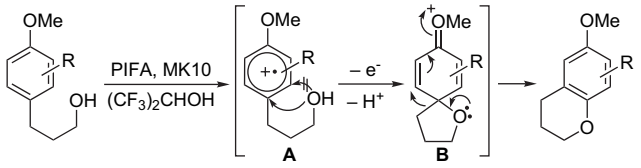
[a] Yield of the isolated products.
[b] In our previous report (Ref. 12), the structures of the products were missed. C-migrated structure is the real structure.



Scheme 2. Rearrangement of the spirodienone derivative.

From these results, the plausible reaction mechanism is assumed as follows (Scheme 3). The cation radical **A** is initially formed by the reaction of the electron-rich aromatic ring with PIFA as mentioned in our previous study.[7] The generation of the cation radical of **1b** under the reaction conditions (PIFA in $(CF_3)_2CHOH$) was detected by electron spin resonance (ESR) spectroscopy (Fig. 2). The intramolecular hydroxyl group was then attacked on the arylic cation radical at the para position of methoxy group to generate the spirodienone-type intermediate **B**. Rearrangement of the spiro

carbon atom then occurred by the electron donation of the spiro oxygen. On the other hand, for the rearrangement reaction of **5b**, a decrease in the conversion was observed in the absence of MK10, which means that MK10 contributes to the migration of the spiro-type intermediate.



Scheme 3. Plausible reaction mechanism.

Next, the reactions of dialkoxy precursors **1a**, **g–j** with PIFA were investigated (Table 3). The chroman derivatives **2a**, **g–i** were produced in moderate yields (entries 1–4). The reactivity of the methyl ether derivative was similar to that of the hydroxyl one (entry 5). However, other protecting derivatives (e.g., R=silyl, acetyl, and THP) gave the chromans in low yield.

Although the chromans **2a**, **g–i** were thought to be produced via the spirodienone-type intermediate (Scheme 4, route **a**), the direct cyclization of the hydroxyl group was also a possible route (route **b**), and the reaction mechanism was not clear from the structures of the products. Therefore, the reactions using the substrates with methoxy and benzyloxy groups **1k**, **l** were examined to clarify the reaction mechanism (Scheme 5). Not only C-migrated chroman, but also the regioisomer chromans were produced in these reactions, and in addition, their ratio was almost same between **1k** and **1l**.[15]

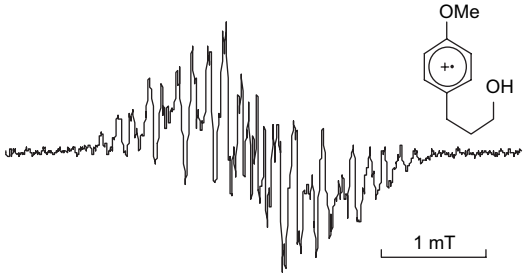
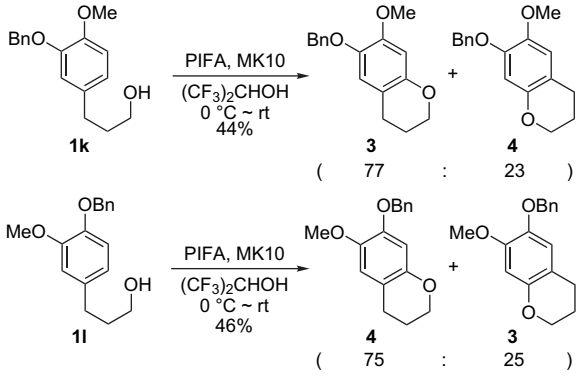
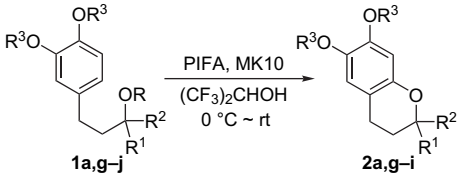


Figure 2. ESR spectra of cation radical **1b** generated by PIFA in $(CF_3)_2CHOH$.



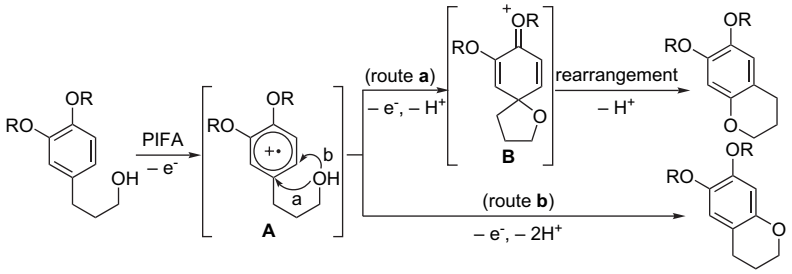
Scheme 5. Oxidative coupling reaction of the substrates with methoxy and benzyloxy groups.

Table 3. Application to other alcohol derivatives



Entry	Substrate	R^1	R^2	OR^3	OR^3	R	Time (h)	Yield[a] (%)
1	**1a**	H	H	OMe	OMe	H	2	55 (**2a**)
2	**1g**	Me	H	OMe	OMe	H	4	49 (**2g**)
3	**1h**	Me	Me	OMe	OMe	H	4	52 (**2h**)
4	**1i**	H	H	OCH_2O		H	1	57 (**2i**)
5	**1j**	H	H	OMe	OMe	Me	1	57 (**2a**)

[a] Yield of the isolated products.



Scheme 4. Assumed reaction mechanism for chroman **2a**, **g–i**.

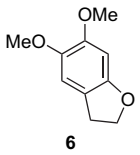
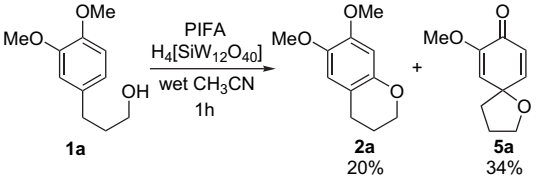
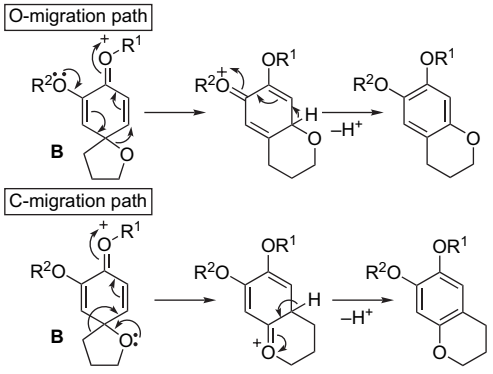


Figure 3.

When the dihydrobenzofuran synthesis using this method was examined, the corresponding product **6** (Fig. 3) was only slightly produced. This is probably because it was difficult to form the spirodienone-type intermediate. In addition, the other condition for producing the cation radical, the combination of PIFA and HPA, which allows the spirodienone-type compounds to be produced, were applied to **1a**. The spirodienone ether **5a** was produced as a major product together with the chroman **2a** (Scheme 6). These results can be regarded as the support for the formation of the spirodienone-type intermediate during the chroman synthesis.



Scheme 6. C–O bond formation reaction using PIFA–HPA.



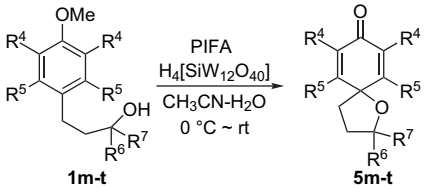
Scheme 7. Plausible migration mechanism.

These results indicated that dialkoxyl chromans were also produced via the spirodienone intermediate. When the dimethoxy substrates were used, the driving force of the rearrangement from the spirodienone intermediate was assumed to be not only the electron donation of the spiro oxygen, but also that of the second alkoxyl group on the aromatics. The electron donation of the spiro oxygen produced the C-migration, and that of the second alkoxyl group on the aromatics favored O-migration,[16] therefore, two kinds of chromans were thought to be produced (Scheme 7).

Recently, we developed an alternative method for the cation radical formation, i.e., the combination of a hypervalent iodine(III) reagent and HPA,[8c,9,17] which is a readily available, inexpensive, easy to handle, non-corrosive, and odorless solid acid. This method has a characteristic behavior that the hydration water of HPA produces spirodienones by a non-phenolic coupling reaction.[9,17] Previously, we developed the hypervalent iodine oxidation of phenol derivatives into spirodienone ethers.[18] However, the use of phenyl ether derivatives for the hypervalent iodine oxidation is considered to be valuable, since the phenyl ether derivatives are more stable and easier to handle than the phenol derivatives themselves under the various reaction conditions. In fact, the spirodienone ether **5a** was obtained using HPA as an activator of PIFA in Scheme 6. Therefore, this spirodienone ether synthesis can be applied to the various alcohols.

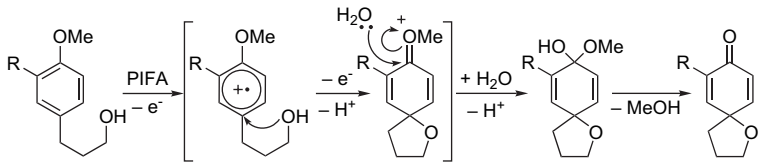
We examined the spirodienone synthesis using **1m** as a substrate to produce a stable spirodienone compound by the combination of PIFA and HPA ($H_4[SiW_{12}O_{40}]$). The corresponding spirodienone **5m** was obtained in 50% yield in acetonitrile (Table 4, entry 1). The reactions of other compounds having terminal hydroxyl groups were investigated under the similar PIFA–HPA conditions and the results are summarized in Table 4. When a symmetrical spirodienone was produced, the yield was good (entries 1–6). Even when the substrate contains other functional groups (alcohol, ester), the corresponding spirodienone was obtained in a moderate yield (entries 7 and 8). Products **5s** and **5t** are possible analogues of the gryndelic acid derivatives, which were isolated from *Grindelia nana*, and the ethanol extract demonstrated in vitro an inhibitory effect on the HIV-1 reverse transcriptase.[19] We

Table 4. Synthesis of spirodienone derivatives



Entry	Substrate	R^4	R^5	R^6	R^7	H_2O (%)	Time (h)	Yield[a] (%)
1	**1m**	Me	H	H	H	0	0.5	50 (**5m**)
2	**1n**	H	Me	H	H	2.5	0.5	79 (**5n**)
3	**1o**	H	Me	Me	H	2.5	0.5	83 (**5o**)
4	**1p**	H	Me	Me	Me	5	2	68 (**5p**)
5	**1q**	OMe	H	H	H	5	0.1	85 (**5q**)
6	**1r**	H	OMe	H	H	5	1.5	63 (**5r**)
7	**1s**	H	Me	CH_2CH_2OH	Me	5	0.5	52 (**5s**)
8	**1t**	H	Me	CH_2CO_2Et	Me	5	2.0	39 (**5t**)

[a] Yield of the isolated products.



Scheme 8. Plausible mechanism of the spirodienone ether synthesis.

Figure 4. ESR spectra of cation radical **1b** generated by PIFA–HPA.

think this approach for the spirodienone could be applied to the synthetic study of many natural products.

The plausible mechanism for the spirodienone ether is assumed as follows (Scheme 8). The spiro-type nucleophilic attack of the hydroxyl group on the cation radical formed by the reaction with PIFA initially occurs. Next, the water attack on the cationic intermediate occurs and the spiroether is produced by the cleavage of the methoxy group. Under this reaction condition, the generation of the cation radical **1b** was also detected by electron spin resonance (ESR) spectroscopy (Fig. 4).

3. Conclusion

We have developed a novel and direct synthetic method for chroman and spirodienone derivatives via the cation radical pathway using a hypervalent iodine reagent. The reaction mechanism was investigated in detail. Under dry reaction conditions, the rearrangement reaction removed off the cation of the spirodienone-type intermediate. On the other hand, under the water containing conditions using HPA, the cation of the spirodienone-type intermediate was readily attacked by the water, and the spirodienone compounds were produced from the phenyl ethers. Selection of the reaction conditions (the dry condition using $(CF_3)_2CHOH$ or the water containing condition using HPA) allows us to control synthesis of desired compounds, i.e., the chromans or spirodienones. The simplicity of the reaction protocol employing unfunctionalized aromatics in mild reaction systems may find many advantages for its application to the synthesis of various types of natural and synthesized products.

4. Experimental section

4.1. General information

All melting points were measured using a Büchi 545 apparatus and are corrected. The infrared (IR) absorption spectra were recorded using a Shimadzu FT/IR-8400 spectrometer with KBr pellets. The ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ using JEOL JNM-AL 300 spectrometers with TMS or $CHCl_3$ as the internal standard. The ESR spectra were taken using a JEOL JES-TE 200 spectrometer. Merck silica gel 60 (70–230 mesh ASTM) and Fuji Silysia Chemical silica gel BW-300 were used for the column chromatography and flash column chromatography, respectively. PIFA is commercially available. $H_4[SiW_{12}O_{40}]$ was purchased from the Kanto Chemical Company.

4.1.1. Measurement of electron spin resonance (ESR) spectra in $(CF_3)_2CHOH$. PIFA (1.0 equiv) was added at room temperature to a 0.05 M solution of **1b** in $(CF_3)_2CHOH$. An aliquot from this mixture was then placed on a flat cell and inserted into the ESR cavity. The spectra were recorded at room temperature using a JEOL JES-TE 200 spectrometer. The instrument conditions were as follows: magnetic field, 335.5±5.0 mT; modulation frequency, 9.42 GHz; output power, 1.0 mW; time constant, 0.03 s; sweep time, 0.5 min.

4.1.2. Measurement of electron spin resonance (ESR) spectra under PIFA–HPA. $H_4[SiW_{12}O_{40}]$ (0.50 g $mmol^{-1}$) and PIFA (1.0 equiv) were added at room temperature to a 0.025 M solution of **1b** in CH_3CN. An aliquot from this mixture was then placed on a flat cell and inserted into the ESR cavity. The spectra were recorded at room temperature using a JEOL JES-TE 200 spectrometer. Instrument conditions were as follows: magnetic field, 335.5±5.0 mT; modulation frequency, 9.42 GHz; output power, 1.0 mW; time constant, 0.03 s; sweep time, 0.5 min.

4.1.2.1. 3-(4-Methoxy-3-methylphenyl)propan-1-ol (1e). Colorless crystals; mp 44.8–44.9 °C; IR (KBr): 3360, 2941, 2860 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.82–1.91 (2H, m), 2.21 (3H, s), 2.62 (2H, t, J=7.5 Hz), 3.67 (2H, t, J=6.3 Hz), 3.81 (3H, s), 6.75 (1H, d, J=8.7 Hz), 6.97–7.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ: 16.2, 31.1, 34.5, 55.3, 62.3, 109.9, 126.3, 126.5, 130.8, 133.4, 156.0; elemental analysis calcd (%) for $C_{11}H_{16}O_2$: C 73.30; H 8.95; found: C 73.38; H 8.84.

4.1.2.2. 3-(3,4-Dimethoxyphenyl)propyl methyl ether (1j). Colorless oil; IR (KBr): 2935, 2866, 2831 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.82–1.92 (2H, m), 2.64 (2H, t, J=7.8 Hz), 3.35 (3H, s), 3.39 (2H, t, J=6.5 Hz), 3.86 (3H, s), 3.87 (3H, s), 6.72–6.81 (3H, m); ^{13}C NMR ($CDCl_3$) δ: 31.5, 31.9, 55.8, 55.9, 58.6, 71.9, 111.2, 111.8, 120.2, 134.6, 147.1, 148.8; elemental analysis calcd (%) for $C_{12}H_{18}O_3$: C 68.54; H 8.63; found: C 68.75; H 8.59.

4.1.2.3. 3-(3,5-Dimethyl-4-methoxyphenyl)propan-1-ol (1m). Colorless oil; IR (KBr): 3356, 2937, 2862 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.81–1.91 (2H, m), 2.26

(6H, s), 2.60 (2H, t, J=6.2 Hz), 3.67 (2H, t, J=6.0 Hz), 3.70 (3H, s), 6.84 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 16.0, 31.3, 34.3, 59.7, 62.4, 128.7, 130.6, 137.0, 155.0; elemental analysis calcd (%) for $C_{12}H_{18}O_2$: C 74.19; H 9.34; found: C 74.35; H 9.31.

4.1.2.4. 3-(2,6-Dimethyl-4-methoxyphenyl)propan-1-ol (1n). Colorless crystals; mp 51.8–51.9 °C; IR (KBr): 3394, 2949, 2878 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.68–1.77 (2H, m), 2.32 (6H, s), 2.62–2.68 (2H, m), 3.73 (2H, t, J=6.3 Hz), 3.77 (3H, s), 6.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 20.2, 25.3, 32.4, 55.1, 63.0, 113.3, 130.8, 137.2, 156.9; elemental analysis calcd (%) for $C_{12}H_{18}O_2$: C 74.19; H 9.34; found: C 73.85; H 9.27.

4.1.2.5. 4-(2,6-Dimethyl-4-methoxyphenyl)butan-2-ol (1o). Colorless crystals; mp 69.4–69.5 °C; IR (KBr): 3350, 2960, 2916 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.26 (3H, d, J=6.3 Hz), 1.57–1.62 (2H, m), 2.31 (6H, s), 2.51–2.77 (2H, m), 3.76 (3H, s), 3.87–3.93 (1H, m), 6.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 20.1, 23.5, 25.2, 38.8, 55.1, 68.4, 113.5, 131.1, 137.2, 157.1; elemental analysis calcd (%) for $C_{13}H_{20}O_2$: C 74.96; H 9.68; found: C 75.15; H 9.63.

4.1.2.6. 4-(2,6-Dimethyl-4-methoxyphenyl)-2-methylbutan-2-ol (1p). Colorless crystals; mp 59.3–59.4 °C; IR (KBr): 3440, 2966, 2920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.32 (6H, s), 1.55–1.60 (2H, m), 2.31 (6H, s), 2.61–2.67 (2H, m), 3.76 (3H, s), 6.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 19.9, 23.7, 29.0, 43.0, 55.1, 71.0, 113.5, 131.1, 137.1, 157.1; elemental analysis calcd (%) for $C_{14}H_{22}O_2$: C 75.63; H 9.97; found: C 75.76; H 9.87.

4.1.2.7. 3-(2,4,6-Trimethoxyphenyl)propan-1-ol (1r). Colorless oil; IR (KBr): 3354, 2939, 2837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.69–1.77 (2H, m), 2.69 (2H, t, J=6.6 Hz), 3.47 (2H, t, J=5.6 Hz), 3.80 (9H, s), 6.14 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 17.9, 31.6, 55.3, 55.7, 61.4, 90.5, 109.6, 158.6, 159.2; elemental analysis calcd (%) for $C_{12}H_{18}O_4$: C 63.70; H 8.02; found: C 63.52; H 7.92.

4.1.2.8. 3-(3,4,5-Trimethoxyphenyl)propan-1-ol (1q). Colorless oil; IR (KBr): 3379, 2939, 2839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.84–1.94 (2H, m), 2.66 (2H, t, J=7.6 Hz), 3.69 (2H, t, J=6.6 Hz), 3.82 (3H, s), 3.84 (6H, s), 6.42 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 32.6, 34.3, 56.0, 60.9, 62.2, 105.1, 135.9, 137.5, 152.9; elemental analysis calcd (%) for $C_{12}H_{18}O_4$: C 63.70; H 8.02; found: C 63.79; H 7.97.

4.1.2.9. 5-(2,6-Dimethyl-4-methoxyphenyl)-3-methylpentane-1,3-diol (1s). Colorless oil; IR (KBr): 3339, 2961, 2920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.37 (3H, s), 1.59–1.65 (2H, m), 1.74–1.88 (2H, m), 2.31 (6H, s), 2.59–2.66 (2H, m), 3.76 (3H, s), 3.92–3.98 (2H, m), 6.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 20.0, 23.3, 26.5, 41.5, 41.8, 55.1, 59.9, 73.7, 113.5, 130.9, 137.1, 157.2; elemental analysis calcd (%) for $C_{15}H_{24}O_3$: C 71.39; H 9.59; found: C 70.65; H 9.46.

4.1.2.10. 3-Hydroxy-5-(2,6-dimethyl-4-methoxyphenyl)-3-methylpentanoic acid ethyl ester (1t). Colorless oil; IR (KBr): 3521, 2976, 2835, 1713, 1606, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.29 (3H, t, J=7.1 Hz), 1.35 (3H, s), 1.62 (2H, dd, J=10.6, 6.8 Hz), 2.30 (6H, s), 2.50–2.69 (4H, m), 3.76 (3H, s), 4.19 (2H, qd, J=7.1, 1.6 Hz), 6.58 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 14.1, 19.9, 23.3, 26.4, 40.9, 44.7, 55.0, 60.7, 70.8, 113.4, 130.8, 137.2, 157.1, 173.1.

4.1.3. A typical procedure for the preparation of 6,7-dimethoxychroman (2a). To a stirred solution of the alcohol (**1a**, 39.2 mg, 0.20 mmol) in $(CF_3)_2CHOH$ (4.0 mL) were added MK10 (100 mg) and PIFA (90.3 mg, 0.21 mmol) at 0 °C. Stirring was continued for 2 h at 0 °C to rt. The solution was then filtered and concentrated in vacuo. Purification of the residue by column chromatography on silica gel gave the corresponding chroman **2a** (21.5 mg, 55%) as colorless crystals; mp 52.6–52.7 °C (lit.[4] mp 51.5–52 °C); IR (KBr): 2934, 2855, 2837, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.94–2.02 (2H, m), 2.71 (2H, t, J=6.5 Hz), 3.81 (6H, s), 4.13 (2H, t, J=5.0 Hz), 6.37 (1H, s), 6.53 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 22.6, 24.3, 55.8, 56.4, 66.3, 100.8, 112.5, 112.6, 142.9, 148.1, 148.6.

4.1.3.1. 6-Methoxychroman (2b).[2c,d] Obtained in 43% yield as colorless oil; IR (KBr): 3153, 2937, 2868, 1790 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.95–2.02 (2H, m), 2.77 (2H, t, J=6.5 Hz), 3.74 (3H, s), 4.13 (2H, t, J=5.1 Hz), 6.58 (1H, d, J=2.7 Hz), 6.66 (1H, dd, J=8.8, 2.7 Hz), 6.72 (1H, d, J=8.8 Hz); ^{13}C NMR ($CDCl_3$) δ: 22.4, 25.1, 55.7, 66.3, 113.2, 114.3, 117.2, 122.7, 149.0, 153.2; elemental analysis calcd (%) for $C_{10}H_{12}O_2$: C 73.15; H 7.37; found: C 73.36; H 7.37.

4.1.3.2. 6-Methoxy-2-methylchroman (2c). Obtained in 45% yield as colorless oil; IR (KBr): 3153, 2977, 2936, 2879, 2835, 1794, 1614 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.38 (3H, d, J=6.2 Hz), 1.63–1.77 (1H, m), 1.92–2.00 (1H, m), 2.67–2.75 (1H, m), 2.80–2.91 (1H, m), 3.74 (3H, s), 4.05–4.11 (1H, m), 6.59 (1H, d, J=2.8 Hz), 6.66 (1H, dd, J=8.7, 2.8 Hz), 6.72 (1H, d, J=8.7 Hz); ^{13}C NMR ($CDCl_3$) δ: 21.3, 25.2, 29.3, 55.7, 72.0, 113.2, 114.1, 117.2, 122.3, 149.1, 153.1; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13; H 7.92; found: C 74.34; H 7.87.

4.1.3.3. 2,2-Dimethyl-6-methoxychroman (2d). Obtained in 46% yield as colorless oil; IR (KBr): 3153, 2978, 2941, 2835, 1774, 1612 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.31 (6H, s), 1.79 (2H, t, J=6.8 Hz), 2.76 (2H, t, J=6.8 Hz), 3.74 (3H, s), 6.62 (1H, s), 6.69–6.70 (2H, m); ^{13}C NMR ($CDCl_3$) δ: 22.8, 26.7, 32.8, 55.7, 73.8, 113.4, 113.9, 117.7, 121.4, 147.9, 152.9; elemental analysis calcd (%) for $C_{12}H_{16}O_2$: C 74.97; H 8.39; found: C 75.15; H 8.41.

4.1.3.4. 6-Methoxy-7-methylchroman (2e). Obtained in 42% yield as colorless oil; IR (KBr): 2934, 2856, 1504 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.94–2.02 (2H, m), 2.15 (3H, s), 2.75 (2H, t, J=6.6 Hz), 3.76 (3H, s), 4.12 (2H, t, J=5.1 Hz), 6.49 (1H, s), 6.60 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 15.9, 22.6, 24.9, 55.9, 66.3, 111.2, 118.7, 119.2, 125.8, 148.3, 151.5; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13; H 7.92; found: C 73.17; H 7.91.

4.1.3.5. 6-Methoxybenzo[*h*]chroman (2f). Obtained in 47% yield as colorless oil; IR (KBr): 2934, 2856, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.06–2.16 (2H, m), 2.88 (2H, t, J=6.5 Hz), 3.97 (3H, s), 4.33 (2H, t, J=5.1 Hz), 6.47 (1H, s), 7.41–7.51 (2H, m), 8.09–8.18 (2H, m);

^{13}C NMR ($CDCl_3$) δ: 27.8, 25.4, 55.7, 66.4, 105.5, 114.8, 120.9, 121.5, 124.9, 125.8, 125.9, 143.5, 148.6; elemental analysis calcd (%) for $C_{14}H_{14}O_2$: C 78.48; H 6.59; found: C 78.21; H 6.69.

4.1.3.6. 6,7-Dimethoxy-2-methylchroman (2g).[20] Obtained in 49% yield as colorless crystals; mp 45.6–45.9 °C (lit.[20] mp 47–48 °C); IR (KBr): 3153, 2936, 2835, 1792 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.38 (3H, d, J=6.2 Hz), 1.63–1.77 (1H, m), 1.93–2.00 (1H, m), 2.60–2.69 (1H, m), 2.74–2.86 (1H, m), 3.81 (6H, s), 4.02–4.12 (1H, m), 6.39 (1H, s), 6.54 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 21.3, 24.4, 29.5, 55.8, 56.4, 72.1, 100.8, 112.2, 112.3, 142.8, 148.2, 148.8.

4.1.3.7. 6,7-Dimethoxy-2,2-dimethylchroman (2h).[21] Obtained in 52% yield as colorless crystals; mp 58.9–59.0 °C (lit.[21] mp 59–60 °C, lit.[21] mp 59–60 °C, lit.[21] mp 60 °C); IR (KBr): 2936, 2853, 2833, 1776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.32 (6H, s), 1.78 (2H, t, J=6.8 Hz), 2.69 (2H, t, J=6.8 Hz), 3.81 (6H, s), 6.37 (1H, s), 6.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 22.2, 26.8, 33.0, 55.8, 56.4, 73.9, 101.1, 111.1, 112.1, 142.4, 147.7, 148.2.

4.1.3.8. 7,8-Dihydro-6*H*-[1,3]dioxolo[4.5-*g*]chromene (2i). Obtained in 57% yield as colorless crystals; mp 44.9–45.8 °C; IR (KBr): 2934, 2876, 2772, 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.92–2.00 (2H, m), 2.68 (2H, t, J=6.5 Hz), 4.11 (2H, t, J=5.1 Hz), 5.85 (2H, s), 6.34 (1H, s), 6.48 (1H, s); ^{13}C NMR ($CDCl_3$) δ: 22.4, 24.8, 66.3, 98.5, 100.7, 108.4, 113.5, 141.2, 146.3, 149.4; elemental analysis calcd (%) for $C_{10}H_{10}O_3$: C 67.41; H 5.66; found: C 67.46; H 5.77.

4.1.3.9. Chroman-6-ol (2b′).[22] Obtained in 97% yield as colorless crystals; mp 97.9–98.0 °C (lit.[22] mp 99–100 °C); IR (KBr): 3315, 3028, 2936, 2866 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.94–2.02 (2H, m), 2.73 (2H, t, J=6.5 Hz), 4.14 (2H, t, J=5.2 Hz), 6.53 (1H, d, J=2.8 Hz), 6.58 (1H, dd, J=8.6, 2.8 Hz), 6.67 (1H, d, J=8.6 Hz); ^{13}C NMR ($CDCl_3$) δ: 22.3, 24.9, 66.3, 114.3, 115.8, 117.2, 123.0, 148.7, 148.8.

4.1.4. The reaction of 1k with PIFA–MK10 in $(CF_3)_2$-CHOH. Obtained in 44% yield as an inseparable mixture of **3** and **4**. The unknown authentic samples **3** and **4** were prepared by the reported method and following hydrogenation.[14]

4.1.5. The reaction of 1l with PIFA–MK10 in $(CF_3)_2$-CHOH. Obtained in 46% yield as an inseparable mixture of **3** and **4**. The unknown authentic samples **3** and **4** were prepared by the reported method and following hydrogenation.[14]

4.1.5.1. 6-Benzyloxy-7-methoxychroman (3). 6-Benzyloxy-7-methoxychromen was synthesized by the reported method.[14] Following hydrogenation using 5% Rh on alumina as catalyst, 6-benzyloxy-7-methoxychroman was obtained as colorless crystals; mp 52.5–53.0 °C; IR (KBr): 2936, 2868, 1512 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.92–2.00 (1H, m), 2.65 (2H, t, J=6.3 Hz), 3.82 (3H, s), 4.12 (2H, t, J=5.3 Hz), 5.05 (2H, s), 6.39 (1H, s), 6.57 (1H, s), 7.29–7.45 (5H, m); ^{13}C NMR ($CDCl_3$) δ: 22.5, 24.2, 55.9, 66.3, 72.2, 101.2, 112.8, 116.3, 127.4, 127.7, 128.4, 137.6, 142.0, 149.2, 149.4; elemental analysis calcd (%) for $C_{17}H_{18}O_3$: C 75.53; H 6.71; found: C 75.56; H 6.79.

4.1.5.2. 7-Benzyloxy-6-methoxychroman (4). 7-Benzyloxy-6-methoxychromen was synthesized by the reported method.[14] Following hydrogenation using 5% Rh on alumina as catalyst, 7-benzyloxy-6-methoxychroman was obtained as colorless crystals; mp 87.7–87.8 °C; IR (KBr): 2936, 2868, 1512 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.90–2.00 (1H, m), 2.67 (2H, t, J=6.5 Hz), 3.80 (3H, s), 4.07 (2H, t, J=5.3 Hz), 5.07 (2H, s), 6.38 (1H, s), 6.54 (1H, s), 7.23–7.42 (5H, m); ^{13}C NMR ($CDCl_3$) δ: 22.5, 24.3, 56.7, 66.2, 70.9, 103.2, 113.3, 113.4, 127.2, 127.7, 128.5, 137.1, 143.5, 147.4, 148.6; elemental analysis calcd (%) for $C_{17}H_{18}O_3$: C 75.53; H 6.71; found: C 75.56; H 6.84.

4.1.6. A typical procedure for the preparation of 7,9-dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5m). To a stirred solution of the alcohol (**1m**, 21.8 mg, 0.112 mmol) in CH_3CN (4.4 mL) were added $H_4[SiW_{12}O_{40}]$ (88 mg) and PIFA (58 mg, 0.134 mmol) at 0 °C. After 0.5 h of stirring at 0 °C to rt, the reaction mixture was diluted with EtOAc. EtOAc containing 3.0% Et_3N (5.0 mL) was then added. The precipitate was observed and the solution was filtered through kieselguhr and concentrated in vacuo. Purification of the residue by column chromatography on silica gel produced the corresponding spirodienone derivatives (**5m**, 10.0 mg, 50%) as yellow oil; IR (KBr): 2955, 2874, 1676, 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.87 (6H, s), 1.98–2.03 (2H, m), 2.08–2.22 (2H, m), 4.04 (2H, t, J=6.6 Hz), 6.55 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 15.7, 26.7, 36.5, 68.8, 77.9, 133.7, 145.0, 187.5; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13; H 7.92; found: C 74.16; H 7.92.

4.1.6.1. 7-Methoxy-1-oxaspiro[4.5]deca-6,9-dien-8-one (5a). Obtained in 34% yield as yellow oil; IR (KBr): 3153, 2936, 2874, 1794, 1678 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.07–2.23 (4H, m), 3.67 (3H, s), 4.02–4.14 (2H, m), 5.70 (1H, d, J=2.7 Hz), 6.14 (1H, d, J=10.0 Hz), 6.81 (1H, dd, J=10.0, 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ: 26.8, 37.7, 54.9, 68.9, 79.4, 116.6, 126.2, 149.7, 150.2, 181.0; elemental analysis calcd (%) for $C_{10}H_{12}O_3$: C 66.65; H 6.71; found: C 66.90; H 6.77.

4.1.6.2. 6,10-Dimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5n). Obtained in 79% yield as colorless crystals; mp 98.5–98.6 °C; IR (KBr): 2959, 2876, 1672, 1632 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.00 (6H, s), 2.01–2.26 (4H, m), 4.20 (2H, t, J=6.5 Hz), 5.94 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 18.8, 27.6, 37.4, 72.2, 83.1, 125.3, 162.6, 185.8; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13; H 7.92; found: C 74.14; H 7.87.

4.1.6.3. 2,6,10-Trimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5o). Obtained in 83% yield as yellow oil; IR (KBr): 2972, 2925, 1670, 1632 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.36 (3H, d, J=5.7 Hz), 1.65–1.79 (1H, m), 1.97–2.06 (7H, m), 2.15–2.27 (2H, m), 4.34–4.45 (1H, m), 5.91 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 18.5, 19.3, 20.3, 34.9, 37.9, 79.4, 83.1, 124.9, 125.4, 162.4, 163.1, 185.8; elemental analysis calcd (%) for $C_{12}H_{16}O_2$: C 74.97; H 8.39; found: C 75.02; H 8.38.

4.1.6.4. 2,2,6,10-Tetramethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5p). Obtained in 68% yield as yellow oil; IR (KBr): 2980, 2930, 1666, 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$)

δ: 1.46 (6H, s), 2.08 (1H, t, J=6.9 Hz), 2.10 (6H, s), 2.22 (1H, t, J=6.9 Hz), 5.97 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 20.8, 29.5, 38.6, 39.3, 85.1, 85.5, 126.0, 163.3, 125.4, 163.3, 185.7; elemental analysis calcd (%) for $C_{13}H_{18}O_2$: C 75.69; H 8.80; found: C 75.69; H 8.83.

4.1.6.5. 7,9-Dimethoxy-1-oxaspiro[4.5]deca-6,9-dien-8-one (5q). Obtained in 85% yield as colorless crystals; mp 130.4–130.5 °C; IR (KBr): 2937, 2847, 1682, 1657, 1622 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.02–2.23 (4H, m), 3.66 (6H, s), 4.06 (2H, t, J=6.5 Hz), 5.73 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 26.8, 38.7, 55.3, 68.5, 78.7, 117.1, 149.1, 176.6; elemental analysis calcd (%) for $C_{11}H_{14}O_4$: C 62.85; H 6.71; found: C 62.88; H 6.65.

4.1.6.6. 6,10-Dimethoxy-1-oxaspiro[4.5]deca-6,9-dien-8-one (5r). Obtained in 63% yield as colorless crystals; mp 113.6–113.7 °C; IR (KBr): 2939, 2849, 1658, 1629, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.12–2.27 (4H, m), 3.73 (6H, s), 4.15 (2H, t, J=6.0 Hz), 5.37 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 27.7, 36.2, 56.1, 72.2, 79.6, 99.9, 173.0, 187.5; elemental analysis calcd (%) for $C_{11}H_{14}O_4$: C 62.85; H 6.71; found: C 62.62; H 6.72.

4.1.6.7. 2-(2-Hydroxyethyl)-2,6,10-trimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5s). Obtained in 52% yield as colorless oil; IR (KBr): 3408, 2966, 2931, 1666, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.69 (3H, s), 1.83–2.04 (1H, m), 2.05–2.39 (5H, m), 2.10 (3H, d, J=1.2 Hz), 2.14 (3H, d, J=1.2 Hz), 3.75–3.81 (1H, m), 3.96–4.04 (1H, m), 5.95 (1H, s), 5.99 (1H, m); ^{13}C NMR ($CDCl_3$) δ: 20.5, 21.4, 26.5, 37.6, 40.1, 43.4, 59.9, 85.7, 88.1, 125.9, 126.7, 162.3, 162.9, 185.6; HRMS (FAB) calcd for $C_{14}H_{21}O_3$ (M^++H): 237.1491; found: 237.1495.

4.1.6.8. 2-(Ethoxycarbonylmethyl)-2,6,10-trimethyl-1-oxaspiro[4.5]deca-6,9-dien-8-one (5t). Obtained in 39% yield as colorless crystals; mp 70.1–70.2 °C; IR (KBr): 3153, 2984, 2903, 1728, 1666, 1626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.28 (3H, t, J=7.1 Hz), 1.56 (3H, s), 2.11 (6H, s), 2.1–2.4 (4H, m), 2.78 (2H, ABq, J=17.7 Hz), 4.17 (2H, q, J=7.1 Hz), 5.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ: 14.2, 20.9, 21.0, 26.9, 38.1, 38.2, 46.6, 60.6, 85.3, 85.6, 126.2, 126.4, 157.2, 162.6, 162.7, 170.5, 185.5; elemental analysis calcd (%) for $C_{16}H_{22}O_4$: C 69.04; H 7.97; found: C 69.00; H 7.88.

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References and notes

1. (a) Hepworth, J. D. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: New York, NY, 1984; Vol. 3, Chapter 2.24; (b) Donnelly, D. M. X.; Meegan, M. J. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: New York, NY, 1984; Vol. 4, Chapter 3.12; (c) Chiuy, C. K.-F. *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: New York, NY, 1995; Vol. 2, Chapter 2.13.
2. (a) Palucki, M.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 10333–10334; (b) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. *J. Am. Chem. Soc.* **2000**, *122*, 10718–10719; (c) Torraca, K. E.; Kuwabe, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 12907–12908; (d) Kuwabe, S.; Torraca, K. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 12202–12206; (e) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553–5566.
3. (a) Knight, D. W.; Little, P. B. *Tetrahedron Lett.* **1998**, *39*, 5105–5108; (b) Birkett, M. A.; Knight, D. W.; Little, P. B.; Mitchell, M. B. *Tetrahedron* **2000**, *56*, 1013–1023; (c) Knight, D. W.; Little, P. B. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2343–2355.
4. Taylor, E. C.; Andrade, J. G.; Rall, G. J. H.; Turchi, I. J.; Steliou, K.; Jagdmann, G. E., Jr.; McKillop, A. *J. Am. Chem. Soc.* **1981**, *103*, 6856–6863.
5. (a) Muraki, T.; Togo, H.; Yokoyama, M. *Tetrahedron Lett.* **1996**, *37*, 2441–2444; (b) Togo, H.; Muraki, T.; Hoshina, Y.; Yamaguchi, K.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 787–793.
6. (a) Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377–407; (b) Koser, G. F. *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, NY, 1983, Chapters 18 and 25; (c) Varvoglis, A. *Synthesis* **1984**, 709–726; (d) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244–250; (e) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123–1178; (f) Kita, Y.; Takeda, T.; Tohma, H. *Pure Appl. Chem.* **1996**, *68*, 627–630; (g) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic: San Diego, CA, 1997; (h) Kitamura, T.; Fujiwara, Y. *Org. Prep. Proced. Int.* **1997**, *29*, 409–458; (i) Moriarty, R. M.; Prakash, O. *Adv. Heterocycl. Chem.* **1998**, *69*, 1–87; (j) Kirschning, A. *Eur. J. Org. Chem.* **1998**, *11*, 2267–2274; (k) Ochiai, M. *Chemistry of Hypervalent Compounds*; Akiba, K., Ed.; John Wiley and Sons: New York, NY, 1999; Chapter 12, pp 359–387; (l) Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89–102; (m) Moriarty, R. M.; Prakash, O. *Org. React.* **2001**, *57*, 327–415; (n) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523–2584; (o) Wirth, T. *Hypervalent Iodine in Chemistry*; Springer: Berlin, 2003.
7. Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684–3691.
8. (a) Kita, Y.; Gyoten, M.; Ohtsubo, M.; Tohma, H.; Takada, T. *Chem. Commun.* **1996**, 1481–1482; (b) Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. *J. Org. Chem.* **1998**, *63*, 7698–7706; (c) Hamamoto, H.; Anilkmar, G.; Tohma, H.; Kita, Y. *Chem. Commun.* **2002**, 450–451.
9. Hamamoto, H.; Anilkmar, G.; Tohma, H.; Kita, Y. *Chem.—Eur. J.* **2002**, *8*, 5377–5383.
10. Kita, Y.; Egi, M.; Okajima, A.; Ohtsubo, M.; Takada, T.; Tohma, H. *Chem. Commun.* **1996**, 1491–1492.
11. Kita, Y.; Egi, M.; Ohtsubo, M.; Saiki, T.; Takada, T.; Tohma, H. *Chem. Commun.* **1996**, 2225–2226.
12. Hamamoto, H.; Hata, K.; Nambu, H.; Shiozaki, Y.; Tohma, H.; Kita, Y. *Tetrahedron Lett.* **2004**, *45*, 2293–2295.
13. There are a few reports to produce the chroman using parabenzoquinone by hypervalent iodine oxidation and the

following 1,4-addition[13a] or radical cyclization–elimination.[13b] (a) Quideau, S.; Pouysegu, L.; Looney, M. A. *J. Org. Chem.* **1998**, *63*, 9597–9600; (b) Clive, D. L.; Fletcher, S. P.; Zhu, M. *Chem. Commun.* **2003**, 526–527.

14. Simas, A. B. C.; Furtado, L. F. O.; Costa, P. R. R. *Tetrahedron Lett.* **2002**, *43*, 6893–6895.
15. Each chroman was prepared by the reported method.[14]
16. The mechanism of selective O-migration is assumed to be a cleavage of the C–O bond by electron donation of OR^2 group followed 1,4-addition of the generated oxy anion to the enone moiety.
17. Hata, K.; Hamamoto, H.; Shiozaki, Y.; Kita, Y. *Chem. Commun.* **2005**, 2465–2467.
18. (a) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *J. Org. Chem.* **1987**, *52*, 3927–3930. The synthesis of spirodienone ether from phenol derivatives has also been reported; (b) Quideau, S.; Pouysegu, L.; Oxiby, M.; Looney, M. A. *Tetrahedron* **2001**, *57*, 319–329.
19. (a) Inada, A.; Murata, H.; Tanaka, K.; Somekawa, M.; Nakazawa, T.; Nishi, M.; Nakanishi, T. *Shoyakugaku Zasshi* **1993**, *47*, 301–304; (b) Roman, L. U.; Cambron, J. I.; del Rio, R. E.; Hernandez, J. D.; Cerda-Garcia-Rojas, C. M.; Joseph-Nathan, P. *J. Nat. Prod.* **2000**, *63*, 226–229; (c) Mahmoud, A. A.; Ahmed, A. A.; Tanaka, T.; Iinuma, M. *J. Nat. Prod.* **2000**, *63*, 378; (d) Al-Musayeib, N. M.; Abbas, F. A.; Ahmad, M. S.; Mossa, J. S.; El-Feraly, F. S. *Phytochemistry* **2000**, *54*, 771–775.
20. Dann, O.; Volz, G.; Huber, O. *Justus Liebigs Ann. Chem.* **1954**, *587*, 16–37.
21. (a) Camps, F.; Coll, J.; Messeguer, A.; Pericas, M. A.; Ricart, S. *Synthesis* **1979**, 126–127; (b) Soladie, G.; Boeffel, D.; Maignan, J. *Tetrahedron* **1996**, *52*, 2065–2074; (c) Bhat, B. H.; Venkataraman, K. *Tetrahedron* **1963**, *19*, 77–80.
22. (a) Fitton, A. O.; Ramage, G. R. *J. Chem. Soc.* **1963**, 5426–5430; (b) Willhalm, B.; Thomas, A. F.; Gautschi, F. *Tetrahedron* **1964**, *20*, 1185–1209.