Synthesis of bicyclo[4.1.0]hept-2-enes (trinorcarenes) by photochemical reaction of bicyclo[2.2.2]oct-5-en-2-ones

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Photochemical reaction of bicyclo[2.2.2[oct-5-en-2-ones has been investigated as a prelude to focused application to the synthesis of sesquiterpenes such as sesquicarene and sirenin. Diels–Alder reaction of cyclohexa-2,4-dienes, having different substituents (methylthiomethyl and methoxy) at the C-6 position, with a dienophile proceeds regio- and stereo-selectively to give bicyclo[2.2.2]oct-5-en-2-ones; their photolysis in benzene upon high-pressure Hg lamp irradiation affords decarbonylation products, bicyclo[4.1.0]hept-2-enes (trinorcarenes), stereoselectively. Replacement of the methylthiomethyl group with a 2-ethoxycarbonylvinyl group improves the sequential reaction.

Introduction

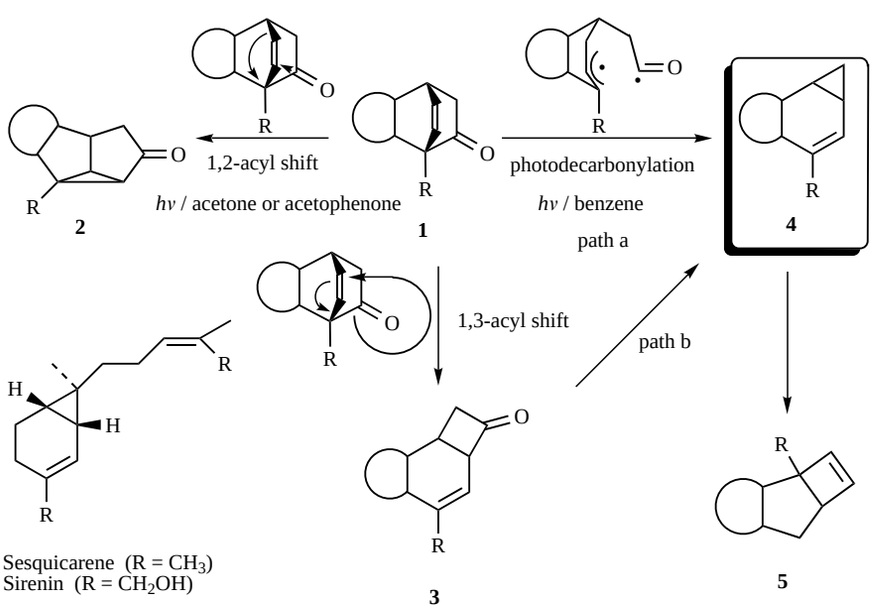
Bicyclo[2.2.2]oct-5-en-2-ones **1** have been versatile intermediates for the synthesis of a variety of natural products and their photochemistry has been widely investigated.[1–6] In their photolysis by direct irradiation, photodecarbonylation, frequently observed in other ring systems such as the 5-norbornen-2-ones,[7] also occurs occasionally after the initial α-cleavage (path a) or the 1,3-acyl shift (path b), although the resulting bicyclo-[4.1.0]hept-2-enes **4**, so-called trinorcarenes, are seldom isolated owing to their successive rapid photoisomerization to the corresponding bicyclo[3.2.0]heptenes **5**[5] except in a few cases.[8] Therefore, it is suggested that if these decarbonylation products can be successfully trapped in the photochemical reaction, a new route for the construction of sesquiterpenes such as sesquicarene **6**[9] and sirenin **7**[10] from the bicyclo[2.2.2]octenones is established (Scheme 1). Our interest in this method focused on the bicyclic compounds **8** and **9** having an appropriate substituent such as a methylthiomethyl or a 2-ethoxycarbonylvinyl group at C-3 on the bicyclo[2.2.2]octenone ring system. Compound **8** would be available by Diels–Alder reaction of 2,6-dimethoxy-6-(methylthiomethyl)cyclohexa-2,4-dienone **13**, whose synthesis has been already developed in our laboratory.[11] Dienone **13** has an unsymmetrical π-plane due to two stereodifferentiating substituents at C-6, hence a stereocontrolled cycloaddition reaction involving π-facial stereoselectivity[12] should be expected upon treatment with a dienophile. Compound **9** is prepared in a two step synthetic sequence starting from **8**.

Here, we report the synthesis of the bicyclo[4.1.0]hept-2-enes (trinorcarenes) **10** and **11** by photochemical reaction of the bicyclo[2.2.2]oct-5-en-2-ones **8** and **9**, available from a route involving the regio- and stereo-selective Diels–Alder reaction of the diene **13** with various dienophiles **14**, in benzene upon high-pressure Hg lamp irradiation (Scheme 2).[13]

Results and discussion

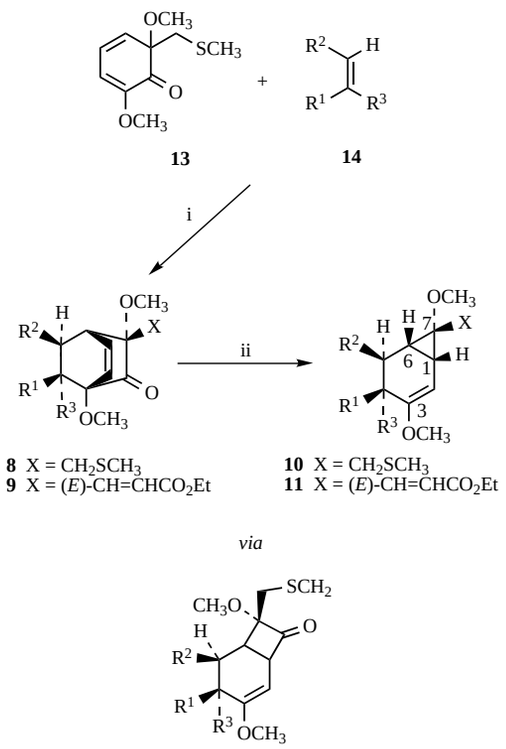
Synthesis of the bicylo[2.2.2]oct-5-en-2-ones 8 and 9

Diene **13**, obtained from 2,6-dimethoxyphenol by treatment with the Corey–Kim reagent,[14] readily dimerized *via* a [4 + 2]



Scheme 1 Photolysis of bicyclo[2.2.2]oct-4-en-2-ones

cycloaddition reaction by being stirred in toluene at 55 °C to give the tricyclic compound **15** as a single *endo* adduct. The ^{1}H NMR spectrum of this dimer showed two singlets at δ_H 2.10 and 2.11 and two AB quartets at δ_H 2.80 and 2.98 due to two methylthio and two thiomethylene hydrogens, respectively, as well as four singlets at δ_H 3.42, 3.50, 3.56 and 3.62 due to four methoxy groups, and two signals at δ_H 5.91 and 6.31 as a doublet and double doublet, respectively, due to vicinal vinyl hydrogens. The stereochemistry of compound **15** was established to be the *endo* adduct by its conversion into a cage compound **16**, photocyclized between C-7–C-8 and C-3–C-2 on structure **15**, together with the [2 + 2] photocycloadduct **17** of monomer **13**. Compound **16** had a two-fold axis of symmetry (as indicated by the broken line in Scheme 3), and its ^{1}H NMR spectrum displayed simple signals; a singlet and an AB quartet at δ_H 2.15 and 2.76 due to a pair of methylthio and thiomethylene hydrogens, and two singlets at δ_H 3.46 and 3.55 due to two methoxy groups.[15] This dimerization is thought to proceed in the manner of an *endo* approach with π-facial selectivity from the less hindered C-6-methoxy face of compound **13**. Dienone **13** was regenerated as a highly purified oil by pyrolysis (Kügelrohr distillation at 165–175 °C) of dimer **15**, and was subsequently supplied to the following Diels–Alder reaction with various dienophiles.

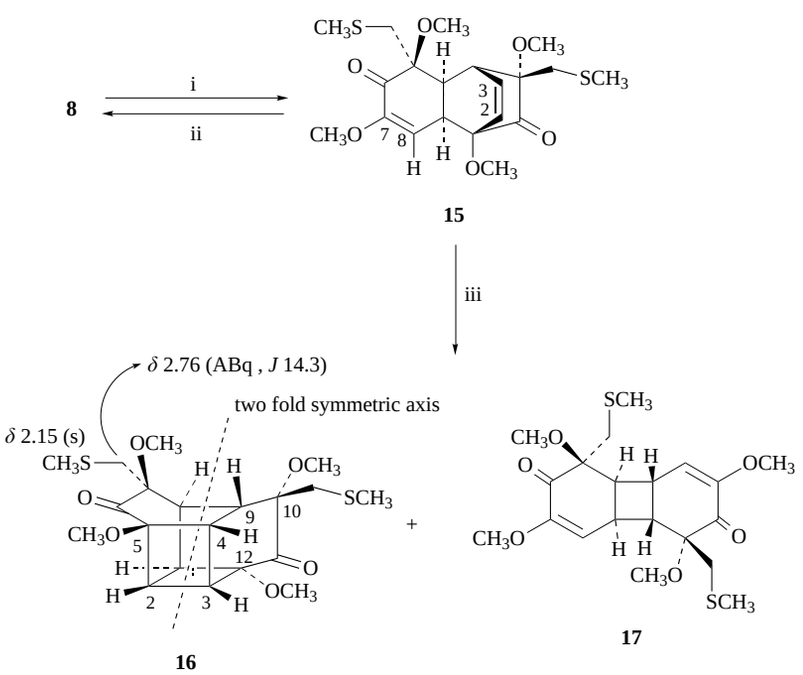


Scheme 2 *Conditions:* i, toluene, 100 °C, sealed tube; ii, toluene, *hv*, Pyrex filter

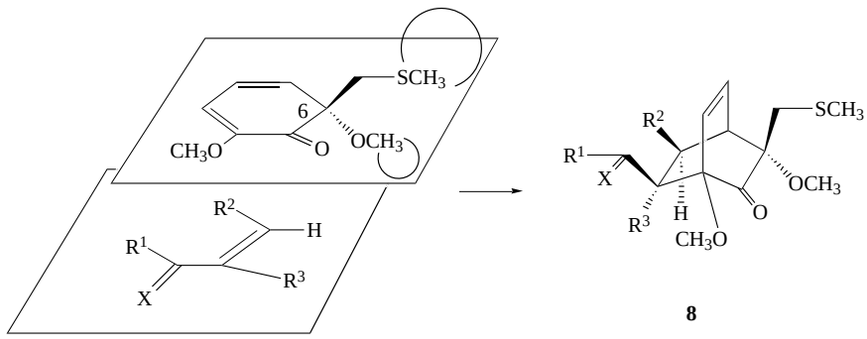
Diels–Alder reaction of substrates **13** and **14** in toluene was carried out by heating them for 24 h in a sealed tube at 100 °C. The solvent was evaporated and purification of the residue by column chromatography afforded the bicyclo[2.2.2]octenones **8** (Table 1). As we expected, the cycloaddition reaction of dienone **13** with the dienophiles **14a–l** proceeded regio- and stereo-selectively to give the corresponding bicyclo[2.2.2]octenone **8** as a single product. The reaction can be explained by the mechanism shown in Scheme 4 involving endoselective attack of the dienophile from the less hindered C-6 methoxy face of the dienone.

The ^{1}H NMR spectra of compounds **8** showed the following characteristic signals; a singlet and an AB quartet at δ_H 2.1–2.2 and 2.8–2.9 due to a pair of the methylthio and thiomethylene hydrogens, and two signals ($J_{5,6}$ 8.4–8.9 Hz) at δ_H 6.0–6.4 and 6.2–6.5 due to vicinal vinyl hydrogens. The stereochemistry was confirmed by ^{1}H–^{1}H vicinal coupling constants ($J_{7,8\text{-}endo}$ 5.4–6.9 Hz, $J_{7,8\text{-}exo}$ 9.4–9.9 Hz) between 7-H and 8-H (9-H and 9a-H in the case of compound **8a**) in the ^{1}H NMR spectra,[16] or by observing the nuclear Overhauser effects (NOEs) between 3-OCH_3 and 7-CH_3 of compounds **8** or between 7a-H and 8-OCH_3 of the desulfurization derivative **18b** (Fig. 1). This relative stereochemistry was finally confirmed by an X-ray crystallographic determination of compound **8k** (Fig. 2).

In the reaction of compound **13** with diethyl fumarate **14m**, 2-*exo*/3-*endo* addition proceeded to give an adduct **8m** as a single product. The stereochemistry was established by observation of the NOEs between 8-OCH_3 and 3-H in the NOE difference spectrum of the desulfurization product **18m** (Scheme 5). This is explained by the supposition that 2-*exo*/3-*endo* addition (path a) is more favourable than 2-*endo*/2-*exo* addition (path b) owing to the steric interaction of the 6-methoxy group of com-



Scheme 3 *Conditions:* i, toluene, 55 °C; ii, pyrolysis (Kugelrohr distillation at 165–175 °C); iii, toluene, *hv*, Pyrex filter



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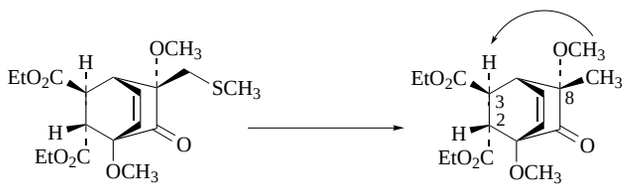
Scheme 4



8m **18m**

Scheme 5 NOEs observed in compound **18m**. *Reagents and conditions:* Raney Ni(w2), EtOH.

Table 1 Preparative data of compounds **8**, **20**, **21** and **9**

				Yield (%)		
R^1	R^2	R^3		**8**	**20** (**21**)	**9**
		H	**a**	77	80 (5)	99
−CH=CH−CH_2−		H	**b**	82	70 (0)	58
$C(CH_3)=CH_2$	H	H	**c**	77	74 (0)	86
CO_2Et	H	H	**d**	86	70 (11)	50
CO_2Bu^t	H	H	**e**	82	58 (14)	79
CO_2Me	H	CH_3	**f**	91	95 (3)	80
CN	H	H	**g**	82	34 (33)	44
COEt	H	H	**h**	77	51 (0)	72
$COCH_3$	H	CH_3	**i**	80		
CHO	H	H	**j**	75	36 (10)	75[a]
CHO	H	CH_3	**k**	74	58 (2)	65
CO_2Et	CO_2Et	H	**l**	75	66 (16)	80
H	CO_2Et	CO_2Et	**m**	58	46 (0)	83

[a] Shows the yield of the 3,7-bis-(2-ethoxycarbonylvinyl) bicyclo[2.2.2]-octenone **9t**.

pound **13** with the ethoxycarbonyl group of the approaching dienophile **14m** in path b (Scheme 6).

3-(2-Ethoxycarbonylvinyl)bicyclo[2.2.2]oct-5-en-2-ones **9** were prepared by Wittig reaction[17] of the corresponding aldehyde **20**, which was obtained by oxidation of an adduct **8** with sodium metaperiodate followed by Pummerer reaction with trifluoroacetic anhydride (TFAA),[18] in 15–77% total yield from adduct **8** (Table 1). In the Pummerer reaction process, bis(methylthio)methyl derivatives **21** were generated as a by-product together with the aldehydes **20**. The presence of a formyl group (δ_H 9.5 and δ_C 196–197) revealed the structure of products **20**. The structure of compounds **21** was confirmed by their ^{1}H NMR spectra which showed three singlets at δ_H 4.13–4.16, 1.97–2.11 and 2.27–2.30 due to a methine and two methyl groups of a 3-[bis(methylthio)methyl] group, and its successful conversion into compound **20** by treatment with $AgClO_4$.[19] The formation of compound **21** together with compounds **20** in the Pummerer reaction was explained by the mechanism shown in Scheme 7. Wittig reaction of the dialdehyde **20j** using an excess of reagent (2.3 mol equiv.) afforded 2,8-bis(2-ethoxycarbonylvinyl) derivative **9t** as a single product. The geometry of products **9** was confirmed to be *E* by the ^{1}H–^{1}H coupling constants (*J* 15.8–

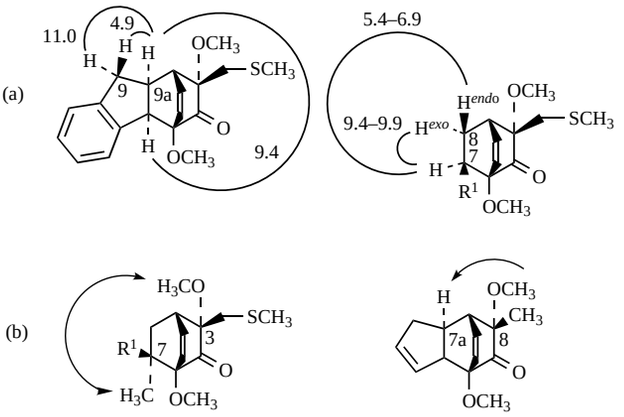


Fig. 1 (a) Coupling constants (Hz) in the ^{1}H NMR spectra of compounds **8a**, **8d**, **8e** and **8j**. (b) NOEs observed in compounds **8f**, **8i**, **8k** and **18b**.

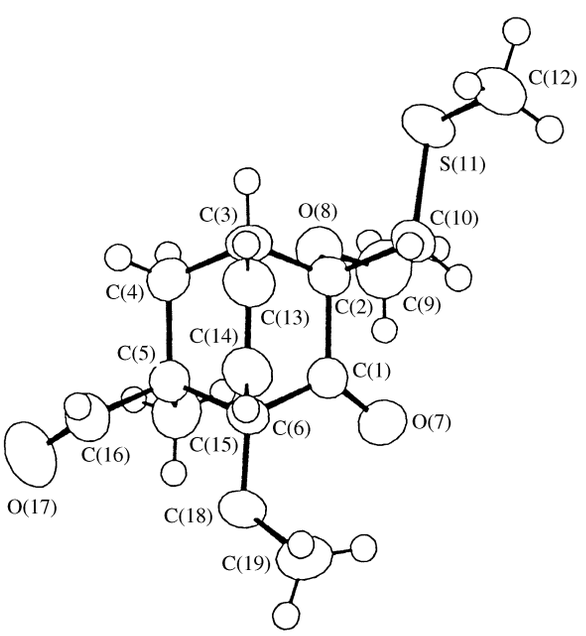
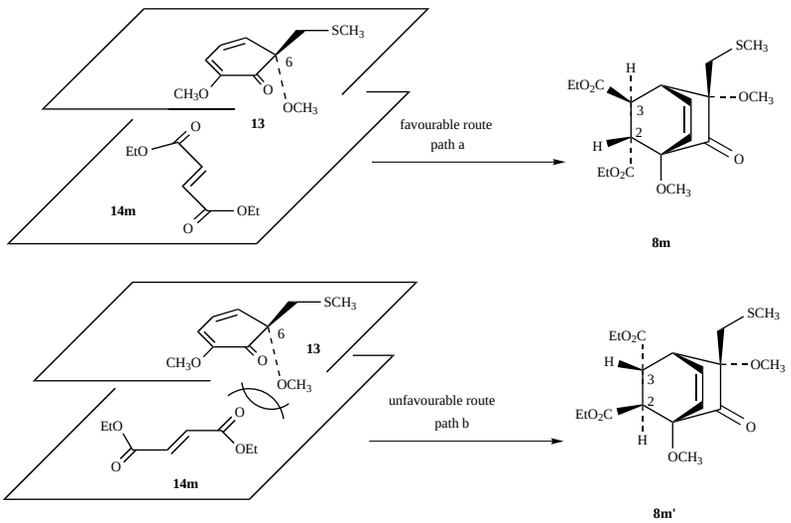


Fig. 2 ORTEP II (Johnson, 1976) diagram[24] of compound **8k**. Displacement ellipsoids are drawn at the 50% probability level.

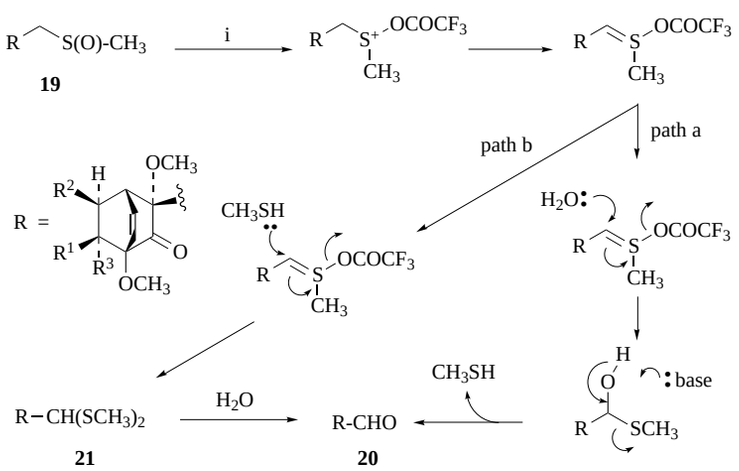
16.2 Hz) of the vicinal ethoxycarbonylvinyl hydrogens at δ_H 6.0–6.1 and 6.6–6.7 in the ^{1}H NMR spectra (Scheme 8).

Synthesis of bicyclo[4.1.0]heptenes (trinorcarenes) by photolysis of the bicyclo[2.2.2]octenones

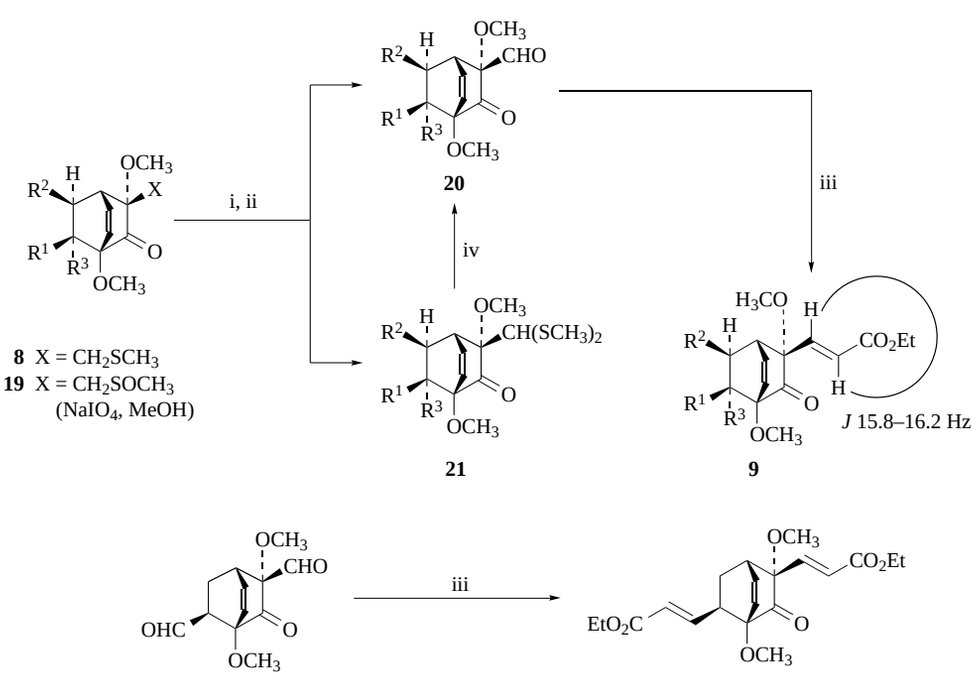
The photolysis of compounds **1** in the presence of a sensitizer such as acetone or acetophenone gave the bicyclo-[3.3.0.0^{2,8}]octanones **2** *via* a 1,2-acyl shift or an oxa-di-π-methane rearrangement upon triplet excitation (^{3}T),[1–3] and this was applied to the synthesis of various cyclopentanoid natural



Scheme 6



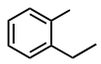
Scheme 7 *Reagent:* i, TFAA



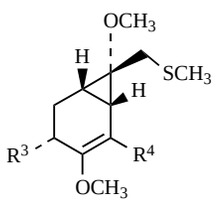
Scheme 8 *Reagents and conditions:* i, TFAA; ii, $NaHCO_3$; iii, $Ph_3\overset{+}{P}CH_2CO_2Et\ Br^-$, K_2CO_3, aq. CH_2Cl_2; iv, $AgClO_4$

products.[1] On the other hand, the photolysis of compounds **1** by direct irradiation in a non-sensitizer solvent such as benzene has been reported to give the bicyclo[4.2.0]oct-2-en-8-ones **3** *via* a 1,3-acyl shift upon singlet excitation (^1S).[4] We tried the photolysis of compounds **8** by direct irradiation, in expectation of the isolation of the photodecarbonylation product (trinorcarenes). The reaction was carried out in a benzene solution of a compound **8** with a 400 W high-pressure Hg lamp, for an

Table 2 Synthesis of compounds **10** by photolysis of substrates **8**

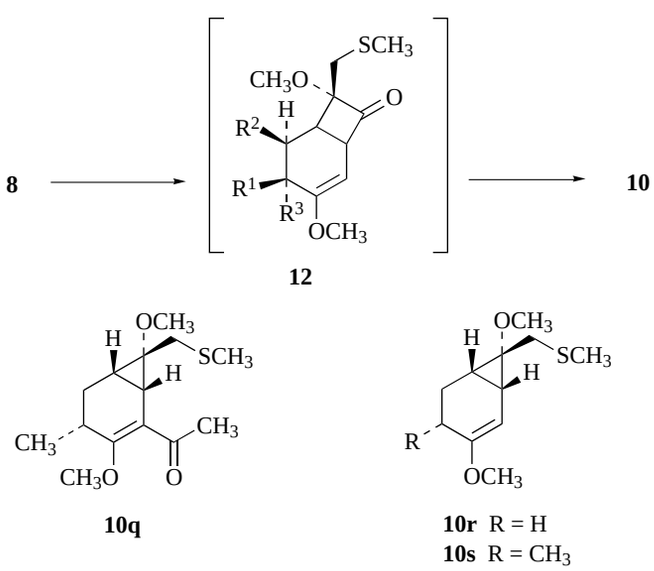
		8				Yield (%)	
Entry		R^1	R^2	R^3	Irradiation time (*t*/h)	**10**	**12**
1	**a**			H	8	46	0
2	**b**	−CH=CH−CH_2−		H	8	59	0
3	**c**	$C(CH_3)=CH_2$	H	H	8	59	0
4	**d**	CO_2Et	H	H	10	71	0
5	**e**	$CO_2{}^tBu$	H	H	4	69	8
6	**f**	CO_2Me	H	CH_3	4	58	14
7	**g**	CN	H	H	4	0[a]	0
8	**h**	COEt	H	H	2	9	66
9	**h**	COEt	H	H	10	48	0
10	**i**	$COCH_3$	H	CH_3	5	26[b]	0
11	**j**	CHO	H	H	5	0[c]	0
12	**k**	CHO	H	CH_3	5	0[d]	0
13	**n**	$C(OCH_2)_2CH_3$	H	CH_3	5	56	0
14	**o**	$CH(OCH_2)_2$	H	H	5	52	0
15	**p**	$CH(OCH_2)_2$	H	CH_3	5	54	0

[a] Unidentified product was obtained. [b] The trinorcarene (**10q**; $R^3 = CH_3$, $R^4 = COCH_3$) was also formed by rearrangement of the acetyl group in 35% yield. [c] The trinorcarene (**10r**; $R^3 = R^4 = H$) was formed after deformylation in 22% yield. [d] The trinorcarene (**10s**; $R^3 = CH_3$ $R^4 = H$) was formed after deformylation in 42% yield.



10q–s

appropriate time, in a Pyrex immersion well at 0 °C. The solvent was evaporated and purification by column chromatography furnished the trinorcarenes **10** in moderate yield (Table 2, Scheme 9). In entries 4–6, the 1,3-acyl shift product was also generated together with the decarbonylation product. Furthermore, short irradiation of compound **8h** gave mainly the 1,3-acyl shift product **12h** (entry 8), which was converted into the decarbonylation product **10h** by prolonged reaction time



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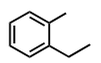
10q

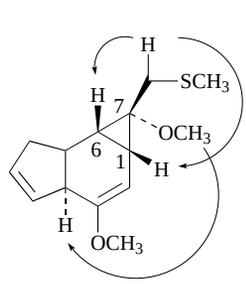
10r R = H
10s R = CH_3

Scheme 9 *Conditions:* i, benzene, *hv*, Pyrex filter

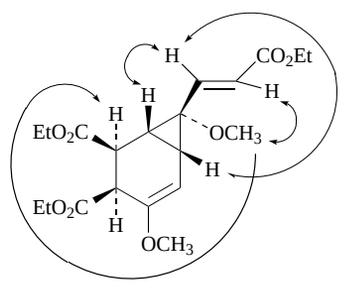
(entry 9). This suggests that the 1,3-acyl shift product, generated by α-cleavage,[5] was subject to photodecarbonylation successively to afford the trinorcarene as the final product (Scheme 1, path b). Similar considerations were described by Singh *et al*. in a closely related experiment with respect to the photodecarbonylation of β,γ-enones.[20] The photolysis of cyano derivative **8g** resulted concurrently in the formation of unidentified product after disappearance of the starting material according to TLC (entry 7). Although photolysis of the compounds having an acyl or a formyl group resulted in

Table 3 Synthesis of compounds **11** by photolysis of substrates **9**

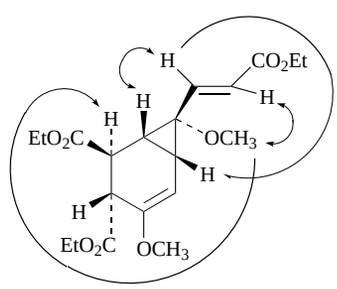
		9				Yield (%)	
Entry		R^1	R^2	R^3	Irradiation time (*t*/h)	**11**	**9** (recovery)
1	**a**			H	5	62	0
2	**b**	−CH=CH−CH_2−		H	5	65	0
3	**c**	$C(CH_3)=CH_2$	H	H	5	60	0
4	**d**	CO_2Et	H	H	5	92	0
5	**e**	$CO_2{}^tBu$	H	H	5	72	0
6	**f**	CO_2Me	H	CH_3	2	77	0
7	**g**	CN	H	H	10	56	14
8	**h**	COEt	H	H	5	69	0
9	**l**	CO_2Et	CO_2Et	H	12	72	0
10	**m**	H	CO_2Et	CO_2Et	12	75	0
11	**p**	$CH(OCH_2)_2$	H	CH_3	5	64	0
12	**t**	CH=$CHCO_2Et$	H	H	8	55	33



10b



11l



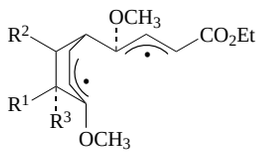
11m

Fig. 3 NOEs observed in compounds **10b**, **11l** and **11m**

rearrangement of the acyl group or deformylation to afford compounds **10q–s** (entries 10–12), the desired trinorcarenes **10n–p** were obtained by protection of these acyl or formyl groups as acetals (entries 13–15). The structures of these trinorcarenes **10a–p** were identified by their spectral data. The infrared (IR) spectra showed a strong absorption based on *ν*(C=C) 1640–1660 cm^{-1}, and no carbonyl absorption. The ^1H NMR spectra displayed a resonance at δ_H 1.1–1.4 ($J_{1,6}$ 9.2–9.6) due to two characteristic hydrogens (NOE) of the cyclopropane ring junction[21] and at δ_H 4.2–4.8 as a doublet due to an olefinic proton of the cyclohexene ring. The final conformation of the photoproducts was determined by NOE difference spectroscopy (Fig. 3), which showed the *cis* arrangement of 1-H and 6-H, and a methylthiomethyl group at C-7. This suggests that the decarbonylation–recyclization sequence proceeds with retention of stereochemistry at the quarternary carbon (C-7 of compounds **10**).

Upon direct irradiation of compounds **9** in benzene in a Pyrex immersion well, the desired trinorcarenes **11** were obtained in much better yields than were their analogues **10** (Table 3). Although the trinorcarene **10g** was not obtained at all in the photolysis of compound **8g** as described above, the desired

product **11g** was generated in moderate yield in the reaction of compound **9g** possessing a cyano group (entry 7). This is thought to be due to the stability of both the biradical intermediate **22** and the cyclopropane ring having an ethoxycarbonylvinyl function as an electron-withdrawing group toward photolysis. In order to complete the reaction, substrates **9a**–**f**,**h**,**p** required only 2–5 h for reaction, but compounds **9g**,**l**,**m** needed a somewhat a longer irradiation time (10–12 h). The IR spectra of compounds **11** also displayed a strong absorption owing to ν(C=C) in the region 1635–1660 cm^{-1}, and no carbonyl absorption except for that of an ethoxycarbonyl group. The ^{1}H NMR spectra showed signals at δ_H 1.5–2.2 ($J_{1,6}$ 9.2–9.4) due to two hydrogens of a cyclopropane ring junction, and δ_H 4.7–4.9 due to an olefinic hydrogen of the cyclohexene ring. The stereochemistry was confirmed by the NOE difference spectra (Fig. 3), and an X-ray crystallographic determination of compound **11l** as shown in Fig. 4, in which the conformation of the vinyl moiety was partially disordered.



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In conclusion, the synthesis of trinorcarenes by photodecarbonylation of the bicyclo[2.2.2]oct-5-en-2-ones, which had been difficult until now, was achieved by direct irradiation of the 2-ethoxycarbonylvinyl or 2-methylthiomethyl analogues in benzene solution. Further exploitation of this transformation as a versatile approach to sesquiterpenes such as sesquicarene and sirenin is under study.

Experimental

Spectral data were obtained using the following appratus: IR spectra on a JASCO IR-810 spectrophotometer; MS on a JEOL JMS-DX300 mass spectrometer by direct insertion at 70 eV; ^{1}H NMR spectra (270 MHz) and ^{13}C NMR spectra (67.8 MHz) on a JEOL EX-270 instrument for solutions in deuteriochloroform ($CDCl_3$), with chemical shifts being reported in δ units from tetramethylsilane as an internal standard and coupling constants (J) in Hz. UV Spectra were obtained on a Hitachi 200-10 spectrophotometer. Column chromatography was carried out on silica gel (100–200 mesh, Micro Bead 4B, Fuji-Davison Chemical Ltd).

(1α,4α,4aα,5*R,8aα,9*S**)-1,5,7,9-Tetramethoxy-5,9-bis(methylthiomethyl)-1,4a,*S*,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4*H*)-dione 15**

A solution of crude 2,6-dimethoxy-6-(methylthiomethyl)-cyclohexa-2,4-dienone **13**, prepared by the previously reported method[11] from 2,6-dimethoxyphenol (14.32 g, 93 mmol), in dry toluene (15 cm^3) was stirred at 55 °C for 5 days. Removal of the solvent under reduced pressure and crystallization from diethyl ether–hexane or chromatography of the residue over silica gel (199 g; eluent hexane–ethyl acetate, 7:3) afforded crystalline adduct **15** (17.91 g, 90%) as a solid from benzene–hexane, mp 117–118.5 °C (Found: C, 56.05; H, 6.6. $C_{20}H_{28}O_6S_2$ requires C, 56.05; H, 6.59%); ν_{max}(KBr)/cm^{-1} 1734, 1700 and 1635; δ_H 2.10 (3 H, s, CH_3S), 2.11 (3 H, s, CH_3S), 2.80 (2 H, ABq, J 14.1, CH_2S), 2.98 (2 H, ABq, J 14.1, CH_2S), 3.31 (1 H, dd, J 8.9 and 4.3, =CHC*H*CH), 3.42 (3 H, s, CH_3O), 3.43–3.45 (1 H, m, 4-H), 3.50 (3 H, s, CH_3O), 3.52 (1 H, br d, J 8.9, CHC*H*CH), 3.56 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 5.39 (1 H, d, J 4.3, =C*H*CH), 5.91 (1 H, d, J 8.5, C*H*=CHCH) and 6.31 (1 H, dd, J 8.5 and 7.1, CH=C*H*CH); δ_C 16.6 (CH_3S), 16.8 (CH_3S), 37.1 (CH_2S), 38.7, 39.9 and 40.1 (C-4, -4a and -8a), 40.4 (CH_2S), 51.0 (CH_3O), 52.3 (CH_3O), 54.2 (CH_3O), 55.6 (CH_3O), 77.3, 81.7 and 88.7 (C-1, -5 and -9), 107.6 (C-8), 131.0 (C-2), 133.2 (C-3), 152.7 (C-7), 192.7 (C=O) and 206.6 (C=O); *m*/*z* (%) 428 (1, M^+), 214 (17) and 61 (base).

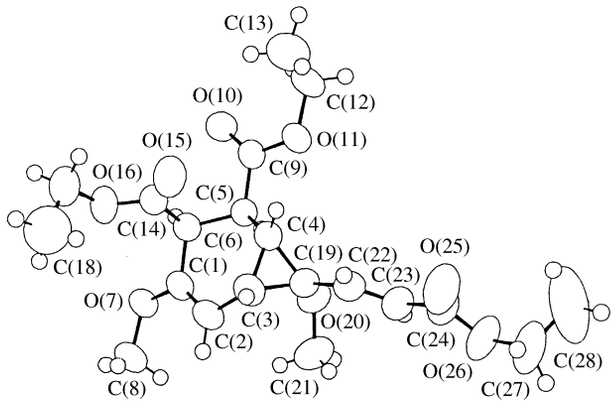

Fig. 4 ORTEP II (Johnson, 1976) diagram[24] of compound **11l**. Displacement ellipsoids are drawn at the 50% probability level.

5,7,10,12-Tetramethoxy-7,10-bis(methylthiomethyl)pentacyclo[6.4.0.0^{2,5}.0^{3,12}.0^{4,9}]dodecane-6,11-dione 16

A solution of compound **15** (1.5 g) in acetophenone (200 cm^3) was irradiated at 0 °C for 3 h under nitrogen. Removal of acetophenone by vacuum distillation at 5×10^{-2} mmHg followed by chromatography over silica gel (20 g; hexane–ethyl acetate, 8:2) afforded the *title compound* **16** (535 mg, 35%) as a crystalline product, recrystallized as a solid from benzene–hexane, mp 112–115 °C (Found: M^+, 428.1310; C, 56.1; H, 6.5. $C_{20}H_{28}O_6S_2$ requires *M*, 428.1328; C, 56.05; H, 6.59%); ν_{max}(KBr)/cm^{-1} 1725; δ_H 2.15 (6 H, s, $CH_3S \times 2$), 2.76 (4 H, ABq, J 14.3, CH_2S), 3.00 (2 H, d, J 5.4, CHC*H*CCH_2S × 2), 3.09–3.15 (2 H, m, 3- and 2-H), 3.36 (2 H, t, J 5.4, 4- and 1-H), 3.46 (6 H, s, $CH_3O \times 2$) and 3.55 (6 H, s, $CH_3O \times 2$); δ_C 17.1 ($CH_3S \times 2$), 34.9 ($CH_2S \times 2$), 38.2 and 38.4 (C-2, -1, -8 and -9), 42.6 (C-3 and -4), 52.3 ($CH_3O \times 2$), 53.8 ($CH_3O \times 2$), 78.7, 84.2 (C-5, -7, -10 and -12) and 207.7 (C-6 and -11); *m*/*z* (%) 429 (3, $M^+ + 1$), 428 (11, M^+) and 61 (base). Continued elution with hexane–ethyl acetate (8:2) gave (1β,4aβ,4bα,5α,8aα,8bβ)-1,3,5,7-tetramethoxy-1,5-bis(methylthiomethyl)-4a,4b,8a,8b-tetrahydrobiphenylene-2,6(1*H*,5*H*)-dione **17** (377 mg, 25%) together with the starting material **15** (413 mg recovery).

Dione **17** was obtained as a solid from benzene–hexane, mp 201–203 °C; ν_{max}(KBr)/cm^{-1} 1710 and 1630; δ_H 2.07 (6 H, s, $CH_3S \times 2$), 2.78 (4 H, ABq, J 13.9, $CH_2S \times 2$), 2.88–2.90 (2 H, m, 4a- and 8a-H), 3.15 (2 H, br d, J 5.9, =CHC*H*CH × 2), 3.55 (6 H, s, $CH_3O \times 2$), 3.71 (6 H, s, $CH_3O \times 2$) and 5.73 (2 H, d, J 4.1, =CH × 2); δ_C 16.6 ($CH_3S \times 2$), 36.0 ($CH_2S \times 2$), 36.6 (C-4b and -8b), 37.3 (C-4a and -8a), 50.5 ($CH_3O \times 2$), 55.6 ($CH_3O \times 2$), 81.7 (C-1 and -5), 114.4 (C-4 and -8), 150.5 (C-3 and -7) and 191.6 (C-2 and -6); *m*/*z* (%) 428 (0.3, M^+) and 61 (base).

General procedure for the preparation of 1,3-dimethoxy-3-(methylthiomethyl)bicyclo[2.2.2]oct-5-en-2-ones 8

A solution of the cyclohexa-2,4-dienone **13** [4.00 g, 18.7 mmol, freshly prepared from its dimer **15** by Kügelrohr distillation (bp 165–175 °C/0.1 mmHg) because of its ready dimerisation and the appropriate dienophile **14** (93.5 mmol) in dry toluene (80 cm^3) was heated in a sealed tube at 100 °C for 24 h. Removal of the solvent under reduced pressure and chromatography of the residue over silica gel (65 g; eluent hexane–ethyl acetate, 9:1) furnished the corresponding adduct **8**.

(1α,4α,4aα,9aα,11*S)-4,11-Dimethoxy-11-methylthiomethyl-1,4,4a,9a-tetrahydro-1,4-ethanofluoren-10-one 8a.** A *solid* from benzene–hexane, mp 129–131 °C (Found: C, 68.8; H, 6.75. $C_{19}H_{22}O_3S$ requires C, 69.06; H, 6.71%); ν_{max}(KBr)/cm^{-1} 1715

and 1605; λ_{max}(EtOH)/nm 210 (15 870), 268 (1772), 274 (1941) and 317 (101); δ_H 2.15 (3 H, s, CH_3S), 2.68 (1 H, dd, *J* 16.8 and 4.9, C*H*^{endo}HCH), 2.84 (2 H, ABq, *J* 13.8, CH_2S), 3.21 (1 H, dd, *J* 16.8 and 11.0, CH*H*^{exo}CH), 3.36–3.41 (1 H, m, 1-H), 3.49 (3 H, s, CH_3O), 3.51–3.62 (1 H, m, 9a-H), 3.64 (3 H, s, CH_3O), 3.81 (1 H, d, *J* 9.4, ArC*H*CH), 5.96 (1 H, br d, *J* 8.9, CH_3OC-C*H*=CH), 6.24 (1 H, dd, *J* 8.9 and 6.4, CH=C*H*CH), 7.07–7.19 (3 H, m, 6-, 7- and 8-H) and 7.41–7.44 (1 H, m, 5-H); δ_C 16.9 (CH_3S), 35.4 (C-9a), 37.4 (CH_2S), 38.0 (C-9), 45.2 (C-1), 50.9 (C-4a), 52.3 (CH_3O), 54.0 (CH_3O), 76.5 and 87.5 (C-4 and -11), 123.8, 126.2 and 127.3 (C-6, -7 and -8), 126.9 (C-5), 130.6 (C-3), 132.3 (C-2), 141.0 and 144.8 (C-4b and -8a) and 206.1 (C-10); *m*/*z* (%) 330 (0.5, M^+), 255 (62), 139 (base) and 61 (43).

(3a*α*,4*α*,7*α*,7a*α*,8*S)-4,8-Dimethoxy-8-methylthiomethyl-3a,4,7,7*α*-tetrahydro-4,7-ethanoindene-9-one 8b.** An *oil*; ν_{max}(neat)/cm^{-1} 1725 and 1613; λ_{max}(EtOH)/nm 204 (4763) and 303 (202); δ_H 2.02 (1 H, br d, *J* 17.1, =CHC*H*^{endo}HCH), 2.22 (3 H, s, CH_3S), 2.62 (1 H, ddd, *J* 17.1, 10.0 and 1.2, =CHCH*H*^{exo}CH), 2.75–2.80 (1 H, m, 7a-H),), 2.89 (2 H, ABq, *J* 14.2, CH_2S), 3.12 (1 H, br d, *J* 9.4, CH_3OCC*H*CH), 3.23 (1 H, br d, *J* 6.6, =CHC*H*$CHCH_2$), 3.33 (3 H, s, CH_3O), 3.55 (3 H, s, CH_3O), 5.60 (1 H, br d, *J* 5.5, 3- or 2-H), 5.76 (1 H, br d, *J* 5.5, 2- or 3-H), 6.09 (1 H, br d, *J* 8.5, CH_3OCC*H*=CH) and 6.32 (1 H, dd, *J* 8.5 and 6.6, CH=C*H*CH); δ_C 16.9 (CH_3S), 34.6 (CH), 37.5 (CH_2S), 38.9 (C-1), 44.6 (CH), 51.4 (CH), 52.2 (CH_3O), 53.4 (CH_3O), 76.9 and 86.7 (C-4 and -8), 128.2 (C-3 or -2), 131.2 (C-5), 131.7 (C-6), 134.3 (C-3 or -2) and 207.6 (C-9); *m*/*z* (%) 280 (1, M^+), 233 (2, $M^+ - CH_3S$), 205 (base) and 61 (47) (Found: M^+, 280.1136. $C_{15}H_{20}O_3S$ requires *M*, 280. 1133).

(1*α*,3*S,4*α*,7*R**)-7-Isopropenyl-1,3-dimethoxy-3-(methylthiomethyl)bicyclo[2.2.2]oct-5-en-2-one 8c.** An *oil*; ν_{max}(neat)/cm^{-1} 1725 and 1640; δ_H 1.30 (1 H, ddd, *J* 12.9, 6.9 and 2.0, CHC*H*^{endo}HCH), 1.66 (3 H, s, $=CCH_3$), 2.13 (3 H, s, CH_3S), 2.52 (1 H, ddd, *J* 12.9, 9.9 and 3.5, CHCH*H*^{exo}CH), 2.81 (2 H, ABq, *J* 13.9, CH_2S), 3.08 (1 H, dd, *J* 9.9 and 6.9, CH_3OCC*H*CH_2), 3.14–3.20 (1 H, m, 4-H), 3.41 (3 H, s, CH_3O), 3.54 (3 H, s, CH_3O), 4.71–4.85 (2 H, m, CH_2=), 6.08 (1 H, d, *J* 8.4, CH_3OC-C*H*=CH) and 6.38 (1 H, dd, *J* 8.4 and 6.9, CH=C*H*CH); δ_C 16.9 (CH_3S), 20.5 (*C*H_3C=), 29.0 (C-8), 37.2 (CH_2S), 39.5 (C-4), 43.5 (C-7), 52.1 (CH_3O), 53.4 (CH_3O), 76.2 and 85.6 (C-1 and -3), 113.8 (CH_2=), 129.6 (C-6), 133.6 (C-5), 145.1 (7-C=) and 203.2 (C-2); *m*/*z* (%) 282 (1, M^+), 254 (1, $M^+ - CO$) and 207 (base) (Found: M^+, 282.1306. $C_{15}H_{22}O_3S$ requires *M*, 282.1290).

Ethyl (1*α*,2*S,4*α*,8*S**)-1,8-dimethoxy-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 8d.** An *oil*; ν_{max}(neat)/cm^{-1} 1735, 1730 and 1610; δ_H 1.26 (3 H, t, *J* 7.1, C*H*$_3$CH$_2$), 1.62 (1 H, ddd, *J* 12.4, 6.4 and 2.4, CHC*H*^{endo}HCH), 2.13 (3 H, s, CH_3S), 2.61 (1 H, ddd, *J* 12.4, 9.9 and 3.2, CHCH*H*^{exo}CH), 2.81 (2 H, ABq, *J* 13.9, CH_2S), 3.22 (1 H, ddd, *J* 9.9, 6.4 and 1.2, CH_2CHCO_2), 3.25–3.32 (1 H, m, 4-H), 3.37 (3 H, s, CH_3O), 3.59 (3 H, s, CH_3O), 4.09–4.21 (2 H, m, CH_2O), 6.18 (1 H, d, *J* 8.5, CH_3OCC*H*=CH), 6.45 (1 H, dd, *J* 8.5 and 6.9, CH=C*H*CH); δ_C 14.1 (*C*H_3CH_2), 16.9 (CH_3S), 27.6 (C-3), 36.9 (CH_2S), 39.8 (C-2), 42.1 (C-4), 52.1 (CH_3O), 53.9 (CH_3O), 60.9 (CH_2O), 76.1 and 84.9 (C-1 and -8), 128.5 (C-6), 134.0 (C-5), 172.6 (CO_2) and 201.6 (C-7); *m*/*z* (%) 314 (0.2, M^+), 238 (base) and 61 (7).

***tert*-Butyl (1*α*,2*S**,4*α*,8*S**)-1,8-dimethoxy-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 8e.** A *solid* from benzene–hexane, mp 46–49 °C (Found: C, 59.3; H, 7.4. $C_{17}H_{26}O_5S$ requires C, 59.62; H, 7.65%); ν_{max}(KBr)/cm^{-1} 1717 and 1615; λ_{max}(EtOH)/nm 211 (3551) and 322 (62); δ_H 1.47 [9 H, s, C(CH_3)$_3$], 1.59 (1 H, ddd, *J* 12.4, 6.4 and 2.4, CHC*H*^{endo}HCH), 2.13 (3 H, s, CH_3S), 2.60 (1 H, ddd, *J* 12.4, 10.1 and 3.1, CHCH*H*^{exo}CH), 2.81 (2 H, ABq, *J* 14.6, CH_2S), 3.11–3.15 (1 H, m, 4- or 2-H), 3.24–3.26 (1 H, m, 2- or 4-H), 3.36 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 6.16 (1 H, dd, *J* 8.4 and 1.5, CH_3OCC*H*=CH) and 6.42 (1 H, dd, *J* 8.4 and 7.0, CH=C*H*CH); δ_C 16.9 (CH_3S), 27.6 (C-3), 28.0 [C(*C*H_3)$_3$], 37.0 (CH_2S), 39.8 and 42.5 (C-2 and -4), 52.1 (CH_3O), 53.8 (CH_3O), 76.1, 81.2 and 85.1 [C-1, -8 and *C*(CH_3)$_3$], 128.9 (C-6), 133.5 (C-5), 171.9 (CO_2) and 201.8 (C-7); *m*/*z* (%) 267 (19, $M^+ - 75$) and 179 (base).

Methyl (1*α*,2*S,4*α*,8*S**)-1,8-dimethoxy-2-methyl-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 8f.** A *solid* from benzene–hexane, mp 105.5–108 °C (Found: C, 57.1; H, 7.0. $C_{15}H_{22}O_5S$ requires C, 57.30; H, 7.05%); ν_{max}(KBr)/cm^{-1} 1725 and 1613; λ_{max}(EtOH)/nm 210 (3925) and 327 (77); δ_H 1.30 (3 H, s, 2-CH_3), 1.95 (1 H, dd, *J* 12.9 and 3.2, C*H*^{endo}HCH), 2.15 (3 H, s, CH_3S), 2.24 (1 H, dd, *J* 12.9 and 2.7, CH*H*^{exo}CH), 2.85 (2 H, ABq, *J* 13.9, CH_2S), 3.22–3.25 (1 H, m, 4-H), 3.43 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 3.66 (3 H, s, CH_3O), 6.40–6.50 (2 H, m, 5- and 6-H); δ_C 16.8 (CH_3S), 20.5 (2-CH_3), 35.6 (C-3), 37.6 (CH_2S), 39.8 (C-4), 50.0 (C-2), 51.5 (CH_3O), 52.1 (CH_3O), 54.9 (CH_3O), 75.7 and 88.9 (C-1 and -8), 128.6 and 133.3 (C-5 and -6), 175.0 (CO_2) and 204.6 (C-2); *m*/*z* (%) 314 (3, M^+), 238 (base) and 61 (13) (Found: M^+, 314.1169. $C_{15}H_{22}O_5S$ requires *M*, 314.1188).

(1*α*,2*R,4*α*,8*S**)-1,8-Dimethoxy-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carbonitrile 8g.** A *solid* from benzene–hexane, mp 91–93.5 °C (Found: M^+, 267.0916; C, 58.5; H, 6.5. $C_{13}H_{17}NO_3S$ requires *M*, 267.0929; C, 58.40; H, 6.4%); ν_{max}(KBr)/cm^{-1} 2230 and 1722; λ_{max}(EtOH)/nm 211 (2944) and 324 (51); δ_H 1.69 (1 H, ddd, *J* 13.0, 5.5 and 3.1, CHC*H*^{endo}HCH), 2.12 (3 H, s, CH_3S), 2.80 (2 H, ABq, *J* 13.9, CH_2S), 2.81 (1 H, ddd, *J* 13.0, 10.1 and 3.1, CHCH*H*^{exo}CH), 3.10–3.28 (1 H, m, 4-H), 3.32 (1 H, ddd, *J* 10.1, 5.5 and 0.9, CH_2C*H*CN), 3.36 (3 H, s, CH_3O), 3.64 (3 H, s, CH_3O), 6.27 (1 H, br d, *J* 8.5, CH_3OCC*H*=CH) and 6.62 (1 H, dd, *J* 8.5 and 7.1, CH=C*H*CH); δ_C 16.8 (CH_3S), 27.2 (C-3), 29.6 (C-2), 36.5 (CH_2S), 39.2 (C-4), 52.2 (CH_3O), 54.0 (CH_3O), 76.1 and 83.1 (C-1 and -8), 119.3 (CN), 128.6 and 136.5 (C-5 and -6) and 200.7 (C-7); *m*/*z* (%) 268 (1, $M^+ + 1$), 267 (6, M^+), 239 (21, $M^+ - CO$) and 178 (base).

(1*α*,3*S,4*α*,7*S**)-1,3*α*-Dimethoxy-3-methylthiomethyl-7-propionylbicylo[2.2.2]oct-5-en-2-one 8h.** An *oil*; ν_{max}(neat)/cm^{-1} 1715 and 1610; δ_H 1.01 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.54 (1 H, ddd, *J* 12.4, 6.6 and 2.3, CHC*H*^{endo}HCH), 2.14 (3 H, s, CH_3S), 2.31–2.47 (1 H, m, 8-H^{exo}), 2.55 (2 H, q ABq, *J* 18.5 and 6.9, C*H*$_2$CH$_3$), 2.80 (2 H, ABq, *J* 13.9, CH_2S), 3.19–3.32 (2 H, m, 4- and 7-H), 3.42 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 6.27 (1 H, d, *J* 8.6, CH_3OCC*H*=CH) and 6.48 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH); δ_C 7.5 (*C*H_3CH_2), 16.9 (CH_3S), 26.8 (C-8), 36.9 (CH_2S), 37.8 (*C*H_2CO), 40.1 and 48.2 (C-4 and -7), 53.0 (CH_3O), 54.4 (CH_3O), 75.9 and 85.8 (C-1 and -3), 126.6 (C-6), 134.3 (C-5), 203.0 and 210.4 (C-2 and 7-CO); *m*/*z* (%) 298 (0.4, M^+), 235 (6), 221 (16), 203 (base) and 61 (5).

(1*α*,3*S,4*α*,7*S**)-7-Acetyl-1,3-dimethoxy-7-methyl-3-(methylthiomethyl)bicyclo[2.2.2]oct-5-en-2-one 8i.** An *oil*; ν_{max}(neat)/cm^{-1} 1725, 1700 and 1613; λ_{max}(EtOH)/nm 211 (2983) and 318 (68); δ_H 1.33 (3 H, s, 7-CH_3), 1.99 (1 H, dd, *J* 13.4 and 2.5, C*H*^{endo}HCH), 2.15 (3 H, s, CH_3S), 2.18 (3 H, s, CH_3CO), 2.20–2.22 (1 H, m, 8-H^{exo}), 2.83 (2 H, ABq, *J* 13.9, CH_2S), 3.21–3.23 (1 H, m, 4-H), 3.51 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O), 6.30 (1 H, dd, *J* 8.7 and 1.5, CH_3OCC*H*=CH) and 6.44 (1 H, dd, *J* 8.7 and 6.9, CH=C*H*CH); δ_C 16.9 (CH_3S), 20.6 (7-CH_3), 28.4 (*C*H_3CO), 32.6 (C-8), 37.5 (CH_2S), 39.7 (C-4), 51.5 (CH_3O), 54.7 (CH_3O and C-7), 75.7 and 89.1 (C-1 and -3), 127.2 (C-6), 134.5 (C-5), 205.1 (7-CO) and 209.2 (C-2); *m*/*z* (%) 298 (4, M^+), 147 (base) and 61 (35) (Found: M^+, 298.1233. $C_{15}H_{22}O_4S$ requires *M*, 298. 1239).

(1*α*,4*α*,8*S)-1,8-Dimethoxy-8-methylthiomethyl-7-oxobicyclo-[2.2.2]oct-5-ene-2β-carbaldehyde 8j.** A *solid* from benzene–hexane, mp 52–53.5 °C (Found: M^+, 270.0925; C, 57.6; H, 6.6. $C_{13}H_{18}O_4S$ requires *M*, 270.0926; C, 57.76; H, 6.71%); ν_{max}(KBr)/cm^{-1} 1720, 1685, 1645 and 1605; δ_H 1.75 (1 H, ddd, *J* 12.9, 5.4 and 2.7, CHC*H*^{endo}HCH), 2.13 (3 H, s, CH_3S), 2.46 (1 H, ddd, *J* 12.9, 9.4 and 3.0, CHCH*H*^{exo}CH), 2.81 (2 H, ABq, *J* 14.0, CH_2S), 3.11–3.18 (1 H, m, 4-H), 3.29–3.34 (1 H, m, 2-H), 3.40 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 6.19 (1 H, d, *J* 8.4, CH_3OCC*H*=CH), 6.53 (1 H, dd, *J* 8.4 and 6.9, CH=C*H*CH) and

9.58 (1 H, d, *J* 3.0, 2-CHO); δ_C 16.9 (CH_3S), 22.8 (C-3), 36.8 (CH_2S), 39.8 (C-2), 48.9 (C-4), 52.1 (CH_3O), 53.9 (CH_3O), 76.2 and 84.9 (C-1 and -8), 127.9 (C-6), 136.0 (C-5), 200.3 (2-CHO) and 202.1 (C-7); *m*/*z* (%) 270 (1, M^+) and 194 (base).

(1α,2*S,4α,8*S**)-1,8-Dimethoxy-2-methyl-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carbaldehyde 8k.** A solid from benzene–hexane, mp 90–93 °C (Found: M^+, 284.1133; C, 58.9; H, 7.0. $C_{14}H_{20}O_4S$ requires *M*, 284.1083; C, 59.13; H, 7.09%); ν_{max}(KBr)/cm^{-1} 1725 and 1610; λ_{max}(EtOH)/nm 207 (2878) and 326 (68); δ_H 1.19 (3 H, s, 2-CH_3), 2.01 (1 H, dd, *J* 13.4 and 3.0, C*H*^{endo}HCH), 2.08 (1 H, dd, *J* 13.4 and 3.0, CH*H*^{exo}CH), 2.15 (3 H, s, CH_3S), 2.83 (2 H, ABq, *J* 13.9, CH_2S), 3.27–3.30 (1 H, m, 4-H), 3.46 (3 H, s, CH_3O), 3.54 (3 H, s, CH_3O), 6.37 (1 H, dd, *J* 8.4 and 2.0, CH_3OCC*H*=CH), 6.56 (1 H, dd, *J* 8.4 and 6.4, CH=C*H*CH) and 9.53 (1 H, s, CHO); δ_C 16.8 (CH_3S), 17.3 (2-CH_3), 30.5 (C-3), 37.2 (CH_2S), 39.9 (C-4), 51.7 (CH_3O), 53.7 (C-2), 55.0 (CH_3O), 75.9 and 88.4 (C-1 and -8), 127.0 (C-6), 136.5 (C-5), 202.4 (CHO) and 204.1 (C-2); *m*/*z* (%) 284 (5, M^+), 208 (base) and 61 (41).

Diethyl (1α,2*S,3*S**,4α,8*S**)-1,8-dimethoxy-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 8l.** A *solid* from benzene, mp 58–61 °C (Found: M^+, 386.1465; C, 55.8; H, 6.7. $C_{18}H_{26}O_7S$ requires *M*, 386.1400; C, 55.94; H, 6.78%); ν_{max}(KBr)/cm^{-1} 1735 and 1617; λ_{max}(EtOH)/nm 208 (1206) and 322 (29); δ_H 1.21 (3 H, t, *J* 7.1, C*H*$_3$CH$_2$), 1.27 (3 H, t, *J* 7.1, C*H*$_3$CH$_2$), 2.16 (3 H, s, CH_3S), 2.83 (2 H, ABq, *J* 14.2, CH_2S), 3.38 (3 H, s, CH_3O), 3.59 (3 H, s, CH_3O), 3.64 (1 H, br d, *J* 6.6, =CHC*H*CH), 3.65 (1 H, dd, *J* 11.9 and 1.3, CH_3OCC*H*-CH), 3.89 (1 H, dd, *J* 11.9 and 2.3, =CHCHC*H*CH), 4.12 (2 H, q, *J* 7.1, C*H*$_2$CH$_3$), 4.13 (2 H, q, *J* 7.1, C*H*$_2$CH$_3$), 6.21 (1 H, br d, *J* 8.4, CH_3OCC*H*=CH) and 6.59 (1 H, dd, *J* 8.4 and 6.6, CH=C*H*CH); δ_C 14.0 (*C*H$_3$CH$_2$), 14.1 (*C*H$_3$CH$_2$), 16.9 (CH_3S), 36.6 (CH_2S), 41.7 (C-4 or -2), 43.6 (C-3), 47.7 (C-2 or -4), 52.3 (CH_3O), 54.1 (CH_3O), 61.0 (CH_2O × 2), 75.5 and 84.9 (C-1 and -8), 128.2 (C-6), 133.7 (C-5), 169.9 (CO_2), 171.5 (CO_2) and 201.5 (C-7); *m*/*z* (%) 386 (1, M^+), 358 (7, $M^+ - CO$), 311 (base) and 61 (13).

Diethyl (1α,2*R,3*S**,4α,8*S**)-1,8-dimethoxy-8-methylthiomethyl-7-oxobicyclo[2.2.2]oct-5-en-2,3-dicarboxylate 8m.** An *oil*; ν_{max}(neat)/cm^{-1} 1750, 1735 and 1615; λ_{max}(EtOH)/nm 209 (7796) and 317 (86); δ_H 1.26 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.28 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 2.17 (3 H, s, CH_3S), 2.85 (2 H, ABq, *J* 14.3, CH_2S), 3.44 (3 H, s, CH_3O), 3.47 (1 H, d, *J* 5.6, CH_3OCC*H*CH), 3.55 (3 H, s, CH_3O), 3.69–3.73 (1 H, m, 4-H), 3.78 (1 H, dd, *J* 5.6 and 2.3, =CHCHC*H*CH), 4.19 (4 H, q, *J* 6.9, C*H*$_2$CH$_3$ × 2) and 6.32–6.42 (2 H, m, 5- and 6-H); δ_C 14.2 (*C*H$_3$CH$_2$ × 2), 16.7 (CH_3S), 37.0 (CH_2S), 42.6 (C-4), 42.8 (C-3), 49.3 (C-2), 52.1 (CH_3O), 53.4 (CH_3O), 61.4 (CH_2O), 61.5 (CH_2O), 75.6 and 84.7 (C-1 and -8), 130.1 and 133.5 (C-5 and -6), 171.4 (CO_2), 172.9 (CO_2) and 201.1 (C-7); *m*/*z* (%) 386 (0.1, M^+), 358 (3, $M^+ - CO$), 237 (base) and 61 (9).

(1′α,4′α,8′*S)-2-(1′,8′-Dimethoxy-2′-methyl-8′-methylthiomethyl-7′-oxobicyclo[2.2.2]oct-5′-en-2′β-yl)-2-methyl-1,3-dioxolane 8n.** A solution of compound **8i** (2.80 g, 9.40 mmol), ethylene glycol (1.17 g, 18.8 mmol) and a trace amount of toluene-*p*-sulfonic acid (PTSA) in benzene (100 cm^3) was stirred at reflux, with azeotropic removal of water, for 24 h. After cooling, the reaction mixture was washed with brine (2 × 30 cm^3) and dried over $MgSO_4$. Removal of solvent under reduced pressure and chromatography of the residue over silica gel (29 g; eluent hexane–ethyl acetate, 9:1) furnished the *title compound* **8n** as an oil (2.83 g, 88%); ν_{max}(neat)/cm^{-1} 1730 and 1620; λ_{max}(EtOH)/nm 205 (3669) and 309 (12); δ_H 1.14 [3 H, s, 2′-CH_3 or $CH_3C(O\text{-})_2$], 1.30 [3 H, s, 2′-CH_3 or $CH_3C(O\text{-})_2$], 1.77 (1 H, dd, *J* 13.5 and 2.6, C*H*^{endo}HCH), 1.99 (1 H, dd, *J* 13.5 and 3.0, CH*H*^{exo}CH), 2.15 (3 H, s, CH_3S), 2.84 (2 H, ABq, *J* 14.2, CH_2S), 3.10–3.17 (1 H, m, 4′-H), 3.43 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 3.88–3.95 (4 H, m, OCH_2CH_2O) and 6.27–6.35 (2 H, m, 5′- and 6′-H); δ_C 16.8 (CH_3S), 20.1 and 22.3 [2′-CH_3 and *C*$H_3C(O\text{-})_2$], 33.5 (C-3′), 37.9 (CH_2S), 39.2 (C-4′), 49.1 (C-2′), 51.3 (CH_3O), 54.6 (CH_3O), 64.3 and 64.8 (OCH_2CH_2O), 75.3 and 90.2 (C-1′ and -8′), 114.2 [$C(O\text{-})_2$], 128.7 and 132.5 (C-5′ and -6′) and 206.0 (C-7′); *m*/*z* (%) 342 (0.1, M^+), 327 (0.1, $M^+ - CH_3$) and 87 (base).

(1′α,4′α,8′*S)-2-(1′,8′-Dimethoxy-8′-methylthiomethyl-7′-oxobicyclo[2.2.2]oct-5′-en-2′β-yl)-1,3-dioxolane 8o.** This compound was prepared from compound **8j** (1.57 g, 5.81 mmol) in a similar procedure to that for the analogue **8n** in 70% yield as an oil (1.27 g); ν_{max}(neat)/cm^{-1} 1720 and 1610; λ_{max}(EtOH)/nm 208 (2635) and 301 (185); δ_H 1.48 (1 H, ddd, *J* 12.9, 6.3 and 2.6, CHC*H*^{endo}HCH), 2.13 (3 H, s, CH_3S), 2.34 (1 H, ddd, *J* 12.9, 9.9 and 3.0, CHCH*H*^{exo}CH), 2.67 (1 H, dddd, *J* 6.6, 6.3, 3.0 and 1.0, =CHC*H*CH$_2$), 2.81 (2 H, ABq, *J* 13.9, CH_2S), 3.15–3.20 (1 H, m, 2′-H), 3.37 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 3.80–3.96 (4 H, m, OCH_2CH_2O), 4.99 [1 H, d, *J* 3.0, CHC*H*$(O\text{-})_2$], 6.11 (1 H, d, *J* 8.6, CH_3OCC*H*=CH) and 6.38 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH); δ_C 16.8 (CH_3S), 22.1 (C-3′), 37.1 (CH_2S), 38.9 (C-4′), 39.0 (C-2′), 52.0 (CH_3O), 53.8 (CH_3O), 64.7 and 65.2 (OCH_2CH_2O), 75.9 and 84.8 (C-1′ and -8′), 102.9 [$CH(O\text{-})_2$], 128.3 (C-6′), 133.9 (C-5′) and 203.5 (C-7′); *m*/*z* (%) 314 (0.1, M^+), 286 (0.2, $M^+ - CO$) and 73 (base).

(1′α,4′α,8′*S)-2-(1′,8′-Dimethoxy-2′-methyl-8′-methylthiomethyl-7′-oxobicyclo[2.2.2]oct-5′-en-2′β-yl)-1,3-dioxolane 8p.** This compound was prepared from compound **8k** (1.50 g, 5.28 mmol) in a similar procedure to that for compound **8n** in 99% yield as an oil (1.73 g); ν_{max}(neat)/cm^{-1} 1723 and 1612; δ_H 1.10 (3 H, s, 2′-CH_3), 1.74 (1 H, dd, *J* 13.2 and 3.0, C*H*^{endo}HCH), 1.93 (1 H, dd, *J* 13.2 and 3.0, CH*H*^{exo}CH), 2.15 (3 H, s, CH_3S), 2.84 (2 H, ABq, *J* 13.9, CH_2S), 3.12–3.18 (1 H, m, 4′-H), 3.43 (3 H, s, CH_3O), 3.53 (3 H, s, CH_3O), 3.77–3.94 (4 H, m, OCH_2CH_2O), 4.77 [1 H, s, $CH(O\text{-})_2$], 6.30 (1 H, dd, *J* 8.6 and 2.0, CH_3OC-C*H*=CH) and 6.36 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH); δ_C 16.9 (CH_3S), 19.5 (C-3′), 30.2 (2′-CH_3), 37.8 (CH_2S), 39.3 (C-4′), 45.0 (C-2′), 51.4 (CH_3O), 54.8 (CH_3O), 64.7 and 65.2 (OCH_2CH_2O), 75.6 and 89.3 (C-1′ and -8′), 106.7 [$CH(O\text{-})_2$], 128.1 and 133.5 (C-5′ and -6′) and 205.7 (C-7′); *m*/*z* (%) 328 (0.3, M^+), 300 (0.4, $M^+ - CO$) and 73 (base).

General procedure of desulfurization of compounds 8

A mixture of a compound **8** (5.31 mmol) and Raney-Ni (W2, 27 g, previously treated in acetone at reflux temperature) in ethanol (100 cm^3) was stirred at 55 °C for 36 h. After cooling, the reaction mixture was filtered through Celite. Removal of the solvent under reduced pressure and chromatography of the residue over silica gel (13 g; eluent hexane–diethyl ether, 2:1) furnished a desulfurized product **18** as an oil.

(3aα,4α,7α,7aα,8*S)-4,8-Dimethoxy-8-methyl-3a,4,7,7a-tetrahydro-4,7-ethanoinden-9-one 18b.** (54% Yield), an oil; ν_{max}(neat)/cm^{-1} 1727 and 1620; δ_H 1.28 (3 H, s, 8-CH_3), 1.92–2.04 (1 H, m, 1-H^{endo}), 2.50–2.63 (1 H, m, 1- H^{exo}), 2.95–2.99 (1 H, m, 7-H), 3.17–3.27 (1 H, m, 7a-H), 3.33–3.37 (1 H, m, 3a-H), 3.37 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O), 5.57–5.60 (1 H, m, 3- or 2-H), 5.74–5.78 (1 H, m, 2- or 3-H), 6.03 (1 H, d, *J* 8.8, CH_3OC-C*H*=CH) and 6.20 (1 H, dd, *J* 8.8 and 6.4, CH=C*H*CH); δ_C 20.0 (8-CH_3), 34.9 (C-7a), 38.9 (C-1), 46.6 (C-7), 51.0 (CH_3O), 51.3 (C-3a), 53.4 (CH_3O), 75.7 and 86.5 (C-4 and -8), 128.4 (C-3 or -2), 130.9 (C-5), 131.7 (C-6), 134.4 (C-2 or -3) and 206.9 (C-9); *m*/*z* (%) 234 (0.3, M^+), 219 (1, $M^+ - CH_3$) and 59 (base).

Diethyl (1α,2*R,3*S**,4α,8*S**)-1,8-dimethoxy-8-methyl-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 18m.** (54% Yield), an oil, ν_{max}(neat)/cm^{-1} 1740; δ_H 1.25 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.27 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.32 (3 H, s, 8-CH_3), 3.28–3.32 (1 H, m, 4-H), 3.40 (3 H, s, CH_3O), 3.49 (1 H, d, *J* 5.5, CH_3OC-C*H*CH), 3.56 (3 H, s, CH_3O), 3.82 (1 H, dd, *J* 5.5 and 2.4, =CHCHC*H*CH), 4.20 (4 H, q, *J* 6.9, C*H*$_2$CH$_3$ × 2), 6.34–6.36 (2 H, m, 5- and 6-H); δ_C 14.2 (*C*H$_3$CH$_2$ × 2), 20.6 (8-CH_3), 42.8 (C-3), 45.5 (C-4), 48.7 (C-2), 51.6 (CH_3O), 53.4 (CH_3O), 61.4 (CH_2O), 61.6 (CH_2O), 73.6 and 84.5 (C-1 and -8), 130.1 and 133.6 (C-5 and -6), 171.7 (CO_2), 173.5 (CO_2) and 201.9 (C-7).

General procedure for the preparation of aldehydes 20

A solution of a bicyclo[2.2.2]octanone **8** (18.4 mmol) in methanol (800 cm^3) was treated with 6.25% aq. $NaIO_4$ (67 cm^3, 19.6 mmol) at 0 °C. After the reaction mixture had been stirred at 0 °C (to room temp.) for 24 h, methanol was removed under reduced pressure. The residue was extracted with dichloromethane (300 cm^3) and the extract was washed with brine (50 cm^3) and dried with anhydrous $MgSO_4$. Removal of the solvent yielded the crude sulfinyl compound **19** as a solid. Subsequently, the crude product in dry benzene (800 cm^3) was treated with TFAA (2.8 cm^3, 19.8 mmol) at 0 °C under argon, and stirring was continued for 5 h at 0 °C (to room temp.). Then, a large excess of aq. $NaHCO_3$ (saturated; 50 cm^3) was added to the reaction mixture at 0 °C, and the mixture was stirred for 1 h at 0 °C (to room temp.). The organic layer was washed successively with aq. NH_4Cl (saturated; 50 cm^3) and brine (50 cm^3), and dried over anhydrous $MgSO_4$. Removal of the solvent gave a pale yellow oil, which was chromatographed on silica gel (eluent hexane–ethyl acetate, 8:2) to afford the corresponding 3-[bis(methylthio)methyl]bicyclo[2.2.2]octenone **21** as an oil. Continued elution with the same solvent furnished the aldehyde **20** as an oil.

(1α,4α,4aα,9aα,11*R)-4,11-Dimethoxy-10-oxo-1,4,4a,9a-tetrahydro-1,4-ethanofluorene-11-carbaldehyde 20a.** An oil; ν_{max}(neat)/cm^{-1} 1742, 1720 and 1610; δ_H 2.74 (1 H, dd, *J* 16.2 and 3.7, C*H*^{endo}HCH), 3.22–3.34 (3 H, m, 1-H, 9-H^{exo} and 9a-H), 3.46 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 3.88 (1 H, d, *J* 8.6, ArC*H*CH), 5.92 (1 H, br d, *J* 8.9, CH_3OCC*H*=CH), 6.37 (1 H, dd, *J* 8.5 and 6.7, CH=C*H*CH), 7.10–7.47 (3 H, m, 6-, 7- and 8-H), 7.47 (1 H, br d, *J* 7.3, 5-H) and 9.50 (1 H, s, CHO); δ_C 35.0 (C-9a or C-1), 38.1 (C-9), 39.8 (C-1 or -9a), 51.9 (C-4a), 53.6 (CH_3O), 54.1 (CH_3O), 84.7 and 87.0 (C-4 and -11), 123.9, 126.5, 127.0 and 127.6 (C-5, -6, -7 and -8), 128.1 (C-3), 131.0 (C-2), 140.2 and 144.3 (C-4b and -8a), 197.2 (CHO) and 200.2 (C-10); *m*/*z* (%) 270 (base, $M^+ - CO$), 154 (40) and 116 (38).

(1α,4α,4aα,9aα,11*S)-11-Bis(methylthio)methyl-4,11-dimethoxy-1,4,4a,9a-tetrahydro-1,4-ethanofluoren-10-one 21a.** An *oil*; ν_{max}(neat)/cm^{-1} 1712; δ_H 2.08 (3 H, s, CH_3S), 2.30 (3 H, s, CH_3S), 2.67 (1 H, dd, *J* 17.0 and 5.4, C*H*^{endo}HCH), 3.20 (1 H, dd, *J* 17.0 and 10.4, CH*H*^{exo}CH), 3.37–3.41 (1 H, m, 1-H), 3.48 (3 H, s, CH_3O), 3.50–3.61 (1 H, m, 9a-H), 3.65 (3 H, s, CH_3O), 3.73 (1 H, d, *J* 9.2, CH_3OCC*H*CH), 4.15 [1 H, s, CH(S-)$_2$], 5.93 (1 H, br d, *J* 8.9, CH_3OCC*H*=CH), 6.26 (1 H, dd, *J* 8.9 and 6.6, CH=C*H*CH), 7.07–7.20 (3 H, m, 6-, 7- and 8-H) and 7.46 (1 H, br d, *J* 6.6, 5-H); δ_C 15.8 (CH_3S), 18.7 (CH_3S), 36.2 (C-4a), 37.7 (C-9), 44.3 (C-1), 52.0 (CH_3O), 52.4 (CH_3O), 54.2 (C-9a), 57.2 [CH(S-)$_2$], 79.4 and 87.5 (C-4 and -11), 123.8, 126.1, 127.1 and 127.3 (C-5, -6, -7 and -8), 128.5 (C-3), 130.9 (C-2), 141.1 and 144.8 (C-4b and -8a) and 203.6 (C-10); *m*/*z* (%) 376 (5, M^+), 329 (11, $M^+ - CH_3S$), 301 (71) and 107 (base) (Found: M^+, 376.1151. $C_{20}H_{24}O_3S_2$ requires *M*, 376.1167).

(3aα,4α,7α,7aα,8*R)-4,8-Dimethoxy-9-oxo-3a,4,7,7a-tetrahydro-4,7-ethanoindene-8-carbaldehyde 20b.** An oil; ν_{max}(neat)/cm^{-1} 1750, 1720 and 1622; δ_H 2.05 (1 H, br d, *J* 17.2, =CHC*H*^{endo}HCH), 2.65 (1 H, br d, *J* 17.2, =CHCH*H*^{exo}CH), 2.95–3.05 (1 H, m, 7a-H), 3.24 (1 H, br dd, *J* 6.6 and 2.6, CH_3OCCH=CHC*H*CH), 3.41 (3 H, s, CH_3O), 3.38–3.46 (1 H, m, 3a-H), 3.57 (3 H, s, CH_3O), 5.58 (1 H, br d, *J* 5.6, 2- or 3-H), 5.80 (1 H, br d, *J* 5.6, 3- or 2-H), 6.00 (1 H, br d, *J* 8.6, CH_3OC-C*H*=CH), 6.37 (1 H, dd, *J* 8.5 and 6.6, CH=C*H*CH) and 9.50 (1 H, s, CHO); δ_C 34.0 (C-7a), 39.0 (C-1), 39.1 (C-7), 52.6 (C-3a), 53.4 (CH_3O), 53.6 (CH_3O), 84.8 and 86.2 (C-4 and -8), 127.5 (C-2 or -3), 128.5 (C-5), 130.5 (C-6), 134.7 (C-3 or -2), 197.4 (CHO) and 199.8 (C-9); *m*/*z* (%) 220 (base, $M^+ - CO$), 205 (13) and 154 (32).

(1α,2*R,4α,8*R**)-8-Isopropenyl-2,4-dimethoxy-3-oxobicyclo-[2.2.2]oct-5-ene-2-carbaldehyde 20c.** An oil; ν_{max}(neat)/cm^{-1} 1734 and 1643; δ_H 1.42 (1 H, ddd, *J* 12.9, 6.9 and 2.3, CHC*H*^{endo}-HCH), 1.68 (3 H, s, CH_3C=), 2.32 (1 H, ddd, *J* 12.9, 10.0 and 3.0, CHCH*H*^{exo}CH), 3.08–3.15 (2 H, m, 1- and 8-H), 3.41 (3 H, s, CH_3O), 3.55 (3 H, s, CH_3O), 4.80–4.86 (2 H, m, CH_2=), 6.11 (1 H, br d, *J* 8.6, CH_3OCC*H*=CH), 6.52 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.53 (1 H, s, CHO); δ_C 20.7 (*C*H_3C=), 28.0 (C-7), 34.2 and 44.2 (C-1 and -8), 53.6 (CH_3O × 2), 83.9 and 85.0 (C-2 and -4), 114.5 (CH_2=), 127.8 (C-5), 132.3 (C-6), 144.4 (8-C=), 197.5 (C-3) and 197.8 (CHO); *m*/*z* (%) 250 (0.3, M^+) and 222 (base, $M^+ - CO$).

Ethyl (1α,2*S,4α,8*R**)-8-formyl-1,8-dimethoxy-7-oxobicyclo-[2.2.2]oct-5-ene-2-carboxylate 20d.** An oil; ν_{max}(neat)/cm^{-1} 1730, 1724 and 1613; δ_H 1.27 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.76 (1 H, ddd, *J* 12.9, 6.0 and 3.0, CHC*H*^{endo}HCH), 2.39 (1 H, ddd, *J* 12.9, 9.9 and 3.0, CHCH*H*^{exo}CH), 3.18–3.28 (2 H, m, 2- and 4-H), 3.40 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 4.08–4.23 (2 H, m, CH_2O), 6.19 (1 H, br d, *J* 8.6, CH_3OCC*H*=CH), 6.58 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.53 (1 H, s, CHO); δ_C 14.1 (*C*H_3CH$_2$), 26.3 (C-3), 34.6 (C-4), 42.7 (C-2), 53.7 (CH_3O), 54.1 (CH_3O), 61.1 (CH_2O), 83.6 and 84.5 (C-1 and -8), 126.8 (C-6), 132.6 (C-5), 172.0 (CO_2), 196.7 (C-7) and 197.4 (CHO); *m*/*z* (%) 282 (0.3, M^+) and 254 (base, $M^+ - CO$).

Ethyl (1α,2*S,4α,8*S**)-8-bis(methylthio)methyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 21d.** An *oil*; ν_{max}(neat)/cm^{-1} 1730 and 1610; δ_H 1.26 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.53–1.58 (1 H, m, 3-H^{endo}), 2.01 (3 H, s, CH_3S), 2.29 (3 H, s, CH_3S), 2.53–2.63 (1 H, m, 3-H^{exo}), 3.16–3.17 (1 H, m, 2-H), 3.19–3.26 (1 H, m, 4-H), 3.35 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 4.10–4.20 (2 H, m, CH_2O), 4.15 [1 H, s, CH(S-)$_2$], 6.07 (1 H, d, *J* 8.5, CH_3OCC*H*=CH) and 6.53 (1 H, dd, *J* 8.5 and 6.7, CH=C*H*CH); *m*/*z* (%) 360 (3, M^+), 313 (6, $M^+ - CH_3S$), 285 (22) and 254 (base) (Found: M^+, 360.1050. $C_{16}H_{24}O_5S_2$ requires *M*, 360.1065).

***tert*-Butyl (1α,2*S**,4α,8*R**)-8-formyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 20e.** An oil; ν_{max}(neat)/cm^{-1} 1725 and 1615; δ_H 1.45 [9 H, s, C(CH$_3$)$_3$], 1.73 (1 H, ddd, *J* 12.9, 5.9 and 2.6, CHC*H*^{endo}HCH), 2.38 (1 H, ddd, *J* 12.5, 10.2 and 3.0, CHCH*H*^{exo}CH), 3.12–3.22 (2 H, m, 2- and 4-H), 3.39 (3 H, s, CH_3O), 3.61 (3 H, s, CH_3O), 6.17 (1 H, br d, *J* 8.6, CH_3OC-C*H*=CH), 6.54 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.53 (1 H, s, CHO); δ_C 26.4 (C-3), 27.8 [C(*C*H$_3$)$_3$], 34.6 and 43.1 (C-2 and -4), 53.7 (CH_3O), 53.9 (CH_3O), 81.6, 83.6 and 84.6 [C-1, -8 and (CH$_3$)$_3$*C*O], 127.2 (C-6), 132.1 (C-5), 171.2 (CO_2), 196.8 (C-7) and 197.5 (CHO); *m*/*z* (%) 282 (3, $M^+ - CO$) and 226 (base).

***tert*-Butyl (1α,2*S**,4α,8*S**)-8-bis(methylthio)methyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 21e.** An *oil*; ν_{max}(neat)/cm^{-1} 1730 and 1610; δ_H 1.45 [9 H, s, C(CH$_3$)$_3$], 1.52 (1 H, ddd, *J* 12.2, 6.6 and 2.3, CHC*H*^{endo}HCH), 2.01 (3 H, s, CH_3S), 2.28 (3 H, s, CH_3S), 2.57 (1 H, ddd, *J* 12.2, 9.6 and 3.3, CHCH*H*^{exo}CH), 3.08 (1 H, ddd, *J* 9.6, 6.6 and 1.0, CHC*H*CO_2), 3.12–3.20 (1 H, m, 4-H), 3.34 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 4.15 [1 H, s, CH(S-)$_2$], 6.05 (1 H, d, *J* 8.6, CH_3OCC*H*=CH) and 6.49 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH); δ_C 15.5 (CH_3S), 18.4 (CH_3S), 28.0 [C(*C*H$_3$)$_3$], 28.6 (C-3), 39.0 (C-4), 43.1 (C-2), 51.9 (CH_3O), 53.9 (CH_3O), 55.4 [CH(S-)$_2$], 79.2, 81.1 and 85.2 [C-1, -8 and (CH$_3$)$_3$*C*O], 124.9 (C-6), 133.0 (C-5), 171.8 (CO_2) and 198.7 (C-7); *m*/*z* (%) 388 (4, M^+), 341 (14, $M^+ - CH_3S$), 313 (47, $M^+ - CO$), 257 (78) and 225 (base) (Found: M^+, 388.1367. $C_{18}H_{28}O_5S_2$ requires *M*, 388.1370).

Methyl (1α,2*S,4α,8*R**)-8-formyl-1,8-dimethoxy-2α-methyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 20f.** An oil; ν_{max}(neat)/cm^{-1} 1722 and 1615; δ_H 1.36 (3 H, s, 2-CH_3), 1.93 (1 H, dd, *J* 13.2 and 2.6, C*H*^{endo}HCH), 2.11 (1 H, dd, *J* 13.2 and 3.3, CH*H*^{exo}CH), 3.18–3.21 (1 H, m, 4-H), 3.38 (3 H, s, CH_3O), 3.50 (3 H, s, CH_3O), 3.68 (3 H, s, CH_3O), 6.40 (1 H, dd, *J* 8.7 and 1.5, CH_3OCC*H*=CH), 6.56 (1 H, dd, *J* 8.7 and 6.8, CH=C*H*CH) and 9.52 (1 H, s, CHO); δ_C 20.5 (2-CH_3), 34.0 (C-4), 34.8 (C-3), 50.1 (C-2), 52.2 (CH_3O), 53.3 (CH_3O), 54.8 (CH_3O), 83.7 and 88.2 (C-1 and -8), 126.3 (C-6), 132.1 (C-5), 174.5 (CO_2), 197.1 (CHO) and 197.7 (C-7); *m*/*z* (%) 282 (0.2, M^+), 254 (base, $M^+ - CO$), 225 (24), 194 (64) and 163 (60).

Methyl (1α,2*S,4α,8*S**)-8-bis(methylthio)methyl-1,8-dimeth-**

oxy-2α-methyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 21f. An *oil*; ν_{max}(neat)/cm^{-1} 1733; δ_H 1.28 (3 H, s, 2-CH_3), 1.92 (1 H, dd, *J* 13.2 and 3.3, C*H*^{endo}HCH), 2.11 (3 H, s, CH_3S), 2.22 (1 H, dd, *J* 13.2 and 2.6, CH*H*^{exo}CH), 2.27 (3 H, s, CH_3S), 3.17–3.23 (1 H, m, 4-H), 3.44 (3 H, s, CH_3O), 3.55 (3 H, s, CH_3O), 3.66 (3 H, s, CH_3O), 4.18 [1 H, s, CH(S-)$_2$] and 6.37–6.39 (2 H, m, 5- and 6-H); δ_C 15.3 (CH_3S), 19.0 (CH_3S), 20.1 (2-CH_3), 36.1 (C-3), 39.2 (C-4), 50.4 (C-2), 51.2 (CH_3O), 52.1 (CH_3O), 54.8 (CH_3O), 56.8 [CH(S-)$_2$], 78.7 and 88.7 (C-1 and -8), 128.2 and 131.1 (C-5 and -6), 175.0 (CO_2) and 202.0 (C-7); *m*/*z* (%) 360 (4, M$^+$), 313 (24, M$^+$ − CH_3S), 285 (69) and 253 (base) (Found: M$^+$, 360.1078. $C_{16}H_{24}O_5S_2$ requires *M*, 360.1065).

(1α,2*R,4α,8*R**)-8-Formyl-1,8-dimethoxy-7-oxobicyco[2.2.2]-oct-5-ene-2-carbonitrile 20g.** An oil; ν_{max}(neat)/cm^{-1} 2250, 1755, 1725 and 1617; δ_H 1.86 (1 H, ddd, *J* 12.9, 4.3 and 4.3, CHC*H*^{endo}-HCH), 2.56 (1 H, ddd, *J* 12.9, 10.2 and 2.3, CHCH*H*^{exo}CH), 3.27–3.30 (1 H, m, 1-H), 3.35–3.41 (1 H, m, 2-H), 3.39 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 6.30 (1 H, d, *J* 8.6, CH_3OC-C*H*=CH), 6.76 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.51 (1 H, s, CHO); δ_C 25.9 (C-3), 30.7 (C-2), 33.8 (C-4), 53.8 (CH_3O), 54.3 (CH_3O), 82.8 and 83.9 (C-8 and -1), 118.9 (CN), 126.7 (C-6), 135.3 (C-5), 196.0 (C-7) and 196.5 (CHO); *m*/*z* (%) 235 (0.2, M$^+$), 207 (82, M$^+$ − CO) and 180 (base).

(1α,2*R,4α,8*S**)-8-Bis(methylthio)methyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carbonitrile 21g.** An *oil*; ν_{max}-(neat)/cm^{-1} 2250, 1735 and 1610; δ_H 1.64 (1 H, ddd, *J* 12.9, 5.9 and 2.6, CHC*H*^{endo}HCH), 1.97 (3 H, s, CH_3S), 2.28 (3 H, s, CH_3S), 2.79 (1 H, ddd, *J* 12.9, 9.6 and 3.0, CHCH*H*^{exo}CH), 3.14–3.19 (1 H, m, 4-H), 3.29–3.41 (1 H, m, 2-H), 3.34 (3 H, s, CH_3O), 3.65 (3 H, s, CH_3O), 4.13 [1 H, s, CH(S-)$_2$], 6.11 (1 H, d, *J* 8.6, CH_3OCC*H*=CH) and 6.70 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH); δ_C 15.4 (CH_3S), 18.4 (CH_3S), 28.4 (C-3), 29.8 (C-4), 38.3 (C-2), 51.9 (CH_3O), 54.0 (CH_3O), 54.7 [CH(S-)$_2$], 79.2 and 83.1 (C-1 and -8), 119.3 (CN), 124.3 (C-6), 136.2 (C-5) and 197.2 (C-7); *m*/*z* (%) 313 (1, M$^+$), 266 (9, M$^+$ − CH_3S), 238 (38) and 107 (base) (Found: M$^+$, 313.0791. $C_{14}H_{19}NO_3S_2$ requires *M*, 313.0806).

(1α,2*R,4α,8*S**)-2,4-Dimethoxy-3-oxo-8-propionylbicylo-[2.2.2]oct-5-ene-2-carbaldehyde 20h.** An oil; ν_{max}(neat)/cm^{-1} 1750, 1720, 1640 and 1610; δ_H 1.01 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.74 (1 H, ddd, *J* 12.5, 5.9 and 2.3, CHC*H*^{endo}HCH), 2.20 (1 H, ddd, *J* 12.5, 9.9 and 3.0, CHCH*H*^{exo}CH), 2.56 (2 H, q ABq, *J* 18.5 and 7.3, C*H*$_2$CH$_3$), 3.23–3.30 (2 H, m, 1- and 8-H), 3.41 (3 H, s, CH_3O), 3.50 (3 H, s, CH_3O), 6.22 (1 H, br d, *J* 8.6, CH_3OC-C*H*=CH), 6.60 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.51 (1 H, s, CHO); δ_C 7.5 (*C*H$_3$CH$_2$), 25.3 (C-7), 34.8 (C-1 or -8), 38.3 (*C*H$_2$CO), 48.7 (C-8 or -1), 53.7 (CH_3O), 54.6 (CH_3O), 83.9 and 85.5 (C-2 and -4), 124.5 (C-5), 133.1 (C-6), 197.1 (CHO) and 209.8 (C=O); *m*/*z* (%) 266 (1, M$^+$), 238 (68, M$^+$ − CO), 181 (47), 149 (base) and 57 (50).

(1α,2*S,4α,5*R**)-1,5-Dimethoxy-6-oxobicylo[2.2.2]oct-7-ene-2,5-dicarbaldehyde 20j.** An oil; ν_{max}(neat)/cm^{-1} 1720 and 1615; δ_H 2.00 (1 H, ddd, *J* 13.4, 4.8 and 3.1, CHC*H*^{endo}HCH), 2.16 (1 H, ddd, *J* 13.4, 9.8 and 2.4, CHCH*H*^{exo}CH), 3.15 (1 H, br dd, *J* 9.8 and 4.8, CH$_2$C*H*CHO), 3.26–3.28 (1 H, m, 4-H), 3.41 (3 H, s, CH_3O), 3.61 (3 H, s, CH_3O), 6.17 (1 H, d, *J* 8.5, CH_3OC-C*H*=CH), 6.63 (1 H, dd, *J* 8.5 and 6.7, CH=C*H*CH), 9.53 (1 H, s, 5-CHO) and 9.69 (1 H, d, *J* 2.1, CHC*H*O); δ_C 20.9 (C-3), 34.1 (C-4), 49.7 (C-2), 53.5 (CH_3O), 54.1 (CH_3O), 84.1 and 84.4 (C-1 and -5), 125.4 (C-7), 134.7 (C-8), 196.9 (5-CHO), 199.7 (2-CHO) and 199.8 (C-6); *m*/*z* (%) 238 (0.4, M$^+$) and 210 (base, M$^+$ − CO).

(1α,2*S,4α,8*S**)-8-Bis(methylthio)methyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carbaldehyde 21j.** An *oil*; ν_{max}-(neat)/cm^{-1} 1725 and 1610; δ_H 1.65 (1 H, ddd, *J* 12.9, 5.6 and 2.5, CHC*H*^{endo}HCH), 2.03 (3 H, s, CH_3S), 2.30 (3 H, s, CH_3S), 2.44 (1 H, ddd, *J* 12.9, 9.6 and 3.3, CHCH*H*^{exo}CH), 3.06–3.14 (1 H, m, 4-H), 3.20–3.26 (1 H, m, 2-H), 3.38 (3 H, s, CH_3O), 3.62 (3 H, s, CH_3O), 4.14 [1 H, s, CH(S-)$_2$], 6.08 (1 H, d, *J* 8.6, CH_3OCC*H*=CH), 6.58 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.56 (1 H, s, CHO); δ_C 15.4 (CH_3S), 18.4 (CH_3S), 23.8 (C-3), 38.9 (C-4), 49.3 (C-2), 51.8 (CH_3O), 53.8 (CH_3O), 55.5 [CH-(S-)$_2$], 79.0 and 84.7 (C-1 and -8), 124.4 (C-6), 135.1 (C-5), 198.9 (C-7) and 200.4 (CHO); *m*/*z* (%) 316 (9, M$^+$), 269 (12, M$^+$ − CH_3S) and 107 (base) (Found: M$^+$, 316.0809. $C_{14}H_{20}O_4S_2$ requires *M*, 316.0803).

(1α,2*S,4α,5*R**)-1,5-Dimethoxy-2-methyl-6-oxobicylo[2.2.2]-oct-7-ene-2,5-dicarbaldehyde 20k.** An oil; ν_{max}(neat)/cm^{-1} 1746, 1723 and 1613; δ_H 1.24 (3 H, s, 2-CH_3), 1.70 (1 H, dd, *J* 13.5 and 2.3, C*H*^{endo}HCH), 2.27 (1 H, dd, *J* 13.5 and 3.3, CH*H*^{exo}CH), 3.21–3.26 (1 H, m, 4-H), 3.40 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 6.27 (1 H, br d, *J* 8.6, CH_3OCC*H*=CH), 6.66 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH), 9.52 (1 H, s, CHO) and 9.58 (1 H, s, CHO); δ_C 17.3 (2-CH_3), 29.5 (C-3), 34.0 (C-4), 52.4 (CH_3O), 53.9 (C-2), 54.8 (CH_3O), 84.3 and 87.8 (C-1 and -5), 124.6 (C-7), 135.4 (C-8), 197.0 (CHO), 197.4 (C-6) and 201.9 (CHO); *m*/*z* (%) 252 (0.3, M$^+$), 224 (54, M$^+$ − CO) and 163 (base).

(1α,2*S,4α,8*S**)-8-Bis(methylthio)methyl-1,8-dimethoxy-2-methyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carbaldehyde 21k.** An *oil*; ν_{max}(neat)/cm^{-1} 1725 and 1610; δ_H 1.17 (3 H, s, 2-CH_3), 2.01–2.22 (2 H, m, 3-H), 2.11 (3 H, s, CH_3S), 2.28 (3 H, s, CH_3S), 3.24–3.30 (1 H, m, 4-H), 3.47 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O), 4.15 [1 H, s, CH(S-)$_2$], 6.29 (1 H, dd, *J* 8.6 and 1.7, CH_3OCC*H*=CH), 6.52 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH) and 9.54 (1 H, s, CHO); δ_C 15.3 (CH_3S), 16.7 (2-CH_3), 19.0 (CH_3S), 31.1 (C-3), 39.2 (C-4), 51.4 (CH_3O), 54.2 (C-2), 54.8 (CH_3O), 56.7 [CH(S-)$_2$], 78.8 and 88.2 (C-1 and -8), 126.5 (C-6), 134.4 (C-5), 202.0 (C-7) and 203.9 (CHO); *m*/*z* (%) 330 (7, M$^+$), 283 (16, M$^+$ − CH_3S) and 107 (base) (Found: M$^+$, 330.0960. $C_{15}H_{22}O_4S_2$ requires *M*, 330.0960).

Diethyl (1α,2*S,3*S**,4α,8*R**)-8-formyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 20l.** An oil; ν_{max}(neat)/cm^{-1} 1740, 1670 and 1640; δ_H 1.23 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.27 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 3.41 (3 H, s, CH_3O), 3.59 (3 H, s, CH_3O), 3.53–3.68 (3 H, m, 2-, 3- and 4-H), 4.10–4.20 (4 H, m, CH_2O × 2), 6.19 (1 H, br d, *J* 8.6, CH_3OCC*H*=CH), 6.69 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH) and 9.51 (1 H, s, CHO); δ_C 13.9 (*C*H$_3$CH$_2$), 14.0 (*C*H$_3$CH$_2$), 36.7, 42.7 and 48.1 (C-2, -3 and -4), 53.9 (CH_3O), 54.2 (CH_3O), 61.3 (CH_2O), 61.4 (CH_2O), 82.8 and 84.6 (C-1 and -8), 126.3 (C-6), 132.0 (C-5), 169.3 (CO_2), 170.6 (CO_2), 196.0 (CHO) and 196.2 (C-7); *m*/*z* (%) 354 (3, M$^+$), 326 (19, M$^+$ − CO), 280 (58) and 207 (base).

Diethyl (1α,2*S,3*S**,4α,8*S**)-8-bis(methylthio)methyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 21l.** An *oil*; ν_{max}(neat)/cm^{-1} 1735 and 1635; δ_H 1.20 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.27 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 2.04 (3 H, s, CH_3S), 2.29 (3 H, s, CH_3S), 3.37 (3 H, s, CH_3O), 3.52–3.57 (1 H, m, CH), 3.60 (3 H, s, CH_3O), 3.65–3.67 (1 H, m, CH), 3.91–4.02 (1 H, m, CH), 4.08–4.17 (4 H, m, CH_2O × 2), 4.16 [1 H, s, CH(S-)$_2$], 6.12 (1 H, br d, *J* 8.6, CH_3OCC*H*=CH) and 6.63 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH); δ_C 13.9 (*C*H$_3$CH$_2$ × 2), 15.3 (CH_3S), 18.4 (CH_3S), 41.1, 44.4 and 48.6 (C-2, -3 and -4), 52.1 (CH_3O), 54.2 (CH_3O), 55.3 [CH(S-)$_2$], 60.8 (CH_2O), 60.9 (CH_2O), 78.4 and 85.0 (C-1 and -8), 124.9 (C-6), 132.7 (C-5), 169.8 (CO_2), 171.3 (CO_2) and 198.5 (C-7); *m*/*z* (%) 432 (3, M$^+$), 385 (26, M$^+$ − CH_3S), 357 (49) and 311 (base) (Found: M$^+$, 432.1289. $C_{19}H_{28}O_7S_2$ requires *M*, 432.1277).

Diethyl (1α,2*R,3*S**,4α,8*R**)-8-formyl-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 20m.** An *oil*; ν_{max}-(neat)/cm^{-1} 1735 and 1635; δ_H 1.27 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.28 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 3.42–3.44 (1 H, m, 4-H), 3.52 (3 H, s, CH_3O), 3.55–3.57 (2 H, m, 2- and 3-H), 3.56 (3 H, s, CH_3O), 4.15–4.24 (4 H, m, CH_2O × 2), 6.32 (1 H, d, *J* 8.6, CH_3OC-C*H*=CH), 6.46 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 9.53 (1 H, s, CHO); δ_C 14.1 (*C*H$_3$CH$_2$ × 2), 38.1 and 42.1 (C-2 and -3), 50.6 (C-4), 53.7 (CH_3O), 54.2 (CH_3O), 61.7 (CH_2O), 61.8 (CH_2O), 82.4 and 84.7 (C-1 and -8), 128.1 (C-6), 132.0 (C-5), 171.1 (CO_2), 171.9 (CO_2), 195.6 (C-7) and 196.9 (CHO); *m*/*z* (%) 354 (3, M$^+$), 326 (24, M$^+$ − CO) and 207 (base) (Found: M$^+$, 354.1287. $C_{17}H_{22}O_8$ requires *M*, 354.1315).

General procedure for the preparation of the 3-(2-ethoxycarbonylvinyl)bicyclo[2.2.2]octenones 9

A mixture of the appropriate aldehyde **20** (5.27 mmol), ethoxycarbonylmethyltriphenylphosphonium bromide (6.85 mmol) and potassium carbonate (8.43 mmol) in dichloromethane–water (1:1; 140 cm^3) was stirred for 24 h. The mixture was extracted with diethyl ether (100 cm^3), and the extracts was washed successively with aq. NH_4Cl (saturated; 30 cm^3) and brine (30 cm^3), and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave a pale brown oil, which was chromatographed on silica gel (eluent hexane–ethyl acetate, 9:1) to afford the corresponding compound **9**.

Ethyl (*E*)-3′-[(1*α*,4*α*,4a*α*,9a*α*,11*S)-4,11-dimethoxy-10-oxo-1,4,4a,9a-tetrahydro-1,4-ethanofluoren-11-yl]acrylate 9a.** An *oil*; ν_{max}(neat)/cm^{-1} 1740, 1720 and 1635; δ_H 1.29 (3 H, t, *J* 7.3, CH_3CH$_2$), 2.69 (1 H, dd, *J* 16.5 and 4.3, CH^{endo}HCH), 3.22–3.26 (1 H, m, 9-H^{exo}), 3.28–3.32 (1 H, m, 1- or 9a-H), 3.38 (3 H, s, CH_3O), 3.35–3.45 (1 H, m, 9a- or 1-H), 3.61 (3 H, s, CH_3O), 3.84 (1 H, d, *J* 9.2, CH_3OCCHCH), 4.20 (2 H, q, *J* 7.3, CH$_2$CH$_3$), 6.02 (1 H, d, *J* 8.9, CH_3OCCH=CH), 6.06 (1 H, d, *J* 16.2, 11-CH=CH), 6.24 (1 H, dd, *J* 8.9 and 6.6, CH=CHCH), 6.65 (1 H, d, *J* 16.2, 11-CH=CH), 7.09–7.22 (3 H, m, 6-, 7- and 8-H) and 7.48 (1 H, br d, *J* 6.6, 5-H); δ_C 14.2 (*C*H$_3$CH$_2$), 35.3 (C-1 or -9a), 38.0 (C-9), 44.9 (C-9a or -1), 51.9 (C-4a), 52.4 (CH_3O), 54.2 (CH_3O), 60.8 (CH_2O), 78.4 and 87.6 (C-4 and -11), 123.8 (C-5), 125.8 (11-CH=*C*H), 126.3, 127.0 and 127.5 (C-6, -7 and -8), 130.2 (C-3), 131.0 (C-2), 140.8 (C-4b or -8a), 143.6 (11-CH=), 144.3 (C-8a or -4b), 165.7 (CO_2) and 204.0 (C-10); *m*/*z* (%) 368 (4, M^+), 340 (71, $M^+ - CO$) and 309 (base) (Found: M^+, 368.1644. $C_{22}H_{24}O_5$ requires *M*, 368.1610).

Ethyl (*E*)-3′-[(3a*α*,4*α*,7*α*,7a*α*,8*S)-4,8-dimethoxy-9-oxo-3a,4,7,7a-tetrahydro-4,7-ethanoinden-8-yl]acrylate 9b.** An oil; ν_{max}(neat)/cm^{-1} 1720 and 1648; λ_{max}(EtOH)/nm 207 (11 990) and 307 (477); δ_H 1.29 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 2.01 (1 H, br d, *J* 17.3, CHC*H*^{endo}HCH), 2.62 (1 H, br dd, *J* 17.3 and 9.6, CHCH*H*^{exo}CH), 3.11–3.21 (2 H, m, 7- and 7a-H), 3.33 (3 H, s, CH_3O), 3.30–3.41 (1 H, m, 3a-H), 3.56 (3 H, s, CH_3O), 4.19 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 5.58–5.61 (1 H, m, 2- or 3-H), 5.75–5.80 (1 H, m, 3- or 2-H), 6.03 (1 H, d, *J* 16.0, 8-CH=C*H*), 6.10 (1 H, br d, *J* 8.6, CH_3OCCH=CH), 6.23 (1 H, dd, *J* 8.6 and 7.3, CH=C*H*CH) and 6.63 (1 H, d, *J* 16.0, 8-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$), 34.4 (C-7 or -7a), 39.9 (C-1), 44.3 (C-7a or -7), 52.4 (CH_3O), 52.6 (C-3a), 53.7 (CH_3O), 60.8 (CH_2O), 78.7 and 86.7 (C-4 and -8), 125.6 (8-CH=*C*H), 128.1 (C-3 or -2), 130.5 and 130.7 (C-5 and -6), 134.5 (C-2 or -3), 143.9 (8-CH=), 165.8 (CO_2) and 203.5 (C-9); *m*/*z* (%) 318 (2, M^+), 290 (52, $M^+ - CO$) and 259 (base) (Found: M^+, 318.1474. $C_{18}H_{22}O_5$ requires *M*, 318.1466).

Ethyl (*E*)-3′-[(1*α*,2*S,4*α*,8*R**)-8-isopropenyl-2,4-dimethoxy-3-oxobicyclo[2.2.2]oct-5-en-2-yl]acrylate 9c.** An *oil*; ν_{max}(neat)/cm^{-1} 1730 and 1645; δ_H 1.29 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.37 (1 H, ddd, *J* 13.2, 6.9 and 2.6, CHC*H*^{endo}HCH), 1.67 (3 H, s, CH_3C=), 2.44 (1 H, ddd, *J* 13.2, 9.9 and 3.0, CHCH*H*^{exo}CH), 2.99–3.05 (1 H, m, 1-H), 3.10 (1 H, dd, *J* 9.9 and 6.9, CH_3OCCHCH), 3.32 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O), 4.20 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 4.80–4.85 (2 H, m, CH_2=), 6.01 (1 H, d, *J* 16.2, 2-CH=C*H*), 6.17 (1 H, br d, *J* 8.9, CH_3OCCH=CH), 6.36 (1 H, dd, *J* 8.9 and 6.9, CH=C*H*CH) and 6.66 (1 H, d, *J* 16.2, 2-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$), 20.7 (*C*H$_3$C=), 28.6 (C-7), 39.4 (C-1), 44.2 (C-8), 52.5 (CH_3O), 53.8 (CH_3O), 60.8 (CH_2O), 78.0 and 85.6 (C-2 and -4), 114.3 (CH_2=), 125.6 (2-CH=*C*H), 129.4 (C-5), 132.4 (C-6), 144.1 (2-CH=), 144.8 (*C*=CH$_2$), 165.8 (CO_2) and 201.3 (C-3); *m*/*z* (%) 320 (10, M^+), 292 (35, $M^+ - CO$) and 261 (base) (Found: M^+, 320.1617. $C_{18}H_{24}O_5$ requires *M*, 320.1624).

Ethyl (1*α*,2*S,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 9d.** An *oil*; ν_{max}(neat)/cm^{-1} 1726 and 1650; λ_{max}(EtOH)/nm 209 (9939) and 318 (235); δ_H 1.26 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.29 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.70 (1 H, ddd, *J* 12.5, 6.3 and 2.6, CHC*H*^{endo}HCH), 2.54 (1 H, ddd, *J* 12.5, 10.1 and 3.0, CHCH*H*^{exo}CH), 3.09–3.13 (1 H, m, 4-H), 3.24 (1 H, br dd, *J* 10.1 and 6.3, CH$_2$C*H*CO$_2$), 3.30 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 4.08–4.21 (2 H, m, CH_2O), 4.20 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 6.00 (1 H, d, *J* 15.8, 8-CH=C*H*), 6.26 (1 H, d, *J* 8.6, CH_3OCCH=CH), 6.44 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 6.66 (1 H, d, *J* 15.8, 8-C*H*=CH); δ_C 14.1 (*C*H$_3$CH$_2$ × 2), 27.1 (C-3), 39.9 (C-4), 42.6 (C-2), 52.7 (CH_3O), 54.2 (CH_3O), 60.9 (CH_2O), 61.0 (CH_2O), 77.6 and 84.9 (C-1 and -8), 125.9 (8-CH=*C*H), 128.4 (C-5), 132.9 (C-6), 143.6 (8-CH=), 165.6 (CO_2), 172.4 (CO_2) and 200.0 (C-7); *m*/*z* (%) 352 (4, M^+), 324 (25, $M^+ - CO$), 293 (63) and 219 (base) (Found: M^+, 352.1523. $C_{18}H_{24}O_7$ requires *M*, 352.1522).

***tert*-Butyl (1*α*,2*S**,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 9e.** An oil; ν_{max}(neat)/cm^{-1} 1730 and 1655; λ_{max}(EtOH)/nm 208 (12 740) and 318 (287); δ_H 1.29 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.45 [9 H, s, C(CH$_3$)$_3$], 1.67 (1 H, ddd, *J* 12.5, 6.3 and 2.3, CHC*H*^{endo}-HCH), 2.52 (1 H, ddd, *J* 12.5, 9.9 and 2.8, CHCH*H*^{exo}CH), 3.07–3.10 (1 H, m, 4-H), 3.15 (1 H, dd, *J* 9.9 and 6.3, CH$_2$C*H*CO$_2$), 3.29 (3 H, s, CH_3O), 3.60 (3 H, s, CH_3O), 4.08–4.24 (2 H, m, CH_2O), 5.99 (1 H, d, *J* 16.0, 8-CH=C*H*), 6.23 (1 H, d, *J* 8.6, CH_3OCCH=CH), 6.40 (1 H, dd, *J* 8.6 and 6.9, CH=C*H*CH) and 6.66 (1 H, d, *J* 16.0, 8-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$), 27.1 (C-3), 28.0 [C(*C*H$_3$)$_3$], 39.9 (C-4), 43.1 (C-2), 52.6 (CH_3O), 54.0 (CH_3O), 60.8 (CH_2O), 77.6 [*C*(CH$_3$)$_3$O], 81.4 and 85.0 (C-1 and -8), 125.8 (8-CH=*C*H), 128.8 (C-6), 132.4 (C-5), 143.8 (8-CH=), 165.7 (CO_2), 171.6 (CO_2) and 200.1 (C-7); *m*/*z* (%) 380 (0.2, M^+), 352 (0.6, $M^+ - CO$) and 295 (base).

Methyl (1*α*,2*S,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-2-methyl-7-oxobicyclo[2.2.2]oct-5-ene-2-carboxylate 9f.** An *oil*; ν_{max}(neat)/cm^{-1} 1730 and 1650; δ_H 1.30 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.35 (3 H, s, 2-CH$_3$), 2.04 (1 H, dd, *J* 13.2 and 3.3, C*H*^{endo}HCH), 2.12 (1 H, dd, *J* 13.2 and 2.6, CH*H*^{exo}CH), 3.04–3.09 (1 H, m, 4-H), 3.31 (3 H, s, CH_3O), 3.51 (3 H, s, CH_3O), 3.67 (3 H, s, CH_3O), 4.21 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 6.02 (1 H, d, *J* 16.0, 8-CH=C*H*), 6.40 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH), 6.48 (1 H, dd, *J* 8.6 and 2.0, CH_3OCCH=CH) and 6.64 (1 H, d, *J* 16.0, 8-C*H*=CH); δ_C 14.1 (*C*H$_3$CH$_2$), 20.5 (2-CH$_3$), 35.2 (C-3), 39.4 (C-4), 50.0 (C-2), 52.1 (CH_3O × 2), 54.8 (CH_3O), 60.8 (CH_2O), 88.6 (C-1 and -8), 125.7 (8-CH=*C*H), 128.5 and 132.2 (C-5 and -6), 144.0 (8-CH=), 165.7 (CO_2), 174.8 (CO_2) and 201.6 (C-7); *m*/*z* (%) 352 (2, M^+), 309 (22, $M^+ - CO$) and 233 (base) (Found: M^+, 352.1517. $C_{18}H_{24}O_7$ requires *M*, 352.1522).

Ethyl (*E*)-3′-[(1*α*,2*S,4*α*,8*R**)-8-cyano-2,4-dimethoxy-3-oxobicyclo[2.2.2]oct-5-en-2-yl]acrylate 9g.** An oil; ν_{max}(neat)/cm^{-1} 2250, 1720 and 1650; λ_{max}(EtOH)/nm 208 (8484) and 310 (569); δ_H 1.30 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.81 (1 H, br d, *J* 13.2, CHC*H*^{endo}HCH), 2.74 (1 H, br d, *J* 13.2, CHCH*H*^{exo}CH), 3.12–3.15 (1 H, m, 1-H), 3.29 (3 H, s, CH_3O), 3.34 (1 H, dd, *J* 10.2 and 4.9, CH$_2$C*H*CN), 3.64 (3 H, s, CH_3O), 4.21 (2 H, q, *J* 6.9, C*H*$_2$CH$_3$), 5.98 (1 H, d, *J* 15.8, 2-CH=C*H*), 6.37 (1 H, d, *J* 8.6, CH_3OCCH=CH), 6.59 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH) and 6.63 (1 H, d, *J* 15.8, 2-C*H*=CH); δ_C 14.1 (*C*H$_3$CH$_2$), 26.5 (C-7), 30.4 (C-8), 39.3 (C-1), 52.7 (CH_3O), 54.1 (CH_3O), 60.9 (CH_2O), 77.3 and 83.1 (C-2 and -4), 119.0 (CN), 126.5 (2-CH=*C*H), 128.7 (C-5), 135.3 (C-6), 142.5 (2-CH=), 165.2 (CO_2) and 199.3 (C-3); *m*/*z* (%) 305 (0.5 M^+), 250 (65) and 204 (base).

Ethyl (*E*)-3′-[(1*α*,2*S,4*α*,8*S**)-2,4-dimethoxy-3-oxo-8-propionylbicylo[2.2.2]oct-5-en-2-yl]acrylate 9h.** An *oil*; ν_{max}(neat)/cm^{-1} 1715, 1650 and 1610; λ_{max}(EtOH)/nm 209 (10 670) and 308 (326); δ_H 1.01 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$CO), 1.29 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$O), 1.67 (1 H, ddd, *J* 12.5, 6.3 and 2.6, CHC*H*^{endo}-HCH), 2.33 (1 H, ddd, *J* 12.5, 9.3 and 3.0, CHCH*H*^{exo}CH), 2.55 (2 H, q, ABq, *J* 18.5 and 7.3, CH$_3$C*H*$_2$CO), 3.12–3.17 (1 H, m, 1-H), 3.27 (1 H, br dd, *J* 9.3 and 6.3, CH$_2$C*H*CO), 3.31 (3 H, s, CH_3O), 3.50 (3 H, s, CH_3O), 4.20 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 6.00 (1 H, d, *J* 16.0, 2-CH=C*H*), 6.28 (1 H, br d, *J* 8.9, CH_3OC-C*H*=CH), 6.46 (1 H, dd, *J* 8.9 and 6.9, CH=C*H*CH) and 6.63 (1 H, d, *J* 16.0, 2-C*H*=CH); δ_C 7.5 (*C*H$_3$CH$_2$CO), 14.2 (*C*H$_3$CH$_2$O), 26.0 (C-7), 38.3 (*C*H$_2$CO), 39.9 (C-1), 48.6 (C-8), 52.5 (CH_3O),

54.6 (CH_3O), 60.8 (CH_2O), 77.6 and 85.9 (C-2 and -4), 125.9 (2-CH=*C*H), 126.4 (C-5), 133.3 (C-6), 143.3 (2-CH=), 165.6 (CO_2), 201.2 (C=O) and 210.1 (C=O); *m*/*z* (%) 337 (2, $M^+ + 1$), 336 (10, M^+), 308 (23, $M^+ - CO$), 251 (72), 219 (base) and 57 (54) (Found: M^+, 336.1556. $C_{18}H_{24}O_6$ requires *M*, 336.1573).

Ethyl (*E*)-3′-[(1*α*,2*S,4*α*,8*S**)-8-formyl-2,4-dimethoxy-8-methyl-3-oxobicyclo[2.2.2]oct-5-en-2-yl]acrylate 9k.** An *oil*; ν_{max}(neat)/cm^{-1} 1725 and 1650; δ_H 1.23 (3 H, d, *J* 2.1, C*H*$_3$C-CHO), 1.30 (3 H, q, *J* 7.3, C*H*$_3$CH$_2$), 1.88 (1 H, br d, *J* 13.5, CH*H*^{endo}HCH), 2.21 (1 H, br d, *J* 13.5, CH*H*^{exo}CH), 3.13–3.15 (1 H, m, 1-H), 3.32 (3 H, s, CH_3O), 3.53 (3 H, s, CH_3O), 4.21 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 6.04 (1 H, d, *J* 16.2, 2-CH=C*H*), 6.37 (1 H, d, *J* 8.6, CH_3OCC*H*=CH), 6.51 (1 H, br d, *J* 8.6, CH=C*H*CH), 6.61 (1 H, d, *J* 16.2, 2-C*H*=CH) and 9.58 (1 H, d, *J* 2.1, CHO); δ_C 14.2 (*C*H$_3$CH$_2$), 17.2 (8-CH_3), 29.9 (C-7), 39.2 (C-1), 52.1 (CH_3O), 53.7 (C-8), 54.8 (CH_3O), 60.9 (CH_2O), 77.8 and 88.2 (C-2 and -4), 126.1 (2-CH=*C*H), 127.0 (C-5), 135.4 (C-6), 143.3 (2-CH=), 165.6 (CO_2), 201.3 (C-3) and 202.2 (CHO); *m*/*z* (%) 322 (2, M^+), 294 ($M^+ - CO$) and 233 (base) (Found: M^+, 322.1407. $C_{17}H_{22}O_6$ requires *M*, 322.1417).

Diethyl (1*α*,2*S,3*S**,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 9l.** An *oil*; ν_{max}(neat)/cm^{-1} 1735 and 1650; λ_{max}(EtOH)/nm 209 (13 990) and 318 (268); δ_H 1.22 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.26 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.27 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 3.30 (3 H, s, CH_3O), 3.44 (1 H, br d, *J* 7.0, =CHC*H*CH), 3.59 (3 H, s, CH_3O), 3.59–3.66 (1 H, m, 3-H), 3.76 (1 H, dd, *J* 11.2 and 2.0, CH_3OC-C*H*CH), 4.07–4.18 (2 H, m, CH_2O), 4.12 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 4.21 (2 H, q, *J* 7.3, CH_2O), 6.01 (1 H, d, *J* 16.2, 8-CH=C*H*), 6.25 (1 H, br d, *J* 8.1, CH_3OCC*H*=CH), 6.55 (1 H, dd, *J* 8.1 and 6.6, CH=C*H*CH) and 6.67 (1 H, d, *J* 16.2, 8-C*H*=CH); δ_C 14.0 (*C*H$_3$CH$_2$), 14.1 (*C*H$_3$CH$_2$), 14.2 (*C*H$_3$CH$_2$), 42.1, 43.1 and 48.2 (C-2, -3 and -4), 52.9 (CH_3O), 54.3 (CH_3O), 60.9 (CH_2O), 61.1 (CH_2O), 61.2 (CH_2O), 76.7 and 85.0 (C-1 and -8), 126.5 (8-CH=*C*H), 127.9 (C-6), 132.5 (C-5), 142.8 (8-CH=), 165.4 (CO_2), 169.7 (CO_2), 171.1 (CO_2) and 199.9 (C-7); *m*/*z* (%) 424 (2, M^+) and 249 (base) (Found: M^+, 424.1702. $C_{21}H_{28}O_9$ requires *M*, 424.1734).

Diethyl (1*α*,2*R,3*S**,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-ene-2,3-dicarboxylate 9m.** An *oil*; ν_{max}(neat)/cm^{-1} 1740, 1725 and 1655; λ_{max}(EtOH)/nm 208 (11 030) and 311 (193); δ_H 1.24–1.32 (9 H, m, C*H*$_3$CH$_2$ × 3), 3.39–3.51 (1 H, m, 4-H), 3.41 (3 H, s, CH_3O), 3.45 (1 H, dd, *J* 5.9 and 4.6, =CHCHC*H*CH), 3.57 (3 H, s, CH_3O), 3.80 (1 H, dd, *J* 5.9 and 2.3, CH_3OCC*H*CH), 4.08–4.25 (6 H, m, CH_2O × 3), 6.00 (1 H, d, *J* 16.2, 8-CH=C*H*), 6.31 (1 H, dd, *J* 8.6 and 6.6, CH=C*H*CH), 6.40 (1 H, dd, *J* 8.6 and 1.7, CH_3OCC*H*=CH) and 6.66 (1 H, d, *J* 16.2, 8-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$ × 3), 42.5 (C-2), 43.9 and 49.9 (C-3 and -4), 53.2 (CH_3O), 53.4 (CH_3O), 60.8 (CH_2O), 61.5 (CH_2O), 61.7 (CH_2O), 76.1 and 84.9 (C-1 and -8), 126.1 (8-CH=*C*H), 130.1 (C-6), 132.6 (C-5), 144.3 (8-CH=), 165.6 (CO_2), 171.1 (CO_2), 172.4 (CO_2) and 199.1 (C-7); *m*/*z* (%) 425 (2, $M^+ + 1$), 424 (9, M^+) and 350 (base) (Found: M^+, 424.1705).

Ethyl (*E*)-3′-[(1*α*,2*S,4*α*,8*S**)-8-(1,3-dioxolan-2-yl)-2,4-dimethoxy-8-methyl-3-oxobicyclo[2.2.2]oct-5-en-2-yl]acrylate 9p.** A solution consisting of compound **9k** (0.67 g, 2.08 mmol), ethylene glycol (0.26 g, 4.16 mmol) and a trace amount of PTSA in benzene (100 cm^3) was stirred at reflux with azeotropic removal of water for 24 h. After cooling, the reaction mixture was washed with brine (2 × 30 cm^3) and dried over $MgSO_4$. Removal of the solvent under reduced pressure and chromatography of the residue over silica gel (13 g; eluent hexane–ethyl acetate, 9:1) furnished the *title compound* **9p** as an oil (0.65 g, 86%), ν_{max}(neat)/cm^{-1} 1730, 1645 and 1620; δ_H 1.30 (3 H, t, *J* 7.2, C*H*$_3$CH$_2$), 1.56 (3 H, s, 8-CH_3), 1.80–1.81 (2 H, m, 7-H), 3.00–3.02 (1 H, m, 1-H), 3.30 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 3.80–3.91 (4 H, m, OCH_2CH_2O), 4.20 (2 H, q, *J* 7.2, C*H*$_2$CH$_3$), 4.80 [1 H, s, CH(O-)$_2$], 6.03 (1 H, d, *J* 15.9, 2-CH=C*H*), 6.32–6.35 (2 H, m, 5- and 6-H), 6.63 (1 H, d, *J* 15.9, 2-C*H*=CH); *m*/*z* (%) 366 (0.2, M^+), 338 (2, $M^+ - CO$) and 73 (base).

Ethyl (*E*)-3′-{(1*α*,2*R,4*α*,8*S**)-8-[(*E*)-2-ethoxycarbonylvinyl]-1,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl}acrylate 9t.** A mixture of the aldehyde **20j** (1.10 g, 4.62 mmol), ethoxycarbonylmethyltriphenylphosphonium bromide (4.56 g, 10.62 mmol) and potassium carbonate (1.81 g, 13.10 mmol) in dichloromethane –water (1:1; 230 cm^3) was stirred for 24 h. Then the reaction mixture was treated in a similar manner to that described above (general procedure for the preparation of compounds **9**) to afford the *title compound* **9t** as a colourless oil (1.31 g, 75%); ν_{max}(neat)/cm^{-1} 1720, 1655 and 1650; λ_{max}(EtOH)/nm 217 (16 450) and 314 (184); δ_H 1.29 (6 H, t, *J* 7.0, C*H*$_3$CH$_2$ × 2), 1.34 (1 H, ddd, *J* 13.4, 4.9 and 3.0, CHC*H*^{endo}HCH), 2.55 (1 H, ddd, *J* 13.4, 9.8 and 2.7, CHCH*H*^{exo}CH), 3.04–3.07 (1 H, m, 4-H), 3.11–3.16 (1 H, m, 2-H), 3.41 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 4.19 (2 H, q, *J* 7.0, C*H*$_2$CH$_3$), 4.20 (2 H, q, *J* 7.0, C*H*$_2$CH$_3$), 5.87 (1 H, d, *J* 15.5, 2-CH=C*H*), 6.01 (1 H, d, *J* 16.1, 8-CH=C*H*), 6.20 (1 H, d, *J* 8.6, CH_3OCC*H*=CH), 6.47 (1 H, dd, *J* 8.6 and 6.7, CH=C*H*CH), 6.64 (1 H, d, *J* 16.1, 8-C*H*=CH) and 6.72 (1 H, dd, *J* 15.5 and 9.2, 2-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$), 14.3 (*C*H$_3$CH$_2$), 28.0 (C-3), 39.4 (C-4), 41.0 (C-2), 52.5 (CH_3O), 53.7 (CH_3O), 60.4 (CH_2O), 60.8 (CH_2O), 77.9 and 85.6 (C-1 and -8), 122.8 (2-CH=*C*H), 126.0 (8-CH=*C*H), 128.9 (C-6), 134.1 (C-5), 143.5 (8-CH=), 147.5 (2-CH=), 165.6 (CO_2), 166.2 (CO_2) and 201.7 (C-7); *m*/*z* (%) 379 (11, $M^+ + 1$), 378 (35, M^+), 332 (25, $M^+ - CH_2$=S) and 304 (base) (Found: M^+, 378.1660. $C_{20}H_{26}O_7$ requires *M*, 378.1679).

General procedure for the photolysis of the 3-(methylthiomethyl)bicyclo[2.2.2]octenones 8

A solution of a compound **8** (1.00 g) in dry benzene (250 cm^3) was irradiated in a Pyrex immersion well with a 400 W mercury vapour lamp (NIKKO SEKIEI WORKS) under nitrogen at 0 °C. After ⩽10 h (TLC test), removal of the solvent gave a pale yellow oil, which was chromatographed on silica gel (eluent hexane–ethyl acetate, 9:1) to afford the bicyclo[4.1.0]heptenes **10**. Continued elution with the same solvent gave the bicyclo-[4.2.0]octenones **12** as oils.

(1*S,1a*β*,3a*α*,8a*α*,8b*β*)-1,3-Dimethoxy-1-methylthiomethyl-1,1a,3a,8,8a,8b-hexahydrocyclopropa[*a*]fluorene 10a.** An oil; ν_{max}(neat)/cm^{-1} 1660; δ_H 1.20 (1 H, br d, *J* 9.6, ArC*H*CH), 1.45 (1 H, dd, *J* 9.6 and 5.6, =CHC*H*CH), 2.21 (3 H, s, CH_3S), 2.78 (2 H, ABq, *J* 13.9, CH_2S), 2.85–2.98 (2 H, m, 8-H), 2.98–3.15 (1 H, m, 8a-H), 3.33 (3 H, s, CH_3O), 3.49 (3 H, s, CH_3O), 3.62 (1 H, d, *J* 7.9, C*H*CHCH$_2$), 4.68 (1 H, d, *J* 5.6, =C*H*CH), 7.01–7.16 (3 H, m, 5-, 6- and 7-H) and 7.26–7.37 (1 H, m, 4-H); δ_C 16.0 (CH_3S), 22.4 (C-1a), 26.4 (C-8b), 36.5 (C-8a), 38.6 (CH_2S), 39.7 (C-8), 46.2 (C-3a), 54.2 (CH_3O), 55.0 (CH_3O), 68.0 (C-1), 86.8 (C-2), 123.8, 125.7 and 126.6 (C-5, -6, -7), 126.9 (C-4), 142.1 and 144.0 (C-3b and -7a) and 154.4 (C-3); *m*/*z* (%) 302 (0.1, M^+), 255 (42, $M^+ - CH_3S$) and 139 (base).

(1*S,1a*β*,3a*α*,6a*α*,6b*β*)-1,3-Dimethoxy-1-methylthiomethyl-1,1a,3a,6,6a,6b-hexahydrocyclopropa[*e*]indene 10b.** An *oil*; ν_{max}(neat)/cm^{-1} 1662; δ_H 1.16 (1 H, br d, *J* 9.6, CH_2CHC*H*CH), 1.41 [1 H, dd, *J* 9.6 and 5.9, CH_3OCC*H*(CH)CH=], 2.20 (3 H, s, CH_3S), 2.28 (1 H, dddd, *J* 15.8, 9.2, 4.6 and 2.6, =CHC*H*^{endo}-HCH), 2.55 (1 H, dddd, *J* 15.8, 8.6, 2.3 and 1.7, =CHCH-*H*^{exo}CH), 2.76 (2 H, ABq, *J* 13.9, CH_2S), 2.81–2.93 (1 H, m, 6a-H), 3.12 [1 H, br d, *J* 9.9, =CHC*H*CH(C=)], 3.27 (3 H, s, CH_3O), 3.50 (3 H, s, CH_3O), 4.63 (1 H, dd, *J* 5.9 and 1.7, CH_3OC=C*H*CH), 5.65–5.72 (1 H, m, 5- or 4-H) and 5.83–5.87 (1 H, m, 4- or 5-H); δ_C 16.4 (CH_3S), 22.2 (C-6b), 26.3 (C-1a), 34.3 (C-6a), 38.5 (CH_2S), 39.6 (C-6), 45.9 (C-3a), 54.1 (CH_3O), 55.0 (CH_3O), 67.7 (C-1), 85.8 (C-2), 129.6 and 132.5 (C-4 and -5) and 156.2 (C-3); *m*/*z* (%) 252 (0.3, M^+), 205 (36, $M^+ - CH_3S$) and 139 (base) (Found: M^+, 252.1182. $C_{14}H_{20}O_2S$ requires *M*, 252.1184).

(1*β*,4*R,6*β*,7*S**)-4-Isopropenyl-3,7-dimethoxy-7-(methylthiomethyl)bicyclo[4.1.0]hept-2-ene 10c.** An oil; ν_{max}(neat)/cm^{-1}

1665; δ_H 1.11 (1 H, ddd, *J* 9.6, 7.6 and 4.9, CH_2CHCH), 1.34 (1 H, dd, *J* 9.6 and 4.3, =CHC*H*CH), 1.74 (3 H, s, CH_3C=), 1.95 (1 H, ddd, *J* 14.2, 7.6 and 5.3, CHC*H*^{endo}HCH), 2.08 (1 H, ddd, *J* 14.2, 6.9 and 4.9, CHCH*H*^{exo}CH), 2.18 (3 H, s, CH_3S), 2.75 (2 H, ABq, *J* 14.2, CH_2S), 2.78 (1 H, dd, *J* 6.9 and 5.3, =CC*H*CH_2), 3.31 (3 H, s, CH_3O), 3.54 (3 H, s, CH_3O) and 4.29 (1 H, d, *J* 4.3, =C*H*CH); δ_C 16.4 (CH_3S), 20.5 (CH_3C=), 20.8 (C-6), 23.1 (C-1), 23.8 (C-5), 39.2 (CH_2S), 44.6 (C-4), 54.6 (CH_3O), 55.5 (CH_3O), 68.9 (C-7), 89.1 (C-2), 111.7 (CH_2=), 146.4 (4-C=) and 159.2 (C-3); *m*/*z* (FAB) (%) 277 [7, $(M + Na)^+$] and 207 (base).

Ethyl (1β,3*S,6β,7*S**)-4,7-dimethoxy-7-(methylthiomethyl)-bicyclo[4.1.0]hept-4-ene-3-carboxylate 10d.** An *oil*; ν_{max}(neat)/cm^{-1} 1730 and 1660; δ_H 1.22–1.30 (1 H, m, 1-H), 1.26 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.41 (1 H, dd, *J* 9.6 and 4.6, =CHC*H*CH), 2.13–2.31 (2 H, m, 2-H), 2.18 (3 H, s, CH_3S), 2.74 (2 H, ABq, *J* 13.9, CH_2S), 3.12 (1 H, t, *J* 6.8, CH_2CHCO_2), 3.28 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O), 4.17 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$) and 4.81 (1 H, d, *J* 4.6, =C*H*CH); δ_C 14.2 (*C*H$_3$CH$_2$), 16.0 (CH_3S), 20.6 (C-1), 22.1 (C-2), 22.3 (C-6), 38.6 (CH_2S), 44.4 (C-3), 54.5 (CH_3O), 55.1 (CH_3O), 60.7 (CH_2O), 68.7 (C-7), 89.6 (C-5), 154.7 (C-4) and 173.2 (CO_2); *m*/*z* (FAB) (%) 309 [33, $(M + Na)^+$], 285 (11) and 239 (base).

***tert*-Butyl (1β,3*S**,6β,7*S**)-4,7-dimethoxy-7-(methylthiomethyl)bicyclo[4.1.0]hept-4-ene-3-carboxylate 10e.** An oil; ν_{max}(neat)/cm^{-1} 1728 and 1663; δ_H 1.23 (1 H, ddd, *J* 9.6, 7.3 and 4.6, CH_2CHCH), 1.39 (1 H, dd, *J* 9.6 and 4.3, =CHC*H*CH), 1.45 [9 H, s, C(CH_3)$_3$], 2.15–2.20 (2 H, m, 2-H), 2.18 (3 H, s, CH_3S), 2.74 (2 H, ABq, *J* 13.9, CH_2S), 2.99 (1 H, dd, *J* 6.6 and 6.3, 3-H), 3.28 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O) and 4.77 (1 H, d, *J* 4.3, =C*H*CH); δ_C 16.3 (CH_3S), 20.5 (C-1), 20.2 (C-2), 22.4 (C-6), 28.0 [C(*C*H$_3$)$_3$], 39.0 (CH_2S), 44.0 (C-3), 54.4 (CH_3O), 55.1 (CH_3O), 68.6 (C-7), 80.4 [*C*(CH$_3$)$_3$], 89.3 (C-5), 155.6 (C-4) and 172.5 (CO_2); *m*/*z* (FAB) (%) 337 [6, $(M + Na)^+$] and 179 (base).

***tert*-Butyl (1β,3*S**,6β,8*S**)-4,8-dimethoxy-8-methylthiomethyl-7-oxobicyclo[4.2.0]oct-4-ene-3-carboxylate 12e.** An oil; ν_{max}(neat)/cm^{-1} 1775, 1695 and 1645; δ_H 1.46 [9 H, s, C(CH_3)$_3$], 1.94 (1 H, ddd, *J* 14.2, 11.2 and 5.1, CHC*H*^{endo}HCH), 2.19 (3 H, s, CH_3S), 2.23 (1 H, ddd, *J* 14.2, 6.6 and 3.3, CHCH*H*^{exo}CH), 2.77 (1 H, ddd, *J* 11.2, 10.2 and 6.6, CH_2CHCH), 2.99 (2 H, ABq, *J* 14.0, CH_2S), 3.10 (1 H, dd, *J* 5.1 and 3.3, CH_2CHCO_2), 3.49 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O), 3.73 (1 H, dd, *J* 10.2 and 4.5, =CHC*H*CH) and 4.72 (1 H, d, *J* 4.5, =C*H*CH); δ_C 16.9 (CH_3S), 24.7 (C-2), 28.0 [C(*C*H$_3$)$_3$], 32.0 (C-1), 36.4 (CH_2S), 44.0 (C-3), 52.1 (C-6), 53.4 (CH_3O), 54.6 (CH_3O), 81.1 [O*C*(CH$_3$)], 87.9 (C-5), 93.0 (C-8), 155.9 (C-4), 171.5 (CO_2) and 208.4 (C-7); *m*/*z* (%) 342 (0.3, M^+), 266 (60), 211 (82) and 179 (base).

Methyl (1β,3*S,6β,7*S**)-4,7-dimethoxy-3-methyl-7-(methylthiomethyl)bicyclo[4.1.0]hept-4-ene-3-carboxylate 10f.** An oil; ν_{max}(neat)/cm^{-1} 1725 and 1650; δ_H 1.22–1.35 (2 H, m, 1- and 6-H), 1.27 (3 H, s, 3-CH_3), 1.78 (1 H, dd, *J* 13.9 and 5.9, C*H*^{endo}HCH), 2.17 (3 H, s, CH_3S), 2.39 (1 H, dd, *J* 13.9 and 8.3, CH*H*^{exo}CH), 2.73 (2 H, ABq, *J* 13.9, CH_2S), 3.34 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O), 3.64 (3 H, s, CH_3O) and 4.65 (1 H, d, *J* 3.0, =C*H*CH); δ_C 16.0 (CH_3S), 20.0 and 23.2 (C-1 and -6), 21.8 (3-CH_3), 31.4 (C-2), 38.6 (CH_2S), 45.4 (C-3), 52.2 (CH_3O), 54.8 (CH_3O), 55.3 (CH_3O), 67.9 (C-7), 89.5 (C-5), 159.5 (C-4) and 176.0 (CO_2); *m*/*z* (FAB) (%) 309 [9, $(M + Na)^+$], 285 (11) and 239 (base).

Methyl (1β,3*S,6β,8*S**)-4,8-dimethoxy-3-methyl-8-methylthiomethyl-7-oxobicyclo[4.2.0]oct-4-ene-3-carboxylate 12f.** An oil; ν_{max}(neat)/cm^{-1} 1782, 1715 and 1642; δ_H 1.37 (3 H, s, 3-CH_3), 1.72 (1 H, dd, *J* 13.9 and 12.9, C*H*^{endo}HCH), 2.18 (3 H, s, CH_3S), 2.26 (1 H, dd, *J* 13.9 and 6.3, CH*H*^{exo}CH), 2.70 (1 H, ddd, *J* 12.9, 9.9 and 6.3, CH_2CHCH), 3.00 (2 H, ABq, *J* 14.2, CH_2S), 3.49 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O), 3.70 (3 H, s, CH_3O), 3.70 (1 H, dd, *J* 9.9 and 4.6, =CHC*H*CH) and 4.68 (1 H, d, *J* 4.6, =C*H*CH); δ_C 16.8 (CH_3S), 22.5 (3-CH_3), 32.2 (C-1), 34.0 (C-2), 36.3 (CH_2S), 45.4 (C-3), 51.8 (C-6), 52.3 (CH_3O), 53.3 (CH_3O), 54.9 (CH_3O), 87.9 (C-5), 93.5 (C-8), 158.1 (C-4), 175.1 (CO_2) and 208.0 (C-7); *m*/*z* (%) 314 (5, M^+), 267 (13, $M^+ - CH_3S$) and 238 (base) (Found: M^+, 314.1195. $C_{15}H_{22}O_5S$ requires *M*, 314.1188).

(1β,4*S,6β,7*S**)-3,7-Dimethoxy-7-methylthiomethyl-4-propionylbicyclo[4.1.0]hept-2-ene 10h.** An oil; ν_{max}(neat)/cm^{-1} 1715 and 1660; δ_H 1.03 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.25–1.31 (1 H, m, 6-H), 1.31 (1 H, dd, *J* 9.6 and 5.6, =CHC*H*CH), 1.92–1.98 (1 H, m, 5-H^{endo}), 2.17 (3 H, s, CH_3S), 2.22–2.30 (1 H, m, 5-H^{exo}), 2.50 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 2.73 (2 H, ABq, *J* 14.0, CH_2S), 3.06 (1 H, dd, *J* 6.3 and 4.6, CH_2CHCO), 3.30 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O) and 4.76 (1 H, d, *J* 3.6, =C*H*CH); δ_C 7.7 (*C*H$_3$CH$_2$), 15.9 (CH_3S), 20.4 and 22.3 (C-1 and -6), 20.8 (C-5), 34.1 (*C*H$_2$CH$_3$), 38.5 (CH_2S), 49.9 (C-4), 54.2 (CH_3O), 55.0 (CH_3O), 68.4 (C-7), 89.8 (C-2), 156.0 (C-3) and 210.6 (CO); *m*/*z* (FAB) (%) 293 [49, $(M + Na)^+$] and 223 (base).

(1β,4*S,6β,7*S**)-3,7-Dimethoxy-7-methylthiomethyl-4-propionylbicyclo[4.2.0]oct-2-en-8-one 12h.** An oil; ν_{max}(neat)/cm^{-1} 1765, 1702 and 1658; δ_H 1.04 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.85 (1 H, ddd, *J* 13.9, 11.6 and 5.3, CHC*H*^{endo}HCH), 2.18 (3 H, s, CH_3S), 2.25 (1 H, ddd, *J* 13.9, 6.9 and 3.0, CHCH*H*^{exo}CH), 2.50–2.59 (2 H, m, C*H*$_2$CH$_3$), 2.82 (1 H, ddd, *J* 11.6, 10.6 and 6.9, CH_2CHCH), 2.99 (2 H, ABq, *J* 14.2, CH_2S), 3.20 (1 H, dd, *J* 5.3 and 3.0, CH_2CHCO), 3.47 (3 H, s, CH_3O), 3.58 (3 H, s, CH_3O), 3.67 (1 H, dd, *J* 10.6 and 4.3, =CHC*H*CH) and 4.74 (1 H, d, *J* 4.3, =C*H*CH); δ_C 7.7 (*C*H$_3$CH$_2$), 16.9 (CH_3S), 23.3 (C-5), 32.0 (C-6), 34.8 (*C*H$_2$CH$_3$), 36.4 (CH_2S), 49.6 (C-4), 51.9 (CH_3O), 53.3 (CH_3O), 54.6 (C-1), 88.4 (C-2), 93.0 (C-7), 155.6 (C-3), 208.1 and 209.8 (4-C=O and C-8); *m*/*z* (%) 298 (0.4, M^+), 222 (57), 165 (57) and 57 (base).

(1β,4*S,6β,7*S**)-4-Acetyl-3,7-dimethoxy-4-methyl-7-(methylthiomethyl)bicyclo[4.1.0]hept-2-ene 10i.** An oil; ν_{max}(neat)/cm^{-1} 1705 and 1643; δ_H 1.17 (3 H, s, 4-CH_3), 1.22 (1 H, dd, *J* 9.5 and 3.2, =CHC*H*CH), 1.27 (1 H, ddd, *J* 9.5, 8.7 and 5.8, CH_2CHCH), 1.67 (1 H, dd, *J* 13.8 and 5.8, C*H*^{endo}HCH) 2.13 (3 H, s, CH_3S), 2.16 (3 H, s, CH_3CO), 2.35 (1 H, dd, *J* 13.8 and 8.7, CH*H*^{exo}CH), 2.72 (2 H, ABq, *J* 14.2, CH_2S), 3.33 (3 H, s, CH_3O), 3.59 (3 H, s, CH_3O) and 4.71 (1 H, d, *J* 3.2, =C*H*CH); δ_C 15.9 (CH_3S), 20.4 (C-1), 20.9 (4-CH_3), 22.8 (C-6), 25.3 (*C*H$_3$CO), 29.7 (C-5), 38.5 (CH_2S), 51.7 (C-4), 54.6 (CH_3O), 55.2 (CH_3O), 67.7 (C-7), 90.5 (C-2), 159.6 (C-3) and 210.0 (CO); *m*/*z* (FAB) (%) 293 [12, $(M + Na)^+$] and 223 (base).

(1β,6β,7*S)-2′-[4,7-Dimethoxy-3-methyl-7-(methylthiomethyl)bicyclo[4.1.0]hept-4-en-3β-yl]-2′-methyl-1′,3′-dioxolane 10n.** An oil; ν_{max}(neat)/cm^{-1} 1650; δ_H 1.05 (3 H, s, 3-CH_3), 1.12 (1 H, br dd, *J* 9.6 and 5.9, CH_2CHCH), 1.31 [3 H, s, $CH_3C(O\text{-})_2$], 1.32 (1 H, dd, *J* 9.6 and 3.6, =CHC*H*CH), 1.67 (1 H, dd, *J* 14.9 and 5.9, C*H*^{endo}HCH), 2.17 (3 H, s, CH_3S), 2.22 (1 H, dd, *J* 14.9 and 9.6, C*H*^{exo}HCH), 2.75 (2 H, ABq, *J* 13.9, CH_2S), 3.34 (3 H, s, CH_3O), 3.53 (3 H, s, CH_3O), 3.89–4.03 (4 H, m, OCH_2CH_2O) and 4.72 (1 H, d, *J* 3.6, =C*H*CH); δ_C 15.9 (CH_3S), 20.7 (C-1), 21.1 and 21.3 [3-CH_3 and *C*H$_3$C(O-)$_2$], 24.4 (C-6), 28.6 (C-2), 38.8 (CH_2S), 44.3 (C-3), 54.3 (CH_3O), 55.3 (CH_3O), 64.7 and 65.2 (OCH_2CH_2O), 68.3 (C-7), 90.7 (C-5), 114.0 [C(O-)$_2$] and 161.4 (C-4); *m*/*z* (FAB) (%) 337 [7, $(M + Na)^+$], 269 (57), 180 (61) and 147 (base).

(1β,6β,7*S)-2′-[4,7-Dimethoxy-7-(methylthiomethyl)bicyclo-[4.1.0]hept-4-en-3β-yl]-1′,3′-dioxolane 10o.** An oil; ν_{max}(neat)/cm^{-1} 1660; δ_H 1.18 (1 H, ddd, *J* 9.6, 7.9 and 5.3, CH_2CHCH), 1.34 (1 H, dd, *J* 9.6 and 4.0, =CHC*H*CH), 2.04–2.10 (2 H, m, 2-H), 2.18 (3 H, s, CH_3S), 2.32–2.38 (1 H, m, 3-H), 2.75 (2 H, ABq, *J* 13.9, CH_2S), 3.31 (3 H, s, CH_3O), 3.57 (3 H, s, CH_3O), 3.82–3.99 (4 H, m, OCH_2CH_2O), 4.75 (1 H, d, *J* 4.0, =C*H*CH) and 5.10 [1 H, d, *J* 4.9, CH(O-)$_2$]; δ_C 16.0 (CH_3S), 18.8 (C-2), 19.9 (C-1), 22.5 (C-6), 38.7 (CH_2S), 40.6 (C-3), 54.4 (CH_3O), 55.1 (CH_3O), 65.0 and 65.4 (OCH_2CH_2O), 68.4 (C-7), 89.5 (C-5), 104.8 [CH(O-)$_2$] and 157.5 (C-4); *m*/*z* (FAB) (%) 309 [1, $(M + Na)^+$], 295 (31) and 73 (base).

(1β,6β,7*S)-2′-[4,7-Dimethoxy-3-methyl-7-(methylthiomethyl)-bicyclo[4.1.0]hept-4-en-3β-yl]-1′,3′-dioxolane 10p.** An oil; ν_{max}(neat)/cm^{-1} 1645; δ_H 0.99 (3 H, s, 3-CH_3), 1.17 (1 H, ddd, *J* 9.9, 9.0 and 6.3, CH_2CHCH), 1.32 (1 H, dd, *J* 9.9 and 3.3, =CHC*H*CH), 1.74 (1 H, dd, *J* 14.4 and 6.3, C*H*^{endo}HCH), 2.14 (1 H, dd, *J* 14.4 and 9.0, CH*H*^{exo}CH), 2.17 (3 H, s, CH_3S), 2.74 (2 H, ABq, *J* 14.2, CH_2S), 3.34 (3 H, s, CH_3O), 3.55 (3 H, s, CH_3O), 3.87–4.07 (4 H, m, OCH_2CH_2O), 4.66 (1 H, d, *J* 3.3, =C*H*CH) and 5.01 [1 H, s, CH(O-)$_2$]; δ_C 15.9 (CH_3S), 17.3 (3-CH_3), 19.2 (C-1), 23.2 (C-6), 28.7 (C-2), 38.7 (CH_2S), 40.7 (C-3), 54.6 (CH_3O), 55.1 (CH_3O), 65.1 and 65.7 (OCH_2CH_2O), 67.8 (C-7), 89.1 (C-5), 107.4 [CH(O-)$_2$] and 161.3 (C-4); *m*/*z* (FAB) (%) 323 [4, (M + Na)$^+$] and 101 (base).

(1β,6β,7*S)-2-Acetyl-3,7-dimethoxy-4-methyl-7-(methylthiomethyl)bicyclo[4.1.0]hept-2-ene 10q.** An oil; ν_{max}(neat)/cm^{-1} 1650 and 1615; δ_H 1.11 (1 H, d, *J* 9.9, =CC*H*CH), 1.21 (1 H, br dd, *J* 9.9 and 6.6, CH_2CHCH), 1.67 (3 H, d, *J* 7.3, CH_3CH), 2.17 (6 H, s, CH_3S and CH_3CO), 2.36 (1 H, br d, *J* 18.4, CHC*H*^{endo}HCH), 2.61 (1 H, br dd, *J* 18.4 and 6.6, CHCH*H*^{exo}CH), 2.76 (2 H, ABq, *J* 13.9, CH_2S), 3.38 (3 H, s, CH_3O), 3.47 (3 H, s, CH_3O) and 3.46–3.48 (1 H, m, 4-H); δ_C 15.7 (4-CH_3), 16.1 (CH_3S), 19.7 (C-1), 24.3 (C-6), 26.6 (*C*H$_3$CO), 26.8 (C-5), 39.3 (CH_2S), 47.0 (C-4), 54.7 (CH_3O), 57.3 (CH_3O), 63.5 (C-7), 117.2 (C-2), 144.4 (C-3) and 209.1 (CO); *m*/*z* (%) 270 (2, M$^+$), 223 (61, M$^+$ − CH_3S) and 147 (base) (Found: M$^+$, 270.1280. $C_{14}H_{22}O_3S$ requires *M*, 270.1290).

(1β,6β,7*S)-3,7-Dimethoxy-7-(methylthiomethyl)bicyclo-[4.1.0]hept-2-ene 10r.** An oil; ν_{max}(neat)/cm^{-1} 1660; δ_H 1.15 (1 H, br d, *J* 9.2, CH_2CHCH), 1.36 (1 H, dd, *J* 9.2 and 5.6, =CHC*H*CH), 1.72–2.26 (4 H, m, 4- and 5-H), 2.19 (3 H, s, CH_3S), 2.74 (2 H, ABq, *J* 14.0, CH_2S), 3.26 (3 H, s, CH_3O), 3.54 (3 H, s, CH_3O) and 4.76 (1 H, dd, *J* 5.6 and 1.3, =C*H*CH); δ_C 16.0 (CH_3S), 17.7 (C-4), 21.7 (C-1), 22.8 (C-6), 25.6 (C-5), 38.9 (CH_2S), 53.9 (CH_3O), 54.9 (CH_3O), 69.1 (C-7), 87.2 (C-2) and 158.1 (C-3); *m*/*z* (FAB) (%) 237 [7, (M + Na)$^+$] and 167 (base).

(1β,6β,7*S)-3,7-Dimethoxy-4-methyl-7-(methylthiomethyl)-bicyclo[4.1.0]hept-2-ene 10s.** An oil; ν_{max}(neat)/cm^{-1} 1645; δ_H 1.00 (3 H, d, *J* 6.9, CH_3CH), 1.17 (1 H, br dd, *J* 9.6 and 5.3, CH_2CHCH), 1.28 (1 H, ddd, *J* 9.6, 3.6 and 1.3, =CHC*H*CH), 1.60 (1 H, ddd, *J* 14.2, 9.8 and 5.3, CHC*H*^{endo}HCH), 2.04 (1 H, ddd, *J* 14.2, 8.6 and 5.9, CHCH*H*^{exo}CH), 2.18 (3 H, s, CH_3S), 2.43 (1 H, m, 4-H), 2.74 (2 H, ABq, *J* 13.9, CH_2S), 3.31 (3 H, s, CH_3O), 3.51 (3 H, s, CH_3O), 4.55 (1 H, dd, *J* 3.9 and 1.7, =C*H*CH); δ_C 16.0 (CH_3S), 17.4 (4-CH_3), 21.0 (C-6), 23.1 (C-1), 27.4 (C-5), 30.2 (C-4), 38.8 (CH_2S), 54.1 (CH_3O), 55.0 (CH_3O), 67.5 (C-7), 86.6 (C-2) and 162.0 (C-3); *m*/*z* (FAB) (%) 251 [39, (M + Na)$^+$], 227 (35), 181 (99) and 139 (base).

General procedure for the photolysis of the 3-(2-ethoxycarbonylvinyl)bicyclo[2.2.2]octenones 9

A solution of a bicyclooctenone **9** (1.00 g) in dry benzene (250 cm^3) was irradiated in a Pyrex immersion well with a 400 W mercury vapour lamp (NIKKO SEKIEI WORKS) under nitrogen at 0 °C. After ≤12 h (TLC test), removal the of solvent gave a pale yellow oil, which was chromatographed on silica gel (eluent hexane-ethyl acetate, 9:1) to afford the bicyclo-[4.1.0]heptenes **11**.

Ethyl(*E*)-3′-[(1*R,1aβ,3aα,8aα,8bβ)-1,3-dimethoxy-1,1a,3a,8,8a,8b-hexahydrocyclopropa[*a*]fluoren-1-yl]acrylate 11a.** An oil; ν_{max}(neat)/cm^{-1} 1715 and 1640; δ_H 1.29 (3 H, t, *J* 6.9, CH_3CH_2), 1.53 (1 H, br d, *J* 9.6, =CHCHC*H*CH), 1.90 (1 H, dd, *J* 9.6 and 5.8, =CHC*H*CH), 2.92 (1 H, dd, *J* 14.8 and 9.2, C*H*^{endo}HCH), 3.10 (1 H, dd, *J* 14.8 and 12.2, CH*H*^{exo}CH), 2.98–3.19 (1 H, m, 8a-H), 3.41 (3 H, s, CH_3O), 3.52 (3 H, s, CH_3O), 3.64 (1 H, d, *J* 7.9, $CH_3OCCHCH$), 4.20 (2 H, q, *J* 6.9, CH_2O), 4.70 (1 H, d, *J* 5.8, =C*H*CH), 5.91 (1 H, d, *J* 15.7, 1-CH=C*H*), 6.63 (1 H, d, *J* 15.7, 1-C*H*=CH), 7.06–7.18 (3 H, m, 5-, 6- and 7-H) and 7.36–7.39 (1 H, m, 4-H); δ_C 14.3 (CH_3CH_2), 27.4 (C-1a), 29.5 (C-8b), 36.2 (C-8a), 39.5 (C-8), 46.0 (C-3a), 54.3 (CH_3O), 56.8 (CH_3O), 60.1 (CH_2O), 69.9 (C-1), 85.9 (C-2), 116.4 (1-CH=*C*H), 123.8, 125.8 and 126.8 (C-5, -6 and -7), 126.8 (C-4), 141.7 and 143.5 (C-3b and -7a), 150.5 (1-CH=), 155.4 (C-3) and 166.6 (CO_2); *m*/*z* (%) 341 (10, M$^+$ + 1), 340 (42, M$^+$), 309 (42) and 151 (base) (Found: M$^+$, 340.1684. $C_{21}H_{24}O_4$ requires *M*, 340.1675).

Ethyl (*E*)-3′-[(1*R,1aβ,3aα,6aα,6bβ)-1,3-dimethoxy-1,1a,3a,6,6a,6b-hexahydrocyclopropa[*e*]inden-1-yl]acrylate 11b.** An *oil*; ν_{max}(neat)/cm^{-1} 1710 and 1635; δ_H 1.29 (3 H, t, *J* 7.1, CH_3CH_2), 1.49 (1 H, br d, *J* 9.6, $CH_2CHCHCH$), 1.88 (1 H, dd, *J* 9.6 and 5.8, CH_3OC=CHC*H*CH), 2.32 (1 H, dddd, *J* 16.0, 9.1, 4.6 and 2.5, CHC*H*^{endo}HCH), 2.58 (1 H, br dd, *J* 16.0 and 8.6, CHCH-*H*^{exo}CH), 2.91 [1 H, br d, *J* 9.4, $CH_2CH(CH)_2$], 3.14 [1 H, br d, *J* 9.4, $CH_3OCCH(CH)_2$], 3.36 (3 H, s, CH_3O), 3.53 (3 H, s, CH_3O), 4.20 (2 H, q, *J* 7.1, OCH_2CH_3), 4.65 (1 H, dd, *J* 5.8 and 1.3, =C*H*CH), 5.70–5.73 (1 H, m, 4- or 5-H), 5.83–5.87 (1 H, m, 5- or 4-H), 5.89 (1 H, d, *J* 15.7, 1-CH=C*H*) and 6.61 (1 H, d, *J* 15.7, 1-C*H*=CH); δ_C 14.3 (*C*H$_3$CH$_2$), 27.4 (C-1a), 29.5 (C-6b), 34.0 (C-6a), 39.7 (C-6), 45.9 (C-3a), 54.2 (CH_3O), 56.9 (CH_3O), 60.2 (CH_2O), 69.8 (C-1), 84.9 (C-2), 116.2 (1-CH=*C*H), 129.7 and 132.2 (C-4 and -5), 150.8 (1-CH=), 157.2 (C-3) and 166.7 (CO_2); *m*/*z* (%) 291 (15, M$^+$ + 1), 290 (75, M$^+$), 275 (11) and 151 (base) (Found: M$^+$, 290.1526. $C_{17}H_{22}O_4$ requires *M*, 290.1518).

Ethyl (*E*)-3′-[(1β,4*R,6β,7*R**)-4-isopropenyl-3,7-dimethoxybicyclo[4.1.0]hept-2-en-7-yl]acrylate 11c.** An *oil*; ν_{max}(neat)/cm^{-1} 1715 and 1640; δ_H 1.29 (3 H, t, *J* 7.1, CH_3CH_2), 1.45 (1 H, ddd, *J* 9.6, 7.6 and 4.6, CH_2CHCH), 1.75 (3 H, s, CH_3C=), 1.80 (1 H, dd, *J* 9.6 and 4.3, =CHC*H*CH), 2.01 (1 H, ddd, *J* 14.5, 7.6 and 5.0, CHC*H*^{endo}HCH), 2.15 (1 H, ddd, *J* 14.5, 6.9 and 4.6, CHCH*H*^{exo}CH), 2.80 (1 H, dd, *J* 6.9 and 5.0, CH_2CHC=), 3.39 (3 H, s, CH_3O), 3.56 (3 H, s, CH_3O), 4.20 (2 H, q, *J* 7.1, CH_2O), 4.77 (1 H, d, *J* 4.3, =C*H*CH), 4.80–4.82 (2 H, m, CH_2=), 5.89 (1 H, d, *J* 15.7, 7-CH=C*H*) and 6.60 (1 H, d, *J* 15.7, 7-C*H*=CH); δ_C 14.7 (*C*H$_3$CH$_2$), 20.5 (CH_3=), 23.5 (C-5), 24.2 (C-6), 28.0 (C-1), 44.5 (C-4), 54.8 (CH_3O), 57.4 (CH_3O), 60.6 (CH_2O), 70.7 (C-7), 88.3 (C-2), 112.0 (CH_2=), 116.8 (7-CH=C*H*), 146.0 (4-C=), 151.4 (7-CH=), 160.0 (C-3) and 167.1 (CO_2); *m*/*z* (%) 293 (8, M$^+$ + 1), 292 (42, M$^+$), 277 (13) and 151 (base) (Found: M$^+$, 292.1679. $C_{17}H_{24}O_4$ requires *M*, 292.1675).

Ethyl (1β,3*S,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxybicyclo[4.1.0]hept-4-ene-3-carboxylate 11d.** An *oil*; ν_{max}(neat)/cm^{-1} 1735, 1713 and 1638; δ_H 1.26 (3 H, t, *J* 6.9, CH_3CH_2), 1.29 (3 H, t, *J* 6.9, CH_3CH_2), 1.58 (1 H, ddd, *J* 9.9, 6.9 and 4.3, CH_2CHCH), 1.84 (1 H, dd, *J* 9.9 and 4.6, =CHC*H*CH), 2.19–2.38 (2 H, m, 2-H), 3.12 (1 H, dd, *J* 6.6 and 6.4, CH_2CHCO_2), 3.36 (3 H, s, CH_3O), 3.59 (3 H, s, CH_3O), 4.12 (2 H, q, *J* 6.9, OCH_2CH_3), 4.20 (2 H, q, *J* 6.9, OCH_2CH_3), 4.83 (1 H, d, *J* 4.6, =C*H*CH), 5.89 (1 H, d, *J* 15.7, 7-CH=C*H*) and 6.59 (1 H, d, *J* 15.7, 7-C*H*=CH); δ_C 14.2 (*C*H$_3$CH$_2$), 14.3 (*C*H$_3$CH$_2$), 21.8 (C-2), 23.7 (C-1), 26.9 (C-6), 43.0 (C-3), 54.7 (CH_3O), 57.0 (CH_3O), 60.3 (CH_2O), 60.9 (CH_2O), 70.3 (C-7), 88.9 (C-5), 116.9 (7-CH=*C*H), 150.3 (7-CH=), 155.1 (C-4), 166.6 (CO_2) and 172.9 (CO_2); *m*/*z* (%) 325 (11, M$^+$ + 1), 324 (48, M$^+$), 293 (66) and 251 (base) (Found: M$^+$, 324.1571. $C_{17}H_{24}O_6$ requires *M*, 324.1573).

***tert*-Butyl (1β,3*S**,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxybicyclo[4.1.0]hept-4-ene-3-carboxylate 11e.** An *oil*; ν_{max}(neat)/cm^{-1} 1720 and 1640; δ_H 1.29 (3 H, t, *J* 7.3, CH_3CH_2), 1.47 [9 H, s, C(CH$_3$)$_3$], 1.55 (1 H, ddd, *J* 9.9, 7.3 and 4.4, CH_2CHCH), 1.82 (1 H, dd, *J* 9.9 and 4.6, =CHC*H*CH), 2.15 (2 H, m, 2-H), 3.00 (1 H, t, *J* 6.3, CH_2CHCO_2), 3.36 (3 H, s, CH_3O), 3.58 (3 H, s, CH_3O), 4.20 (2 H, q, *J* 7.3, CH_2CH_3), 4.79 (1 H, d, *J* 4.6, =C*H*CH), 5.93 (1 H, d, *J* 16.8, 7-CH=C*H*) and 6.59 (1 H, d, *J* 16.8, 7-C*H*=CH); δ_C 14.2 [C(*C*H$_3$)$_3$], 14.3 (*C*H$_3$CH$_2$), 21.8 (C-2), 23.7 (C-1), 27.0 (C-6), 28.0 [*C*(CH$_3$)$_3$], 44.1 (C-3), 54.6 (CH_3O), 57.0 (CH_3O), 60.3 (CH_2O), 70.3 (C-7), 88.5 (C-5), 116.8 (7-CH=*C*H), 150.5 (7-CH=), 156.4 (C-4), 166.7 (CO_2) and 172.1 (CO_2); *m*/*z* (%) 352 (2, M$^+$) and 295 (base) (Found: M$^+$, 352.1865. $C_{19}H_{28}O_6$ requires *M*, 352.1886).

Methyl (1β,3*S,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxy-3-methylbicyclo[4.1.0]hept-4-ene-3-carboxylate 11f.**

An *oil*; ν_{max}(neat)/cm^{-1} 1730, 1713 and 1636; δ_H 1.29 (3 H, t, *J* 7.1, C*H*$_3$CH$_2$), 1.30 (3 H, s, 3-CH$_3$), 1.61 (1 H, ddd, *J* 9.7, 8.9 and 5.9, CH$_2$C*H*CH), 1.74 (1 H, dd, *J* 9.7 and 3.6, =CHC*H*CH), 1.86 (1 H, dd, *J* 14.2 and 5.9, C*H*^{endo}HCH), 2.42 (1 H, dd, *J* 14.2 and 8.9, CH*H*^{exo}CH), 3.40 (3 H, s, CH$_3$O), 3.59 (3 H, s, CH$_3$O), 3.70 (3 H, s, CH$_3$O), 4.19 (2 H, q, *J* 7.1, C*H*$_2$CH$_3$), 4.68 (1 H, d, *J* 3.6, =C*H*CH), 5.89 (1 H, d, *J* 15.5, 7-CH=C*H*) and 6.59 (1 H, d, *J* 15.5, 7-C*H*=CH); δ_C 14.3 and 21.7 (*C*H$_3$CH$_2$, 3-CH$_3$), 23.5 (C-1), 27.7 (C-6), 30.8 (C-2), 45.3 (C-3), 52.3 (CH$_3$O), 54.9 (CH$_3$O), 57.2 (CH$_3$O), 60.3 (CH$_2$O), 69.7 (C-7), 88.7 (C-5), 116.7 (7-CH=*C*H), 150.7 (7-*C*H=), 160.1 (C-4), 166.6 (CO$_2$) and 175.6 (CO$_2$); *m*/*z* (%) 325 (11, M$^+$ + 1), 324 (52, M$^+$), 309 (22) and 233 (base) (Found: M$^+$, 324.1579. $C_{17}H_{24}O_6$ requires *M*, 324.1573).

Ethyl (*E*)-3′-[(1β,4*R,6β,7*R**)-4-cyano-3,7-dimethoxybicyclo[4.1.0]hept-2-en-7-yl]acrylate 11g.** A *solid*, mp 74–76 °C (from benzene–hexane) (Found: M$^+$, 277.1318; C, 64.9; H, 6.9; N, 4.9%. $C_{15}H_{19}NO_4$ requires *M*, 277.1314; C, 64.97; H, 6.91; N, 5.05%); ν_{max}(neat)/cm^{-1} 2240, 1710 and 1640; δ_H 1.30 (3 H, t, *J* 7.1, C*H*$_3$CH$_2$), 1.60 (1 H, ddd, *J* 9.6, 6.5 and 3.3, CH$_2$C*H*CH), 1.92 (1 H, dd, *J* 9.6 and 5.3, =CHC*H*CH), 2.28 (1 H, ddd, *J* 14.2, 7.9 and 6.5, CHC*H*^{endo}HCH), 2.48 (1 H, ddd, *J* 14.2, 7.3 and 3.3, CHCH*H*^{exo}CH), 3.31 (3 H, s, CH$_3$O), 3.41 (1 H, dd, *J* 7.9 and 7.3, CH$_2$C*H*CN), 3.64 (3 H, s, CH$_3$O), 4.21 (2 H, q, *J* 7.1, C*H*$_2$CH$_3$), 4.93 (1 H, dd, *J* 5.3 and 1.3, =C*H*CH), 5.90 (1 H, d, *J* 15.5, 7-CH=C*H*) and 6.57 (1 H, d, *J* 15.5, 7-C*H*=CH); δ_C 14.3 (*C*H$_3$CH$_2$), 23.0 (C-5), 23.3 (C-6), 25.9 (C-1), 28.3 (C-4), 55.1 (CH$_3$O), 57.0 (CH$_3$O), 60.5 (CH$_2$O), 70.3 (C-7), 89.6 (C-2), 117.9 (7-CH=*C*H), 119.5 (CN), 140.9 (7-*C*H=), 150.7 (C-3) and 166.3 (CO$_3$); *m*/*z* (%) 278 (2, M$^+$ + 1), 277 (9, M$^+$), 250 (43) and 204 (base).

Ethyl (*E*)-3′-[(1β,4*S,6β,7*R**)-3,7-dimethoxy-4-propionylbicylo[4.1.0]hept-2-en-7-yl]acrylate 11h.** An *oil*; ν_{max}(neat)/cm^{-1} 1710 and 1638; δ_H 1.04 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$CO), 1.29 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$O), 1.61 (1 H, ddd, *J* 9.6, 7.9 and 4.6, CH$_2$C*H*CH), 1.74 (1 H, dd, *J* 9.6 and 4.3, =CHC*H*CH), 2.06 (1 H, ddd, *J* 14.2, 6.6 and 4.6, CHC*H*^{endo}HCH), 2.31 (1 H, ddd, *J* 14.2, 7.9 and 4.3, CHCH*H*^{exo}CH), 2.43–2.67 (2 H, m, CH$_2$CO), 3.08 (1 H, dd, *J* 6.6 and 4.3, CH$_2$C*H*CO), 3.38 (3 H, s, CH$_3$O), 3.59 (3 H, s, CH$_3$O), 4.19 (2 H, q, *J* 7.3, C*H*$_2$CH$_3$), 4.78 (1 H, d, *J* 4.3, =C*H*CH), 5.88 (1 H, d, *J* 15.8, 7-CH=C*H*) and 6.58 (1 H, d, *J* 15.8, 7-C*H*=CH); δ_C 7.8 (*C*H$_3$CH$_2$CO), 14.3 (*C*H$_3$CH$_2$O), 20.5 (C-5), 23.8 (C-6), 27.0 (C-1), 34.2 (*C*H$_2$CO), 49.8 (C-4), 54.5 (CH$_3$O), 57.1 (CH$_3$O), 60.3 (CH$_2$O), 70.3 (C-7), 89.2 (C-2), 116.9 (7-CH=*C*H), 150.4 (7-*C*H=), 156.8 (C-3), 166.6 (CO$_2$) and 210.0 (C=O); *m*/*z* (%) 309 (8, M$^+$ + 1), 308 (42, M$^+$), 279 (21), 251 (81), 219 (91) and 57 (base) (Found: M$^+$, 308.1631. $C_{17}H_{24}O_5$ requires *M*, 308.1624).

Diethyl (1β,2*S,3*S**,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxybicyclo[4.1.0]hept-4-ene-2,3-dicarboxylate 11l.** A *solid*, mp 102–103 °C (from diethyl ether–hexane) (Found: M$^+$, 396.1793; C, 60.42; H, 7.1%. $C_{20}H_{28}O_8$ requires *M*, 396.1785; C, 60.59; H, 7.12%); ν_{max}(KBr)/cm^{-1} 1735, 1725, 1705 and 1660; δ_H 1.24 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.25 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.30 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.86 (1 H, dd, *J* 9.9 and 3.1, =CHC*H*CH), 2.19 (1 H, dd, *J* 9.9 and 6.6, =CHCHC*H*), 3.16 (1 H, dd, *J* 6.6 and 4.8, CH$_3$OCCHC*H*CH), 3.39 (3 H, s, CH$_3$O), 3.51 (1 H, d, *J* 4.8, CH$_3$OCC*H*CH), 3.62 (3 H, s, CH$_3$O), 4.16 (2 H, q, *J* 6.9, C*H*$_2$CH$_3$), 4.18 (2 H, q, *J* 6.9, C*H*$_2$CH$_3$), 4.21 (2 H, q, *J* 6.9, C*H*$_2$CH$_3$), 4.75 (1 H, d, *J* 3.1, =C*H*CH), 5.95 (1 H, d, *J* 15.5, 7-CH=C*H*) and 6.69 (1 H, d, *J* 15.5, 7-C*H*=CH); δ_C 14.1 (*C*H$_3$CH$_2$ × 2), 14.3 (*C*H$_3$CH$_2$), 25.4 (C-1), 27.6 (C-6), 38.8 (C-2), 45.8 (C-3), 55.0 (CH$_3$O), 57.2 (CH$_3$O), 60.4 (CH$_2$O), 61.0 (CH$_2$O), 61.2 (CH$_2$O), 69.9 (C-7), 89.3 (C-5), 117.6 (7-CH=*C*H), 149.5 (7-*C*H=), 156.8 (C-4), 166.5 (CO$_2$), 170.5 (CO$_2$) and 172.0 (CO$_2$); *m*/*z* (%) 397 (2, M$^+$ + 1), 396 (7, M$^+$), 381 (19) and 249 (base).

Diethyl (1β,2*S,3*R**,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxybicyclo[4.1.0]hept-4-ene-2,3-dicarboxylate 11m.** An *oil*; ν_{max}(neat)/cm^{-1} 1735 and 1643; δ_H 1.25 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.28 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.30 (3 H, t, *J* 7.3, C*H*$_3$CH$_2$), 1.81 (1 H, dd, *J* 9.9 and 3.6, =CHCHC*H*CH), 1.87 (1 H, dd, *J* 9.9 and 4.5, =CHC*H*CH), 3.31 (3 H, s, CH$_3$O), 3.60 (3 H, s, CH$_3$O), 3.64 (1 H, d, *J* 6.6, CH$_3$OCC*H*CH), 3.73 (1 H, dd, *J* 6.6 and 3.6, CH$_3$OCCHC*H*CH), 4.13–4.25 (6 H, m, CH$_2$O × 3), 4.83 (1 H, d, *J* 4.3, =C*H*CH), 5.93 (1 H, d, *J* 15.7, 7-CH=C*H*) and 6.63 (1 H, d, *J* 15.7, 7-C*H*=CH); δ_C 14.0 (*C*H$_3$CH$_2$), 14.1 (*C*H$_3$CH$_2$), 14.3 (*C*H$_3$CH$_2$), 26.3 (C-6), 27.0 (C-1), 39.0 (C-2), 45.6 (C-3), 54.9 (CH$_3$O), 56.9 (CH$_3$O), 60.4 (CH$_2$O), 61.0 (CH$_2$O), 61.4 (CH$_2$O), 69.2 (C-7), 88.3 (C-5), 117.9 (7-CH=*C*H), 149.3 (7-*C*H=), 154.0 (C-4), 166.5 (CO$_2$), 170.8 (CO$_2$) and 173.1 (CO$_2$); *m*/*z* (%) 397 (3, M$^+$ + 1), 396 (15, M$^+$), 367 (3) and 350 (base) (Found: M$^+$, 396.1793).

Ethyl (*E*)-3-{(1β,4*S,6β,7*R**)-4-(1,3-dioxolan-2-yl)-3,7-dimethoxy-4-methylbicyclo[4.1.0]hept-2-en-7-yl}acrylate 11p.** An *oil*; ν_{max}(neat)/cm^{-1} 1715 and 1635; δ_H 1.02 (3 H, s, 4-CH$_3$), 1.29 (3 H, t, *J* 6.9, C*H*$_3$CH$_2$), 1.51 (1 H, ddd, *J* 9.2, 9.2 and 5.6, CH$_2$C*H*CH), 1.74–1.79 (1 H, m, 1-H), 1.79 (1 H, dd, *J* 14.5 and 5.6, C*H*^{endo}HCH), 2.18 (1 H, dd, *J* 14.5 and 9.2, CH*H*^{exo}CH), 3.40 (3 H, s, CH$_3$O), 3.58 (3 H, s, CH$_3$O), 3.89 (4 H, br s, OCH$_2$CH$_2$O), 4.20 (2 H, q, *J* 6.9, C*H*$_2$CH$_3$), 4.70 (1 H, d, *J* 3.6, =C*H*CH), 4.97 [1 H, s, CH(O-)$_2$], 5.89 (1 H, d, *J* 15.8, 7-CH=C*H*) and 6.60 (1 H, d, *J* 15.8, 7-C*H*=CH); δ_C 14.3 (*C*H$_3$CH$_2$), 17.8 (4-CH$_3$), 23.1 (C-6), 27.6 (C-5), 28.0 (C-1), 40.7 (C-4), 54.7 (CH$_3$O), 57.1 (CH$_3$O), 60.2 (CH$_2$O), 65.1 and 65.7 (OCH$_2$CH$_2$O), 69.9 (C-7), 88.5 (C-2), 107.4 [CH(O-)$_2$], 116.3 (7-CH=*C*H), 151.2 (7-*C*H=), 161.8 (C-3) and 166.7 (CO$_2$); *m*/*z* (%) 338 (2, M$^+$) and 73 (base) (Found: M$^+$, 338.1721. $C_{18}H_{26}O_6$ requires *M*, 338.1730).

Ethyl (*E*)-3′-{(1β,3*R,6β,7*R**)-7-[(*E*)-2-ethoxycarbonylvinyl]-4,7-dimethoxybicyclo[4.1.0]hept-4-en-3-yl}acrylate 11t.** An oil; ν_{max}(neat)/cm^{-1} 1715 and 1640; δ_H 1.29 (6 H, t, *J* 6.9, C*H*$_3$CH$_2$ × 2), 1.49 (1 H, ddd, *J* 9.6, 7.9 and 5.0, CH$_2$C*H*CH), 1.80 (1 H, dd, *J* 9.6 and 4.3, =CHC*H*CH), 1.98 (1 H, ddd, *J* 14.4, 7.9 and 7.2, CHC*H*^{endo}HCH), 2.24 (1 H, ddd, *J* 14.4, 6.6 and 5.0, CHCH*H*^{exo}CH), 2.93 (1 H, m, 3-H), 3.39 (3 H, s, CH$_3$O), 3.56 (3 H, s, CH$_3$O), 4.20 (4 H, q, *J* 6.9, C*H*$_2$CH$_3$ × 2), 4.75 (1 H, d, *J* 4.3, =C*H*CH), 5.86 (1 H, dd, *J* 15.8 and 1.3, CHCH=C*H*), 5.90 (1 H, d, *J* 15.7, 7-CH=C*H*), 6.58 (1 H, d, *J* 15.7, 7-C*H*=CH) and 6.96 (1 H, dd, *J* 15.8 and 7.6, CHC*H*=CH); δ_C 14.3 (*C*H$_3$CH × 2), 23.1 (C-1), 23.7 (C-2), 27.1 (C-6), 39.6 (C-3), 54.5 (CH$_3$O), 57.0 (CH$_3$O), 60.3 (CH$_2$O), 60.5 (CH$_2$O), 69.9 (C-7), 87.9 (C-5), 116.9 (7-CH=*C*H), 121.3 (3-CH=*C*H), 148.8 (3-*C*H=), 150.5 (7-*C*H=), 158.5 (C-4), 166.6 (CO$_2$) and 166.7 (CO$_2$); *m*/*z* (%) 351 (2, M$^+$ + 1), 350 (11, M$^+$) and 151 (base) (Found: M$^+$, 350.1757. $C_{19}H_{26}O_6$ requires *M*, 350.1730).

X-Ray analysis of compound 8k

A plate-shaped crystal of dimensions 0.3 × 0.3 × 0.2 mm was used for X-ray crystallography. Formula $C_{14}H_{20}O_4S$, M_r = 284.1083; monoclinic, space group $P2_1/c$; cell parameters a = 6.823(1), b = 12.398(1), c = 16.790(1) Å, β = 91.05(1)°; V = 1420.0(2) Å^3, Z = 4, D_c = 1.330 g cm^3. Intensity data were collected by the 2θ/ω scan technique using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å) on a four-circle diffractometer (Rigaku AFC5R) at 293 K. Of the 2327 reflections up to θ_{max} = 65.03°, 2153 with $|F_o| > 2(|F_o|)$ were considered to be significant and were used in the refinement. The structure was solved by direct methods using SHELXS-86[22] and refined by full-matrix least-squares using SHELXL-93.[23] The final *R* factors converged to *R* = 0.050, w*R* = 0.122. Full crystallographic details for the structure determination have been deposited with the Cambridge Crystallographic Data Centre, under the accession number 207/67.†

X-Ray analysis of compound 11l

A plate-shaped crystal of dimensions 0.4 × 0.3 × 0.2 mm was

† *Supplementary material*. See the Instructions for Authors, in the January issue.

used for X-ray crystallography. Formula $C_{20}H_{28}O_8$, $M_r = 396.1785$; triclinic, space group $P\bar{1}$; cell parameters $a = 10.675(1)$, $b = 11.006(1)$, $c = 9.167(1)$ Å, $\alpha = 89.93(1)$, $\beta = 92.71(1)$, $\gamma = 99.92(1)°$, $V = 1059.7(1)$ Å^3, $Z = 2$, $D_c = 1.236$ g cm^{-3}. Intensity data were collected by the $2\theta/\omega$ scan technique using graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) on a four-circle diffractometer (Rigaku AFC5R) at 263 K. Of the 3444 reflections up to $\theta_{max} = 65.07°$, 3091 with $|F_o| > 2(|F_o|)$ were considered to be significant and were used in the refinement. The structure was solved by direct methods using SHELXS-86, and was refined by full-matrix least-squares using SHELXL-93. At this stage, a difference map showed disorder at one of the ethyl ester side chains. Occupancy factors of these atoms after refinement were 0.55 and 0.45 respectively. Residual electron densities in the final difference map were in the range -0.19 e/Å^3 to 0.29 e/Å^3. The final R factors converged to $R = 0.050$, w$R = 0.115$. Full crystallographic details for the structure determination have been deposited with the Cambridge Crystallographic Data Centre, under the accession code 207/67.

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