Role of the methoxy group in product formation via $TiCl_4$ promoted 4-phenyldioxolane isomerizations

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Abstract
The product distribution obtained from the $TiCl_4$ initiated intramolecular isomerizations of 4-methoxyphenyl- and trimethoxyphenyldioxolanes at -78 ^oC, -30 ^oC and 0 ^oC provided insights into the important regiochemical role played by these groups in such Mukaiyama- type rearrangements through their resonance effects on the aryl ring of the dioxolanes.

Keywords: Low temperature studies, substituent effects, rearrangement, isomerizations, oxygen heterocycles

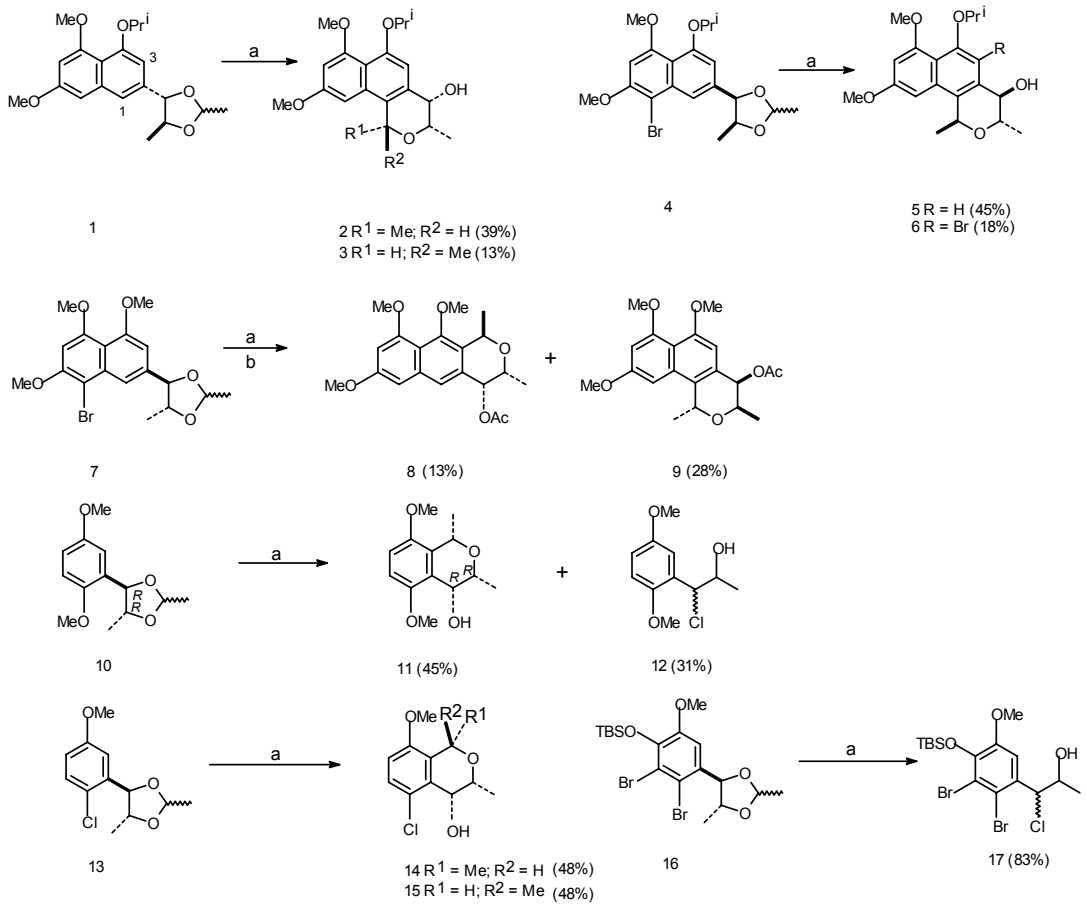
Introduction

Our interest in naphthopyranquinones as potential antimicrobial and antibiotic agents has extended over two decades[1-6] as a result of their well documented importance.[7,8] Additionally, the synthesis of benzopyrans as model systems has received attention by ourselves[6,9-13] and others.[14-16] Of particular interest to us was our earlier discovery of a $TiCl_4$ - induced intramolecular isomerization in which phenyl- and naphthyldioxolanes were stereoselectively transformed into their corresponding benzo- and naphthopyrans.[17]

Thus, treatment of the naphthyldioxolane **1** with $TiCl_4$ at -78 ^oC in dichloromethane afforded the two angular naphthopyrans **2** and **3** in yields of 39% and 13% respectively (Scheme 1). In an attempt to promote linear naphthopyran formation, the bromonaphthyldioxolane **4**, in which it was hoped the Br would sterically inhibit cyclization at C-1′, was similarly treated to again afford angular naphthopyrans **5** (45%) and **6** (18%) representing both debromination for the former product and an example of bromine- migration for the latter. This result indicated that the steric environment of the C4′-isopropoxy group was sufficient to prevent formation of the linear naphthopyran which required cyclization at C-3 in the naphthyldioxolanes **1** and **4**. Subsequently, the C4′-methoxy analog **7**, was treated with $TiCl_4$ at -78 ^oC, and indeed small

quantities of the debrominated linear naphthopyran were isolated as its acetate **8** (13%) together with the debrominated angular naphthopyran, also isolated as its acetate **9** (28%).[18] These results support, in part, our hypothesis that the steric environment at C-3′ of the naphthyl ring plays a significant role in these intramolecular cyclizations.

Kaufman *et al*.[19] investigated the structural consequences of substituents at the C-2 and C-4 positions in the dioxolane ring on the relative relationship of the formed 1,3-disubstituted 4-hydroxybenzopyrans, while Giles *et al*.[20] investigated the influence of two substituents on the phenyl ring of 4-phenyldioxolanes on the formation of benzopyrans at different temperatures when treated with $TiCl_4$. This latter work established that when a C-4 phenyl ring of a dioxolane has an *ortho*- and *meta*- methoxy group viz., **10**, upon treatment with $TiCL_4$ at -78 ^oC, the benzopyran **11** was formed in 45% yield and the stereochemistry at C-4 and C-5 of the dioxolane ring of **10** had been transferred unaltered to C-4 and C-3, respectively, in the benzopyran **11**. The second product isolated from this reaction proved to be the ring-opened chlorohydrin **12** in a yield of 31%. Since the third stereogenic centre, C-1 of the benzopyran, is derived from C-2 of the parent dioxolane, its temperature dependence has also been investigated.[20]



Scheme 1. Examples of $TiCl_4$ induced isomerizations of dioxolanes.

Replacing the electron-donating *ortho*- methoxy group in **10** by Cl, *i.e.* in **13** and treating this compound with $TiCl_4$ at -78 ^oC, served to dramatically increase the formation of benzopyrans **14** and **15** to give a combined yield of 97%, in a 1:1 ratio.[21] On the other hand, attempted isomerization of the aryldioxolane **16**, which has a *para*- TBSO group at C4 in the aryl ring, failed to produce any benzopyran products. Only ring-opened products were isolated viz., the diastereoisomeric chlorohydrins **17**, in a yield of 83%.[22] It is thus possible that the increased availability of electrons from the aryl ring attached at C4 of the dioxolane favors ring- opening rather than intramolecular cyclization.

It was recently reported that a 4-(3′-methoxy-2′-tosyloxyphenyl)-1,3-dimethyldioxolane produced the corresponding benzopyran in 95% yield when treated under the standard conditions with $TiCl_4$.[23] To the best of our knowledge, investigations of the electronic role played by a *meta*- or *para*-methoxyphenyl group in 4-phenyldioxolanes when treated with $TiCl_4$ has neither been established nor published. In this Paper, we address the above issues, and extend them to include C-4- substituted trimethoxyphenyl-1,3-dimethyldioxolanes as well as the influence of temperature on the product profile.

Results and Discussion

Methylation of *m*-hydroxybenzaldehyde with methyl iodide and potassium carbonate in dimethylformamide afforded the corresponding *m*-methoxybenzaldehyde **18a** in 91% yield. Wittig olefination with ethyltriphenylphosphorane afforded the olefin **18b** as a 1:2 ratio (by NMR) of an E/*Z*- mixture, in a combined yield of 96%. Isomerization of this mixture into the virtually pure *E*- isomer **18c** was achieved by the use of bis-acetonitriledichloropalladium (II),[24] in 95% yield. This was necessary since we required stereochemically pure products in the subsequent transformations. Thus, treatment of olefin **18c** with osmium tetroxide and *N*-methylmorpholine *N*-oxide in aqueous acetone afforded the *threo*- diol **18d**, in 92% yield, which was then converted into the C-2 epimeric dioxolane mixture **18e** by reaction with 1,1-dimethoxyethane in the presence of a catalytic amount of camphorsulfonic acid, in a yield of 95% (summarized in Fig. 1 and Table 1). In an analogous manner, the *p*-methoxybenzaldehyde **19a** was transformed *via* the same sequence 19a > **19b** > **19c** > **19d** > **19e**, in similar yields (Fig. 1 and Table 1).

Since our broader intention was aimed at investigating the electronic influence of three methoxy groups in the phenyl ring of 4-phenyldioxolanes upon the nature of the products of $TiCl_4$- induced isomerizations, other 4-trimethoxyphenyldioxolanes viz., **20e** and **21e,** were synthesized using the same protocols, with the yields illustrated in Fig 1 and Table 1.

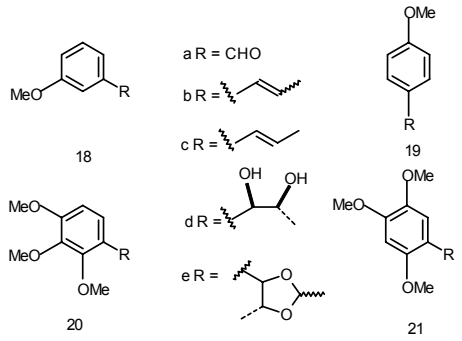


Figure 1. The conversion of aldehydes **18-21** into the dioxolanes **18e**–**21e.**

Table 1. Yields of products of transformations of methoxybenzaldehydes in Figure 1

	a	b	c	d	e
18	91	96	95	92	95
19		97	94	92	77
20		87	84	99	99
21		94	50	80	52

In a further study, we investigated the effect the all-*cis* relative stereochemistry of the groups in the dioxolane ring had on the products of isomerization, under our conditions. Thus, we required a molecule in which there was no *para*- methoxy group in the C-4- aryldioxolane. Thus, the 4-trimethoxyphenyldioxolanes **22f** and **22h** were synthesized as shown in Figure 2. For the former molecule, the *E*-olefin 22c was treated with *m*-CPBA in the presence of solid sodium hydrogen carbonate to afford the pure *trans*- epoxide **22d**, in an un-optimized yield of 57%. This epoxide was subsequently ring-opened in a *trans*- manner, using dilute aqueous potassium hydroxide in dimethyl sulfoxide, giving the pure *erythro*- diol **22e**, in 88% yield after chromatography. Finally, conversion of **22e** into the corresponding dioxolane **22f** was effected by treatment with dimethoxyethane in the presence of camphorsulfonic acid, in quantitative yield. For the latter molecule, the *E*-olefin **22c** was converted into the *threo*- diol **22g** and subsequently into the dioxolane **22h**, as described earlier. The yields are given in Fig. 2 and Table 2.

Thus, having all the methoxyphenyldioxolanes in hand, each was treated under a standard set of conditions. Namely, the dioxolane in dry dichloromethane at -78 ^{o}C, -30 ^{o}C, or 0 ^{o}C was treated under nitrogen with four equivalents of $TiCl_4$ and stirred for 30 min. The product was then quenched with methanol and allowed to reach 24 ^{o}C, and the products isolated by PLC.

Treatment of the C-2- epimeric *trans*- 4-(3′-methoxyphenyl)-2,5-dimethyldioxolanes **18e** under the standard set of conditions afforded the all- *cis*- 2-benzopyran **23** in 78% yield, together with the ring-opened chlorohydrins **24** in 20% yield (Scheme 2).

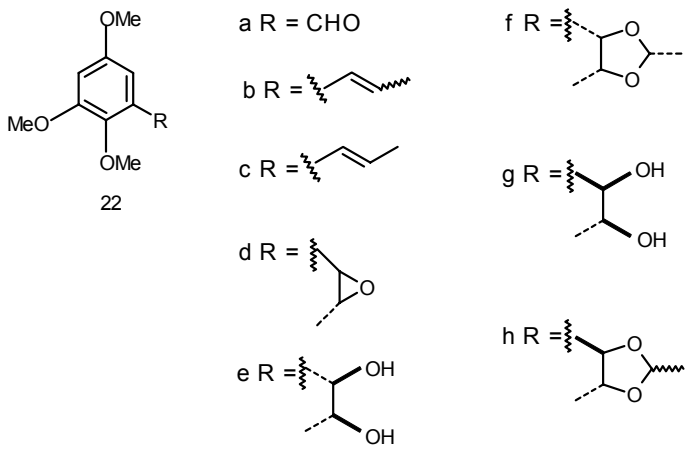


Figure 2. Conversion of the aldehydes **22** into dioxolanes **22f** – **22h.**

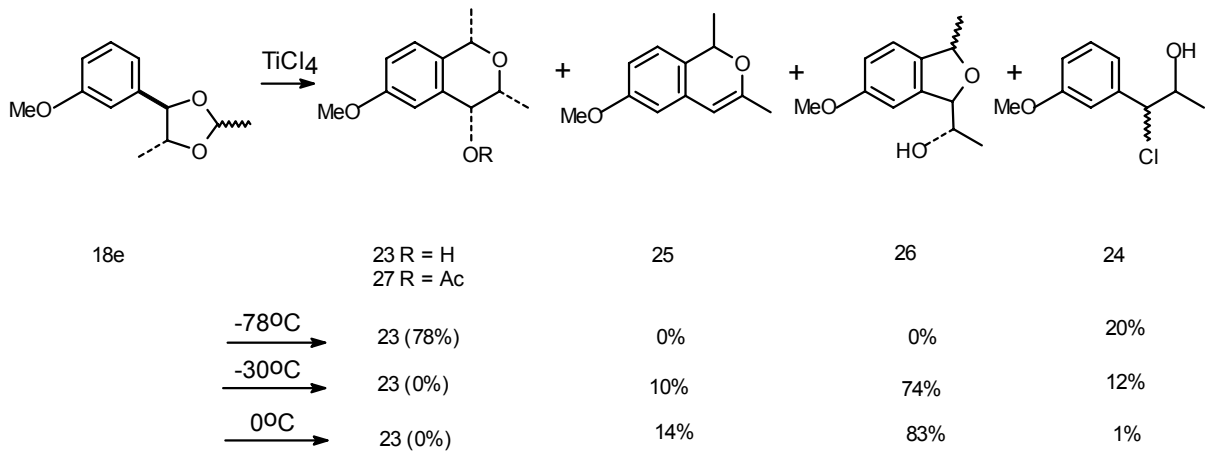
Table 2. Yields of products of transformation of the trimethoxybenzaldehydes **22a**

Product	**22b**	**22c**	**22d**	**22e**	**22f**	**22g**	**22h**
Yield	91	95	57	88	99	87	94

The stereochemistry of the pyran ring in **23** was assigned on the basis of the ^{1}H- NMR spectrum which demonstrated *inter alia* the following signals; a 1-proton doublet at δ = 1.95 (*J* = 7.0 Hz) assigned to the 4-OH; a 1-proton doublet of quartets at δ = 3.80 (*J* = 6.6 and 1.5 Hz) assigned to 3-H; a 1-proton doublet of doublet of doublets at δ = 4.19 (*J* = 7.0, 1.5 and 1.0 Hz), 4-H, and a 1-proton doublet of quartets at δ = 4.76 (*J* = 6.2 and 1.0) assigned to 1-H. The relatively small *J* of 1.5 Hz between 3-H and 4-H signifies that the 4-OH- and C-3- methyl groups are *cis*- related. Additionally, the greater shielding value for 3-H at δ = 3.80 is typical for 3-H in *cis*-1,3-dimethyl-2-benzopyrans compared to their *trans*-1,3-dimethyl- epimers.[20,21] The ^5J of ~ 1.0 Hz observed for coupling between the *pseudo*- axial 1-H and *pseudo*- equatorial 4-H is also noted for these systems.[20,21] Further confirmation for the 4-hydroxypyran ring was provided by acetylation of the hydroxyl group to form the corresponding acetate **27** in 84% yield, in which the ^{1}H- NMR spectrum indicated a strong deshielding effect of the 4-H signal from the ddd at δ = 4.19 to a doublet of doublets at δ = 5.78 with ^3J = 1.8 Hz, illustrating coupling with 3-H, and with ^5J = 1.0 Hz showing coupling with the *pseudo*- axial 1-H.

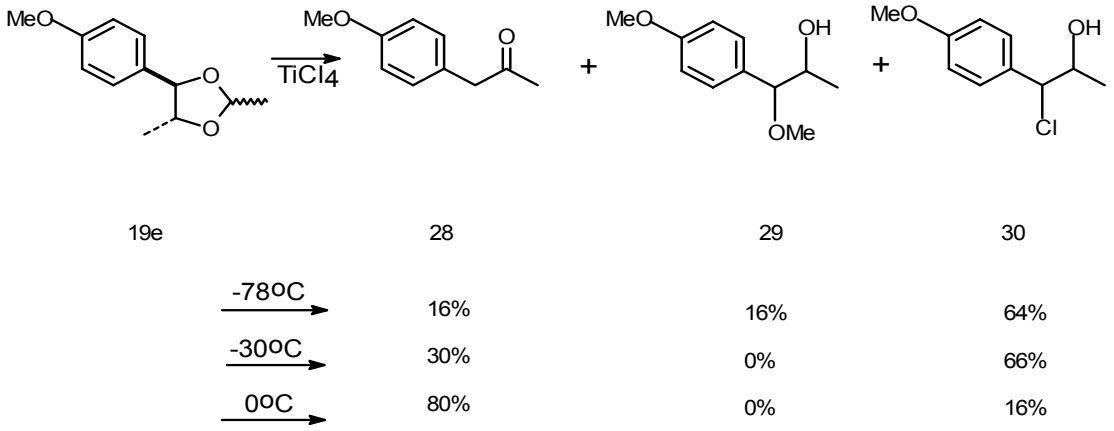
Conducting the reaction at -30 ^{o}C produced quite a large change in the product distribution. The only benzopyran isolated was the dehydrated analog **25**, in 10% yield, while the major product was the benzofuran mixture **26**, isolated in 74% yield, with the chlorohydrins **24** accounting for the rest. It is known that similar benzofuran mixtures are formed from initially formed benzopyrans' rearranging under these reaction conditions.[20] It is of interest to note that in the ^{1}H-NMR spectrum of **25** the signal for the C-3- Me group appeared at δ = 1.92 as a doublet (^4J = 0.7 Hz) and 4-H appeared at δ = 5.57 as a quartet (^4J = 0.7 Hz). The same three products were

formed at 0 °C but with increased proportions of the benzopyrene **25** to 14%, while that of the benzofurans **26** increased to 83% (Scheme 2).



Scheme 2. Products of reaction of **18e** with $TiCl_4$.

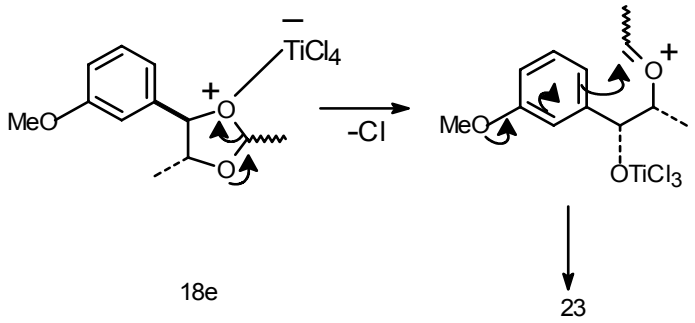
Treatment of the *para*- methoxyphenyldioxolane **19e** under the standard conditions produced no benzopyran products. The only products isolated were the ring-opened methoxyphenylpropanone, **28** (16%), and the methoxyphenylpropanols, **29** and **30**, in yields of 16% and 64% respectively (Scheme 3). From the same reaction at -30 °C only two products were isolated, the arylpropanone **28** and the corresponding propanol **30**, in yields of 30% and 66% respectively, while at 0°C the yield of the propanone **28** increased to 80% and the substituted propanol **30** was reduced to 16%.



Scheme 3. Products of the reaction of **19e** with $TiCl_4$.

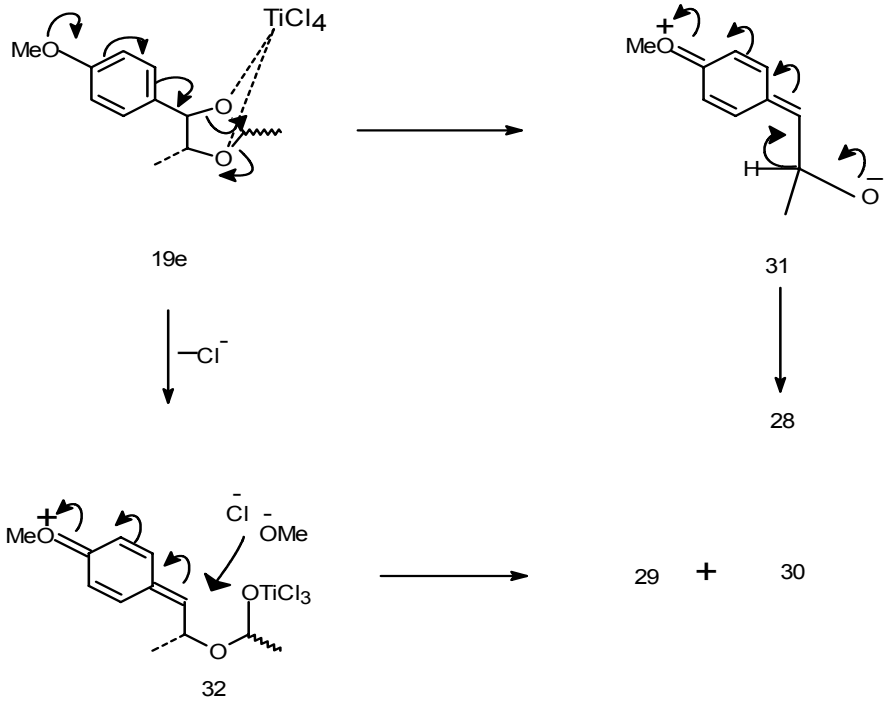
In formulating a plausible mechanism for the formation of the benzopyran **18e** it is more than likely that electronic effects play a major role. Thus, subsequent to initial complexation with

$TiCl_4$ at O-3 in the dioxolane ring, fission occurs between C-2 and O-3 to produce the intermediate oxonium ion which undergoes cyclization as a result of the nucleophilicity of the aryl ring C- *para* to the methoxy group to afford the benzopyran **23** as illustrated in Scheme 4.



Scheme 4. Mechanism of isomerization of the dioxolane **18e.**

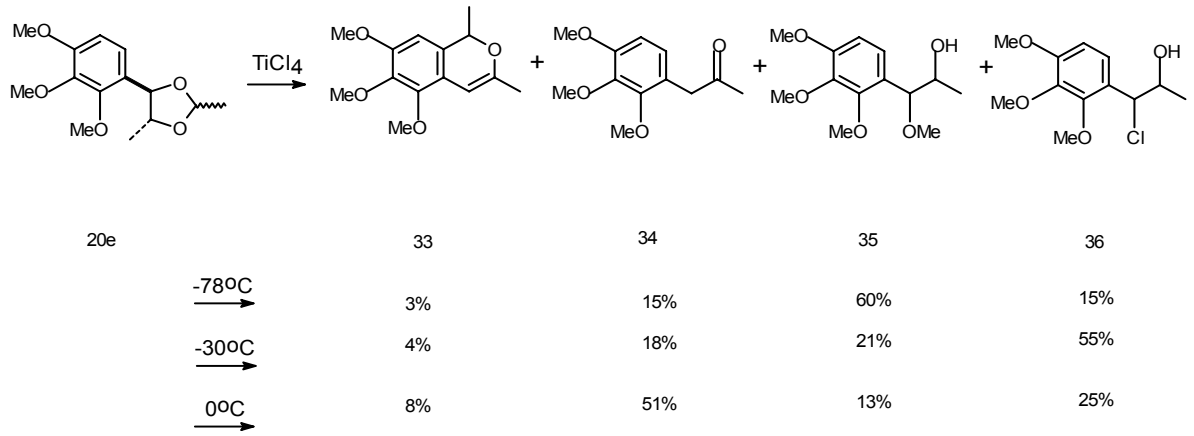
On the other hand, complexation by $TiCl_4$ at O-1 and O-3 of **19e** induces fission between O-3 and C-4 owing to the electron-donating ability of the *para*- methoxy group ring at C-4 of the dioxolane ring, to produce the *para*-quinone methides, **31** arising from further fission between O-1 and C-2, and **32** from the alternative loss of chloride. In the former case, a hydride migration would give the arylpropanone **28** while the latter intermediate might afford the substituted propanol **29** resulting from attack by methoxide, and **30** from attack by chloride (Scheme 5).



Scheme 5. Mechanism of formation of pyran-ring opened products **28–30.**

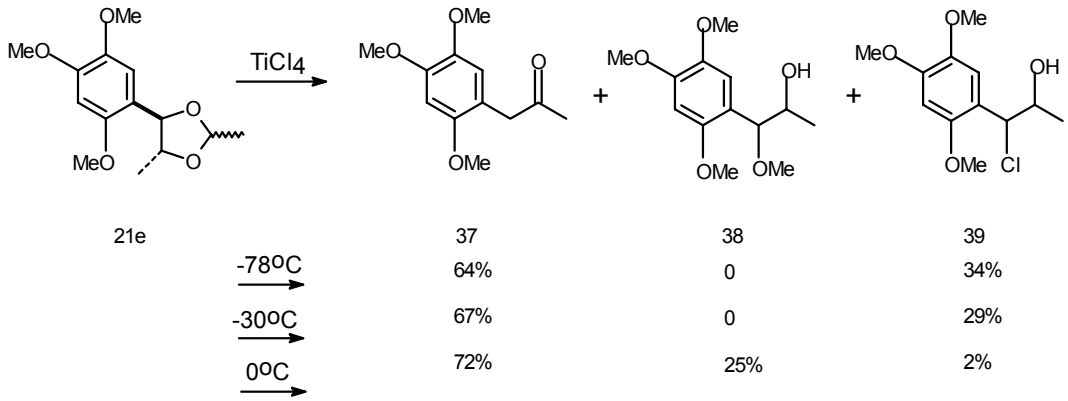
As a consequence of the study by Giles *et al.*[20] in which the influence of a C-4- *ortho*-methoxyphenyl dioxolane was investigated when treated under the standard conditions, we wished to broaden the scope of our investigations to include C-4- phenyl scaffolds having combinations of *ortho*-, *meta*- and *para*- trimethoxy groups. Our research required investigation of the influence of three methoxy groups on the product distribution of 4-(trimethoxyphenyl)-2,5-dimethyldioxolanes when treated under the standard conditions, and to define the regiochemical pattern needed for benzopyran ring formation.

The first trimethoxyphenyl-dioxolane investigated was **20e** which has *ortho-, meta*- and *para*- methoxy groups relative to the ring- C attached to C-4 of the dioxolane moiety, viz., two groups favoring ring-opening of the dioxolane moiety and one group favoring benzopyran ring formation. Thus treatment of **20e** under the standard conditions afforded a low yield of the benzopyrene **33** (3%) together with the products of ring opening viz., the substituted propanone **34** (15%), the trimethoxyarylpropanol **35** (60%) and the substituted propanol **36** (15%) illustrated in Scheme 6. As the temperature of reaction was increased, so too did the proportions of the trimethoxyarylpropanone **34,** and – to a much lesser extent – the benzopyrene **33**.



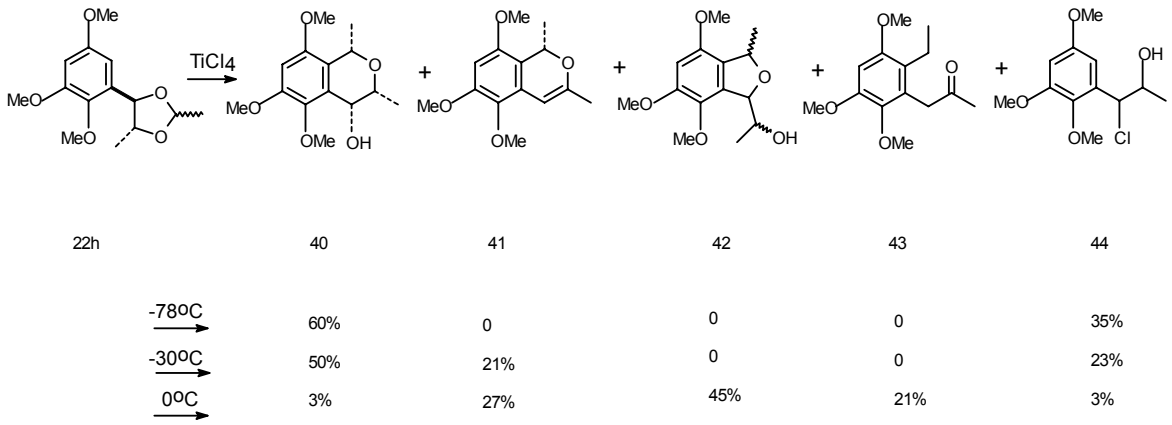
Scheme 6. Products of reaction of dioxolanes **20e** with $TiCl_4$.

The second trimethoxyphenyldioxolane investigated, viz. **21e**, represents a molecule with a subtle change in the regiochemistry of the methoxy groups. Not only does it have *ortho-, meta*- and *para*-methoxy groups relative to the ring-C attached to C-4 of the dioxolane moiety, but additionally it has steric and electronic effects that do not support pyran ring formation, as shown in Schemes 4 and 5. Thus, it was not surprising that treatment of **21e** under the standard set of conditions yielded only ring- opened products viz., the aryl propanone **37** together with the two arylpropanols **38** and **39**, as illustrated in Scheme 7.



Scheme 7. Products of reaction of the dioxolane with $TiCl_4$.

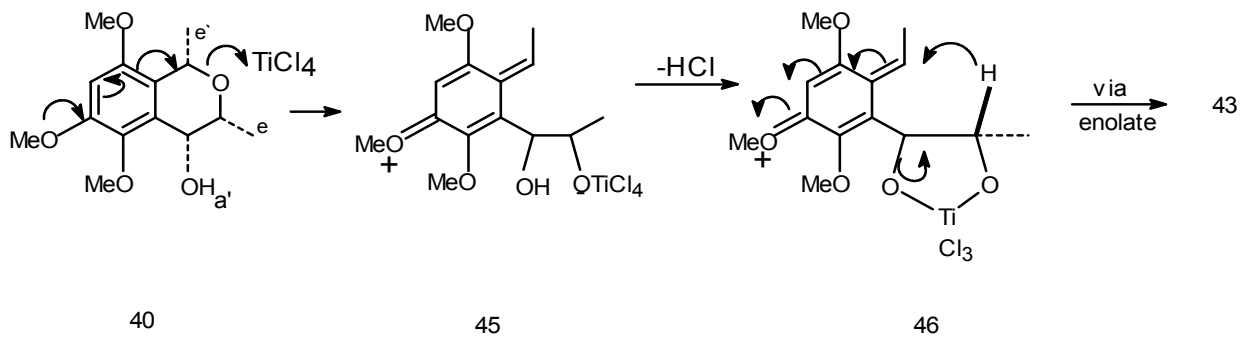
The third of the trimethoxyphenyldioxolanes investigated was **22h**, having two *meta*- and one *ortho*-methoxy groups relative to the phenyl ring-C attached to C-4 of the dioxolane moiety. In this case, there was only one methoxy group that strongly favored cyclization, in spite of the steric demand at the C-6′ position which is similar to that found in **21e**. The results of the treatment regime are shown in Scheme 8. The influence of the C-3′-methoxy group is clear at low temperature since it induces sufficient nucleophilic character at C-6′ to attack the intermediate oxonium ion depicted in Scheme 4 to subsequently form the benzopyran **40**, and it thus overrides any adverse steric effects of the C-5′-methoxy group. An increase in the reaction temperature results in a decrease in formation of benzopyran **40** and chloropropanols **44**, and an increase in the formation of benzofurans **42** resulting from the rearrangement of the initially formed benzopyran **40.**[20]



Scheme 8. Products of reaction of **22h** with $TiCl_4$.

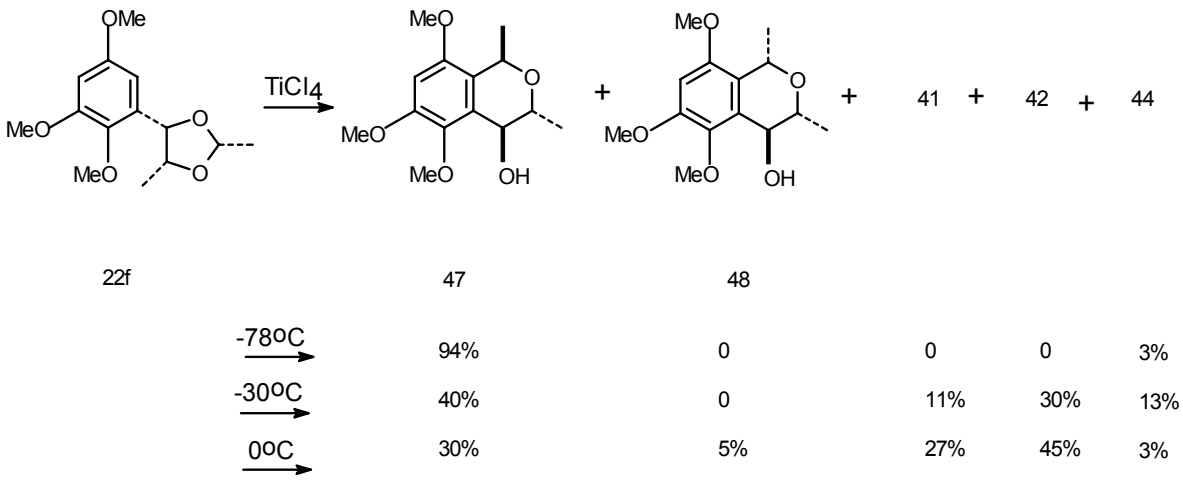
A rather intriguing new product was isolated for the first time in this work at 0 ^{o}C – the trimethoxyphenylpropanone **43** – which was isolated in 21% yield. Assignment of the structure

follows from ^{1}H- and ^{13}C-NMR spectral data which had *inter alia*; a 3-proton triplet at δ = 1.02 (*J* = 7.4 Hz) coupled to a 2-proton quartet at δ = 2.50 (*J* = 7.4 Hz), a 3-proton singlet at δ = 2.18, a 2-proton singlet at δ = 3.77, and a 1-proton singlet at δ = 6.44. The ketone group was evident from a signal at δ = 207.0 in the ^{13}C NMR spectrum. A proposed mechanism for the formation of compound **43** is illustrated in Scheme 9, in which the C6-methoxy group in **40** and $TiCl_4$ cause the C-1–O-2 bond of the pyran ring to cleave and generate intermediate **45**. The driving force behind this fission is the unfavorable *peri*- interaction between the *pseudo*- equatorial C-1-methyl and C-8-methoxy group being relieved as a consequence of this ring opening. Loss of the elements of HCl from the complex **45** would yield the $TiCl_3$-co-coordinated transition intermediate **46**, followed by a hydride migration and subsequent enolate formation. Hydrolysis of the latter enolate would then produce the substituted propanone **43**.



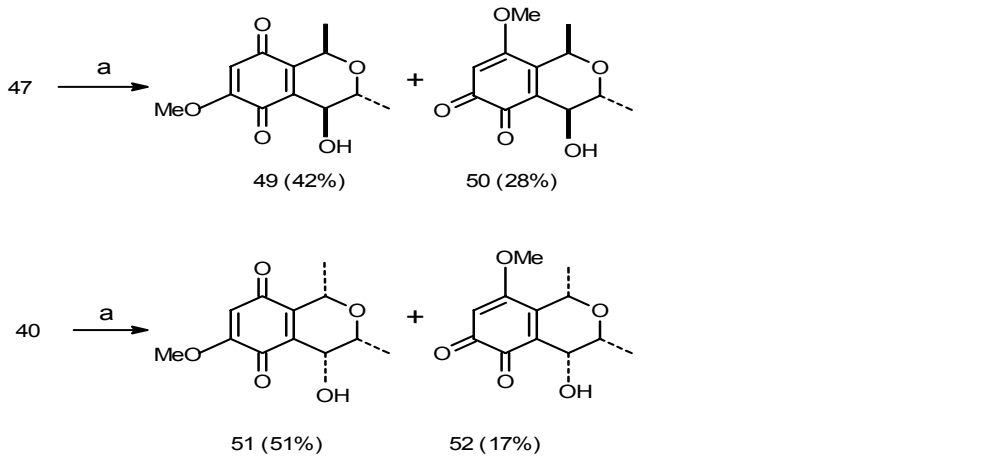
Scheme 9. Mechanism of formation of the ketone **43**.

The results of treatment of the all-*cis* trimethoxyphenyldioxolane **22f** under the standard conditions are summarized in Scheme 10. At -78 °C, by far the major product is the benzopyran **47**, isolated in 94% yield, in which the stereochemistries of C-4 and C-5 of the dioxolane ring have been incorporated unaltered at C-4 and C-3 respectively in the pyran ring. In addition, the C-1- methyl group is in the *pseudo*-axial position, owing to the steric environment of the *peri*-C-8-methoxy group. At -30 °C the yield of the benzopyran **47** dropped to 40% while the amount of dehydration product **41** increased to 11%, and the rearranged benzofurans **42** increased to 30%. This trend continued at 0 °C where it was noted that the C-1 epimer of **47,** *viz.*, the benzopyran **48** was isolated in 5% yield. It is of interest that the yield of benzofurans **42** is the same starting from either **22f** or **22h,** but that the proportion of the benzopyrans **47** and **40** differed by more than 44%. This differential trend is maintained, although not to the same extent, as the temperature increased to 0 °C.



Scheme 10. Products of reaction of the dioxolane **22f** with $TiCl_4$.

Finally, the benzopyrans **47** and **40** were oxidized to the corresponding quinones **49** (42%) and **51** (51%) in aqueous cerium(IV) ammonium nitrate. In this procedure the two corresponding *ortho*- quinones, **50** (28%) and **52** (17%) were also produced as unstable red oils (Scheme 11).



a) Aqueous cerium(IV) ammonium nitrate in acetonitrile

Scheme 11. Oxidation products of the benzopyrans **47** and **40.**

Conclusions

The *meta*-methoxyphenyl group attached to C-4 of the dioxolane moiety, viz., **18e**, is sufficient, through resonance, to provide the necessary nucleophilic character to C-6′ in order to promote the intramolecular Mukaiyama- type cyclization at -78 ^{o}C. This produces the corresponding 2-

benzopyran **23**, while at higher temperatures the initially formed 2-benzopyran **23** is further isomerized to the benzofurans **26**. When there is a *para*- methoxyphenyl group attached to C-4 of the dioxolane moiety, *i.e.*, **19e**, no benzopyran formation occurs under the same conditions, but rather products of dioxolane ring opening, viz., the propanone **28,** as a consequence of the electron-releasing property of the methoxy group.

The trimethoxyphenyldioxolanes **20e** and **21e**, in which the methoxy groups are *ortho-, meta*- and *para*- in the phenyl ring at C4 of the dioxolane moiety, do not yield benzopyran products of isomerization, although with **20e** minor quantities (~5%), of 2-benzopyrene **33** were detected. Thus, since *ortho*- and *meta*-methoxy groups favor intramolecular cyclization under the standard conditions, the presence of the *para*- methoxy group is sufficient to direct the course of reaction to that of dioxolane ring opening. On the other hand, the dioxolanes **22h** and **22f**, both of which possess one *ortho*- and two *meta*-, but no *para*-methoxy substituents in the phenyl ring, the products of $TiCl_4$ - induced isomerization are indeed the 2-benzopyrans **40** and **47** respectively. In comparing the relative yields of this latter isomerization, it appears that the all-*cis*- phenyldioxolane **22f** affords a much higher quantity of the 2-benzopyran **47** (94%) than that of the epimeric mixture **22h** which produces **40** (60%). It is our contention that the reason for this is the fact that in **47** the C-1-methyl group adopts a *pseudo*-axial orientation and thus experiences relatively less steric interaction with the C-8 –*peri*- methoxy group, while in **40** the C-1- methyl group adopts a *pseudo*-equatorial orientation resulting in an unfavorable *peri*-interaction with the C-8- methoxy group.

Experimental Section

General. ^{1}H- and ^{13}C- NMR spectra were recorded on a Varian 200 MHz spectrometer using deuteriochloroform with TMS as internal standard; δ values are recorded in ppm. In the ^{13}C-spectra, assignments with the same superscripts may be interchanged. IR spectra were recorded on a Perkin Elmer FT-IR Paragon 2000 spectrometer either as oils or Nujol mulls. Mass spectra were performed on a Finnigan-MAT GCQ, and elemental analyses were performed on a Carlo Erba 1500 NA analyzer. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Preparative chromatography was done on dry columns using Merck Silica Gel 60, particle size 0.063-0.2 mm. Hexane refers to the fraction boiling between 67-70 ^{o}C and the term, "residue obtained upon work-up" refers to drying of the extract over magnesium sulfate, filtration, and removal of solvent under reduced pressure.

***E*-(3′-Methoxyphenyl)prop-1-ene (18c). General procedure.** *n*-Butyllithium (14.5 mmol) was added dropwise to a stirred suspension of ethyltriphenylphosphonium bromide (5.30 g; 14.29 mmol) in dry THF (50 mL) under a nitrogen flow, and at -78 ^{o}C. The temperature of the mixture was allowed to rise to 0 ^{o}C for 30 min after which it was again cooled to -78 ^{o}C and then the 3-methoxybenzaldehyde **(18a,** 1.39 g; 10.2 mmol) dissolved in THF (10 mL) was added dropwise

over 30 min. The reaction mixture was stirred for an additional 20 min at this temperature, then allowed to warm to 25 ^{o}C, and stirred for a further 3 h. It was then quenched with water and extracted with EtOAc, and the residue obtained upon work-up was chromatographed using EtOAc: hexane (1:9) as eluent to afford an *E/Z*- mixture of olefins **18b** as an oil (1.45 g; 96%) in a ratio of 1:2 (determined by NMR). This mixture was taken up in chloroform (50 mL) to which bis-(acetonitrile)dichloropalladium(II) [20] (35 mg) was added, the mixture was stirred at 25 ^{o}C for 72 h and then chromatographed on a short column using EtOAc: hexane (1:9) as eluent to yield the *(E)*-alkene **18c** (1.38 g; 95%) as a colorless oil. IR (NaCl, film): ν_{max} = 1666 (C=C) cm^{-1}. ^{1}H-NMR (200 MHz,$CDCl_3$): δ = 1.93 (dd, *J* = 6.6 and 1.8 Hz, 3H, 3-H), 3.86 (s, 3H, 3′-OCH_3), 6.32 (dq, *J* = 11.8 and 6.2 Hz, 1H, 2-H), 6.80 (dq, *J* = 11.8 and 1.8 Hz, 1H, 1-H), 6.92 (m, 3H, 2′-, 4′- and 6′-H), 7.26 (t, *J* = 8.0 Hz, 1 H, 5'-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.4 (C-3), 55.2 (OCH_3), 111.2 (C-4')^{a}, 112.3 (C-2')^{a}, 118.5 (C-2), 126.0 (C-5')^{b}, 129.4 (C-6')^{b}, 130.9 (C-1'), 139.4 (C-1), 159.8 (C-3'). MS (EI 70 eV): *m/z* (%) = 148 (100) $[M]^+$, 133 (7), 117 (26), 105 (70), 91 (8). Anal. Calcd for $C_{10}H_{12}O$ (148.2): C, 81.1; H, 8.1. Found C, 81.3; H, 7.9%.

***E*-(4′-Methoxyphenyl)prop-1-ene (19c).** Starting from the *p*-methoxybenzaldehyde **19a** (2.01g; 14.8 mmol) the *E/Z* (1:2) olefin **19b** was obtained as an oil (2.12g; 97%) which was isomerized into the pure (*E)*-alkene **19c** (2.00g; 94%), a white solid, m.p. 59-62 ^{o}C (from hexane). IR (Nujol mull): ν_{max} 1600 (C=C) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.86 (dd, *J* = 6.6 and 1.6 Hz, 3H, 3-H), 3.80 (s, 3H, 4'-OCH_3), 6.10 (dq, *J* = 15.8 and 6.6 Hz, 1H, 2-H), 6.35 (dq, *J* = 15.8 and 1.6 Hz, 1H, 1-H), 6.83 (d, *J* = 8.8 Hz, 2H, 3'- and 5'-H), 7.27 (d, *J* = 8.8 Hz, 2H, 2'- and 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.5 (C-3), 55.4 (OCH_3), 113.7 (C-2), 114.0 (C-3'/5'), 123.6 (C-2'/6'), 126.9 (C-1'), 130.4 (C-1), 158.7 (C-4'). MS (EI 70 eV): *m/z* (%) = 148 (100) $[M]^+$, 133 (5), 117 (16), 105 (9). Anal. Calcd for $C_{10}H_{12}O$ (148.2): C, 81.1; H, 8.1. Found C, 81.0; H, 8.3%.

***E*-(2′,3′,4′-Trimethoxyphenyl)prop-1-ene (20c).** Starting from 2,3,4-trimethoxy-benzaldehyde **20a**[20] (1.84g; 10.22 mmol), the *E/Z* (1:2) olefin **20b** was obtained as an oil (1.85g; 87%) and was isomerized into the pure *(E)*-alkene **20c** (1.56g; 84%), as an oil. IR (NaCl, film): ν_{max} = 1604 (C=C) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.88 (dd, *J* = 6.6 and 1.6 Hz, 3H, 3-H), 3.84, 3.85 and 3.87 (s, each 3H, 2'-,3'-,4'-OCH_3), 6.13 (dq, *J* = 16.2 and 6.6 Hz, 1H, 2-H), 6.58 (dq, *J* = 16.2 and 1.6 Hz, 1H, 1-H), 6.64 (d, *J* = 8.8 Hz, 1H, 5'-H), 7.11 (d, *J* = 8.8 Hz, 1H, 6'-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.9 (C-3), 56.2, 60.9, 61.1 (OCH_3), 107.9 (C-5'), 120.6 (C-6'), 125.1 (C-2)^{a}, 125.2 (C-1')^{a}, 125.3 (C-1)^{a}, 142.5 (C-2')^{b}, 151.0 (C-3')^{b}, 152.7 (C-4'). MS (EI 70 eV): *m/z* (%) = 208 (100) $[M]^+$, 193 (18), 179 (43), 161 (16), 151 (16), 133 (32). Anal. Calcd for $C_{12}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.0; H, 7.9%.

***E*-(2′,4′,5′-Trimethoxyphenyl)prop-1-ene (21c).** From 2,4,5-trimethoxy-benzaldehyde **21a** [20] (1.84g; 10.22 mmol), the *E/Z* (1:2) olefin **21b** was obtained as an oil (2.00g; 94%) and was isomerized into pure *(E)*-alkene **21c** (1.00g; 50%) – a white solid, m.p. 35-36 ^{o}C (from hexane). IR (Nujol mull): ν_{max} 1604 (C=C) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.89 (dd, *J* = 6.6 and 1.8 Hz, 3H, 3-H), 3.82, 3.86, 3.89 (s, each 3H, 2'-,4'-, 5'-OCH_3), 6.09 (dq, *J* = 16.0 and 6.6 Hz, 1H, 2-H), 6.66 (dq, *J* = 16.6 and 1.8 Hz, 1H, 1-H), 6.50 (s, 1H, 3'-H), 6.94 (s, 1H, 6'-H). ^{13}C

NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 56.3, 56.6, 56.9 (OCH_3), 98.2 (C-3'), 110.0 (C-6'), 119.2 (C-1'), 124.5 (C-1)[a], 125.2 (C-2)[a], 143.6 (C-2')[b], 148.9 (C-4')[b], 150.8 (C-5')[b]. MS (EI 70 eV): *m/z*(%) = 208 (100) $[M]^+$, 193 (38), 177 (7), 165 (22), 137 (19). Anal. Calcd for $C_{12}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.4; H, 7.9%.

***E*-(2′,3′,5′-Trimethoxyphenyl)prop-1-ene (22c).** Starting from 2,3,5-trimethoxybenzaldehyde **22a**[25,26] (1.85g; 10.30 mmol), the *E/Z* (1:2) olefins **22b** were isolated as an oil (2.03g, 95%), and then isomerized into the pure *(E)*-alkene **22c** (1.95g; 96%), a pale yellow oil. IR (NaCl, film): ν_{max} = 1654 (C=C) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.91 (dd, *J* = 6.6 and 1.8 Hz, 3H, 3-H), 3.74, 3.79, 3.83 (s, each 3H, 2'-,3'-,5'-OCH_3), 6.24 (dq, *J* = 15.6 and 6.6 Hz, 1H, 2-H), 6.38 (d, *J* = 2.8 Hz, 1H, 4'-H), 6.54 (d, *J* = 2.4 Hz, 1H, 6'-H), 6.66 (dq, *J* = 15.6 and 1.8 Hz, 1H, 1-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 55.6, 55.9, 61.1 (OCH_3), 99.2 (C-4')[a], 100.6 (C-6')[a], 125.4 (C-2), 127.2 (C-1), 131.9 (C-1'), 140.6 (C-2')[b], 153.7 (C-3')[b], 156.1 (C-5')[b]. MS (EI 70 eV): *m/z*(%) = 208 (100) $[M]^+$, 193 (95), 178 (%), 165 (75), 150 (30). Anal. Calcd for $C_{12}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.5; H, 7.6%.

***rel*-(1*R*,2*R*)-1-(3′-Methoxyphenyl)-propane-1,2-diol (18d). The following general procedure was applied to all the alkenes**

To the *(E)*-alkene **18c** (200 mg; 1.35 mmol) in acetone-water (10:9.9 mL) was added *N*-methylmorpholine *N*-oxide (563 mg; 4.80 mmol) and osmium tetroxide (8mg; 0.03 mmol) in *tert*-butyl alcohol (0.4 mL) and the resulting solution was stirred at 25 °C for 24 h. The aqueous layer obtained after removal of the acetone under vacuum at 25 °C was poured into aqueous hydrogen chloride (2*M*, 3.0 mL) and stirred for 15 min. The residue obtained from extraction of the acid solution with EtOAc was chromatographed using EtOAc: hexane (1:1) to afford the diol **18d** (226 mg; 92%) as a thick pale brown oil. IR (NaCl, film): ν_{max} = 3600 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 6.6 Hz, 3H, 3-H), 2.65 (bs, 1H, 2-OH), 3.98 (bs, 1H, 1-OH), 3.80 (s, 3H, 3'-OCH_3), 3.83 (dq, *J* = 6.6 and 7.4 Hz, 1H, 2-H), 4.32 (d, *J* = 7.4 Hz, 1H, 1-H), 6.88 (m, 3H, 2'-, 4'-, 6'-H), 7.26 (t, *J* = 8.0 Hz, 1H, 5'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 55.3 (OCH_3), 72.2 (C-2), 79.4 (C-1), 112.5 (C-2')[a], 113.5 (C-4')[a], 119.3 (C-6')[b], 129.6 (C-5')[b], 142.9 (C-1'), 159.8 (C-3'). MS (EI 70 eV): *m/z* (%) = 182 (3) $[M]^+$, 138 (100), 109 (79), 105 (18). Anal. Calcd for $C_{10}H_{14}O_3$ (182.2): C, 65.9; H, 7.7. Found C, 65.7; H, 7.9%.

***rel*-(1*R*,2*R*)-1-(4′-Methoxyphenyl)propane-1,2-diol (19d).** The *(E)*-alkene **19c** (200 mg; 1.35 mmol) was converted into the diol **19d** (226 mg, 92%); white needles, m.p. 61-62 °C (from hexane). IR (Nujol mull): ν_{max} = 3600 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.6 Hz, 3H, 3-H), 2.02 (s, 1H, 2-OH), 2.42 (bs, 1H, 1-OH), 3.80 (s, 3H, 4'-OCH_3), 3.82 (dq, *J* = 6.6 and 7.6 Hz, 1H, 2-H), 4.30 (d, *J* = 7.6 Hz, 1H, 1-H), 6.88 (d, *J* = 8.8 Hz, 2H, 3'- and 5'-H), 7.25 (d, *J* = 8.8 Hz, 2H, 2'- and 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 55.4 (OCH_3), 72.4 (C-2), 79.2 (C-1), 114.0 (C-3' and C-5'), 128.0 (C-2')[a], 128.1 (C-6')[a], 133.3 (C-1'), 159.6 (C-4'). MS (EI 70 eV): *m/z* (%) = 182 (3) $[M]^+$, 137 (100), 109 (51). Anal. Calcd for $C_{10}H_{14}O_3$ (182.2): C, 65.9; H, 7.7. Found C, 65.8; H, 7.5%.

***rel*-(1*R*,2*R*)-1-(2′, 3′,4′-Trimethoxyphenyl)propane-1,2-diol (20d)**. The *(E)*-alkene **20c** (200 mg; 0.96 mmol) was converted into the diol **20d** (231 mg; 99%), a thick pale brown oil. IR (NaCl, film): ν_{max} = 3600 (OH) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.2 Hz, 3H, 3-H), 2.40 (bs, 1H, 2-OH), 3.50 (bs, 1H, 1-OH), 3.82, 3.88, 3.89 (s, each 3H, 2'-,3'-,4'-OCH_3), 3.90 (dq, *J* = 6.2 and 7.4 Hz, 1H, 2-H), 4.54 (d, *J* = 7.4 Hz, 1H, 1-H), 6.63 (d, *J* = 8.8 Hz, 1H, 5'-H), 6.97 (d, *J* = 8.8 Hz, 1H, 6'-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.7 (C-3), 55.9, 60.7, 61.2 (OCH_3), 71.6 (C-2), 75.6 (C-1), 107.4 (C-5'), 122.5 (C-6'), 126.5 (C-1'), 142.0 (C-2')[a], 151.5 (C-3')[a], 153.4 (C-4')[a]. MS (EI 70 eV): *m/z* (%) = 242 (24) $[M]^+$, 197 (100), 169 (25), 154 (30), 138 (15). Anal. Calcd for $C_{12}H_{18}O_5$ (242.3): C, 59.5; H, 7.4. Found C, 59.7; H, 7.2%.

***rel*-(1*R*,2*R*)-1-(2′,4′,5′-Trimethoxyphenyl)propane-1,2-diol (21d).** The *(E)*-alkene **21c** (200 mg; 0.96 mmol) was converted into the diol **21d** (185 mg; 80%), a thick pale brown oil. IR (NaCl, film): ν_{max} = 3582 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.2 Hz, 3H, 3-H), 1.60 (bs, 1H, 2-OH), 2.90 (bs, 1H, 1-OH), 3.84, 3.89, 3.90 (s, each 3H, 2'-,4'-, 5'-OCH_3), 3.90 (dq, *J* = 6.6 and 6.2 Hz, 1H, 2-H), 4.54 (d, *J* = 6.6 Hz, 1H, 1-H), 6.52 (s,1H, 3'-H), 6.84 (s, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 56.3 (X2), 56.7 (OCH_3), 71.3 (C-2), 77.3 (C-1), 97.6 (C-3'), 112.3 (C-6'), 114.1 (C-1'), 142.2 (C-2')[a], 149.3 (C-4')[a], 151.2 (C-5')[a]. MS (EI 70 eV): *m/z*(%) = 224 (18) $[M-18]^+$, 181 (100), 151 (32). Anal. Calcd for $C_{12}H_{18}O_5$ (242.3): C, 59.5; H, 7.4. Found C, 59.3; H, 7.6%.

***rel*-(1*R*,2*R*)-1-(2′,3′,5′-Trimethoxyphenyl)propane-1,2-diol (22g).** The *(E)*-Alkene **22c** (200 mg; 0.96 mmol) was converted into the diol **22g** (203 mg; 87%), a thick pale brown oil. IR (NaCl, film): ν_{max} = 3590 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 6.6 Hz, 3H, 3-H), 2.25 (bs, 1H, 2-OH), 2.98 (bs, 1H, 1-OH), 3.79,3.80, 3.85 (s, each 3H, 2'-, 3'-, 5'-OCH_3), 4.10 (dq, *J* = 6.6 and 4.4 Hz, 1H, 2-H), 4.92 (d, *J* = 4.4 Hz, 1H, 1-H), 6.44 (d, *J* = 2.6 Hz, 1H, 4'-H), 6.54 (d, *J* = 2.6 Hz, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.9 (C-3), 55.7, 55.8, 61.2 (OCH_3), 71.8 (C-2),75.2 (C-1), 100.0 (C-4'), 102.7 (C-6'), 134.6 (C-1'), 140.9 (C-2')[a], 153.4 (C-3')[a], 156.3 (C-5')[a]. MS (EI 70 eV): *m/z*(%) = 242 (24) $[M]^+$, 197 (100), 183 (33), 169 (77), 154 (43), 138 (34), 123 (24). Anal. Calcd for $C_{12}H_{18}O_5$ (242.3): C, 59.5; H, 7.4. Found: C, 59.3; H, 7.6%.

***trans*-1-(2′,3′,5′-Trimethoxyphenyl)-1,2-epoxypropane (22d).** To a stirred suspension of the *(E)*-alkene **22c** (500 mg; 2.40 mmol) and sodium hydrogencarbonate (700 mg; 8.33 mmol) in chloroform (8 mL) at 0 °C was added dropwise *m*-chloroperbenzoic acid (1.03 g; 5.99 mmol) in chloroform (50 mL). The resultant mixture was stirred at this temperature for 24 h, filtered, and the filtrate was poured into saturated aqueous sodium hydrogencarbonate (20 mL) and vigorously shaken. The residue obtained upon workup was chromatographed using EtOAc: hexane (1:9) as eluent to afford the epoxide **22d** (306 mg; 57%) as a light orange oil. IR (NaCl, film): ν_{max} = 1280 (C-O) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.47 (d, *J* = 5.2 Hz, 3H, 3-H), 2.95 (dq, *J* = 2.2 and 5.2 Hz, 1H, 2-H), 3.75, 3.81, 3.84 (s, each 3H, 2'-,3'- ,5'-OCH_3), 3.93 (d, *J* = 2.2 Hz, 1H, 1-H), 6.22 (d, *J* = 2.6 Hz, 1H, 4'-H), 6.42 (d, *J* = 2.6 Hz, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.8 (C-3), 55.2, 55.6, 55.8 (OCH_3), 58.2 (C-2), 61.3 (C-1), 99.4 (C-4'), 99.9 (C-6'), 131.9 (C-1'), 141.9 (C-2')[a], 153.1 (C-3')[a], 156.6 (C-5')[a]. MS (EI 70 eV): *m/z* (%) = 224

(100) $[M]^+$, 209 (86), 193 (48), 181 (25), 166 (22). Anal. Calcd for $C_{12}H_{16}O_4$ (224.3): C, 64.3; H, 7.2. Found C, 64.1; H, 7.3%.

***rel*-(1*S*,2*R*)-1-(2′,3′,5′-Trimethoxyphenyl)-1,2-diol (22e).** To a stirred solution of the epoxide **22d** (200 mg; 0.89 mmol) in dimethyl sulfoxide (10 mL) was added aqueous potassium hydroxide (22 mL, 0.4*M*, 8.8 mmol) and the resulting solution was stirred at 80 ^oC for 24 h. The cooled reaction mixture was poured into water (120 mL) and extracted with EtOAc. The residue obtained upon workup was chromatographed using EtOAc: hexane (1:1) as eluent to afford the diol **22e** (190 mg; 88%) as a thick pale brown oil. IR (NaCl, film): ν_{max} = 3490 (OH) cm $^{-1}$. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 6.6 Hz, 3H, 3-H), 2.20 (bs, 1H, 2-OH), 2.80 (bs, 1H, 1-OH), 3.48, 3.49, 3.54 (s, each 3H, 2'-, 3'-, 5'-OCH_3), 3.79 (dq, *J* = 6.6 and 4.4 Hz, 1H, 2-H), 4.65 (d, *J* = 4.4 Hz, 1H, 1-H), 6.14 (d, *J* = 3 Hz, 1H, 4'-H), 6.27 (d, *J* = 3 Hz, 1H, 6'-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 17.7 (C-3), 55.7, 55.8, 61.1 (OCH_3), 70.7 (C-2), 73.7 (C-1), 99.9 (C-4'), 102.6 (C-6'), 134.1 (C-1'), 140.5(C-2')[a], 153.3 (C-3')[a], 156.4 (C-5'). MS (EI 70 eV): *m/z* (%) = 242 (24) $[M]^+$, 197 (100), 183 (33), 169 (77), 154 (43), 138 (34), 123 (34). Anal. Calcd for $C_{12}H_{18}O_5$ (242.3): C, 59.5; H, 7.4. Found C, 59.7; H, 7.2%.

***rel*-(2*S*,4*R*,5*R*)-and *rel*-(2*R*,4*R*,5*R*)-4-(3′-Methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (18e). The following general protocol was employed for all syntheses of the dioxolanes.** To a solution of the diol **18d** (200 mg; 1.10 mmol) in dry dichloromethane (30 mL) containing camphorsulfonic acid (30 mg; 0.12 mmol) was added 1,1-dimethoxyethane (0.4 mL, 471 mg; 5.9 mmol) and the resulting mixture was stirred under gentle reflux for 2 h. The cooled mixture was quenched with saturated aqueous sodium hydrogencarbonate (5 mL) and then poured into water (100 mL). The residue obtained from dichloromethane extraction was chromatographed using EtOAc: hexane (1:4) as eluent to afford the dioxolane mixture **18e** (243 mg; 95%) as a colorless oil. IR (NaCl, film): ν_{max} = 1100 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.31 and 1.38 (d, *J* = 6.4 Hz, each 3H, 5-CH_3 for each isomer), 1.47 and 1.50 (d, *J* = 4.8 Hz, each 3H, 2-CH_3 for each isomer), 3.82 (s, 6H, 3'-OCH_3 for each isomer), 3.89 (dq, *J* = 7.6 and 6.4 Hz, 2H, 5-H for each isomer), 4.44 and 4.46 (d, *J* = 7.6 Hz, each 1H, 4-H of each isomer), 5.39 (q, *J* = 4.8 Hz, 2H, 2-H for each isomer), 6.89 (m, 6H, 2'-,4'-,6'-H for each isomer), 7.28 (t, *J* = 7.4 Hz, 2H, 5'-H for each isomer). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.6 and 17.3 (C5-CH_3), 20.5 and 20.6 (C2-CH_3), 55.2 (OCH_3), 79.1 and 81.1 (C-5), 84.2 and 85.9 (C-4), 100.9 and 101.9 (C-2), 111.7 and 111.9 (C-2')[a], 113.3 and 113.6 (C-4')[a], 118.4 and 118.7 (C-6'), 129.6 (C-5'), 139.7 and 140.9 (C-1'), 159.8 (C-3'). MS (EI 70 eV): *m/z* (%) = 208 (28) $[M]^+$, 191 (18), 164 (100), 148 (60), 133 (44), 120 (20). Anal. Calcd for $C_{10}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.0; H, 7.9%.

***rel*-(2*S*,4*R*,5*R*)- and *rel*-2*R*,4*R*,5*R*)-4-(4′-methoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (19e).** The diol **19d** (200 mg; 1.1 mmol) was converted into an inseparable mixture of dioxolanes **19e** (200 mg; 77%), as a colorless oil. IR (NaCl, film): ν_{max} = 1100 (C-O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.28 and 1.35 (d, *J* = 6.4 Hz, each 3H, 5-CH_3 for each isomer), 1.46 and 1.48 (d, *J* = 4.8 Hz, each 3H, 2-CH_3 for each isomer), 3.80 (s, 6H, 4'-OCH_3 for each isomer), 3.89 (dq, *J* = 6.4 and 7.2 Hz, 2H, 5-H for each isomer), 4.39 and 4.43 (d, *J* = 7.6 Hz, 2H, 4-H for each isomer), 5.36 and 5.45 (q, *J* = 4.8 Hz, 2H, 2-H for each isomer), 6.90 (d, *J* = 8.8 Hz, 4H, 3'- and

5'-H for each isomer), 7.28 (d, J = 8.8 Hz, 4H, 2'- and 6'-H for each isomer). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 16.5 and 17.2 (C5-CH_3), 20.7 and 20.9 (C2-CH_3), 55.4 (OCH_3), 79.1 and 81.2 (C-5), 84.2 and 85.9 (C-4), 100.9 and 101.9 (C-2), 113.6 and 114.1 (C-3'/5'), 127.7 and 127.9 (C-2'/6'), 128.3 (C-1'), 159.6 and 159.8 (C-4'). MS (EI 70 eV): *m/z* (%) 208 (16) $[M]^+$, 164 (100), 133 (35), 121 (19). Anal. Calcd for $C_{10}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.4; H, 7.5%.

***rel*-(2*S*,4*R*,5*R*)- and *rel*-2*R*,4*R*,5*R*)-4-(2′,3′,4′-Trimethoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (20e).** The diol **20d** (200 mg; 0.83 mmol) was converted into an inseparable mixture of dioxolanes **20e** (220 mg; 99%) as a colorless oil. IR (NaCl, film): ν_{max} = 1096 (C-O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.33 and 1.38 (d, J = 6.4 Hz, each 3H, C5-CH_3 for each isomer), 1.46 and 1.48 (d, J = 6.2 Hz, each 3H, C2-CH_3 for each isomer), 3.84, 3.85, 3.86, 3.88, 3.89, 3.91 (s, each 3H, 2'-,3'-,4'-OCH_3 for each isomer), 3.99 (dq, J = 6.6 and 6.4 Hz, 2H, 5-H for each isomer), 4.73 and 4.82 (each d, J = 6.6 Hz, each 1H, 4-H of each isomer), 5.38 (m, 2H, 2-H of each isomer), 6.66 and 6.70 (each d, J = 8.4 and 8.8 Hz, each 1H, 5'-H for each isomer), 7.06 and 7.16 (each d, J = 8.4 and 8.8 Hz, each 1H, 6'-H for each isomer). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.4 and 17.8 (C5-CH_3), 20.5 and 20.8 (C2-CH_3), 56.1 (X2), 60.8 (X2), 61.0, 61.2 (OCH_3), 79.0 and 80.6 (C-5), 84.4 and 85.8 (C-4), 100.6 and 101.5 (C-2), 107.5 and 107.7 (C-5'), 121.8 (C-6'), 124.5 and 125.2 (C-1'), 151.9, 152.0, 153.6 (X4) (C-2',C-3',C-4'). MS (EI 70 eV): *m/z* (%) = 268 (11) $[M]^+$, 224 (100), 193 (78), 181 (20), 165 (22). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H,7.5. Found C, 62.9; H, 7.3%.

***rel*-(2*S*,4*R*,5*R*)- and *rel*-2*R*,4*R*,5*R*)-4-(2′,4′,5′-Trimethoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (21e).** The diol **21d** (a colorless oil, 200 mg; 0.83 mmol) was converted into an inseparable mixture of dioxolanes **21e** (166 mg; 75%). IR (NaCl, film): ν_{max} = 1200 (C-O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.30 and 1.35 (d, J = 6.2 Hz, each 3H, C5-CH_3 for each isomer), 1.43 and 1.45 (d, J = 6.4 Hz, each 3H, C2-CH_3 for each isomer), 3.76, 3.78, 3.82, 3.83, 3.86 (x2) (s, each 3H, 2'-,4'-,5'-OCH_3), 3.90 (m, 2H, 5-H), 4.83 and 4.92 (d, J = 6.6 Hz, each 1H, 4-H of each isomer), 5.36 (m, 2H, 2-H of each isomer), 6.47 (s, 2H, 3'-H of each isomer), 6.93 and 7.02 (s, each 1H, 6'-H of each isomer). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.5 and 17.8 (C5-CH_3), 20.4 and 20.6 (C2-CH_3), 56.1, 57.4, 58.8, 60.8, 61.2, 61.3 (OCH_3). 79.6 and 80.1 (C-5), 84.3 and 85.8 (C-4), 100.9 and 101.5 (C-2), 104.3 (C-3'), 107.6 (C-6'), 124.6 and 125.2 (C-1'), 151.6, 153.4, 155.8 (C-2', C-4', C-5'). MS (EI 70 eV): *m/z* (%) = 268 (51) $[M]^+$, 224 (67), 209 (100), 193 (64), 181 (29), 165 (28). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H,7.5. Found C, 62.5; H, 7.7%.

***rel*-(2*S*,4*R*,5*R*)- and *rel*-2*R*,4*R*,5*R*)-4-(2′,3′,5′-Trimethoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (22h).** The diol **22g** (200 mg; 0.83 mmol) was converted into an inseparable mixture of dioxolanes **22h** (212 mg; 94%), as a colorless oil. IR (NaCl, film): ν_{max} = 1150 (C-O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.35 and 1.42 (each d, J = 6.2 and 5.8 Hz, each 3H, C5-CH_3 for each isomer), 1.48 and 1.50 (each d, J = 6.2 Hz, 3H, C2-CH_3 for each isomer), 3.76, 3.78, 3.79(X2), 3.84(X2) (s, 18H, 2'-,3'-,5'-OCH_3), 3.95 (m, 2H, 5-H), 4.81 and 4.91 (d, J = 7.8 and 6.6 Hz, each 1H, 4-H for each isomer), 5.39 (q, J = 6.2 Hz, 2H, 2-H), 6.43 (d, J = 3.0 Hz, 2H, 4'-

H), 6.51 and 6.60 (d, J = 3.0 Hz, each 1H, 6'-H for each isomer).^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.4 and 17.9 (C5-CH_3), 20.3 and 20.6 (C2-CH_3), 55.5, 55,6(X2), 55.8, 60.7,60.9 (OCH_3), 79.4 and 79.7 (C-5), 80.0 and 80.1 (C-4), 99.7 and 99.9 (C-2), 100.5, 101.4, 101.7(X2) (C-4' and C-6'), 132.8 and 133.5 (C-1'), 140.9(X2), 153.2, 153.4, 156.4(X2) (C-2',C-3', C-5'). MS (EI 70 eV): *m/z* (%) = 268 (60) $[M]^+$, 224 (97), 209 (100), 193 (66), 182 (22). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H,7.5. Found 62.6; H, 7.8%.

***rel*-2*R*,4*S*,5*R*)-4-(2′,3′,5′-Trimethoxyphenyl)-2,5-dimethyl-1,3-dioxolanes (22f).** Diol **22e** (200 mg; 0.83 mmol) was converted into the pure dioxolane **22f** (220 mg; 99%) as a colorless oil. IR (NaCl, film): ν_{max} = 1150 (C-O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.4 Hz, 3H, C5-CH_3), 1.55 (d, J = 5.2 Hz, 3H, C2-CH_3), 3.76, 3.79, 3.84 (s, each 3H, 2'-,3'-,5'-OCH_3), 4.44 (dq, J = 7.4 and 6.4 Hz, 1H, 5-H), 5.18 (q, J = 5.2 Hz, 1H, 2-H), 5.35 (d, J = 7.4 Hz, 1H, 4-H), 6.43 (d, J = 3.0 Hz, 1H, 4'-H), 6.56 (d, J = 3.0 Hz, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 16.3 (C5-CH_3), 19.9 (C2-CH_3), 55.5, 55.7, 60.5 (OCH_3), 75.8 (C-5)[a], 76.0 (C-4)[a], 99.6 (C-4'), 99.6 (C-2), 100.4 (C-4'), 102.6 (C-6'), 132.3 (C-1'), 140.0, 152.8, 156.0 (C-2',C-3',C-5'). MS (EI 70 eV): *m/z* (%) = 268 (50) $[M]^+$, 224 (96), 209 (100), 193 (65), 182 (22). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H,7.5. Found 62.9; H, 7.3%.

Standard conditions for treatment of dioxolanes with $TiCl_4$.

To a solution of the dioxolane mixtures (200 mg) in dichloromethane (20 mL) at the specified temperature was added $TiCl_4$ (4 mol equivalents of a 9.2*M* solution in dichloromethane) *via* syringe under a nitrogen atmosphere, and stirring was continued for 30 min. The reaction mixture was quenched by the addition of methanol (0.6 mL) and allowed to reach 24 ^oC. Water (20 mL) and saturated aqueous sodium hydrogencarbonate (10 mL) were added and the aqueous solution exhaustively extracted with dichloromethane. The residue obtained upon workup was chromatographed using PLC with EtOAc: hexane (1:4) as eluent to afford the products in order of Rf.

Products of treatment of dioxolanes 18e at -78 ^oC. *rel*-(1*R*,3*S*,4*S*)-4-hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran (23) (156 mg; 78%) as white needles, m.p. 89-91 ^oC (from hexane). IR (Nujol mull): ν_{max} = 3586 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.39 (d, J = 6.6 Hz, 3H, C3-CH_3), 1.51 (d, J = 6.2 Hz, 3H, C1-CH_3), 1.95 (bd, J = 7.0 Hz, 1H, 4-OH), 3.80 (dq, J = 6.6 and 1.5 Hz, 1H, 3-H), 3.81 (s, 3H, C6-OCH_3), 4.19 (ddd, J = 7.0, 1.5 and 1.0 Hz, 1H, 4-H), 4.76 (dq, J = 6.2 and 1.0 Hz, 1H, 1-H), 6.86 (dd, J = 8.4 and 2.4 Hz, 1H, 7-H), 6.91 (d, J = 2.4 Hz, 1H, 5-H), 7.05 (d, J = 8.4 Hz,1H, 8-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.1 (C3-CH_3), 21.9 (C1-CH_3), 55.4 (OCH_3), 69.3 (C-3), 73.4 (C-1)[a], 73.8 (C-4)[a], 114.1 (C-7)[b], 115.4 (C-5)[b], 125.6 (C-8), 131.5 (C-4a)[c], 137.5 (C-8a)[c], 158.6 (C-6). MS (EI 70 eV): *m/z* (%) = 208 (4) $[M]^+$, 193 (23), 175 (30), 164 (100), 147 (33), 135 (55), 121 (29). Anal. Calcd for $C_{12}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found: C, 69.2; H, 7.9%.

***rel*-(1*R*,3*S*,4*S*)-4-Acetoxy-6-methoxy-1,3-dimethyl-2-benzopyran (27)**. The pyran **23** (160 mg; 0.59 mmol) in acetic anhydride (3.6 mL) and pyridine (0.9 mL) was stirred under nitrogen at 24

^{o}C for 24 h and then poured into ice-cold aqueous hydrogen chloride (0.5*M*, 25 mL) and extracted with dichloromethane. The residue obtained upon workup was chromatographed by PLC using EtOAc: hexane (1:4) as eluent to afford the acetate **27** (125 mg; 84%) as an oil. IR (NaCl, film): ν_{max} = 1738 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.30 (d, *J* = 6.4 Hz, 3H, C3-CH_3), 1.58 (d, *J* = 6.6 Hz, 3H, C1-CH_3), 2.12 (s, 3H, $COCH_3$), 3.78 (s, 3H, OCH_3), 3.85 (dq, *J* = 6.4 and 1.8 Hz, 1H, 3-H), 4.78 (dq, *J* = 6.6 and 1.2 Hz, 1H, 1-H), 5.78 (dd, *J* = 1.8 and 1.2 Hz, 1H, 4-H), 6.88 (dd, *J* = 8.4 and 2.2 Hz, 1H, 7-H), 6.90 (d, *J* = 2.2 Hz, 1H, 5-H), 7.08 (d, *J* = 8.4 Hz, 1H, 8-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.0 (C-3-CH_3), 21.2 (C-1-CH_3), 22.7 (CH_3CO), 55.5 (OCH_3), 69.3 (C-3), 72.3 (C-1)^{a}, 73.1 (C-4)^{a}, 114.2 (C-7)^{b}, 115.8 (C-5)^{b}, 125.6 (C-8), 132.4 (C-4a)^{c}, 133.4 (C-8a)^{c}, 158.6 (C-6), 171.4 (C=O). MS (EI 70 eV): *m/z* (%) = 250 (3) [M]$^{+}$, 235 (14), 175 (100), 164 (32). Anal. Calcd for $C_{14}H_{18}O_4$ (250.3): C, 67.2, H, 7.25. Found: C, 67.0, H, 7.4%.

1-Chloro-2-hydroxy-1-(3'-methoxyphenyl)propane (24). (40 mg; 20%) as an oil. IR (NaCl, film): ν_{max} = 3584 (OH) cm $^{-1}$. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.05 (d, *J* = 6.6 Hz, 3H, 3-CH_3), 2.98 (s, 1H, 2-OH), 3.80 (s, 3H, C3'-OCH_3), 3.83 (dq, *J* = 7.4 and 6.6 Hz, 1H, 2-H), 4.32 (d, *J* = 7.4 Hz, 1H, 1-H), 6.88 (m, 3H, 2'-,4'-, 6'-H), 7.26 (t, *J* = 8.0 Hz, 1H, 5'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 55.3 (OCH_3), 72.2 (C-2), 79.4 (C-1), 112.5 (C-4')^{a}, 113.5 (C-2')^{a}, 119.3 (C-6')^{b}, 129.6 (C-5')^{b}, 142.8 (C-1')^{b}, 159.8 (C-3'). MS (EI 70 eV): *m/z* (%) = 182 (3) [M^{+}-18], 137 (100), 109 (51), 94 (26). Anal. Calcd for $C_{10}H_{13}ClO_2$ (200.7): C, 59.9; H, 6.5. Found C, 60.2; H, 6.7%.

Products of treatment of dioxolanes (18e) at -30 ^{o}C

6-Methoxy-1,3-dimethyl-1*H*-2-benzopyrene (25) (18 mg; 10%), a colorless oil. IR (NaCl, film): ν_{max} = 1614 (C=C) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.57 (d, *J* = 6.6 Hz, 3H, C1-CH_3), 1.92 (d, *J* = 0.7 Hz, 3H, C3-CH_3), 3.78 (s, 3H, OCH_3), 5.15 (q, *J* = 6.6 Hz, 1H. 1-H), 5.57 (q, *J* = 0.7 Hz, 1H, 4-H), 6.46 (d, *J* = 2.4 Hz, 1H, 5-H), 6.64 (dd, *J* = 8.4 and 2.4 Hz, 1H, 7-H), 6.91 (d, *J* = 8.4 Hz, 1H, 8-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 20.2 (C1-CH_3), 22.8 (C3-CH_3), 56.8 (OCH_3), 68.8 (C-1), 97.6 (C-7)^{a}, 97.9 (C-4)^{a}, 108.0 (C-5), 112.8 (C-4a)^{b}, 122.0 (C-8), 124.2 (C-8a)^{b}, 139.0 (C-3), 151.2 (C-6). MS (EI 70 eV): *m/z* (%) = 190 (27) [M]$^{+}$, 175 (100), 253 (10), 91 (10). Anal. Calcd for $C_{12}H_{14}O_2$ (190.2): C, 75.8; H, 7.4. Found C, 75.6; H, 7.6%.

***rel*-(1*R*,1′*S*,3*S*)- and *rel*-(1*R*,1′*S*,3*R*)-1-(1′-Hydroxyethyl)-6-methoxy-3-methyl-1,3-dihydro-isobenzofurans (26)** (148 mg; 74%), a light pale olive-colored oil. IR (NaCl, film): ν_{max} = 3584 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.30 (d, *J* = 6.2 Hz, 3H, 2'-CH_3), 1.44 (d, *J* = 6.2 Hz, 3H, 3–CH_3), 2.40 (bs, 1H, 1'-OH), 3.80 (s, 3H, OCH_3), 3.85 (dq, *J* = 6.2 and 5.6 Hz, 1H, 1'-H), 4.96 (dd, *J* = 5.6 and 2.4 Hz, 1H, 1-H), 5.33 (dq, *J* = 6.2 and 2.4 Hz, 1H, 3-H), 6.76 (d, *J* = 2.2 Hz, 1H, 7-H), 6.86 (dd, *J* = 8.2 and 2.2 Hz, 1H, 5-H), 7.04 (d, *J* = 8.2 Hz, 1H, 4-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.4 (C2'-CH_3), 22.4 (C3-CH_3), 55.6 (OCH_3), 69.9 (C-1'), 79.1 (C-1)^{a}, 89.9 (C-3)^{a}, 107.5 (C-5), 114.1 (C-4), 121.8 (C-7), 138.5 (C-3a)^{b}, 140.4 (C-7a)^{b}, 159.6 (C-6). MS (EI 70 eV): *m/z* (%) = 208 (3) [M]$^{+}$, 163 (100), 145 (16), 135 (12), 121 (65), 105 (9). Anal.

Calcd for $C_{12}H_{16}O_3$ (208.3): C, 69.2; H, 7.7. Found C, 69.4; H, 7.4%. The third band afforded **24** (24 mg; 12%).

Products of treatment of dioxolanes 18e at 0 °C. Compounds (**25)** (25 mg; 14%), **26** (166 mg; 83%) and (**24)** (2 mg; 1%) were isolated.

Products of treatment of dioxolanes (19e) at -78 °C. 1-(4'-Methoxyphenyl)-2-propanone (28) (26 mg; 16%) as yellow needles, m.p. 194-195 °C (from hexane). IR (Nujol mull): ν_{max} = 1710 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 3H, 3-H), 3.63 (s, 2H, 1-H), 3.80 (s, 3H, OCH_3), 6.87 (d, *J* = 8.6 Hz, 2H, 3'-, 5'-H), 7.12 (d, *J* = 8.6 Hz, 2H, 2'-, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 29.2 (C-3), 50.2 (C-1), 55.3 (OCH_3), 114.3 (C-3' and C-5'), 126.4 (C-1'), 130.5 (C-2' and C-6'), 158.8 (C-4'), 207.0 (C=O). MS (EI 70 eV): *m/z* (%) = 164 (19) $[M]^+$, 121 (100), 91 (16). Anal. Calcd for $C_{10}H_{12}O_2$ (164.2): C, 73.2; H, 7.4. Found C, 73.0; H, 7.5%. **2-Hydroxy-1-methoxy-1-(4′-methoxyphenyl)propane (29)** (30 mg; 16%) as an oil. IR (NaCl, film): ν_{max} = 3446 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 0.94 (d, *J* = 5.8 Hz, 3H 3-H), 2.62 (bs, 1H, 2-OH), 3.20 (s, 3H, 1-OCH_3), 3.78 (m, 2H, 1-, 2-H), 3.81 (s, 3H, 4'-OCH_3), 6.89 (d, *J* = 8.6 Hz, 2H, 3'- , 5'-H), 7.19 (d, J = 8.6 Hz, 2H, 2'-, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.1 (C-3), 55.3 (C1-OCH_3), 55.6 (C4'-OCH_3), 71.6 (C-2), 89.2 (C-1), 114.0 (C-3' and C-5'), 128.9 (C-2' and C-6'), 130.5 (C-1'), 159.7 (C-4'). MS (EI 70 eV): *m/z* (%) = 196 (0.3) $[M]^+$, 151 (100), 131 (15), 108 (9). Anal. Calcd for $C_{11}H_{16}O_3$ (196.25): C, 67.3; H, 8.2. Found C, 67.1; H, 8.4%. **1-Chloro-2-hydroxy-1-(4′-methoxyphenyl)propane (30)** (124 mg; 64%) as an oil. IR (NaCl, film): ν_{max} = 3464 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 6.2 Hz, 3H, 3-H), 1.60 (bs, 1H, 2-OH), 3.75 (s, 3H, OCH_3), 3.81 (m, 1H, 2-H), 4.27 (d, *J* = 9.2 Hz, 1H, 1-H), 6.79 (d, *J* = 8.8 Hz, 2H, 3'-, 5'-H), 7.19 (d, *J* = 8.8 Hz, 2H, 2'-,6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 55.4 (OCH_3), 72.4 (C-2), 79.2 (C-1), 113.9 (C-3')^a, 114.0 (C-5')^a, 128.0 (C-2')^b, 128.1 (C-6')^b, 133.3 (C-1'), 159.6 (C-4'). MS (EI 70 eV): *m/z* (%) = 182 (3) $[M]^+$, 137 (100), 109 (51), 94 (26). Anal. Calcd for $C_{10}H_{13}ClO_2$ (200.7): C, 59.9; H, 6.5. Found C, 60.2; H, 6.7%.

Products of treatment of dioxolanes 19e at -30 °C. The propanone **28** (47 mg; 30%) and the chlorohydrin **30** (127 mg; 66%) were isolated.

Products of treatment of dioxolanes 19e at 0 °C. The propanone **28** (126 mg; 80%) and the chlorohydrin **30** (31 mg; 16%) were isolated.

Products of treatment of dioxolanes (20e) at -78 °C. 5,6,7-Trimethoxy-1,3-dimethyl-1*H*-2-benzopyrene 33 (6 mg; 3%); an olive- colored oil. IR (NaCl, film): ν_{max} = 1606 (C=C) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 6.6 Hz, 3H, 1-CH_3), 1.93 (s, 3H, 3-CH_3), 3.84, 3.85 (x2) (s, 9H, OCH_3), 5.10 (q, *J* = 6.6 Hz, 1H, 1-H), 5.80 (s, 1H, 4-H), 6.37 (s, 1H, 8-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 19.9 (C1-CH_3), 21.2 (C3-CH_3), 56.2, 57.8, 61.1 (OCH_3), 65.5 (C-

1), 93.7 (C-4)[a], 94.6 (C-8)[a], 112.3 (C-4a)[b], 125.0 (C-8a)[b], 136.3 (C-3), 150.2 (C-5)[c], 152.3 (C-6)[c], 152.5 (C-7)[c]. MS (EI 70 eV): *m/z*(%) = 250 (34) $[M]^+$, 235 (100), 191 (27), 174 15). Anal. Calcd for $C_{14}H_{18}O_4$ (250.3): C, 67.2; H, 7.25. Found C, 67.4; H, 7.0%.

1-(2′,3′,4′-Trimethoxyphenyl)-2-propanone 34 (25 mg; 15%); yellow crystals, m.p. 161-162 ^oC (from hexane). IR (Nujol mull): ν_{max} = 1717 (C=O) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 2.16 (s, 3H, 3-H), 3.61 (s, 2H, 1-H), 3.82, 3.83, 3.84 (s, 9H, OCH_3), 6.61 (d, *J* = 8.6 Hz, 1H, 5'-H), 6.79 (d, *J* = 8.6 Hz, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 29.3 (C-3), 45.1 (C-1), 56.1, 60.6, 60.7 (OCH_3), 107.5 (C-5'), 121.0 (C-1'), 124.9 (C-6'), 142.3 (C-2')[a], 151.9 (C-3')[a], 153.2 (C-4')[a], 206.9 (C=O. MS (EI 70 eV): *m/z* (%) = 224 (31) $[M]^+$, 181 (100), 166 (90). Anal. Calcd for $C_{12}H_{16}O_4$ (224.3): C, 64.3; H, 7.2. Found C, 64.1; H, 7.3%.

2-Hydroxy-1-methoxy-(2′,3′,4′-trimethoxyphenyl)propane 35 (116 mg; 60%), as a light olive-colored oil. IR (NaCl, film): ν_{max} = 3590 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.2 Hz, 3H, 3-H), 3.19 (s, 3H, 1-OCH_3), 3.48(x2), 3.87 (s, 9H, OCH_3), 3.85 (m, 1H, 2-H), 4.25 (d, *J* = 8.0 Hz, 1H, 1-H), 6.67 (d, *J* = 8.8 Hz, 1H, 5'-H), 6.93 (d, *J* = 8.8 Hz, 1H, 6'-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 18.0 (C-3), 56.6, 56.7, 60.8, 61.0 (OCH_3), 71.4 (C-2), 82.7 (C-1), 107.7 (C-5'), 122.1 (C-1'), 124.4 (C-6'), 142.0 (C-2')[a], 152.8 (C-3')[a], 153.4 (C-4')[a] . MS (EI 70 eV): *m/z* (%) = 256 (0.6) $[M]^+$, 224 (50), 211 (100), 181 (23), 166 (29). Anal. Calcd for $C_{13}H_{20}O_5$ (256.3): C, 60.9; H, 7.9. Found: C, 60.8; H, 7.6%.

1-Chloro-2-hydroxy-(2′,3′,4′-trimethoxyphenyl)propane 36 (29 mg; 15%), as an oil. IR (NaCl, film): ν_{max} = 3495 (OH) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 1.08 (d, 6.6 Hz, 3H, 3-H), 2.50 (bs, 1H, 2-OH), 3.56, 3.57, 3.66 (s, 9H, OCH_3), 3.62 (dq, *J* = 6.6 and 7.2 Hz, 1H, 2-H), 3.64 (d, *J* = 7.2 Hz, 1H, 1-H), 6.38 (d, *J* = 8.4 Hz, 1H, 5'-H), 6.69 (d, *J* = 8.4 Hz, 1H, 6'-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 18.9 (C-3), 55.9, 60.7, 61.2 (OCH_3), 71.2 (C-2), 75.6 (C-1), 107.4 (C-5'), 122.6 (C-6'), 126.5(C-1'), 142.0 (C-2')[a], 151.5 (C-3')[a], 153.5 (C-4'). MS (EI 70 eV): *m/z* (%) = 262 (8) $[M]^+$ for ^{37}Cl, 260 (23) $[M]^+$ for ^{35}Cl, 216 (50), 201 (100). Anal. Calcd for $C_{12}H_{17}ClO_4$ (260.7): C, 55.3; H, 6.6. Found: C, 55.2; C, 6.3%.

Products of treatment of dioxolanes (20e) at -30 ^oC. The benzopyrene **33** (8 mg; 4%), the propanone **34** (30 mg; 18%), the methoxypropanol **35** (40 mg; 21%) and the chloropropanol **36** (107 mg; 55%) were isolated.

Products of treatment of dioxolanes (20e) at 0 ^oC. The benzopyrene **33** (15 mg; 8%), the propanone **34** (85 mg; 51%), the methoxypropanol **35** (25 mg; 13%) and the chloropropanol **36** (48 mg; 25%) were isolated.

Products of treatment of dioxolanes (21e) at -78 ^oC. 1-(2′,4′,5′-Trimethoxyphenyl)-2-propanone 37 (108 mg; 64%); yellow needles, m.p. 191-192 ^oC (from hexane). IR (Nujol mull): ν_{max} = 1714 (C=O) cm^{-1}. ^1H- NMR (200 MHz, $CDCl_3$): δ = 2.13 (s, 3H, 3-H), 3.61 (s, 2H, 1-H), 3.79, 3.82, 3.89 (s, 9H, OCH_3), 6.54 (s, 1H, 3'-H), 6.66 (s, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 29.1 (C-3), 44.9 (C-1), 56.3, 56.4, 56.7 (OCH_3), 97.9 (C-3'), 114.9 (C-1')[a], 115.0

(C-6')[a], 143.2 (C-2')[b], 149.0 (C-4')[b], 151.7 (C-5')[b], 207.4 (C=O). MS (EI 70 eV): *m/z* (%) = 224 (2) $[M]^+$, 181 (100), 151 (36). Anal. Calcd for $C_{12}H_{16}O_4$ (224.3): C, 64.3; H, 7.2. Found C, 64.1; H, 7.3%. **1-Chloro-2-hydroxy-1-(2′,4′,5′-trimethoxyphenyl)propane (39)** (66 mg; 34%); a light yellow oil. IR (NaCl, film): ν_{max} = 3584 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.2 Hz, 3H, 3-H), 1.60 (bs, 1H, 2-OH), 3.83, 3.85, 3.89 (s, 9H, OCH_3), 3.90 (m, 1H, 2-H), 4.54 (d, *J* = 6.6 Hz, 1H, 1-H), 6.52 (s, 1H, 3'-H), 6.84 (s, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-3), 56.3 (X2), 56.7 (OCH_3), 71.3 (C-2), 75.8 (C-1), 97.6 (C-3'), 112.3 (C-6'), 114.1 (C-1'), 143.3 (C-2')[a], 149.3 (C-4')[a], 151.2 (C-5'). MS (EI 70 eV): *m/z* (%) = 242 (24) $[M-18]^+$, 197 (100), 183 (33), 169 (77), 154 (43), 138 (34). Anal. Calcd for $C_{12}H_{17}ClO_4$ (260.7): C, 53.6; H, 6.6. Found C, 55.5; H, 6.7%.

Products of treatment of dioxolanes (21e) at -30 °C. The propanone **(37)** (112 mg; 67%) and the chloropropane **39** (58 mg; 29%) were isolated

Products of treatment of dioxolanes (21e) at 0 °C. The propanone **(37)** (120 mg; 72%), and **2-hydroxy-1-methoxy-1-(2′,4′,5′-trimethoxyphenyl)propane (38)** (48 mg; 25%) were obtained as yellow needles, m.p. 193-194 °C (from hexane). IR (Nujol mull): ν_{max} = 3536 (OH) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.2 Hz, 3H, 3-H), 1.70 (bs, 1H, 2-OH), 3.22 (s, 3H, 1-OCH_3), 3.80, 3.82, 3.89 (s, 9H, OCH_3), 3.85 (m, 1H, 2-H), 4.40 (d, *J* = 7.8 Hz, 1H, 1-H), 6.52 (s, 1H, 3'-H), 6.81 (s, 1H, 6'-H). MS (EI 70 eV): *m/z* (%) = 256 (0.5) $[M]^+$, 211 (100), 181 (23), 166 (29). Anal. Calcd for $C_{13}H_{20}O_5$ (256.3): C, 60.9; H, 7.9. Found C, 60.7; H, 7.6%. Due to decomposition of the molecule a ^{13}C- spectrum could not be obtained and thus the compound **38** was converted into the corresponding acetate with acetic anhydride and pyridine to give **2-acetoxy-1-methoxy-1-(2′,4′,5′-trimethoxyphenyl)propane** as an oil in 70% yield. IR (NaCl, film): ν_{max} = 1734 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 6.6 Hz, 3H, 3-H), 2.03 (s, 3H, $COCH_3$), 3.26 (s, 3H, 1-OCH_3), 3.76(X2), 3.82 (s, 9H, OCH_3), 4.63 (d, *J* = 5.4 Hz, 1H, 1-H), 5.10 (dq, *J* = 5.4 and 6.6 Hz, 1H, 2-H), 6.50 (s, 1H, 3'-H), 6.66 (s, 1H, 6'-H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 16.3 (C-3), 21.2 ($COCH_3$), 56.2, 56.4, 57.5 (OCH_3), 72.6 (C-2), 78.6 (C-1), 111.1 (C-3'), 115.0 (C-6'), 125.3 (C-1'), 146.7 (C-2')[a], 157.1 (C-4')[a], 158.2 (C-5')[a], 165.8 (C=O). MS (EI 70 eV): *m/z* (%) = 298 (3) $[M]^+$, 211 (100), 181 (18), 151 (14). Anal. Calcd for $C_{15}H_{22}O_6$ (298.3): C, 60.4; H, 7.4. Found C, 60.6; H, 7.2%. The final product of elution was the propane **39** (4 mg; 2%).

Products of treatment of dioxolanes (22h) at -78 °C. *rel*-(1*S*,3*R*,4*R*)-4-Hydroxy-5,6,8-trimethoxy-1,3-dimethyl-2-benzopyran (40) (120 mg; 60%) was obtained as a light yellow oil. IR (NaCl, film): ν_{max} = 3550 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 6.6 Hz, 3H, 3-CH_3), 1.55 (d, *J* = 6.2 Hz, 3H, 1-CH_3), 2.15 (bs, 1H, 4-OH), 3.63 (dq, *J* = 6.6 and 1.0 Hz, 1H, 3-H), 3.80, 3.88, 3.89 (s, 9H, OCH_3), 4.57 (d, *J* = 1.0 Hz, 1H, 4-H), 4.86 (q, *J* = 6.2 Hz, 1H, 1-H), 6.48 (s, 1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 17.1 (C3-CH_3), 22.2 (C1-CH_3), 55.6, 56.3, 62.0 (OCH_3), 63.8 (C-3), 71.0 (C-1), 72.4 (C-4), 97.6 (C-7), 120.0 (C-4a)[a], 132.2 (C-8a)[a],

140.9 (C-5)[b], 151.6 (C-6)[b], 152.4 (C-8)[b]. MS (EI 70 eV): *m/z*(%) = 268 (24) $[M]^+$, 253 (100), 235 (23), 225 (22), 209 (35), 194 (41). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H, 7.5. Found C, 63.0; 7.3%. **1-Chloro-2-hydroxy-1-(2′,3′,5′-trimethoxyphenyl)propane (44)** (68 mg; 35%) was isolated as an olive colored oil. IR (NaCl, film): ν_{max} = 3600 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.6 Hz, 3H, 3-H), 3.82, 3.85, 3.87 (s, 9H, OCH_3), 4.15 (m, 1H, 2-H), 5.23 (d, *J* = 7.6 Hz, 1H, 1-H), 6.46 (d, *J* = 3.0 Hz, 1H, 4'-H), 6.51 (d, *J* = 3.0 Hz, 1H, 6'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.9 (C-3), 55.7, 55.8, 61.2 (OCH_3), 71.8 (C-2), 75.2 (C-1), 100.0 (C-4'), 102.7 (C-6'), 134.6 (C-1'), 140.9 (C-2')[a], 153.4 (C-3')[a], 156.3 (C-5')[a]. MS (EI 70 eV): *m/z*(%) = 261 (8) $[M]^+$ for ^{37}Cl, 259 (25) $[M]^+$ for ^{35}Cl, 216 (50), 201 (100), 173 (25). Anal. Calcd for $C_{12}H_{17}ClO_4$ (260.7): C, 55.3; H, 6.6. Found C, 55.2; H, 6.7%.

Products of treatment of dioxolanes 22h at -30 °C. The **benzopyran 40** (100 mg; 50%) and **2′,3′,5′-Trimethoxy-1,3 dimethyl-1*H*-2-benzopyrene, 41,** (40 mg; 21%) were given as white needles m.p. 73-75 °C (from hexane). IR (Nujol mull): ν_{max} = 1612 (C=C) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 6.6 Hz, 3H, 1-CH_3), 1.92 (s, 3H, 3-CH_3), 3.74, 3.79, 3.85 (s, 9H, OCH_3), 5.56 (q, *J* = 6.6 Hz, 1H, 1-H), 5.79 (s, 1H, 4-H), 6.28 (s, 1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 19.8 (C1-CH_3), 20.7 (C3-CH_3), 55.8, 56.2, 61.1 (OCH_3), 69.5 (C-1), 93.7 (C-7)[a], 94.6 (C-4)[a], 112.2 (C-4a)[b], 125.0 (C-8a)[b], 136.3 (C-3), 150.6 (C-5)[c], 152.3 (C-6)[c], 152.7 (C-8)[c]. MS (EI 70 eV): *m/z*(%) = 250 (26) $[M]^+$, 235 (100), 220 (11), 205 (14), 191 (13). Anal. Calcd for $C_{14}H_{18}O_4$ (250.3): C, 67.2; H, 7.25. Found C, 67.0; H, 7.4%. The final product of elution was the **substituted propane 44** (45 mg; 23%).

Products of treatment of dioxolanes 22h at 0 °C. The substituted benzopyran 40 (6 mg; 3%), the **benzopyrene 41** (50 mg; 27%), and **2-(6′-ethyl-2′,3′,5′-trimethoxyphenyl)propanone 43** (40 mg; 21%) was obtained as a light yellow oil. IR (NaCl, film): ν_{max} = 1718 (C=O) cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.4 Hz, 3H, 2"-H), 2.18 (s, 3H, 3-H), 2.50 (q, *J* = 7.4 Hz, 1H, 1"-H), 3.72, 3.81, 3.87 (s, 9H, OCH_3), 3.77 (s, 2H, 1-H), 6.44 (s, 1H, 4'-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 14.4 (C-2"), 19.7 (C-3), 29.8 (C-1"), 42.1 (C-1), 56.0(X2), 60.6 (OCH_3), 96.7 (C-4'), 139.3 (C-6'), 142.4 (C-1'), 150.8 (C-2')[a], 153.9 (C-3')[a], 154.1 (C-5'), 207.6 (C=O). MS (EI 70 eV): *m/z* (%) = 252 (51) $[M]^+$, 237 (18), 209 (25), 195 (100), 180 (32). Anal. Calcd for $C_{14}H_{20}O_4$ (252.3): C, 66.65; H, 8.0. Found, C, 66.5; H, 8.0%, ***rel*-(1*R*,1′*S*,3*S*)- and *rel*-(1*R*,1′*S*,3*R*)-1-(1′-Hydroxyethyl)-4,6,7-trimethoxy-3-methyl-1,3-dihydroisobenzofurans (42)** (90 mg; 45%) was isolated as a 1:1 mixture; a pale yellow oil. IR (NaCl, film): ν_{max} = 3500 (OH) cm^{-1}. ^{1}H- NMR for the *trans*- isomer (200 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.2 Hz, 3H, 2'-H), 1.46 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 3.81, 3.88, 3.89 (s, 9H, OCH_3), 3.63 (m, 1H, 1'-H), 5.11 (dd, *J* = 6.6 and 2.8 Hz, 1H, 1-H), 5.35 (dq, *J* = 6.2 and 2.8 Hz, 1H, 3-H), 6.42 (s, 1H, 5-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C-2'), 22.1 (C3-CH_3), 55.8, 56.7, 60.9 (OCH_3), 70.7 (C-1'), 79.1 (C-1)[a], 86.4 (C-3)[a], 97.6 (C-5), 121.3 (C-7a)[b], 134.1 (C-3a)[b], 150.4 (C-4)[c], 150.5 (C-6)[c], 153.0 (C-7)[c]. MS (EI 70 eV): *m/z* (%) = 268 (7) $[M]^+$, 253 (8), 223 (100), 208 (38), 193 (15). Anal. Calcd for

$C_{14}H_{20}O_5$ (268.3): C, 62.7; H, 7.5. Found C, 62.6; H, 7.3%. The final product of elution was the substituted **propanol (44)** (5mg; 3%).

Products of treatment of the pure dioxolane (22f) at –78 °C. *rel*-(1*R*, 3*R*,4*S*)-4-Hydroxy-5,6,8-trimethoxy-1,3-dimethyl-2-benzopyran (47) (188 mg; 94%) as a colorless oil. IR (NaCl, film): ν_{max} = 3600 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 1.51 (d, *J* = 6.6 Hz, 3H, 1-CH_3), 3.80. 3.86, 3.87 (s, 9H, OCH_3), 3.94 (dq, *J* = 8.0 and 6.2 Hz, 1H, 3-H), 4.12 (s, 1H, 4-OH), 4.55 (dq, *J* = 6.6 and 1.0 Hz, 1H, 1-H), 4.95 (dd, *J* = 8.0 and 1.0 Hz, 1H, 4-H), 6.42 (s, 1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.8 (C3-CH_3), 19.2 (C1-CH_3), 55.7, 56.3, 61.0 (OCH_3), 67.7 (C-3)[a], 67.9 (C-1)[a], 69.0 (C-4)[a], 96.6 (C-7), 121.0 (C-4a)[b], 130.7 (C-8a)[b], 141.2 (C-5)[c], 151.3 (C-6)[c], 151.6 (C-8)[c]. MS (EI 70 eV): *m/z*(%) = 268 (31) $[M]^+$, 253 (100), 235 (27), 225 (23), 209 (36), 194 (50). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H, 7.5. Found C, 62.6; H, 7.4%. The final product of elution was **the propanol 44** (6 mg; 3%).

Products of treatment of pure dioxolane 22f at -30 °C. The benzopyrene **(41)** (20 mg; 11%), the hydroxybenzopyran **(47)** (80 mg; 40%), the **benzofurans (42)** (60 mg; 30%) were obtained as a 1:1 mixture and the **propanol (44)** (25 mg; 13%).

Products of treatment of pure dioxolane (22f) at 0 °C. The benzopyrene **(41)** (51 mg; 27%), the hydroxybenzopyran **(47)** (60 mg; 30%), the benzofurans **(42)** (90 mg; 45%) were followed by ***rel*-(1*S*, 3*R*,4*S*)-4-hydroxy-5,6,8-trimethoxy-1,3-dimethyl-2-benzopyran (48)** (10 mg; 5%) as a light yellow oil. IR (NaCl, film): ν_{max} = 3600 (OH) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.44 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 1.50 (d, *J* = 6.2 Hz, 3H, 1-CH_3), 3.43 (dq, *J* = 8.4 and 6.2 Hz, 1H. 3-H), 3.79, 3.88(X2) (s, 9H, OCH_3), 4.58 (dd, *J* = 8.4 and 1.2 Hz, 1H, 4-H), 4.62 (s, 1H, 4-OH), 4.84 (dq, *J* = 6.2 and 1.2 Hz, 1H, 1-H), 6.44 (s, 1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.7 (C3-CH_3), 21.9 (C1-CH_3), 55.7, 56.2, 61.2 (OCH_3), 70.0 (C-1)[a], 71.2 (C-3)[a], 73.7 (C-4)[a], 96.7 (C-7), 121.4 (C-4a)[b], 133.9 (C-8a)[b], 140.8 (C-5)[c], 151.2 (C-6)[c], 152.5 (C-8)[c]. MS (EI 70 eV): *m/z*(%) = 268 (24) $[M]^+$, 253 (100), 235 (23), 225 (22), 209 (35), 194 (41). Anal. Calcd for $C_{14}H_{20}O_5$ (268.3): C, 62.7; H, 7.5. Found C, 62.5; H, 7.7%. The final product was the substituted propanol **44** (6mg; 3%).

Cerium(IV) ammonium nitrate oxidations

***rel*-(1*R*,3*R*,4*S*)-4-Hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran-5,8-dione (49) and r*el*-(1*R*,3*R*,4*S*)-4-Hydroxy-8-methoxy-1,3-dimethyl-2-benzopyran-5,6-dione (50).** To an aqueous solution of the benzopyran **47** (40 mg; 0.15 mmol) in acetonitrile (15 mL) and water (2 mL) was added dropwise cerium(IV)ammonium nitrate (215 mg; 0.39 mmol) in water (1 mL) and after stirring at 25 °C for 20 min, water (100 mL) was added and the solution was extracted with dichloromethane. The residue obtained after workup was chromatographed using EtOAc: hexane (2:3) as eluent to afford the *p*-quinone **49** (15 mg; 42%) as yellow needles, m.p. 122-123 °C (from hexane). IR (Nujol mull): ν_{max} = 3400 (OH) and 1668 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz,

$CDCl_3$): δ = 1.35 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 1.51 (d, *J* = 6.6 Hz, 3H, 1-CH_3), 3.40 (s, 1H, 4-OH), 3.82 (s, 3H, OCH_3), 3.82 (m, 1H, 3-H), 4.35 (dd, *J* = 7.8 and 1.0 Hz, 1H, 4-H), 4.76 (dq, *J* = 6.6 and 1.0 Hz, 1H, 1-H), 5.88 (s, 1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 18.4 (C3-CH_3), 20.9 (C1-CH_3), 56.8 (OCH_3), 67.7 (C-3)[a], 70.3 (C-1)[a], 73.1 (C-4)[a], 108.1 (C-7), 138.7 (C-4a)[b], 146.2 (C-8a)[b], 158.2 (C-6), 183.2 (C=O), 186.4 (C=O). MS (EI 70 eV): *m/z* (%) = 238 (1) $[M]^+$, 194 (84), 166 (100), 151 (94). Anal. Calcd for $C_{12}H_{14}O_5$ (238.2): C, 60.5; H, 5.9. Found C, 60.7; H, 5.7%. The next compound to elute was the *o*-quinone **50** (10 mg; 28%) as a red oil. IR (NaCl, film): ν_{max} = 3560 (OH) and 1766 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 1.57 (d, *J* = 6.6 Hz, 3H, 1-CH_3), 1.70 (bs, 1H, 4-OH), 3.80 (m, 1H, 3-H), 3.98 (s, 3H, OCH_3), 4.31 (dd, *J* = 7.2 and 1.0 Hz, 1H, 4-H), 4.78 (dq, *J* = 7.4 and 1.0 Hz, 1H, 1-H), 5.78 (s, 1H, 7-H). HR-EIMS: *m/z* = 238.0836 (Calcd for $C_{12}H_{14}O_5$, 238.0841).

***rel*-(1*S*,3*R*,4*S*)-4-Hydroxy-6-methoxy-1,3-dimethyl-2-benzopyran-5,8-dione (51) and r*el*-(1*S*,3*R*,4*S*)-4-Hydroxy-8-methoxy-1,3-dimethyl-2-benzopyran-5,6-dione (52).** Treatment of the benzopyran **40** (40 mg; 0.15 mmol) as above gave the *p*-quinone **51** (18 mg; 51%) as a yellow oil. IR (NaCl, film): ν_{max} = 3595 (OH) and 1658 (C=O) cm^{-1}. ^{1}H- NMR (200 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 6.6 Hz, 3H, 3-CH_3), 1.52 (d, *J* = 7.0 Hz, 3H, 1-CH_3), 2.20 (bs, 1H, 4-OH), 3.55 (dq, *J* = 6.6 and 1.4 Hz, 1H, 3-H), 3.82 (s, 3H, OCH_3), 4.40 (d, *J* = 1.4 Hz, 1H, 4-H), 4.65 (dq, *J* = 7.0 and 1.4 Hz, 1H, 1-H), 5.89 (s,1H, 7-H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ = 16.2 (C3-CH_3), 21.1 (C1-CH_3), 56.4 (OCH_3), 61.7 (C-3)[a], 70.2 (C-1)[a], 72.4 (C-4)[a], 108.2 (C-7), 138.7 (C-4a)[b], 145.9 (C-8a)[b], 158.5 (C-6), 180.9 C=O), 186.7 (C=O). MS (EI 70 eV): *m/z* (%) = 238 (1) $[M]^+$, 194 (86), 166 (100), 151 (93), 133 (10).. Anal. Calcd for $C_{12}H_{14}O_5$ (238.2): C, 60.5; H, 5.9. Found C, 60.2; H, 6.2%. The next compound to elute was the *o*-quinone **52** (6 mg; 17%) as a red oil. IR (NaCl, film): ν_{max} = 3560 (OH) and 1766 (C=O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 6.2 Hz, 3H, 3-CH_3), 1.57 (d, *J* = 7.4 Hz, 3H, 1-CH_3), 1.70 (bs, 1H, 4-OH), 3.48 (m, 1H, 3-H), 3.98 (s, 3H, OCH_3), 4.31 (d, *J* = 1.0 Hz, 1H, 4-H), 4.78 (dq, *J* = 7.4 and 1.0 Hz, 1H, 1-H), 5.78 (s, 1H, 7-H). HREIMS: *m/z* = 238.0834. (Calcd for $C_{12}H_{14}O_5$, 238.0841).

Acknowledgements

We thank the National Research Foundation for providing a bursary to N.O.

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