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Novel stereoconvergent transformation of 1,2a-disubstituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones to 1,3-disubstituted 1,2,4a,9b-tetrahydrodibenzofuran-4-ols and its application to the second-generation synthesis of (±)-linderol A†

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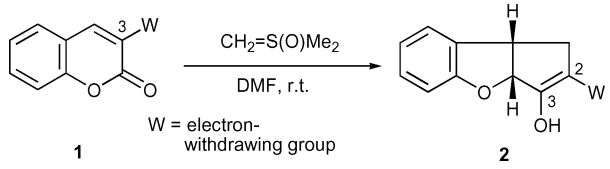
1,2a-Disubstituted 1,2,2a,8b-tetrahydro-3*H*-benzo[*b*]cyclobuta[*d*]pyran-3-ones (**10**) bearing an electron-withdrawing group at the 2a-position were treated with two equivalents of dimethylsulfoxonium methylide to give *r*-1,*t*-4a,*t*-9b-1,3-disubstituted 1,2,4a,9b-tetrahydrodibenzofuran-4-ols (**11**) stereoconvergently regardless of the stereochemistry of the 1-position on the benzocyclobutapyran ring. This methodology was applied to the second-generation synthesis of (±)-linderol A (**12**), a melanin biosynthesis inhibitory natural product.

Introduction

Small ring size cycloalkanes such as cyclopropanes and cyclobutanes have been found as a basic structural constituent in a wide range of natural products.[2] In organic synthesis, their cycloalkanes also play an important role owing to their diversity of reactions,[3] and their high reactivity toward ring-opening reactions is attributable to both angle and torsional strains. We have been interested in the small ring size cycloalkanes and reported several reactions including cyclopropane ring-opening.[4] One report dealt with a novel transformation of the coumarin derivatives (**1**) having an electron-withdrawing group at the 3-position to 2-substituted cyclopenta[*b*]benzofuran-3-ol derivatives (**2**) by treatment with 2.4 equivalents of dimethylsulfoxonium methylide[5] (Scheme 1).[4a,e]



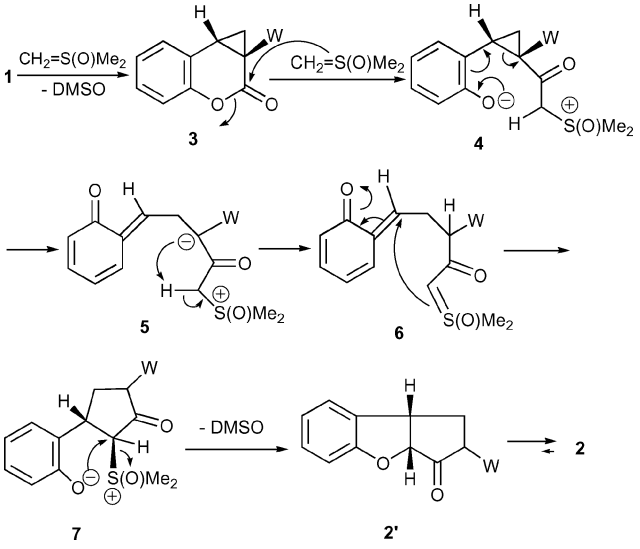
Scheme 1 The previous transformation of **1** to **2**.

A plausible reaction mechanism of **1** to **2** is shown in Scheme 2. The driving force of the reaction would be release of the ring strain from the cyclopropane intermediate (**4**)[6] to the ring-opened orthoquinone methide (**5**).

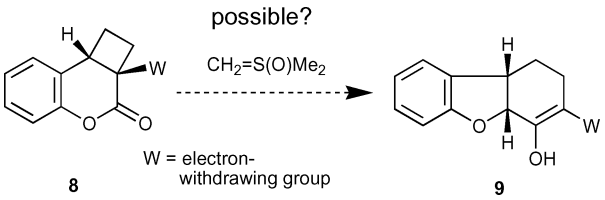
We expected that a similar ring-opening reaction as **1** to **2** would also occur in the strained cyclobutane derivatives (**8**) to give dibenzofuran derivatives (**9**) (Scheme 3).

In continuation of our study related to small ring size cycloalkanes, we would like to describe here a novel stereoconvergent transformation of the cyclobutane compounds, 1,2a-disubstituted benzo[*b*]cyclobuta[*d*]pyran-3-one derivatives (**10**), by treatment with dimethylsulfoxonium methylide to 1,3-disubstituted dibenzofuran-4-ol derivatives (**11**) (Scheme 4), and its application to the second-generation synthesis of (±)-linderol A (**12**) (Fig. 1).[7–9]

† See ref. 1



Scheme 2 The plausible reaction mechanism of **1** to **2**.



Scheme 3 A working hypothesis.

Results and discussion

Stereoconvergent transformation reaction of 10 to 11

The photochemical [2 + 2] cycloaddition of alkenes has been a well-known methodology for the preparation of cyclobutane compounds[10] and there are several reports on the photocycloaddition between coumarin derivatives and alkenes.[11] A solution of 3-ethoxycarbonylcoumarin and six equivalents of styrene in benzene was irradiated with a high-pressure mercury lamp (400 W) to afford [2 + 2] adducts (**10a**) in 78% yield.[11e] The

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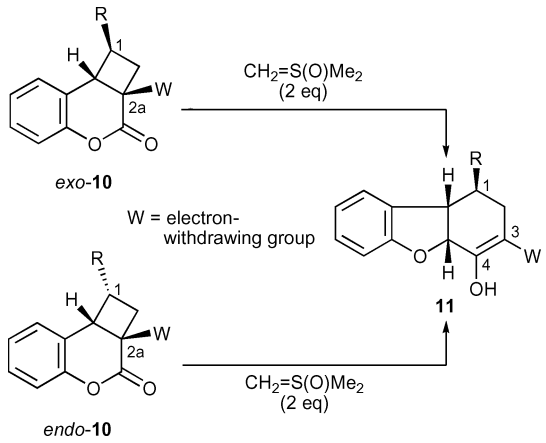
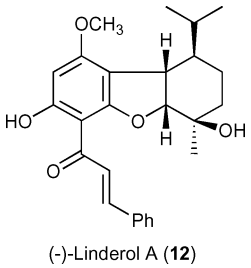


Scheme 4 The stereoconvergent transformation of **10** to **11**.

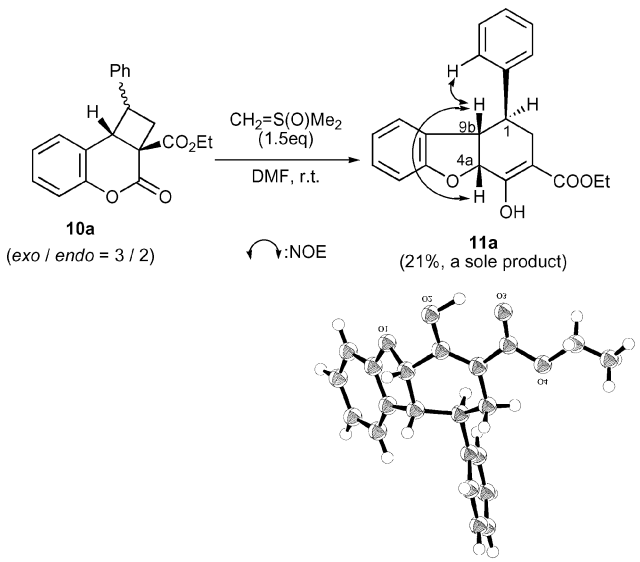


(-)-Linderol A (**12**)

Fig. 1 Structure of natural (−)-linderol A (**12**).

obtained **10a** was a diastereomeric mixture of 1-*exo*-phenyl cyclobutane (*exo*-**10a**) and 1-*endo*-phenyl cyclobutane (*endo*-**10a**) in the ratio of 3 : 2 on the basis of the ^{1}H NMR spectrum. The mixture **10a** was treated with one equivalent of dimethylsulfoxonium methylide in DMF at room temperature, and this reaction condition was almost the same as that of **3** to **2** in Scheme 1.[4a] Though the starting material (**10a**) disappeared completely, the expected dibenzofuran (**11a**) was not found at all in the reaction mixture. When the cyclobutane (**10a**) was treated with 1.5 equivalents of dimethylsulfoxonium methylide, the desired product (**11a**) was obtained as a single isomer, which had the molecular formula $C_{21}H_{20}O_4$ on the basis of HRMS (336.1354) and elemental analysis (EA). Its plane structure and stereostructure were confirmed as shown in Scheme 5 on the basis of ^{1}H NMR and NOE correlations, namely, the NOEs were observed between 4a-H and 9b-H, and 9b-H and 1-phenyl-H (Scheme 5). Finally, the plane structure and the stereochemistry of **11a** were determined by X-ray crystallographic analysis.[12]

Because the yield of **11a** was only 21%, several reaction conditions were examined in order to improve the yield of **11a**, and the results are shown in Table 1. The best yield was obtained by the use of two equivalents of dimethylsulfoxonium methylide in DMF (Table 1, run 3); however, more than three equivalents



Scheme 5 The stereoconvergent transformation of **10a** and X-ray structure of **11a**.

of dimethylsulfoxonium methylide rather decreased the yield of **11a** (runs 4–5). In THF, dichloromethane, and other polar aprotic solvents such as *N*,*N*-dimethylacetamide (DMA), 1,3-dimethyl-2-imidazolidinone (DMI), and DMSO, the yields of **11a** were lower than that obtained in DMF (runs 6–10). When chloroform, DME, toluene, and methanol were used as solvents, **11a** was not afforded at all.

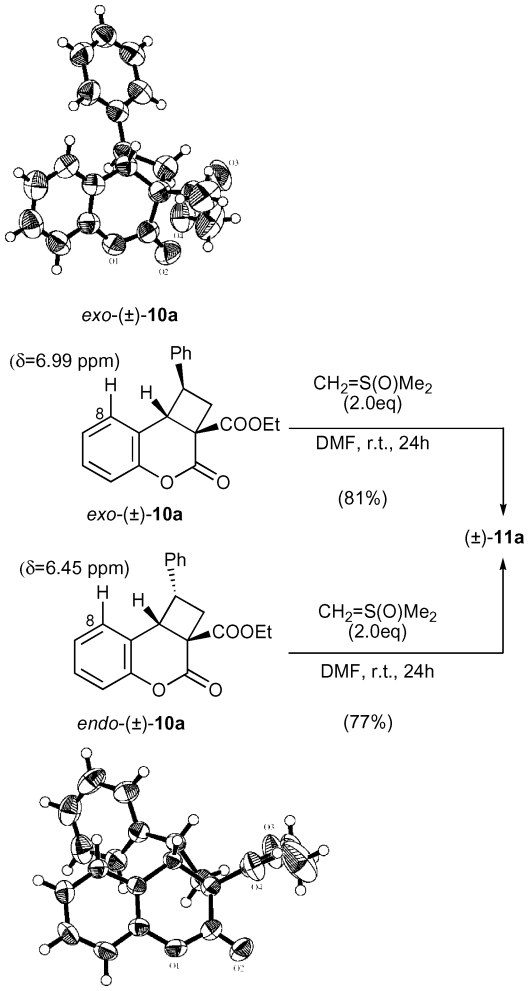
It is very interesting that, in spite of the use of the *exo*–*endo* mixture (3 : 2) of **10a**, the sole product (**11a**) was obtained in 75% yield (run 3). This phenomenon means that the same product (**11a**) might be derived from both diastereomeric isomers (*exo*-**10a** and *endo*-**10a**) regardless of the stereochemistry of the 1-position. Both diastereomeric isomers (*exo*-**10a** and *endo*-**10a**) were separated with flash column chromatography,[13] and their stereochemistries were confirmed on the basis of spectral data and X-ray crystallography.[14] As the phenyl group at the 1-position of *endo*-**10a** strongly shields the C_8-proton as shown in Scheme 6, the ^{1}H NMR signal of the C_8–H in *endo*-**10a** was observed at higher field (6.45 ppm, d) than that (6.99 ppm, dd) of *exo*-**10a**. *Exo*-**10a** and *endo*-**10a** were each treated with two equivalents of dimethylsulfoxonium methylide to give the same product (**11a**) in 81 and 77% yields, respectively (Scheme 6). It is noteworthy that the present transformation proceeded stereoconvergently irrespective of the stereochemistry of the 1-position in **10a**.

In order to examine the generality of the present stereoconvergent transformation reaction, several cyclobutane compounds (**10b–10n**) were prepared as diastereomeric mixtures in various ratios by the photochemical cycloaddition of monosubstituted

Table 1 Effects of solvents and amounts of CH_2=S(O)Me_2 for **11a**[a]

Run	CH_2=S(O)Me_2 (eq)	Solvent	Reaction time/h	Isolated yield of **11a** (%)
1	1.0	DMF	8	0
2	1.5	DMF	8	21[b]
3	2.0	DMF	8	75[c]
4	3.0	DMF	8	52
5	5.0	DMF	8	42
6	2.0	DMA	83	52
7	2.0	DMI	36	50
8	2.0	DMSO	168	48
9	2.0	THF	36	38
10	2.0	CH_2Cl_2	36	21

[a] The reaction was carried out at rt under an N_2 atmosphere. [b] The yield was 14% when the reaction temperature was 60 °C. [c] The yield was 76% when the reaction time was 24 h.

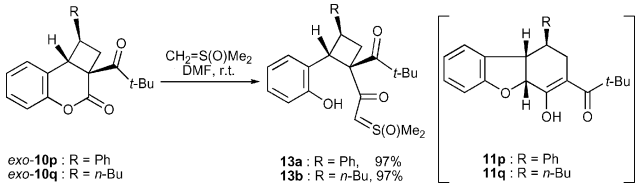


Scheme 6 The stereoconvergent transformation and X-ray structures of *exo*- and *endo*-**10a**.

alkenes with coumarins or β-naphthocoumarins, which had an electron-withdrawing group at the 3-position (Table 2). The diastereomeric mixtures of the cyclobutane compounds (**10b–10n**) were subjected to the above-mentioned reaction conditions (run 3 in Table 1), and the results are listed in Table 2. It was found that all reactions proceeded stereoconvergently to give the dibenzofuran derivatives (**11b–11k**) and benzo[*b*]naphtho[1,2-*d*]furan derivatives (**11m–11n**) as single isomers. The yields of **11b–11n** were 21 to 93%, and in the cases of **10** having an aliphatic acyl group at the 2a-position, the yields were relatively low except for **11j** (runs 8–11). On the other hand, benzonaphthofuran derivatives (**11m** and **11n**) were obtained in relatively high yields (runs 12–13).

Elucidation of the reaction mechanism

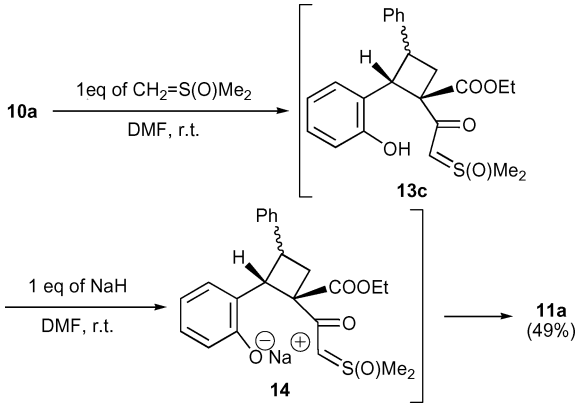
Next, our attention was focused on elucidation of the reaction mechanism. When cyclobutanes (*exo*-**10p** and *exo*-**10q**)[15] with a pivaloyl group at the 2a-position were treated with two or more equivalents of dimethylsulfoxonium methylide, the desired dibenzofurans (**11p** and **11q**) were not obtained at all, and the ylides (**13a** and **13b**) were isolated in 97% yield each (Scheme 7).



Scheme 7 The reaction of **10p** and **10q** with CH_2=S(O)Me_2.

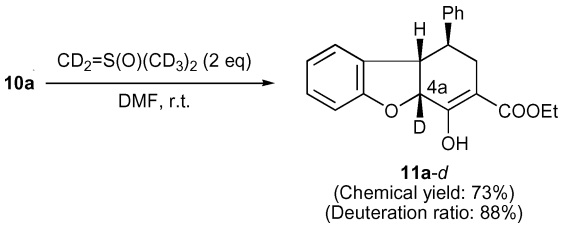
These structures were confirmed on the basis of EA and their spectral data. The ylides **13a** and **13b** would be the key intermediates in the present transformation to **11**. In the presence of a bulky pivaloyl group in **13**, subsequent cyclobutane ring-opening would not proceed because the appropriate conformation for obtaining the best stereoelectronic effect in the ring-opening could not be taken.

From the consideration of these results, we assumed that the first equivalent of dimethylsulfoxonium methylide would be used for opening of the lactone ring to give the ylide (**13**), and the second equivalent of dimethylsulfoxonium methylide would act as a base for extraction of the phenolic proton from **13**, and the generated phenoxide ion would advance the cyclobutane ring-opening. When one equivalent of sodium hydride instead of the second equivalent of dimethylsulfoxonium methylide was added after treatment of **10a** with one equivalent of dimethylsulfoxonium methylide, the benzofuran (**11a**) was obtained in 49% yield as was expected (Scheme 8).



Scheme 8 The reaction of **10a** with one equivalent of CH_2=S(O)Me_2 and subsequent one equivalent of NaH.

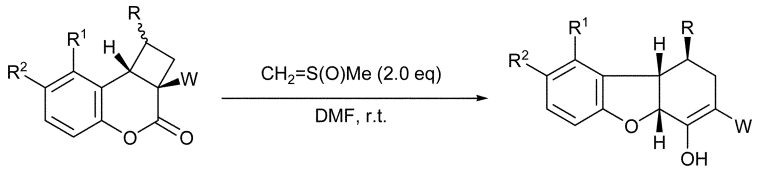
Next, a reaction of **10a** with di(methyl-d_3)sulfoxonium methylide-d_2 [CD_2=S(O)$(CD_3)_2$][16] was performed. When the cyclobutane (**10a**) was treated with two equivalents of CD_2=S(O)$(CD_3)_2$instead of dimethylsulfoxonium methylide, **4a**-*D*-dibenzofuran (**11a**-*d*) was obtained in 73% chemical yield and 88% deuteration ratio[17] (Scheme 9).



Scheme 9 Treatment of **10a** with CD_2=S(O)$(CD_3)_2$.

From these experimental results, we presumed a plausible reaction mechanism as follows (Scheme 10). (1) Due to good leaving ability of the phenoxide ion, the carbonyl group at the 3-position of **10** would be more reactive than that at the 2a-position against dimethylsulfoxonium methylide; therefore, one equivalent of dimethylsulfoxonium methylide would attack the lactone carbonyl group to open the lactone ring of *exo*-**10** and *endo*-**10**. (2) The generated phenoxide ion (**15** and **15'**) would extract the α-proton of the dimethylsulfoxonium methylene moiety to give the ylide (**13** and **13'**). (3) Another one equivalent of dimethylsulfoxonium methylide as a base would pull out the phenolic proton of **13** and **13'** to reproduce the phenoxide ion and then cyclobutane ring-opening would occur to form an orthoquinone methide (**16** and **16'**). (4) Owing to *equatorial*-like orientation of the orthoquinone methide group, intramolecular 1,4-addition of dimethylsulfoxonium ylide to the orthoquinone

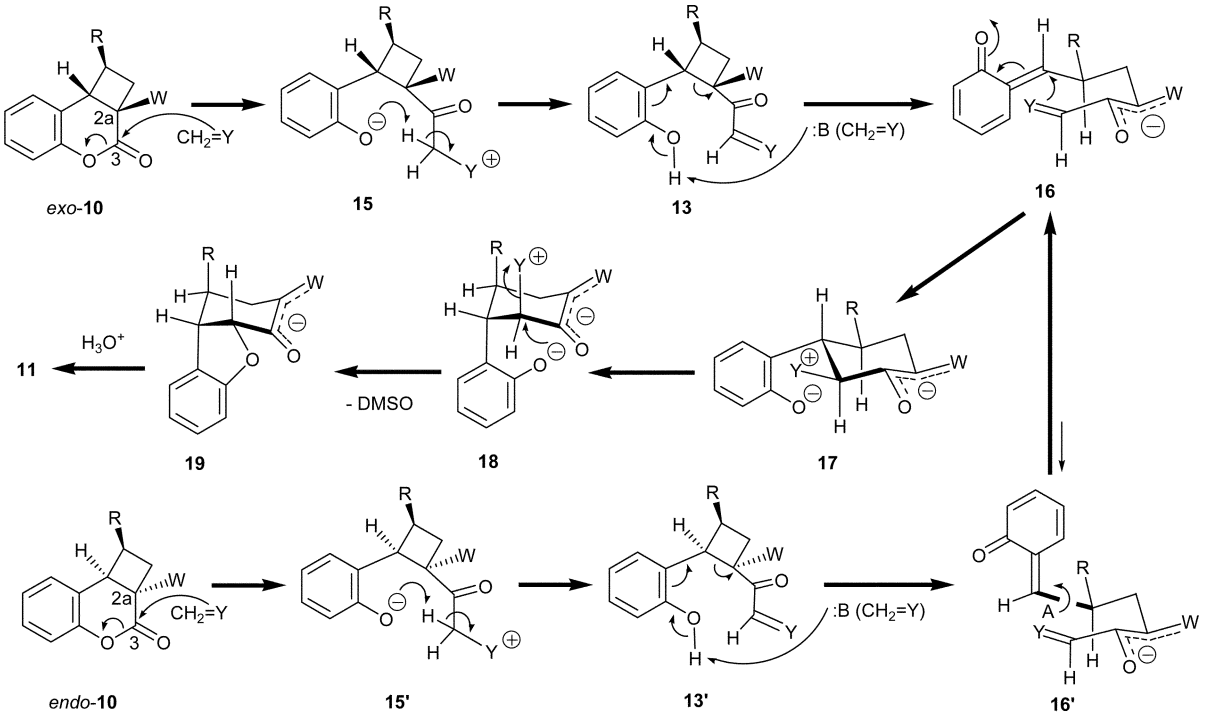
Table 2 The stereoconvergent transformation of **10** to **11**



10 **11**

Run	Starting material (**10**)						Product (**11**)	
		Exo–endo ratio[a]	W	R^1	R^2	R	Isolated yield (%)	
1	**10a**	3 : 2	COOEt	H	H	Ph	**11a**	75
2	**10b**	11 : 2	COOEt	H	H	*n*-Butyl	**11b**	79
3	**10c**	5 : 3	COOEt	H	H	2-Pyridinyl	**11c**	51
4	**10d**	10 : 3	COOEt	H	H	Acetyloxymethyl	**11d**[b]	74
5	**10e**	5 : 1	COPh	H	H	Ph	**11e**	62
6	**10f**	6 : 1	COPh	H	H	*n*-Butyl	**11f**	51
7	**10g**	7 : 2	COPh	H	H	2-Pyridinyl	**11g**	44
8	**10h**	9 : 2	COMe	H	H	Ph	**11h**	21
9	**10i**	9 : 2	COEt	H	H	Ph	**11i**	22
10	**10j**	4 : 1	CO *n*-C_3H_7	H	H	Ph	**11j**	56
11	**10k**	5 : 1	CO *i*-C_3H_7	H	H	Ph	**11k**	30
12	**10m**	19 : 5	COOMe			Ph	**11m**	86
13	**10n**	6 : 1	COPh			Ph	**11n**	93

[a] The ratio was estimated on the basis of ^{1}H NMR spectrum after purification by using column chromatography. [b] The structure was confirmed by X-ray crystallography (CCDC 257345).



Scheme 10 A plausible reaction mechanism of **10** to **11**.

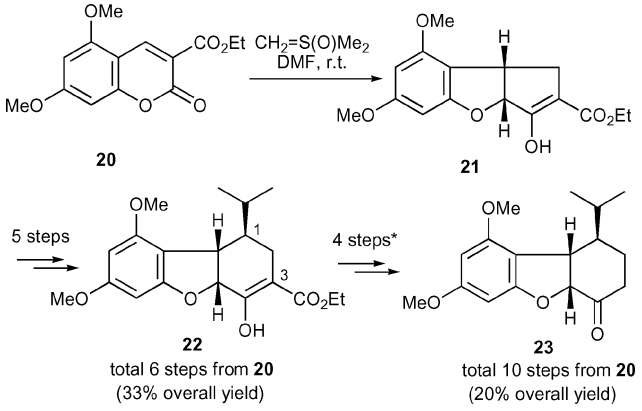
methide portion would easily proceed in only **16** to produce a cyclohexane derivative (**17**). (5) The regenerated phenoxide ion would attack the α-position carbon of dimethylsulfoxonium salt (**18**) to give the tricyclic product (**19**) with an accompanying release of DMSO. (6) After work-up, the dibenzofuran (**11**) was obtained.

On the other hand, because of *axial*-like orientation of the orthoquinone methide group in **16'**, the single bond A of **16'** rotated prior to the intramolecular 1,4-addition to give the more stable intermediate **16**. As a result, the present transformation proceeded stereoconvergently from mixtures of *exo*-**10** and *endo*-**10**.

Application to the second-generation synthesis of (±)-linderol A

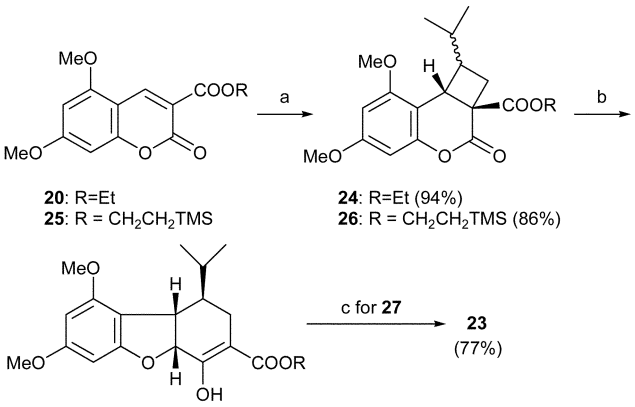
We have already reported the first total synthesis of (±)-linderol A (**12**).[9] (−)-Linderol A (**12**) was isolated from the fresh bark of *Lindera umbellata* (Lauraceae) and showed potent inhibitory activity in melanin biosynthesis of cultured B-16 melanoma cells without causing any cytotoxicity in the cultured cells or skin irritation in guinea pigs (Fig. 1).[7] We planned an application of the present transformation reaction to the second-generation synthesis of (±)-**12**.

In the previous synthesis of (±)-**12**, it took six steps to prepare a dibenzofuran intermediate (**22**) having the proper stereochemistry from 5,7-dimethoxycoumarin (**20**), namely, the steps included transformation of **20** to **21** with dimethylsulfoxonium methylide, regio- and stereoselective introduction of the isopropyl group at the 1-position, and ring enlargement of cyclopentane to cyclohexane. Contrary to our expectation, alkaline and acidic hydrolysis of the ethoxycarbonyl group of **22** was difficult, and decarboethoxylation at the 3-position of **22** took four steps to obtain a dibenzofuranone (**23**) as shown in Scheme 11.



Scheme 11 The previous synthetic route from **20** to **23**.

The present methodology would be applicable to improvement of the route to **22** from **20**. A benzene solution of the coumarin (**20**) and 3-methyl-1-butene was irradiated by a high-pressure mercury lamp (400 W) to give the cyclobutane derivative (**24**) in 94% yield as a diastereomeric mixture (*exo*–*endo* = 8 : 1). The cyclobutane (**24**) was treated with two equivalents of dimethylsulfoxonium methylide to give the dibenzofuran derivative (**22**) as a single isomer in 88% yield. In order to shorten the route to **23**, 3-[2-(trimethylsilyl)ethoxycarbonyl]coumarin (**25**) was prepared and subjected to photo [2 + 2] cycloaddition with 3-methyl-1-butene to afford the cyclobutane derivative (**26**) in 86% yield as a diastereomeric mixture (*exo*–*endo* = 9 : 1). The cyclobutane (**26**) was converted to the dibenzofuran derivative (**27**) as a single isomer in 83% yield. Finally, **27** was treated with TBAF and then refluxed to give **23** (Scheme 12). The spectral data of the obtained **22** and **23** were identical with those of **22** and **23** synthesized previously.[9]



a) 3-methyl-1-butene, *hν*, benzene. b) $Me_3S(O)I$, 60% NaH, DMF, r.t. c) 1) TBAF, THF, r.t.; 2) xylene, reflux.

Scheme 12 The present synthetic route from **20** to **22** and **23**.

Therefore, the preparation of **22** was achieved in 83% overall yield in two steps from **20** and that of **23** was done in 55% overall yield in four steps from **25**. As a result, the synthesis of (±)-**12** would be much improved from the previous route.

Conclusion

We have developed a novel stereoconvergent transformation reaction to dibenzofuran derivatives (**11**) from benzo[*b*]cyclobuta[*d*]pyran derivatives (**10**), which were prepared by the photochemical [2 + 2] cycloaddition of coumarins with an electron-withdrawing group at the 3-position and alkenes, regardless of the stereochemistry of the 1-position in **10**. This methodology could be applied to the second-generation synthesis of (±)-linderol A (**12**) to shorten the synthetic route. Now, further work on an asymmetric synthesis of **12** and its derivatives by applying the present methodology is in progress.

Experimental

Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. NMR spectra were measured on a JEOL AL-300 (^{1}H; 300 MHz, ^{13}C; 75.5 MHz) and a Varian INOVA 400NB (^{1}H; 400 MHz, ^{13}C; 100 MHz). IR spectra were taken with a Shimadzu IR-435 spectrophotometer. A JEOL JMS-GC mate spectrometer and a Shimadzu GCMS-QP5050A spectrometer were used for low-resolution electron ionization MS (MS) and a JEOL JMS-GC mate spectrometer was used for high-resolution electron ionization MS (HRMS). Elemental analysis was performed with a PERKIN ELMER Series II CHNS/O Analyzer 2400. X-Ray crystal structure analyses were performed on a Rigaku AFC7R diffractometer. All extracts were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure in the usual work-up procedure. Silica gel 60 (grade 7734, 60–230 mesh, Merck) for column chromatography and silica gel 60 PF_{254} (5–50 μm, Nacalai tesque) for preparative TLC were used.

Ethyl *rac*-(1*R*,2a*R*,8b*R*)-1,8b-dihydro-3-oxo-1-phenyl-2*H*-benzo[*b*]cyclobuta[*d*]pyran-2a(3*H*)-carboxylate (*exo*-10a) and ethyl *rac*-(1*R*,2a*S*,8b*S*)-1,8b-dihydro-3-oxo-1-phenyl-2*H*-benzo[*b*]cyclobuta[*d*]pyran-2a(3*H*)-carboxylate (*endo*-10a)

A solution of 3-ethoxycarbonylcoumarin[18] (2.18 g, 10.0 mmol) and styrene (6.24 g, 6.86 ml, 60.0 mmol) in benzene (20 ml) was added in a photochemical reactor vessel with a 400 W high-pressure mercury lamp in a water-cooled quartz immersion well. The stirred solution was irradiated for 24 h. After evaporation of the volatile materials, the residue was chromatographed on

silica gel with ethyl acetate–*n*-hexane (1 : 3) to give a mixture of *exo*-**10a** and *endo*-**10a** (2.52 g, 78%, *exo*–*endo* = 3 : 2). *Exo*-**10a** and *endo*-**10a** were separated with silica gel flash column chromatography[13] with ethyl acetate–*n*-hexane (1 : 10). *Exo*-**10a** (less polar isomer): colorless powder (found: C, 74.4; H, 5.7. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.6%), mp 90.2–90.6 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.21 (3H, t, J = 7.1 Hz), 2.99 (1H, ddd, J = 11.7, 8.2, 0.7 Hz), 3.26 (1H, dd, J = 11.7, 11. 1 Hz), 3.56 (1H, dt, J = 11.2, 8.9 Hz), 3.82 (1H, d, J = 9.3 Hz), 4.15 (1H, dq, J = 10.8, 7.1 Hz), 4.23 (1H, dq, J = 10.8, 7.1 Hz), 6.99 (1H, dd, J = 7.5, 1.6 Hz), 7.08 (1H, dt, J = 1.1, 7.5 Hz), 7.14 (1H, ddd, J = 8.2, 0.7, 0.4 Hz), 7.24–7.38 (6H, m). δ_C (100 MHz; $CDCl_3$; Me_4Si) 13.9, 35.9, 44.5, 47.8, 49.0, 62.4, 117.3, 121.1, 124.8, 126.5, 127.2, 127.5, 128.7, 129.2, 140.8, 151.5, 167.4, 168.8. $\nu_{max}(CHCl_3)/cm^{-1}$ 1751, 1730, 1637, 1584. *m*/*z* (EI) 322.1203 (M^+, $C_{20}H_{18}O_4$ requires 322.1205, 1.1%), 104 (100). Crystal data. $C_{20}H_{18}O_4$, M = 322.36, orthorhombic, a = 8.471(1), b = 11.811(2), c = 16.531(3) Å, V = 1653.9(9) Å^3, T = 296 K, space group $Pna2_1$ (no. 33), Z = 4, μ(Cu–Kα) = 7.33 cm^{-1}, 1460 reflections measured, 1283 unique (R_{int} = 0.0) which were used in all calculations. The final R_1 was 0.061 (all data). *Endo*-**10a** (more polar isomer): colorless plates (found: C, 74.5; H, 5.7. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.6%), mp 139.8–140.2 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.31 (3H, t, J = 7.1 Hz), 2.98 (1H, ddd, J = 12.6, 8.2, 0.9 Hz), 3.38 (1H, ddd, J = 12.6, 8.9, 2.6 Hz), 4.13 (1H, q, J = 8.8 Hz), 4.27 (1H, dd, J = 8.8, 2.0 Hz), 4.29 (1H, dq, J = 10.6, 7.1 Hz), 4.35 (1H, dq, J = 10.8, 7.1 Hz), 6.45 (1H, d, J = 7.7 Hz), 6.81 (1H, dt, J = 1.3, 7.5 Hz), 6.88–6.91 (2H, m), 6.95 (1H, dd, J = 8.2, 1.3 Hz), 7.09–7.17 (4H, m). δ_C (100 MHz; $CDCl_3$; Me_4Si) 14.0, 33.1, 42.5, 45.3, 48.0, 62.5, 116.9, 117.5, 124.2, 127.0, 128.0, 128.1, 128.7, 129.6, 137.2, 151.1, 165.4, 169.9. $\nu_{max}(CHCl_3)/cm^{-1}$ 1744, 1614, 1582. *m*/*z* (EI) 322.1195 (M^+, $C_{20}H_{18}O_4$ requires 322.1205, 0.8%), 104 (100). Crystal data. $C_{20}H_{18}O_4$, M = 322.36, monoclinic, a = 11.759(1), b = 9.091(2), c = 15.774(1) Å, β = 103.766(6)°, V = 1637.8(3) Å^3, T = 296 K, space group $P2_1/n$ (no. 14), Z = 4, μ(Cu–Kα) = 7.41 cm^{-1}, 2731 reflections measured, 2539 unique (R_{int} = 0.025) which were used in all calculations. The final R_1 was 0.061 (all data).

General procedure for stereoconvergent transformation of 10 to 11. Ethyl *rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-tetrahydro-4-hydroxy-1-phenyl-3-dibenzofurancarboxylate (11a) as an example

Trimethylsulfoxonium iodide (440 mg, 2.0 mmol) was added in one portion to a suspension of NaH (60% in mineral oil, 80 mg, 2.0 mmol) in DMF (2 ml) under ice-cooling and the whole mixture was stirred for 30 min under an N_2 atmosphere at room temperature. To the reaction mixture was added dropwise a solution of **10a** (322 mg, 1.0 mmol, *exo*–*endo* = 3 : 2) in DMF (1 ml) at room temperature and the whole mixture was stirred for an additional 24 h. After acidification with 3% HCl solution under ice-cooling, the product was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over sodium sulfate, and evaporated. The residue was purified by silica gel column chromatography (eluent; AcOEt–*n*-hexane = 1 : 5) to give **11a** (256 mg, 76%). Colorless needles (found: C, 74.9; H, 6.1. $C_{21}H_{20}O_4$ requires C, 75.0; H, 6.0%), mp 179.7–181.6 °C (AcOEt–*n*-hexane). δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.28 (3H, t, J = 7.2 Hz), 2.48 (1H, dd, J = 15.2, 11.0 Hz), 2.64 (1H, td, J = 11.2, 3.9 Hz), 2.73 (1H, dd, J = 15.2, 3.9 Hz), 3.57 (1H, dd, J = 11.4, 8.1 Hz), 4.24 (2H, q, J = 7.2 Hz), 5.12 (1H, d, J = 8.1 Hz), 6.15 (1H, d, J = 7.2 Hz), 6.59 (1H, t, J = 7.4 Hz), 6.88 (1H, d, J = 8.1 Hz), 7.05–7.16 (3H m), 7.23–7.37 (3H, m), 12.21 (1H, s). δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 14.1, 30.3, 44.3, 47.1, 61.0, 79.4, 101.5, 110.0, 120.3, 125.3, 127.0, 128.3, 128.5, 128.6, 129.2, 141.9, 158.1, 164.3, 171.7. $\nu_{max}(CHCl_3)/cm^{-1}$ 3011, 1656, 1625, 1592. *m*/*z* (EI) 336.1354 (M^+, $C_{21}H_{20}O_4$ requires 336.1361, 100%), 290 (35), 118 (74), 104 (51). Crystal data. $C_{21}H_{20}O_4$, M = 336.39, orthorhombic, a = 22.3809(9), b = 17.2516(8), c = 9.034(1) Å, V = 3488.1(7) Å^3, T = 296 K, space group *Pbca* (no. 61), Z = 8, μ(Cu–Kα) = 7.16 cm^{-1}, 2982 reflections measured, 2597 unique (R_{int} = 0.011) which were used in all calculations. The final R_1 was 0.057 (all data).

Ethyl *rac*-(1*R*,4a*S*,9b*R*)-1-butyl-1,2,4a,9b-tetrahydro-4-hydroxy-3-dibenzofurancarboxylate (11b)

Yield, 79% (eluent; AcOEt–*n*-hexane = 1 : 5). Colorless needles (found: C, 72.0; H, 7.6. $C_{19}H_{24}O_4$ requires C, 72.1; H, 7.7%), mp 94.1–95.1 °C (from *n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.90 (3H, t, J = 7.1 Hz), 1.32 (3H, t, J = 7.1 Hz), 1.16–1.48 (5H, m), 1.63–1.73 (2H, m), 1.98 (1H, ddd, J = 16.1, 8.8, 0.7 Hz), 2.50 (1H, dd, J = 16.3, 4.0 Hz), 3.17 (1H, t, J = 8.6 Hz), 4.24 (1H, dq, J = 10.8, 7.1 Hz), 4.27 (1H, dq, J = 11.0, 7.1 Hz), 5.01 (1H, d, J = 8.1 Hz), 6.80–7.00 (2H, m), 7.13–7.19 (1H, m), 7.20–7.24 (1H, m), 12.08 (1H, s). δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 14.0, 14.2, 22.9, 26.1, 28.9, 31.4, 35.6, 46.3, 60.9, 79.5, 100.8, 110.3, 120.6, 125.2, 128.6, 129.6, 158.7, 164.3, 171.9. $\nu_{max}(CHCl_3)/cm^{-1}$ 3500–3000, 1659, 1627, 1591. *m*/*z* (EI) 316.1682 (M^+, $C_{19}H_{24}O_4$ requires 316.1674, 100%), 270 (55), 242 (52), 213 (95), 185 (73), 118 (46).

Ethyl *rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-tetrahydro-4-hydroxy-1-(2-pyridyl)-3-dibenzofurancarboxylate (11c)

Yield, 51% (eluent; AcOEt–*n*-hexane = 1 : 3). Colorless plates (found: C, 71.0; H, 5.7; N, 4.2. $C_{20}H_{19}NO_4$ requires C, 71.2; H, 5.7; N, 4.2%), mp 166.3–166.8 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.28 (3H, t, J = 7.1 Hz), 2.64 (1H, ddd, J = 16.1, 10.0, 0.8 Hz), 2.70 (1H, dd, J = 16.1, 5.3 Hz), 2.85 (1H, ddd, J = 11.2, 10.0, 5.3 Hz), 4.04 (1H, dd, J = 11.2, 8.1 Hz), 4.25 (2H, q, J = 7.1 Hz), 5.17 (1H, d, J = 8.2 Hz), 6.18 (1H, dt, J = 7.3, 0.7 Hz), 6.62 (1H, td, J = 7.5, 0.9 Hz), 6.89 (1H, dt, J = 8.1, 0.5 Hz), 6.96 (1H, dt, J = 7.7, 0.9 Hz), 7.09 (1H, tdd, J = 7.7, 1.1, 0.4 Hz), 7.22 (1H, ddd, J = 7.5, 4.9, 1.1 Hz), 7.59 (1H, td, J = 7.6, 1.8 Hz), 8.68 (1H, ddd, J = 4.9, 1.7, 0.9 Hz), 12.21 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 14.1, 29.0, 45.2, 45.7, 61.0, 79.3, 101.0, 110.1, 120.4, 122.0, 124.5, 124.7, 128.6, 129.5, 136.2, 149.5, 158.2, 161.1, 164.3, 171.7. $\nu_{max}(CHCl_3)/cm^{-1}$ 3500–3000, 1657, 1625, 1590, 1577. *m*/*z* (EI) 337.1313 (M^+, $C_{20}H_{19}NO_4$ requires 337.1314, 76%), 264 (99), 219 (93), 209 (82), 173 (68), 79 (100).

Ethyl *rac*-(1*R*,4a*S*,9b*R*)-1-acetoxymethyl-1,2,4a,9b-tetrahydro-4-hydroxy-3-dibenzofurancarboxylate (11d)

Yield, 74% (eluent; AcOEt–*n*-hexane = 1 : 5). Colorless plates (found: C, 65.2; H, 6.1. $C_{18}H_{20}O_6$ requires C, 65.1; H, 6.1%), mp 120.8–121.8 °C (from AcOEt–*n*-hexane). δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.33 (3H, t, J = 7.2 Hz), 1.88–2.08 (1H, m), 2.11 (3H, s), 2.23 (1H, dd, J = 16.2, 9.6 Hz), 2.53 (1H, dd, J = 16.3, 4.4 Hz), 3.38 (1H, dd, J = 9.7, 8.3 Hz), 4.21 (1H, dd, J = 11.4, 5.5 Hz), 4.26 (1H, dd, J = 11.4, 3.9 Hz), 4.27 (2H, q, J = 7.2 Hz), 5.05 (1H, d, J = 7.9 Hz), 6.80–6.95 (2H, m), 7.15–7.22 (2H, m), 12.10 (1H, s). δ_C (67.8 MHz; $CDCl_3$; Me_4Si) 14.3, 21.0, 24.7, 35.7, 42.5, 61.1, 64.6, 79.2, 100.4, 110.5, 121.0, 125.0, 128.3, 128.9, 158.3, 163.9, 170.8, 171.5. $\nu_{max}(CHCl_3)/cm^{-1}$ 1729, 1660, 1627, 1592. *m*/*z* (EI) 332.1262 (M^+, $C_{18}H_{20}O_6$ requires 332.1260, 69%), 272 (23), 226 (100), 198 (44). Crystal data. $C_{18}H_{20}O_6$, M = 332.35, triclinic, a = 9.275(1), b = 13.425(2), c = 7.830(1) Å, α = 106.14(1), β = 114.52(1), γ = 71.40(1)°, V = 828.7(2) Å^3, T = 296 K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Cu–Kα) = 8.36 cm^{-1}, 2649 reflections measured, 2471 unique (R_{int} = 0.038) which were used in all calculations. The final R_1 was 0.056 (all data).

Phenyl[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-tetrahydro-4-hydroxy-1-phenyl-3-dibenzofuranyl]methanone (11e)

Yield, 62% (eluent; AcOEt–*n*-hexane = 1 : 3). Pale yellow needles (found: C, 81.4; H, 5.6. $C_{25}H_{20}O_3$ requires C, 81.5; H, 5.5%), mp 190.3–191.2 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$;

Me_4Si) 2.62 (1H, dd, $J = 15.8$, 3.4 Hz), 2.58–2.66 (1H, m), 2.88 (1H, dd, $J = 15.8$, 12.3 Hz), 3.78 (1H, dd, $J = 11.4$, 8.9 Hz), 5.30 (1H, d, $J = 8.9$ Hz), 6.15 (1H, d, $J = 7.0$ Hz), 6.60 (1H, td, $J = 7.5$, 0.9 Hz), 6.91 (1H, dd, $J = 8.1$, 0.3 Hz), 7.08–7.16 (3H, m), 7.24–7.48 (6H, m), 7.55–7.58 (2H, m), 16.16 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 34.1, 45.9, 47.4, 80.3, 107.8, 110.0, 120.5, 125.2, 127.2, 127.9, 128.1, 128.3, 128.6, 128.7, 128.8, 131.4, 136.7, 141.7, 158.1, 178.7, 194.6. $\nu_{max}(CHCl_3)/cm^{-1}$ 1608. *m/z* (EI) 368.1409 (M^+, $C_{25}H_{20}O_3$ requires 368.1412, 62%), 264 (17), 105 (100).

[*rac*-(1*R*,4a*S*,9b*R*)-1-Butyl-1,2,4a,9b-tetrahydro-4-hydroxy-3-dibenzofuranyl]phenylmethanone (11f)

Yield, 51% (eluent; AcOEt–*n*-hexane = 1 : 10). Colorless needles (found: C, 79.1; H, 7.0. $C_{23}H_{24}O_3$ requires C, 79.3; H, 6.9%), mp 130.9–132.4 °C (from AcOEt–*n*-hexane). δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.83 (3H, t, $J = 7.0$ Hz), 1.03–1.39 (5H, m), 1.58–1.74 (2H, m), 2.26 (1H, dd, $J = 15.0$, 8.4 Hz), 2.52 (1H, dd, $J = 15.0$, 3.3 Hz), 3.37 (1H, t, $J = 8.6$ Hz), 5.14 (1H, d, $J = 8.8$ Hz), 6.88–6.94 (2H, m), 7.15–7.24 (2H, m), 7.40–7.53 (3H, m), 7.53–7.58 (2H, m), 15.95 (1H, s). δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 13.9, 22.8, 28.8, 29.5, 31.6, 37.7, 46.4, 80.7, 107.2, 110.3, 120.8, 125.2, 128.0, 128.2, 128.7, 129.2, 131.3, 136.7, 158.8, 179.5, 193.8. $\nu_{max}(CHCl_3)/cm^{-1}$ 1606, 1590, 1567. *m/z* (EI) (M^+, 348.1733, $C_{23}H_{24}O_3$ requires 348.1725, 27%), 105 (100), 77 (39).

[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-Tetrahydro-4-hydroxy-1-(2-pyridyl)-3-dibenzofuranyl]phenylmethanone (11g)

Yield, 44% (eluent; AcOEt–*n*-hexane = 1 : 10). Pale yellow needles (found: C, 77.8; H, 5.4; N, 3.7. $C_{24}H_{19}NO_3$ requires C, 78.0; H, 5.2; N, 3.8%), mp 187.6–188.4 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.58 (1H, dd, $J = 15.2$, 3.5 Hz), 2.81 (1H, td, $J = 11.0$, 3.5 Hz), 3.06 (1H, dd, $J = 15.0$, 11.0 Hz), 4.23 (1H, dd, $J = 10.9$, 9.1 Hz), 5.34 (1H, d, $J = 9.0$ Hz), 6.15 (1H, dt, $J = 7.9$, 0.7 Hz), 6.62 (1H, td, $J = 7.4$, 0.9 Hz), 6.86–6.93 (2H, m), 7.10 (1H, td, $J = 7.6$, 1.5 Hz), 7.21 (1H, ddd, $J = 7.5$, 4.9, 1.1 Hz), 7.37–7.49 (3H, m), 7.51–7.60 (3H, m), 8.68 (1H, ddd, $J = 4.8$, 1.7, 0.9 Hz), 16.12 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 32.6, 45.5, 47.2, 80.3, 107.4, 110.1, 120.5, 122.2, 124.5, 124.7, 128.0, 128.2, 128.7, 129.1, 131.4, 136.3, 136.7, 149.5, 158.2, 160.8, 178.7, 194.4. $\nu_{max}(CHCl_3)/cm^{-1}$ 3008, 1606, 1590, 1567. *m/z* (EI) 369.1371 (M^+, $C_{24}H_{19}NO_3$ requires 369.1365, 22%), 251 (100), 209 (55), 105 (40), 77 (29).

1-[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-Tetrahydro-4-hydroxy-1-phenyl-3-dibenzofuranyl]ethanone (11h)

Yield, 21% (eluent; AcOEt–*n*-hexane = 1 : 5). Colorless prisms (found: C, 78.2; H, 6.0. $C_{20}H_{18}O_3$ requires C, 78.4; H, 5.9%), mp 183.5–184.2 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.23 (3H, s), 2.63–2.74 (3H, m), 3.62 (1H, t, $J = 8.2$ Hz), 5.15 (1H, d, $J = 8.2$ Hz), 6.16 (1H, d, $J = 7.5$ Hz), 6.61 (1H, td, $J = 7.5$, 0.9 Hz), 6.89 (1H, d, $J = 8.1$ Hz), 7.10 (1H, td, $J = 7.7$, 1.4 Hz), 7.15–7.19 (2H, m), 7.29–7.39 (3H, m), 15.22 (1H, s). δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 26.3, 32.2, 44.7, 46.9, 79.8, 108.9, 110.1, 120.5, 125.3, 127.3, 128.2, 128.7, 128.8, 129.0, 141.7, 158.1, 170.6, 202.1. $\nu_{max}(CHCl_3)/cm^{-1}$ 1630, 1610, 1589. *m/z* (EI) 306.1250 (M^+, $C_{20}H_{18}O_3$ requires 306.1256, 100%), 215 (30), 187 (29), 145 (55), 104 (56), 91 (40).

1-[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-Tetrahydro-4-hydroxy-1-phenyl-3-dibenzofuranyl)]-1-propanone (11i)

Yield, 22% (eluent; AcOEt–*n*-hexane = 1 : 10). Colorless needles (found: C, 78.5; H, 6.3. $C_{21}H_{20}O_3$ requires C, 78.7; H, 6.3%), mp 148.0–148.5 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.12 (3H, t, $J = 7.2$ Hz), 2.50 (1H, dq, $J = 10.3$, 7.3 Hz), 2.57 (1H, dq, $J = 10.3$, 7.3 Hz), 2.62–2.73 (3H, m), 3.61 (1H, dd, $J = 10.9$, 8.4 Hz), 5.15 (1H, d, $J = 8.3$ Hz), 6.16 (1H, dt, $J = 7.4$, 0.6 Hz), 6.61 (1H, td, $J = 7.4$, 1.0 Hz), 6.89 (1H, d, $J = 8.1$ Hz), 7.10 (1H, td, $J = 7.7$, 1.4 Hz), 7.15–7.19 (2H, m), 7.30–7.39 (3H, m), 15.20 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 7.8, 31.5, 31.9, 44.6, 46.8, 79.8, 108.5, 110.1, 120.4, 125.3, 127.2, 128.2, 128.6, 128.8, 129.0, 141.8, 158.1, 169.1, 205.5. $\nu_{max}(CHCl_3)/cm^{-1}$ 3010, 1634, 1609, 1587. *m/z* (EI) 320.1415 (M^+, $C_{21}H_{20}O_3$ requires 320.1412, 100%), 229 (22), 145 (41), 104 (41), 91 (31).

1-[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-Tetrahydro-4-hydroxy-1-phenyl-3-dibenzofuranyl)-1-butanone (11j)

Yield, 56% (eluent; AcOEt–*n*-hexane = 1 : 5). Colorless needles (found: C, 78.8; H, 6.7. $C_{22}H_{22}O_3$ requires C, 79.0; H, 6.6%), mp 138.3–138.8 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.94 (3H, t, $J = 7.4$ Hz), 1.65 (2H, sextet, $J = 7.4$ Hz), 2.44 (1H, dq, $J = 16.3$, 7.3 Hz), 2.50 (1H, dq, $J = 16.3$, 7.3 Hz), 2.63–2.73 (3H, m), 3.61 (1H, dd, $J = 10.9$, 8.3 Hz), 5.15 (1H, d, $J = 8.4$ Hz), 6.16 (1H, dt, $J = 7.5$, 0.7 Hz), 6.60 (1H, td, $J = 7.5$, 0.9 Hz), 6.89 (1H, dd, $J = 7.9$, 0.5 Hz), 7.10 (1H, td, $J = 7.7$, 1.4 Hz), 7.15–7.19 (2H, m), 7.29–7.39 (3H, m), 15.35 (1H, s). δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 13.7, 17.3, 31.7, 40.2, 44.7, 46.8, 79.8, 108.6, 110.0, 120.4, 125.2, 127.2, 128.2, 128.6, 128.7, 129.0, 141.8, 158.0, 170.1, 204.5. $\nu_{max}(CHCl_3)/cm^{-1}$ 3005, 1628, 1586. *m/z* (EI) 334.1567 (M^+, $C_{22}H_{22}O_3$ requires 334.1569, 35%), 145 (37), 104 (55), 71 (100).

1-[*rac*-(1*R*,4a*S*,9b*R*)-1,2,4a,9b-Tetrahydro-4-hydroxy-1-phenyl-3-dibenzofuranyl)-2-methyl-1-propanone (11k)

Yield, 30% (eluent; AcOEt–*n*-hexane = 1 : 1). Colorless needles (found: C, 79.0; H, 6.7. $C_{22}H_{22}O_3$: C, 79.0; H, 6.6%), mp 178.6–179.4 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.10 (3H, d, $J = 6.6$ Hz), 1.11 (3H, d, $J = 6.8$ Hz), 2.63–2.74 (3H, m), 2.94 (1H, hept, $J = 6.8$ Hz), 3.58–3.67 (1H, m), 5.17 (1H, d, $J = 8.1$ Hz), 6.16 (1H, dt, $J = 7.4$, 0.7 Hz), 6.61 (1H, td, $J = 7.4$, 1.0 Hz), 6.89 (1H, d, $J = 8.1$ Hz), 7.10 (1H, td, $J = 7.8$, 1.2 Hz), 7.16–7.21 (2H, m), 7.30–7.40 (3H, m), 15.64 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 18.5, 31.6, 34.6, 44.9, 46.9, 79.9, 107.6, 110.1, 120.4, 125.3, 127.3, 128.2, 128.6, 128.8, 129.0, 141.8, 158.1, 171.4, 208.4. $\nu_{max}(CHCl_3)/cm^{-1}$ 1622, 1586. *m/z* (EI) 334.1567 (M^+, $C_{22}H_{22}O_3$ requires 334.1569, 80%), 291(100), 145 (26), 104 (33), 91(29), 71 (21).

Methyl *rac*-(7a*R*,11*S*,11a*S*)-7a,10,11,11a-tetrahydro-8-hydroxy-11-phenylbenzo[*b*]naphtho[1,2-*d*]furan-9-carboxylate (11m)

Yield, 86% (eluent; AcOEt–*n*-hexane = 1 : 10). Colorless plates (found: C, 77.4; H, 5.6. $C_{24}H_{20}O_4$ requires C, 77.4; H, 5.4%), mp 191.5–193.0 °C (from AcOEt). δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.74–2.88 (3H, m), 3.80 (1H, dd, $J = 10.9$, 7.2 Hz), 3.81 (3H, s), 5.19 (1H, d, $J = 7.5$ Hz), 6.28 (1H, dd, $J = 8.5$, 0.8 Hz), 6.80 (1H, ddd, $J = 8.2$, 6.8, 1.3 Hz), 6.94–7.00 (2H, m), 7.06 (1H, ddd, $J = 8.1$, 6.8, 1.1 Hz), 7.12 (1H, dd, $J = 8.3$, 1.4 Hz), 7.14 (1H, d, $J = 7.5$ Hz), 7.20 (1H, tt, $J = 7.2$, 1.4 Hz), 7.21 (1H, d, $J = 8.8$ Hz), 7.66 (1H, t, $J = 8.1$ Hz), 12.10 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 29.3, 44.4, 48.3, 52.0, 80.8, 101.6, 112.2, 121.8, 122.5, 123.1, 125.6, 127.0, 128.1, 128.3, 128.6, 129.3, 130.0, 130.9, 142.5, 156.2, 163.9, 172.0. $\nu_{max}(CHCl_3)/cm^{-1}$ 3082, 1662, 1622, 1590. *m/z* (EI) 372.1362 (M^+, $C_{24}H_{20}O_4$ requires 372.1361, 100%), 340 (30), 281 (39), 168 (55).

Phenyl[*rac*-(7a*R*,11*S*,11a*S*)-7a,10,11,11a-tetrahydro-8-hydroxy-11-phenylbenzo[*b*]naphtho[1,2-*d*]furan-9-yl]methanone (11n)

Yield, 93% (eluent; AcOEt–*n*-hexane = 1 : 10). Pale yellow needles (found: C, 83.0; H, 5.3. $C_{29}H_{22}O_3$ requires C, 83.2; H, 5.3%), mp 174.5–175.5 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 2.70 (1H, dd, $J = 15.1$, 3.4 Hz), 2.91 (1H, td, $J = 10.4$, 3.3 Hz), 3.07 (1H, dd, $J = 15.1$, 10.7 Hz), 4.01 (1H, dd, $J = 10.1$, 8.0 Hz), 5.35 (1H, d, $J = 7.9$ Hz), 6.43 (1H, d, $J = 7.7$ Hz), 6.87 (1H, ddd, $J = 8.5$, 6.8, 1.2 Hz), 6.94–7.00 (2H, m), 7.06–7.24 (4H, m), 7.37–7.47 (3H, m), 7.52–7.57 (2H, m),

7.65–7.71 (2H, m), 16.05 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 32.3, 45.3, 48.3, 81.9, 108.0, 112.1, 121.2, 122.6, 122.8, 125.8, 127.1, 127.7, 128.0, 128.1, 128.26, 128.29, 128.7, 129.4, 130.1, 130.8, 131.3, 136.9, 142.4, 156.2, 177.3, 195.3. $\nu_{max}(CHCl_3)/cm^{-1}$ 1616, 1594. *m/z* (EI) 418.1564 (M^+, $C_{29}H_{22}O_3$ requires 418.1569, 9%), 300 (59), 271 (18), 105 (100), 77 (61).

Dimethylsulfoxonium 2-[*rac*-(1*R*,2*R*,3*R*)-1-(2,2-dimethyl-1-oxoprop-1-yl)-2-(2-hydroxyphenyl)-3-phenylcyclobut-1-yl]-2-oxoethylide (13a)

Yield, 97% (eluent; AcOEt). Colorless powder (found: C, 70.4; H, 7.1. $C_{25}H_{30}O_4S$ requires C, 70.2; H, 7.2%), mp 182.5–187.1 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.28 (9H, s), 2.31 (1H, dd, $J = 10.4$, 8.8 Hz), 2.67 (3H, s), 3.14 (3H, s), 3.38 (1H, dd, $J = 10.7$, 8.5 Hz), 3.89 (1H, s), 4.14 (1H, d, $J = 10.8$ Hz), 4.19 (1H, dt, $J = 10.8$, 8.7 Hz), 6.78 (1H, td, $J = 7.5$, 1.3 Hz), 6.90 (1H, dd, $J = 8.1$, 1.3 Hz), 7.10–7.22 (5H, m), 7.24–7.29 (2H, m), 9.51 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 28.7, 32.3, 35.3, 41.2, 41.3, 44.9, 47.8, 67.3, 70.8, 116.5, 119.0, 124.0, 126.3, 126.4, 127.7, 128.4, 128.5, 143.0, 155.7, 179.9, 221.9. $\nu_{max}(CHCl_3)/cm^{-1}$ 3210, 1658, 1576, 1550. *m/z* (EI) 426.1862 (M^+, $C_{25}H_{30}O_4S$: requires 426.1865, 1.4%), 348 (6), 291 (14), 231 (30), 153 (51), 104 (100).

Dimethylsulfoxonium 2-[*rac*-(1*R*,2*R*,3*R*)-3-butyl-1-(2,2-dimethyl-1-oxoprop-1-yl)-2-(2-hydroxyphenyl)cyclobut-1-yl]-2-oxoethylide (13b)

Yield, 97% (eluent; AcOEt). Colorless needles (found: C, 67. 7; H, 8.2. $C_{23}H_{34}O_4S$ requires C, 67.9; H, 8.4%), mp 182.3–183.9 °C (from AcOEt–*n*-hexane). δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.84 (3H, t, $J = 7.1$ Hz), 1.13–1.50 (6H, m), 1.24 (9H, s), 1.81 (1H, dd, $J = 10.6$, 8.8 Hz), 2.65 (3H, s), 2.82–2.96 (1H, m), 3.01 (1H, dd, $J = 10.4$, 8.8 Hz), 3.07 (3H, s), 3.60 (1H, d, $J = 10.1$ Hz), 3.82 (1H, s), 6.77 (1H, td, $J = 7.4$, 1.0 Hz), 6.87 (1H, dd, $J = 7.9$, 1.1 Hz), 7.07–7.12 (2H, m), 9.41 (1H, s). δ_C (100 MHz; $CDCl_3$; Me_4Si) 13.9, 22.7, 28.7, 29.1, 31.5, 31.6, 35.8, 41.1, 41.3, 44.8, 47.6, 67.6, 70.3, 116.3, 118.8, 124.6, 127.5, 128.1, 155.8, 180.4, 222.2. $\nu_{max}(CHCl_3)/cm^{-1}$ 3205, 1656, 1578, 1549. *m/z* (EI) 406.2184 (M^+, $C_{23}H_{34}O_4S$ requires 406.2178, 10%), 328 (19), 271 (74), 231 (53), 153 (100), 119 (56).

Ethyl *rac*-(1*R*,2a*S*,8b*S*)- and *rac*-(1*R*,2a*R*,8b*R*)-1,8b-dihydro-1-(1-methylethyl)-6,8-dimethoxy-3-oxo-2*H*-benzo[*b*]cyclobuta[*d*]pyran-2a(3*H*)-carboxylate (24)

Cyclobutane (**24**) was prepared from **20** (1.39 g, 5.0 mmol) with 3-methyl-1-butene (8.8 g, 126 mmol) in benzene (50 ml) according to the procedure for **10a**. After evaporation of the volatile materials, the residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 3) to give a mixture of *exo*-**24** and *endo*-**24** (1.6 g, 94%, *exo*–*endo* = 8 : 1). Colorless oil. δ_H (400 MHz; $CDCl_3$; Me_4Si) for *exo*-**24** 0.85 (3H, d, $J = 6.4$ Hz), 0.86 (3H, d, $J = 6.4$ Hz), 1.19 (3H, t, $J = 7.1$ Hz), 1.71 (1H, octet, $J = 6.8$ Hz), 2.05 (1H, dq, $J = 10.6$, 8.3 Hz), 2.55 (1H, dd, $J = 11.4$, 8.3 Hz), 2.61 (1H, dd, $J = 11.4$, 10.8 Hz), 3.67 (1H, d, $J = 9.0$ Hz), 3.79 (3H, s), 3.80 (3H, s), 4.10 (1H, dq, $J = 10.8$, 7.1 Hz), 4.18 (1H, dq, $J = 10.8$, 7.1 Hz), 6.23 (1H, d, $J = 2.2$ Hz), 6.26 (1H, d, $J = 2.2$ Hz). δ_C (100 MHz; $CDCl_3$; Me_4Si) 13.9, 18.7, 19.1, 32.3, 33.1, 40.1, 47.4, 48.2, 55.3, 55.4, 61.9, 93.9, 94.8, 103.9, 152.9, 156.9, 160.4, 168.2, 169.1. $\nu_{max}(CHCl_3)/cm^{-1}$ 1745, 1730, 1623, 1590. *m/z* (EI) 348.1565 (M^+, $C_{19}H_{24}O_6$ requires 348.1573, 1.4%), 278 (100), 233 (40), 206 (78).

Ethyl *rac*-(1*R*,4a*R*,9b*S*)-1,2,4a,9b-tetrahydro-4-hydroxy-7,9-dimethoxy-1-(1-methylethyl)-3-dibenzofurancarboxylate (22)

Dibenzofuran (**22**) was prepared from **24** (110 mg, 0.32 mmol) with trimethylsulfoxonium iodide (141 mg, 0.64 mmol) and NaH (60% in mineral oil, 26 mg, 0.64 mmol) in DMF (1 ml) according to the general procedure for stereoconvergent transformation. The crude product was purified by silica gel column chromatography to give **22** (101 mg, 88%). Colorless plates (AcOEt–*n*-hexane), mp 101.0–102.8 °C (lit.[9a] 102.0–102.9 °C from AcOEt–petroleum ether).

3-[2-(Trimethylsilyl)ethoxycarbonyl]coumarin (25)[19]

A solution of 3-coumarincarboxylic acid[20] (1.00 g, 4.00 mmol) and DMF (2 drops) in thionyl chloride (4 ml) was refluxed for 2 h and evaporated to give a crude acid chloride. 2-(Trimethylsilyl)ethanol (472 mg, 4.00 mmol) was added to a solution of the crude acid chloride, triethylamine (808 mg, 8.00 mmol) and a catalytic amount of DMAP in dichloromethane (10 ml) under ice-cooling and the whole mixture was stirred for 15 h at rt. After addition of water, the mixture was extracted with $CHCl_3$. The combined extracts were washed with 5% HCl, saturated $NaHCO_3$, water, and brine, dried, and evaporated. The residue was recrystallized from benzene to give **25** (1.29 g, 92%). Colorless needles (found: C, 58.2; H, 6.3. $C_{17}H_{22}O_6Si$ requires C, 58.3; H, 6.3%), mp 168.0–170.0 °C (from benzene). δ_H (300 MHz; $CDCl_3$) 0.06 (9H, s), 1.14 (2H, t, $J = 8.5$ Hz), 3.85 (3H, s), 3.90 (3H, s), 4.39 (2H, t, $J = 8.6$ Hz), 6.24 (1H, d, $J = 2.0$ Hz), 6.36 (1H, d, $J = 2.0$ Hz), 8.76 (1H, s). δ_C (75.5 MHz; $CDCl_3$) −1.6, 17.4, 56.0, 56.1, 63.7, 92.5, 94.9, 103.5, 111.8, 144.3, 157.3, 158.2, 158.3, 163.7, 166.3. $\nu_{max}(CHCl_3)/cm^{-1}$ 1749, 1692, 1613, 1600, 1561. *m/z* (EI) 350.1184 (M^+, $C_{17}H_{22}O_6Si$ requires 350.1185, 12%), 307 (100), 233 (47), 73 (55), 57 (29).

2-(Trimethylsilyl)ethyl *rac*-(1*R*,2a*S*,8b*S*)- and *rac*-(1*R*,2a*R*,8b*R*)-1,8b-dihydro-1-(1-methylethyl)-6,8-dimethoxy-3-oxo-2*H*-benzo[*b*]cyclobuta[*d*]pyran-2a(3*H*)-carboxylate (26)

Cyclobutane (**26**) was prepared from **25** (180 g, 0.514 mmol) with 3-methyl-1-butene (983 mg, 14.0 mmol) in benzene (4 ml) according to the procedure for **10a**. After evaporation of the volatile materials, the residue was chromatographed on silica gel with ethyl acetate–*n*-hexane (1 : 3) to give a mixture of *exo*-**26** and *endo*-**26** (187 mg, 86%, *exo*–*endo* = 9 : 1). Colorless oil. δ_H (300 MHz; $CDCl_3$) for *exo*-**26** −0.04 (9H, s), 0.84 (3H, d, $J = 6.6$ Hz), 0.85 (3H, d, $J = 6.6$ Hz), 0.92 (2H, t, $J = 8.5$ Hz), 1.59–1.75 (1H, m), 1.98–2.12 (1H, m), 2.49–2.64 (2H, m), 3.66 (1H, d, $J = 9.0$ Hz), 3.78 (6H, s), 4.08–4.26 (2H, m), 6.21 (1H, d, $J = 2.4$ Hz), 6.24 (1H, d, $J = 2.4$ Hz). δ_C (75.5 MHz; $CDCl_3$) for *exo*-**26** −1.65, 17.0, 18.7, 19.2, 32.4, 33.2, 40.2, 47.5, 48.2, 55.3, 55.5, 64.5, 94.0, 94.9, 104.0, 153.0, 156.9, 160.4, 168.3, 169.3. $\nu_{max}(CHCl_3)/cm^{-1}$ 1749, 1724, 1624, 1598. *m/z* (EI) 420.1965 (M^+, $C_{22}H_{32}O_6Si$ requires 420.1968, 0.6%), 350 (20), 307 (100), 233 (31), 73 (60).

2-(Trimethylsilyl)ethyl *rac*-(1*R*,4a*R*,9b*S*)-1,2,4a,9b-tetrahydro-4-hydroxy-7,9-dimethoxy-1-(1-methylethyl)-3-dibenzofurancarboxylate (27)

Dibenzofuran (**27**) was prepared from **26** (138 mg, 0.298 mmol) with trimethylsulfoxonium iodide (132 mg, 0.600 mmol) and NaH (60% in mineral oil, 24 mg, 0.600 mmol) in DMF (1 ml) according to the general procedure for stereoconvergent transformation. The crude product was purified by silica gel column chromatography to give **27** (119 mg, 83%). Colorless powder (found: C, 63.5; H, 7.9. $C_{23}H_{34}O_6Si$ requires C, 63.6; H, 7.9%), mp 110.0–112.0 °C (from isopropyl ether). δ_H (300 MHz; $CDCl_3$) 0.07 (9H, s), 0.936 (3H, d, $J = 7.0$ Hz), 0.944 (3H, d, $J = 6.8$ Hz), 1.06 (2H, t, $J = 8.3$ Hz), 1.58–1.70 (1H, m), 1.75–1.90 (1H, m), 2.03 (1H, dd, $J = 16.1$, 9.1 Hz), 2.33 (1H, dd, $J = 16.1$, 3.9 Hz), 3.37 (1H, dd, $J = 10.0$, 7.5 Hz), 3.75 (3H, s), 3.77 (3H, s), 4.31 (2H, t, $J = 8.3$ Hz), 4.95 (1H, d, $J = 7.3$ Hz), 6.04 (1H, d, $J = 2.0$ Hz), 6.14 (1H, d, $J = 2.0$ Hz), 12.04 (1H, s). δ_C (75.5 MHz; $CDCl_3$) −1.5, 16.9, 17.3, 21.0, 21.8, 27.1, 42.2, 42.7, 55.1, 55.4, 63.2, 81.2, 89.2, 91.6, 101.6, 109.3, 157.3, 160.9, 161.7, 164.0, 172.2. $\nu_{max}(CHCl_3)/cm^{-1}$ 1656, 1618, 1594. *m/z*

(EI) 434.2121 (M^+, $C_{23}H_{34}O_6Si$ requires 434.2124, 7%), 237 (22), 178 (30), 1543 (79), 121 (23), 73 (100).

rel-(1*R*,4a*R*,9b*S*)-2,3,4a,9b-Tetrahydro-7,9-dimethoxy-1-(1-methylethyl)-4(1*H*)-dibenzofuranone (23)

A solution of TBAF (0.37 ml, 1.0 M in THF, 0.37 mmol) was added dropwise to a solution of **27** (79 mg, 0.182 mmol) in THF (0.5 ml) under ice-cooling and the whole mixture was stirred for 1 h at rt. After addition of water, the mixture was extracted with AcOEt. The combined extracts were washed with water, and brine, dried, and evaporated. The residue was dissolved in xylene and refluxed for 5 min. After concentration, the residue was purified with preparative TLC (AcOEt–*n*-hexane = 1 : 5) to give **23** (41 mg, 77%). Colorless plates, mp 92.0–94.0 °C (from *n*-hexane, lit.,[9a] 78.2–80.4 °C).

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13 A FLASH 40 chromatography module (Biotage) and prepacked cartridge system [Wakogel® LP-40 Cartridge Column (4 ϕ × 15 cm) (Wako Pure Chemical Industries, Ltd.)] were used.

14 CCDC 257344 for *exo*-**10a**. CCDC 257506 for *endo*-**10a**[12].

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