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The Preparation of Substituted 3,4-Dihydro-1(2*H*)-naphthalenones from Benzocyclobutenones *via* Sequential Thermal Electrocyclic Reactions

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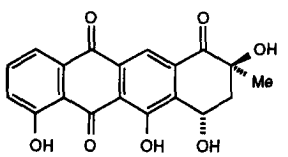
Abstract: 1-Alkenylbenzocyclobutenols, prepared from benzocyclobutenones *via* the addition of alkenyl Grignard reagents or the addition of alkynyllithium reagents followed by (*E*)-selective reduction, undergo successive thermal 4π and 6π electrocyclisations to give substituted 3,4-dihydro-1(2*H*)-naphthalenones. An analogous sequence gave 3,4-dihydro-1(2*H*)-anthracenone from naphtho[*b*]cyclobuten-1(2*H*)-one.

Substituted 3,4-dihydro-1(2*H*)-naphthalenones (α-tetralones) and their linear fused homologues have various synthetic uses, especially in the context of the anthracyclines,[1,2] where they feature both as intermediates[3] and targets, *e.g.* 8-demethoxyaranciamycinone **1**,[4] and the aureolic acid anticancer agents,[5] *e.g.* olivomycin and chromomycin A_3, which are based on the tricyclic aglycones olivin **2** and chromomycinone **3** respectively.[6] In



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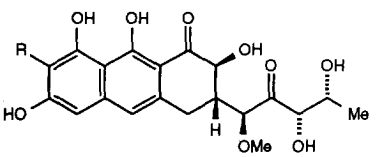
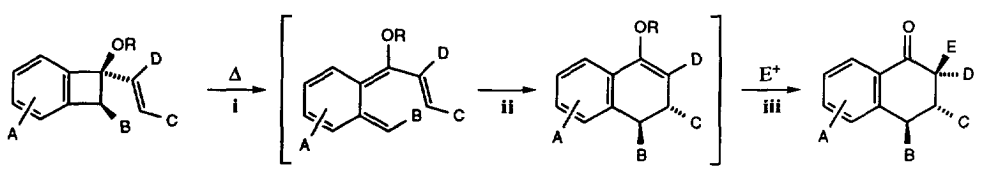


2 R = H
3 R = Me

seeking a route to structures of this type, we were attracted by the potential of a reaction sequence in which an alkenylbenzocyclobutenol **4** might be transformed thermally into an *o*-quinone dimethide **5** and thence the enol derivative **6**, treatment of which with an electrophile E^+ should produce the substituted α-tetralone **7** (Scheme 1). The stereochemical outcome of this sequence, whose prototype was described by Sammes and coworkers over 20 years ago,[7,8] can be predicted on the basis of the control elements of each step. In step **i**, the OR group



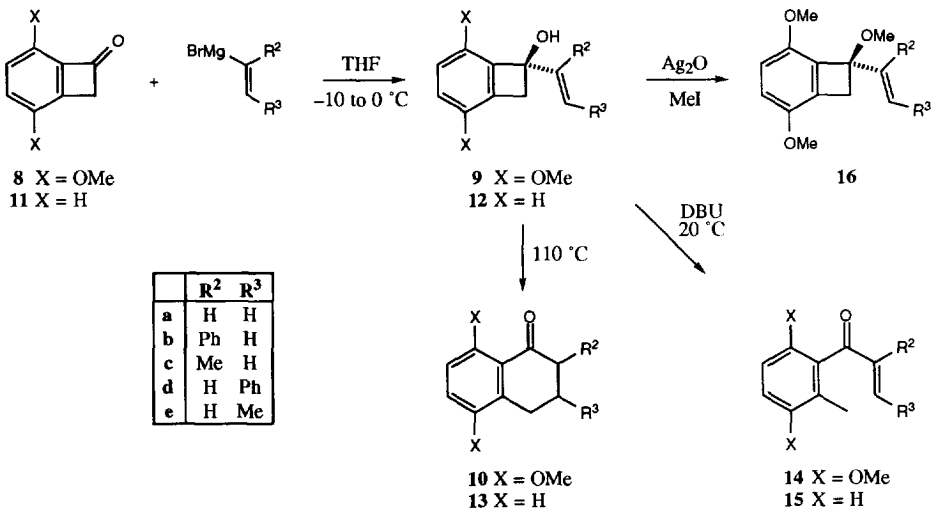
4 **5** **6** **7**

SCHEME 1

will prefer 'outward' conrotation during thermal electrocyclic ring-opening;[7,9] in step **ii**, the electrocyclic process is of the disrotatory (6π) type, which will give rise to a *trans* relationship between B and C;[10] and in step **iii** the assumption is made that the electrophile E^+ will tend to avoid the substituent C while approaching the enol derivative **6**. We decided to evaluate the scope of this sequence and herein describe our results in detail.[11]

We first studied the reactions of simple alkenyl Grignard reagents with 3,6-dimethoxybenzocyclobutenone **8**,[12] which was selected as a model because of the need to establish that *peri* substituents would not suppress the electrocyclic ring-opening reactions. Treatment of the ketone **8** with vinylmagnesium bromide gave the expected carbinol **9a** in good yield, while analogous reactions produced the α-styryl and isopropenyl analogues **9b** and **9c** (Scheme 2 and Table 1). Heating the benzocyclobutenols **9a–c** under reflux in toluene for 2–3 days produced the desired tetralones **10a–c** in good yields.

The addition of Grignard reagents derived from β-bromostyrene or 1-bromoprop-1-ene to the ketone **8** produced neither of the desired carbinols. The β-styryl reagent gave the tetralone **10d** directly in 56% yield, while the propenyl system gave rise to a complex mixture of products. Although the latter result can be partly attributed to the presence of both isomers of the Grignard reagent,[13] the destabilising influence of the β-substituents in the carbinols **9d** and **9e** can be rationalised in terms of their effects on the electron density at the α-position, to which the stability of the four-membered ring is particularly sensitive.[14] Similar trends were observed in the analogous reactions of benzocyclobutenone **11**,[15] with the α-styryl and isopropenyl carbinols **12b** and **12c** proving readily accessible, while attempts to prepare the β-styryl compound **12d** were abortive. Electrocyclic ring-expansions of the carbinols **12** were much more rapid than those of **9**, being complete within 2 h. We presume that this difference in rate is at least partly a manifestation of steric inhibition of ring-opening to the planar *o*-quinone dimethide species (*cf.* **5**) by the *peri* substituents in the dimethoxy series.



8 X = OMe
11 X = H

9 X = OMe
12 X = H

16

	R^2	R^3
a	H	H
b	Ph	H
c	Me	H
d	H	Ph
e	H	Me

10 X = OMe
13 X = H

14 X = OMe
15 X = H

SCHEME 2

Under the conditions used for the Grignard addition reactions, *in situ* ring-opening of the intermediate alkoxy species was a potential pitfall.[8f,16] However, careful analysis of the crude Grignard addition products by 300 MHz ^{1}H n.m.r. spectroscopy revealed only traces of the putative ring-opened products **14** and **15**, samples of which were obtained by treating the carbinols with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in

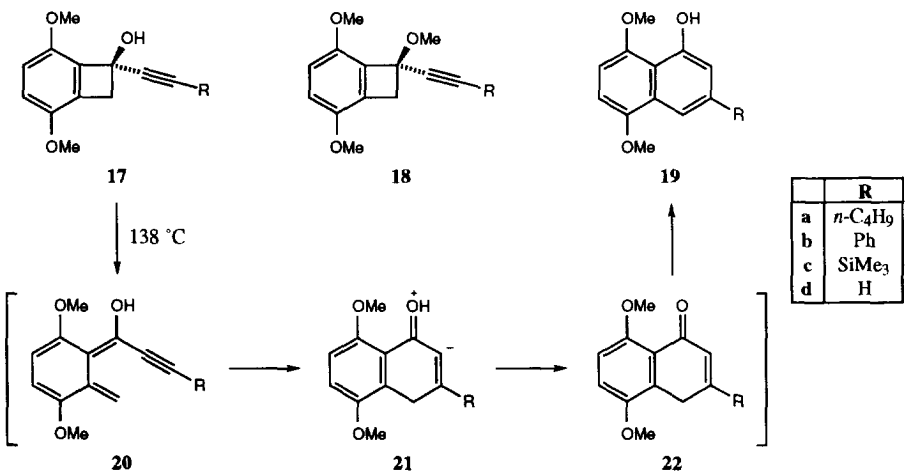
chloroform. The base-induced ring-opening reactions also showed an interesting variation in rate, which we assume is the result of the electronic effect of the alkenyl substituent.[17] Because of their potential sensitivity to base, the method of choice for protecting the carbinols **9a–c** was methylation using iodomethane and silver oxide, which gave the corresponding ethers **16** in good yields.

TABLE 1 The Preparation and Reactions of Alkenylbenzocyclobutenols **9** and **12**

			PREPARATION		*THERMOLYSIS*			*BASE TREATMENT*			*METHYLATION*	
Ketone	R^2	R^3	Product	Yield (%)	Time (h)	Product	Yield (%)	Time (d)	Product	Yield (%)	Product	Yield (%)
8	H	H	**9a**	88	56	**10a**	90	2	**14a**	100	**16a**	85
8	Ph	H	**9b**	75	48	**10b**	71	3	**14b**	99	**16b**	84
8	Me	H	**9c**	91	48	**10c**	65	8	**14c**	99	**16c**	80
8	H	Ph	**9d**	(–)†		**10d**	56		–		–	
8	H	Me	**9e**	(–)‡		–			–		–	
11	H	H	**12a**	80	0.5	**13a**	96	6	**15a**	97	–	
11	Ph	H	**12b**	80	2	**13b**	91	2	**15b**	100	–	
11	Me	H	**12c**	87	2	**13c**	94	6	**15c**	97	–	
11	H	Ph	**12d**	(–)‡		–			–		–	

† The carbinol **9d** was not isolated. Rearrangement to the tetralone **10d** occurred *in situ*.
‡ The reaction produced a complex mixture from which no product was isolated.

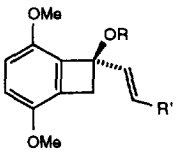
Alkynyllithium reagents were also found to add cleanly to the benzocyclobutenone **8** without inducing ring-opening. Thus reacting **8** with 1-hexynyllithium in tetrahydrofuran (THF) - hexane at –78 °C gave the alcohol **17a** in 77% yield. Analogous procedures gave the alcohols **17b** and **17c** in good yield. The alcohols **17a–c** could also be methylated using iodomethane/silver(I) oxide, and the ether **18c** was desilylated using tetra-*n*-butylammonium fluoride in THF (88% yield) to obtain the parent ethynyl compound **18d**. On heating at 110 °C for 60 h, the carbinol **17a** was smoothly transformed into the naphthol **19a** (65%), a possible sequence of events being shown in Scheme 3. Similar treatment of **17b** gave the naphthol **19b** (68%). The silyl compound **17c** appeared to behave similarly, but the product proved labile and was not characterised.



	R
a	*n*-C_4H_9
b	Ph
c	$SiMe_3$
d	H

SCHEME 3

In working towards an approach to 3-substituted cyclenones related to olivin **2**, we sought a more flexible route from the ketone **8** to β-substituted 1-alkenylbenzocyclobuten-1-ol derivatives **23**, and reasoned that an aldehyde **24** might serve as the carbonyl component of various olefination protocols which could yield the desired *trans*-1-alkenylbenzocyclobutenes. Attempts to prepare **24** *via* ozonolysis of **9a** or **16a** followed by a dimethylsulphide work-up gave no identifiable products. When the ozonolysis product from **16a** was worked up with sodium borohydride, the hydroxymethyl compound **25** was obtained in good yield, suggesting that the earlier problems might derive from the product rather than the process. In an alternative approach, a Peterson sequence was used to prepare **26** and hence **27** (81% over two steps), and the latter was transformed into the diol **28** by treatment with osmium(VIII) oxide/*N*-methylmorpholine oxide. Attemped oxidation of **28** to **24a** under Swern conditions was unsuccessful. Finally, the dithiane **29** was prepared from **8** by reaction with 2-lithio-1,3-dithiane (77% yield), but attempts to effect dethioacetalisation to **24a** were fruitless.



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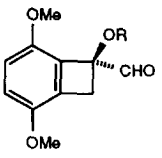
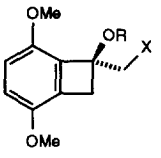
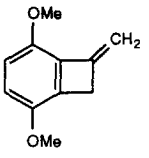


24a R = H
b R = Me



	R	X
25	Me	OH
26	H	$SiMe_3$
28	H	OH



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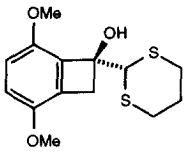
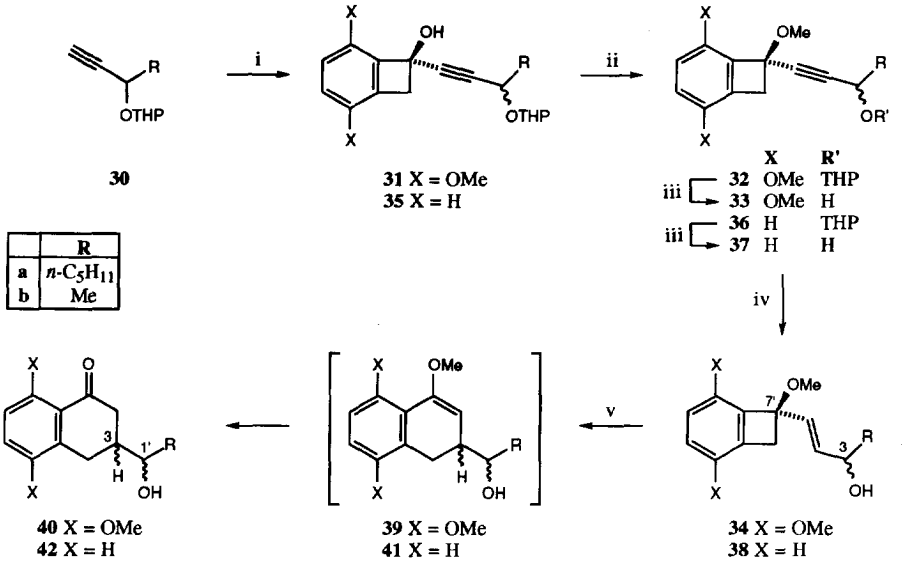


29

The inaccessibility of **24a** is in retrospect unsurprising for two reasons. Firstly, it is now well established that the activation barrier to thermal electrocyclic ring-opening of a substituted 2-cyclobutene is influenced by the electronic effects of the 1- and 4-substituents, and that the effects of the hydroxyl and formyl groups are both strong and complementary, the hydroxyl group preferring to undergo 'outward' conrotation while the formyl group is a very powerful 'inward' conrotator.[9,18] The combined effect of these two groups at C-1 can therefore be expected to render **24a** highly susceptible to electrocyclic ring-opening. Secondly, a structure **24a** is also set up to undergo ring expansion to a hydroxyindanone, with the concomitant release of ring strain.[19]

A more successful route to β-substituted 1-alkenylbenzocyclobuten-1-ols was developed using the (*E*)-selective hydride reduction of an alkynol[20] as the key step (Scheme 4). Addition of the lithium derivative of the tetrahydropyranyl (THP) ether **30a** of 1-octyn-3-ol to the benzocyclobutenone **8** produced the carbinol **31a** in good yield. Methylation then gave the ether **32a**, which was hydrolysed to the corresponding alkynol **33a**, and the latter was reduced to the (*E*)-alkenol **34a** using sodium bis(2-methoxyethoxy)aluminium hydride (SMEAH, Red-Al®). Analogous reaction sequences efficiently provided the homologues **34b**, **38a** and **38b** (Table 2).

Heating **34a** in toluene at 110 °C led to the disappearance of the starting material in 24 h, and gave rise to a mixture which was presumed to contain the enol ether **39a**. Accordingly, brief acid treatment followed by chromatography gave the desired tetralone **40a**, but only in modest yield. Similar treatment of **34b** appeared to give a complex mixture, and no products were isolated. Initially the thermal ring expansions of **38a** and **38b**, which were effected at 76 °C, also gave disappointing yields of the respective tetralones **42**, but significant improvement was brought about by increasing the vigour of the acid treatment of the intermediate enol ethers **41**, whereupon the formation of the tetralone became almost quantitative and purification by chromatography became unnecessary. The low yields in the initial experiments can thus be attributed to incomplete hydrolysis of the intermediate methyl enol ethers **39** and **41**.



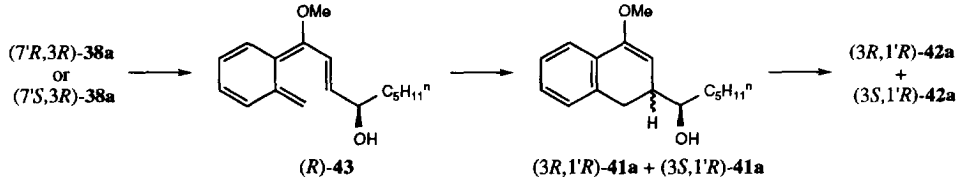
SCHEME 4 *Reagents:* i, *n*BuLi, hexane - THF, 20 °C; then –78 °C, **8** or **11**; then –50 °C, 0.5 h; ii, MeI, Ag_2O, 24 h; iii, MeOH, H^+, 24 h; iv, Red-Al®, toluene, THF, 0–20°C, 2 h; v, toluene or tetrachloromethane, reflux, 24 h, then H_3O^+.

TABLE 2 The Preparation and Thermolysis of Benzocyclobutenyl Ethers **34** and **38**†

		PREPARATION OF INTERMEDIATES								*THERMOLYSIS*		
Ketone	X		Yield (%)		Yield (%)		Yield (%)		Yield (%)	Temp. (°C)	Product	Yield‡ (%)
8	OMe	**31a**	75	**32a**	83	**33a**	82	**34a**	95	110	**40a**	(38)
8	OMe	**31b**	68	**32b**	87	**33b**	86	**34b**	91	110	**40b**	(–)
11	H	**35a**	83	**36a**	87	**37a**	85	**38a**	94	76	**42a**	97(43)
11	H	**35b**	85	**36b**	85	**37b**	86	**38b**	94	76	**42b**	93(52)

† All products were isolated and used as mixtures of diastereoisomers.
‡ The yields in parentheses were later ascribed to incomplete hydrolysis of the enol ethers **39** and **41**.

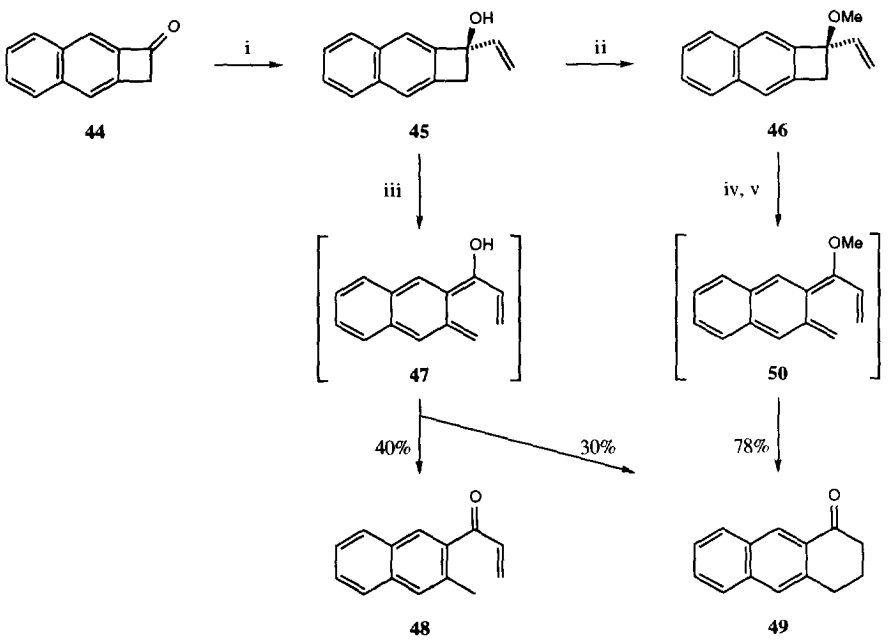
In each of the sequences shown in Scheme 4 it was apparent (from 300 MHz ^{1}H n.m.r. spectra) that the products were formed as mixtures of diastereoisomers, and those of **38a** were separated (into enantiomer pairs) by HPLC. Each diastereoisomer of **38a**, when thermolysed, gave rise to essentially the same (*ca.* 1:1) mixture of diastereoisomers of **42a**, confirming that the ring closure step is not significantly influenced by the original configuration of the stereogenic centre on the cyclobutene ring. This is consistent with the proposed sequence of electrocyclic reactions, and in particular the intermediacy of **43**, *en route* to **42a** (Scheme 5).



SCHEME 5 (All compounds are racemic; one diastereoisomeric series is represented)

Before this work could be applied to the preparation of anthracenones analogous to the core of olivin **2**, it was necessary to establish that the electrocyclic reaction sequence would operate with naphtho[*b*]cyclobutenes. This was not guaranteed since the thermal ring-opening of a naphtho[*b*]cyclobutene involves the disruption of a complete naphthalene π-system, and the activation barrier to *o*-quinone dimethide formation might therefore be expected to be higher than that of monocyclic or naphtho[*a*]-fused analogues.[11b,21]

In order to address this issue, we prepared the naphthocyclobutenes **45** and **46** and studied their thermal electrocyclic ring opening reactions (Scheme 6). The addition of vinylmagnesium bromide to **44**[22] in THF at −10 °C gave the crystalline alcohol **45** (67%), methylation of which gave the ether **46** as an oil. Thermolysis of the alcohol **45** at 110 or 140 °C resulted in its disappearance within two hours, the major products being the enone **48** and the known anthracenone **49**,[23] which were isolated by chromatography. The formation of a significant amount of **48**, which is formally derived from **47** *via* a 1,5-hydrogen shift, has no analogy in the monocyclic series and is possibly a manifestation of the higher energy (greater diradical character) of dienes of the naphtho[*b*]-fused series. It does not seem likely that the ground-state (*Z*)-isomer of **47** is the major precursor of **48**.[7] As expected, the formation of **48** was suppressed by the simple expedient of *O*-methylation. When the methyl ether **46** was heated at 110 °C for 8 h, acid hydrolysis of the intermediate enol ether gave the desired anthracenone **49** cleanly and in good yield.



SCHEME 6 *Reagents:* i, CH_2=CHMgBr (67%); ii, MeI, Ag_2O (86%); iii, toluene, 110 °C, 2 h; iv, toluene, 110 °C, 8 h; v, HCl–H_2O, 2 h

The efficient transformation of the naphthocyclobutene **46** into the ketone **49** suggests that the sequence of reactions shown in Scheme 4 might indeed form the basis of a synthetic approach to olivin **2** and related structures. We are currently seeking routes to highly oxygenated naphtho[*b*]cyclobutenones for use in such a context, and will describe our findings in due course.

EXPERIMENTAL

All compounds are racemic. Melting points were determined using an Electrothermal apparatus and are uncorrected. Unless otherwise stated, i.r. spectra were of thin films on sodium chloride plates, recorded on a Perkin-Elmer 1710FT spectrometer. N.m.r. spectra were measured at 300 MHz (^{1}H) or 75.47 MHz (^{13}C) for solutions in deuteriochloroform with tetramethylsilane as the internal standard, on a Bruker AC300 instrument unless otherwise indicated. Mass spectra were measured on a Finnegan 4500 (low resolution EI; ammonia CI), or Kratos Concept S1 (high resolution ammonia CI) instruments. Data for most of the peaks of intensity <20% of that of the base peak are omitted. Preparative high performance liquid chromatography (HPLC) was carried out using a Gilson system comprising a Model 131 refractive index (RI) detector, Model 303 pump and Model 803C manometric module, fitted with a Rheodyne 7125 loop (175 μl).

Starting materials and solvents were routinely purified by conventional techniques.[24] Organic solutions were dried using anhydrous magnesium sulphate and concentrated by rotary evaporation. Analytical thin layer chromatography (t.l.c.) was carried out on Camlab Polygram SIL G/UV$_{254}$ plates. Preparative (column) chromatography was carried out using 60H silica gel (Merck 9385) and the flash technique.[25] Compositions of solvent mixtures are quoted as ratios of volume. 'Petroleum' refers to a light petroleum fraction, b.p. 60–80 °C, unless otherwise stated. 'Ether' refers to diethyl ether.

1-Ethenyl-3,6-dimethoxybenzocyclobuten-1-ol **9a**

The following is the typical procedure used for the addition of Grignard reagents to benzocyclobutenones. In a 25 ml 3-necked flask was placed dry THF (3 ml) to which was added vinylmagnesium bromide solution (1.0 M, 2.7 ml, 2.7 mmol) and the mixture was stirred in an ice/acetone bath at –10 °C. The solution was observed to go slightly cloudy. A solution of 3,6-dimethoxybenzocyclobutenone **8**[12] (0.10 g, 0.56 mmol) in THF (6 ml) was added slowly dropwise, during which a deep wine-red coloration was observed. The solution was then stirred for 1.5 h at –10 °C, cooled to –50 °C in an acetone/CO_2 bath, and treated slowly with cold saturated aqueous ammonium chloride (10 ml), whereupon the red coloration was immediately discharged. Ether (20 ml) was added and the mixture was allowed to warm to 0 °C before separation of the phases was carried out. The aqueous phase was then extracted with more ether (4 x 5 ml) and the combined ethereal extract was washed successively with water (10 ml), sodium bicarbonate (5% w/w; 5 ml), and saturated aqueous sodium chloride (10ml). The extract was then dried over magnesium sulphate and evaporated to yield a colourless oil, which was purified by flash chromatography, eluting with petroleum - ethyl acetate (8:1). The eluate was evaporated to yield the *title compound* **9a** (0.102 g, 88%) as a colourless oil, which on cooling gave a solid, m.p. 54–56 °C (petroleum - ethyl acetate 4:1) (Found: C, 70.04; H, 6.96. $C_{12}H_{14}O_3$ requires C, 69.89; H, 6.84%); ν_{max} (film) 3401, 2963, 1494, 1433, 1260, 1050, 801 and 666 cm^{-1}; δ (300 MHz) 2.50 (1 H, br s, OH), 3.33 (1 H, d, *J* 13.7 Hz, 2-H), 3.48 (1 H, d, *J* 13.7 Hz, 2-H), 3.78 (3 H, s, OCH_3), 3.79 (3 H, s, OCH_3), 5.16 (1 H, dd, *J* 1.1, 10.6 Hz, 2'-H), 5.39 (1 H, dd, *J* 1.1, 17.2 Hz, 2'-H), 6.19 (1 H, dd, *J* 10.6, 17.2 Hz, 1'-H), 6.64 (1 H, d, *J* 8.9 Hz, ArH), 6.70 (1 H, d, *J* 8.9 Hz, ArH); m/z (CI) 207 (M + H$^+$, 43%), 189 (100); (EI) 206 (M$^+$, 100), 205 (31), 191 (63), 179 (20), 176 (24), 175 (35), 151 (38), 121 (50), 91 (35), 77 (38); R_f (petroleum - ethyl acetate 4:1) 0.33.

3,6-Dimethoxy-1-(1-phenylethenyl)benzocyclobuten-1-ol **9b**

1-Phenylethenylmagnesium bromide, prepared from α-bromostyrene (1.82 ml, 2.57 g, 14 mmol) and Mg turnings (0.34 g, 14 mmol), was reacted with 3,6-dimethoxybenzocyclobutenone **8** (0.50 g, 2.8 mmol) as described above. Formation of the Grignard reagent was initiated by sonication (using an ultrasonic bath) for 0.5 h. There was no coloration on addition of the electrophile at –78 °C. Work-up and evaporation gave a yellow oil, which was chromatographed using petroleum - ethyl acetate (8:1) as eluent. The main fraction gave the *title compound* **9b** (0.595 g, 75%) as a colourless oil (*M*$^+$, 282.1255. $C_{18}H_{18}O_3$ requires 282.1256); ν_{max} (neat) 3435, 2928, 2835, 1496, 1433, 1257, 1068, 1047, 1022, 987, 916, 887, 808, 780, 760 and 701

cm^{-1}; δ (300 MHz) 7.55–7.45 (2 H, m, 2",6"-H), 7.35–7.25 (3 H, m, 3",4",5"-H), 6.73 (1 H, d, *J* 9.1 Hz, 4-H or 5-H), 6.725 (1 H, d, *J* 9.1 Hz, 5-H or 4-H), 5.46 (1 H, d, *J* 0.8 Hz, 2'-H), 5.42 (1 H, d, *J* 0.8 Hz, 2'-H), 3.86 (3 H, s, OCH_3), 3.75 (3 H, s, OCH_3), 3.61 (1 H, d, *J* 13.4 Hz, 2-H), 3.49 (1 H, d, *J* 13.4 Hz, 2-H), 2.78 (1 H, br s, OH); m/z (CI) 282 (23%), 265 (100).

3,6-Dimethoxy-1-(1-methylethenyl)benzocyclobuten-1-ol **9c**

Isopropenylmagnesium bromide, prepared from 2-bromopropene (0.15 ml, 204 mg, 1.69 mmol) and Mg turnings (0.041 g, 1.69 mmol), was reacted with 3,6-dimethoxybenzocyclobutenone **8** (0.10 g, 0.56 mmol) as described above. Formation of the Grignard reagent was initiated by vigorous stirring or by sonication (using an ultrasonic bath) for 0.5 h. There was a pink coloration on addition of the electrophile at –10 °C. After work up and evaporation a white oil remained, and was chromatographed using petroleum - ethyl acetate (8:1) as eluent. The main fraction contained the *title compound* **9c** (0.113 g, 91%) (*M* + H, 221.1177. $C_{13}H_{17}O_3$ requires 221.1178), ν_{max} (neat) 3436, 2948, 1495, 1433, 1257, 1134, 1051, 1054, 988, 905 and 807 cm^{-1}; δ (300 MHz) 6.69 (1 H, d, *J* 9.0 Hz, ArH), 6.64 (1 H, d, *J* 9.0 Hz, ArH), 5.10 (1 H, narrow m, 2'-H), 4.90 (1 H, narrow m, 2'-H), 3.77 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.49 (1 H, d, *J* 13.8 Hz, 2-H), 3.26 (1 H, d, *J* 13.8, 2-H), 2.59 (1 H, br s, OH), 1.79 (3 H, narrow m, 1'-CH_3); m/z (CI) 238 (M + NH_4^+, 32%), 221 (65), 220 (26), 219 (23), 203 (100); (EI) 220 (M^+, 40%), 205 (36), 203 (100), 191 (21).

3,4-Dihydro-5,8-dimethoxy-1(2H)-naphthalenone **10a**

A solution of 1-ethenyl-3,6-dimethoxybenzocyclobuten-1-ol **9a** (60 mg, 0.29 mmol) in dry toluene (15 ml) under N_2 was heated under reflux for 56 h. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (2:1), afforded a yellow oil which solidified on standing and was recrystallised from petroleum (40–60°) to give the *title compound* **10a** (54 mg, 90%) as white crystals, m.p. 61–63 °C (lit.[26] 63 °C, 60–61 °C) (*M* + H, 207.1017. $C_{12}H_{15}O_3$ requires 207.1021); ν_{max} (film) 3350, 2927, 1682, 1586, 1476, 1435, 1272, 1086 and 1032 cm^{-1}; δ (300 MHz) 6.94 (1 H, d, *J* 9.0 Hz, 6-H), 6.75 (1 H, d, *J* 9.0 Hz, 7-H), 3.81 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 2.83 (2 H, t, *J* 6.1 Hz, 4-H_2), 2.57 (2 H, t, *J* 6.4 Hz, 2-H_2), 2.00 (2 H, overlapping dt, *J* 6.1, 6.4 Hz, 3-H_2); m/z (CI) 207 (M + H^+, 100%).

3,4-Dihydro-5,8-dimethoxy-2-phenyl-1(2H)-naphthalenone **10b**

A solution of 3,6-dimethoxy-1-(1-phenylethenyl)benzocyclobuten-1-ol **9b** (0.10 g, 0.35 mmol) in dry toluene (5 ml) under N_2 was heated under reflux for 48 h. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (2:1), afforded the *title compound* **10b** (71 mg, 71%) as a yellow oil (M^+, 282.1253. $C_{18}H_{18}O_3$ requires 282.1256); ν_{max} (neat) 2933, 1676, 1586, 1494, 1434, 1263, 1078 and 804 cm^{-1}; δ (300 MHz) 7.35–7.15 (5 H, m, Ar'H), 6.97 (1 H, d, *J* 9.0 Hz, 6-H), 6.80 (1 H, d, *J* 9.0 Hz, 7-H), 3.82 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3), 3.10 (1 H, dt, *J* 5.0, 17.9 Hz, 4-H_{eq}), 2.90–2.75 (1 H, m, 4-H_{ax}), 2.40–2.30 (2 H, m, 3-H_2) (2-H signal obscured by the two methoxy signals); m/z (CI) 284 (20 %), 283 (M + H^+, 100), 282 (60), 194 (12), 179 (10), 94 (11).

3,4-Dihydro-5,8-dimethoxy-2-methyl-1(2H)-naphthalenone **10c**

A solution of 1-(1-methylethenyl)-3,6-dimethoxybenzocyclobuten-1-ol **9c** (66 mg, 0.30 mmol) in dry toluene (5 ml) under N_2 was heated under reflux for 48 h. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (2:1), afforded the *title compound* **10c** (43 mg, 65%) as a yellow oil (*M* + H, 221.1170. $C_{13}H_{17}O_3$ requires 221.1178); ν_{max} (neat) 2932, 1688, 1587, 1476, 1435, 1308, 1262, 1205, 1097, 1057, 1028, 980, 803 and 720 cm^{-1}; δ (300 MHz) 6.91 (1 H, d, *J* 9.0 Hz, 6-H), 6.75 (1 H, d, *J* 9.0 Hz, 7-H), 3.81 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.03 (1 H, dt, *J* 4.5, 18 Hz, 4-H_{eq}), 2.70 (1 H, ddd, *J* 5.2, 10.8, 18 Hz, 4-H_{ax}), 2.60–2.50 (1 H, m, 2-H), 2.15–2.05 (1 H, m, 3-H_{eq}), 1.80–1.65 (1 H, m, 3-H_{ax}), 1.17 (3 H, d, *J* 6.7 Hz, 2-CH_3); m/z (CI) 221 (M + H^+, 100%), 94 (11).

*3,4-Dihydro-5,8-dimethoxy-3-phenyl-1(2*H*)-naphthalenone* **10d**

A procedure analogous to that described above for the preparation of **9b** was followed, using β-bromostyrene (0.21 ml, 300 mg, 1.64 mmol), Mg turnings (0.041 g, 1.69 mmol), and the ketone **8** (0.10 g, 0.56 mmol). The initial formation of the β-styryl Grignard reagent was very slow and heating under reflux in the presence of a crystal of iodine was necessary. The addition of the ketone **8** was carried out –78 °C, and a deep purple coloration was observed. Work-up furnished a yellow oil which was chromatographed using petroleum - ethyl acetate (4:1) as eluent. The main fraction gave a buff coloured solid which was identified by ^{1}H n.m.r. as the *title compound* **10d** (89 mg, 56%), m.p. 163–165 °C (*M*, 282.1255. $C_{18}H_{18}O_3$ requires 282.1256); ν_{max} (film) 2923, 1678, 1586, 1494, 1476, 1434, 1260, 1081, 804 and 666 cm^{-1}; δ (300 MHz) 7.4–7.2 (5 H, m, Ar'H), 6.99 (1 H, d, *J* 9.1 Hz, 6-H), 6.81 (1 H, d, *J* 9.1 Hz, 7-H), 3.86 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.45–3.25 (2 H, m, 3-H, 4-H_{eq}), 2.9–2.7 (3 H, m, 2-H_2, 4-H_{ax}); m/z (CI) 283 (M + H$^+$, 100%); m/z (EI) 282 (M$^+$, 64%), 191 (22), 179 (100), 163 (38), 121 (27), 120 (29), 91 (63) and 77 (39).

1-Ethenylbenzocyclobuten-1-ol **12a**[7a]

Into a 25 ml 3-necked flask was placed dry THF (3 ml) to which was added vinylmagnesium bromide solution (1.0 M, 2.7 ml, 2.7 mmol) and the mixture was stirred in an ice/acetone bath at –10 °C. The solution was observed to go slightly cloudy, then a solution of benzocyclobutenone **11**[15] (0.10 g, 0.85 mmol) in THF (6 ml) was added slowly dropwise. On this addition, a pink coloration was observed and the solution stirred for 1.5 h at –10 °C. The reaction mixture was then cooled to –50 °C in an acetone/CO_2 bath and cold sat. aq. ammonium chloride (10 ml) was added slowly, whereupon the pink coloration was immediately discharged. Cold ether (20 ml) was added and the mixture allowed to warm to 0 °C before rapid separation of the phases was carried out. The aqueous phase was then extracted with ether (4 x 5 ml) and the organic extracts combined, washed with ice-cold water (10 ml), sodium bicarbonate (5% w/w, 5 ml) and then finally with saturated aqueous sodium chloride (10ml). The organic extract was dried overnight in a refrigerator, and evaporated to yield a colourless oil. This was chromatographed, eluting with petroleum - ethyl acetate (6:1), yielding two main fractions (ratio *ca.* 1:9; total 0.109 g, 88%) of α-tetralone and the title compound **12a** (*M* + NH_4, 164.1070. $C_{10}H_{14}NO$ requires 164.1075); ν_{max} (neat) 3400, 2935, 1640, 1498, 1433, 1258, 1055 and 924 cm^{-1}; δ (300 MHz) 7.3–7.1 (4 H, m, ArH), 6.18 (1 H, dd, *J* 10.6, 17.1 Hz, 1'-H), 5.34 (1 H, d, *J* 17.1 Hz, 2'-H), 5.15 (1 H, dd, *J* 1.3, 10.6 Hz, 2'-H), 3.45 (1 H, d, *J* 14.1 Hz, 2-H), 3.30 (1 H, d, *J* 14.1 Hz, 2-H), 2.45 (1 H, br s, OH); m/z (CI) 164 (M + NH_4^+, 22%), 163 (15), 147 (10), 146 (62) and 129 (100).

1-(1-Phenylethenyl)benzocyclobuten-1-ol **12b**

The method was the same as described above for **9b**, using α-bromostyrene (0.775 g, 0.55 ml, 4.24 mmol), Mg turnings (0.103 g, 4.24 mmol), and benzocyclobutenone **11** (0.10 g, 0.85 mmol). Work-up and evaporation gave a yellow oil, which was chromatographed using petroleum - ethyl acetate (8:1) as eluent. The main fraction afforded the title compound **12b** (0.150 g, 80%) as a colourless oil; ν_{max} (neat) 3392, 2923, 1599, 1494, 1459, 1391, 1209, 1152, 1051, 1029, 912 and 777 cm^{-1}; δ (300 MHz) 7.58–7.16 (4 H, m, ArH), 5.41 (1 H, narrow m, 2'-H), 5.37 (1 H, s, 2'-H), 3.66 (1 H, d, *J* 14.0 Hz, 2-H), 3.46 (1 H, d, *J* 14.0 Hz, 2-H), 2.71 (1 H, br s, OH). The constitution of **12b** was confirmed by conversion to **13b** and **15b**.

1-(1-Methylethenyl)benzocyclobuten-1-ol **12c**

The method was the same as described above for **9c**, using 2-bromopropene (0.23 ml, 0.31 g, 2.56 mmol), Mg turnings (0.061 g, 2.54 mmol), and benzocyclobutenone **11** (0.10 g, 0.85 mmol). The work-up gave a colourless oil which, after chromatography with petroleum - ethyl acetate (12:1) as eluent, yielded the title compound **12c** (0.118 g, 87%) which solidified upon cooling in a refrigerator; ν_{max} (neat) 3350, 2921, 1459, 1208, 1121, 1054, 902, 757 and 716 cm^{-1}; δ (300 MHz) 7.3–7.1 (4 H, m, ArH), 5.04 (1 H, narrow m, 2'-

H), 4.89 (1 H, narrow m, 2'-H), 3.50 (1 H, d, *J* 14.1 Hz, 2-H), 3.23 (1 H, d, *J* 14.1 Hz, 2-H), 2.52(1 H, br s, OH), 1.83 (3 H, narrow m, 1'-CH_3); m/z (CI, methane) 161 ($M + H^+$, 9%), 145 (31), 143 (100), 91 (25). The constitution of **12c** was confirmed by conversion to **13c** and **15c**.

3,4-Dihydro-1(2H)-naphthalenone **13a**[7a]

A solution of 1-ethenylbenzocyclobuten-1-ol **12a** (20 mg, 0.137 mmol) in dry toluene (10 ml) under N_2 was heated under reflux for 0.5 h, after which time none of the starting material could be detected by t.l.c. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (4:1), gave the title compound **13a** (19.2 mg, 96%) as a yellow oil; ν_{max} (neat) 3067, 2945, 1683, 1602, 1455, 1324, 1287, 1226 and 1025 cm^{-1}; δ (300 MHz) 7.99 (1 H, dd, *J* 2.0, 7.5 Hz, ArH), 7.43 (1 H, dt, *J* 2.0, 7.5 Hz, ArH), 7.24 (2 H, m, ArH), 2.93 (2 H, t, *J* 6 Hz, 2-H_2), 2.62 (2 H, t, *J* 6 Hz, 4-H_2) and 2.10 (2 H, overlapping dt, *J* 6 Hz, 3-H_2). The product was identical (n.m.r., i.r., t.l.c.) with commercial α-tetralone.

3,4-Dihydro-2-phenyl-1(2H)-naphthalenone **13b**

A solution of 1-(1-phenylethenyl)benzocyclobuten-1-ol **12b** (0.10 g, 0.45 mmol) in dry toluene (10 ml) under N_2 was heated under reflux for 0.5 h, after which time none of the starting material could be detected by t.l.c. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (4:1), gave the *title compound* **13b** (91 mg, 91%) as colourless crystals, m.p. 70–72 °C (petroleum) [lit.[27] 76–77 °C (ethanol); lit.[28] 78 °C] (*M* + NH_4, 240.1384. $C_{16}H_{18}ON$ requires 240.1388); ν_{max} (film) 3061, 3028, 2930, 1682, 1599, 1453, 1306, 1223, 1156, 1026, 896 and 759 cm^{-1}; δ (300 MHz) 8.10 (1 H, d, *J* 7.8 Hz, 8-H), 7.50 (1 H, dt, *J* 1.4, 7.4 Hz, 6-H), 7.4–7.15 (7 H, m, ArH), 3.79 (1 H, t, *J* 8 Hz, 2-H), 3.2–3.0 (2 H, m, 4-H_2), 2.45–2.35 (2 H, m, 3-H_2); m/z (CI) 240 ($M + NH_4^+$, 10%), 223 (100), 118 (28).

3,4-Dihydro-2-methyl-1(2H)-naphthalenone **13c**

A solution of 1-(1-methylethenyl)benzocyclobuten-1-ol **12c** (0.10 g, 0.62 mmol) in dry toluene (10 ml) under N_2 was heated under reflux for 2 h, after which time none of the starting material could be detected by t.l.c. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (4:1), gave the *title compound* **13c** (94 mg, 94%) as a colourless oil (*M* + NH_4, 178.1238. $C_{11}H_{16}ON$ requires 178.1232); ν_{max} (neat) 2931, 2859, 1686, 1602, 1454, 1433, 1375, 1358, 1323, 1267, 1227, 1156, 1018 and 968 cm^{-1}; δ (300 MHz) 8.02 (1 H, dd, *J* 1.3, 7.8 Hz, 8-H), 7.43 (1 H, dt, *J* 1.3, 7.5 Hz, 6-H), 7.27 (1 H, t, *J* 7.5 Hz, 7-H), 7.20 (1 H, d, *J* 7.5 Hz, 5-H), 3.1–2.9 (2 H, m, 4-H_2), 2.56 (1 H, ddd, *J* 4.5, 6.8, 12.0 Hz, 2-H), 2.25–2.10 (1 H, m, 3-H), 1.95–1.75 (1 H, m, 3-H), 1.25 (3 H, d, *J* 6.8 Hz, 2-CH_3); m/z (CI) 178 ($M + NH_4^+$, 10%), 161 (100), 131 (4), 118 (17) [lit.[29] δ 1.26 (3 H, d, *J* 7.3 Hz), 1.72–1.92 (1 H, m), 2.08–2.22 (1 H, m), 2.48–2.60 (1 H, m), 2.88–3.08 (2 H, m, benzylic), 7.16–8.04 (4 H, m)].

1-(3,6-Dimethoxy-2-methylphenyl)prop-2-en-1-one **14a**

A solution of 1-ethenyl-3,6-dimethoxybenzocyclobuten-1-ol **9a** (50 mg, 0.243 mmol) in $CDCl_3$ (1 ml) was placed into an n.m.r. tube, and the 300 MHz ^1H n.m.r. spectrum recorded. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 5% w/w in $CDCl_3$, 74 μl) was added and another spectrum recorded. The reaction was followed by n.m.r. over a period of 2 days at room temperature, after which time full conversion was observed. Some deuteration of the product was evident from the ^1H n.m.r. spectrum. The experiment was repeated in $CHCl_3$ and the product chromatographed, eluting with petroleum - ethyl acetate (12:1), to obtain the *title compound* **14a** (50 mg, 100%) as a colourless oil (*M* + H, 207.1020. $C_{12}H_{15}O_3$ requires 207.1021); ν_{max} (neat) 2932, 1665, 1598, 1481, 1260, 1086, 965, 801 and 713 cm^{-1}; δ (300 MHz) 6.78 (1 H, d, *J* 9.0 Hz, 4'-H), 6.69 (1 H, d, *J* 9.0 Hz, 5'-H), 6.55 (1 H, dd, *J* 10.4, 17.5 Hz, 2-H), 6.01 (1 H, dd, *J* 1.0, 10.4 Hz, 3-H), 5.93 (1 H, dd, *J* 1.0, 17.5 Hz, 3-H), 3.78 (3 H, s, OCH_3), 3.69 (3 H, s, OCH_3), 2.01 (3 H, s, $ArCH_3$); m/z (CI) 224 ($M + NH_4^+$, 61%), 207 (100).

1-(3,6-Dimethoxy-2-methylphenyl)-2-phenylprop-2-en-1-one **14b**

The procedure used was as described for the preparation of **14a**, starting with 3,6-dimethoxy-1-(1-phenylethenyl)benzocyclobuten-1-ol **9b** (68.5 mg, 0.243 mmol). The reaction took 3 days to reach completion, and was repeated in $CHCl_3$. The product of the latter run was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **14b** (68 mg, 99%) as a white crystalline solid, m.p. 91–93 °C (petroleum) (*M*, 282.1252. $C_{18}H_{18}O_3$ requires 282.1256); ν_{max} (nujol) 2935, 1667, 1479, 1435, 1256 and 1019 cm^{-1}; δ (300 MHz) 7.50–7.30 (5 H, m, Ph), 6.80 (1 H, d, *J* 8.9 Hz, 4'-H), 6.71 (1 H, d, *J* 8.9 Hz, 5'-H), 6.13 (1 H, s, 3-H), 5.84 (1 H, s, 3-H), 3.79 (3 H, s, OCH_3), 3.70 (3 H, s, OCH_3), 2.11 (3 H, s, $ArCH_3$); m/z (EI) 282 (M^+, 13%), 180 (100).

1-(3,6-Dimethoxy-2-methylphenyl)-2-methylprop-2-en-1-one **14c**

The procedure used was as described for the preparation of **14a**, starting with 3,6-dimethoxy-1-(1-methylethenyl)benzocyclobuten-1-ol **9c** (53.6 mg, 0.243 mmol). The reaction took 8 days to reach completion, and was repeated in $CHCl_3$. The product of the latter run was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **14c** (53 mg, 99%) as a colourless oily solid (*M*, 220.1096. $C_{13}H_{16}O_3$ requires 220.1099); ν_{max} (neat) 2936, 1668, 1479, 1437, 1324, 1255, 1083, 1025 and 800 cm^{-1}; δ (300 MHz) 6.76 (1 H, d, *J* 8.9 Hz, 4'-H), 6.67 (1 H, d, *J* 8.9 Hz, 5'-H), 5.88 (1 H, narrow m, 3-H), 5.60 (1 H, narrow m, 3-H), 3.77 (3 H, s, OCH_3), 3.67 (3 H, s, OCH_3), 2.00 (3 H, br s, 2-CH_3), 1.97 (3 H, s, $ArCH_3$); m/z (CI) 238 (M + NH_4, 66%), 221 (100).

1-(2-Methylphenyl)prop-2-en-1-one **15a**

The procedure used was as described for the preparation of **14a**, starting with 1-ethenylbenzocyclobuten-1-ol **12a** (36 mg, 0.247 mmol). The reaction took 6 days to reach completion. The product was chromatographed, eluting with petroleum - ethyl acetate (12:1), to obtain the *title compound* **15a** (35 mg, 97%) as a colourless oil (*M* + H, 147.0813. $C_{10}H_{11}O$ requires 147.0810); ν_{max} (neat) 2925, 1667, 1603, 1546, 1509, 1445 and 1023 cm^{-1}; δ (300 MHz) 7.51–7.09 (4 H, m, 3',4',5',6'-H), 6.56 (1 H, dd, *J* 10.5, 17.6 Hz, 2-H), 5.94 (1 H, narrow m, 3-H), 5.55 (1 H, s, 3-H), 2.26 (3 H, s, $ArCH_3$), 2.24 (3 H, narrow m, $ArCDH_2$) (*ca.* 30% deuteration); m/z (CI) 164 (M + NH_4, 20%), 147 (100).

1-(2-Methylphenyl)-2-phenylprop-2-en-1-one **15b**

The procedure used was as described for the preparation of **14a**, starting with the benzocyclobutenol **12b** (54 mg, 0.243 mmol). The reaction took 2 days to reach completion. The product was chromatographed, eluting with petroleum - ethyl acetate (12:1), to obtain the *title compound* **15b** (54 mg, 100%) as a colourless oil (*M* + NH_4, 240.1396. $C_{16}H_{18}NO$ requires 240.1388); ν_{max} (neat) 2925, 1665, 1599, 1495, 1446, 1212, 1019 and 977 cm^{-1}; δ (300 MHz) 7.60–7.00 (9 H, m, ArH), 6.16 (1 H, s, 3-H), 5.73 (1 H, s, 3-H), 2.45 (3 H, s, $ArCH_3$) (*ca.* 35% deuteration); m/z (CI) 240 (M + NH_4^+, 15%), 223 (100), 205 (3), 187 (18), 119 (52).

1-(2-Methylphenyl)-2-methylprop-2-en-1-one **15c**

The procedure used was as described for the preparation of **14a**, starting with the benzocyclobutenol **12c** (39 mg, 0.244 mmol). The reaction took 6 days to reach completion. The product was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **15c** (38 mg, 97%) as a colourless oil (*M* + H, 161.0961. $C_{11}H_{13}O$ requires 161.0966); ν_{max} (neat) 2925, 1669, 1601, 1548, 1514, 1445, 1261 and 1020 cm^{-1}; δ (300 MHz) 7.35–7.10 (4 H, m, ArH), 5.93 (1 H, narrow m, 3-H), 5.53 (1 H, narrow m, 3-H) 2.26 (1.5 H, s, $ArCH_3$), 2.24 (*ca.* 2 H, narrow m, $ArCH_3$ with partial deuteration) 2.00 (3 H, narrow m, 2-CH_3); m/z (CI) 178 (M + NH_4^+, 15%), 161 (85), 143 (100).

1-Ethenyl-1,3,6-trimethoxybenzocyclobutene **16a**

A mixture of iodomethane (2.0 ml, 4.56 g, 32 mmol), silver oxide (0.58 g, 2.5 mmol), and 1-ethenyl-3,6-dimethoxybenzocyclobuten-1-ol **9a** (110 mg, 0.53 mmol) was stirred under argon overnight. Ethyl acetate (5 ml) was added and the silver residues were filtered off through a plug of anhydrous magnesium sulphate. Water (5 ml) was added and the two layers were separated. The water layer was extracted with ether (2 x 5ml), and the combined organic phases were washed with saturated aqueous sodium chloride (5 ml), dried, and evaporated. The residual oil was chromatographed, eluting with petroleum - ethyl acetate (12:1), to obtain the *title compound* **16a** (100 mg, 85%) as an oil (*M* + NH_4, 238.1446. $C_{13}H_{20}NO_3$ requires 238.1443); ν_{max} (film) 2933, 2834, 1496, 1434, 1260, 1050, 804 and 712 cm^{-1}; δ (300 MHz) 3.24 (1 H, d, *J* 13.9 Hz, 2-H), 3.38 (3 H, s, 1-OCH_3), 3.49 (1 H, d, *J* 13.9 Hz, 2-H), 3.77 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 5.19 (1 H, dd, *J* 1.5, 10.6 Hz, 2'-H), 5.33 (1 H, dd, *J* 1.5, 17.3 Hz, 2'-H), 6.13 (1 H, dd, *J* 10.6, 17.3 Hz, 1'-H), 6.67 (1 H, d, *J* 9.0 Hz, ArH), 6.71 (1 H, d, *J* 9.0 Hz, ArH); m/z (CI) 238 (M + NH_4^+, 10%), 205 (13), 189 (100).

1,3,6-Trimethoxy-1-(1-phenylethenyl)benzocyclobutene **16b**

Using the procedure described for the preparation of **16a**, the carbinol **9b** (100 mg, 0.35 mmol) was methylated using iodomethane (2.0 ml, 4.56 g, 32 mmol) and silver oxide (0.30 g, 1.29 mmol). Work-up gave an oil which was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **16b** (88 mg, 84%) as a waxy solid, m.p. 30 °C (*M*, 296.1414. $C_{19}H_{20}O_3$ requires 296.1412); ν_{max} (film) 2934, 2832, 1496, 1463, 1435, 1258, 1146, 1056, 805, 779 and 712 cm^{-1}; δ (300 MHz) 7.59–7.55 (2 H, m, 2',6'-ArH), 7.35–7.25 (3 H, m, 3',4',5'-ArH), 6.74 (1 H, d, *J* 9.1 Hz, ArH), 6.73 (1 H, d, *J* 9.1 Hz, ArH), 5.60 (1 H, d, *J ca.* 1 Hz, 2'-H), 5.55 (1 H, d, *J ca.* 1 Hz, 2'-H), 3.83 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.51 (1 H, d, *J* 13.4 Hz, 2-H), 3.40 (3 H, s, 1-OCH_3), 3.40 (1 H, d, *J* 13.4 Hz, 2-H); m/z (CI) 234 (M + NH_4^+, 1%), 208 (2), 194 (11), 177 (100); m/z (CI) 296 (M^+, 17%), 265 (100).

1,3,6-Trimethoxy-1-(1-methylethenyl)benzocyclobutene **16c**

Using the procedure described for the preparation of **16a**, the carbinol **9c** (100 mg, 0.45 mmol) was methylated using iodomethane (2.0 ml, 4.56 g, 32 mmol) and silver oxide (0.30 g, 1.29 mmol). Work-up gave an oil which was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **16c** (85 mg, 80%) as a colourless oil which solidified on cooling in a refrigerator (*M*, 234.1253. $C_{14}H_{18}O_3$ requires 234.1256); ν_{max} (film) 2930, 2833, 1496, 1435, 1258, 1136, 1067, 906, 846 and 804 cm^{-1}; δ (300 MHz) 6.72 (1 H, d, *J* 9.0 Hz, ArH), 6.67 (1 H, d, *J* 9.0 Hz, ArH), 5.05 (1 H, narrow m, 2'-H), 4.98 (1 H, narrow m, 2'-H), 3.79 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 3.35 (1 H, d, *J* 13.5 Hz, 2-H), 3.34 (3 H, s, 1-OCH_3), 3.25 (1 H, d, *J* 13.5 Hz, 2-H), 1.80 (3 H, narrow m, 1'-CH_3); m/z (EI, peaks >20%) 234 (M^+, 81%), 219 (100), 205 (51), 204 (38), 203 (60), 193 (20), 191 (33), 189 (38), 188 (43), 175 (23), 173 (26), 163 (27), 161 (41), 159 (20), 145 (22), 115 (46).

1-(1-Hexynyl)-3,6-dimethoxybenzocyclobuten-1-ol **17a**

A solution of 1-hexyne (0.13 ml, 93 mg, 1.13 mmol) in THF (5 ml) at 0 °C in a 25 ml 3-necked flask was treated dropwise with *n*-butyllithium in hexane (1.245 M, 0.93 ml, 1.16 mmol), whereupon a yellow coloration was observed. The solution was stirred for 20 minutes, cooled to –78 °C and treated dropwise with a solution of the ketone **8** (0.10 g, 0.56 mmol) in THF (5 ml). The mixture was allowed to warm to –50 °C to ensure that all the ketone had dissolved, and then recooled to –78 °C and stirred for a further 1 h. The reaction was then quenched at –78 °C by the dropwise addition of saturated aqueous ammonium chloride (5 ml). Ether (5 ml) was added and the mixture was stirred and allowed to warm to 0 °C. The two layers were rapidly separated and the aqueous phase was extracted with ether (4 x 5 ml). The organic phases were combined, washed with ice-cold water (10 ml), aqueous sodium bicarbonate (5% w/w; 5 ml), and saturated aqueous

sodium chloride (10 ml), dried, and evaporated. The residual yellow oil was chromatographed, eluting with petroleum - ethyl acetate (8:1), to obtain the *title compound* **17a** (112 mg, 77%) as colourless crystals, m.p. 53–55 °C (*M* + H, 261.1477. $C_{16}H_{21}O_3$ requires 261.1491); ν_{max} (neat) 3400, 2932, 2235, 1588, 1495, 1463, 1432, 1258, 1142, 1110, 1050 and 814 cm^{-1}; δ (300 MHz) 6.70 (1 H, d, *J* 8.9 Hz, ArH), 6.65 (1 H, d, *J* 8.9 Hz, ArH), 4.00 (3 H, s, OCH_3), 3.77 (1 H, d, *J* 13.7 Hz, 2-H), 3.77 (3 H, s, OCH_3), 3.48 (1 H, d, *J* 13.7 Hz, 2-H), 2.68 (1 H, s, OH), 2.21 (2 H, t, *J* 6.9 Hz, 3'-H_2), 1.50–1.30 (4 H, m, 4'-H_2, 5'-H_2), 0.87 (3 H, t, *J* 7.1 Hz, 6'-H_3); m/z (CI) 261 (M + H^+, 100%), 243 (51).

1-Phenylethynyl-3,6-dimethoxybenzocyclobuten-1-ol **17b**

The procedure used to prepare **17a** (see above) was followed, using phenylacetylene (0.123 ml, 114 mg, 1.12 mmol) as the alkyne. The *title compound* **17b** (128 mg, 81%) was isolated as a white solid, m.p. 74–76 °C (*M* + NH_4, 298.1446. $C_{18}H_{20}O_3N$ requires 298.1443); ν_{max} 3400, 2929, 2358, 1495, 1432, 1258, 1142, 1051 and 818 cm^{-1}; δ (300 MHz) 7.45–7.40 (2 H, m, PhH), 7.31–7.27 (3 H, m, PhH), 6.74 (1 H, d, *J* 8.9 Hz, ArH), 6.68 (1 H, d, *J* 8.9 Hz, ArH), 4.05 (3 H, s, OCH_3), 3.92 (1 H, d, *J* 13.5 Hz, 2-H), 3.80 (3 H, s, OCH_3), 3.59 (1 H, d, *J* 13.5 Hz, 2-H), 2.89 (1 H, br s, OH); m/z (CI) 298 (M + NH_4^+, 6%), 281 (5), 264 (20), 263 (100).

1-Trimethylsilylethynyl-3,6-dimethoxybenzocyclobuten-1-ol **17c**

The procedure used to prepare **17a** (see above) was followed, using trimethylsilylacetylene (0.16 ml, 110 mg, 1.12 mmol) as the alkyne. The *title compound* **17c** (126 mg, 81%) was isolated as a white solid, m.p. 88–90 °C (ethyl acetate - petroleum) (*M* + NH_4, 294.1516. $C_{15}H_{24}NO_3Si$ requires 294.1525); ν_{max} 3385, 2956, 2167, 1497, 1433, 1258, 1143, 1052, 903, 844, 812, 760 and 666 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 8.9 Hz, ArH), 6.65 (1 H, d, *J* 8.9 Hz, ArH), 4.01 (3 H, s, OCH_3), 3.81 (1 H, d, *J* 13.5 Hz, 2-H), 3.77 (3 H, s, OCH_3), 3.47 (1 H, d, *J* 13.5 Hz, 2-H), 2.87 (1 H, br s, OH), 0.14 (9 H, s, $Si(CH_3)_3$); m/z (CI) 294 (M + NH_4^+, 17%), 259 (100), 207 (15), 151 (16).

1-(1-Hexynyl)-1,3,6-trimethoxybenzocyclobutene **18a**

Using the procedure described for the preparation of **16a**, the carbinol **17a** (0.10 g, 0.38 mmol) was methylated using iodomethane (2.0 ml, 4.56 g, 32 mmol) and silver oxide (0.30 g, 1.29 mmol). After stirring the mixture overnight, work-up gave an oil which was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **18a** (89 mg, 84%) as a colourless oil (*M* + NH_4, 292.1912. $C_{17}H_{26}NO_3$ requires 292.1913); ν_{max} (film) 2929, 1496, 1462, 1433, 1264, 1117, 1049 and 1018 cm^{-1}; δ (300 MHz) 6.70 (1 H, d, *J* 9.0 Hz, ArH), 6.65 (1 H, d, *J* 9.0 Hz, ArH), 3.91 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.50 (2 H, s, 2-H_2), 3.46 (3 H, s, 1-OCH_3), 2.23 (2 H, t, *J* 6.8 Hz, 3'-H_2), 1.51–1.34 (4 H, m, 4'-H_2, 5'-H_2), 0.88 (3 H, t, *J* 7.0 Hz, 6'-H_3); m/z (CI) 292 (M + NH_4^+, 10%), 243 (100), 196 (24).

1,3,6-Trimethoxy-1-(2-phenylethynyl)benzocyclobutene **18b**

Using the procedure described for the preparation of **16a**, the carbinol **17b** (0.10 g, 0.36 mmol) was methylated using iodomethane (2.0 ml, 4.56 g, 32 mmol) and silver oxide (0.30 g, 1.29 mmol). After stirring the mixture overnight, work-up gave an oil which was chromatographed, eluting with petroleum - ethyl acetate, to obtain the *title compound* **18b** (79 mg, 75%) as a colourless oil (*M* + NH_4, 312.1600. $C_{19}H_{22}NO_3$ requires 312.1600); ν_{max} (film) 2933, 1589, 1497, 1462, 1433, 1259, 1143, 1112, 1063, 1013, 807 and 757 cm^{-1}; δ (300 MHz) 7.45–7.40 (2 H, m, 2',6'-ArH), 7.30–7.25 (3 H, m, 3',4',5'-ArH), 6.74 (1 H, d, *J* 8.9 Hz, ArH), 6.69 (1 H, d, *J* 8.9 Hz, ArH), 3.96 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3), 3.68 (1 H, d, *J* 13.3 Hz, 2-H), 3.60 (1 H, d, *J* 13.3 Hz, 2-H), 3.57 (3 H, s, 1-OCH_3); m/z (CI) 312 (M + NH_4^+, 2%), 263 (100).

1,3,6-Trimethoxy-1-trimethylsilylethynylbenzocyclobutene **18c**

1-Trimethylsilylethynyl-3,6-dimethoxybenzocyclobuten-1-ol **17c** (0.10 g, 0.36 mmol) was methylated as described for the preparation of **16a**. After stirring overnight, the reaction was worked up as before to afford the *title compound* **18c** (89 mg, 85%) as a white crystalline solid, m.p. 74–76 °C (*M* + NH_4, 308.1671. $C_{16}H_{26}NO_3Si$ requires 308.1682); ν_{max} 2958, 2164, 1498, 1434, 1264, 1157, 1114 and 1050 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 8.9 Hz, ArH), 6.66 (1 H, d, *J* 8.9 Hz, ArH), 3.93 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.56 (1 H, d, *J* 13.4 Hz, 2-H), 3.49 (1 H, d, *J* 13.4 Hz, 2-H), 3.47 (3 H, s, OCH_3), 0.15 (9 H, s, $Si(CH_3)_3$); m/z (CI) 308 (M + NH_4^+, 54%), 259 (100).

1-Ethynyl-1,3,6-trimethoxybenzocyclobutene **18d**

To a magnetically stirred solution of 1,3,6-trimethoxy-1-trimethylsilylethynylbenzocyclobutene **18c** (100 mg, 0.34 mmol) in THF (5 ml) at 0 °C was added tetra-*n*-butylammonium fluoride (TBAF) in THF (1.0 M; 1.0 ml, 1.0 mmol) slowly dropwise. The resulting solution was stirred for a further 2 h, when the reaction appeared to be complete by t.l.c. The mixture was treated with water (5 ml), extracted with ether (3 x 5 ml), and the combined extracts washed with saturated aqueous sodium chloride (5 ml), dried, and evaporated. The resulting white solid was chromatographed, eluting with petroleum - ethyl acetate (15:1), to obtain the *title compound* **18d** (66 mg, 88%) as a white solid (m.p. 40–41 °C) (*M*, 218.0952. $C_{13}H_{14}O_3$ requires 218.0943); ν_{max} (film) 3284, 2934, 2834, 1497, 1463, 1433, 1263, 1155, 1116, 1064, 1012 and 796 cm^{-1}; δ (300 MHz) 6.73 (1 H, d, *J* 9.0 Hz, ArH), 6.67 (1 H, d, *J* 9.0 Hz, ArH), 3.90 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.59 (1 H, d, *J* 13.2 Hz, 2-H), 3.51 (3 H, s, OCH_3), 3.50 (1 H, d, *J* 13.2 Hz, 2-H), 2.62 (1 H, s, C≡CH); m/z (CI) 236 (M + NH_4^+, 3%), 218 (95), 187 (100).

3-(n-Butyl)-5,8-dimethoxynaphth-1-ol **19a**

A solution of 1-(1-hexynyl)-3,6-dimethoxybenzocyclobuten-1-ol **17a** (0.10 g, 0.38 mmol) and toluene (5 ml) was heated under reflux for 60 h, after which time the starting material was not detectable by t.l.c. The solvent was evaporated and the residual oil was chromatographed, eluting with petroleum - ethyl acetate (2:1). The main fraction gave the *title compound* **19a** (65 mg, 65%) as white crystals, m.p. 60–62 °C (ethanol) (*M* + H, 261.1476. $C_{16}H_{21}O_3$ requires 261.1491); ν_{max} (nujol) 3419, 2955, 1640, 1494, 1464, 1432, 1256, 1155, 1054, 991 and 805 cm^{-1}; δ (300 MHz) 9.34 (1 H, s, OH), 7.48 (1 H, d, *J* 1.3 Hz, 4-H), 6.78 (1 H, d, *J* 1.3 Hz, 2-H), 6.59 (2 H, s, 6,7-H), 3.98 (3 H, s, OCH_3), 3.92 (3 H, s, OCH_3), 2.68 (2 H, t, *J* 7.6 Hz, 1'-H_2), 1.7–1.6 (2 H, m, 2'-H_2), 1.4–1.3 (2 H, m, 3'-H_2), 0.91 (2 H, t, *J* 7.3 Hz, 4'-H_3); m/z (CI) 261 (M + H^+, 100%); R_f 0.65 (petroleum - ethyl acetate 2:1).

3-Phenyl-5,8-dimethoxynaphth-1-ol **19b**

The procedure used for the preparation of the naphthol **19a** was followed, starting with 1-phenylethynyl-3,6-dimethoxybenzocyclobuten-1-ol **17b** (84 mg, 0.30 mmol). The same work-up gave the *title compound* **19b** (57 mg, 68%) as white crystals, m.p. 165–167 °C (ethanol) (*M* + H, 281.1186. $C_{18}H_{17}O_3$ requires 281.1178); ν_{max} 3424, 1697, 1633, 1497, 1266, 1200, 1066 and 985 cm^{-1}; δ (300 MHz) 9.51 (1 H, s, OH), 7.69–7.34 (7 H, m, PhH, 2-H, 4-H), 7.01 (1 H, d, *J* 8.8 Hz, 7-H), 6.78 (1 H, d, *J* 8.8 Hz, 6-H), 3.93 (3 H, s, OCH_3), 3.88 (3 H, s, OCH_3); m/z (CI) 281 (M + H^+, 100%).

Attempted preparation of 3-trimethylsilyl-5,8-dimethoxynaphth-1-ol **19c**

The procedure used for the preparation of **19a** was followed, starting with **17c** (100 mg, 0.36 mmol). The glassware and solvent were washed with sodium hydroxide solution in anticipation of the lability of the trimethylsilyl group. The reaction was worked up as before and the residue chromatographed over Florisil®, eluting with petroleum - ethyl acetate (4:1). It was found that a compound observed on t.l.c and considered to be the title compound **19c**, did not emerge from the column, presumably due to decomposition.

Attempted preparation of 1-formyl-3,6-dimethoxybenzocyclobuten-1-ol **24a**

A solution of 1-ethenyl-3,6-dimethoxybenzocyclobuten-1-ol **9a** (100 mg, 0.48 mmol) in dichloromethane (5 ml) in a 10 ml 3-necked round bottomed flask was cooled to –78 °C and dry ozone was passed through the solution. Monitoring the reaction by t.l.c., after 0.5 h the starting material was no longer apparent. Dimethylsulphide (175 µl, 148 mg, 2.4 mmol) was added, and the mixture was allowed to warm up to room temperature with stirring overnight. The methanol and excess of dimethylsulphide was removed by rotary evaporation under reduced pressure, and the residue was partitioned between dichloromethane (5 ml) and water (5 ml). The two layers were separated and the aqueous layer was extracted with dichloromethane (3 x 5 ml). The combined organic phases were washed with saturated aqueous sodium chloride (5 ml), dried over $MgSO_4$, and concentrated to give an orange oil. T.l.c. did not indicate any major product, and chromatography over silica failed to produce an identifiable compound.

Attempted preparation of 1-formyl-1,3,6-trimethoxybenzocyclobutene **24b**

A solution of 1-ethenyl-1,3,6-trimethoxybenzocyclobutene **16a** (0.10 g, 0.45 mmol) in methanol (5 ml) in a 10 ml 3-necked round bottomed flask was cooled to –78 °C and dry ozone was passed through the solution. Monitoring the reaction by t.l.c., after 0.5 h the starting material was no longer apparent and a more polar product (R_f 0.15 using petroleum - ethyl acetate 2:1) was observed which was thought to be the corresponding ozonide. Dimethylsulphide (175 µl, 148 mg, 2.4 mmol) was added, and the mixture was allowed to warm up to room temperature with stirring overnight. The methanol and excess of dimethylsulphide was removed by rotary evaporation under reduced pressure, and the residue was partitioned between ether (10 ml) and water (5 ml). The two layers were separated and the aqueous layer was extracted with ether (2 x 5 ml). The combined organic phases were washed with saturated aqueous sodium chloride (5 ml), dried over $MgSO_4$, and concentrated to give a yellow oil. T.l.c. did not indicate any major product, and chromatography over silica failed to produce an identifiable compound.

1-Hydroxymethyl-1,3,6-trimethoxybenzocyclobutene **25**

1-Ethenyl-1,3,6-trimethoxybenzocyclobutene **16a** (0.10 g, 0.45 mmol) was ozonised in methanol as described above. Following the disappearance of the starting material and the formation of the (presumed) ozonide, the mixture was added slowly dropwise to a stirred solution of sodium borohydride (20 mg, 0.52 mmol) in methanol (5 ml) at –78 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The bulk of the methanol was removed by rotary evaporation under reduced pressure, and the residue was partitioned between ether (10 ml) and water (5 ml). The two layers were separated and the aqueous layer was extracted with ether (2 x 5 ml). The combined organic phases were washed with saturated aqueous sodium chloride (5 ml), dried over $MgSO_4$, and concentrated. The residual oil was chromatographed, eluting with petroleum - ethyl acetate (2:1), to obtain the *title compound* **25** (0.83 g, 83%) as a colourless oil (*M* + NH_4, 242.1386. $C_{12}H_{20}NO_4$ requires 242.1392); ν_{max} (film) 3410, 2930, 1615, 1495, 1434, 1257, 1050 and 796 cm^{-1}; δ (300 MHz) 6.72 (1 H, d, *J* 8.9 Hz, ArH), 6.66 (1 H, d, *J* 8.9 Hz, ArH), 3.94 (1 H, d, *J* 11.5 Hz, 1'-H) (other 1'-H signal obscured by methoxy signals), 3.80 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3), 3.40 (1 H, d, *J* 14.0 Hz, 2-H), 3.36 (3 H, s, OCH_3), 3.20 (1 H, d, *J* 14.0 Hz, 2-H), 2.20 (1 H, br s, OH); m/z (CI) 242 (M + NH_4^+, 15%), 224 (34), 210 (25), 193 (100).

1-Trimethylsilylmethyl-3,6-dimethoxybenzocyclobuten-1-ol **26**

A solution of the ketone **8** (1.00 g, 5.61 mmol) in THF (50 ml) under nitrogen was cooled to –78 °C and treated slowly dropwise with a solution of trimethylsilylmethyllithium in pentane (1.0 M, 10.0 ml, 10.0 mmol), taking care to maintain an internal temperature below –70 °C. After the addition the mixture was stirred for a further 5 min, whereupon the reaction appeared to be complete by t.l.c. Saturated aqueous ammonium chloride

(10 ml) was added slowly dropwise, again taking care to prevent the temperature from rising above –70 °C until the addition was complete. The mixture was then allowed to warm to room temperature, ether (25 ml) was added and the layers were separated. The aqueous layer was extracted with ether (3 x 25 ml), and the combined organic phases were washed with saturated aqueous sodium chloride (50 ml), dried, and concentrated. The residual oil was chromatographed, eluting with petroleum - ethyl acetate (12:1), yielding the *title compound* **26** (1.48 g, 99%) as a white crystalline solid, m.p. 45–47 °C (*M* + H, 267.1418. $C_{14}H_{23}O_3Si$ requires 267.1416); ν_{max} (film) 3356, 2933, 1589, 1490, 1430, 1264, 1143, 1063, 1013, 807 and 757 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 8.3 Hz, ArH), 6.62 (1 H, d, *J* 8.3 Hz, ArH), 3.84 (3 H, s, OCH_3), 3.79 (3 H, s, OCH_3), 3.45 (1 H, d, *J* 12.9 Hz, 2-H), 3.27 (1 H, d, *J* 12.9 Hz, 2-H), 2.26 (1 H, br s, OH), 1.63 (1 H, d, *J* 15.4 Hz, 1'-H), 1.34 (1 H, d, *J* 15.4 Hz, 1'-H), 0.06 (9 H, s, 3 x $SiCH_3$); m/z (CI) 267 ($M + H^+$, 30%), 249 (100), 236 (8), 179 (10), 90 (27).

1-Methylene-3,6-dimethoxybenzocyclobutene **27**

A solution of the carbinol **26** (1.37 g, 5.14 mmol) in ether (50 ml) was treated dropwise with conc. sulphuric acid (5 drops), and the mixture stirred overnight at room temperature. The solution was then shaken with water (20 ml), and the separated ether layer washed with saturated aqueous sodium chloride (20 ml), dried, and evaporated. The residual white solid was chromatographed, eluting with petroleum - ethyl acetate (100:1), to obtain the *title compound* **27** (0.748 g, 82%) as a white crystalline solid, m.p. 67–69 °C (*M* + H, 194.1198. $C_{11}H_{16}NO_2$ requires 194.1181); ν_{max} (film) 2963, 2834, 1500, 1434, 1262, 1176, 1110, 1068, 1034, 879, 821 and 813 cm^{-1}; δ (300 MHz) 6.66 (1 H, d, *J* 8.9 Hz, ArH), 6.63 (1 H, d, *J* 8.9 Hz, ArH), 5.26 (1 H, t, *J* 1.5 Hz, C=CH), 4.93 (1 H, br s, C=CH), 3.83 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.68 (2 H, br s, 2-H_2); m/z (CI) 178 (12%), 177 ($M + H^+$, 100), 176 (23), 161 (8). The two steps described above were also carried out without purification of the intermediate carbonol **26** with the same overall yield.

1-Hydroxymethyl-3,6-dimethoxybenzocyclobuten-1-ol **28**

A mixture of 1-methylene-3,6-dimethoxybenzocyclobutene **27** (0.842 g 4.78 mmol), *N*-methylmorphine-*N*-oxide (0.87 g, 7.4 mmol), osmium tetroxide (4 mg, 0.016 mmol), *t*-butanol (1.5 ml), water (5 ml), and acetone (1 ml) was stirred for 0.5 h and then allowed to warm to room temperature and stirred overnight. A slurry of sodium dithionite (47 mg) and talc (0.57 g) in water (5 ml) was then added, followed by ethyl acetate (20 ml). The mixture was filtered and the filtrate neutralised to pH 7 with sulphuric acid (1.0 M, 3 drops). The acetone was removed under reduced pressure and the acidity of the remaining solution was adjusted to pH 2. The solution was saturated with sodium chloride and extracted with ethyl acetate (4 x 10 ml). The organic extracts were combined, dried, and concentrated in the normal manner. The residual white solid was chromatographed, eluting with petroleum - ethyl acetate (2:1), to obtain the *title compound* **28** (0.638 g, 63%) as a white solid, m.p. 75–77 °C (ethyl acetate - petroleum) (*M*, 210.0895. $C_{11}H_{14}O_4$ requires 210.0892); ν_{max} (film) 3305, 2955, 1497, 1462, 1434, 1254, 1176, 1068, 1042, 803 and 708 cm^{-1}; δ (300 MHz) 6.70 (1 H, d, *J* 9.0 Hz, ArH), 6.63 (1 H, d, *J* 9.0 Hz, ArH), 3.92 (1 H, d, *J* 11.2 Hz, 1'-H), 3.80 (1 H, d, *J* 11.2 Hz, 1'-H), 3.79 (6 H, s, 2 x OCH_3), 3.40 (1 H, d, *J* 13.8 Hz, 2-H), 3.24 (1 H, d, *J* 13.8 Hz, 2-H), 2.35 (2 H, br s, 2 x OH); m/z (CI) 228 ($M + NH_4^+$, 100%), 210 (15).

1-(1',3'-Dithian-2'-yl)-3,6-dimethoxybenzocyclobuten-1-ol **29**

A solution of 1,3-dithiane (freshly sublimed, 1.27 g, 10.6 mmol) in THF (25 ml) in a flame-dried 100 ml 3-necked flask under argon was cooled to –5 °C and treated slowly dropwise with *n*-butyllithium in hexane (1.35 M, 8.5 ml, 11.5 mmol). The solution was then stirred for 10 min, during which a yellow coloration developed. The mixture was cooled to –78 °C and treated slowly dropwise with a solution of 3,6-dimethoxybenzocyclobutenone **8** (1.00 g, 5.60 mmol) in THF (25 ml), ensuring that the temperature did not rise above –50 °C. Stirring was continued for 0.5 h, after which time no starting material was detected by t.l.c.

The mixture was then allowed to warm to 0 °C and water (15 ml) slowly added, whereupon the yellow colour was discharged. Ether (15 ml) was added and the two layers were separated. The aqueous layer was extracted with ether (3 x 15 ml), and the combined organics were washed with potassium hydroxide solution (7%, 15 ml) and saturated aqueous sodium chloride (15 ml), dried, and concentrated. The residual yellow oil was chromatographed, eluting with petroleum - ethyl acetate (4:1), to isolate the *title compound* **29** (1.288 g, 77%) as white crystals, m.p. 92–94 °C (*M* + NH_4, 316.1024. $C_{14}H_{22}NO_3S_2$ requires 316.1041); ν_{max} (film) 3423, 2925, 1494, 1432, 1259, 1040, 801 and 701 cm^{-1}; δ (300 MHz) 6.72 (1 H, d, *J* 9.0 Hz, ArH), 6.65 (1 H, d, *J* 9.0 Hz, ArH), 4.61 (1 H, s, 2'-H), 3.82 (3 H, s, OCH_3), 3.80 (1 H, partly obscured d, *J* 13.6 Hz, 2-H), 3.79 (3 H, s, OCH_3), 3.20 (1 H, d, *J* 13.6 Hz, 2-H), 3.12 (1 H, s, OH), 2.90–2.80 (4 H, m, 4'-H_2, 6'-H_2), 2.15–2.00 (1 H, m, 5'-H), 1.90–1.75 (1 H, m, 5'-H); m/z (CI) 316 (M + NH_4^+, 11%), 299 (87), 281 (100), 193 (18), 179 (19), 119 (56).

Attempted dethioacetalisation of 1-(1',3'-dithian-2'-yl)-3,6-dimethoxybenzocyclobuten-1-ol **29**

Method 1:[30] A mixture of 1-(1',3'-dithian-2-yl)-3,6-dimethoxybenzocyclobuten-1-ol **29** (0.10 g, 0.34 mmol), Claycop [10:15 w/w copper(II) nitrate:clay, 0.5 g], and dichloromethane (20 ml) was stirred overnight. The clay was then filtered off washed with dichloromethane (2 x 10 ml). The pale yellow filtrate was passed through a plug of neutral alumina and then concentrated. The residual off-white solid was shown by t.l.c. to be identical to the starting material. Purification of the residue by chromatography gave only a 41% return of the starting material.

Method 2:[31] To a stirred solution of 1-(1',3'-dithian-2-yl)-3,6-dimethoxybenzocyclobuten-1-ol **29** (0.10 g, 0.34 mmol) in acetonitrile (5 ml) was added [bis(trifluoroacetoxy)iodo]benzene (0.219 g, 0.51 mmol). The stirring was continued for 0.3 h until the starting material had been consumed as judged by t.l.c. However no product spot was evident in the chromatogram (*cf.* the ozonolysis reaction). The reaction mixture was poured into saturated aqueous sodium bicarbonate (10 ml) and extracted with ether (4 x 10 ml). The combined extracts were washed with saturated aqueous sodium chloride (10 ml), dried, and concentrated. The residual yellow oil was chromatographed, eluting with petroleum - ethyl acetate mixtures of increasing polarity, but no products were obtained. A small quantity of the starting material (7%) was recovered.

*2-[(1-Ethynylhexyl)oxy]tetrahydro-2*H*-pyran* **30a**[32]

A mixture of (±)-1-octyn-3-ol (5.0 ml, 4.32 g, 0.034 mol), *p*-toluenesulphonic acid (20 mg), and dichloromethane (50 ml) was cooled to 0 °C. 3,4-Dihydro-2*H*-pyran (3.44 ml, 3.17 g, 0.038 mol) was added slowly dropwise over 0.5 h. The reaction was observed to be exothermic. The mixture was stirred for 2 h, and the solvent was then evaporated and the residue chromatographed, eluting with petroleum - ethyl acetate (100:1), yielding the title compound **30a** (6.58 g, 91%) as an oil (*M* + NH_4, 228.1978. $C_{13}H_{26}O_2N$ requires 228.1963); ν_{max} (neat) 3436, 2923, 1457, 1422, 1276, 1232, 1184, 1151, 1061, 1017, 753 and 716 cm^{-1}; δ (300 MHz) 4.95 (1 H, narrow m, 2-H), 4.38 (1 H, dt, *J* 1.9, 6.7 Hz, 1'-H), 3.82–3.74 (1 H, m, 6-H), 3.54–3.48 (1 H, m, 6-H), 2.34 (1 H, d, *J* 1.9 Hz, C≡CH), 1.85–1.55 (4 H, m), 1.55–1.30 (8 H, m), 1.30–0.90 (4 H, m), 0.87 (3 H, t, *J* 6.5 Hz, 6'-H_3); m/z (CI) 228 (M + NH_4^+, 18%), 119 (33), 102 (100).

*Tetrahydro-2-[(1-methyl-2-propynyl)oxy]-2*H*-pyran* **30b**[33]

The procedure utilised to form 2-[(1-ethynylhexyl)oxy]tetrahydro-2*H*-pyran (above) was followed, starting with (±)-3-butyn-2-ol (2.63 ml, 2.35 g, 0.034 mol). The isolation procedure was identical, and gave the title compound **30b** (4.61 g, 89%) as a colourless oil; ν_{max} (neat) 3310, 2943, 2872, 1467, 1379, 1353, 1202, 1184, 1127, 1078, 1023, 980, 908 and 870 cm^{-1}; δ (300 MHz) 4.94 (1 H, m, 2-H), 4.49 (1 H, dq, *J* 2.0, 6.7 Hz, 1'-H), 3.77 (1 H, m, 6-H), 3.51 (2 H, m, 6-H), 2.34 (1 H, d, *J* 2.0 Hz, 3'-H), 1.85–1.60 (2 H, m, 3-H_2), 1.60–1.50 (4 H, m, 4-H_2, 5-H_2), 1.43 (3 H, d, *J* 6.8 Hz, 1'-H_3).

7-[3-(Tetrahydro-2H-pyran-2-yl)oxy-1-octynyl]-2,5-dimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-ol **31a**
A solution of 2-[(1-ethynylhexyl)oxy]tetrahydro-2*H*-pyran **30a** (1.30 g, 6.19 mmol) in THF (20 ml) at 0 °C was treated dropwise with *n*-butyllithium in hexane (1.55 M, 4.0 ml, 6.2 mmol). The yellow solution was stirred for 20 minutes, cooled to –78 °C and treated dropwise with a solution of the ketone **8** (1.00 g, 5.62 mmol) in THF (15 ml). The mixture was allowed to warm to –50 °C to ensure that all the ketone had dissolved, and then recooled to –78 °C and stirred for a further 1 h. The reaction was then quenched at –78 °C by the dropwise addition of saturated aqueous ammonium chloride (20 ml). Ether (20 ml) was added and the mixture was stirred and allowed to warm to 0 °C. The two layers were rapidly separated and the aqueous phase was extracted with ether (4 x 20 ml). The organic phases were combined, washed with ice-cold water (25 ml), aqueous sodium bicarbonate (5% w/w; 25 ml), and sat. aq. sodium chloride (25 ml), dried and evaporated. The residual yellow oil was chromatographed, eluting with petroleum - ethyl acetate (4:1), which afforded the *title compound* **31a** (1.63 g, 75%) as a colourless oil (*M*, 388.2251. $C_{23}H_{32}O_5$ requires 388.2250); ν_{max} (neat) 3400, 2931, 1496, 1432, 1259, 1115, 1020, 866 and 814 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 8.9 Hz, ArH), 6.65 (1 H, d, *J* 8.9 Hz, ArH), 4.94 (1 H, narrow m, 2"-H), 4.43 (1 H, t, *J* 6.8 Hz, 3'-H), 4.00 (3 H, s, OCH_3), 3.80–3.70 (1 H, obscured m, 6"-H), 3.77 (3 H, s, OCH_3), 3.77 (1 H, partly obscured d, *J* 13.3 Hz, 6-H), 3.55–3.40 (1 H, m, 6"-H), 3.47 (1 H, d, *J* 13.3 Hz, 6-H), 1.85–1.20 (14 H, m), 0.86 (3 H, t, *J* 6.5 Hz, 8'-H_3) (OH signal obscured); m/z (CI) 406 (M + NH_4^+, 3%), 389 (7), 371 (16), 305 (24), 287 (100).

7-[3-(Tetrahydro-2H-pyran-2-yl)oxy-1-butynyl]-2,5-dimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-ol **31b**
The procedure used for the preparation of the benzocyclobutenol **31a** was followed, starting with tetrahydro-2-[(1-methyl-2-propynyl)oxy]-2*H*-pyran **30b** (0.95 g, 6.16 mmol) and benzocyclobutenone **8** (1.00 g, 5.6 mmol). The usual work-up afforded the *title compound* **31b** (1.26 g, 68%) as a colourless oil (*M* + NH_4, 350.1934. $C_{19}H_{28}O_5N$ requires 350.1967); ν_{max} (neat) 3391, 2940, 1496, 1433, 1259, 1125, 1036, 1020 and 986 cm^{-1}; δ (300 MHz) 6.67 (1 H, d, *J* 8.9 Hz, ArH), 6.62 (1 H, d, *J* 8.9 Hz, ArH), 4.85 (1 H, br s, 2"-H), 4.53 (1 H, q, *J* 6.7 Hz, 3'-H), 3.95 (3 H, s, OCH_3), 3.80–3.70 (1 H, obscured m, 6"-H), 3.74 (3 H, s, OCH_3), 3.74 (1 H, d, *J* 13.5 Hz, 6-H), 3.50–3.40 (1 H, obscured m, 6"-H), 3.44 (1 H, d, *J* 13.5 Hz, 6-H), 1.80–1.40 (6 H, m, 3",4",5"-H), 1.40 (3 H, d, *J* 6.7 Hz, 4'-H_3) (OH signal obscured); m/z (CI) 350 (M + NH_4^+, 55%), 315 (18), 231 (55), 102 (100).

Tetrahydro-2-[[1-[(2,5,7-trimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)ethynyl]hexyl]oxy]-2H-pyran **32a**
The carbinol **31a** (0.776 g, 2.0 mmol) was stirred with silver(I) oxide (1.85 g, 8 mmol) and iodomethane (8 ml, 18.24 g, 128 mmol) under argon for 16 h. Ethyl acetate (10 ml) was added and the silver residues were filtered off through a plug of anhydrous magnesium sulphate. Water (10 ml) was added and the two layers were separated. The aqueous layer was extracted with ether (2 x 10 ml), and the combined organic phases were washed with saturated aqueous sodium chloride (15 ml) and dried over $MgSO_4$. The solvent was removed and the residual oil chromatographed, eluting with petroleum - ethyl acetate (12:1), to isolate the *title compound* **32a** (0.67 g, 83%) as a colourless oil (*M* + NH_4, 420.2753. $C_{24}H_{38}O_5N$ requires 420.2750); ν_{max} (neat) 2935, 1497, 1433, 1264, 1201, 1115, 1051, 1021 and 814 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 9.1 Hz, ArH), 6.65 (1 H, d, *J* 9.1 Hz, ArH), 4.91 (1 H, narrow m, 2-H), 4.46 (1 H, t, *J* 6.7 Hz, 1'-H), 3.89 (3 H, s, $ArOCH_3$), 3.80–3.70 (1 H, obscured m, 6-H), 3.78 (3 H, s, $ArOCH_3$), 3.55–3.45 (1 H, obscured m, 6-H), 3.53 (1 H, d, *J* 13.5 Hz, 6"-H), 3.49 (1 H, partly obscured d, *J* 13.5 Hz, 6"-H), 3.48 (3 H, s, 7"-OCH_3), 1.80–1.25 (14 H, m), 0.86 (3 H, t, *J* 6.8 Hz, 6'-H_3); m/z (CI) 420 (M + NH_4^+, 75%), 371 (73), 301 (26), 287 (100), 217 (98), 102 (78), 85 (36).

Tetrahydro-2-[[3-(2,5,7-trimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-methyl-2-propynyl]oxy]-2H-pyran **32b**
The procedure utilised to prepare **32a** was followed, starting with the benzocyclobutenol **31b** (1.20 g, 3.61

mmol). Chromatography gave the *title compound* **32b** (1.09 g, 87%) as a colourless oil (*M* + NH_4, 364.2106. $C_{20}H_{30}O_5N$ requires 364.2124); ν_{max} (neat) 2937, 1497, 1264, 1125, 1074, 1051, 1034, 1020, 984, 873 and 814 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 8.9 Hz, ArH), 6.65 (1 H, d, *J* 8.9 Hz, ArH), 4.88 (1 H, br s, 2"-H), 4.59 (1 H, q, *J* 6.7 Hz, 3'-H), 3.89 (3 H, s, OCH_3), 3.85–3.70 (1 H, obscured m, 6"-H), 3.77 (3 H, s, OCH_3), 3.53 (1 H, d, *J* 13.5 Hz, 6-H), 3.55–3.35 (1 H, obscured m, 6"-H), 3.48 (1 H, d, *J* 13.5 Hz, 6-H), 3.47 (3 H, s, 7-OCH_3), 1.80–1.40 (6 H, m, 3",4",5"-H), 1.44 (3 H, d, *J* 6.7 Hz, 4'-H_3); m/z (CI) 364 (M + NH_4^+, 100%), 332 (5), 315 (13), 231 (36), 102 (76).

1-(2,5,7-Trimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-octyn-3-ol **33a**

A solution of the tetrahydropyranyl compound **32a** (100 mg, 0.248 mmol) and *p*-toluenesulphonic acid (10 mg) in methanol (5 ml) was stirred for 2 h at room temperature until the reaction appeared to be complete by t.l.c. The mixture was washed with water (3 ml) and the two layers separated. The organic layer was washed with saturated aqueous sodium chloride (3 ml), dried and concentrated. The resulting yellow oil was chromatographed, eluting with petroleum - ethyl acetate (8:1), to isolate the *title compound* **33a** (65 mg, 82%) as a colourless oil (*M* + NH_4, 336.2181. $C_{19}H_{30}O_4N$ requires 336.2175); ν_{max} (neat) 3390, 2934, 1498, 1434, 1264, 1124, 1048 and 820 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 9.0 Hz, ArH), 6.66 (1 H, d, *J* 9.0 Hz, ArH), 4.41 (1 H, br t, *J* 6.4 Hz, 3-H), 3.89 (3 H, s, $ArOCH_3$), 3.78 (3 H, s, $ArOCH_3$), 3.54 (1 H, d, *J* 13.3 Hz, 6'-H), 3.51 (1 H, d, *J* 13.3 Hz, 6'-H), 3.48 (3 H, s, 7'-OCH_3), 1.9–1.2 (8 H, m), 0.86 (total 3 H, 2 x overlapping t, *J ca.* 6.5 Hz, 8-H_3 of diastereoisomers) (OH signal obscured); m/z (CI) 336 (M + NH_4^+, 68%), 287 (100); R_f 0.35 (petroleum - ethyl acetate 2:1).

4-(2,5,7-Trimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-3-butyn-2-ol **33b**

The tetrahydropyran **32b** (1.00 g, 2.89 mmol) was deprotected in the same manner as the analogue **32a**. Isolation gave the *title compound* **33b** (0.65 g, 86%) as a colourless oil (*M* + H, 263.1290. $C_{15}H_{19}O_4$ requires 263.1283); ν_{max} (neat) 3391, 2933, 1589, 1498, 1434, 1264, 1124, 1048, 939 and 820 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 9.0 Hz, ArH), 6.65 (1 H, d, *J* 9.0 Hz, ArH), 4.56 (1 H, q, *J* 6.7 Hz, 2-H), 3.88 (3 H, s, $ArOCH_3$), 3.77 (3 H, s, $ArOCH_3$), 3.54 (1 H, d, *J* 13.4 Hz, 6'-H), 3.50 (1 H, d, *J* 13.4 Hz, 6'-H), 3.47 (3 H, s, 7'-OCH_3), 2.1 (1 H, br s, OH), 1.43 (3 H, d, *J* 6.7 Hz, 1-H_3); m/z (CI) 263 (M + H^+, 100%), 249 (11), 245 (34), 231 (19).

(E)-1-(2,5,7-Trimethoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-octen-3-ol **34a**

A mixture of sodium bis(2-methoxyethoxy)aluminium hydride (Red-Al®; 1.30 g, 6.43 mmol, 4 equiv.) and THF (20 ml) in a 50 ml flask was cooled to 0 °C in an ice bath, and the octynol **33a** (0.514 g, 1.616 mmol) in THF (20 ml) was added slowly dropwise. Once the exotherm was complete, the mixture was allowed to warm up to room temperature and stirred for 2 h, whereupon the reaction appeared complete by t.l.c. The solution was recooled to 0 °C and cautiously treated dropwise with wet ether until the exotherm was complete. The solution was then washed with water (5 ml) and the two layers separated. The organic phase was washed with saturated aqueous sodium chloride (10 ml), dried, and concentrated. Chromatography of the residual yellow oil, eluting with petroleum - ethyl acetate (8:1), gave the *title compound* **34a** (0.49 g, 95%) as a colourless oil (*M*, 320.1992. $C_{19}H_{28}O_4$ requires 320.1987); ν_{max} (neat) 3413, 2931, 2858, 1587, 1496, 1433, 1261, 1072 and 806 cm^{-1}; δ (300 MHz) 6.70 (1 H, d, *J* 8.9 Hz, ArH), 6.64 (1 H, d, *J* 8.9 Hz, ArH), 5.93 (total 1 H, 2 x overlapping d, *J* 15.6 Hz, 1-H of diastereoisomers), 5.83–5.74 (total 1 H, 2 x overlapping dd, *J* 6.3, 15.6 Hz, 2-H of diastereoisomers), 4.13 (1 H, m, 3-H), 3.77 (3 H, s, $ArOCH_3$), 3.74 (total 3 H, 2 x s, $ArOCH_3$ of diastereoisomers), 3.49 (total 1 H, 2 x d, *J* 13.7 Hz, 6'-H of diastereoisomers), 3.35 (3 H, s, 7'-OCH_3), 3.21 (1 H, d, *J* 13.7 Hz, 6'-H), 1.6–1.2 (8 H, m, 4,5,6,7-H), 0.86 (total 3 H, 2 x t, *J* 6.5 Hz, 8-H_3 of diastereoisomers); m/z (CI) 338 (M + NH_4^+, 35%), 306 (25), 289 (100).

(E)-4-(7-Methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-3-buten-2-ol **34b**
The butynol **33b** (0.60 g, 2.29 mmol) was treated with Red-Al® in the same manner as the analogue **33a**. Isolation gave the *title compound* **34b** (0.55 g, 91%) as a colourless oil (*M* + NH_4, 282.1716. $C_{15}H_{24}O_4N$ requires 282.1705); ν_{max} (neat) 3391, 2929, 1586, 1497, 1259, 1070 and 806 cm^{-1}; δ (300 MHz) 6.71 (1 H, d, *J* 9.0 Hz, ArH), 6.66 (1 H, d, *J* 9.0 Hz, ArH), 5.95 (1 H, d, *J* 15.6 Hz, 4-H), 5.84 (1 H, dd, *J* 6.2, 15.6 Hz, 3-H), 4.33 (1 H, m, 2-H), 3.79 (3 H, s, $ArOCH_3$), 3.76 (3 H, s, $ArOCH_3$), 3.49 (1 H, d, *J* 13.9 Hz, 6'-H), 3.35 (3 H, s, 7'-OCH_3), 3.23 (1 H, d, *J* 13.9 Hz, 6'-H), 1.25 and 1.24 (total 3 H, 2 x d, each *J* *ca.* 7 Hz, 1-H_3 of diastereoisomers); m/z (CI) 282 (M + NH_4^+, 7%), 267 (3), 250 (37), 233 (100).

7-[3-(Tetrahydro-2H-pyran-2-yl)oxy-1-octynyl]bicyclo[4.2.0]octa-1,3,5-trien-7-ol **35a**
The procedure used for the preparation of the benzocyclobutenol **31a** was followed, starting with 2-[(1-ethynylhexyl)oxy]tetrahydro-2*H*-pyran **30a** (1.30 g, 6.19 mmol) and benzocyclobutenone **11** (0.66 g, 5.6 mmol). The usual work-up, followed by chromatography (elution with petroleum - ethyl acetate 5:1), afforded the *title compound* **35a** (1.52 g, 83%) as a colourless oil (*M* + NH_4, 346.2401. $C_{21}H_{32}O_3N$ requires 346.2382); ν_{max} (neat) 3392, 2930, 2859, 1460, 1183, 1127, 1037, 1020, 981, 756 and 715 cm^{-1}; δ (300 MHz) 7.30–7.12 (4 H, m, ArH), 4.92 (1 H, narrow m, 2"-H), 4.41 (1 H, t, *J* 6.7 Hz, 3'-H), 3.8–3.7 (1 H, m, 6"-H), 3.69 (1 H, d, *J* 13.8 Hz, 6-H), 3.5–3.4 (1 H, m, 6"-H), 3.44 (1 H, d, *J* 13.8 Hz, 6-H), 3.16 (1 H, br s, OH), 1.85–1.20 (14 H, m), 0.85 (3 H, t, *J* 6.5 Hz, 8'-H_3); m/z (CI) 346 (M + NH_4^+, 75%), 311 (25), 262 (10), 244 (25), 102 (100).

7-[3-(Tetrahydro-2H-pyran-2-yl)oxy-1-butynyl]bicyclo[4.2.0]octa-1,3,5-trien-7-ol **35b**
The procedure used for the preparation of the benzocyclobutenol **31a** was followed, starting with tetrahydro-2-[(1-methyl-2-propynyl)oxy]-2*H*-pyran **30b** (0.95 g, 6.16 mmol) and benzocyclobutenone **11** (0.66 g, 5.6 mmol). The usual work-up followed by chromatography (elution with petroleum - ethyl acetate 4:1) afforded the *title compound* **35b** (1.30 g, 85%) as a colourless oil (*M* + NH_4, 290.1740. $C_{17}H_{24}O_3N$ requires 290.1756); ν_{max} (neat) 3379, 2937, 1602, 1335, 1184, 1125, 1090, 1074, 1035, 1019, 983, 757 and 715 cm^{-1}; δ (300 MHz) 7.30–7.10 (4 H, m, ArH), 4.89 (1 H, br s, 2"-H), 4.56 (1 H, q, *J* 6.7 Hz, 3'-H), 3.80–3.70 (1 H, m, 6"-H), 3.70 (1 H, d, *J* 13.5 Hz, 6-H), 3.50–3.40 (1 H, obscured m, 6"-H), 3.43 (1 H, d, *J* 13.5 Hz, 6-H), 3.12 (1 H, br s, OH), 1.80–1.40 (6 H, m, 3",4",5"-H), 1.42 and 1.41 (total 3 H, 2 x d, *J* 6.7 Hz, 4'-H_3 of diastereoisomers); m/z (CI) 290 (M + NH_4^+, 4%), 255 (4), 188 (92), 171 (65), 102 (100).

Tetrahydro-2-[[1-[(7-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)ethynyl]hexyl]oxy]-2H-pyran **36a**
The procedure utilised to prepare **32a** was followed, starting with the benzocyclobutenol **35a** (1.50 g, 4.57 mmol). When the reaction was complete by t.l.c., the mixture was filtered through a pad of Celite, which was washed with ether. Evaporation of the filtrate, followed by chromatography (elution with petroleum - ethyl acetate 10:1), gave the *title compound* **36a** (1.36 g, 87%) as a colourless oil (*M* + NH_4, 360.2529. $C_{22}H_{34}O_3N$ requires 360.2539); ν_{max} (neat) 2932, 1461, 1201, 1111, 1021 and 752 cm^{-1}; δ (300 MHz) 7.34–7.14 (4 H, m, ArH), 4.92 (1 H, narrow m, 2-H), 4.45 (1 H, t, *J* 6.6 Hz, 1'-H), 3.80–3.70 (1 H, m, 6-H), 3.54 (1 H, d, *J* 13.9 Hz, 6"-H), 3.50 (3 H, s, 7"-OCH_3), 3.55–3.45 (1 H, obscured m, 6-H), 3.43 (1 H, d, *J* 13.9 Hz, 6"-H), 1.80–1.25 (14 H, m), 0.86 (3 H, t, *J* 6.8 Hz, 6'-H_3); m/z (CI) 360 (M + NH_4^+, 50%), 311 (25), 244 (23), 102 (100).

Tetrahydro-2-[[3-(7-methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-methyl-2-propynyl]oxy]-2H-pyran **36b**
The procedure utilised to prepare **32a** was followed, starting with the benzocyclobutenol **35b** (1.25 g, 4.59 mmol). Chromatography (elution with petroleum - ethyl acetate 10:1) gave the *title compound* **36b** (1.12 g, 85%) as a colourless oil (*M* + NH_4, 304.1925. $C_{18}H_{26}O_3N$ requires 304.1913); ν_{max} (neat) 2936, 1459, 1335, 1237, 1202, 1178, 1112, 1076, 1034, 1020, 983, 753 and 716 cm^{-1}; δ (300 MHz) 7.32–7.14 (4 H, m,

ArH), 4.89 (1 H, br s, 2"-H), 4.59 (1 H, q, *J* 6.7 Hz, 3'-H), 3.85–3.75 (1 H, m, 6"-H), 3.54 (1 H, d, *J* 13.4 Hz, 6-H), 3.55–3.45 (1 H, obscured m, 6"-H), 3.50 (3 H, s, OCH_3), 3.44 (1 H, d, *J* 13.5 Hz, 6-H), 1.80–1.40 (6 H, m, 3",4",5"-H), 1.44 and 1.43 (total 3 H, 2 x d, *J* 6.6 Hz, 4'-H_3 of diastereoisomers); m/z (CI) 304 (M + NH_4^+, 32%), 119 (18), 102 (100).

1-(7-Methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-octyn-3-ol **37a**

The tetrahydropyran **36a** (1.30 g, 3.80 mmol) was deprotected in the same manner as the analogue **32a**. When the reaction was complete by t.l.c., the excess of methanol was evaporated and the residue chromatographed (elution with petroleum - ethyl acetate 6:1), which gave the *title compound* **37a** (0.83 g, 85%) as a colourless oil (*M* + H, 259.1704. $C_{17}H_{23}O_2$ requires 259.1698); ν_{max} (neat) 3400, 2931, 2859, 1460, 1335, 1237, 1201, 1175, 1152, 1107, 1072, 752 and 715 cm^{-1}; δ (300 MHz) 7.35–7.10 (4 H, m, ArH), 4.36 (1 H, t, *J* 6.5 Hz, 3-H), 3.54 (1 H, d, *J* 13.8 Hz, 6'-H), 3.49 (3 H, s, 7-OCH_3), 3.44 (1 H, d, *J* 13.8 Hz, 6'-H), 2.6 (1 H, br s, OH), 1.7–1.3 (8 H, m, 4-H_2, 5-H_2, 6-H_2, 7-H_2), 0.86 (3 H, t, *J* 6.3 Hz, 8-H_3); m/z (CI) 276 (M + NH_4^+, 100%), 227 (30), 157 (14).

4-(7-Methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-3-butyn-2-ol **37b**

The tetrahydropyran **36b** (1.10 g, 3.84 mmol) was deprotected in the same manner as the analogue **32a**. Chromatography (elution with petroleum - ethyl acetate 5:1) gave the *title compound* **37b** (0.67 g, 86%) as a colourless oil (*M* + H, 220.1347. $C_{13}H_{18}O_2N$ requires 220.1337); ν_{max} (neat) 3400, 2982, 2933, 2824, 1459, 1418, 1370, 1332, 1277, 1237, 1201, 1177, 1153, 1136, 1118, 1102, 1072, 1030, 962, 930, 754 and 716 cm^{-1}; δ (300 MHz) 7.32–7.14 (4 H, m, ArH), 4.51 (1 H, q, *J* 6.6 Hz, 2-H), 3.54 (1 H, d, *J* 13.9 Hz, 6'-H), 3.48 (3 H, s, 7'-OCH_3), 3.44 (1 H, d, *J* 13.9 Hz, 6'-H), 2.78 (1 H, br s, OH), 1.40 and 1.39 (total 3 H, 2 x d, *J* 6.6 Hz, 1-H_3 of diastereoisomers, ratio *ca.* 1:1); m/z (CI) 220 (M + NH_4^+, 45%), 203 (90), 188 (30), 171 (100), 157 (33).

(E)-1-(7-Methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-1-octen-3-ol **38a**

The octynol **37a** (0.80 g, 3.10 mmol) was treated with Red-Al® in the same manner as the analogue **34a**. Chromatography (elution with petroleum - ethyl acetate 4:1) gave the *title compound* **38a** (0.76 g, 94%) as a colourless oil (*M* + NH_4, 276.1958. $C_{17}H_{26}O_2N$ requires 276.1963); ν_{max} (neat) 3391, 2929, 1495, 1434, 1260, 1070 and 806 cm^{-1}; δ (300 MHz) 7.35–7.15 (4 H, m, ArH), 5.95 (1 H, d, *J* 15.6 Hz, 1-H), 5.71 (1 H, dd, *J* 6.9, 15.6 Hz, 2-H), 4.12 (1 H, m, 3-H), 3.40 (1 H, d, *J* 14.0 Hz, 6'-H), 3.33 (total 3 H, 2 x s, 7'-OCH_3 of diastereoisomers), 3.24 and 3.22 (total 1 H, 2 x d, each *J* 14.0 Hz, 6'-H of diastereoisomers), 1.6–1.2 (8 H, m, 4,5,6,7-H), 0.86 (3 H, br t, *J* 6.7 Hz, 8-H_3) (OH signal broad, obscured); m/z (CI) 278 (M + NH_4^+, 1%), 261 (2), 246 (6), 229 (100). Samples of the pure diastereoisomers of **38a** were isolated (as enantiomeric pairs) by HPLC, using a Rainin Dynamax®-60A column (Si 83-101-C) and eluting with THF - dichloromethane (1:20) at 1 ml/min (retention times 320 and 400 s).

(E)-4-(7-Methoxybicyclo[4.2.0]octa-1,3,5-trien-7-yl)-3-buten-2-ol **38b**

The butynol **37b** (0.60 g, 2.97 mmol) was treated with Red-Al® in the same manner as the analogue **33a**. Chromatography (elution with petroleum - ethyl acetate 3:1) gave the *title compound* **38b** (0.57 g, 94%) as a colourless oil (*M* + NH_4, 222.1477. $C_{13}H_{20}O_2N$ requires 222.1494); ν_{max} (neat) 3400, 2969, 2929, 1458, 1260, 1150, 1132, 1074, 973 and 716 cm^{-1}; δ (300 MHz) 7.35–7.15 (4 H, m, ArH), 5.94 (1 H, d, *J* 15.6 Hz, 4-H), 5.76 (1 H, dd, *J* 5.8, 15.6 Hz, 3-H), 4.32 (1 H, m, 2-H), 3.40 (1 H, d, *J* 13.9 Hz, 6'-H), 3.32 and 3.31 (total 3 H, 2 x s, 7'-OCH_3 of diastereoisomers), 3.22 (total 1 H, 2 x d, each *J* 13.9 Hz, 6'-H of diastereoisomers), 1.90 (1 H, br s, OH), 1.24 and 1.23 (total 3 H, 2 x d, each *J ca.* 6.3 Hz, 1-H_3 of diasteroisomers); m/z (CI) 222 (M + NH_4^+, 5%), 190 (54), 173 (100).

3,4-Dihydro-3-(1-hydroxyhexyl)-5,8-dimethoxy-1(2H)-naphthalenone **40a**

A solution of the benzocyclobutene **34a** (0.10 g, 0.31 mmol) in toluene (10 ml) was heated under reflux for 24 h, after which time no starting material could be detected by t.l.c. The solution was shaken with 0.1M sulphuric acid (5 ml), and then extracted with ether (3 x 5 ml). The combined ether extract was washed with saturated aqueous sodium chloride (10 ml), dried and evaporated, and the residual yellow oil was chromatographed, eluting with petroleum - ethyl acetate (2:1), to obtain the *title compound* **40a** (36 mg, 38%) as an orange solid (*M* + H, 307.1905. $C_{18}H_{27}O_4$ requires 307.1909); ν_{max} (film) 3487, 2931, 1679, 1587, 1477, 1436, 1263, 1087, 804 and 723 cm^{-1}; δ (300 MHz) 6.95 (1 H, d, *J* 9.0 Hz, 6-H), 6.76 (1 H, d, *J* 9.0 Hz, 7-H), 3.83 (3 H, s, OCH_3), 3.79 (3 H, s, OCH_3), 3.6–3.5 (1 H, m, 1'-H), 3.21 (dd, *J* 3.5, 17 Hz, 4-H_{eq}), 3.09 (ddd, *J* 2, 3.5, 17 Hz, 4-H_{eq} of other diastereoisomer), 2.75–2.4 (total 3 H, m, 4-H_2 and 2-H_{ax}), 2.2–2.05 (1 H, m, 3-H), 1.7–1.2 (9 H, m, 2',3',4',5'-H and OH), 0.86 (3 H, t, *J* 6.5 Hz, 6'-H_3); m/z (CI) 307 (M + H^+, 100%).

Attempted preparation of 3,4-dihydro-3-(1-hydroxyethyl)-5,8-dimethoxy-1(2H)-naphthalenone **40b**

The benzocyclobutene **34b** (100 mg, 0.38 mmol) was thermolysed in refluxing toluene (110 °C) in the same manner as the analogue **34a**. T.l.c. showed a complex mixture, and no products were identified or isolated.

3,4-Dihydro-3-(1-hydroxyhexyl)-1(2H)-naphthalenone **42a**

The benzocyclobutene **38a** (100 mg, 0.385 mmol) was heated under reflux in tetrachloromethane and worked up as for the analogue **34a**. Chromatography gave the *title compound* **42a** (41 mg, 43%) as a yellow oil; ν_{max} (neat) 3372, 2928, 1676, 1490, 1434, 1260 and 806 cm^{-1}; δ (300 MHz) 7.97 (1 H, d, *J* 7.5 Hz, 8-H), 7.44 (1 H, t, *J* 7.5 Hz, 6-H), 7.25 (2 H, apparent q, *J ca.* 7.5 Hz, 5,7-H), 3.62–3.53 (1 H, m, 1'-H of diastereoisomers), 3.05–2.75 and 2.70–2.45 (4 H, m, 2-H_2 and 4-H_2 of diastereoisomers), 2.30–2.15 (1 H, m, 3-H of diastereoisomers), 2.04 (1 H, br s, OH), 1.55–1.20 (8 H, m, 2',3',4',5'-H), 0.86 (3 H, br t, *J* 6 Hz, 6'-H_3); δ_C (H decoupled) 196, 143.7, 133.6 (two peaks), 132.2, 129.2, 128.9, 126.94, 126.89, 126.62, 74.1, 42.5, 40.8, 39.8, 34.44, 34.36, 33.0, 31.8, 30.5, 25.5, 25.4, 22.6, 14.0.

Repeating the reaction, the alcohol **38a** (200 mg, 0.77 mmol) was heated under reflux in tetrachloromethane (15 ml) for 18 h, after which time no starting material could be detected by t.l.c. The solution was allowed to cool, stirred with hydrochloric acid (1 M, 5 ml) for 20 min., and the layers then separated. The organic phase was washed with saturated aqueous sodium chloride (10 ml), dried and evaporated to obtain the essentially pure *title compound* **42a** (184 mg, 97%) as a yellow oil (*M* + NH_4, 264.1960. $C_{16}H_{26}O_2N$ requires 264.1963); m/z (CI) [peaks ≥ 10%] 264 (M + NH_4^+, 26%), 209 (12), 208 (100), 191 (30), 83 (15). This reaction was repeated with each of the diastereoisomers of **38a** (separated by HPLC as above). In each experiment the ratio of diastereoisomers of **42a** generated was *ca.* 1:1 [HPLC analysis conditions as for **38a**; refractive index and UV (260 nm) detection, uncorrected].

3,4-Dihydro-3-(1-hydroxyethyl)-1(2H)-naphthalenone **42b**

The benzocyclobutene **38b** (100 mg, 0.49 mmol) was heated under reflux in tetrachloromethane as described for **34a** (and worked up by briefly shaking with 0.1M H_2SO_4). Chromatography gave the *title compound* **42b** (48 mg, 52%) as a yellow oil; ν_{max} (neat) 3406, 2932, 1678, 1494, 1434, 1262 and 804 cm^{-1}; δ_C (H decoupled) 198, 144, 134, 132, 129, 127, 70, 43 (two peaks), 41, 32 (two peaks), 21 (two peaks).

In a repeat reaction, the substrate **38b** (200 mg, 0.98 mmol) was heated under reflux in tetrachloromethane (15 ml) for 18 h, after which time no starting material could be detected by t.l.c. The solution was allowed to cool, stirred with hydrochloric acid (1 M, 5 ml) for 20 min and the layers then separated. The organic phase was washed with saturated aqueous sodium chloride (10 ml), dried and evaporated to obtain the essentially pure *title compound* **42b** (173 mg, 93%) as a yellow oil (*M* + NH_4, 208.1332. $C_{12}H_{18}O_2N$ requires 208.1337); δ (300 MHz) 7.99 (1 H, d, *J* 7.7 Hz, 8-H), 7.46 (1 H, t, *J* 7.4 Hz, 6-H), 7.27 (2 H, apparent q, *J ca.* 7.8

Hz, 5,7-H), 3.9–3.7 (total 1 H, 2 x dq, 1'-H of diastereoisomers), 3.12 (0.5 H, br d, *J* 16.5 Hz, 4-H_{eq} of diastereoisomer), 2.95–2.80 (2 H, m, 2-H_2 of diastereoisomers), 2.70 (0.5 H, br d, *J* 16.5 Hz, 4-H_{eq} of diastereoisomer), 2.46 (1 H, ddd, *J* 3.5, 13.0, 16.5 Hz, 4-H_{ax}), 2.25–2.10 (1 H, m, 3-H), 1.79 (1 H, br s, OH), 1.27 and 1.26 (total 3 H, 2 x d, *J* 6.3 Hz, 2'-H_3 of diastereoisomers); m/z (CI) [peaks ≥ 10%] 209 (14%), 208 (M + NH_4^+, 100), 191 (60), 146 (12). The n.m.r. spectrum clearly indicated a diastereoisomer ratio of 1:1.

*Naphtho[*b*]cyclobutenone* **44**

CAUTION – DIAZONIUM SALTS ARE POTENTIALLY EXPLOSIVE. READ THE INFORMATION IN REF. 34. USE A SAFETY SCREEN, PLASTIC BÜCHNER FUNNELS AND PLASTIC SPATULAS.

The following procedure was adapted from that described by McOmie and coworkers:[22] In a 100 ml round-bottomed flask, a mixture of 3-amino-2-naphthoic acid (1.0 g, 5.34 mmol) and concentrated hydrochloric acid (1.0 ml) in THF (45 ml) at 20 °C was treated dropwise with isoamyl nitrite (97%; 1.3 g, 11.1 mmol), and the mixture was stirred at 20 °C for 2 h. The solution was then cooled in an ice bath, and the solid was collected on a plastic Büchner funnel and washed with cold dry dioxane, using minimal suction for draining so as to prevent complete drying. The salt, still moist with solvent, was immediately transferred to a flask and mixed with dry dioxane (60 ml), propylene oxide (0.4 ml), and 1,1-dichloroethene (12 ml). The mixture was then heated at 100 °C with stirring for 2 h. The reaction mixture was then cooled, evaporated *in vacuo*, and the red residue chromatographed (elution with dichloromethane) to give 1,1-dichloronaphtho[*b*]cyclobutene (0.53 g, 44%) as a white crystalline solid, m.p. 130–131 °C (lit.[22] 129–130 °C); δ (300 MHz) 7.90–7.75 (3 H, m, 4-H, 7-H, 8-H), 7.60 (1 H, s, 3-H), 7.50–7.40 (2 H, m, 5-H, 6-H) and 4.28 (2 H, s, 2-H_2). A mixture of 1,1-dichloronaphtho[*b*]cyclobutene (1.0 g, 4.48 mmol), aq. silver(I) nitrate (0.05 M, 90 ml, 4.5 mmol), and ethanol (30 ml) was heated under reflux for 3 h and then cooled. The ethanol was evaporated under reduced pressure and the residue dissolved in hot aqueous ethanol, filtered through a glass sinter, and the filtrate allowed to cool, giving the title compound **44** (563 mg, 75%) as an off-white solid, m.p. 161–162 °C [lit.[22] 163–164 °C (CCl_4)]; δ (300 MHz) 7.94 (1 H, d, *J* 8 Hz, 7-H), 7.90–7.85 (3 H, m, 3-H, 4-H, 8-H), 7.59 (1 H, t, *J* 8 Hz, 5-H), 7.48 (1 H, t, *J* 8 Hz, 6-H) and 4.18 (2 H, s, 2-H_2).

*1-Ethenylnaphtho[*b*]cyclobuten-1-ol* **45**

In a 25 ml 3-necked flask was placed vinylmagnesium bromide in THF (1.0 M, 5.0 ml, 5.0 mmol) and the mixture was stirred in an ice/acetone bath at –5 to –10 °C. A solution of naphtho[*b*]cyclobutenone **44** (168 mg, 1.0 mmol) in THF (5 ml) was added slowly dropwise, during which a dark brown coloration was observed. The solution was then stirred for 1.5 h at –10 °C and then treated dropwise with cold saturated aqueous ammonium chloride (5 ml), whereupon the brown coloration was immediately discharged. Ether (25 ml) was added and the mixture was allowed to warm to 0 °C before separation of the phases was carried out. The aqueous phase was then extracted with more ether (4 x 10 ml) and the combined ethereal extract was washed successively with water (25 ml), sodium bicarbonate (5% w/w; 25 ml), and saturated aqueous sodium chloride (25 ml). The extract was then dried over magnesium sulphate and evaporated to yield a beige solid, which was purified by flash chromatography, eluting with petroleum - ethyl acetate (8:1). The eluate was evaporated to yield the *title compound* **45** (130 mg, 67%) as colourless needles, m.p. 95–96 °C (petroleum - ethyl acetate) (Found: C, 85.60; H, 5.96. $C_{14}H_{12}O$ requires C, 85.68; H, 6.16%); ν_{max} (nujol) 3233, 1147, 1051, 988, 916, 855 and 746 cm^{-1}; δ (300 MHz) 7.85–7.75 (2 H, m, 4-H, 7-H), 7.61 (1 H, s, 8-H), 7.58 (1 H, s, 3-H), 7.45–7.35 (2 H, m, 5-H, 6-H), 6.26 (1 H, dd, *J* 10.5, 17.1 Hz, 1'-H), 5.40 (1 H, dd, *J ca.* 1, 17.1 Hz, 2'-H), 5.17 (1 H, dd, *J ca.* 1, 10.5 Hz, 2'-H), 3.62 (1 H, d, *J* 15.0 Hz, 2-H), 3.49 (1 H, d, *J* 15.0 Hz, 2-H) and 2.50 (1 H, br s, OH); R_f (petroleum - ethyl acetate 4:1) 0.5.

Thermolysis of **45** *at 110 °C*

A solution of the carbinol **45** (50 mg, 0.25 mmol) in dry toluene (15 ml) under N_2 was heated under reflux for 2 h. Evaporation of the solvent and chromatography of the residue, eluting with petroleum - ethyl acetate (8:1), gave *1-(3-methylnaphth-2-yl)prop-2-en-1-one* **48** (20 mg, 40%) as a white solid, m.p. 86 °C (*M* + NH_4^+, 214.1238. $C_{14}H_{16}NO$ requires 214.1232); ν_{max} (nujol) 1655 cm^{-1}; δ (300 MHz) 7.96 (1 H, s, 1'-H), 7.82 (1 H, d, *J* 8.0 Hz, 8'-H), 7.76 (1 H, d, *J* 8.0 Hz, 5'-H), 7.66 (1 H, s, 4'-H), 7.55–7.40 (2 H, m, 6'-H and 7'-H), 6.90 (1 H, dd, *J* 10.6, 17.5 Hz, 2-H), 6.20 (1 H, dd, *J* 1.0, 17.5 Hz, 3-H), 6.04 (1 H, dd, *J* 1.0, 10.6 Hz, 3-H), 2.56 (3 H, s, 2'-CH_3); m/z (CI) 214 (M + NH_4^+, 70%), 198 (15), 197 (100), 196 (18); R_f (petroleum - ethyl acetate 8:1) 0.66. A more polar fraction afforded *3,4-dihydro-1(2H)-anthracenone* **49** (15 mg, 30%) as white crystals, m.p. 85 °C [lit.[23a] 95–96 °C (petroleum); lit.[23b] 94–96 °C (EtOAc - hexane)] (*M* + NH_4^+, 214.1231. $C_{14}H_{16}NO$ requires 214.1232); ν_{max} (nujol) 1680 cm^{-1}; δ (300 MHz) 8.60 (1 H, s, 10-H), 7.93 (1 H, d, *J* 8.2 Hz, 9-H), 7.77 (1 H, d, *J* 8.2 Hz, 6-H), 7.67 (1 H, s, 5-H), 7.54 (1 H, t, *J* 8 Hz, 7-H), 7.44 (1 H, t, *J* 8 Hz, 8-H), 3.12 (2 H, t, *J* 6.1 Hz, 4-H_2), 2.74 (2 H, t, *J* 6.5 Hz, 2-H_2), 2.18 (2 H, overlapping dt, *J* 6.1, 6.5 Hz, 3-H_2); m/z (CI) 214 (M + NH_4^+, 34%), 198 (14), 197 (100), 196 (16), 191 (12); R_f (petroleum - ethyl acetate 8:1) 0.35.

Thermolysis of **45** *at 140 °C*

A solution of the carbinol **45** (50 mg, 0.25 mmol) in dry *o*-xylene (10 ml) under N_2 was heated under reflux for 2 h. The solvent was removed *in vacuo* and the residue examined by 300 MHz ^{1}H-n.m.r. spectroscopy, which indicated that the product was a mixture of **48** and **49** (ratio *ca.* 1:1).

1-Ethenyl-1-methoxynaphtho[b]cyclobutene **46**

A mixture of the carbinol **45** (90 mg, 0.46 mmol), silver(I) oxide (425 mg, 1.83 mmol) and iodomethane (1.75 ml, 4.0 g, 28 mmol) was stirred under N_2 at room temperature for 20 h. After the addition of ethyl acetate (5 ml), the mixture was filtered and the residue washed with more ethyl acetate (20 ml). The combined filtrate was concentrated and the residual oil chromatographed, eluting with ether - petroleum (1:20), which gave the *title compound* **46** (83 mg, 86%) as a colourless oil (*M*$^+$, 210.1040. $C_{15}H_{14}O$ requires 210.1045); ν_{max} (neat) 3059, 2981, 2930, 2822, 1507, 1410, 1265, 1224, 1202, 1176, 1140, 1111, 1087, 992, 922, 886, 838 and 747 cm^{-1}; δ (300 MHz) 7.9–7.8 (2 H, m, 4-H, 7-H), 7.69 (1 H, s, 3-H), 7.61 (1 H, s, 8-H), 7.5–7.4 (2 H, m, 5-H, 6-H), 6.21 (1 H, dd, *J* 10.5, 17.2 Hz, 1'-H), 5.32 (1 H, dd, *J ca.* 1, 17.2 Hz, 2'-H), 5.26 (1 H, dd, *J ca.* 1, 10.5 Hz, 2'-H), 3.59 (1 H, d, *J* 14.9 Hz, 2-H), 3.45 (1 H, d, *J* 14.9 Hz, 2-H) and 3.42 (3 H, s, OCH_3); m/z (EI, peaks >40%) 210 (M$^+$, 74%), 195 (85), 179 (67), 178 (65), 167 (59), 165 (100), 152 (49), 139 (42); R_f (ether - petroleum 1:10) 0.6; R_f (petroleum - ethyl acetate 8:1) 0.7.

Thermolysis of **46** *at 110 °C*

A solution of the naphthocyclobutene **46** (40 mg, 0.19 mmol) in freshly distilled toluene (5 ml) under N_2 was heated under reflux for 8 h, and then allowed to cool to room temperature. T.l.c. at this point indicated that the starting material [R_f (petroleum - ethyl acetate 8:1) 0.7] had given way to a more mobile major product (R_f *ca.* 0.75), presumed to be the methyl enol ether of **49**, together with a less mobile minor product (R_f *ca.* 0.35) corresponding to **49**. To ensure complete conversion into **49**, the solution was stirred with 4M hydrochloric acid (5 ml) for 2 h. The layers were separated and the organic phase was washed with brine (5 ml), dried and evaporated to afford almost pure **49** (29 mg, 78%) as a colourless solid, which was identical (t.l.c., n.m.r., i.r.) to material obtained from the carbinol **45**; δ (300 MHz) 8.60 (1 H, s, 10-H), 7.93 (1 H, d, *J* 8.2 Hz, 9-H), 7.77 (1 H, d, *J* 8.2 Hz, 6-H), 7.67 (1 H, s, 5-H), 7.54 (1 H, t, *J* 8 Hz, 7-H), 7.44 (1 H, t, *J* 8 Hz, 8-H), 3.12 (2 H, t, *J* 6.1 Hz, 4-H_2), 2.74 (2 H, t, *J* 6.5 Hz, 2-H_2), 2.18 (2 H, overlapping dt, *J* 6.1, 6.5 Hz, 3-H_2); R_f (petroleum - ethyl acetate 8:1) 0.35.

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