A General Synthesis of (±)-Dibenzocyclooctadiene Lignans

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We have established a new general synthesis for (±)-dibenzocyclooctadiene lignans, including (±)-schizandrin (1a), (±)-gomisin A (1b), (±)-isoschizandrin (3a), and (±)-isogomisin A (3b), *via* the spiro-dienone ethers E- and T-11 as the key intermediates, prepared from the corresponding bisarylbutanol derivatives E- and T-10 by the oxidation with Weitz' aminium salt, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA). These syntheses consist of 13 steps from the phenylpropanone 5.

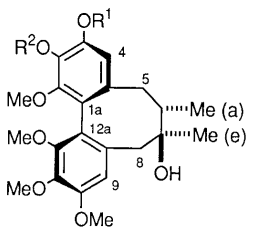
Key words general synthesis; lignan; dibenzocyclooctadiene; spirodienone ether; Weitz' aminium salt; oxidative aryl–aryl coupling

The fruits of *Schizandra chinesis* BAIL. (Schizandraceae) are used for the treatment of asthmatic cough, dry mouth, diarrhea, insomnia, amnesia, *etc.*, in Chinese traditional medicine,[1] and more than three dozen dibenzocyclooctadiene (DBCO) lignans have been isolated from the plant since 1961.[2] Among these compounds, (±)-gomisin A (**1b**) showed a potent antihepatoxic activity against liver injuries induced by various chemicals in *in vivo* and *in vitro* studies.[3] Recently, it was also reported that (±)-schizandrin (**1a**) showed a restorative effect on functional depression of the brain and a protective effect against oxotremorine-induced tremor in mice.[4] Several attempts to synthesize these lignans have been made in connection with their intriguing biological activities as described above.[5] In the preceding papers,[2,6] we reported a new concise synthesis of DBCO lignan group compounds, (±)-(**1a**), (±)-(**1b**), (±)-isoschizandrin (**3a**), (±)-isogomisin A (**3b**), and related stereo-isomers, utilizing the recently developed samarium-Grignard and samarium-Barbier reactions.

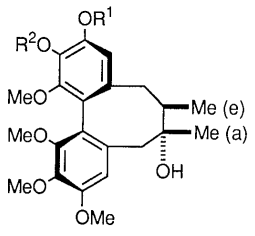
The following problems face any general synthesis of lignans. (i) How can the symmetrical and unsymmetrical compounds on the biaryl moiety be synthesized from a common intermediate? (ii) How can the desired compounds having different relative configuration between the C-6 and C-7 positions be constructed from common intermediates?

During the investigations for the synthesis of DBCO lignans, we found that oxidations of the alcohols E- and T-**10** with $Fe(ClO_4)\cdot 9H_2O$–MeCN gave the spiro-dienone ethers E- and T-**11**, respectively. These results suggested that the spiro-dienone ethers might be useful intermediates for the synthesis of lignans from the viewpoint described above. Thus, we started in the investigations for a general synthesis of DBCO lignans starting from the spiro-dienone ether as a key intermediate, based on the retro synthetic plan shown in Chart 2. This plan involves, (i) cleavage of the ether bond in **11** by hydrogenation followed by protection of the hydroxyl groups, (ii) transformation to the *ortho*-quinones **18** by oxidation of **16**, and (iii) finally reduction of **18** to the catechols followed by oxidative aryl–aryl coupling reaction of the catechols or catechol-ethers to construct the desired dibenzocyclooctadiene rings.

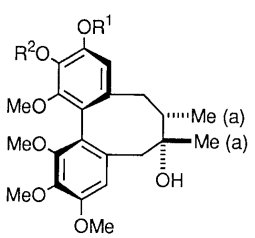
According to the synthetic plan described above, we first investigated the syntheses of the key intermediates E- and T-**11** from 3,4,5-trimethoxy-phenylpropanone **5**. The (*Z*)- and (*E*)-bisarylbutenes **8** and **9** were synthesized based upon previously reported procedures[7] with a few modifications. Treatment of the diol **6** with ethyl orthoformate in the presence of pyridinium *p*-toluenesulfonate afforded **7**. Without isolation of **7**, the reaction mixture was treated with acetic anhydride to furnish the (*Z*)- and (*E*)-diarylbutenes **8** and **9** in yields of 63% and 25%, respectively.[8] These olefins **8** and **9** can be separated easily by simple recrystallization from EtOH. Hydroborations of **8** and **9** with BH_3–tetrahydrofuran (THF) followed by treatments with 30% H_2O_2 and aqueous 3 N NaOH gave the *erythro*- and *threo*-butanols E- and T-**10** in yields of 80% and 82%, respectively. The key intermediates E- and T-**11** were synthesized from E- and T-**10** by oxidations with various reagents. The results are summarized in Table 1. The best result was obtained with Weitz' aminium salt, tris(4-bromophenyl)aminium hexa-



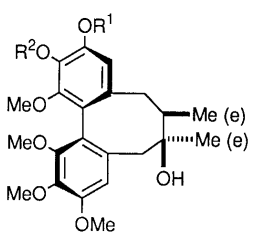
1a: R^1=R^2=Me (schizandrin)
1b: R^1+R^2=CH_2 (gomisin A)



2a: R^1=R^2=Me
2b: R^1+R^2=CH_2



3a: R^1=R^2=Me (isoschizandrin)
3b: R^1+R^2=CH_2 (isogomisin A)



4a: R^1=R^2=Me
4b: R^1+R^2=CH_2

Chart 1

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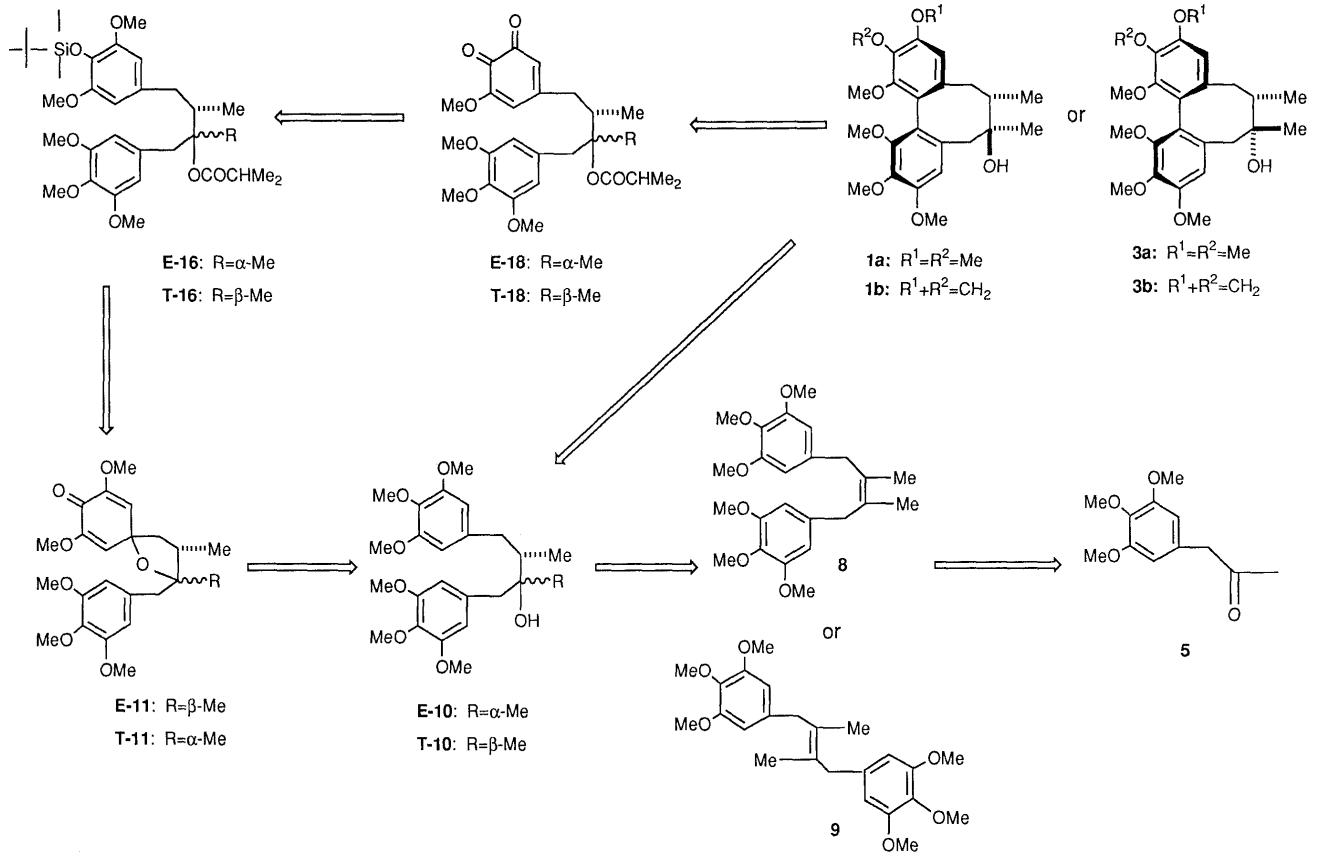


Chart 2

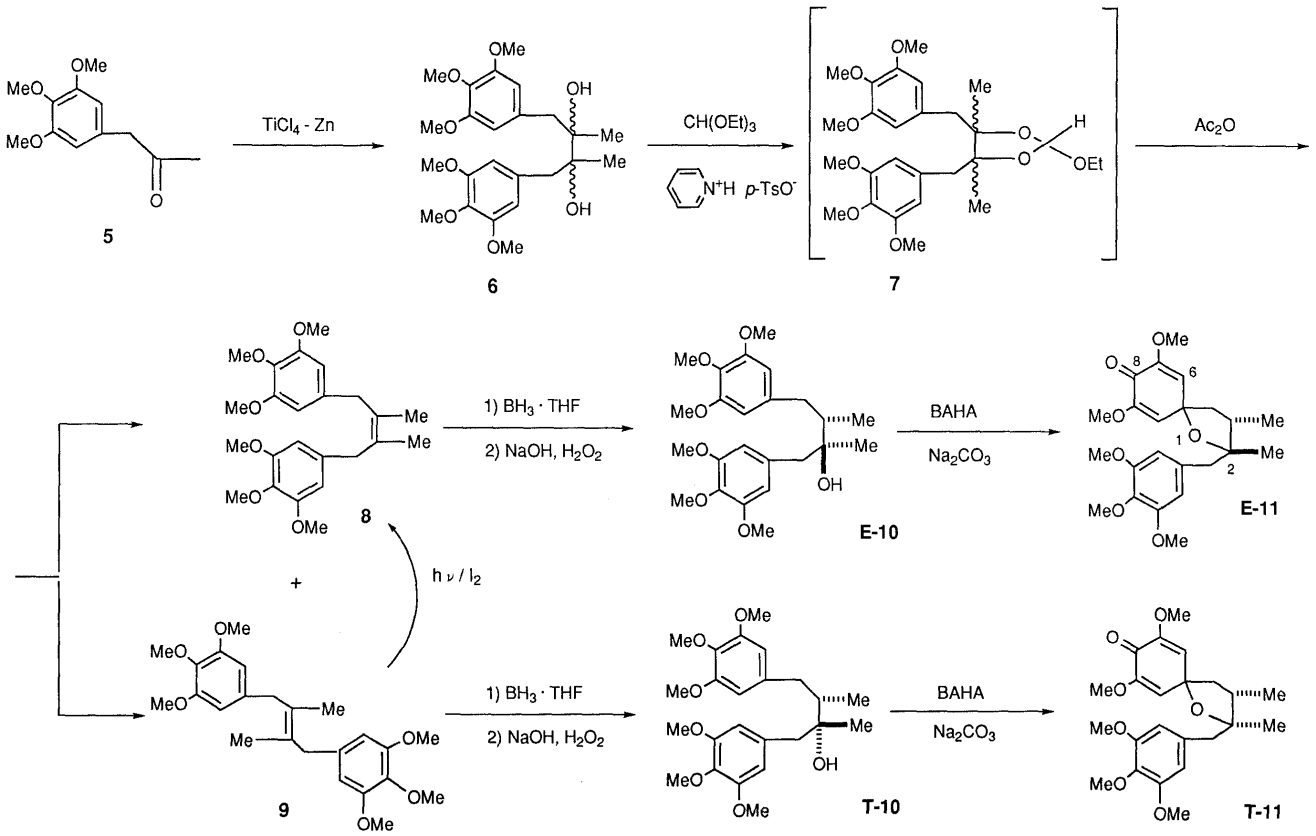


Chart 3

chloroantimonate (BAHA),[9] in both cases.

Next, we investigated the syntheses of E-**21a** and E-**21b** from E-**11**. The transformation of E-**11** into the phenol E-**12** was achieved by catalytic hydrogenation of E-**11** with 10% Pd/C in excellent yield (Table 2). Reactions of E-**11** with various acids were explored to obtain the DBCO

skeleton by acid-catalyzed conjugate addition of the trimethoxyphenyl moiety of E-**11**, but the only product were the tetralin **13**, and a novel bicyclo-adduct **15** (Table 2).

The planar structure of the cyclization product **15** was assigned by means of spectral analyses, including IR, ^{1}H- and ^{13}C-NMR spectra, ^{1}H–^{13}C shift correlation spectroscopy (^{1}H–^{13}C COSY), and ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) experiments (Tables 4 and 5). (i) It formed deep purple crystals, mp 223—225 °C. (ii) It has *ortho*-quinone absorptions at 1700 and 1640 cm^{-1} in the IR spectrum. (iii) The molecular ion peak at *m/z* 400 (M^+) was observed in the mass spectrum (MS), and the molecular formula was determined by elemental analysis and high-resolution MS (HR-MS) to be $C_{22}H_{24}O_7$. (iv) In the HMBC spectrum, the proton at δ 4.37 (C_{12}-H) showed long-range correlations with the carbons at δ 114.1 (C-1a), 123.0 (C-11a), 152.7 (C-4a), 36.8 (C-13) and 127.5 (C-7a); the proton at δ 2.02 (C_{13}-H) showed long-range correlations with the carbons at δ 14.6 (C_{13}-Me), 26.5 (C_6-Me), 28.7 (C-12), 40.1 (C-7), 83.7 (C-6), and 123.0 (C-11a). These data indicate that the **15** has the 6,12-methano-5-dibenz[*b*,*e*]oxocine skeleton, as shown in Table 2. The stereochemistry of **15** was established from a nuclear Overhauser effect (NOE) experiment and the coupling constants, respectively. When the signal of C_{12}-H at δ 4.37 was irradiated, 10.1% and 3.2% increments of the C_{13}-H and C_{13}-Me signals, respectively, were observed in the ^{1}H-NOE. Similarly, when the signal of C_{13}-Me at δ 0.95 was irradiated, 12.9% and 5.8% increments of the C_{12}-H and C_6-Me signals, respectively, were obtained. Furthermore, the coupling constant between C_{12}-H and C_{13}-H was 2.44 Hz in the ^{1}H-NMR. Consequently, C_{12}-H and C_{13}-H, and C_6-Me and C_{13}-Me in **15** may have *cis* relative configurations.

Table 1. Oxidation of E-**10** and T-**10** with Various Reagents

Run	Substrate	Reagent[a)]	Product	Yield (%)
1	E-**10**	A	E-**11**	21
2	E-**10**	B	E-**11**	25
3	E-**10**	C	E-**11**	36
4	E-**10**	D	E-**11**	26
5	E-**10**	E	E-**11**	35
6	E-**10**	F	E-**11**	38
7	E-**10**	G	E-**11**	45
8	E-**10**	H	E-**11**	50
9	E-**10**	I	E-**11**	53
10	T-**10**	B	T-**11**	16
11	T-**10**	E	T-**11**	53
12	T-**10**	G	T-**11**	74
13	T-**10**	H	T-**11**	73
14	T-**10**	I	T-**11**	80

a) A, $FeCl_3$–MeCN; B, anodic oxidation; C, AgO; D, $Fe(bpy)_3(ClO_4)_3$–HBF_4–MeCN; E, $Fe(ClO_4)_3 \cdot 9H_2O$–MeCN; F, $Fe(ClO_4)_3 \cdot 9H_2O$–CH_2Cl_2–MeCN; G, $Pb(OAc)_4$; H, $Ce(NH_4)_2(NO_3)_6$ [CAN]; I, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA).

The mechanism for the formation of the bicyclo-adduct **15** from the spiro-dienone ether E-**11** can be postulated to be as follows (Chart 5). The Lewis acid ($BF_3 \cdot OEt_2$)-catalyzed dienone-phenol rearrangement of E-**11a** may afford an intermediate E-**11c** through E-**11b**. Then, the air oxidation of E-**11c** may take place to give E-**11d**. This speculation is supported by the reaction of E-**11** with

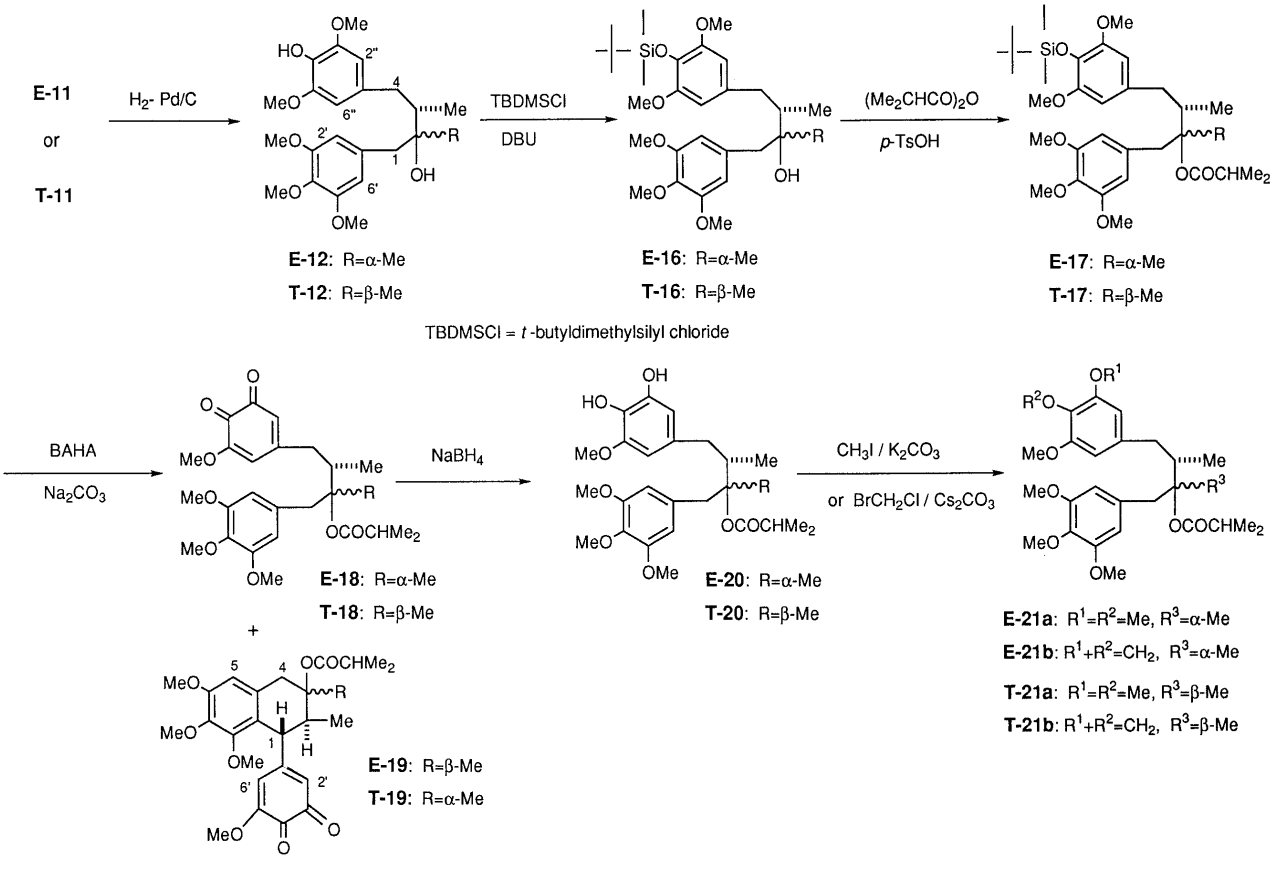
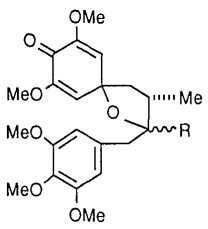
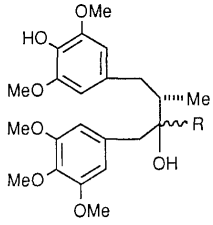


Chart 4

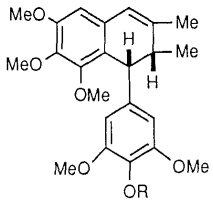
Table 2. The Reactions of E-**11** and T-**11** with Various Reagents



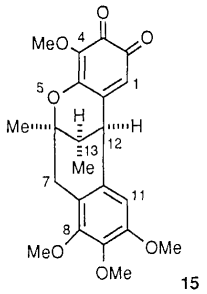
E-**11**: R=β-Me
T-**11**: R=α-Me



E-**12**: R=α-Me
T-**12**: R=β-Me



13: R=Ac
14: R=H



15

Run	Substrate	Reagent	Solvent	Temperature	Product (yield)
1	E-**11**	10% Pd/C–H_2	EtOH	r.t.	E-**12** (96%)
2	E-**11**	P_2O_5–$MeSO_3H$	CH_2Cl_2	r.t.	E-**12** (76%)
3	E-**11**			−20 °C	E-**12** (60%)+**15** (30%)
4	E-**11**	$BF_3 \cdot OEt_2$	CH_2Cl_2	r.t.	E-**12** (37%)+**15** (15%)
5	E-**11**	$ZnCl_2$	Ac_2O	r.t.	**13** (43%)
6	E-**11**	$Fe(bpy)_3(ClO_4)_3$–$HClO_4$–O_2	MeCN	r.t.	**15** (45%)
7	T-**11**	10% Pd/C–H_2	EtOH	r.t.	T-**12** (98%)
8	T-**11**	P_2O_5–$MeSO_3H$	CH_2Cl_2	r.t.	**14** (90%)

r.t., room temperature.

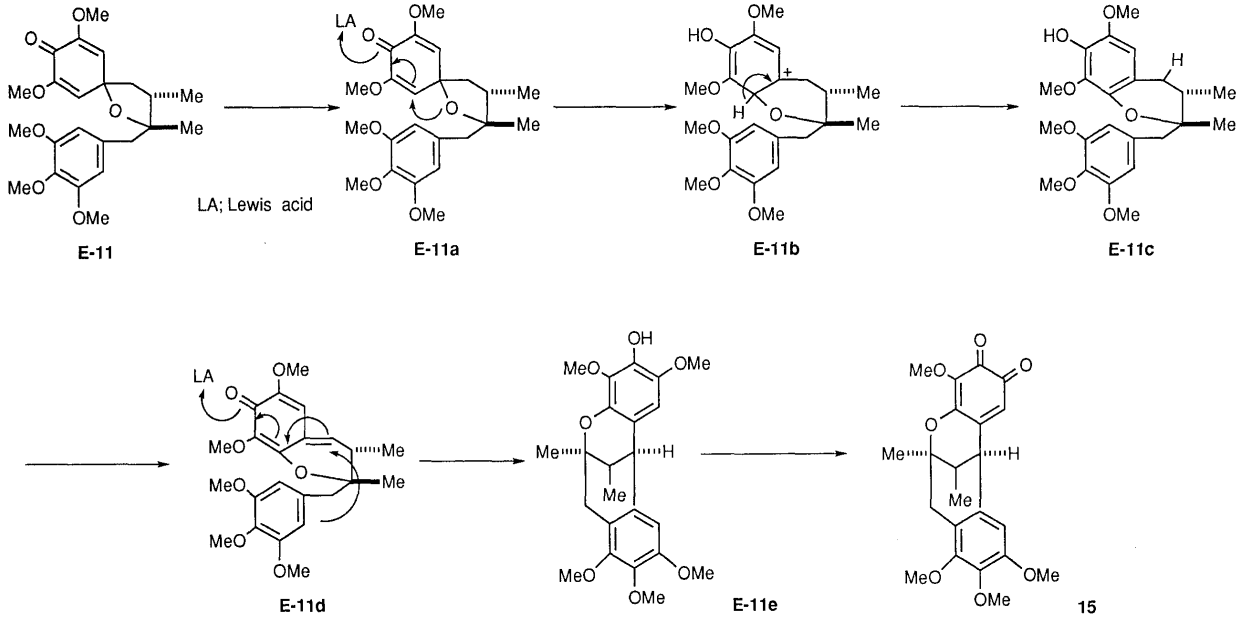


Chart 5. A Proposed Mechanism for the Formation of **15** from E-**11**

the reagent system $Fe(bpy)_3(ClO_4)_3$–$HClO_4$–O_2 (bpy = bipyridyl) to yield exclusively **15** (Table 2). Of course, we can not rule out the possibility of direct formation of E-**11d** from E-**11b**. Finally, nucleophilic addition reaction of the trimethoxyphenyl ring in E-**11d** may lead to an intermediate E-**11e** which would be further oxidized by air to afford the *ortho*-quinone **15**. Because the transformation of **12** to the catechol derivative **20** by *ortho*-demethylation with various Lewis acids was unsuccessful,[10] we tried to another approach. That is, according to the synthetic plan, the phenolic hydroxyl group of E-**12** was treated with *tert*-butyldimethylsilyl chloride (TBDMSCl) in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) to afford selectively the corresponding *O*-silylated compound E-**16** in 92% yield, followed by estification using isobutyric anhydride to give the corresponding *O*-silylated isobutyrate E-**17** in 86% yield. The conversion of E-**17** into the *ortho*-quinone derivative E-**18** is problematic and we tried an oxidative method for this reaction. Oxidation of E-**17** using $Fe(ClO_4)_3$–MeCN gave only the tetralin **14** in 42% yield. However, oxidation of E-**17** with BAHA afforded the desired *ortho*-quinone E-**18** in 65% yield along with the tetralin-quinone E-**19** (5% yield). Compound E-**18** could be easily purified from the reaction mixture by silica gel chromatography, but was rather unstable on storage, and so was used as soon as possible in the next step.

Reduction of E-**18** with $NaBH_4$ followed by treatment of the resulting catechol derivative E-**20** with CH_3I in the presence of K_2CO_3 in *N*,*N*-dimethylformamide (DMF)

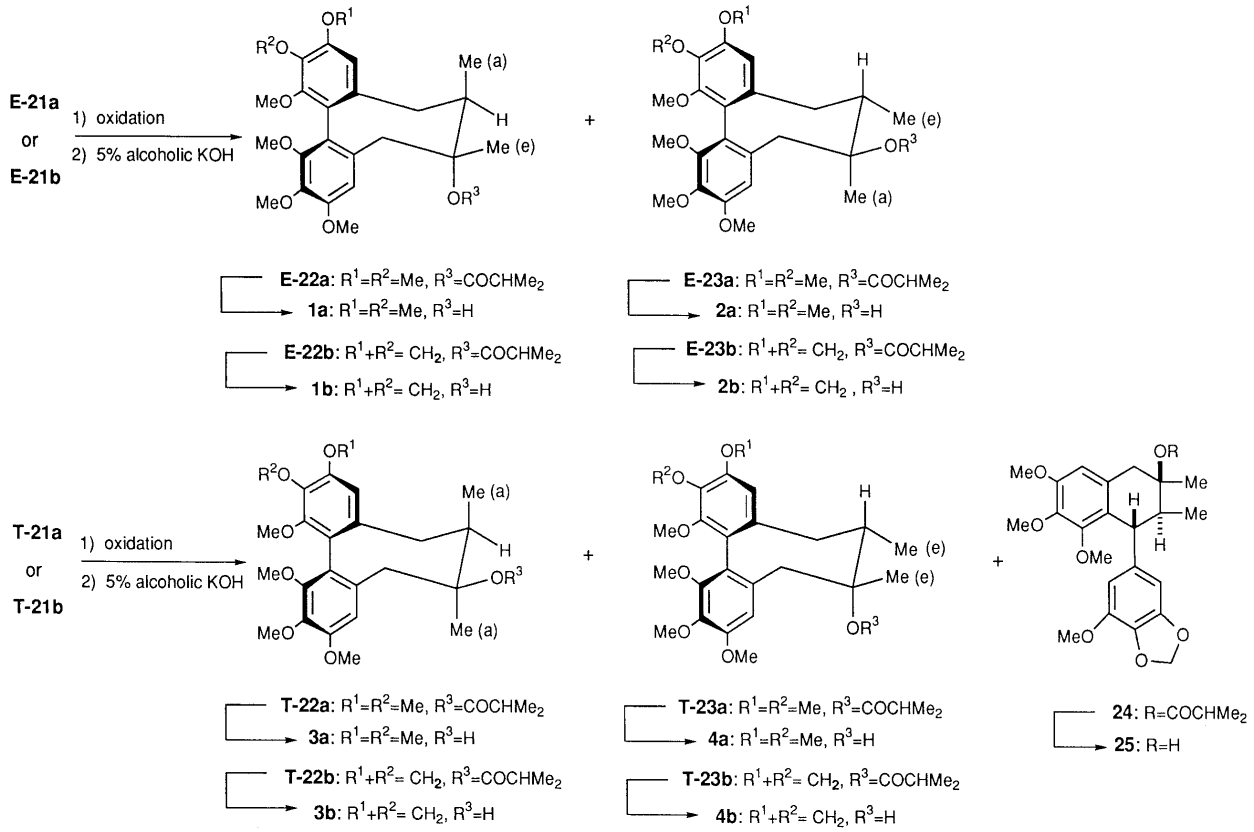
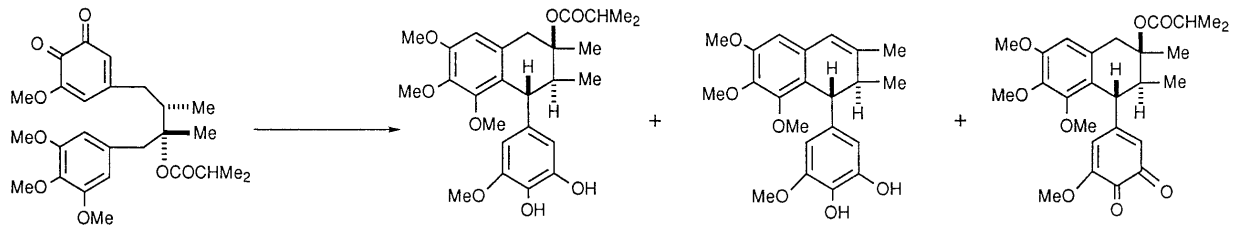


Chart 6

Table 3. Reaction of T-**18** with Various Reagents



Run	Substrate	Reagent	Temperature	Product (yield, %)		
				26	**27**	T-**19**
1	T-**18**	$BF_3 \cdot OEt_2$	−78 °C	72	8	—
2	T-**18**		0 °C	36	42	—
3	T-**18**		r.t.	—	79	—
4	T-**18**	$TiCl_4$	r.t.	10	65	—
5	T-**18**	$SnCl_4$	−20 °C	—	67	—
6	T-**18**	$ZnCl_2$	r.t.	—	43	38
7	T-**18**	*p*-TsOH	r.t.	—	45	40
8	T-**18**	Air	r.t.	—	—	86

r.t., room temperature.

gave the corresponding bisarylbutane E-**21a**. On the other hands, E-**21b** was obtained by treatment of E-**20** with $BrCH_2Cl$ in the presence of Cs_2CO_3[11] in 92% yield. Further, T-**21a** and T-**21b** were synthesized from T-**11** by methods similar to those used for E-**21a** and E-**21b**.

We have reported already the oxidative aryl–aryl coupling reactions of the four isobutyrates, E-**21a** and **21b**, and T-**21a** and **21b**, employing several reagent systems based on iron(III) salts.[2,6] In this investigation, we found that (i) the best yields were obtained in the reactions with the reagent system $Fe(ClO_4)_3 \cdot 9H_2O$–CH_2Cl_2–MeCN, (ii) two coupling products E-**22a** and E-**23a** (in the ratio of 4:1, 36% yield) were obtained in the reactions of E-**21a**; E-**22b** and E-**23b** (in the ratio of 4:1, 41% yield) in the reaction of E-**21b**; T-**22a** and T-**23a** (in the ratio of 7:3, 36% yield) in the reaction of T-**21a**, (iii) E-**22a**, E-**22b**,

Table 4. ^{1}H-NMR Spectral Data for E- and T-**12**, **16**, **17**, **18**, and **20**[a]

	E-**12**	T-**12**	E-**16**	T-**16**	E-**17**	T-**17**	E-**18**	T-**18**	E-**20**	T-**20**
H-2′ and H-6′	6.51, s	6.46, s	6.50, s	6.46, s	6.46, s	6.42, s	6.45, s	6.38, s	6.46, s	6.42, s
H-2″ and H-6″	6.37, s	6.39, s	6.32, s	6.34, s	6.28, s	6.31, s	5.67, d	5.76, d	6.39, d	6.41, d
(J=Hz)							(1.2)	(1.5)	(1.5)	(1.5)
							5.97, d	5.98, d	6.20, d	6.25, d
							(1.2)	(1.5)	(1.5)	(1.5)
H-1 (J=Hz)	2.77, d	2.74, d	2.76, d	2.73, d	3.05, d	2.95, d	2.93, d	2.96, d	3.02, d	2.96, d
	(13.4)	(13.4)	(13.4)	(13.4)	(14.0)	(14.0)	(14.0)	(13.1)	(14.0)	(14.0)
	2.86, d	2.79, d	2.86, d	2.80, d	3.23, d	3.39, d	3.05, d	3.42, d	3.23, d	3.36, d
	(13.4)	(13.4)	(13.4)	(13.4)	(14.0)	(14.0)	(14.0)	(13.1)	(14.0)	(14.0)
H-4 (J=Hz)	2.12, dd	2.13, dd	2.12, dd	2.12, dd	2.14, dd	2.12, dd	2.10, dd	2.10, dd	2.10, dd	2.10, dd
	(13.1)	(13.4)	(13.1)	(13.1)	(13.1)	(13.1)	(12.8)	(13.1)	(13.1)	(13.4)
	(11.6)	(11.6)	(11.6)	(11.6)	(11.6)	(11.9)	(11.6)	(11.5)	(11.6)	(11.3)
	3.15, dd	3.18, dd	3.13, dd	3.15, dd	2.94, dd	2.94, dd	2.61, dd	2.58, dd	2.91, dd	2.91, dd
	(13.1)	(13.4)	(13.1)	(13.1)	(13.1)	(13.1)	(12.8)	(13.1)	(13.1)	(13.4)
	(2.7)	(3.1)	(2.8)	(2.8)	(2.1)	(2.4)	(2.1)	(2.1)	(2.1)	(2.1)
H-3 (m)	1.82—1.88	1.81—1.88	1.80—1.95	1.79—1.92	2.71—2.80	2.71—2.78	2.95—3.01	2.85—2.93	2.72—2.79	2.67—2.74
C-2-Me (s)	1.17	1.15	1.16	1.15	1.43	1.43	1.46	1.38	1.43	1.43
C-3-Me (J=Hz)	0.88, d	0.91, d	0.87, d	0.89, d	0.84, d	0.87, d	1.02, d	1.03, d	0.86, d	0.88, d
	(6.7)	(7.0)	(6.6)	(6.7)	(6.7)	(7.0)	(7.0)	(6.7)	(7.0)	(7.7)
Ar-OMe (s)	3.86	3.85	3.85	3.78	3.83	3.77	3.75	3.77	3.84	3.83
		3.86	3.86	3.85	3.84	3.83	3.84	3.84	3.85	3.84
		3.87		3.86		3.84	3.85			3.85
OCOCH (m)	—	—	—	—	2.43—2.54	2.43—2.51	2.48—2.56	2.43—2.50	2.44—2.52	2.43—2.51
$CHMe_2$	—	—	—	—	1.13, d	1.12, d	1.13, d	1.11, d	1.12, d	1.12, d
					(6.7)	(7.0)	(7.0)	(7.0)	(6.7)	(7.0)
					1.16, d	1.13, d	1.17, d	(×2)	1.15, d	1.13, d
					(6.7)	(7.0)	(7.0)		(6.7)	(7.0)
Si-Me	—	—	0.12, s	0.12, s	0.11, s	0.12, s	—	—	—	—
Si-*tert*-Bu	—	—	1.01, s	1.01, s	1.00, s	1.01, s	—	—	—	—
C2-OH	1.65, s	1.50, s	1.50, s	1.49, s	—	—	—	—	—	—
Ar-OH	5.41, s	5.46, s	—	—	—	—	—	—	5.28, s	5.25, s
									5.34, s	5.29, s

a) δ in $CDCl_3$, ^{1}H-NMR at 270 MHz.

Table 5. ^{13}C-NMR Spectral Data for E- and T-**12**, **16**, **17**, and **20**[a]

Carbon No.	E-**12**	T-**12**	E-**16**	T-**16**	E-**17**	T-**17**	E-**20**	T-**20**
1	44.9	46.5	45.0	46.4	41.3	41.7	41.31	41.6
2	74.5	74.6	74.6	74.6	86.9	86.9	86.9	86.9
3	44.9	45.2	44.7	45.0	41.2	41.3	41.25	41.4
4	38.2	37.7	38.3	37.7	38.0	37.8	37.7	37.6
1′	132.8	132.8	133.2	133.0	132.9	132.9	132.9	132.9
2′	107.7	107.8	107.7	107.7	107.9	107.8	107.9	107.8
3′	153.0	153.0	153.0	153.0	152.7	152.7	152.7	152.7
4′	136.8	136.8	136.7	136.7	136.7	136.7	136.7	136.7
5′	153.0	153.0	153.0	153.0	152.7	152.7	152.7	152.7
6′	107.7	107.8	107.7	107.7	107.9	107.8	107.9	107.8
1″	132.6	132.9	133.9	134.2	132.9	132.5	130.5	130.5
2″	105.6	105.7	106.0	106.2	106.0	106.1	109.4	109.4
3″	146.9	146.9	151.4	151.4	151.4	151.4	143.6	143.6
4″	133.1	132.9	133.2	133.0	133.4	133.6	132.8	133.1
5″	146.9	146.9	151.4	151.4	151.4	151.4	146.9	146.8
6″	105.6	105.7	106.0	106.2	106.0	106.1	103.6	103.7
C-3-Me	13.7	14.6	13.7	14.5	13.9	14.2	14.0	14.2
C-2-Me	24.3	22.5	24.2	25.7	21.0	20.6	21.0	20.6
Ar-OMe	56.2	56.2	55.8	55.8	55.8	55.8	56.1	56.1
	56.3	56.3	56.2	56.2	56.1	56.1	60.9	60.9
	60.9	60.9	60.9	60.9	60.9	60.9		
–CO–	—	—	—	—	176.4	176.6	176.4	176.6
–COCH–	—	—	—	—	35.3	35.2	35.3	35.2
$–COCHMe_2$	—	—	—	—	19.1	19.1	19.1	19.1
					19.2	19.2	19.2	19.2
Si-Me	—	—	−4.7	−4.7	−4.7	−4.7	—	—
Si-*tert*-Bu	—	—	25.8	25.8	25.8	25.8	—	—

a) δ in $CDCl_3$, ^{13}C-NMR at 125.65 MHz.

and T-**22a** were formed in preference to E-**23a**, E-**23b**, and T-**23a**, respectively, and (iv) three products were produced in the reaction of T-**21b**, namely, two DBCO lignans T-**22b** and T-**23b** and the 1-aryltetralin **24** (in the ratio of 38 : 11 : 51, 55.8% yield).

The above coupling products were hydrolyzed with 5% KOH to give the corresponding alcohols, (±)-schizandrin (**1a**), (±)-gomisin A (**1b**), **2a**, **2b**, (±)-isoschizandrin (**3a**), (±)-isogomisin A (**3b**), **4a**, **4b** and **25**.

Acid-catalyzed conjugate addition reaction by the attack of trimethoxyphenyl ring at the C-6″ position in T-**18** using various acids in order to construct the desired DBCO skeleton were examined, but the expected reaction did not take place, and the tetralins **26**, **27**, and T-**19** were formed (Table 3). Also, when T-**18** was kept under air, it gave the tetralin-quinone T-**19** in 86% yield. The formation of T-**19** may proceed as follows. Proton elimination at the C-4 position in T-**18** followed by the ionic-addition of the trimethoxyphenyl ring to the C-4 position in the resulting product may give the corresponding tetralin **26**. Then, further oxidation of **26** by air may proceed to provide the *ortho*-quinone derivative T-**19**.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer, and ^{1}H- and ^{13}C-NMR spectra with JEOL JNM-EX90, JNM-GX270 and JNM-GSX500 spectrometers, with tetramethylsilane as an internal standard ($CDCl_3$ and C_6D_6 solution). Mass spectra were recorded on a JEOL JMS-D300 spectrometer. Elemental analyses were done using a Yanaco CHN-MT-3 apparatus. Wako Silica gel C-200 (200 mesh) and Merck Kieselgel 60 F_{254} were used for column chromatography and thin-layer chromatography (TLC), respectively. Each organic extract was dried over Na_2SO_4. High-performance liquid chromatography (HPLC) was performed on a Wakosil 5C4-200 column (25 cm × 4.6 mm i.d. for analytical scale or 25 cm × 20 mm i.d. for preparative scale) with aqueous methanol (40—60%), using a Shimadzu LC-6A apparatus for monitoring at 254 nm.

(*Z*)-1,4-Bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butene (8) and (*E*)-1,4-Bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butene (9) A solution of the butanediol **6** (4.50 g, 10 mmol), ethyl orthoformate (7.41 g, 50 mmol) and pyridium *p*-toluenesulfonate (PPTS, 1.26 g, 5 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature for 30 min. The solution was passed though a short column of silica gel using hexane–CH_2Cl_2 (3 : 2, v/v). The resulting compound **7** was dissolved in acetic anhydride (30 ml) and the solution was refluxed under a nitrogen atmosphere for 10 h. The reaction mixture was poured into ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was recrystallized from EtOH to yield 0.97 g (23%) of **9** as colorless crystals, mp 119—121 °C. IR (KBr): 1590 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.80 (6H, s, 2 × olefinic-Me), 3.42 (4H, s, 2 × Ar-CH_2), 3.82 and 3.85 (18H, each s, 6 × Ar-OMe), and 6.42 (4H, s, Ar-H). *Anal.* Calcd for $C_{24}H_{32}O_6$: C, 69.20; H, 7.74. Found: C, 68.90; H, 7.86. MS *m/z*: 416 (M^+). The above mother liquor was concentrated and the residue was distilled in a bulb-to-bulb distillation apparatus to yield 2.62 g (63%) of **8** as a colorless oil, bp 210—220 °C (3 mm). IR (KBr): 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.72 (6H, s, 2 × olefinic-Me), 3.50 (4H, s, 2 × Ar-CH_2), 3.80 and 3.82 (18H, each s, 6 × Ar-OMe), 6.40 (4H, s, Ar-H). *Anal.* Calcd for $C_{24}H_{32}O_6$: C, 69.20; H, 7.74. Found: C, 68.91; H, 7.88. MS *m/z*: 416 (M^+).

Isomerization of the (*E*)-Butene (9) to the (*Z*)-Butene (8) A solution of the (*E*)-butene (**9**, 100 mg) in cyclohexane (100 ml) was irradiated using 100W low-pressure UV lamp for 1 h in the presence of I_2 (10 mg). Gas chromatographic measurement showed that this solution consisted of *ca.* 60% (*E*)-isomer and 40% (*Z*)-isomer.

***erythro*-1,4-Bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butanol (E-10)** A 1.0 M BH_3 · THF solution (100 ml, Aldrich) was added under a nitrogen atmosphere to a solution of the (*Z*)-butene **8**[9] (14 g, 34 mmol) in anhydrous THF (135 ml) at 0 °C, and the whole was stirred at room temperature for 3 h. A solution prepared from aqueous 30% H_2O_2 (135 ml) and aqueous 3 M NaOH (27 ml) was added slowly, and the reaction mixture was stirred at room temperature for 2 h, then poured into saturated aqueous NaCl and the whole was extracted with $CHCl_3$–ether (1 : 3, v/v). The organic layer was washed with H_2O, then dried and concentrated. The residue was recrystallized from $CHCl_3$–ether to yield 11.7 g (80%) of E-**10** as colorless prisms, mp 138.5—139 °C (ether–hexane). IR (KBr): 3450, 1595 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.96 (3H, d, J = 6.8 Hz, C3-Me), 1.17 (3H, s, C2-Me), 1.65 (1H, br s, C2-OH), 1.84—1.91 (1H, m, C3-H), 2.15 (1H, dd, J = 13.1, 11.5 Hz, C4-H), 2.76 and 2.86 (each 1H, d, J = 13.4 Hz, 2 × C1-H), 3.16 (1H, dd, J = 13.1, 2.5 Hz, C4-H), 3.83 (3H, s, Ar-OMe), 3.84 (6H, s, 2 × Ar-OMe), 3.85 (3H, s, Ar-OMe), 3.86 (6H, s, 2 × Ar-OMe), 6.39 (2H, s, Ar-H), 6.51 (2H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 13.7 (C3-Me), 24.3 (C2-Me), 38.4 (C4), 44.7 (C3), 44.8 (C1), 56.0 (2 × Ar-OMe), 60.8 (4 × Ar-OMe), 74.4 (C2), 105.9, 107.7, 132.7, 136.1, 136.7, 137.2, 152.9 (each Ar-C). *Anal.* Calcd for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.38; H, 8.00. MS *m/z*: 434 (M^+).

***threo*-1,4-Bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butanol (T-10)** T-**10**, colorless prisms, mp 119—120 °C, was synthesized from **9** in 82% yield by a procedure similar to that used for E-**10**.

T-**10**: Colorless prisms, mp 119—120 °C (ether–hexane). IR (KBr): 3450, 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (3H, d, J = 6.8 Hz, C3-Me), 1.15 (3H, s, C2-Me), 1.50 (1H, br s, C2-OH), 1.84—1.91 (1H, m, C3-H), 2.15 (1H, dd, J = 13.5, 11.5 Hz, C4-H), 2.74 and 2.80 (each 1H, d, J = 13.4 Hz, 2 × C1-H), 3.19 (1H, dd, J = 13.1, 2.7 Hz, C4-H), 3.83 (3H, s, Ar-OMe), 3.84 (6H, s, 2 × Ar-OMe), 3.85 (3H, s, Ar-OMe), 3.86 (6H, s, 2 × Ar-OMe), 6.39 (2H, s, Ar-H), 6.47 (2H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 14.4 (C3-Me), 22.3 (C2-Me), 37.7 (C4), 44.8 (C3), 46.2 (C1), 55.9 (2 × Ar-OMe), 60.9 (4 × Ar-OMe), 74.3 (C2), 105.8, 107.6, 132.7, 136.9, 137.4, 152.8 (each Ar-C). *Anal.* Calcd for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.15; H, 7.90. MS *m/z*: 434 (M^+).

Oxidation of *erythro*-Butanol (E-10) Method A: With $FeCl_3$–MeCN (Reagent A): A solution of E-**10** (43 mg, 0.1 mmol) in dry MeCN (1.5 ml) was added to a solution of $FeCl_3$ (146 mg, 0.9 mmol) in dry MeCN (1.5 ml), and the whole was stirred at room temperature for 1 min. The reaction mixture was poured into ice-water and the whole was extracted with ether. The organic layer was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (2 : 3, v/v) gave 8.8 mg (21%) of 7,9-dimethoxy-2β,3α-dimethyl-8-oxo-2-(3,4,5-trimethoxybenzyl)-1-oxaspiro[4.5]deca-6,9-diene (E-**11**) as colorless crystals (ether–hexane), mp 139—140 °C. IR (KBr): 1680, 1660, 1620, 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.21 (3H, d, J = 6.8 Hz, C3-Me), 1.25 (3H, s, C2-Me), 2.20 (1H, t, J = 12.7 Hz, C4-H), 2.28 (1H, dd, J = 12.7, 6.6 Hz, C4-H), 2.47 and 2.85 (2H, each d, J = 13.7 Hz, Ar-CH_2), 2.48—2.60 (1H, m, C3-H), 3.66 and 3.70 (6H, each s, Ar-OMe), 3.80 (3H, s, Ar-OMe), 3.82 (6H, s, 2 × Ar-OMe), 5.81 (2H, s, 2 × olefinic-H), 6.53 (2H, s, 2 × Ar-H). *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.13; H, 7.43. HR-MS Calcd for $C_{23}H_{30}O_7$: 418.1991, Found: 418.2017.

Method B: By Anodic Oxidation (Reagent B): E-**10** (43.4 mg, 0.1 mmol) was oxidized in the presence of Et_4NClO_4 (400 mg) as an electrolyte in MeCN (17 ml) at 1.05 V saturated calomel electrode (SCE) using platinum electrodes and a Hg–Hg_2Cl_2 reference electrode for 20 min. The reaction mixture was worked up as described in method A to give 10.4 mg (25%) of E-**11**.

Method C: With AgO (Reagent C): Silver(II)oxide (246 mg, 2 mmol), was slowly added to a suspension of E-**10** (174 mg, 0.4 mmol) and pyridine-2,6-dicarboxylic acid *N*-oxide (386 mg, 2 mmol) in a mixture of MeCN (2.8 ml) and H_2O (1.2 ml) with vigorous stirring within 30 min. During this addition, the reaction mixture was cooled in an ice-water bath. Then the reaction mixture was diluted with water (10 ml) and insoluble compounds were removed by filtration. The solid was washed several times with CH_2Cl_2. The same solvent was used for extraction of the filtrate. The combined extracts were washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 60.3 mg (36%) of E-**11**.

Method D: With $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$–$HBF_4$–MeCN (Reagent D): A solution of E-**10** (43.4 mg, 0.1 mmol) in dry MeCN (5 ml) was added to a solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (220 mg, 0.25 mmol) and HBF_4 (0.04 ml) in dry MeCN (5 ml), and the whole was stirred at room temperature for 20 min. The reaction mixture was poured into ice-water and extracted with ether. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method

A to give 10.9 mg (26%) of E-**11**.

Method E: With $Fe(ClO_4)_3 \cdot 9H_2O$–MeCN (Reagent E): A solution of E-**10** (43.4 mg, 0.1 mmol) in dry MeCN (1.5 ml) was added to a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (134 mg, 0.25 mmol) in dry MeCN (1.5 ml), and the whole was stirred at room temperature for 1 min. The reaction mixture was poured into ice-water and the whole was extracted with ether. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 14.6 mg (35%) of E-**11**.

Method F: With $Fe(ClO_4)_3 \cdot 9H_2O$–CH_2Cl_2–MeCN (Reagent F): A solution of the *erythro*-butanol E-**10** (87 mg, 0.2 mmol) in anhydrous MeCN (1 ml) and CH_2Cl_2 (1 ml) was added to a solution of $Fe(ClO_4)_3$ (259 mg, 0.5 mmol) in anhydrous MeCN (1.5 ml) and CH_2Cl_2 (1.5 ml), and the whole was stirred at room temperature for 5 min. The reaction mixture was poured into ice-water and the whole was extracted with ether. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 31.8 mg (38%) of E-**11**.

Method G: With $Pb(OAc)_4$ (Reagent G): A solution of the *erythro*-butanol E-**10** (260 mg, 0.6 mmol) and $Pb(OAc)_4$ (797 mg, 1.8 mmol) in AcOH (10 ml) was heated at 60 °C for 7 min. The reaction mixture was poured into ice-water, and the whole was neutralized with saturated $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with saturated $NaHCO_3$ and H_2O, dried and concentrated. The residue was purified as described in method A to give 112.7 mg (45%) of E-**11**.

Method H: With $Ce(NH_4)_2(NO_3)_6$ [CAN][12] (Reagent H): A cooled solution of $Ce(NH_4)_2(NO_3)_6$ (548 mg, 1 mmol) in a mixture of MeCN (2 ml) and H_2O (2 ml) was slowly added to a suspension of E-**10** (174 mg, 0.4 mmol) and pyridine-2,6-dicarboxylic acid *N*-oxide (193 mg, 1 mmol) in MeCN (2 ml) and water (1 ml) with vigorous stirring within 20 min. During this addition, the reaction vessel was cooled in an ice-water bath. Then, the mixture was stirred for an additional 20 min. The bath was removed and, after 10 min, the mixture was poured into ice-water. The whole was extracted several times with $CHCl_3$. The combined extracts were washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 183.8 mg (50%) of E-**11**.

Method I: With BAHA (Reagent I): Anhydrous Na_2CO_3 (1.46 g, 13.8 mmol), followed by BAHA (753 mg, 0.92 mmol), was added to a solution of E-**10** (100 mg, 0.23 mmol) in THF (20 ml) under a nitrogen atmosphere at 0 °C. The mixture was stirred for 4.5 h, when the deep blue color of the BAHA had faded. At this time, the light yellow reaction mixture was passed through a short column of silica gel with AcOEt–hexane (1 : 2, v/v). The eluate was concentrated, and the residue was purified as described in method A to give 51 mg (53%) of E-**11**.

Oxidation of *threo*-Butanol (T-10) Method A: By Anodic Oxidation (Reagent B): Oxidation of T-**10** was carried out by the procedure described for the oxidation of E-**10** with reagent B, to give 7,9-dimethoxy-2α,3α-dimethyl-8-oxo-2-(3,4,5-trimethoxylbenzyl)-1-oxaspiro-[4.5]deca-6,9-diene (T-**11**), as colorless crystals, mp 134—135 °C (acetone–ether). IR (KBr): 1680, 1660, 1620, 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (3H, d, J=6.9 Hz, C3-Me), 1.26 (3H, s, C2-Me), 2.34 (3H, m, 2×C4-H and C3-H), 2.64 and 2.99 (each 1H, d, J=13.9 Hz, $ArCH_2$), 3.39, 3.68, and 3.81 (15H, each s, 5×Ar-OMe), 5.05 and 5.60 (each 1H, d, J=2.4 Hz, 2×olefinic-H), 6.47 (2H, s, 2×Ar-H). *Anal.* Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.05; H,7.30. HR-MS Calcd for $C_{23}H_{30}O_7$: 418.1991, Found: 418.1979. Yield is listed in Table 1.

Method B: With $Fe(ClO_4)_3 \cdot 9H_2O$–MeCN (Reagent E): Oxidation of T-**10** was carried out by the procedure described for the oxidation of E-**10** with reagent E, to give T-**11**. Yield is listed in Table 1.

Method C: With $Pd(OAc)_4$ (Reagent G): Oxidation of T-**10** was carried out by the procedure described for the oxidation of E-**10** with reagent G, to give T-**11**. Yield is listed in Table 1.

Method D: With $Ce(NH_4)_2(NO_3)_6$ [CAN] (Reagent H): Oxidation of T-**10** was carried out by the procedure described for the oxidation of E-**10** with reagent H, to give T-**11**. Yield is listed in Table 1.

Method E: With BAHA (Reagent I): Oxidation of T-**10** was carried out by the procedure described for the oxidation of E-**10** with reagent I, to give T-**11**. Yield is listed in Table 1.

Reactions of the Spiro-Dienone Ether (E-11) with Various Reagents Method A: By Hydrogenation with 10% Pd/C: E-**11** (500 mg, 1.2 mmol) was hydrogenated in the presence of 10% Pd/C (mg) in EtOH (ml). The catalyst was removed, and the filtrate was concentrated. The residue was subjected to silica gel chromatography. The eluate with benzene–$CHCl_3$–acetone (20 : 5 : 1, v/v) gave 482 mg (96%) of *erythro*-4-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butanol (E-**12**), as colorless crystals, mp 109—110 °C (ether–hexane). IR (KBr): 3450, 1610, 1590 cm^{-1}. *Anal.* Calcd for $C_{23}H_{32}O_7$: C, 65.69; H, 7.67. Found: C, 65.77; H, 7.65. HR-MS Calcd for $C_{23}H_{32}O_7$: 420.2148. Found: 420.2140. Yield and physical data of E-**12** are listed in Tables 2, 4, and 5.

Method B: With P_2O_5 and $MeSO_3H$ in CH_2Cl_2 at Room Temperature[13]: A solution of the quinol ether E-**11** (500 mg, 1.2 mmol) in dry CH_2Cl_2 (156 ml) was added to a solution of P_2O_5 (341 mg, 2.4 mmol) and $MeSO_3H$ (0.018 ml, 2.4 mmol) in dry CH_2Cl_2 at room temperature, and the solution was stirred for 2.5 h. The reaction mixture was poured into ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 382 mg (76.0%) of E-**12**.

Method C: With P_2O_5 and $MeSO_3H$ in CH_2Cl_2 at −20 °C: A solution of quinol ether E-**11** (500 mg, 1.2 mmol) in dry CH_2Cl_2 (25 ml) was added to a solution of P_2O_5 (341 mg, 2.4 mmol) and $MeSO_3H$ (0.018 ml, 2.4 mmol) in dry CH_2Cl_2 at −20 °C. The reaction mixture was kept in a refrigerator for 2.5 h, then poured into ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 144 mg (30%) of 7,12-dihydro-4,8,9,10-tetramethoxy-6α,13α-dimethyl-2,3-dioxo-6,12-methano-5-dibenz[*b*,*e*]oxocine (**15**) and 301 mg (60%) of E-**12**. **15**: deep purple crystals, mp 223—225 °C (acetone). IR (KBr): 1700, 1640, 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.95 (3H, d, J=6.8 Hz, C13-Me), 1.58 (3H, s, C6-Me), 2.02 (1H, dq, J=6.8, 2.4 Hz, C13-H), 3.00 and 3.10 (each 1H, d, J=18.8 Hz, 2×C7-H), 3.72, 3.80, 3.81, and 3.94 (each 3H, s, 4×Ar-OMe), 4.37 (1H, d, J=2.4 Hz, C12-H), 5.68 (1H, s, C1-H), 6.35 (1H, s, C11-H). ^{13}C-NMR ($CDCl_3$) δ: 14.6 (C13-Me), 26.5 (C6-Me), 28.7 (C12), 36.8 (C13), 40.1 (C7), 55.9, 60.6, and 61.5 (4×Ar-OMe), 83.7 (C6), 106.6 (C11), 107.1 (C1), 114.1 (C1a), 123.0 (C11a), 127.5 (C7a), 140.7 (C9), 152.0 (C8), 152.2 (C10), 152.7 (C4a), 165.4 (C4), 173.1, 176.8 (C2 and C3). *Anal.* Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04. Found: C, 65.81: H, 5.86. MS *m/z*: 400 (M^+).

Method D: With $BF_3 \cdot OEt_2$ in CH_2Cl_2: $BF_3 \cdot OEt_2$ (2.7 ml) was added to a solution of the quinol ether E-**11** (500 mg, 1.2 mmol) in dry CH_2Cl_2 (25 ml) at room temperature and the solution was stirred for 2 h. The reaction mixture was poured into ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 72 mg (15%) of **15** and 186 mg (37%) of E-**12**.

Method E: With $ZnCl_2$ in Ac_2O: $ZnCl_2$ (136 mg, 1 mmol) was added to a solution of the quinol ether E-**11** (208 mg, 0.5 mmol) in Ac_2O (10 ml) at room temperature and the solution was stirred for 15 min. The reaction mixture was poured into ice-water and the whole was extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1 : 9, v/v) gave 95 mg (43%) of 1,2-*cis*-1-(4-acetoxy-3,5-dimethoxyphenyl)-3,4-dehydro-6,7,8-trimethoxy-2,3-dimethyltetralin (**13**), as colorless crystals, mp 158—158.5 °C (ether). IR (KBr): 1760, 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.09 (3H, d, J=7.1 Hz, C2-Me), 1.81 (3H, s, C3-Me), 2.29 (3H, s, –OCOMe), 2.29—2.42 (1H, m, C2-H), 3.59 (3H, s, C8-OMe), 3.69 (6H, s, 2×Ar-OMe), 3.85 (6H, s, 2×Ar-OMe), 3.93 (1H, d, J=3.2 Hz, C1-H), 6.10 (1H, s, C4-H), 6.39 (2H, s, Ar-H), 6.43 (1H, s, Ar-H). *Anal.* Calcd for $C_{25}H_{30}O_7$: C, 67.86; H, 6.83. Found: C, 67.66; H, 6.76. MS *m/z*: 442 (M^+). Yield is listed in Table 1.

Method F: With $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$–$HClO_4$–$O_2$ in MeCN: A solution of E-**11** (42 mg, 0.1 mmol) in MeCN (5 ml) was added to a solution of $Fe(bpy)_3(ClO_4)_3 \cdot 3H_2O$ (220 mg, 0.25 mmol) and 70% $HClO_4$ (0.04 ml) in MeCN (5 ml) and the mixture was stirred under an oxygen atmosphere for 1 h, stirred at room temperature for 75 min. The reaction mixture was poured into ice-water and the whole was extracted with ether–CH_2Cl_2 (3 : 1, v/v). The organic layer was washed with saturated $NaHCO_3$ and H_2O, then dried and concentrated. The residue was purified as described in method A to give 18 mg (45%) of **15**.

Reactions of the Spiro-Dienone Ether (T-11) with Various Reagents Method A: By Hydrogenation with 10% Pd/C: Reaction of T-**11** was carried out by the procedure described for the reaction of E-**11**, by hydrogenation with 10% Pd/C to give *threo*-4-(4-hydroxy-3,5-dimethoxyphenyl)-1-(3,4,5-trimethoxyphenyl)-2,3-dimethyl-2-butanol (T-**12**) as

colorless crystals, mp 102—104 °C (ether–hexane). IR (KBr): 3558, 1575 cm^{-1}. *Anal.* Calcd for $C_{23}H_{32}O_7$: C, 65.69; H, 7.67. Found: C, 65.59; H, 7.49. HR-MS Calcd for $C_{23}H_{32}O_7$: 420.2148. Found: 420.2159. Yield and physical data of **T-12** are listed in Tables 2, 4 and 5.

Method B: With P_2O_5 and $MeSO_3H$ in CH_2Cl_2 at Room Temperature: Reaction of **T-11** was carried out by the procedure described for the reaction of **E-11** with P_2O_5 and $MeSO_3H$ in CH_2Cl_2 at room temperature to give 1,2-*cis*-3,4-dehydro-1-(4-hydroxy-3,5-dimethoxyphenyl)-6,7,8-trimethoxy-2,3-dimethyltetralin (**14**), as a colorless oil. IR (KBr): 3450, 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.08 (3H, d, J=7.1 Hz, C2-Me), 1.74 (3H, s, C3-Me), 2.24—2.40 (1H, m, C2-H), 3.56(3H, s, C8-OMe), 3.76 (6H, s, 2×Ar-OMe), 3.80 (6H, s, 2×Ar-OMe), 4.06 (1H, d, J=3.2 Hz, C1-H), 5.37 (1H, br s, Ar-OH), 6.10 (1H, s, C4-H), 6.34 (2H, s, Ar-H), 6.44 (1H, s, Ar-H). *Anal.* Calcd for $C_{23}H_{28}O_6$: C, 69.98; H, 7.05. Found: C, 69.88; H, 7.00. MS m/z: 400 (M^+). Yield is listed in Table 2.

***erythro*-4-(4-*tert*-Butyldimethylsilyloxy-3,5-dimethoxyphenyl)-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)-2-butanol (E-16)** TBDMSCl (94 mg, 0.63 mmol) and DBU (95 mg, 0.63 mmol) was added to a solution of **E-12** (105 mg, 0.25 mmol) in anhydrous benzene (5 ml) and the whole was stirred for 1 min. The precipitates were separated from the solution by filtration and the filtrate was washed with H_2O, then dried and concentrated to give 145 mg (92%) of **E-16**, as colorless crystals, mp 66—67 °C (hexane). IR (KBr): 3654, 1283, 1160 cm^{-1}. *Anal.* Calcd for $C_{29}H_{46}O_7Si$: C, 65.13; H, 8.67. Found: C, 65.10; H, 8.57. HR-MS Calcd for $C_{29}H_{46}O_7Si$: 534.3012. Found: 534.2986. MS m/z: 534 (M^+). ^{1}H- and ^{13}C-NMR data are listed in Tables 4 and 5.

***threo*-4-(4-*tert*-Butyldimethylsilyloxy-3,5-dimethoxyphenyl)-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)-2-butanol (T-16)** **T-16**, colorless crystals, mp 121—122 °C (hexane), was synthesized from **T-12** in 90% yield by a procedure similar to that used for **E-16**. IR (neat): 3622, 1573, 1283, 1160 cm^{-1}. *Anal.* Calcd for $C_{29}H_{46}O_7Si$: C, 65.13; H, 8.67. Found: C, 65.11; H, 8.54. HR-MS Calcd for $C_{29}H_{46}O_7Si$: 534.3012. Found: 534.3009. MS m/z: 534 (M^+). ^{1}H- and ^{13}C-NMR data for **T-16** are listed in Tables 4 and 5.

***erythro*-4-(4-*tert*-Butyldimethylsilyloxy-3,5-dimethoxyphenyl)-2-isopropylcarbonyloxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (E-17)** *p*-Toluenesulfonic acid (400 mg) was added to a solution of **E-16** (3.58 g, 6.7 mmol) in isobutyric anhydride (5 ml), and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into ice-water and the whole was stirred for 48 h, then extracted with ether. The ether layer was washed with saturated $NaHCO_3$ and H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1 : 6, v/v) gave 3.48 g (86%) of **E-17** as a colorless oil. IR (oil): 1284, 1160 cm^{-1}. HR-MS Calcd for $C_{33}H_{52}O_8Si$: 604.3431. Found: 604.3414. MS m/z: 604 (M^+). ^{1}H- and ^{13}C-NMR data for **E-17** are listed in Tables 4 and 5.

***threo*-4-(4-*tert*-Butyldimethylsilyloxy-3,5-dimethoxyphenyl)-2-isopropylcarbonyloxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (T-17)** **T-17**, colorless oil, was synthesized from **T-16** in 84% yield by a procedure similar to that used for **E-17**. IR (oil): 1654, 1284, 1159 cm^{-1}. HR-MS Calcd for $C_{33}H_{52}O_8Si$: 604.3431, Found: 604.3426. MS m/z: 604 (M^+). ^{1}H- and ^{13}C-NMR data for **T-17** are listed in Tables 4 and 5.

Reaction of E-17 with BAHA in THF Anhydrous Na_2CO_3 (2 g), followed by BAHA[8] (296 mg, 0.37 mmol), was added to a solution of **E-17** (100 mg, 0.16 mmol) in THF (20 ml) under a nitrogen atmosphere at −20 °C. The mixture was stirred at room temperature for 3 min, when the deep blue color of the BAHA had faded. The red reaction mixture was passed through a short column of silica gel with AcOEt–hexane (1 : 2, v/v). The eluate was concentrated, and the residue was subjected to silica gel column chromatography. The first eluate with AcOEt–hexane (1 : 3, v/v) gave 4 mg (5%) of *c*-3-isopropylcarbonyloxy-*r*-1-(3,4-dioxo-5-methoxyphenyl)-*t*-2,*t*-3-dimethyl-6,7,8-trimethoxytetralin (**E-19**). The second eluate gave 51 mg (65%) of *erythro*-4-(3,4-dihydro-3,4-dioxo-5-methoxyphenyl)-2-isopropylcarbonyloxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (**E-18**). **E-18**: red oil. IR (oil): 1704, 1659, 1634, 1568 cm^{-1}. MS m/z: 474 (M^+). ^{1}H- and ^{13}C-NMR data for **E-18** are listed in Tables 4 and 5. **E-19**: red crystals, mp 158—159 °C (ether–hexane). IR (KBr): 1700, 1670, 1632 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.13 and 1.15 (each 3H, d, J=7.1 Hz, –COCH$\underline{Me}_2$), 1.36 (3H, s, C3-Me), 1.40 (3H, d, J=7.0 Hz, C2-Me), 2.33—2.37 (1H, m, C2-H), 2.39—2.49 (1H, m, –COCH–), 3.21 and 3.42 (each 1H, d, J=16.6 Hz, C4-H), 3.68, 3.76, 3.79, and 3.85 (each 3H, s, 4×Ar-OMe), 3.43 (1H, d, J=8.9 Hz, C1-H), 5.62 (1H, d, J=1.5 Hz, C2′-H), 5.98 (1H, d, J=1.5 Hz, C6′-H), 6.42 (1H, s, C5-H). *Anal.* Calcd for $C_{26}H_{32}O_8$: C, 66.08; H, 6.83. Found: C, 66.10; H, 6.93. MS m/z: 472 (M^+).

Reaction of T-17 with BAHA Reaction of **T-17** (100 mg, 0.16 mmol) was carried out by the procedure described for the reaction of **E-17** with BAHA to give 5 mg (6%) of **T-19** and 49 mg (63%) of *threo*-4-(3,4-dihydro-3,4-dioxo-5-methoxyphenyl)-2-isopropylcarbonyloxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (**T-18**). **T-18**: red oil. IR (neat): 1705, 1659, 1635 cm^{-1}. MS m/z: 474 (M^+). ^{1}H- and ^{13}C-NMR data for **T-18** are listed in Tables 4 and 5. **T-19**: red crystals, mp 129—129.5 °C. IR (KBr): 1725, 1655, 1626 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.73 and 0.85 (each 3H, d, J=7.0 Hz, –COCH$\underline{Me}_2$), 1.21 (3H, d, J=6.7 Hz, C2-Me), 1.64—1.66 (1H, m, C2-H), 1.67 (3H, s, C3-Me), 2.22—2.31 (1H, m, –COCH–), 2.77 and 3.83 (each 1H, d, J=16.5 Hz, C4-H), 3.58 (1H, d, J=9.5 Hz, C1-H), 3.67, 3.76, and 3.83 (12H, each s, 4×Ar-OMe), 5.61 (1H, d, J=1.5 Hz, C2′-H), 6.05 (1H, d, J=1.5 Hz, C6′-H), 6.39 (1H, s, C5-H). MS m/z: 472 (M^+).

***erythro*-4-(3,4-Dihydroxy-5-methoxyphenyl)-2-isopropylcarbonyl-oxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (E-20)** A solution of $NaBH_4$ (2 mg, 0.05 mmol) in anhydrous MeOH (1 ml) was added portionwise to a solution of **E-18** (47.4 mg, 0.1 mmol) in anhydrous MeOH (2 ml), and the mixture was stirred at room temperature for 30 min. The reaction mixture was poured into ice-water and extracted the whole was with $CHCl_3$. The organic layer was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1 : 3, v/v), gave 46 mg (97%) of **E-20** as colorless crystals, mp 161—163 °C (petroleum ether). IR (KBr): 3556, 1715 cm^{-1}. *Anal.* Calcd for $C_{26}H_{36}O_8$: C, 65.53; H, 7.61. Found: C, 65.43; H, 7.60. MS m/z: 476 (M^+). ^{1}H- and ^{13}C-NMR data are listed in Tables 4 and 5.

***threo*-4-(3,4-Dihydroxy-5-methoxyphenyl)-2-isopropylcarbonyl-oxy-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (T-20)** **T-20**, colorless oil, was synthesized from **T-18** in 96% yield by a procedure similar to that used for **E-20**. IR (oil): 3410, 1716, 1589 cm^{-1}. HR-MS Calcd for $C_{26}H_{36}O_8$: 476.2410. Found: 476.2420. MS m/z: 476 (M^+). ^{1}H- and ^{13}C-NMR data for **T-20** are listed in Tables 4 and 5.

***erythro*-2-Isopropylcarbonyloxy-2,3-dimethyl-1,4-bis(3,4,5-trimethoxyphenyl)butane (E-21a)** CH_3I (142 mg, 1 mmol) was added to a solution of **E-20** (95 mg, 0.2 mmol) and anhydrous K_2CO_3 (50 mg) in dry DMF, and the solution was stirred at room temperature for 2 h with vigorous stirring. The reaction mixture was poured into ice-water, and the whole was neutralized with 10% HCl, and extracted with ether. The organic layer was washed with H_2O, dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1 : 6, v/v) gave 97 mg (96%) of **E-21a**, as colorless crystals, mp 78—79 °C (ether–hexane). IR (KBr): 1717 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, d, J=6.7 Hz, C3-Me), 1.14 and 1.16 (each 3H, d, J=7.0 Hz, CH-$\underline{Me}_2$), 1.15 (3H, s, C2-Me), 2.15 (1H, dd, J=13.0, 11.6 Hz, C4-H), 2.44—2.54 (1H, m, –CO–C$\underline{H}$), 2.78—2.86 (1H, m, C3-H), 2.96 (1H, dd, J=13.0, 1.6 Hz, C4-H), 3.04 and 3.22 (each 1H, d, J=14.4 Hz, C1-H), 3.82 (3H, s, Ar-OMe), 3.83 (6H, s, 2×Ar-OMe), 3.84 (9H, s, 3×Ar-OMe), 6.32 and 6.47 (each 2H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (C3-$\underline{Me}$), 19.1 and 19.2 (–CH$\underline{Me}_2$), 21.1 (C2-$\underline{Me}$), 35.3 (–CO–$\underline{C}$H), 41.3 (C3), 56.06, 56.08, 60.85, 60.88, and 60.8 (each Ar-O$\underline{Me}$), 86.9 (C2), 105.9, 107.9, 132.8, 136.2, 136.8, 152.7, and 153.1 (each Ar-C), 176.4 (–$\underline{CO}$–CH). *Anal* Calcd for $C_{28}H_{40}O_8$: C, 66.64; H, 7.99. Found: C, 66.73; H, 8.01. MS m/z: 504 (M^+).

***erythro*-2-Isopropylcarbonyloxy-4-(3-methoxy-4,5-methylenedioxyphenyl)-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (E-21b)** $BrCH_2Cl$ (0.2 ml, 3.1 mmol) was added to a stirred degassed suspension of **E-20** (129 mg, 0.27 mmol) and Cs_2CO_3 (1 g, 3 mmol) in anhydrous DMF (5 ml), and the resulting mixture was heated to 110 °C for 2 h. The reaction mixture was cooled to room temperature and filtered through a pad of Celite with AcOEt washing. The filtrate was concentrated almost to dryness and the residue was diluted with water and extracted with AcOEt. The extracts were combined, washed with brine, dried and concentrated. The residue was subjected to silica gel chromatography using AcOEt–hexane (1 : 7, v/v) to give 122 mg (92%) of **E-21b**, colorless crystals, mp 103—103.5 °C (ether–hexane). IR (KBr): 1718, 1636, 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, d, J=6.7 Hz, C3-Me), 1.13 and 1.15 (each 3H, d, J=7.0 Hz, CH-$\underline{Me}_2$), 1.14 (3H, s, C2-Me), 2.13 (1H, dd, J=13.0, 11.6 Hz, C4-H), 2.43—2.53 (1H, m, –CO–C$\underline{H}$), 2.74—2.81 (1H, m, C3-H), 2.93 (1H, dd, J=13.0, 2.1 Hz, C4-H), 2.99 and 3.23 (each 1H, d, J=14.0 Hz, C1-H), 3.88 (3H, s, Ar-OMe), 3.85 (9H, s, 3×Ar-OMe), 5.93 (2H, s, OCH_2O), 6.27, and 6.33 (4H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ:

13.9 (C3-Me), 19.1 and 19.2 (–CHMe$_2$), 21.1 (C2-Me), 35.2 (–CO–CH), 37.8 (C4-Me), 41.3 (C3), 41.4 (C1), 56.1, 56.5, and 60.9 (each Ar-OMe), 86.8 (C2), 103.1, 107.9, 108.1, 132.8, 133.4, 135.5, 136.7, 143.4, 148.7, and 152.7 (each Ar-C), 176.4 (–CO–CH). *Anal.* Calcd for $C_{27}H_{36}O_8$: C, 66.37; H, 7.43. Found: C, 66.47; H, 7.60. MS *m/z*: 488 (M^+).

***threo*-2-Isopropylcarbonyloxy-2,3-dimethyl-1,4-bis(3,4,5-trimethoxyphenyl)butane (T-21a)** T-**21a**, colorless crystals, mp 88—89 °C (ether–hexane), was synthesized from T-**20** in 92% yield by a procedure similar to that used for E-**21a**. IR (KBr): 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, d, J=6.7 Hz, C3-Me), 1.14 and 1.16 (each 3H, d, J=7.0 Hz, CH-Me$_2$), 1.15 (3H, s, C2-Me), 2.15 (1H, dd, J=13.0, 11.6 Hz, C4-H), 2.44—2.54 (1H, m, –CO–CH), 2.78—2.86 (1H, m, C3-H), 2.96 (1H, dd, J=13.0, 1.6 Hz, C4-H), 3.04 and 3.22 (each 1H, d, J=14.4 Hz, C1-H), 3.83 (3H, s, Ar-OMe), 3.84 (9H, s, 3×Ar-OMe), 3.85 (6H, s, 2×Ar-OMe), 6.32 and 6.47 (each 2H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (C3-Me), 19.1 and 19.2 (–CHMe$_2$), 21.1 (C2-Me), 35.3 (–CO–CH), 38.2 (C4), 41.2 (C1), 41.3 (C3), 56.06, 56.08, 60.85, 60.88, and 60.8 (each Ar-OMe), 86.9 (C2), 105.9, 107.9, 132.8, 136.2, 136.8, 152.7, and 153.1 (each Ar-C), 176.4 (–CO–CH). *Anal.* Calcd for $C_{28}H_{40}O_8$: C, 66.64; H, 7.99. Found: C, 66.64; H, 7.92. MS *m/z*: 504 (M^+).

***threo*-2-Isopropylcarbonyloxy-4-(3-methoxy-4,5-methylenedioxyphenyl)-2,3-dimethyl-1-(3,4,5-trimethoxyphenyl)butane (T-21b)** T-**21b**, colorless plates, mp 78—78.5 °C (ether–hexane), was synthesized from T-**20** in 90% yield by a procedure similar to that used for E-**21b**. IR (KBr): 1718, 1636, 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, d, J=6.7 Hz, C3-Me), 1.13 and 1.15 (each 3H, d, J=7.0 Hz, CH-Me$_2$), 1.14 (3H, s, C2-Me), 2.13 (1H, dd, J=13.0, 11.6 Hz, C4-H), 2.43—2.53 (1H, m, –CO–CH), 2.74—2.81 (1H, m, C3-H), 2.93 (1H, dd, J=13.0, 1.6 Hz, C4-H), 2.99 and 3.23 (each 1H, d, J=14.0 Hz, C1-H), 3.83 (9H, s, 3×Ar-OMe), 3.88 (3H, s, Ar-OMe), 5.93 (2H, s, OCH_2O), 6.30, 6.34 (each 1H, s, Ar-H), 6.41 (2H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 13.9 (C3-Me), 19.1 and 19.2 (–CHMe$_2$), 21.1 (C2-Me), 35.2 (–CO–CH), 37.8 (C4-Me), 41.3 (C3), 41.4 (C1), 56.1, 56.5, and 60.9 (each Ar-OMe), 86.8 (C2), 103.1, 107.9, 108.1, 132.8, 133.4, 135.5, 136.7, 143.4, 148.7, and 152.7 (each Ar-C), 176.4 (–CO–CH). *Anal.* Calcd for $C_{27}H_{36}O_8$: C, 66.37; H, 7.43. Found: C, 66.51; H, 7.52. MS *m/z*: 488 (M^+).

Reaction of T-18 with Various Reagents Method A: With $BF_3 \cdot OEt_2$ at −78 °C: $BF_3 \cdot OEt_2$ (0.15 mmol) was added to a solution of T-**18** (47 mg, 0.1 mmol) in anhydrous CH_2Cl_2 (5 ml) at −78 °C and the solution was stirred for 2 h. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1:6, v/v) gave a mixture of **26** and **27**. The mixture was further subjected to preparative HPLC with MeOH–H_2O (60:40, v/v). The first eluate gave 34 mg (72%) of *r*-1-(4-hydroxy-3,5-dimethoxyphenyl)-3-isopropylcarbonyloxy-6,7,8-trimethoxy-*t*-2,*c*-3-dimethyltetralin (**26**) as a colorless oil. The second eluate gave 3.1 mg (8%) of 1,2-*trans*-3,4-dehydro-(3,4-dihydroxy-5-methoxyphenyl)-6,7,8-trimethoxy-2,3-dimethyltetralin (**27**) as colorless crystals, mp 61—62 °C, (ether–hexane). **26**: IR (oil): 3580, 1675, 1598 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.70 and 0.81 (each 3H, d, J=7.0 Hz, –COCHMe$_2$), 1.10 (3H, d, J=6.7 Hz, C2-Me), 1.61 (3H, s, C3-Me), 1.64—1.74 (1H, m, C2-H), 2.19—2.27 (1H, m, –COCH–), 2.90 and 3.76 (each 1H, d, J=16.2 Hz, C4-H), 3.64 (1H, d, J=11.0 Hz, C1-H), 3.16 (3H, s, C8-OMe), 3.70, 3.81, and 3.85 (9H, each s, 4×Ar-OMe), 5.27 (2H, s, Ar-OH), 6.35 (2H, s, Ar-H), 6.37 (1H, s, Ar-H). HR-MS Calcd for $C_{26}H_{34}O_8$: 474.2253. Found: 474.2253. MS *m/z*: 474 (M^+). **27**: IR (KBr): 3428, 1604 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.10 (3H, d, J=6.0 Hz, C2-Me), 1.77 (3H, s, C3-Me), 2.31—2.41 (1H, m, C2-H), 3.83 (1H, d, J=10.8 Hz, C1-H), 3.58 (3H, s, C8-OMe), 3.78, 3.84, and 3.87 (each 3H, s, 3×Ar-OMe), 5.15 and 5.18 (each 1H, s, Ar-OH), 5.80 (1H, s, C4-H), 6.27 (2H, s, C2′ and C-6′-H), 6.43 (1H, s, C5-H). *Anal.* Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 68.35; H, 6.75. HR-MS Calcd for $C_{22}H_{26}O_6$: 386.1729. Found: 386.1732. MS *m/z*: 386 (M^+).

Method B: With $BF_3 \cdot OEt_2$ at 0 °C: Reaction of T-**18** was carried out at 0 °C for 4 h by the same procedure as described for the reaction of T-**18** in method A to give **26** and **27**.

Method C: With $BF_3 \cdot OEt_2$ at Room Temperature: Reaction of T-**18** was carried out at room temperature for 3 h by using the procedure described for the reaction of T-**18** in method A to give **27**.

Method D: With $TiCl_4$: $TiCl_4$ (1.5 mmol) was added to a solution of T-**18** (0.1 mmol) in CH_2Cl_2 (5 ml) at room temperature and the solution was stirred for 1 h. The reaction mixture was worked up as described in method A to give **26** and **27**.

Method E: With $SnCl_4$: $SnCl_4$ (0.15 mmol) was added to a solution of T-**18** (47 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) at 0 °C and the solution was stirred for 1 h. The reaction mixture was worked up as described in method A to give **26** and **27**.

Method F: With $ZnCl_2$: $ZnCl_2$ (0.15 mmol) was added to a solution of T-**18** (47 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) at room temperature and the solution was stirred for 2 h. The reaction mixture was worked up as described in method A to give **27** and T-**19**.

Method G: With *p*-TsOH: *p*-TsOH (0.15 mmol) was added to a solution of T-**18** (0.1 mmol) in CH_2Cl_2 (5 ml) at room temperature and the solution was stirred for 3 h. The reaction mixture was worked up as described in method A to give **27** and T-**19**.

Method H: With Air: A solution of T-**18** (0.1 mmol) in CH_2Cl_2 (5 ml) under air was stirred at room temperature for 48 h. The reaction mixture was worked up as described in method A to give T-**19**. Yields are listed in Table 3.

Reaction of T-19 with $NaBH_4$ Reaction of T-**19** with $NaBH_4$ was carried out by using the procedure described for the reaction of E-**17** with $NaBH_4$ to give **26** in 90% yield.

References and Notes

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