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The Synthesis of 8a-Methoxy-*2H,6H*-Chromen-6-ones and corresponding *2H*-Chromenes by a Unique Process utilising Phenolic Oxidation

By Andrew Pelter,*† Amjad Hussain, Gareth Smith and Robert S. Ward*

Chemistry Department, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK

Abstract: (*Z*)-1-Hydroxy-3-(3′-hydroxyphenyl)prop-2-enes undergo phenolic oxidation by phenyliodonium diacetate (PIDA) in methanol to give 8a-methoxy-*2H,6H*-dihydrochromen-6-ones. These are reduced by DIBAL-H to 2-substituted-$\Delta^{3,4}$-chromenes, the overall process being a unique heterocyclic synthesis in which the heteroatom is not initially attached to a benzene ring, but is introduced from a side chain. Parallel oxidations using *cis*-1-hydroxy-3-(3′-hydroxyphenyl)prop-2,3-oxiranes have also been achieved despite the presence of the sensitive oxirane ring.

INTRODUCTION

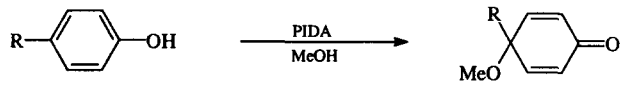
We have recently described oxidations of phenols that have all the characteristics of 2-electron oxidations and proposed general equations that could be used to rationalise the initiation of such oxidations.[1,2] Two of these (equations 1,2) are given below.

$$\text{ArOH} \longrightarrow \text{Ar-O-}\overset{(+)}{\text{X}} \longrightarrow \underset{\mathbf{1}}{\overset{(+)}{\text{ArO}}} + \text{X} \qquad (1)$$

$$\text{ArOH} \longrightarrow \text{ArOX(N)} \longrightarrow \mathbf{1} + \text{X(N-2)} \qquad (2)$$

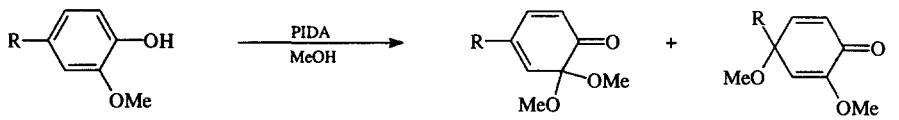
To exemplify equation 1 we used X = SMe_2 and SPh_2 and explored the advantages and limitations of each series, the latter being both new and especially useful. We paid particular attention to equation 2 in which X = I, the driving force for the oxidation being the transformation of trivalent iodine to monovalent iodine.[3-5] For this purpose we explored a variety of reagents and found that phenyliodonium diacetate ($PhI(OAc)_2$, PIDA) was particularly appropriate and that the closely related phenyliodonium bis(trifluoroacetate)($PhI(OCOCF_3)_2$, PIFA) could also be utilised. These compounds have distinct environmental advantages over reagents such as $Pb(OAc)_4$[6,7] or thallium (III) nitrate[8] as the by-products are only acetic acid and iodobenzene, the latter being readily recycled.[3-5] The intermolecular reactions we explored are shown in equations 3 and 4.

†Dedicated to Arthur Birch, friend, colleague and creative chemist.



(3)

(R= alkyl, alkoxy, bromine)



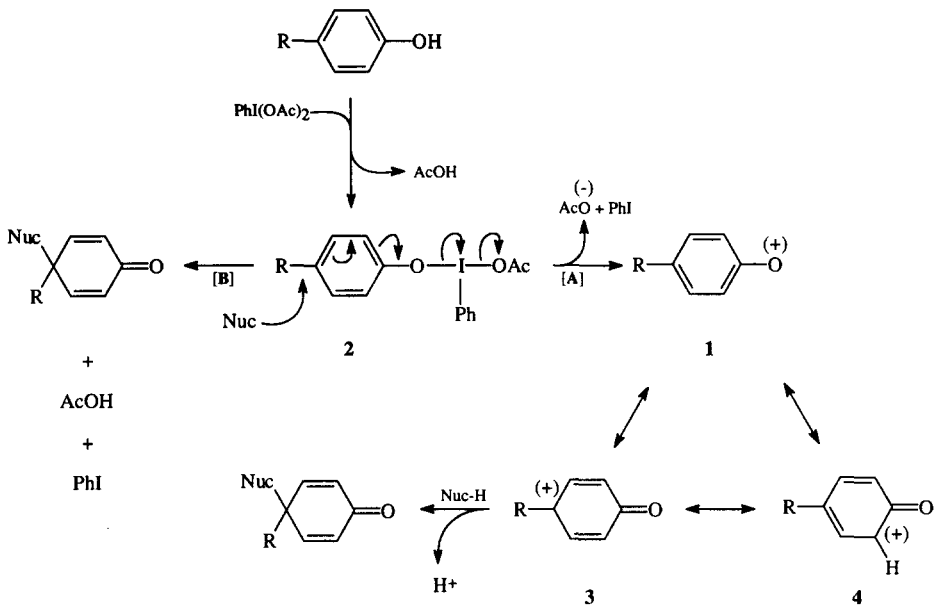
(4)

(R= alkyl)

The products may be formed either by routes A or B (Scheme 1). Route A involves the production of discrete (solvated) phenoxenium ions **1** (**3**, **4**) whilst route B involves direct displacement from undissociated intermediates **2**. The results of our experiments strongly favour route A, and are in line with extensive MOPAC calculations (to be published separately) that we have carried out on substituted phenoxenium ions, the electron distribution of which accords very well with the point of attack by nucleophiles. Thus when the phenol has a C-2 substituent such as an alkoxy group which is capable of stabilising a positive charge then attack occurs at C-2, regardless of the steric situation which would favour attack at C-4 or C-6. On the other hand, in phenols lacking such a substituent, calculation indicates that **3** most accurately reflects the species present and nucleophilic attack is predominantly or exclusively at C-4. Previous calculations[9] on **3** (R=H) at the STO-3G and 4-31G levels strongly support our conclusions. The calculated C-O bond length for **3** (R=H) is 1.241Å, close to that calculated for acetone and the ring charge increased by +1.002, most being at C-4 with little charge at oxygen.

The electrochemical oxidation of phenols can unequivocally yield phenoxenium ions,[10,11] and the chemical behaviour of the species so generated are completely in accord with the results of our PIDA oxidations. Attack by O-, N- and C-nucleophiles all proceed to give predominantly 4-substituted cyclohexa-2,5-dienones,[11] except when the phenol has a 2-methoxy group in which case *ortho*-substitution predominates. There is a similar situation for arylnitrenium ions for which the conclusion has been reached that an 'arylnitrenium ion is perhaps better viewed as a cyclohexadienyl cation bearing an imine substituent'.[12] Others studying PIDA oxidations of phenols have reached similar conclusions.[13,14]

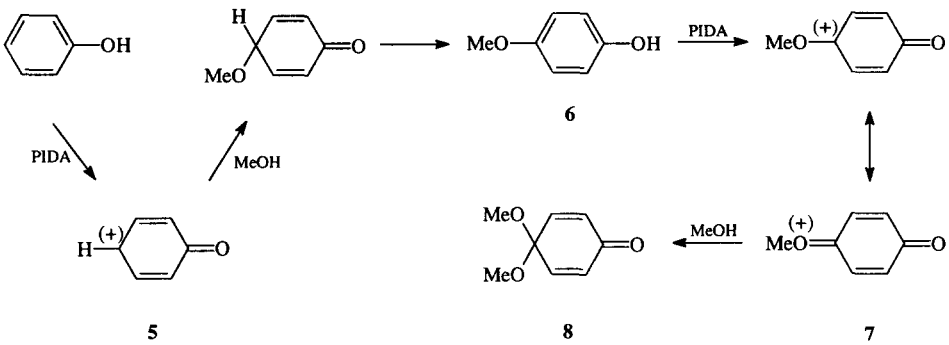
It should be noted that the oxidative reactions described are high yielding methods for the transformation of benzenoid substrates into highly functionalised cyclohexane derivatives. As such they are the oxidative analogues to the Birch reduction, which *via* anions or anion radicals does the same thing.[15] They have therefore similar potential in organic synthesis.



Scheme 1

We shall, in this paper, use the simple symbolism of path A, with due regard to its limitations.

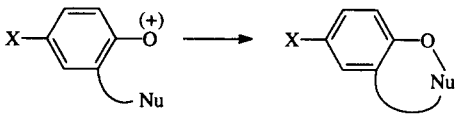
We draw particular attention to the oxidation of phenol itself,[2] which we were unable to stop at 4-methoxyphenol **6** but which gave 4,4-dimethoxycyclohexa-2,5-dienone **8** even when only one equivalent of PIDA was used (Scheme 2).



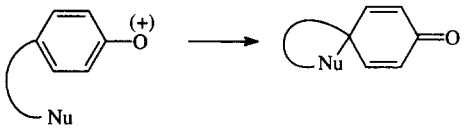
Scheme 2

This result is to be expected as the phenoxenium intermediate **7** would be stabilised by a factor of at least 2000 with respect to phenoxenium ion **5**.[12]

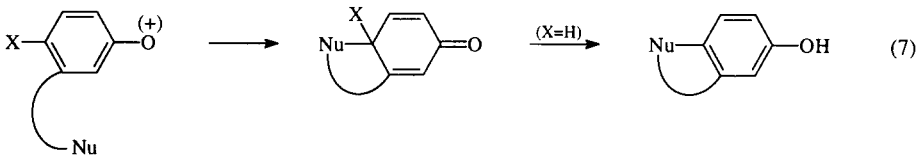
In view of the above we decided to examine *intramolecular* nucleophilic attack upon phenoxenium ions, with a view to introducing novel cyclisation reactions. Some of our general reactions are shown in equations 5-7.



(5)

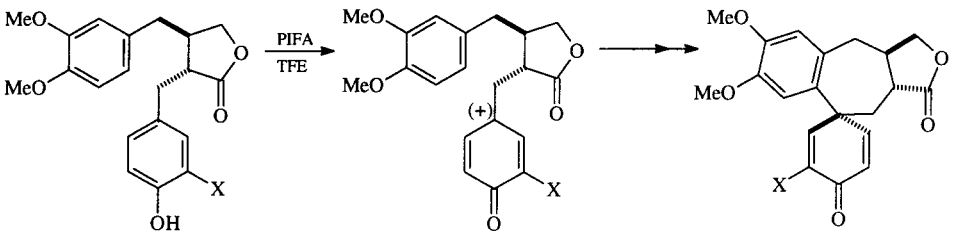


(6)



(7)

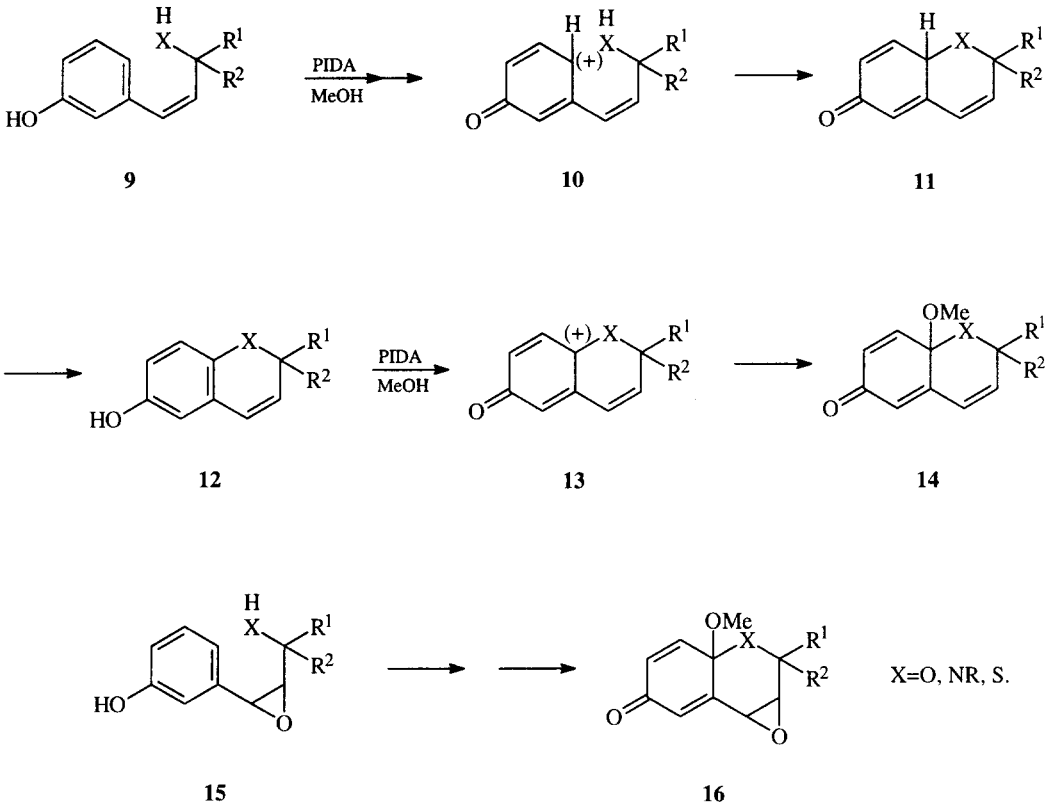
We have provided examples of equation 6, one of which is shown in equation 8.[16,17]



(8)

In this case the nucleophile is an activated benzene ring attached by a four carbon chain to the 4-position of the phenol being oxidised. It is important to note that when the four carbon linker was unsubstituted, oxidation occurred without cyclisation to give 4-methoxycyclohexa-2,5-dienones. *The rigidity conferred by the* trans-*butyrolactone substituent was essential to obtain good yields of spirodienones.*

With this background we turned to equation 7, with the linker in the *meta* position to the phenolic hydroxy group. This paper details results when the nucleophile is an hydroxyl group linked by a three carbon chain to which some rigidity had been imparted either by incorporation of *Z*-alkenyl group or by a *cis*-oxiranyl group. Our expectations are summarised in Scheme 3.

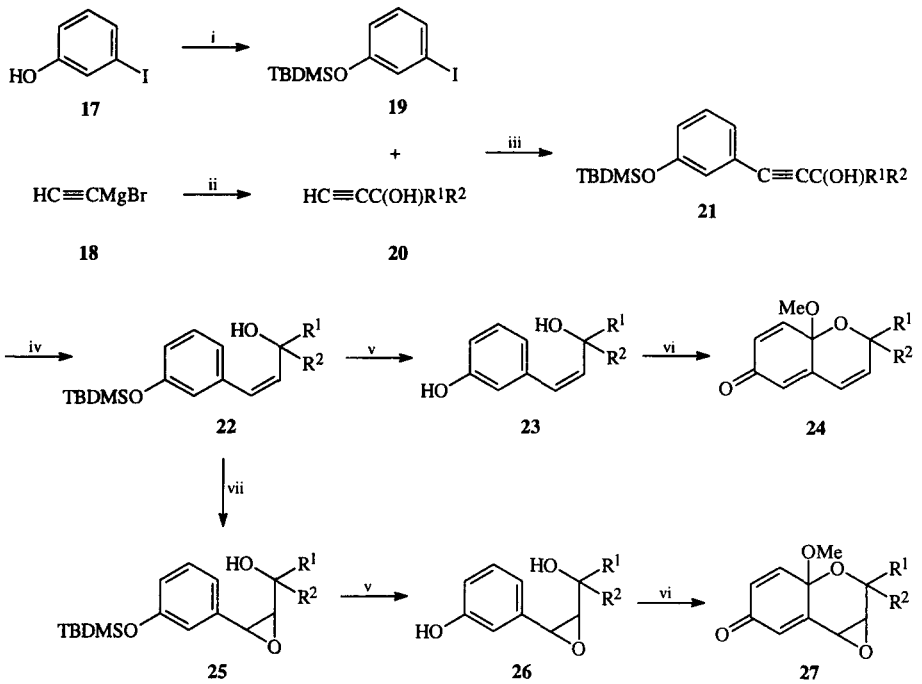


Scheme 3

Oxidation of **9** with PIDA should give rise to phenoxenium ion **10** which could undergo cyclisation to **11** which would then isomerise to **12**. In turn **12** would give **13**, which would be a highly favoured process (Scheme 2) as compared with the production of **10**. Attack by methanol would yield the unusual products **14**. From **15** a similar set of reactions would yield the highly functionalised products **16**, which could be homochiral if derived from homochiral **15**. Scheme 3 outlines the possibility of producing oxygen, nitrogen and sulfur heterocycles in a unique fashion, in that the heterocyclic atom is not present on the benzene ring of the precursors, but is introduced from an external source.

RESULTS AND DISCUSSION

In the first instance we decided to examine Scheme 3 with X = OH, with the idea of producing chromene derivatives. The processes used are shown in Scheme 4.



(a) $R^1 = R^2 = Me$; (b) $R^1, R^2 = -(CH_2)_5-$; (c) $R^1 = Me, R^2 = Ph$; (d) $R^1 = R^2 = Ph$; (e) $R^1 = Ph, R^2 = H$; (f) $R^1 = C_{11}H_{17}; R^2 = Me$;

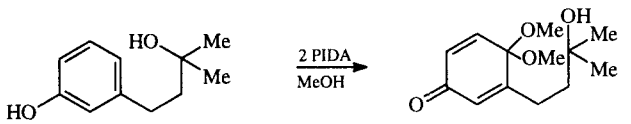
(i) $Me_2BuᵗSiCl$, imidazole; (ii) R^1R^2CO; (iii) $PdCl_2(PPh_3)_2$, CuI, Pri_2NH;
(iv) H_2, Lindlar catalyst or $TiCp_2Cl_2$, $BuⁱMgCl$;(v) CsF, MeOH; (vi) 2xPIDA, MeOH; (vii) MCPBA;

Scheme 4

Compound **19** was readily available from commercially available **17** and compounds **20** were produced from commercially available solutions of **18**. Palladium/copper salt induced condensations[18] of **19** and **20** gave alcohols **21**, reductions of which using Lindlar catalyst proved to be somewhat tedious and erratic. Despite rigorous purification of **21** after the coupling reactions, a minute amount of impurity always seemed to be present and this poisoned the catalyst so that three additions and stirring were frequently required before hydrogenation started. Moreover stopping the reaction before over-hydrogenation occurred required careful monitoring and even then some alkane was produced. Hydroboration with solid dicyclohexylborane followed by protonolysis[19] gave better results but the best results were obtained using titanocene dichloride and *iso*-butylmagnesium chloride[20,21] a process that is operationally simple and gave excellent yields in every case tried. Removal of the silicon protecting group was best done with caesium fluoride in solution in methanol which allowed a simpler work-up procedure than did the use of tetrabutylammonium fluoride. The epoxides **25** were prepared in racemic form by reaction of **22** with *meta*-chloroperbenzoic acid (MCPBA) and were transformed into precursors **26** by careful removal of the silicon protecting group. With both **23** and **26**

available it was now possible to check whether or not the oxidations conformed to our general ideas as set out in Scheme 3.

With one equivalent of PIDA in methanol the product from **23a** was **24a** plus unused **23a**, as expected. When two equivalents of PIDA were used then **24a** was isolated in 83% yield. Very interestingly when **28**, with a saturated C_3 linker was used, only the 4,4-dimethoxycyclohexa-2,5-dienone **29** was obtained, with no cyclisation at all (equation 9). This emphasises the need for some steric restriction in the linker unit. Nor could cyclisation be accomplished by the action of acid on **29**.



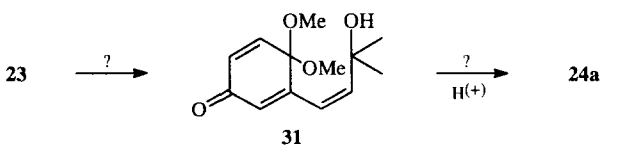
28 **29** (9)

Yields in the cases of **23b** (95%) and **23f** (69%) were reasonable but dropped somewhat with **23c** (57%), **23d** (56%) and more so with **23e** (25%). This may be due to competing benzylic carbocation formation either from **22** or an intermediate chromene. In the case of **23e**, there is also the possibility of oxidation of the alcohol group.

In Scheme 3 it is postulated that a chromene (**12**, X=O) is an intermediate on the way to the final cyclic quinone ketal (**14**). To check whether this was feasible the chromene **30** (*vide infra*) was mixed with an equivalent of PIDA under the same conditions as used for the oxidations of **23**. There was a rapid and quantitative reaction to give **24a** (equation 10).

30 **24a** (10)

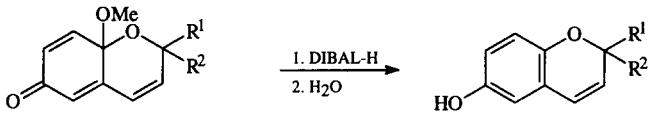
An alternative mode for the production of **24a** is *via* the quinone ketal **31**. We were never able to check this route due to our inability to produce **31** (equation 11).



31 (11)

However the successful reaction shown in equation 10 opens the way to rapid and unique oxidative modifications of a variety of natural products that, like chromenes, have interesting physiological properties.[22]

With compounds **24** available, we turned our attention to the production of the corresponding 2-substituted chromenes **32**. In practice, addition of one equivalent of di-*iso*-butylaluminium hydride (DIBAL-H) rapidly gave the required products in good to excellent yields (**32a**, 87%; **32b**, 65%; **32c**, 85%; **32d**, 88%; **32e**, 98%; **32f**, 82%) (equation 12).



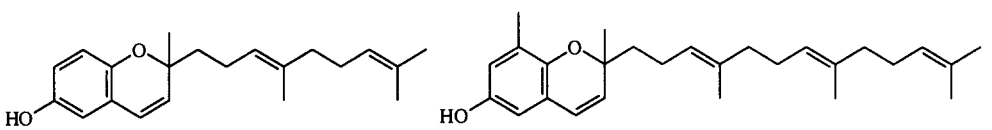
24 **32** (12)

A further point to note is that in the cases of **24c**, **24e** and **24f**, diastereoisomeric products were obtained.

24c, R^1 = Ph, R^2 = Me,	2	:	3
24e, R^1 = Ph, R^2 = H,	6	:	11
24f, $R^1 = C_{11}H_{17}$, R^2 = Me,	1	:	3

In the cases of **24c** and **24e** the 8a-methoxyl groups of the minor isomers give signals at the very high field values of δ2.57 and 2.70 respectively, compared with the major isomers at δ3.27 and 3.36. The diphenyl product, **24d** *must* have a C-2 phenyl group *syn* to the 8a-methoxyl group and in this compound the methoxyl signal is at δ2.51. The equivalent signals for **24a** and **24b** are at δ3.12 and 3.18 and therefore in both **24c** and **24e** the minor isomers have the methoxyl and phenyl groups *syn* to each other. The NOESY spectrum of the major isomer of **24f** indicates that the methyl group at C-2 is *syn* to the 8a-methoxyl. Therefore in all three cases the 8a-methoxyl is *trans* to the largest group at C-2 in the major isomer.

Product **32f** is very closely related to the cytotoxic meroterpenoid sargaol **33**,[23] and its facile synthesis by our route serves as a model for the synthesis of sargaol.

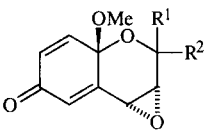


32f **33**

We next turned our attention to the PIDA oxidations of the epoxides **26**. These were of interest for several reasons. Firstly we wished to assess the effectiveness of the oxirane ring in providing the rigidity

required for the intramolecular cyclisation reaction. Secondly we were interested to find out whether the oxirane ring would withstand the reaction conditions for the PIDA oxidation. Thirdly we were attracted by the prospect of using a homochiral precursor in order to stereoselectively synthesise highly functionalised homochiral chromene derivatives.

Treatment of **26a** with two equivalents of PIDA in methanol gave a 4:1 mixture of the diastereoisomeric chromene derivatives **34a** and **35a** in 58% yield. Separation of the two isomers by column chromatography followed by examination of their NOESY spectra showed conclusively that the major isomer was **34a** in which the methoxyl group introduced at C-8a was *trans* to the oxirane ring. Thus a strong NOE interaction was observed between the hydrogens of the methoxyl group and the methine hydrogens of the oxirane.



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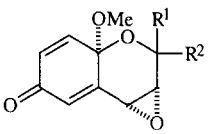
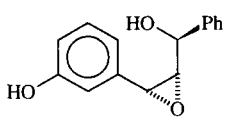


35

(a) $R^1 = R^2 = Me$; (b) $R^1, R^2 = -(CH_2)_5-$

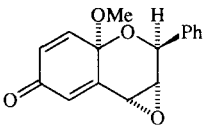
Similarly treatment of **26b** with two equivalents of PIDA gave **34b** and **35b** in 65% yield and in a 4.7:1 ratio. The *trans* isomer **34b** was once again shown to be the major isomer.

Racemic **26e** was obtained as outlined in Scheme 4 as a single diastereoisomer, which on the basis of the evidence presented below is assigned the *erythro* configuration. Treatment of **26e** with PIDA in methanol gave two cyclised products **36** and **37** in a 3:2 ratio and the uncyclised quinone-monoketal **38** (equation 13).



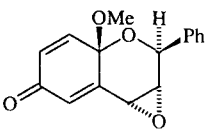
26e

PIDA
MeOH



36

+



37

(13)

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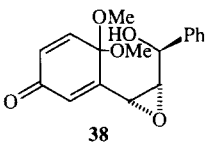
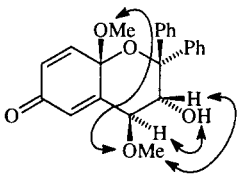


38

The structures of the two cyclised products were established on the basis of their NOESY spectra. Thus the spectrum of the major isomer **36** showed a clear interaction between the protons of the methoxyl group and the methine proton at C-2, but showed no interaction between either of these signals and the

methine protons at C-3 and C-4. In contrast in the minor isomer **37** there was a strong interaction between the methoxyl group and H-4 and a weak interaction between the methoxyl group and H-3. There was no interaction between H-2 and either the methoxyl protons or the methine protons at C-3 and C-4. Based on the structures assigned to **36** and **37** the stereochemistry of the precursor **26e** was deduced as the *erythro* isomer as shown. The structure of the uncyclised quinone-monoketal **38** was assigned on the basis of its spectroscopic data and by comparison with other similar compounds (*vide infra*).

Treatment of **26d** with PIDA gave a single product. However it was immediately obvious that this was not the expected cyclised epoxide since it contained two methoxyl groups, one of which gave a signal at δ2.64 in the ^{1}H nmr spectrum. This strongly suggested that this methoxyl group was held very close to one of the phenyl rings and lead to the conclusion that this was a cyclised product in which the oxirane ring had been opened by attack of methanol. Of the possible isomeric compounds which could be formed in this way the product was assigned as **39** on the basis of its NOESY spectrum. This showed a clear interaction between the two methoxyl groups, and also between the low field methoxyl group (δ3.27) and H-3 and between the OH group and H-4. There was no such interaction between the high field methoxyl group and H-4 or between H-3 and H-4, as would be expected.



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CONCLUSION

We have proposed a series of general equations 5, 6 and 7 in which oxidatively generated phenoxonium ions are trapped intramolecularly by a nucleophile attached by a suitable linker. The present work illustrates general equation 7 using a three carbon side chain and an hydroxyl group as the nucleophile. As with equation 6 we find that a degree of constraint must be present in the linker chain, and this has been provided by either a (*Z*)-alkenyl or a *cis*-oxiranyl group. With the former, PIDA oxidation directly yields 8a-methoxy-*2H,6H*-dihydrochromen-6-ones **24**, whilst the latter yields the corresponding 3,4-oxiranes **27**. Compounds **24** are readily reduced with DIBAL-H to give 2-substituted chromenes. This is a unique chromene synthesis as the heterocyclic oxygen atom is introduced from the side chain and was not present on the benzene ring of the phenolic precursor. We are currently attempting to extend equation 7 by using amino and thiol groups as nucleophiles (Scheme 3, X = NR, S) so as to provide new oxidatively induced heterocyclic syntheses. Very recently Kita[24] has adopted a similar approach using cation radicals derived not from phenols but from methoxybenzenes.

Table 1. ^{1}*H nmr spectra of chromenone derivatives* **24.**

	24a	**24b**	**24c** (major isomer)	**24c** (minor isomer)	**24d**	**24e** (major isomer)	**24e** (minor isomer)	**24f** (major isomer)	**24f** (minor isomer)
H-2	–	–	–	–	–	5.58 (br.s)	5.52 (t, J=2.7Hz)	–	–
H-3	6.65 (d, J=10.2Hz)	6.34 (d, J=10.3Hz)	6.82 (d, J=10.2Hz)	6.78 (d, J=10. 2Hz)	6.85 (d, J=10.3Hz)	6.82 (d, J=10.1Hz)	6.78 (d, J=10.3Hz)	6.72 (d, J=10.2Hz)	6.69 (d, J=10.2Hz)
H-4	6.10 (d, J=10.2Hz)	6.24 (d, J=10.3Hz)	6.21 (d, J=10.2Hz)	6.28 (d, J=10.2Hz)	6.18 (d, J=10.3Hz)	6.24 (dd, J=2.0, 10.1Hz)	6.22 (dd, J=2.0, 10.3Hz)	6.10 (d, J=10.2Hz)	6.24 (d, 10.2Hz)
H-5	5.93 (d, J=2.0Hz)	5.98 (s)	6.05 (d, J=2.0Hz)	5.99 (d, J=2.0Hz)	5.91 (s)	6.07 (br.s)	6.02 (br.s)	5.99 (d, J=2.0Hz)	5.60 (d, J=2.0Hz)
H-7	6.18 (dd, J=2.0, 10.2Hz)	6.26 (d, J=10.1Hz)	6.30 (dd, J=2.0, 10.2Hz)	6.56 (dd, J=2.0, 10.3Hz)	6.4 (d, J=10.2Hz)	6.33 (dd, J=2.0, 10.1Hz)	6.54 (dd, J=2.8, 10.3Hz)	6.24 (dd, J=2.0, 10.3Hz)	6.23 (dd, J=2.0, 10.3Hz)
H-8	6.25 (d, J=10.2Hz)	6.76 (d, J=10.1Hz)	6.37 (d, J=10.2Hz)	6.70 (d, J=10.3Hz)	6.62 (d, J=10.2Hz)	6.46 (dd, J=2.7, 10.1Hz)	6.66 (dd, J=2.1, 10.3Hz)	6.40 (d, J=10.3Hz)	6.30 (d, J=10.3Hz)
O*Me*	3.12 (s)	3.18 (s)	3.27 (s)	2.57 (s)	2.51 (s)	3.36 (s)	2.70 (s)	3.19 (s)	3.12 (s)
2-CH_3	1.26 (s) 1.47 (s)	–	1.93 (s)	1.64 (s)	–	–	–	1.58 (s)	1.60 (s)
$(CH_2)_5$	–	1.3-2.0 (10H, m)	–	–	–	–	–	–	–
Ph	–	–	7.3-7.4 (m)	7.3-7.5 (m)	7.1-7.4 (m)	7.3-7.4 (m)	7.3-7.4 (m)	–	–
geranyl group	–	–	–	–	–	–	–	1.52, 1.53 (6H, 2 x CH_3) 1.66 (3H, s) 1.68, 1.94, 2.20 (8H, m, H-1', 2', 5', 6') 5.05 (2H, m, H-3', 7')	1.26, 1.29 (6H, 2 x CH_3) 1.64 (3H, s,) 1.68, 1.94, 2.20 (8H, m, H-1', 2', 5', 6') 5.14 (2H, m, H-3', 7')

Table 2. ^{13}C *nmr spectra of chromenone derivatives* **24**[a].

	24a	**24b**	**24c** (major isomer)	**24c** (minor isomer)	**24d**	**24e** (major isomer)	**24e** (minor isomer)	**24f** (major isomer)	**24f** (minor isomer)
C-2	75.0	76.0	76.7	77.9	78.3	73.6	75.1	77.1	77.18
C-3	120.2	120.5	121.5	121.5	121.3	122.4	121.8	121.5	120.05
C-4	121.7	121.3	122.0	122.2	121.6	122.5	124.0	121.6	121.67
C-4a	146.6	147.1	146.2	146.9	146.9	146.7	146.7	146.8	146.61
C-5	142.9	142.7	142.5	142.4	142.3	138.7	138.7	142.7	142.60
C-6	186.1	186.2	185.9	185.9	185.8	185.8	185.9	186.1	186.10
C-7	129.4	129.3	129.6	129.5	129.7	130.9	129.5	129.3	129.29
C-8	142.6	142.5	141.7	140.6	139.8	137.8	135.2	141.7	141.69
C-8a	91.5	91.4	92.1	91.3	91.8	91.6	90.0	91.7	91.68
OMe	50.6	50.6	50.8	50.3	50.3	51.3	50.2	50.5	50.62
2-CH_3	28.7, 30.4	--	27.6	31.3	--	--	--	25.7	25.68
$(CH_2)_5$	–	21.4, 22.1, 25.2, 36.8, 38.7	–	–	–	–	–	–	–
Ph	–	–	125.2 127.1 128.5 144.2	126.4 127.4 128.0 145.2	126.7 127.8 128.5 145.3	127.5 128.4 128.8 142.1	128.2 128.4 129.2 138.7	–	–
geranyl group	–	–	–	–	–	–	–	15.9 (2 x CH_3) 22.0, 26.6 (C-1', 5') 27.7 (C-9') 39.6, 42.7 (C-2', 6') 123.6, 122.4 (C-3', 7') 131.3, 135.4, (C-4', 8')	15.9 (2 x CH_3) 22.8, 26.4 (C-1', 5') 26.9 (C-9') 39.7, 40.9 (C-2', 6') 123.9, 124.4 (C-3', 7') 131.3, 135.4, (C-4', 8')

[a]All assignments are supported by DEPT spectra.

Table 3. ^{1}H *nmr spectra of chromenes* **32**

	32a	**32b**	**32c**	**32d**	**32e**	**32f**
H-2	--	--	--	--	5.80 (m)	--
H-3	5.63 (d, J=9.8Hz)	5.66 (d, J=9.8Hz)	5.93 (d, J=9.8Hz)	6.17 (d, J=9.8Hz)	5.80 (m)	5.59 (d, J=9.9Hz)
H-4	6.23 (d, J=9.8Hz)	6.24 (d, J=9.8Hz)	6.31 (d, J=9.8Hz)	6.48 (d, J=9.8Hz)	6.40 (d, 10.8Hz)	6.26 (d, J=9.9Hz)
H-5	6.49 (d, J=2.9Hz)	6.47 (d, J=2.9Hz)	6.40 (d, J=2.9Hz)	6.43 (d, J=2.9Hz)	6.47 (d, J=2.9Hz)	6.47 (d, J=2.9Hz)
H-7	6.58 (dd, J=2.9, 8.6Hz)	6.55 (dd, J=2.9, 8.6Hz)	6.52 (dd, J=2.9, 8.6Hz)	6.51 (dd, J=2.9, 8.6Hz)	6.53 (dd, J=2.9, 8.6Hz)	6.56 (dd, J=2.9, 8.6Hz)
H-8	6.65 (d, J=8.6 Hz)	6.68 (d, J=8.6Hz)	6.72 (d, J=8.6Hz)	6.76 (d, J=8.6Hz)	6.63 (d, J=8.6Hz)	6.64 (d, J=8.6Hz)
OH	5.17 (s)	5.1 (s)	5.50 (s)	4.76 (s)	--	4.95 (s)
2-CH_3	1.40 (s)	--	1.73 (s)	--	--	1.59 (s)
$(CH_2)_5$	_	1.5, 1.7, 1.9 (m)	_	_	_	_
(Ph)	_	_	7.19 (m) 7.28 (t, J=8.0Hz) 7.46 (d, J=7.5Hz)	7.22 (t, J=7.2Hz) 7.29 (t, J=7.6Hz) 7.40 (d, J=7.0Hz)	7.3 (m) 7.41 (d, J=8.3Hz)	_
geranyl group	_	_	_	_	_	1.37, 1.57 (6H, 2 x CH_3) 1.66 (3H, s,) 1.9-2.2 (8H, m, H-1', 2', 5', 6') 5.08 (2H, m, H-3', 7')

Table 4. ^{13}C *nmr spectra of chromenes* **32**[a].

	32a	**32b**	**32c**	**32d**	**32e**	**32f**
C-2	75.9	76.5	78.4	82.3	77.1	78.2
C-3	112.9	112.9	113.1	113.0	113.3	112.9
C-4	115.4	115.3	115.8	116.0	116.0	115.4
C-4a	122.2	123.1	122.0	121.9	122.3	122.0
C-5	116.9	117.0	117.0	117.2	116.7	116.7
C-6	146.5	146.5	145.6	144.7	146.9	146.9
C-7	131.9	131.7	130.6	130.0	128.6	131.0
C-8	122.2	112.6	122.8	123.3	124.1	122.6
C-8a	149.4	149.4	149.4	149.5	149.7	149.3
2-CH_3	27.5	--	29.1	--	--	25.7
$(CH_2)_5$	–	21.4 25.3 35.3	–	–	–	–
Ph	–	–	125.2 127.2 128.2 146.6	127.0 127.5 128.1 146.4	126.0 127.2 128.7 140.5	–
geranyl group	–	–	–	–	–	16.0, 17.7 (2 x CH_3) 22.6, 26.7, (C-1', 5') 26.0 (C-9') 39.7, 40.9 (C-2', 6') 124.0, 124.3 (C-3', 7') 131.3, 135.3 (C-4', 8')

[a]All assignments supported by DEPT spectra.

Table 5. ^{1}H *nmr spectra of oxiranes* **34-37**

	34a	**35a**	**34b**	**35b**	**36**	**37**	**39**
H-2	-	-	-	-	5.22 (s)	5.22 (d, J= 2.4Hz)	-
H-3	3.28 (d, J= 4.4Hz)	3.28 (d, J= 3.8Hz)	3.38 (d, J= 3.9Hz)	3.54 (d, J= 4.4Hz)	3.59 (d, J= 3.8Hz)	3.89 (dd, J= 2.4, 4.4Hz)	3.60 (d, J= 2.0Hz)
H-4	3.63 (d, J= 4.4Hz)	3.85 (d, J= 3.8Hz)	3.83 (d, J= 3.9Hz)	3.83 (d, J= 4.4Hz)	3.84 (d, J= 3.8Hz)	3.93 (d, J= 4.4Hz)	4.06 (d, J= 2.0Hz)
H-5	6.26 (d, J= 2.0Hz)	6.46 (d, J= 2.0Hz)	6.46 (d, J= 2.0Hz)	6.45 (d, J= 2.0Hz)	6.49 (d, J= 2.0Hz)	6.51 (d, J= 2.0Hz)	6.66 (d, J= 2.1Hz)
H-7	6.01 (dd, J= 2.0, 10.1Hz)	6.23, (dd, J=2.0,10.3Hz)	6.22 (dd, J= 2.0, 10.3Hz)	6.19 (dd, J= 2.0, 10.2Hz)	6.28 (dd, J= 2.0, 10.3Hz)	6.22 (dd, J= 2.0, 10.2Hz)	6.34 (dd, J= 2.1, 10.2Hz)
H-8	6.39 (d, J= 10.1Hz)	6.68 (d, J= 10.3Hz)	6.68 (d, J= 10.3Hz)	6.64 (d, J= 10.2Hz)	6.78 (d, J= 10.3Hz)	6.66 (d, J= 10.2Hz)	6.66 (d, J= 10.2Hz)
OMe	2.97 (s)	3.22 (s)	3.18 (s)	3.16 (s)	3.36 (s)	3.10 (s)	2.64 (s) 3.27 (s)
2-CH_3	1.15 (s) 1.41 (s)	1.37 (s) 1.59 (s)	-	-	-	-	-
$(CH_2)_5$	-	-	1.44-2.13 (m)	1.54-2.04 (m)	-	-	-
Ph	-	-	-	-	7.36-7.5 (m)	7.34-7.66 (m)	7.24-7.52 (m)
OH	-	-	-	-	-	-	2.76 (s)

Table 6. ^{13}C *nmr spectra of oxiranes* **34-37**[a].

	34a	**35a**	**34b**	**35b**	**36**	**37**	**39**
C-2	73.8	72.5	74.0	73.8	69.7	73.5	75.7
C-3	53.0	51.0	52.8	51.0	51.0	52.4	50.5
C-4	61.4	55.9	60.6	54.7	53.0	57.2	67.8
C-4a	147.9	145.6	148.6	145.9	145.7	147.8	154.6
C-5	127.7	129.1	127.4	120.0	130.4	128.3	128.6
C-6	184.8	185.1	184.8	185.3	184.8	184.6	184.6
C-7	128.1	130.0	127.8	129.8	130.7	128.5	128.4
C-8	144.9	143.6	145.0	143.5	142.9	144.6	144.5
C-8a	92.1	90.6	90.0	90.6	90.6	92.5	95.0
O*Me*	51.0	49.6	51.0	49.3	49.7	51.4	50.6, 51.3
2-CH_3	26.8, 28.1	27.1 27.4	-	-	-	-	-
$(CH_2)_5$	-	-	21.6, 21.8, 25.3, 35.3, 36.2	21.6, 22.2, 25.5, 35.3, 36.2	-	-	-
Ph	-	-	-	-	127.6, 128.7, 128.8, 136.9	127.8, 128.1, 128.6, 138.2	125.6, 126.6, 126.7, 127.3 127.6, 127.9, 132.1, 142.4, 143.3

[a]All assignments supported by DEPT spectra.

EXPERIMENTAL

^{1}H and ^{13}C Nmr spectra were recorded on a Bruker AC 400 spectrometer at 400 MHz and 100 MHz respectively. All spectra used tetramethylsilane as the internal standard, and were run in deuterated chloroform, unless otherwise stated. The mass spectra were recorded on a VG-12-250 low resolution quadrupole mass spectrometer, while a ZAB-E, high resolution, double focusing mass spectrometer was used for accurate mass measurements. Infra-red spectra were recorded as films on NaCl discs using a Perkin-Elmer Fourier transform 1725X spectrometer and ultra-violet spectra were recorded on a Philips PU8720 scanning spectrometer. Melting points were recorded on an Electrothermal 9100 melting point apparatus, and are uncorrected.

Thin layer chromatography was carried out on Merck 5785 Kieselgel $60F_{254}$ fluorescent plates. Analytical hplc was carried out on a Milton Roy system using a 3100 SpectroMonitor, 3000 ConstaMetric pump and CI-4100 integrator. Flash chromatography was performed with silica gel (Fisons Matrex 60, 35-70 micron).

Reactions carried out under nitrogen refer to the use of 'white spot' nitrogen which was dried by bubbling through concentrated sulphuric acid and passing through calcium chloride granules. Low temperature baths were prepared by making a slurry of solid carbon dioxide with acetone (-78°C). Diethyl ether and dichloromethane were dried by passing down an alumina column and distilling from calcium hydride. Ethyl acetate was dried over potassium carbonate and distilled from calcium hydride. Tetrahydrofuran was passed down a dry alumina column and distilled from sodium metal and benzophenone.

*Preparation of 3-*tert*-butyldimethylsilyloxy-1-iodobenzene* (**19**)

To a round bottomed flask (100ml) containing a magnetic follower was added 3-iodophenol (**17**) (10.42g, 0.047mol), *tert*-butyldimethylsilyl chloride (7.142g, 0.047mol), and imidazole (6.452g, 0.095mol) in dichloromethane (60ml). The mixture was then stirred for 18 hours, during which time a white solid precipitated, and was removed by filtration. The filtrate was concentrated under vacuum, and the residue purified by flash column chromatography on silica using dichloromethane. The product (**19**) (15.67g, 0.047mol, 99.7%) was obtained as a colourless oil.

Observed mass = 334.0250. Calc. for $C_{12}H_{19}OSiI$ is 334.0252. δ_H, 0.19 (6H, s, 2 x $SiCH_3$), 0.97 (9H, s, $SiC(CH_3)_3$), 6.85 (1H, d, J=8.2Hz, H-4), 6.94 (1H, t, J=8.0Hz, H-5), 7.22 (1H, s, H-2), 7.28 (1H, d, J=7.8, H-6). δ_C, ppm, -4.5 ($Si(CH_3)_2$), 18.1 ($SiC(CH_3)_3$), 25.6 ($SiC(CH_3)_3$), 94.1 (C-1), 119.4 (C-4), 129.4 (C-2), 130.4 (C-6), 130.6 (C-5), 156.2 (C-3). *m/z* (EI), 334(M^+,35), 227(80), 150(100), 135(58), 115(28), 91(24), 75(18), 73(56), 57(33). ν_{max} (cm^{-1}), 2956, 2930, 2886, 2858 (C-H), 1584, 1471. λ_{max} (MeOH), 210.9nm (ε, 36185), 228.2nm (ε, 16254), 273.8nm (ε, 4784).

*Preparation of 4-(3′-*tert*-butyldimethylsilyloxyphenyl)-2-methylbut-3-yn-2-ol* (**21a**)

To a round bottomed flask (100ml) containing a magnetic follower was added **19** (1g, $2.99x10^{-3}$ mol), 2-methylbut-3-yn-2-ol (0.6g, $7.2x10^{-3}$mol), $Pd(PPh_3)_2Cl_2$ (0.057g, $8.1x10^{-5}$ mol) and CuI (0.015g, $8.1x10^{-5}$ mol) in di-*iso*-propylamine (50ml). A water condenser was then attached to the top of the flask, and the stirred solution was then raised to 75°C using an oil bath. This temperature was maintained for 16 hours before the solution was allowed to cool to room temperature. A white solid (10.57g) formed, and this was removed by filtration. The filtrate was then concentrated under vacuum to yield a black tar which was purified by flash column chromatography using gradient elution with pet. spirit (bp 30-40°) and dichloromethane. Elution with pure dichloromethane afforded **21a** (1.17g, $2.99x10^{-3}$ mol, 100%) as a brown oil.

Observed mass = 290.1702. Calc. for $C_{17}H_{26}O_2Si$ is 290.1702. δ_H, 0.20 (6H, s, $Si(CH_3)_2$), 0.99 (9H, s, $SiC(CH_3)_3$), 1.62 (6H, s, CCH_3), 6.79 (1H, d, J=8.2Hz, H-4′), 6.90 (1H, s, H-2′), 7.02 (1H, d, J=7.6Hz, H-6′), 7.15 (1H, t, J=7.8Hz, H-5′). δ_C, ppm, -4.4 ($SiC(CH_3)_2$), 18.1 ($SiC(CH_3)_3$), 25.6 ($SiC(CH_3)_3$), 31.5 (C-1), 65.6 (C-2), 82.0 (C-3), 93.5 (C-4), 120.5 (C-4′), 123.2 (C-2′), 123.7 (C-1′), 124.9 (C-6′), 129.3 (C-5′), 155.4 (C-3′). *m/z* (EI), 290(M^+,48), 273(11), 233(100), 215(29), 159(17), 115(13), 75(57), 73(15), 57(12). ν_{max} (cm^{-1}), 3348 (O-H), 2981, 2956, 2930,2896, 2859 (C-H), 1596, 1576, 1480. λ_{max} (MeOH), 210.6nm (ε, 23973), 240.4nm (ε, 10682), 250.4nm (ε, 12663), 285.6nm (ε, 1402).

Preparation of (Z)*-4-(3′-*tert*-butyldimethylsilyloxyphenyl)-2-methylbut-3-en-2-ol* (**22a**)

To a round bottomed flask (100ml) containing a magnetic follower was added **21a** (2.019g, $6.95x10^{-3}$ mol), Lindlar catalyst (0.198g) and methanol (25ml). The flask was then placed on a hydrogenator at atmospheric pressure, and the apparatus evacuated, purged with hydrogen, evacuated again, and repurged with hydrogen. The reaction was monitored until one equivalent of hydrogen had been consumed. The Lindlar catalyst was filtered off, and the filtrate concentrated under vacuum. The products were separated by flash chromatography using gradient elution with pet. spirit (bp 40-60°) and dichloromethane. Elution with pure dichloromethane afforded **22a** (1.81g, $6.26x10^{-3}$ mol, 90%) as a yellow oil.

Observed mass = 292.1859. Calc. for $C_{17}H_{28}O_2Si$ is 292.1858. δ_H, 0.19 (6H, s, $Si(CH_3)_2$), 0.98 (9H, s, $SiC(CH_3)_3$), 1.34 (6H, s, CCH_3)), 1.78 (1H, s, O*H*), 5.73 (1H, d, J=12.6, H-3), 6.40 (1H, d, J=12.6, H-4), 6.72 (1H, d, J=8.0Hz, H-4′), 6.85 (1H, s, H-2′), 6.90 (1H, d, J=7.5Hz, H-6′), 7.16 (1H, t, J=7.8Hz, H-5′). δ_C, ppm, -4.4 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 31.1 (C-1), 72.0 (C-2), 118.8 (C-3), 120.6 (C-4), 122.0 (C-2′), 127.6 (C-6′), 129.1 (C-4′), 138.9 (C-1′), 139.3 (C-5′), 155.9 (C-3′). *m/z* (EI), 292(M^+,23), 277(15), 235(35), 217(75), 115(8), 75(100). ν_{max} (cm^{-1}), 3417 (O-H), 2958, 2859 (C-H). λ_{max} (MeOH), 208.7nm (ε, 18360), 246.0nm (ε, 5512).

Preparation of (Z)-*4-(3′-hydroxyphenyl)-2-methylbut-3-en-2-ol* (**23a**)

To a round bottomed flask (100ml) containing a magnetic follower was added **22a** (0.206g, $7.043x10^{-4}$ mol), and tetrabutylammonium fluoride (1M in THF) (2.11ml, $2.11x10^{-3}$ mol, 3eq), and the mixture stirred for one hour. Distilled water (40ml) was then added. The mixture was extracted with dichloromethane (2x40ml), and washed with distilled water (40ml), before drying over $MgSO_4$, and concentrating under vacuum. The products were separated by flash column chromatography on silica, using gradient elution with CH_2Cl_2 and EtOAc. Elution with a 4:6 ratio of solvents afforded **23a** (0.124g, $6.966x10^{-4}$ mol, 99%) as a yellow oil.

Observed mass = 178.0994. Calc. for $C_{11}H_{14}O_2$ is 178.0994. δ_H, 1.37 (6H, s, H-1), 2.44 (1H, s, O*H*), 5.7 (1H, d, J=12.6Hz, H-3), 6.40 (1H, d, J=12.6Hz, H-4), 6.68 (1H, d, J=8.1Hz, H-4′), 6.79 (1H, d, J=7.5Hz, H-6′), 6.85 (1H, s, H-2′), 7.10 (1H, s, O*H*), 7.14 (1H, t, 7.7Hz, H-5′). δ_C, ppm, 31.0 (C-1), 72.9 (C-2), 114.5 (C-3), 116.0 (C-4), 120.7 (C-2′), 127.9 (C-6′), 129.4 (C-4′), 138.6 (C-5′), 138.8 (C-1′), 155.8 (C-3′). *m/z* (EI), 178(M^+,27), 163(17), 107(88), 91(40), 77(21), 43(100). ν_{max} (cm^{-1}), 3382 (O-H), 3020-2930 (C-H). λ_{max} (MeOH), 205.3nm (ε, 18968), 281.0nm (ε, 4895).

*Preparation of 6-hydroxy-8a-methoxy-2,2-dimethyl-*2H,6H-*dihydrochromen-6-one* (**24a**)

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and magnetic follower, was added **23a** (2.015g, 0.0113mol), in dry methanol (10ml). To the stirred solution was added PIDA (7.283g, 0.0226mol), and stirring continued for 45 minutes before concentration under vacuum. The products were immediately separated by flash chromatography on neutral silica using CH_2Cl_2, to give the product (**24a**) (1.934g, 0.0094mol, 83%) as a brown oil.

Observed mass = 206.0943. Calc. for $C_{12}H_{14}O_3$ is 206.0943. *m/z* (EI), 206(M^+,4), 191(8), 175(29), 164(91), 103(20), 91(47), 77(46), 43(100). ν_{max} (cm^{-1}), 2977, 2828 (C-H), 1667 (C=O). λ_{max} (MeOH), 215.5nm (ε, 22982), 313.6nm (ε, 7532). See Tables 1 and 2 for ^1H and ^{13}C nmr spectra.

*Preparation of 6-hydroxy-2,2-dimethyl-*2H-*chromene* (**32a**)

To a dry round bottomed flask (100ml) under nitrogen, fitted with a septum and a magnetic follower, was added **24a** (0.539g, 0.0026mol) in dry CH_2Cl_2 (10ml), and to the stirred solution was added DIBAL-H (1M solution in CH_2Cl_2) (2.61ml, 0.0026mol). The mixture was stirred for 170 minutes before the addition of 1M HCl (2.61ml, 0.0026mol). After being stirred for a further 20 minutes the mixture was washed with water (2 x 40ml), dried over $MgSO_4$ and evaporated to dryness. The residue was separated by flash chromatography on neutral silica using gradient elution with pet. spirit (bp 40-60°) and CH_2Cl_2. The product (**32a**) (0.40g, 0.0023mol, 87%) was obtained as a brown solid from CH_2Cl_2.

Observed mass for $M+H^+$ = 177.0915. Calc. for $C_{11}H_{13}O_2$ is 177.0915. *m/z* (CI), 177($M+H^+$,100), 161(56), 91(1), 74(1). ν_{max} (cm^{-1}), 3397 (O-H), 3020, 2979, 2933 (C-H). λ_{max} (MeOH), 219.8nm (ε, 21648), 264.4nm (ε, 3890), 331.0nm (ε, 4365). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

*Preparation of 2-(3′-*tert*-butyldimethylsilyloxyphenyl)-1-(1″-hydroxycyclohexyl)ethyne* (**21b**)

To a round bottomed flask (250ml) containing a magnetic follower, was added **19** (13.46g, 0.04 mol), 1-ethynylcyclohexanol (5g, 0.04 mol), $Pd(PPh_3)_2Cl_2$ (0.76g, $1.087x10^{-3}$ mol), CuI (0.2g, $1.087x10^{-3}$ mol) in di-*iso*-propylamine (20ml) and dichloromethane (120ml). A water condenser was then attached to the top of the flask, and the stirred solution was then raised to 60°C using an oil bath. This temperature was maintained for 18 hours before the solution was allowed to cool to room temperature, after which the mixture was concentrated under vacuum, and dissolved in diethyl ether (50ml). A white solid had been formed, and this was removed by filtration. The filtrate was then concentrated under vacuum to yield a yellow oil which was purified by flash chromatography on silica using dichloromethane. The product (**21b**) (13.099g, 0.0396mol, 98%) was obtained as a pale yellow oil.

Observed mass = 330.2015. Calc. for $C_{20}H_{30}O_2Si$ is 330.2015. δ_H, 0.19 (6H, s, $Si(CH_3)_2$), 0.98 (9H, s, $SiC(CH_3)_3$), 1.15, (1H, s, *OH*), 1.59-1.75 (6H, complex m, $(CH_2)_3$), 2.0 (4H, complex m, $C(CH_2)_2$), 6.78 (1H, d, J=8.1Hz, H-4′), 6.90 (1H, s, H-2′), 7.03 (1H, d, J=7.6Hz, H-6′), 7.15(1H,t,J=7.7Hz,H-5′). δ_C,ppm, -4.4 ($Si(CH_3)_2$), 18.1 ($SiC(CH_3)_3$), 23.4 ($CH_2CH_2CH_2CH_2CH_2$), 25.2 ($CH_2CH_2CH_2CH_2CH_2$), 25.6 ($SiC(CH_3)_3$), 40.0 ($C(CH_2CH_2CH_2CH_2CH_2)$), 69.1 (C-1″), 84.17 (C-1), 92.5 (C-2), 120.42 (C-4′), 123.2 (C-2′), 123.9 (C-1′), 124.9 (C-6′), 129.3 (C-5′), 155.4 (C-3′). *m/z* (EI), 330(M^+,63), 313(12), 273(45), 255(50), 213(12), 205(53), 199(32), 189(13), 115(26), 91(6),75(100). *m/z* (CI), 330(M^+,12), 313(100), 91(5). ν_{max}(cm^{-1}), 3360 (O-H), 2920, 2840 (C-H), 1590, 1560, 1470. λ_{max} (MeOH), 242.8nm (ε, 84884), 254.6nm (ε, 83003), 285.4nm (ε, 17326), 294.2nm (ε, 16831).

*Preparation of (Z)-2-(3′-*tert*-butyldimethylsilyloxyphenyl)-1-(1″-hydroxycyclohexyl)ethene* (**22b**)

To a round bottomed flask (250ml) containing a magnetic follower, was added, **21b** (7.47g, 0.0226mol), Lindlar catalyst (0.92g) and methanol (50ml). The flask was then placed on a hydrogenator at atmospheric pressure, the apparatus twice evacuated, and purged with hydrogen, and the reaction monitored until one equivalent of hydrogen had been consumed. The Lindlar catalyst was removed by filtration, and the filtrate concentrated under vacuum. The products were separated by flash chromatography using gradient elution with pet. spirit (bp 40-60°) and dichloromethane. Elution with pure dichloromethane afforded **22b** (4.242g, 0.0128mol, 57%) as a yellow oil.

Observed mass = 332.2170. Calc. for $C_{20}H_{32}O_2Si$ is 332.2171 δ_H, 0.20 (6H, s, $(SiCH_3)_2$), 0.98 (9H, s, $SiC(CH_3)_3$), 1.26 (1H, s, *OH*), 1.43-1.61 (10H, complex m, $(CH_2CH_2CH_2CH_2CH_2)_5$), 5.67 (1H, d, J=12.7, H-1), 6.42 (1H, d, J=12.7, H-2), 6.71 (1H, d, J=7.9Hz, H-4′), 6.93 (1H, s, H-2′), 6.94 (1H, d, J=7.9Hz, H-6′), 7.14 (1H, t, J=7.9Hz, H-5′). δ_C, ppm, -4.4 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 22.1 ($CH_2CH_2CH_2CH_2CH_2$), 25.5 ($CH_2CH_2CH_2CH_2CH_2$), 25.7 ($SiC(CH_3)_3$), 39.0 ($CH_2CH_2CH_2CH_2CH_2$), 72.7 (C-1″), 118.8 (C-1), 120.7 (C-2), 122.2 (C-2′), 128.6 (C-6′), 129.1 (C-4′), 138.9 (C-5′), 139.1 (C-1′), 155.3 (1C, C-3′). *m/z* (EI),

332(M^+,27), 315(23), 275(100), 257(25), 207(13), 115(13), 75(32). *m/z* (CI), 332(M^+,15), 315(100), 275(35), 257(8), 115(2), 91(9), 74(3). ν_{max} (cm^{-1}), 3560, 3420 (O-H), 2900-2800 (C-H). λ_{max} (MeOH), 215.2nm (ε, 38778), 247.1nm (ε, 18548), 281.2nm (ε, 3213).

Preparation of (Z)-2-(3′-hydroxyphenyl)-1-(1″-hydroxycyclohexyl)ethene **(23b)**

To a round bottomed flask (100ml) containing a magnetic follower was added **22b** (1.952g, $5.87x10^{-3}$ mol), and tetrabutylammonium fluoride (1M in THF) (17.61ml, 0.0176mol, 3eq), and the mixture was stirred for 18 hours. The mixture was then concentrated under vacuum, and the products separated using flash chromatography on silica using CH_2Cl_2. The product **(23b)** (1.03g, $4.72x10^{-3}$ mol, 80%) was obtained as white crystals.

Observed mass = 218.1307. Calc. for $C_{14}H_{18}O_2$ is 218.1307. Elemental analysis. Observed C, 76.9%; H, 8.68%. $C_{14}H_{18}O_2$ requires C, 77.03%; H, 8.83%. δ_H, 1.28, 1.45, 1.62 (10H, complex m, $(CH_2)_5$), 5.69 (1H, d, J=12.7Hz, C-1), 6.45 (1H, d, J=12.7Hz, C-2), 6.67 (1H, d, J=8.2Hz, H-4′), 6.80 (1H, d,J=7.5Hz, H-6′), 6.93 (1H, s, H-2′), 7.13 (1H, t, 7.9Hz, H-5′). δ_C, ppm, 22.1 ($CH_2CH_2CH_2CH_2CH_2$), 25.3 ($CH_2CH_2CH_2CH_2CH_2$), 38.8 ($CH_2CH_2CH_2CH_2CH_2$), 73.9 (C-1″), 114.5 (C-1), 116.0 (C-2), 121.4 (C-2′), 129.0 (C-6′), 129.5 (C-4′), 139.0 (C-5′), 139.0 (C-1′), 155.8 (C-3′). *m/z* (EI), 218(M^+,35), 200(100), 147(46), 133(28), 120(20), 107(45), 91(70), 77(56). ν_{max} (cm^{-1}), 3416 (O-H), 2932 (C-H). λ_{max} (MeOH), 233.3nm (ε, 13030), 290.7nm (ε, 4156), 304.6nm (ε, 3176), 324.6nm (ε, 1322).

Preparation of 6-hydroxy-8a-methoxy-2-spirocyclohexyl-2H,6H-*dihydrochromen-6-one* **(24b)**

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower, was added **23b** (0.65g, $2.982x10^{-3}$ mol), in dry methanol (5ml). PIDA (1.92g, $5.963x10^{-3}$ mol) was added to the stirred solution, and stirring was continued for 45 minutes when the solvent was removed under vacuum. The products were separated immediately by flash chromatography on neutral silica using gradient elution with CH_2Cl_2 and EtOAc. After elution with 100% CH_2Cl_2 the product **(24b)** (0.7g, $2.8x10^{-3}$ mol, 95%) was obtained as a brown oil.

Observed mass for $M+H^+$ = 247.1334. Calc. for $C_{15}H_{19}O_3$ is 247.1334. *m/z* (EI), 246(M^+,12), 218(51), 203(10), 187(20), 164(65), 137(100), 105(41), 91(39), 77(44), 65(20), 55(37). *m/z* (CI), 247($M+H^+$,75), 215(100), 187(3). ν_{max} (cm^{-1}), 2935, 2859 (C-H), 1666 (C=O). λ_{max} (MeOH), 233.0nm (ε, 10824), 314.5nm (ε, 10588). See Tables 1 and 2 for ^1H and ^{13}C nmr spectra.

Preparation of 6-hydroxy-2-spirocyclohexyl-2H-*chromene* **(32b)**

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower, was added **24b** (0.215g, $8.94x10^{-4}$ mol) in dry CH_2Cl_2 (10ml). To the stirred solution was added DIBAL-H (1M solution in CH_2Cl_2) (0.87ml, $8.94x10^{-4}$ mol), and the mixture was stirred for 2 hours before the addition

of 2M HCl (0.45ml, $8.94x10^{-4}$ mol), and then stirred for a further 30 minutes. The mixture was then washed with water (2 x 40ml), dried over $MgSO_4$ and concentrated under vacuum. The residue was separated by flash chromatography on neutral silica with CH_2Cl_2, to give the product **(32b)** (0.126g, $5.83x10^{-4}$ mol, 65%) as a brown oil.

Observed mass = 216.1150. Calc. for $C_{14}H_{16}O_2$ is 216.1150. *m/z* (EI), 216(M^+,23), 179(20), 83(30), 49(100). *m/z* (CI), 234($M+NH_4^+$,2), 217($M+H^+$,100), 179(11). ν_{max} (cm^{-1}), 3385 (O-H), 3020-2856 (C-H). λ_{max} (MeOH), 224.3nm (ε, 19969), 264.9nm (ε, 3974), 331.2nm (ε, 3596). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

*Preparation of 4-(3′-*tert*-butyldimethylsilyloxyphenyl)-2-phenylbut-3-yn-2-ol* **(21c)**

To a round bottomed flask (250ml) containing a magnetic follower,was added **19** (16.05g, 0.048mol), 2-phenyl-3-butyn-2-ol (10g, 0.048mol), $Pd(PPh_3)_2Cl_2$ (0.91g, $1.269x10^{-3}$ mol), CuI (0.247g, $1.269x10^{-3}$ mol) in di-*iso*-propylamine (25ml) and dichloromethane (100ml). A water condenser was attached to the top of the flask, and the stirred solution was then raised to 60°C using an oil bath. This temperature was maintained for 18 hours after which the solution was allowed to cool to room temperature. The mixture was then concentrated under vacuum, and dissolved in pet. spirit (bp 30-40°). A white solid was removed by filtration, the filtrate was then concentrated under vacuum to yield a black tar which was purified by flash column chromatography with dichloromethane. The product **(21c)** (17.09g, 0.048mol, 100%) was obtained as a brown oil.

Observed mass = 352.1859. Calc. for $C_{22}H_{28}O_2Si$ is 352.1858. δ_H, 0.20 (6H, s, $Si(CH_3)_2$), 0.98 (9H, s, $SiC(CH_3)_3$), 1.86 (3H, s, H-1), 2.57 (1H, s, O*H*), 6.81 (1H, d, J=8.1Hz, H-4′), 6.95 (1H, s, H-2′), 7.07 (1H, d, J=7.6Hz, H-6′), 7.16 (1H, t, J=7.7Hz, H-5′), 7.30 (1H, complex m, *Ph*), 7.37 (2H, complex m, *Ph*), 7.72 (2H, complex m, *Ph*). δ_C, ppm, -4.5 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 33.3 (C-1), 70.4 (C-2), 84.8 (C-3), 92.2 (C-4), 120.8 (C-4′), 123.2 (C-2′), 123.6 (C-1′), 125.0 (C-6′), 125.0 (*Ph*), 127.7 (*Ph*), 128.4 (*Ph*), 129.4 (C-5′), 145.6 (*Ph*), 155.5 (C-3′). *m/z* (EI), 352(M^+,20), 337(32), 295(100), 277(20), 261(15), 221(23), 202(10), 189(8), 115(12), 101(42), 91(18), 75(48). *m/z* (CI), 352(M+,1), 335(100), 295(7), 91(20). ν_{max} (cm^{-1}), 3360 (O-H), 2940-2820 (C-H), 2220 (C C), 1580, 1560, 1460. λ_{max} (MeOH), 225nm (ε, 32887), 242nm (ε, 44260), 252nm (ε, 45563), 284nm (ε, 7746).

*Preparation of (Z)-4-(3′-*tert*-butyldimethylsilyloxyphenyl)-2-phenylbut-3-en-2-ol* **(22c)**

To a dry round bottomed flask (250ml) under nitrogen, fitted with a septum and a magnetic follower, was added cyclohexene (7.94g, 0.096mol) in dry THF (40ml), and the solution stirred. To a second dry round bottomed flask (100ml) under nitrogen, was added borane dimethyl sulfide complex (3.667g, 0.048mol), in dry THF (30ml). The borane dimethyl sulphide complex was then added to the cyclohexene through a double ended needle, and the reaction mixture stirred. After 5 minutes a white precipitate was seen to be forming,

but stirring was continued for 0.5 hours. To a third dry round bottomed flask (250ml) under nitrogen, was added **21c** (7.03g, 0.024mol) in dry THF (50ml), and this was then added through a double ended needle to the reaction mixture. After 5 minutes the white precipitate disappeared, and stirring was continued for 0.5 hours, after which the reaction was worked up by addition of glacial acetic acid (2.88g, 2.747ml, 0.048mol). The reaction mixture was left to stir for 18 hours, before concentration under vacuum, dissolving in CH_2Cl_2 (50ml), washing with distilled water (2 x 30ml) and evaporation under vacuum. The products were separated by flash chromatography on silica with CH_2Cl_2, to give **22c** (3.6g, 0.01mol, 45%) as a brown oil.

Observed mass = 354.2015. Calc. for $C_{22}H_{30}O_2Si$ is 354.2015. δ_H, 0.19 (6H, s, Si(CH_3)$_2$), 0.95 (9H, s, SiC(CH_3)$_3$), 1.64 (3H, s, H-1), 2.42 (1H, s, O*H*), 6.16 (1H, d, J=12.5, H-3), 6.55, 1H, d, J=12.5, H-4), 6.30 (1H, s, H-2′), 6.68 (1H, d, J=8.1Hz, H-4′), 6.73 (1H, d, J=6.9Hz, H-6′), 7.09 (1H, t, J=7.8Hz, H-5′), 7.25 (1H, complex m, *Ph*), 7.35 (2H, t, J=7.35Hz, *Ph*), 7.52 (2H, d, J=7.1Hz, *Ph*). δ_C, ppm, -4.5 (Si(CH_3)$_2$), 18.1 (SiC(CH$_3$)$_3$), 25.6 (SiC(CH_3)$_3$), 33.0 (C-1), 75.1 (C-2), 119.1 (C-3), 120.3 (C-4), 121.8 (C-2′), 125.1 (*Ph*), 126.8 (*Ph*), 128.3 (*Ph*), 128.7 (C-6′), 129.3 (C-4′), 138.3 (C-1′), 138.5 (C-5′), 148.8 (*Ph*), 155.5 (C-3′). *m/z* (EI), 354(M^+,10), 339(5), 297(30), 219(12), 205(13), 181(90), 163(20), 151(15), 129(100), 105(45), 91(29), 75(40). *m/z* (CI), 354(M^+,1), 337(100), 297(5). ν_{max} (cm^{-1}), 3567-3450 (O-H), 3027-2859 (C-H), 1599, 1579, 1486. λ_{max} (MeOH), 233nm (ε, 6311), 246.7nm (ε, 5929), 268.3nm (ε, 2839), 293.2nm (ε, 736).

Preparation of (Z)-*4-(3′*-tert-*butyldimethylsilyloxyphenyl)-2-phenylbut-3-en-2-ol* **(22c)**

To a round bottomed flask (250ml) containing a magnetic follower, was added **21c** (5.865g, 0.017mol), Lindlar catalyst (0.6g) and methanol (10ml). The flask was then placed on a hydrogenator at atmospheric pressure, and the apparatus evacuated, purged with hydrogen, evacuated again, and repurged with hydrogen. The reaction was monitored until one eqivalent of hydrogen had been consumed. The Lindlar catalyst was removed by filtration, and the filtrate concentrated under vacuum. The product **(22c)** (4.793g, 0.0135mol, 81%) was obtained as a brown oil. The spectral data were identical to those of the compound prepared above.

Preparation of (Z)-*4-(3′-hydroxyphenyl)-2-phenylbut-3-en-2-ol* **(23c)**

To a round bottomed flask (250ml) containing a magnetic follower, was added **22c** (7.297g, 0.02mol) and CsF (3.12g, 0.02mol) in methanol (50ml). The reaction was stirred for 18 hours, concentrated under vacuum, dissolved into CH_2Cl_2 (50ml), washed with water (2 x 50ml), dried over $MgSO_4$ and reconcentrated under vacuum. The product **(23c)** (4.4g, 0.0183mol, 99%) was obtained as a brown oil.

Observed mass = 240.1150. Calc. for $C_{16}H_{16}O_2$ is 240.1150. δ_H, 1.62 (3H, s, H-1), 6.12 (1H, d, J=12.4Hz, H-3), 6.53 (1H, d, J=12.4Hz, H-4), 6.56 (1H, d, J=7.9Hz, H-4′), 6.58 (1H, d, J=7.5Hz, H-6′), 6.60 (1H, s, H-2′), 6.98 (1H, t, 7.4Hz, H-5′), 7.2 (1H, complex m, *Ph*), 7.3 (2H, complex m, *Ph*), 7.46 (2H, complex m, *Ph*). δ_C, ppm, 32.5 (C-1), 75.8 (C-2), 114.7 (C-3), 115.7 (C-4), 120.5 (C-2′), 125.1 (*Ph*), 127.0

(*Ph*), 128.3 (*Ph*), 128.9 (C-6'), 129.6 (C-4'), 138.1 (C-5'), 138.4 (C-1'), 148.3 (*Ph*) 155.7 (C-3'). *m/z* (EI), 240(M^+,3), 222(50), 207(48), 197(100), 119(95), 105(60), 91(80), 77(78). *m/z* (CI), 240(M^+,2), 223(100). ν_{max} (cm^{-1}), 3354 (O-H), 2979-2859 (C-H). λ_{max} (MeOH), 208.9nm (ε, 29400).

*Preparation of 6-hydroxy-8a-methoxy-2-methyl-2-phenyl-*2H,6H*-dihydrochromen-6-one* (**24c**)

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower, was added **23c** (0.442g, $1.841x10^{-3}$ mol), in dry methanol (10ml). To the stirred solution was added PIDA (1.186g, $3.68x10^{-3}$ mol). The solution was stirred for 15 minutes before concentrating under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2. The product (**24c**) (0.28g, $1.045x10^{-3}$ mol, 57%) was obtained as a brown oil, ratio of isomers = 3:2.

Observed mass = 268.1099. Calc. for $C_{17}H_{16}O_3$ is 268.1099. *m/z* (EI), 268(M^+,5), 253(3), 237(12), 165(17), 84(100), 77(10). *m/z* (CI), 269(M+H^+,90), 237(100) ν_{max} (cm^{-1}), 2984-2881 (C-H), 1665 (C=O). λ_{max} (MeOH), 214.7nm (ε, 15204), 310.0nm (ε, 8415). See Tables 1 and 2 for ^1H and ^{13}C nmr spectra.

*Preparation of 6-hydroxy-2-methyl-2-phenyl-*2H*-chromene* (**32c**)

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower, was added **24c** (0.42g, $1.567x10^{-3}$ mol) in dry CH_2Cl_2 (4ml), and DIBAL-H (1M solution in CH_2Cl_2) (1.567ml, $1.567x10^{-3}$ mol), the mixture was stirred for 1.5 hours before the addition of 2M HCl (0.784ml, $1.567x10^{-3}$ mol), after which it was stirred for a further 30 minutes, washed with water (2 x 50ml), dried over $MgSO_4$, filtered and evaporated to dryness. The residue was separated by flash chromatography on neutral silica with CH_2Cl_2. The product (**32c**) (0.3g, $1.26x10^{-3}$ mol, 80%) was obtained as a brown oil.

Observed mass = 238.0994. Calc. for $C_{16}H_{14}O_2$ is 238.0994. *m/z* (EI), 238(M^+,17), 223(100), 161(15), 77(11). *m/z* (CI), 239(M+H^+,100), 223(20), 161(3). ν_{max} (cm^{-1}), 3388 (O-H), 3060-2864 (C-H). λ_{max} (MeOH), 227.2nm (ε, 15865), 332.2nm (ε, 2055). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

*Preparation of 3-(3'-*tert*-butyldimethylsilyloxyphenyl)-1,1-diphenylprop-2-yn-1-ol* (**21d**)

To a round bottomed flask (1 litre) containing a magnetic follower, was added **19** (30.85g, 0.092mol), 1,1-diphenylprop-2-yn-1-ol (19.22g, 0.092mol), $Pd(PPh_3)_2Cl_2$ (1.2g), CuI (0.35g,) in di-iso-propylamine (100ml) and dichloromethane (300ml). A water condenser was then attached to the top of the flask, and the stirred solution was refluxed using an oil bath. This temperature was maintained for 18 hours before the solution was allowed to cool to room temperature, washed with 2M HCl (2 x 300ml), and distilled water (2 x 100ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The products were separated by flash chromatography on silica with pet. spirit (bp 30-40°). The product (**21d**) (38g, 0.092mol, 99.7%) was obtained as a brown oil.

Observed mass = 414.2015. Calc. for $C_{27}H_{30}O_2Si$ is 414.2015. δ_H, 0.18 (6H, s, Si(C*H*$_3$)$_2$), 0.98 (9H, s, SiC(C*H*$_3$)$_3$), 3.01 (1H, s, O*H*), 6.81 (1H, d, J=7.9Hz, H-4′), 6.98 (1H, s, H-2′), 7.10 (1H, d, J=7.65Hz, H-6′), 7.13 (1H, t, J=7.6Hz, H-5′), 7.24 (2H, d, J=7.4Hz, *Ph*), 7.30 (4H, t, J=7.1Hz, *Ph*), 7.65 (4H, d, J=7.1Hz, *Ph*). δ_C, ppm, -4.4 (Si(*C*H$_3$)$_2$), 18.1 (Si*C*(CH$_3$)$_3$), 25.6 (SiC(*C*H$_3$)$_3$), 71.1 (C-1), 87.0 (C-2), 91.5 (C-3), 120.8 (C-4′), 123.2 (C-2′), 123.4 (C-1′), 125.0 (C-6′), 126.0 (*Ph*), 129.3 (*Ph*), 130.6 (*Ph*), 132.4 (C-5'), 144.9 (*Ph*), 155.4 (C-3′). *m/z* (EI), 414(M$^+$,45), 357(100), 341(16), 279(42), 265(16), 175(75), 165(18), 105(73), 77(28). *m/z* (CI), 415(M+H$^+$,9), 397(100), 183(90), 105(11). ν_{max} (cm^{-1}), (O-H), (C-H), (C C). λ_{max} (MeOH), 220nm (ε, 44761), 243nm (ε, 41600), 254nm (ε, 39936), 285nm (ε, 7654), 292nm (ε, 7488).

Preparation of (Z)-*3-(3′*-tert-*butyldimethylsilyloxyphenyl)-1,1-diphenylprop-2-en-1-ol* (**22d**)

To a dry round bottomed flask (250ml) under nitrogen at 0°C, fitted with a septum and a magnetic follower, was added titanocene dichloride (0.32g, 1.28x10^{-3} mol) and *iso*-butyl magnesium chloride (20ml, 0.0256mol) in dry diethyl ether (40ml), and the mixture stirred for 10 minutes. To a second dry round bottomed flask (100ml) under nitrogen, fitted with a septum, was added **21d** (5.316g, 0.0128mol), in dry diethyl ether (30ml), and the solution was added to the reaction mixture through a double ended needle. The mixture was then allowed to warm to room temperature, and stirred for 2 hours before the careful addition of distilled water (50ml), after which it was stirred for a further hour, before removing the solid by filtration. The filtrate was then concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The product (**22d**) (4.047g, 0.0097mol, 76%), was obtained as a brown oil.

Observed mass = 416.2172. Calc. for $C_{27}H_{32}O_2Si$ is 416.2171. δ_H, 0.00 (6H, s, Si(C*H*$_3$)$_2$), 0.85 (9H, s, SiC(C*H*$_3$)$_3$), 2.82 (1H, s, O*H*), 6.28 (1H, d, J=12.5, H-2), 6.59 (1H, d, J=12.5, H-3), 6.61 (1H, s, H-2′), 6.61 (1H, d, J=7.6 H-4′), 6.71 (1H, d, J=7.8Hz, H-6′), 7.01 (1H, t, J=7.7Hz, H-5′), 7.15 (2H, complex m, *Ph*), 7.23 (4H, t, J=7.2Hz, *Ph*), 7.37 (4H, d, J=7.1Hz, *Ph*). δ_C, ppm, -4.6 (Si(*C*H$_3$)$_2$), 18.1 (Si*C*(CH$_3$)$_3$), 25.6 (SiC(*C*H$_3$)$_3$), 79.5 (C-1), 119.3 (C-2), 120.3 (C-3), 121.9 (C-2′), 126.5 (*Ph*), 127.0 (*Ph*), 128.2 (*Ph*), 129.2 (C-6′), 129.4 (C-4′), 137.9 (C-5′), 138.2 (C-1′), 147.8 (*Ph*), 155.5 (C-3′). *m/z* (EI), 416(M$^+$,10), 400(33), 359(20), 211(27), 263(15), 191(61), 105(100), 91(15). *m/z* (CI), 417(M+H$^+$,2), 399(100), 359(2), 105(6), 91(2). ν_{max} (cm^{-1}), 3567 (O-H), 3061-2712 (C-H), 1597, 1578, 1486. λ_{max} (MeOH), 207.7nm (ε, 36400), 255.2nm (ε, 11714).

Preparation of (Z)-*3-(3'-hydroxyphenyl)-1,1-diphenyl-prop-2-en-1-ol* (**23d**)

To a round bottomed flask (250ml) containing a magnetic follower, was added **22d** (0.205g, 0.49x10^{-3} mol) and CsF (0.075g, 0.49x10^{-3} mol) in methanol (50ml). The reaction was stirred for 18 hours, concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50ml), dried over $MgSO_4$,

filtered and evaporated under vacuum. The product (**23d**) (0.15g, $0.49x10^{-3}$ mol, 100%) was obtained as a pale yellow oil.

Observed mass = 302.1307. Calc. for $C_{21}H_{18}O_2$ is 302.1307. δ_H, 2.97 (1H, s, O*H*), 6.24 (1H, d, J=12.5Hz, H-2), 6.47 (1H, d, J=7.9Hz, H-4'), 6.51 (1H, s, H-2'), 6.54 (1H, d, J=12.5Hz, H-3), 6.59 (1H, d, J=7.5Hz, H-6'), 6.92 (1H, t, 7.4Hz, H-5'), 7.12 (2H, t, J=7.5Hz, *Ph*), 7.19 (4H, t, J=7.5Hz, *Ph*), 7.32 (4H, d, J=8.4Hz, *Ph*). δ_C, ppm, 80.0 (C-1), 114.8 (C-2), 115.8 (C-3), 120.9 (C-2'), 126.6 (*Ph*), 127.2 (*Ph*), 128.6 (*Ph*), 129.4 (C-6'), 129.7 (C-4'), 137.6 (C-5'), 138.3 (C-1'), 147.4 (*Ph*) 155.5 (C-3'). *m/z* (EI), 207(2), 119(8), 105(100), 91(16), 77(42). *m/z* (CI), 302(M^+,1), 285(100), 105(12). λ_{max} (MeOH), 211.4nm, (ε, 16874), 250.7nm, (ε, 6116).

*Preparation of 6-hydroxy-8a-methoxy-2,2-diphenyl-*2H,6H-*dihydrochromen-6-one* (**24d**)

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower was added **23d** (0.848g, $2.81x10^{-3}$ mol), in dry methanol (30ml), and PIDA (1.81g, $5.62x10^{-3}$ mol) was added with good stirring. The solution was stirred for 12 minutes then concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2. The product (**24d**) (0.52g, $1.57x10^{-3}$ mol, 56%) was obtained as a yellow solid from CH_2Cl_2.

Observed mass = 330.126. Calc. for $C_{22}H_{18}O_3$ is 330.1256. *m/z* (EI), 330(M^+,12), 300(20), 223(41), 105(80), 84(100), 77(24), 49(80). *m/z* (CI), 331(M+H^+,4), 301(100), 105(10). ν_{max} (cm^{-1}), 3062-2937 (C-H), 1665 (C=O). λ_{max} (MeOH), 212.4nm (ε, 3346), 310.4nm (ε, 1385). See Tables 1 and 2 for ^1H and ^{13}C nmr spectra.

*Preparation of 6-hydroxy-2,2-diphenyl-*2H-*chromene* (**32d**)

To a dry round bottomed flask (100ml) under nitrogen, fitted with a septum and a magnetic follower, was added **24d** (0.144g, $4.36x10^{-4}$ mol) in dry CH_2Cl_2 (10ml), and then DIBAL-H (1M solution in CH_2Cl_2) (0.48ml, $4.36x10^{-4}$ mol) was added with vigorous stirring. The mixture was stirred for 2.5 hours before the addition of 2M HCl (10ml), after which it was stirred for a further hour, washed with water (2 x 50ml), dried over $MgSO_4$, filtered and evaporated to dryness. The residue was separated by flash chromatography on neutral silica with CH_2Cl_2, to give **32d** (0.115g, $308x10^{-4}$ mol, 88%) as a brown oil.

Observed mass = 300.1150. Calc. of $C_{21}H_{16}O_2$ is 300.1150. *m/z* (EI), 300(M^+,18), 284(5), 207(11), 223(16), 183(15), 137(20), 121(10), 105(70), 91(30), 84(100), 77(43). *m/z* (CI), 301(M+H^+,100), 285(80), 200(75), 183(92), 167(40), 146(60). ν_{max} (cm^{-1}), 3227 (O-H), 3061-2856 (C-H). λ_{max} (MeOH), 221.2nm (ε, 34680), 267.4nm (ε, 10440), 334.4nm (ε, 5280). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

Preparation of 1-phenylprop-2-yn-1-ol (**20e**)

To a round bottomed flask (250ml) under nitrogen, fitted with a pressure equalising dropping funnel

(100ml), a septum and a magnetic follower, was added distilled benzaldehyde (5.3g, 0.05mol), in dry THF (20ml). The dropping funnel was filled with ethynylmagnesium chloride (0.5M in THF) (100ml, 0.05mol), and the solution was added slowly to the stirred mixture. After the addition was complete the mixture was stirred for a further 30 minutes, before addition of 2M HCl (25ml, 0.05mol), then stirred for 20 minutes, concentrated under vacuum, dissolved into CH_2Cl_2 (100ml), washed with water (2 x 50ml), dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by flash chromatography on silica using CH_2Cl_2, to give **20e** (5.43g, 0.041mol, 82%), as a brown oil.

Observed mass = 132.0575. Calculated for C_9H_8O is 132.0575. δ_H, 2.56 (1H, d, J=2.3Hz, H-3), 3.58 (1H, s, O*H*), 5.31 (1H, d, J=2.3, H-1), 7.2-7.3 (3H, complex m, *Ph*), 7.44 (2H, d, J=6.1, *Ph*). δ_C, ppm, 64.1 (C-1), 75.0 (C-3), 83.8 (C-2), 126.8 (*Ph*), 128.5 (*Ph*), 128.7 (*Ph*), 140.2 (*Ph*). *m/z* (EI), 132(M^+,100), 115(56), 89(12), 77(50), 53(22). *m/z* (CI), 132(M^+,100),115(30). ν_{max} (cm^{-1}), 3293 (O-H), 3088-3034 (C-H), 2119 (C C). λ_{max} (MeOH), 220.1nm (ε, 988), 252.5nm (ε, 162), 258.3nm (ε, 187), 264.1nm (ε, 148).

*Preparation of 3-(3′-*tert*-butyldimethylsilyloxyphenyl)-1-phenylprop-2-yn-1-ol* (**21e**)

To a round bottomed flask (250ml) containing a magnetic follower, was added **20e** (13.77g, 0.040mol), 1-phenylprop-2-yn-1-ol (5.2g, 0.040mol), $Pd(PPh_3)_2Cl_2$ (280mg), CuI (76mg,) in di-*iso*-propylamine (50ml) and dichloromethane (150ml). A water condenser was then attached to the top of the flask, and the stirred solution was heated under reflux for 18 hours before the solution was allowed to cool to room temperature, quenched with 2M HCl (40ml), washed with distilled water (2 x 50ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash chromatography on silica with CH_2Cl_2, to give **21e** (12.19g, 0.036mol, 70%) as a brown oil.

δ_H, 0.17 (6H, s, $Si(CH_3)_2$), 0.97 (9H, s, $SiC(CH_3)_3$), 3.10 (1H, d, J=4.7Hz, O*H*), 5.60 (1H, d, J=4.7Hz, H-1), 6.79 (1H, d, J=8.0Hz, H-4′), 6.95 (1H, s, H-2′), 7.05 (1H, d, J=7.7Hz, H-6′), 7.12 (1H, t, J=7.8Hz, H-5′), 7.28 (1H, d, J=7.1Hz, *Ph*), 7.33 (2H, t, J=7.6, 6.85Hz, *Ph*), 7.54 (2H, d, J=7.2Hz, *Ph*). δ_C, ppm, -4.5 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 64.8 (C-1), 86.4 (C-2), 89.0 (C-3), 120.9 (C-4′), 123.3 (C-2′), 123.7 (C-1′), 125.2 (C-6′), 126.4 (*Ph*), 128.4 (*Ph*), 128.7 (*Ph*), 129.5 (C-5′), 140.8 (*Ph*), 155.5 (C-3′). ν_{max} (cm^{-1}), 3330 (O-H), 3000-2800 (C-H), 2200 (C C). λ_{max} (MeOH), 224.2nm (ε, 10740), 237.6nm (ε, 10816), 254.4nm (ε, 10440), 285.8nm (ε, 3042), 292.9nm (ε, 2891).

Preparation of (Z)*-3-(3′-tert-butyldimethylsilyloxyphenyl)-1-phenylprop-2-en-1-ol* (**22e**)

To a dry round bottomed flask (100ml) under nitrogen at 0°C, fitted with a septum and a magnetic follower, was added titanocene dichloride (0.069g, $2.76x10^{-4}$ mol) and *iso*-butylmagnesium chloride (3.2ml, $5.52x10^{-3}$ mol) in dry diethyl ether (20ml), and the mixture stirred for 10 minutes. To a second dry round bottomed flask (100ml) under nitrogen, fitted with a septum, was added **21e** (1g, $2.76x10^{-3}$ mol), in dry diethyl ether (30ml), and the solution added to the reaction mixture through a double ended needle. The

mixture was then raised to room temperature, and stirred for 1 hour before the careful addition of distilled water (10ml). The stirring was continued for a further hour, before the mixture was washed with water (2 x 50ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The product (**22e**) (0.093g, $2.73x10^{-3}$ mol, 99%), was obtained as a brown oil.

Observed mass = 340.1859. Calc. for $C_{21}H_{28}O_2Si$ is 340.1861. δ_H, 0.19 (6H, s, $Si(CH_3)_2$), 1.00 (9H, s, $SiC(CH_3)_3$), 1.29 (1H, s, O*H*), 5.67 (1H, d, J=9.3Hz, H-1), 5.93 (1H, dd, J=9.3, 11.5Hz, H-2), 6.64 (1H, d, J=11.5Hz, H-3), 6.80 (1H, d, J=8.0Hz, H-4′), 6.83 (1H, s, H-2′), 6.94 (1H, d, J=7.6Hz, H-6′), 7.23 (1H, t, J=7.8Hz, H-5′), 7.33 (1H, t, J=7.1Hz, *Ph*), 7.40 (2H, t, J=7.1Hz, *Ph*), 7.67 (2H, d, J=7.0Hz, *Ph*). δ_C, ppm, -4.3 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.7 ($SiC(CH_3)_3$), 70.1 (C-1), 119.26 (C-2), 120.4 (C-3), 121.9 (C-2′), 126.3 (*Ph*), 127.7 (*Ph*), 128.5 (*Ph*), 129.3 (C-6′), 131.1 (C-4′), 133.2 (C-5′), 137.7 (C-1′), 143.1 (*Ph*), 155.6 (C-3′). *m/z* (EI), 340(M^+,45), 323(5), 265(42), 249(12), 235(8), 191(33), 115(100), 105(31), 91(42), 75(73). *m/z* (CI), 340(M^+,6), 323(100). ν_{max} (cm^{-1}), 3363 (O-H), 3063-2859 (C-H). λ_{max} (MeOH), 216.8nm (ε, 1539), 245.7nm (ε, 917), 284.3nm (ε, 250).

Preparation of (Z)-3-(3′-hydroxyphenyl)-1-phenyl-prop-2-en-1-ol (**23e**)

To a round bottomed flask (100ml) containing a magnetic follower, was added **22e** (4.106g, 0.012mol) and CsF (1.836g, 0.012mol) in methanol (20ml). The reaction was stirred for 14 hours, concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50ml), dried over $MgSO_4$, filtered, evaporated under vacuum, and the residue purified by flash chromatography on silica using gradient elution with CH_2Cl_2 and EtOAc. The product (**23e**) (2.402g, 0.010mol, 86%) was obtained as a pale brown oil.

Observed mass = 226.0994. Calc. for $C_{15}H_{14}O_2$ is 226.0994. δ_H, 5.4 (1H, s, O*H*), 5.5 (1H, d, 9.4Hz, H-1), 5.7 (1H, dd, J=9.4, 11.4Hz, H-2), 6.4 (1H, d, J=11.4Hz, H-3), 6.7 (1H, d, J=8.45Hz, H-4′), 6.7 (1H, d, J=7.9Hz, H-6′), 6.8 (1H, s, H-2′), 7.1 (1H, t, 7.9Hz, H-5′), 7.18 (1H, t, J=7.0Hz, *Ph*), 7.23 (2H, t, J=6.65Hz, *Ph*), 7.28 (2H, d, J=6.9Hz, *Ph*), 9.3 (1H, s, O*H*). δ_C, ppm, 70.3 (C-1), 114.6 (C-2), 115.6 (C-3), 121.1 (C-2′), 126.5 (*Ph*), 127.6 (*Ph*), 128.6 (*Ph*), 129.6 (C-6′), 131.2 (C-4′), 132.5 (C-5′), 137.6 (C-1′), 142.7 (*Ph*) 155.7 (C-3′). *m/z* (EI), 226(M^+,51), 209(30), 131(21), 121(100), 105(80), 91(35), 77(55). *m/z* (CI), 226(M^+,8), 209(100), 105(3). λ_{max} (cm^{-1}), 220.0nm (ε, 6109), 224.8nm (ε, 6177), 244.9nm (ε, 4981), 289.6nm (ε, 1080).

*Preparation of 6-hydroxy-8a-methoxy-2-phenyl-*2H,6H*-dihydrochromen-6-one* (**24e**)

To a dry round bottomed flask (100ml) under nitrogen, fitted with a septum and a magnetic follower, was added **23e** (1.177g, $5.2x10^{-3}$ mol), in dry methanol (70ml). To the stirred solution was added PIDA (3.15g, $10.4x10^{-3}$ mol). The solution was stirred for 30 minutes before concentrating under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2, to yield **24e** (0.310g, $1.28x10^{-3}$ mol, 25%) as a brown oil, ratio of isomers = 11:6.

Observed mass = 254.0943. Calc. for $C_{16}H_{14}O_3$ is 254.0943. *m/z* (EI), 254(M^+,1), 223(8), 165(12), 152(8), 139(8), 105(100), 91(8), 77(21). *m/z* (CI), 272($M+NH_4^+$,3), 255($M+H^+$,33), 223(100). ν_{max} (cm^{-1}), 3062-2853 (C-H), 1666 (C=O). λ_{max} (MeOH), 217.3nm (ε, 13721), 309.6nm (ε, 7605). See Tables 1 and 2 for ^1H and ^{13}C nmr spectra.

*Preparation of 6-hydroxy-2-phenyl-*2H*-chromene* (**32e**)

To a dry round bottomed flask (100ml) fitted with a septum and a magnetic follower and flushed with nitrogen was added **24e** (0.31g, $1.28x10^{-3}$ mol) in dry CH_2Cl_2 (15ml), and then DIBAL-H (1M solution in CH_2Cl_2) (1.28ml, $1.28x10^{-3}$ mol) was added with vigorous stirring. The mixture was stirred for 1 hour before the addition of 2M HCl (10ml), after which it was stirred for a further 30 minutes, washed with water (2 x 20ml), dried over $MgSO_4$, filtered and evaporated to dryness. The residue was separated by flash chromatography on neutral silica with CH_2Cl_2, to give **32e** (0.28g, $1.25x10^{-3}$ mol, 98%) as a brown oil.

Observed mass for $M+H^+$ = 225.0916. Calc. for $C_{15}H_{13}O_2$ is 225.0916. *m/z* (EI), 224(M^+,80), 223(100), 207(5), 165(15), 147(30), 84(20). *m/z* (CI), 225($M+H^+$,100). ν_{max} (cm^{-1}), 3389 (O-H), 3062-2851 (C-H). λ_{max} (MeOH), 213.4nm (ε, 26365), 232.0nm (ε, 26141), 331.3nm (ε, 3248). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

Preparation of (E)*-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol* (**20f**)

To a round bottomed flask (100ml) under nitrogen, fitted with a pressure equalising dropping funnel (100ml), a septum and a magnetic follower was added geranylacetone (0.96g, $5x10^{-3}$ mol), in dry THF (20ml). The dropping funnel was filled with ethynylmagnesium chloride (0.5M in THF) (10ml, $5x10^{-3}$ mol), and the solution was added slowly to the stirred mixture. After addition was complete the mixture was stirred for a further hour, followed by addition of 2M HCl (2.5ml, $5x10^{-3}$ mol), and further stirring for 30 minutes. The mixture was concentrated under vacuum, and the residue was dissolved in CH_2Cl_2 (20ml), washed with water (2 x 20ml), dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by flash chromatography on silica using gradient elution with pet. spirit (bp 30-40°) and CH_2Cl_2, to give **20f** (0.855g, $3.88x10^{-3}$ mol, 76%), as a brown oil.

Observed mass of $M+NH_4^+$ = 238.2171. Calc. for $C_{15}H_{28}ON$ is 238.2171. δ_H, 1.49 (3H, s, C*H*$_3$), 1.59 (3H, s, C*H*$_3$), 1.64 (3H, s, C*H*$_3$), 1.67 (3H, s, C*H*$_3$), 1.72 (2H, complex m, H-5 or 9), 1.98 (2H, t, J=7.9Hz, H-4 or 8), 2.06 (2H, t, J=7.3Hz, H-4 or 8), 2.23 (2H, complex m, H-5 or 9), 2.45 (1H, s, H-1), 2.67 (1H, s, O*H*), 5.08 (1H, t, J=6.8Hz, H-6 or 10), 5.17 (1H, t, J=6.6Hz, H-6 or 10). δ_C, ppm, 16.0, 17.6 (2 x *C*H$_3$), 23.4 (C-4), 25.6 (C-12), 26.6 (C-8), 29.7 (*C*H$_3$), 39.6, 43.1 (C-5, 9), 68.1 (C-3), 71.4 (C-1), 87.7 (C-2), 123.6, 124.2 (C-6, 10), 131.3, 135.9 (C-7, 11). *m/z* (EI), 205(4), 187(12), 136(30), 121(23), 105(62), 91(45), 77(15), 69(100). *m/z* (CI), 238($M+NH_4^+$,72), 220(M^+,30), 203(100), 137(22), 121(17). ν_{max} (cm^{-1}), 3396 (O-H), 2974-2858 (C-H). λ_{max} (MeOH), 207.3nm (ε, 7106).

Preparation of (E)-*1-(3'*-tert-*butyldimethylsilyloxyphenyl)-3,7,11-trimethyldodeca-6,10-dien-1-yn-3-ol* (**21f**)

To a round bottomed flask (250ml) containing a magnetic follower, was added **19** (7.1g, 0.0318mol), **20f** (3.502g, 0.0159mol), $Pd(PPh_3)_2Cl_2$ (11mg), CuI (30mg,) in di-*iso*-propylamine (25ml) and dichloromethane (150ml), and the solution stirred at room temperature for 18 hours before adding 2M HCl (40ml). After stirring for a further 0.5 hours the mixture was washed with distilled water (2 x 40ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash chromatography on silica with CH_2Cl_2, to give **21f** (4.1g, $9.6x10^{-3}$ mol, 61% based on the alcohol) as a brown oil.

Observed mass for $M+H-H_2O$ = 409.2925. Calc. for $C_{27}H_{41}OSi$ is 409.2925. δ_H, 0.19 (6H, s, $Si(CH_3)_2$), 0.98 (9H, s, $SiC(CH_3)_3$), 1.57 (3H, s, CH_3), 1.60 (3H, s, CH_3), 1.67 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.79 (2H, t, J=7.8Hz, H-5 or 9), 2.00 (2H, t, J=7.8Hz, H-4 or 8), 2.07 (2H, t, J=7.0Hz, H-4 or 8), 2.23 (2H, complex m, H-5 or 9), 5.09 (1H, t, J=6.9Hz, H-6 or 10), 5.23 (1H, t, J=6.7Hz, H-6 or 10), 6.79 (1H, dd, 8.1, 2.46Hz, H-4'), 6.90 (1H, t, J=2.2Hz, H-2'), 7.02 (1H, d, 7.7Hz, H-6'), 7.15 (1H, t, J=7.9Hz, H-5'). δ_C, ppm, -4.4 ($Si(CH_3)_2$), 16.1, 17.7 (2 x CH_3), 18.2 ($SiC(CH_3)_3$), 23.8 (C-4), 25.6 ($SiC(CH_3)_3$), 25.7 (C-12), 26.6 (C-8), 29.9 (CH_3), 39.7, 43.5 (C-5, 9), 68.9 (C-3), 83.4 (C-2), 92.5 (C-1), 120.5 (C-2'), 123.2, 123.8 (C-6, 10), 124.2 (C-6'), 124.9 (C-4'), 129.3 (C-5'), 131.5, 136.4 (C-7, 11), 155.4 (C-3'). *m/z* (EI), 339(100), 299(73), 215(20), 187(10), 175(80), 149(48), 109(13), 69(72). *m/z* (CI), 427($M+H^+$,2), 409(100). ν_{max} (cm^{-1}), 3406 (O-H), 2959-2859 (C-H). λ_{max} (MeOH), 210.3nm (ε, 81043), 241.3nm (ε, 37433), 251.5nm (ε, 38019), 285.2nm (ε, 4260).

Preparation of (Z,E)-*1-(3'*-tert-*butyldimethylsilyloxyphenyl)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol* (**22f**)

To a dry round bottomed flask (250ml) fitted with a septum and a magnetic follower, and flushed with nitrogen was added titanocene dichloride (0.23g, $9.29x10^{-4}$ mol) and *iso*-butylmagnesium chloride (25ml, $9.29x10^{-3}$ mol) in dry diethyl ether (50ml), and the mixture stirred for 10 minutes. To a second dry round bottomed flask (100ml) under nitrogen, fitted with a septum, was added **21f** (3.96g, $9.29x10^{-3}$ mol), in dry diethyl ether (50ml), and the solution added to the reaction mixture through a double ended needle. The mixture was then stirred for 1 hour before the careful addition of distilled water (40ml). The stirring was continued for a further 0.5 hours, before the mixture was washed with water (2 x 50ml), dried over $MgSO_4$, filtered and concentrated under vacuum. The product (**22f**) (3.584g, $8.37x10^{-3}$ mol, 90%), pure as indicated by all the physical data, was obtained as a brown oil.

Observed mass for $M+H^+$ = 429.3189. Calc. for $C_{27}H_{45}O_2Si$ is 429.3189. δ_H, 0.15 (6H, s, $Si(CH_3)_2$), 0.94 (9H, s, $SiC(CH_3)_3$), 1.27 (3H, s, CH_3), 1.56 (3H, s, CH_3), 1.57 (2H, t, J=8.0Hz, H-4 or 8), 1.57 (3H, s, CH_3), 1.63 (3H, s, CH_3), 1.77 (O*H*), 1.92 (2H, t, J=7.0Hz, H-4 or 8), 2.02 (4H, t, J=7.8Hz, H-5, 9), 5.07 (2H, complex m, H-6, 10), 5.59 (1H, d, J=12.75Hz, H-2), 6.39 (1H, d, J=12.76Hz, H-1), 6.67 (1H, dd, 8.0, 1.64Hz, H-4'), 6.81 (1H, s, H-2'), 6.86 (1H, d, 7.6Hz, H-6'), 7.10 (1H, t, J=7.7Hz, H-5'). δ_C, ppm, -4.4 ($Si(CH_3)_2$),

16.0, 17.7 (2 x CH_3), 18.2 ($SiC(CH_3)_3$), 22.9 (C-4), 25.7 ($SiC(CH_3)_3$), 25.8 (C-12), 26.7 (C-8), 29.1 (CH_3), 39.7, 43.5 (C-5, 9), 74.5 (C-3), 118.8 (C-2), 120.6 (C-1), 122.0 (C-2′), 124.3, 124.3 (C-6, 10), 128.0 (C-6′), 129.1 (C-4′), 131.2 (C-5′), 138.5, 138.9 (C-7, 11), 155.3 (C-3′). *m/z* (EI), 327(6), 277(18), 259(10), 217(10), 203(12), 189(14), 177(8), 149(15), 109(5), 91(4), 69(100). *m/z* (CI), 429($M+H^+$,1) 411(100), 317(20), 261(15). ν_{max} (cm^{-1}), 3592, 3454 (O-H), 2961-2859 (C-H). λ_{max} (MeOH), 208.3nm (ε, 86211), 246.5nm (ε, 20972), 266.1nm (ε, 9905), 281.1nm (ε, 4769).

Preparation of (Z,E)-*1-(3′-hydroxyphenyl)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol* **(23f)**

To a round bottomed flask (250ml) containing a magnetic follower, was added **22f** (3.086g, $7.2x10^{-3}$ mol) and CsF (1.096g, $7.2x10^{-3}$ mol) in methanol (30ml). The reaction was stirred for 18 hours, concentrated under vacuum, and the residue dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50ml), dried over $MgSO_4$, filtered, and evaporated under vacuum to give **23f** (2.2g, $7.0x10^{-3}$ mol, 97%), pure as indicated by all the physical data, as a pale brown oil.

Observed mass for $M+H^+$ = 315.2324. Calc. for $C_{21}H_{31}O_2$ is 315.2324. δ_H, 1.34 (3H, s, CH_3), 1.59 (6H, s, 2 x CH_3), 1.62 (2H, t, J=6.9Hz, H-4 or 8), 1.67 (3H, s, CH_3), 1.97 (2H, t, J=8.2Hz, H-4 or 8), 2.06 (4H, complex m, H-5, 9), 5.08 (1H, t, J=7.0Hz, H-6 or 10), 5.10 (1H, t, J=7.3Hz, H-6 or 10), 5.62 (1H, d, J=12.7Hz, H-2), 6.45 (1H, d, J=12.7Hz, H-1), 6.66 (1H, dd, 8.1, 2.19Hz, H-4′), 6.79 (1H, d, J=7.5Hz, H-6′), 6.85 (1H, s, H-2′), 7.12 (1H, t, J=7.8Hz, H-5′). δ_C, ppm, 16.0, 17.7 (2 x CH_3), 22.9 (C-4), 25.7 (C-12), 26.7 (C-8), 28.9 (CH_3), 39.7, 43.6 (C-5, 9), 75.3 (C-3), 114.5 (C-2), 116.0 (C-1), 120.7 (C-2′), 124.0, 124.3 (C-6, 10), 128.4 (C-6′), 129.3 (C-4′), 131.4 (C-1′), 135.5, 138.7 (C-7, 11), 137.7 (C-5′), 155.9 (C-3′). *m/z* (EI), 213(8), 185(12), 159(13), 145(100), 127(20), 107(40), 91(25, 77(15), 69(95). *m/z* (CI), 315($M+H^+$,1) 297(100). ν_{max} (cm^{-1}), 3343 (O-H), 2968-2730 (C-H). λ_{max} (MeOH), 204.8nm (ε, 29950), 246.1nm (ε, 4952), 284.0nm (ε, 1389).

Preparation of (E)-*8a-methoxy-2-methyl-2-(4′,8′-dimethylnona-3′,7′-diene)*-2H,6H-*dihydrochromen-6-one* **(24f)**

To a dry round bottomed flask (100ml) under nitrogen, fitted with a septum and a magnetic follower, was added **23f** (0.12g, $3.82x10^{-4}$ mol), in dry methanol (20ml). To the stirred solution was added PIDA (0.246g, $7.64x10^{-4}$ mol). The solution was stirred for 35 minutes before it was concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2, to yield **24f** (0.09g, $2.63x10^{-4}$ mol, 69%) as a brown oil, with an isomer ratio of 3:1.

Observed mass for $M+H^+$ = 343.2273. Calc. for $C_{22}H_{31}O_3$ is 343.2273. *m/z* (EI), 191(20), 175(15), 161(100), 132(18), 105(12), 91(15), 69(65). *m/z* (CI), 343($M+H^+$,20), 311(100), 161(40). ν_{max} (cm^{-1}), 2968-2858 (C-H), 1667 (C=O). λ_{max} (MeOH), 209.1nm (ε, 18114), 314.4nm (ε, 11837). See Tables 1 and 2 for ^1H

and ^{13}C nmr spectra.

Preparation of (E)-6-*hydroxy-2-methyl-2-(4',8'-dimethylnona-3',7'-dienyl)*-2H-*chromene* (**32f**)

To a dry round bottomed flask (50ml) fitted with a septum and a magnetic follower and flushed with nitrogen was added **24f** (0.47g, $1.17x10^{-3}$ mol) in dry CH_2Cl_2 (30ml), and then DIBAL-H (1M solution in CH_2Cl_2) (1.17ml, $1.17x10^{-3}$ mol) was added with vigorous stirring. The mixture was stirred for 1 hour before the addition of 2M HCl (5ml), after which it was stirred for a further 30 minutes, washed with water (2 x 20ml), dried over $MgSO_4$, filtered and evaporated to dryness. The residue was separated by flash chromatography on neutral silica with CH_2Cl_2, to give **32f** (0.3g, 82%) as a brown oil.

Observed mass for $M+H^+$, = 313.2168. Calc. for $C_{21}H_{29}O_2$ is 313.2168. *m/z* (EI), 312(M^+,4), 161(100). *m/z* (CI), 330($M+NH_4^+$,40), 313($M+H^+$,100), 231(25), 161(78). ν_{max} (cm^{-1}), 3396 (O-H), 3037-2730 (C-H). λ_{max} (MeOH), 206.6nm (ε, 37270), 224.6nm (ε, 31777), 263.7nm (ε, 5953), 332.3nm (ε, 5460). See Tables 3 and 4 for ^1H and ^{13}C nmr spectra.

Preparation of cis-*4-(3'*-tert-*Butyldimethylsilyloxyphenyl)-2-methyl-3,4-oxiranylbutan-2-ol* (**25a**)

A dry round bottomed flask (50ml) was charged with a magnetic follower, fitted with a septum and flushed three times with nitrogen. **24a** (0.245g,8.548 x 10^{-3} mol) in dry CH_2Cl_2 (10ml) was added by syringe and kept at 0°C, and to this solution was added a solution of *m*-chloroperbenzoic acid (1.475g,8.548 x 10^{-3} mol) in dry CH_2Cl_2(3ml) at 0°C *via* a double ended needle. The reaction mixture was stirred under nitrogen at 0°C for 2 hours and precipitated *m*-chlorobenzoic acid was removed by filtration, the precipitate washed with CH_2Cl_2 (2 x 10ml) and the combined filtrates dried ($MgSO_4$). Any remaining *m*-chloroperbenzoic acid was precipitated using $Ca(OH)_2$ (0.2g) and the precipitate removed by filtration. The filtrate was concentrated under vacuum to yield a yellow oil which was purified by flash chromatography on neutral silica using CH_2Cl_2 as eluent. The product **25a**, (1.703g, 7.671 x 10^{-3}mol, 67%) was obtained as a colourless oil.

Observed mass = 308.1808. Calc. for $C_{17}H_{28}SiO_3$ is 308.1808. δ_H, 0.20(6H,s, Si(CH_3)$_2$) , 0.98 (9H,s, SiC(CH_3)$_3$), 1.04 (3H, s, CCH_3) , 1.26 (3H, s, CCH_3), 1.55 (1H, s, O*H*), 3.16 (1H, d, J=4.4Hz, H-3), 4.11 (1H, d, J=4.4Hz, H-4), 6.76 (1H, d, J=7.3Hz, H-4'or 6'), 6.86(1H, s, H-2'), 6.96 (1H, d, J=7.6Hz, H-4' or 6'),7.20 (1H, t, J=7.8Hz, H-5'). δ_c, ppm, -4.4 (Si(CH_3)$_2$), 18.2 (SiC(CH_3)$_3$), 25.6 (SiC(CH_3)$_3$), 25.8 (CCH_3), 28.1 (CCH_3), 57.5(C-3), 64.9(C-4), 69.6(C-2), 117.9(C-2'), 119.1(C-6'), 119.4(C-4'), 129.4(C-5'), 136.8(C-1'), 155.7(C-3'). *m/z* (EI), 308(M^+,7), 291(8), 237(53), 193(47), 179(43), 151(90). ν_{max}(cm^{-1}) 3446(O-H), 3021,2861 (C-H). λ_{max}($CHCl_3$) 242.8nm (ε=1106), 273.5nm (ε=1781).

Preparation of cis-*4-(3'-hydroxyphenyl)-2-methyl-3,4-oxiranylbutan-2-ol* (**26a**)

To a round bottomed flask (100ml) containing a magnetic follower was added **25a** (0.321g, 1.042 x 10^{-3} mol) and CsF (0.159g,1.042 x 10^{-3} mol), in methanol (50ml). The reaction mixture was stirred for 8 hours,

concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50 ml), dried over $MgSO_4$ and concentrated under vacuum to yield a yellow oil. The product was purified by flash chromatography on neutral silica, using gradient elution with CH_2Cl_2 and EtOAc. The product **26a** (0.180g, 0.928 x 10^{-3}mol, 88%) was obtained as a pale yellow oil.

Observed mass = 194.0943. Calc. for $C_{12}H_{14}O_3$ is 194.0943. δ_H ppm 1.10(3H, s, C*H*$_3$), 1.29 (3H, s, C*H*$_3$) , 2.02 (1H, s, O*H*), 3.17(1H, d, J= 4.42Hz,H-3), 4.14 (1H, d, J=4.4Hz, H-4), 6.69 (1H, d, J=8.2Hz, H-4′ or 6′) , 6.88 (1H, d, J=7.5Hz, H-4′ or 6′), 6.92 (1H, s, H-2′), 6.96(1H, s, O*H*), 7.18 (1H, t, J=7.8Hz, H-5′). δ_C ppm 25.7 (C*C*H$_3$), 28.2 (C*C*H$_3$), 57.8 (C-3), 64.9 (C-4), 70.1 (C-2), 113.2 (C-6′), 114.9 (C-4′), 117.9 (C-2′), 129.8 (C-5′), 136.5 (C-1′), 156.3 (C-3′). *m/z* (EI) 194 (M^+,2), 177 (100) , 161 (10), 137 (70), 123 (10), 107(15). *m/z* (CI) 212(M+NH_4^+, 60), 177(100), 137(98). ν_{max}(cm^{-1}) 3413 (O-H), 3058, 2984 (C-H). λ_{max}(MeOH) 223.2 (ε= 922), 276.9 (ε= 761)

Preparation of rel(3R,4R,8aS)-8a-methoxy-2,2-dimethyl-3,4-oxiranyl-6H-chroman-6-one (**34a**) and rel(*3S,4S,8aS*)-*8a-methoxy-2,2-dimethyl-3,4-oxiranyl-6H-chroman-6-one* (**35a**)

To a dry round bottomed flask (50ml) under nitrogen, fitted with a septum and a magnetic follower was added **26a** (0.203g,1.046 x 10^{-3}mol) in dry methanol (10ml) and PIDA (0.674g,2.093 x 10^{-3}mol) in dry methanol (5ml) with good stirring. The solution was stirred for 45 mins before addition of anhyd. K_2CO_3 (0.2g) to remove acetic acid. The reaction mixture was filtered, then concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2 as eluent giving **34a** (0.086g, 3.87 x 10^{-4} mol, 37%) as a yellow oil. (See Tables 5 and 6 for ^{1}H and ^{13}C nmr spectra).

m/z (EI) 191(M-OMe, 100), 163(12), 149(32) , 134(40), 121(20), 107(20). *m/z* (CI) 192(100). ν_{max} (cm^{-1}) 2981,2934 (C-H), 1670 (C=O). λ_{max} ($CHCl_3$) 230.4nm (ε= 327), 244.5nm (ε= 858). A further product, **35a** (0.024g, 1.08 x 10^{-4} mol, 10%) was also obtained as a yellow oil.(See Tables 5 and 6 for ^{1}H and ^{13}C nmr spectra).

Preparation of cis-*3-(3′*-tert-b*utyldimethylsilyloxyphenyl)-1-spirocyclohexyl-2,3-oxiranylpropan-1-ol* (**25b**)

A dry round bottomed flask (50ml) was charged with a magnetic follower, fitted with a septum and flushed three times with nitrogen. Compound **24b** (0.501g,1.509 x 10^{-3} mol) in dry CH_2Cl_2 (20ml) was added by syringe and kept at 0°C. To this solution was added a solution of *m*-chloroperbenzoic acid (0.302g,1.886 x 10^{-3} mol) in dry CH_2Cl_2 (5ml) at 0°C *via* a double ended needle. The reaction mixture was stirred under nitrogen at 0°C for 4 hours.The precipitated *m*-chlorobenzoic acid was removed by filtration, the precipitate washed with CH_2Cl_2 (2 x 10ml) and the combined filtrates dried ($MgSO_4$). Any remaining *m*-chloroperbenzoic acid was precipitated using Na_2CO_3 (0.2g) and the precipitate removed by filtration. The filtrate was concentrated under vacuum to yield a yellow oil which was purified by flash chromatography on

neutral silica using CH_2Cl_2 as eluent. The product **25b**, (0.309g,0.888 x 10^{-3}mol, 59%) was obtained as a pale yellow oil.

Observed mass = 348.2121. Calc. for $C_{20}H_{32}SiO_3$ is 348.2121. δ_H, 0.19(6H,s, Si(CH_3)$_2$), 0.98 (9H, s, SiC(CH_3)$_3$), 134,1.47,1.56,1.67 (10H, complex m, (CH_2)$_5$, 3.11 (1H, d, J=4.4Hz, H-2), 4.09 (1H, d, J=4.4Hz, H-3), 6.74 (1H, dd , J=2.4Hz, J=8.1Hz, H- 4'or 6'), 6.87(1H, d,J=2.4Hz, H-2'), 7.00 (1H, d, J= 7.6Hz, H-4' or 6'),7.21 (1H, t, J=7.8Hz, H-5'). δ_c, ppm, -4.4 (SiC(CH_3)$_2$), 18.2 (SiC(CH_3)$_3$), 25.6 (Si C(CH_3)$_3$), 21.1, 21.13, 25.5, 34.0, 36.7 ((CH_2)$_5$), 57.3(C-2), 64.7(C-3), 69.9(C-1), 117.9(C-2'), 119.0(C-6'), 119.3(C-4'), 129.5(C-5'), 137.2(C-1'), 155.7(C-3'). *m/z* (CI), 366(M+NH_4^+10), 348(M^+,1) 331(10), 268(20), 251(100), 116(35). ν_{max}(cm^{-1}) 3560,3440(O-H), 2900,2840 (C-H). λ_{max}($CHCl_3$) 240.4nm (ε=491), 273.5nm (ε=1234).

Preparation of cis-*3-(3'-hydroxyphenyl)-1-spirocyclohexyl-2,3-oxiranylpropan-1-ol* (**26b**)

To a round bottomed flask (50ml) containing a magnetic follower was added **25b** (1.411g,4.243 x 10^{-3} mol) and CsF (0.645g,4.243 x 10^{-3} mol), in methanol (25ml). The reaction mixture was stirred for 8 hours, concentrated under vacuum, dissolved in CH_2Cl_2 (50ml),washed with water (2 x 50 ml), dried ($MgSO_4$), filtered and concentrated under vacuum to yield a yellow oil. The mixture was purified by flash chromatography on neutral silica, using gradient elution with CH_2Cl_2 and EtOAc. The product **26b** (0.943g, 4.031 x 10^{-3} mol, 95%) was obtained as a pale yellow oil.

Observed mass M+NH_4^+ = 252.1600. Calc. for $C_{14}H_{22}O_3N$ is 252.1600. δ_H ppm 1.25,1.49,1.77 (10H, complex m, (CH_2)$_5$, 3.12(1H, d, J= 4.4Hz,H-2), 4.12 (1H, d, J=4.4Hz, H-3), 6.13(1H, s, OH), 6.70 (1H, d, J=8.1Hz, H-4' or 6') , 6.92 (1H, d, J=7.6Hz, H-4' or 6'), 6.96 (1H, d,J=1.4Hz, H-2'), 7.19 (1H, t, J=7.8Hz, H-5'). δ_C ppm 21.1, 21.1, 25.5, 33.9, 36.7 ((CH_2)$_5$) , 57.3 (C-2), 64.6 (C-3), 70.4 (C-1), 113.1 (C-6'), 114.8 (C-4'), 118.0 (C-2'), 129.8 (C-5'), 137.1 (C-1'), 156.2 (C-3'). *m/z* (CI) 252 (M+NH_4^+,20) , 234 (M^+,5), 217 (55), 201 (10), 154(14), 137(50), 116(100). ν_{max}(cm^{-1}) 3365 (O-H), 3016, 2935, 2839 (C-H). λ_{max}($CHCl_3$) 239.8 (ε= 126), 275.5 (ε= 345), 282.1 (ε= 318)

Preparation of rel(3R,4R,8aS)-8a-methoxy-2-spirocyclohexyl-3,4-oxiranyl-6H-chroman-6-one(**34b**) and rel(*3S,4S,8aS)-8a-methoxy-2-spirocyclohexyl-3,4-oxiranyl-6H-chroman-6-one* (**35b**)

To a dry nitrogen flushed round bottomed flask (50ml), fitted with a septum and a magnetic follower was added **26b** (0.760g, 3.248 x 10^{-3}mol) in dry methanol (20ml) and PIDA (2.092g, 6.496 x 10^{-3}mol) in dry methanol (10ml) with good stirring. The solution was stirred for 1 hour before addition of anhyd. K_2CO_3 (0.4g) to remove acetic acid. The reaction mixture was filtered, then concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2 as eluent giving **34b** (0.422g, 1.611 x 10^{-3} mol, 50%) as a yellow oil.(See Tables 5 and 6 for ^{1}H and ^{13}C nmr spectra).

Observed mass for M+H^+ = 263.1283. Calc. for $C_{15}H_{19}O_4$ is 263.1283. *m/z* (CI) 263 (M+H^+,8), 231

(100), 215 (20), 189 (4). $\nu_{max}(cm^{-1})$ 2937, 2860, 2829 (C-H) , 1676 (C=O). $\lambda_{max}(CHCl_3)$ 222.1nm (ε= 754), 259.4 (ε=2638). A minor product **35b** (0.129g, 4.930 x 10^{-4}mol, 15%) was also obtained as a yellow oil. (See Tables 5 and 6 for ^1H and ^{13}C nmr spectra).

Preparation of cis-*3-(3′-*tert-*butyldimethylsilyloxyphenyl)-1,1-diphenyl-2,3-oxiranylpropan-1-ol* (**25d**)

A dry round bottomed flask (50ml) was charged with a magnetic follower, fitted with a septum and flushed three times with nitrogen. **24d** (0.724g, 1.729 x 10^{-3} mol) in dry CH_2Cl_2 (20ml) was added by syringe and kept at 0°C. A solution of *m*-chloroperbenzoic acid (0.298g,1.729 x 10^{-3} mol) in dry CH_2Cl (5ml) was added at 0°C *via* a double ended needle and the reaction mixture was stirred under nitrogen at 0°C for 4 hours. The precipitated *m*-chlorobenzoic acid was removed by filtration, the precipitate washed with CH_2Cl_2 (2 x 10ml) and the combined filtrates dried ($MgSO_4$). Any remaining *m*-chloroperbenzoic acid was precipitated using Na_2CO_3 (0.2g) and the precipitate removed by filtration. The filtrate was concentrated under vacuum to yield a yellow oil which was purified by flash chromatography on neutral silica using CH_2Cl_2 as eluent. The product **25d** (0.362g,8.367 x 10^{-4} mol, 49 %) was obtained as a yellow oil.

Observed mass for $M+NH_4^+$ = 450.2464. Calc. for $C_{27}H_{36}SiNO_3$ is 450.2464. δ_H, 0.17(6H,s, $Si(CH_3)_2$) , 0.97 (9H,s, $SiC(CH_3)_3$), 3.05 (1H,s,O*H*), 3.74 (1H, d, J=2.2Hz, H-2), 4.06 (1H, d, J=2.12Hz, H-3), 6.74 (1H, d, J=1.5Hz, H-2′), 6.76 (1H, m, H-4′ or 6'), 6,85 (1H, d, J= 7.7Hz, H-4′ or 6′), 7.14 (1H, t, J=7.7Hz, H-5′), 7.15-7.79 (10H,complex m, Ph). δ_c, ppm, -4.4 ($SiC(CH_3)_2$), 18.1 ($SiC(CH_3)_3$), 25.6(Si $C(CH_3)_3$), 53.4(C-2), 67.2(C-3), 75.6(C-1), 117.3(C-2′), 118.6(C-6′), 119.8(C-4′), 126.4(Ph), 127.4(Ph), 130.0(C-5′), 132.3(Ph), 137.5(C-1′), 143.1(Ph), 145.0 (Ph), 155.8(C-3′). *m/z*(CI) 450 ($M+NH_4^+$,2), 268(10), 251(17), 183(100), 105(9). $\nu_{max}(cm^{-1})$ 3457(O-H), 3064, 3019, 2958, 2932 (C-H). $\lambda_{max}(CHCl_3)$ 231.2nm (ε=2091), 253.9nm (ε=4326).

Preparation of cis-*3-(3′-hydroxyphenyl)-1,1-diphenyl-2,3-oxiranylpropan-1-ol* (**26d**)

To a round bottomed flask (50ml) containing a magnetic follower was added **25d** (0,351g 9.27 x 10^{-4} mol) and CsF (0.141g, 9.27 x 10^{-4} mol), in methanol (25ml). The reaction mixture was stirred for 8 hours, concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 25 ml), dried over $MgSO_4$ and concentrated under vacuum to yield a yellow oil. The product was purified by flash chromatography on neutral silica, using gradient elution with CH_2Cl_2 and EtOAc. The product **26d** (0.191g,5.99 x 10^{-4} mol, 75%) was obtained as a pale yellow oil.

Observed mass of $M+NH_4^+$ = 336.1600. Calc. for $C_{21}H_{22}O_3N$ = 336.1600. δ_H ppm 2.90(1H, s ,O*H*), 3.78(1H, d, J= 2.1Hz,H-2), 4.10 (1H, d, J=2.1Hz, H-3), 5.20(1H, s, O*H*), 6.72-6.75 (2H, m, H-2′ and H-4′ or 6′) H-4′ or 6′), 6.85 (1H, d, J=7.7Hz, H-4′ or 6′), 7.17 (1H, t, J=7.03Hz, H-5′), 7.20-7.52 (10H,complex m, Ph). δ_C ppm 55.5 (C-2), 67.2 (C-3), 75.6 (C-1), 112.4 (C-6′), 115.4 (C-4′), 118.3 (C-2′), 126.3(Ph),

126.8(Ph), 126.9(Ph), 127.9(Ph), 128.3(Ph), 128.4(Ph), 128.5(Ph), 129.9 (C-5′), 138.3 (C-1′), 142.9 (Ph), 144.9 (Ph), 155.9 (C-3′). *m/z* (CI) 336 ($M+NH_4^+$,4) , 318 (M^+,4), 301 (15), 200 (30), 183(100). $\nu_{max}(cm^{-1})$ 3436 (O-H), 3020, (C-H). $\lambda_{max}(CHCl_3)$ 239.3 (ε= 1004), 276.1 (ε= 1808).

Preparation of rel(3R,4S,8aS)-3-hydroxy-4,8a-dimethoxy-2,2-diphenyl-6H-chroman-6-one (**39**)

To a dry round bottomed flask (50ml) fitted with a septum and a magnetic follower was added under nitrogen **26d** (0.170g, 5.399 x 10^{-4}mol) in dry methanol (10ml) and PIDA (0.344g, 1.068 x 10^{-3}mol) in dry methanol (5ml) with good stirring. The solution was stirred for 45 mins before addition of anhyd. K_2CO_3 (0.15g) to remove acetic acid. The reaction mixture was filtered, then concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2 as eluent. The product **39** (0.122g , 3.364 x 10^{-3} mol, 60%) was obtained as an oil.

Observed mass for M-OMe = 347.1283. Calc. for $C_{22}H_{19}O_4$ is 347.1283. *m/z* (EI) 347 (M-OMe,22), 196 (22), 183 (100), 164 (36), 77 (36). ν_{max} cm^{-1} 3464 (OH), 3061,3032, 3004,2943 (C-H), 1679 (C=O). λ_{max} (MeOH) 217.6nm (ε= 6842), 254.0 nm (ε= 2705), 277.8 nm (ε= 1876). See Tables 5 and 6 for ^1H and ^{13}C nmr spectra.

Preparation of cis-*3-(3′*-tert-*butyldimethylsilyloxyphenyl)-1-phenyl-2,3-oxiranylpropan-1-ol* (**25e**)

A dry round bottomed flask (50ml) was charged with a magnetic follower, fitted with a septum and flushed three times with nitrogen. **24e** (1.601g, 4.709 x 10^{-3} mol) in dry CH_2Cl_2 (15ml) was added by syringe and kept at 0°C. A solution of *m*-chloroperbenzoic acid (1.014g, 5.886 x 10^{-3} mol) in dry CH_2Cl_2 (10ml) was added at 0°C *via* a double ended needle and the reaction mixture stirred under nitrogen at 0°C for 2 hours. The precipitated *m*-chlorobenzoic acid was removed by filtration, the precipitate washed with CH_2Cl_2 (2 x 10ml) and the combined filtrates dried ($MgSO_4$). Any remaining *m*-chloroperbenzoic acid was precipitated using Na_2CO_3 (0.2g) and the precipitate was removed by filtration. The filtrate was concentrated under vacuum to yield a yellow oil which was purified by flash column chromatography on neutral silica using CH_2Cl_2 as eluent.The product **25e**, was obtained (0.957g, 2.688 x 10^{-3}mol, 57.1 %) as a colourless oil.

Observed mass for $M+NH_4^+$ = 374.2151. Calc. for $C_{21}H_{32}SiNO_3$ = 374.2151. δ_H, 0.20(6H,s, $Si(CH_3)_2$) , 0.99 (9H,s, $SiC(CH_3)_3$), 3.39 (1H, dd, J=4.3Hz, J=8.6Hz, H-2), 4.16 (1H, d, J=4.3Hz, H-4), 4.30 (1H, d, J= 8.6 Hz, H-1), 6.81 (1H, dd, J=2.3, 8.0Hz, H-4′or 6′), 6.84(1H, s, H-2′), 6.94 (1H, d, J= 7.6Hz, H-4′ or 6′), 7.00 (1H, t, J=7.8Hz, H-5′) 7.22-7.26 (5H, complex m, Ph) . δ_c, ppm, -4.4 ($Si(CH_3)_2$), 18.2 ($SiC(CH_3)_3$), 25.7($SiC(CH_3)_3$), 58.0(C-3), 63.3(C-4), 71.6(C-2), 118.1(C-2′), 119.4(C-6′), 119.9(C-4′), 125.9 (Ph), 128.1 (Ph), 128.3 (Ph), 128.4 (Ph), 129.4(C-5′), 129.8 (Ph), 136.3(C-1′), 139.2 (Ph) 155.8(C-3′). *m/z* (EI) 339 (8), 327 (13), 281 (42), 251 (31), 221 (100). *m/z* (CI) 374($M+NH_4^+$,4), 356($M+H^+$,2), 339(10), 251(100). $\nu_{max}(cm^{-1})$ 3420 (OH), λ_{max}(MeOH) 217.8nm (ε= 7108), 279.1nm (ε= 1230).

Preparation of cis-*3-(3'-hydroxyphenyl)-1-phenyl-2,3-oxiranylpropan-1-ol* (**26e**)

To a round bottomed flask (100ml) containing a magnetic follower was added **25e** (0.897g, 2.52 x10^{-3} mol) and CsF (0.382g, 2.52 x 10^{-3} mol) in methanol (50ml). The reaction mixture was stirred for 10 hours, concentrated under vacuum, dissolved in CH_2Cl_2 (50ml), washed with water (2 x 50 ml), dried over $MgSO_4$ and concentrated under vacuum to yield a yellow oil. The product was purified by flash chromatography on neutral silica, using gradient elution with CH_2Cl_2 and EtOAc. The product **26e** (0.601g, 2.481 x 10^{-3} mol, 98.6%) was obtained as a pale yellow oil.

Observed mass for M+H-H_2O = 225.0916. Calc. for $C_{15}H_{13}O_2$ = 225.0916. δ_H ppm 2.91(1H, s ,O*H*), 3.40(1H, dd, J=8.7Hz, J=4.04Hz, H-2), 4.03 (1H, s, O*H*), 4.12 (1H, d, J=4.4Hz, H-3), 4.39 (1H, d, J=8.7Hz, H-1), 6.70 (1H, d, J=7.6Hz, H-4′ or 6′) , 6.82 (1H, dd, J=2.4Hz, J=8.1Hz, H-4′ or 6′), 6.90-6.95 (3H, m, H-2′, H-5′, Ph), 7.18 (4H,complex m, Ph). δ_C ppm 58.1 (C-2), 63.3 (C-3), 71.6 (C-1), 112.9 (C-6′), 115.4 (C-4′), 118.8(C-2′), 125.9 (Ph), 128.2 (Ph), 128.5 (Ph), 129.8 (C-5′), 136.0 (C-1′), 138.9 (Ph), 144.9 (Ph), 156.2 (C-3′). *m/z* (CI) 260 (M+NH_4^+,4), 251 (12), 225 (70), 209 (40), 154 (23). ν_{max}(cm^{-1}) 3376 (O-H), 3066, 3032,2930 (O-H). λ_{max} (MeOH) 220.1 nm (ε= 2653), 277.9 nm (ε= 1693).

Preparation of rel(2R,3S,4S,8aS)-8a-methoxy-2-phenyl-3,4-oxiranyl-6H-chroman-6-one (**36**), rel(*2R,3S,4S,8aR*)-*8a-methoxy-2-phenyl-3,4-oxiranyl-6H-chroman-6-one* (**37**) and cis-*3-(6',6'-dimethoxy-3'-oxocyclohexa-1',4'-dienyl)-1-phenyl-2,3-oxiranyl propan-1-ol* (**38**)

To a dry round bottomed flask (100ml), fitted with a septum and a magnetic follower was added under nitrogen **26e** (0.551g, 2.274 x 10^{-3}mol) in dry methanol (15ml) and PIDA (1.465g, 4.548 x 10^{-3}mol) in dry methanol (10ml) with good stirring. The solution was stirred for 45 mins before addition of anhyd. K_2CO_3 (0.5g) to remove acetic acid. The reaction mixture was filtered, then concentrated under vacuum, and the products immediately separated by flash chromatography on neutral silica using CH_2Cl_2 as eluent to give isomers **36** and **37** (0.161g, 5.763 x 10^{-4}mol, 26.2%). Hplc showed a 3:2 ratio of isomers present. Further column chromatography on neutral silica of the mixed isomers using CH_2Cl_2 gave **36** (0.081g, 3.00 x 10^{-4} mol,13.2 %). (See Tables 5 and 6 for ^{1}H and ^{13}C nmr spectra).

Observed mass for M+H-MeOH = 239.0708. Calc. for $C_{15}H_{11}O_3$ = 239.0708 *m/z* (CI) 271 (M+H^+,5), 239 (100), 223 (7), 211 (10), 139 (20). ν_{max} (cm^{-1}) 3008,2938 (C-H), 1679 (C=O). λ_{max} (MeOH) 254.0 nm (ε= 3308) 278.7nm (ε= 1777). The minor isomer **37** was obtained in a 3:1 ratio (by ^{1}H nmr) with the major isomer (0.059g). (See Tables 5 and 6 for ^{1}H and ^{13}C nmr spectra).

Further elution of the initial column gave an additional product **38** (0.181g, 5.793 x 10^{-4} mol,26.4%) as a yellow oil. Observed mass for M+NH_4^+ = 320.1498. Calculated mass for $C_{17}H_{22}O_5N$ = 320.1498. δ_H ppm 3.01(1H, s, O*H*), 3.19 (3H, s, OCH_3), 3.23 (3H, s, OCH_3), 3.56 (1H, dd, J=4.5Hz, J= 8.5Hz, H-2), 3.98 (1H, d, J= 4.5Hz, H-3), 4.36 (1H, d, J=8.5Hz ,H-1), 6.40 (1H, d, J= 10.0Hz, H-5′), 6.43 (1H, s, H-2′), 6.89 (1H, d, J=

10.0 Hz, H-4′), 7.25-7.38 (5H, complex m, Ph). δ_C ppm 50.3 (OCH_3), 51.4 (OCH_3), 55.2 (C-2), 60.4 (C-3), 70.2 (C-1), 94.2 (C-6′), 126.8 (Ph), 127.1 (Ph), 128.1 (Ph), 128.2 (Ph), 131.5 (C-5′), 139.3 (Ph), 142.1 (C-2′), 152.2 (C-1′), 184.3 (C-3′). *m/z* (CI) 320 ($M+NH_4$,3), 271 (54), 255 (20), 239 (100), 225 (10), 184 (53), 167 (55) ν_{max} (cm^{-1}) 3452 (OH), 3063,3011,2943 (C-H), 1677 (C=O). λ_{max} (MeOH) 208.5 (ε= 4543), 228.4 (ε= 3006), 275.0 (ε=926).

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