Utility of Weitz' Aminium Salt for Obtaining Quinones as Potential Synthetic Precursors of Quassinoids

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Reactions of phenols and phenolic silyl ethers 5, 6, and 7 using Weitz' aminium salt, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA), gave the corresponding quinone derivatives 8, 9, and 10, which may be useful synthons for obtaining quassinoids, the bitter principle of *Simaroubaceous* plants. Treatment of 10a with silica gel powder resulted in the intramolecular conjugate addition to afford the indanone 11 in good yield.

Key words synthesis; quinone; synthon; quassinoid; Weitz' aminium salt; oxidation

Quinone derivatives are considered to be not only versatile compounds for organic synthesis, but also intermediates in the biosynthesis of various natural products, and several applications of quinone derivatives as synthons for the synthesis of natural products have been reported.[1)]

In the preceding paper,[2)] we reported a general synthesis for (±)-dibenzocyclooctadiene lignans, including (±)-schizandrin, (±)-gomisin A, (±)-isoschizandrin, and (±)-isogomisin A, utilizing quinone derivatives as the key intermediates. In the investigation of the preparations of these key intermediates from the corresponding phenol-ethers by oxidations with various reagents, namely, $Ce(NH_4)_2(NO_3)_6$ [CAN], $Pb(OAc)_4$, AgO, *etc.*, we found that the best yields were obtained in the reactions with Weitz' aminium salt, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA),[3)] a stable cation radical salt, in all cases.

Quassinoids are highly oxgenated triterpenes which were isolated as bitter principles from *Simaroubaceous* plants. Their synthesis has attracted much attention because of the wide spectrum of their biological properties.[4)]

Our retro-synthetic studies indicated that quinone derivatives such as **10** and **11** might be useful synthons for quassinoids such as quassin (**1**) as shown in Chart 1. Herein, we report a novel synthetic method for quinone derivatives such as **8**, **9**, and **10** from **5**, **6**, and **7** by oxidation with BAHA.

The phenols **5a** and E-**5b**, the alcoholic monosilyl ethers **6a** and E-**6b**, and the disilyl ethers **7a** and E-**7b** were obtained from **2**[5)] through the following reaction sequence (Chart 2).

The phenolic hydroxyl group of **2** was protected with *tert*-butyldimethylsilyl chloride (TBDMSCl) in the presence of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) to afford the corresponding *O*-silylated compound **3** in 83% yield. Diisobutylaluminium hydride (DIBAL) effected selective reduction of the ester group of **3** to afford the corresponding aldehyde **4** in 85% yield. The nitro-Aldol reaction[6)] of **4** with nitromethane proceeded in the presence of potassium fluoride (KF) and 18-crown-6 to give **5a** in 60% yield. The similar reaction of **4** with 1-(3-benzyloxy-4-methoxyphenyl)-3-nitropropane[7)] gave the *erythro*- and

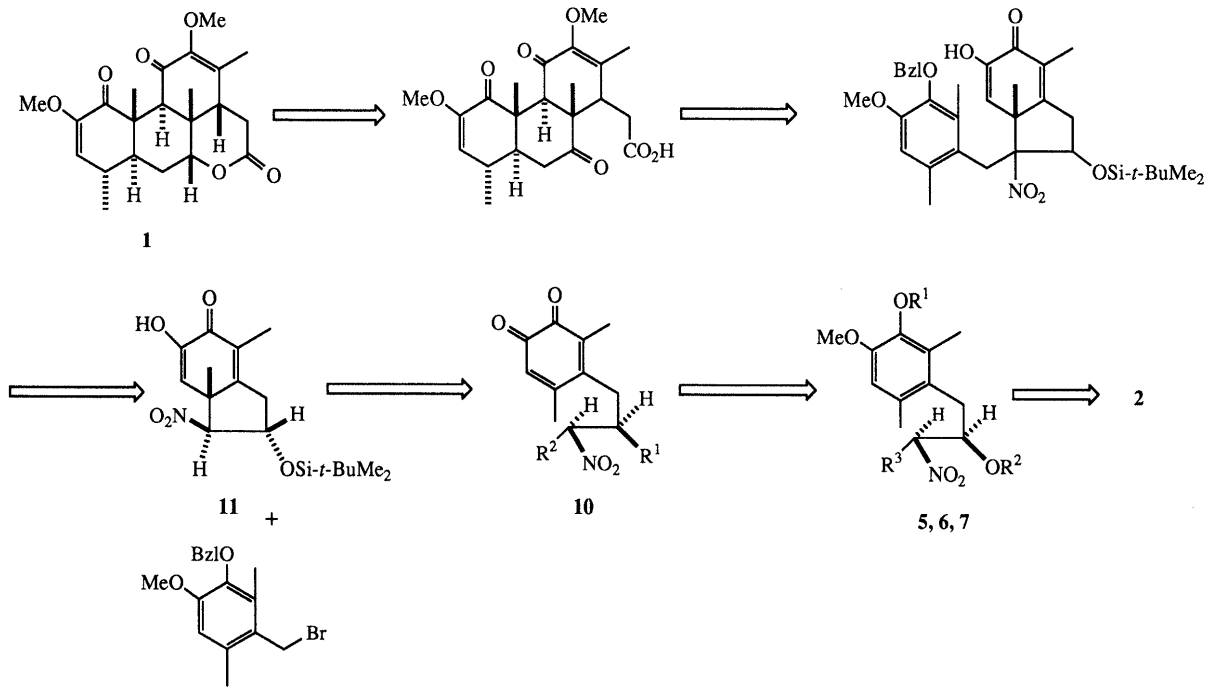

Chart 1

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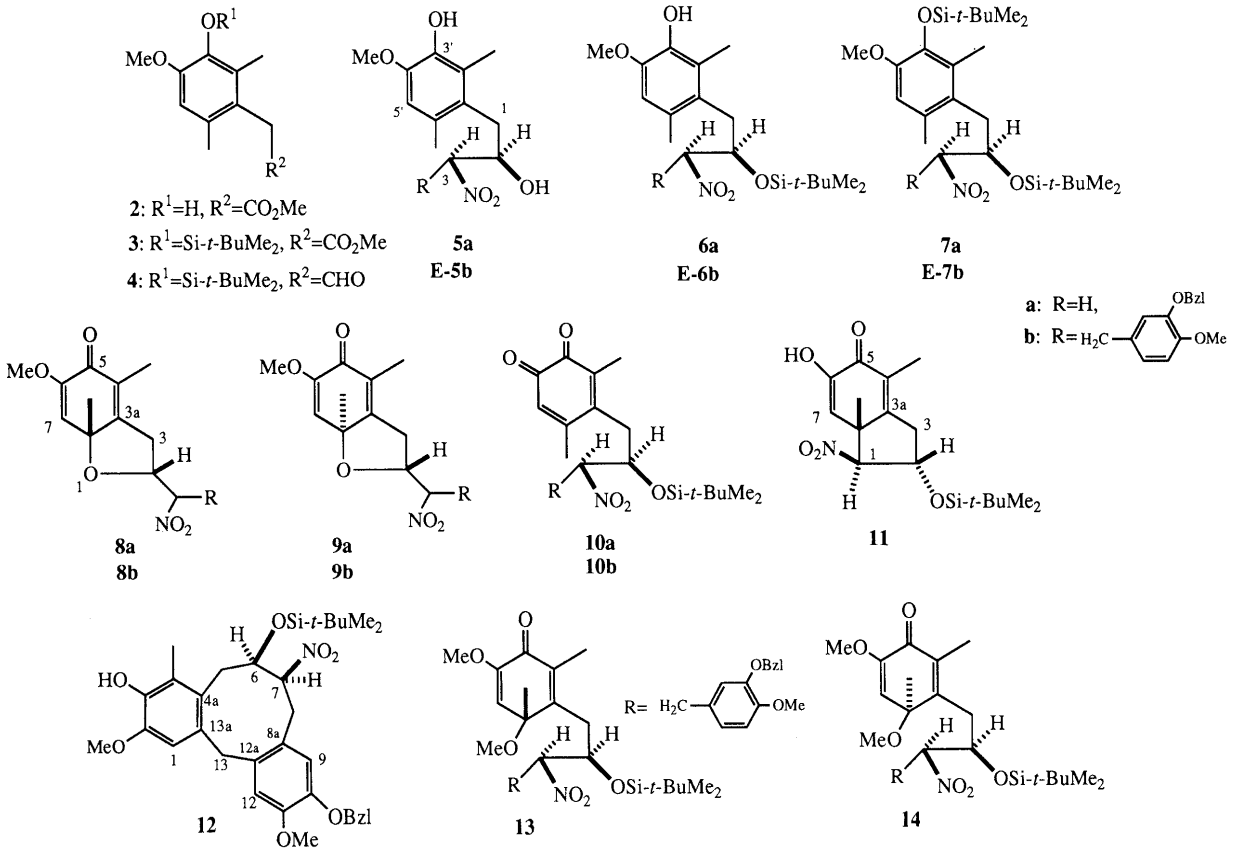

Chart 2

Table 1. Oxidation of Phenols and Phenolic-silyl Ethers

Run	Substrate	Reagent[a]	Solvent	Temp. (°C)	Product (yield)
1	**5a**	A	THF	0	**8a** (40%)+**9a** (32%)
2	**5a**	B	CH_2Cl_2	0	**8a** (32%)+**9a** (8%)
3	E-**5b**	A	THF	0	**8b** (20%)+**9b** (16%)
4	E-**5b**	B	CH_2Cl_2	0	**8b** (13%)+**9b** (6%)
5	**6a**	A	THF	0	**10a** (71%)
6	**6a**	B	CH_2Cl_2	0	No reaction
7	E-**6b**	A	THF	0	**10b** (28%)
8	**7a**	A	THF	0	**10a** (77%)+**11** (trace)
9	**7a**	B	CH_2Cl_2	0	No reaction
10	E-**7b**	A	THF	−20	**10b** (78%)
11	E-**7b**	B	CH_2Cl_2	r.t.	No reaction
12	E-**7b**	A	CH_2Cl_2	−20	**12** (17%)
13	E-**7b**	B	MeOH	r.t.	**13** (32%)+**14** (34%)

a) A, tris(4-bromophenyl)aminium hexachloroantimonate (BAHA); B, $Fe(bpy)_3(ClO_4)_3$. r.t., room temperature.

threo-phenols E-**5b** and T-**5b**[8] in 61% yield (in the ratio of 3:1). Compounds E-**5b** can be easily separated from the mixture of E-**5b** and T-**5b** by simple recrystallization from ether–hexane. The stereochemistry of the *erythro*-compound, E-**5b**, was elucidated from the relative configuration between the C_6-OSi-*tert*-$BuMe_2$ (TBDMS) group and C_7-NO_2 in the oxidation product **12** as described below. The phenolic and alcoholic hydroxyl groups of **5a** or E-**5b** were protected with TBDMSCl to yield the corresponding disilyl ether **7a** or E-**7b**, and the phenolic silylated group was selectively deprotected with *n*-butylammonium fluoride (*n*-$Bu_4N^+F^-$)[9] to furnish the alcoholic monosilyl ether **6a** or E-**6b**.

We next investigated oxidation of the phenols **5a**, E-**5b**, the alcoholic monosilyl ethers **6a**, E-**6b**, and the disilyl ethers **7a**, E-**7b** (Table 1). First, reaction of the phenol **5a** with 2.5 eq of BAHA in tetrahydrofuran (THF) under a nitrogen atmosphere in the presence of Na_2CO_3 as a base at 0 °C was performed to give two quinol-ethers having a benzofuran moiety, **8a** and **9a**, in yields of 40% and 32%, respectively (run 1 in Table 1). Compounds **8a** and **9a** were separated by preparative HPLC using MeOH: H_2O=6:4 as an eluent. The similar reaction of E-**5b** with BAHA gave the benzofurans, **8b** and **9b** (run 3).

Subsequently, we investigated the reactions of **5a** and E-**5b** with another mild one-electron oxidation reagent, $Fe(byp)_3(ClO_4)_3$, in methylene chloride (CH_2Cl_2)[10] for comparison with the reaction with BAHA (runs 2 and 4).

The reactions of **5a** and E-**5b** with the above reagent provided the same oxidation products, but the yields were lower than with BAHA used as the oxidant.

The BAHA oxidation of **6a** and E-**6b** protected at the alcoholic hydroxyl group in THF afforded respectively, the corressponding *ortho*-quinones **10a** and **10b** in yields of 71% and 28%, without cleavage of the alcoholic silyl ether (runs 5 and 7).

Treatment of **7a** protected with TBDMSCl at the phenolic and alcoholic hydroxyl groups using BAHA in THF afforded the *ortho*-quinone **10a** in 71% yield and a trace of the indanone **11** (run 8). Treatment of pure **10a** with silica gel powder (Merck 60 F_{254}) fortuitously afforded the desired conjugate addition product having the indanone moiety **11**, indicating that the minor product **11** formed in the above oxidation reaction is a secondary product generated from **10a** by silica gel used for column chromatography during purification. The similar reaction of E-**7b** gave the *ortho*-quinone E-**10b** in good yield.

As shown in Table 1, the *ortho*-quinones **10a** and **10b** were obtained from **7a** and E-**7b** in better yields than from **6a** and E-**6b**, respectively. This may be attributed to the promotion of one-electron transfer (oxidation) and the stabilization of the resultant cation radical by the TBDMS group (β-effect)[11]; see the compound **15** in Chart 3.

The structure of the indanone **11** was assigned on the basis of the following spectral considerations. (i) It has dienone absorptions at 1665 and 1635 cm^{-1} in the IR spectrum. (ii) The proton signal of C_{7a}-Me (δ 1.59) in **11** is observed at higher field in the ^{1}H-NMR spectrum as compared with the signal of $C_{6'}$-Me (δ 2.27) in **7a**. This suggests that C_{7a}-Me is the aliphatic-Me group. (iii) The signal of C_4-Me (δ 1.92) was observed as doublet because of homoallyl coupling (long-range coupling) between C_4-Me and C_3-Hα. The stereochemistry of **11** was established from a nuclear Overhauser effect (NOE) experiment, (i) when the signal of C_{7a}-Me was irradiated, a 6.5% increment of C_3-Hβ was observed, but the proton signal of C_3-Hα was not enhanced, (ii) similarly, when the signal of C_3-Hβ at δ 3.38 was irradiated, the signal of C_2-Hβ at δ 4.82 was increased by 6.9%, (iii) upon irradiation of the signal of C_7-H at δ 6.06, a 5.4% increment of C_1-Hα was observed. These data suggest that the structure of **11** may be as shown in Fig 1.

We found that the reaction products changed drastically depending on the solvent and oxidizing reagent. In the reactions of **6a**, **7a**, and E-**7b** with $Fe(byp)_3(ClO_4)_3$ using CH_2Cl_2 as the solvent, the corresponding *ortho*-quinones could not be obtained. Oxidation of E-**7b** with BAHA using CH_2Cl_2 instead of THF afforded a novel compound **12** possessing a nine-membered ring moiety in 17% yield. Further, in the reaction of E-**7b** with $Fe(byp)_3(ClO_4)_3$ in MeOH, the quinol-ethers **13** and **14** were produced in 32% and 34% yields, respectively.

The planar structure of **12** was elucidated by spectral analysis, as well as comparison of ^{1}H- and ^{13}C-NMR spectra, with the aid of ^{1}H–^{13}C shift correlation spectroscopy (^{1}H–^{13}C COSY), with those of E-**7b**. First, (i) the proton signal due to the phenolic-hydroxyl group was observed at δ 5.62 in the ^{1}H-NMR spectrum of **12**; (ii) the signal of $C_{6'}$-Me (δ 2.24) in E-**7b** disappeared, and

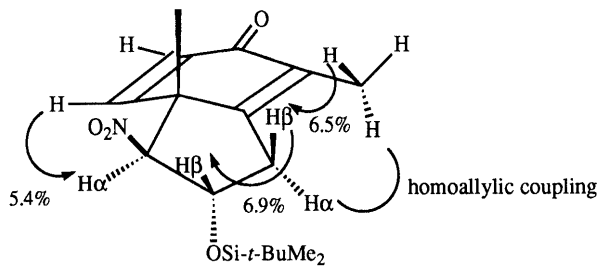

Fig. 1. Significant Enhancements of Signal Intensity in NOE Experiments on **11**

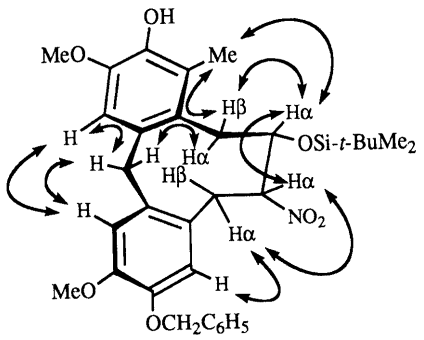

Fig. 2. The Conformation of **12** (twist-boat-chair form) Indicated by Correlations in the NOESY Experiment

the new signals of C_{13}-Hα and -Hβ were observed at δ 3.54 and 4.30 in **12**, each as a doublet. These data suggested that **12** contains a nine-membered ring bound with the methylene-bridge between C_{12a} and C_{13a}. The stereochemistry of **12** was established from a nuclear Overhauser enhancement and exchange spectroscopy (NOESY) experiment and the coupling constants, respectively. In the NOESY experiment on **12**, the correlation cross peaks shown in Fig. 2 were observed. Further, the results suggest that the bond angles between C_5-Hα and C_6-Hα, C_6-Hβ and C_7-Hα, C_5-Hβ and C_6-Hα, C_7-Hα and C_8-Hα, and C_7-Hα and C_8-Hβ of **12** may be about 180°, 45°, 0°, 30°, and 90°, based on the values of the corresponding coupling constants, $J_{C_5\text{-H}\alpha,C_6\text{-H}\alpha}=11.6$ Hz, $J_{C_5\text{-H}\beta,C_6\text{-H}\alpha}=6.1$ Hz, $J_{C_6\text{-H}\alpha,C_7\text{-H}\alpha}=11.6$ Hz, $J_{C_7\text{-H}\alpha,C_8\text{-H}\alpha}=5.8$ Hz, and $J_{C_7\text{-H}\alpha,C_8\text{-H}\beta}=0$ Hz, respectively. Hence, the structure of **12** can be illustrated as shown in Fig. 2, where the molecule takes a twist-boat-chair form of the nine-membered ring, and the C_7-OSi-*tert*-$BuMe_2$ group and C_8-NO_2 group adopt *cis* relative configuration.

The formations of **10b**, **12**, **13**, and **14** from E-**7b** by oxidation with BAHA or $Fe(bipy)_3(ClO_4)_3$ can be explained as follows (Chart 3): Compound E-**7b** undergoes one-electron oxidation with BAHA or $Fe(byp)_3(ClO_4)_3$ to generate the cation radical **15**, followed by desilylation to the radical **16a**. Further one-electron oxidation of **16a** may take place to afford the cation **17**, and water (H_2O) contained in the reagent (BAHA) is introduced at the cationic position to give the *ortho*-quinone **10b** *via* the hemiketal **18**. Similarly, formation of **12** by oxidation with BAHA in CH_2Cl_2 may proceed as follows: Further one-electron oxidation of **16b** derived from E-**7b** with BAHA may generate the cation **19**, followed by proton elimination of **19** to yield **20**. Then, ionic-conjugate addition reaction by the attack of the benzene ring in **20**

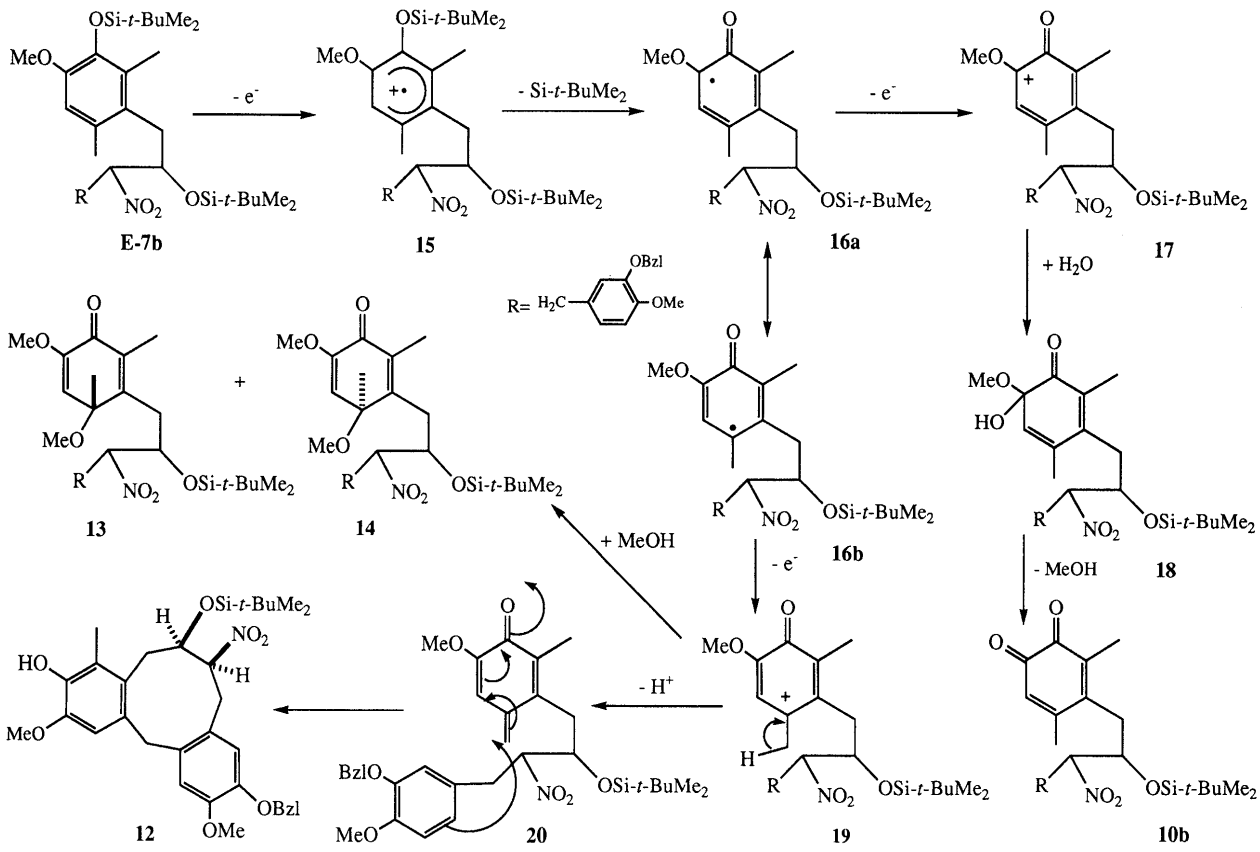

Chart 3

may proceed to provide **12**. Further, formation of **13** and **14** by oxidation with $Fe(bipy)_3(ClO_4)_3$ in MeOH may proceed as follows: Two one-electron oxidations of E-**7b** may generate the cation **19**, and methanol (MeOH) from the solvent is introduced at the cationic position to afford **13** and **14**.

The above results show that (i) BAHA is a useful reagent for synthesis of *ortho*-quinones; (ii) the TBDMS group that protects the phenolic functionality promotes the oxidation and increases the yield of the quinone derivatives.

Investigations on the synthesis of quassin utilizing the indanone **11** as a synthon are in progress.

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 MeOH (40—60%), using a Shimadzu LC-6A apparatus for monitoring at 254 nm.

Methyl (3-*tert*-Butyldimethylsilyloxy-4-methoxy-2,6-dimethylphenyl)-acetate (3) TBDMSCl (56 mg, 0.75 mmol) and DBU (95 mg, 0.63 mmol) were added to a solution of **2** (56 mg, 0.25 mmol) in anhydrous benzene (1 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 77 mg (90.1%) of **3**, as colorless crystals, mp 41—42 °C (hexane). IR (KBr) cm^{-1}: 1737, 1593, 1247. ^{1}H-NMR ($CDCl_3$) δ: 0.15 (6H, s, Si-Me_2), 1.00 (9H, s, Si-*tert*-Bu), 2.20, 2.26 (6H, each s, 2 × Ar-Me), 3.61 (2H, s, Ar-CH_2), 3.66 (3H, s, CO_2Me), 3.75 (3H, s, OMe), 6.54 (1H, s, Ar-H). HR-MS Calcd for $C_{18}H_{30}O_4Si$: 338.1913. Found: 338.1924. *Anal.* Calcd for $C_{18}H_{30}O_4Si$: C, 63.86; H, 8.93. Found: C, 63.83; H, 8.92.

(3-*tert*-Butyldimethylsilyloxy-4-methoxy-2,6-dimethylphenyl)acetaldehyde (4) **3** (304 mg, 0.9 mmol) was dissolved in anhydrous ether and the flask was purged with nitrogen then cooled to −78 °C. A 1.4 ml sample (1.34 mmol) of 0.93 M diisobutylaluminum hydride in hexane was added dropwise to the solution and the mixture was stirred at −78 °C over 2 h. The reaction was quenched with saturated ammmonium chloride and the whole was stirred for 1 h. The precipitate was separated from the solution by filtration and the filtrate was extracted 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 $CHCl_3$–hexane (1 : 1, v/v) gave 260 mg (94.0%) of **4** as a colorless oil. IR (oil) cm^{-1}: 1721, 1594, 1253. ^{1}H-NMR ($CDCl_3$) δ: 0.16 (6H, s, Si-Me_2), 1.00 (9H, s, Si-*tert*-Bu), 2.17, 2.87 (6H, each s, 2 × Ar-Me), 3.65 (2H, d, J = 2.2 Hz, Ar-CH_2), 3.76 (3H, s, Ar-OMe), 6.58 (1H, s, Ar-H), 9.59 (1H, t, J = 2.2 Hz, $ArCH_2$–CHO). HR-MS Calcd for $C_{17}H_{28}O_3Si$: 308.1807. Found: 308.1770.

1-(3-Hydroxy-4-methoxy-2,6-dimethylphenyl)-3-nitro-2-propanol (5a) KF (29 mg, 0.5 mmol), followed by 18-crown-6 (132 mg, 0.5 mmol), was added to a solution of **4** (308 mg, 1.0 mmol) and $MeNO_2$ (61 mg, 1.0 mmol) in isopropanol (1.0 ml). The mixture was stirred at room temperature for 33 h, then poured into ice water, and the whole was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with benzene–acetone (20 : 1, v/v) gave 154 mg (60.4%) of **5a**, as colorless crystals, mp 81—82 °C (ether–hexane). IR (KBr) cm^{-1}: 3506, 1614, 1552. ^{1}H-NMR ($CDCl_3$) δ: 2.24 (3H, s, C2′-Me), 2.29 (3H, s, C6′-Me), 2.42 (1H, d, J = 3.7 Hz, C2-OH), 2.79 (1H, dd, J = 14.4, 6.0 Hz, C3-H), 2.95 (1H, dd, J = 14.4, 7.9 Hz, C3-H), 3.86 (3H, s, Ar-OMe), 4.39 (1H, dd, J = 12.5, 2.1 Hz, C1-H), 4.49 (1H, dd, J = 8.9, 12.9 Hz, C1-H), 4.51—4.56 (1H, m, C2-H), 5.63 (1H, s, C3″-OH), 6.58 (1H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 12.3 (C2′-Me), 20.4 (C6′-Me), 33.5 (C1), 56.0 (Ar-OMe), 68.7 (C2), 80.0 (C3), 110.6 (C5′), 123.0 (C2′), 125.6 (C6′),

127.7 (C1′), 142.2 (C3′), 144.9 (C4′). HR-MS Calcd for $C_{12}H_{17}NO_5$: 255.1106. Found: 255.1079. MS *m/z*: 255 (M^+). *Anal.* Calcd for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.45; H, 6.71; N, 5.48.

***erythro*-4-(3-Benzyloxy-4-methoxyphenyl)-1-(3-hydroxy-4-methoxy-2,6-dimethylphenyl)-3-nitro-2-butanol (E-5b)** Reaction of **4** and 1-(3-benzyloxy-4-methoxyphenyl)-3-nitropropane was carried out by a procedure similar to that used for **5a** to give a crude product (containing the *erythro*-compound E-**5b**, and the *threo*-compound T-**5b**). This crude product was recrystalized from ether–hexane to yield E-**5b** as colorless prisms in 61% yield. mp 155—156 °C (ether–hexane). IR (KBr) cm^{-1}: 3520, 1609, 1548, 1251. ^{1}H-NMR ($CDCl_3$) δ: 1.98 (1H, d, J=3.4 Hz, C2-OH), 2.20 (1H, s, C2′-H), 2.25 (1H, s, C6′-Me), 2.74 (1H, dd, J=14.0, 3.7 Hz, C1-H), 2.87 (1H, dd, J=14.0, 10.4 Hz, C1-H), 3.25—3.31 (2H, m, C4-H), 3.85, 3.86 (6H, each s, 2×Ar-OMe), 4.21—4.17 (1H, m, C2-H), 4.67-4.72 (1H, m, C3-H), 5.12 (2H, s, OCH_2Ar), 5.63 (1H, s, Ar-OH), 6.58 (1H, s, C5′-H), 6.73 (1H, d, J=2.1 Hz, C2″-H), 6.75 (1H, dd, J=8.2, 2.1 Hz, C6″-H), 6.82 (1H, d, J=8.2 Hz, C5″-H), 7.26—7.43 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: 12.2 (C3-Me), 20.4 (C2-Me), 32.9 (C4), 35.1 (C1), 55.9 and 56.0 (Ar-OMe), 71.1 (OCH_2-Ar), 71.7 (C2), 93.5 (C3), 110.5 (C5‴), 112.1 (C5′), 114.9 (C2′), 121.7 (C6′), 123.3 (C2″), 127.4 (C2‴ and C6‴), 127.8 (C4‴), 128.1 (C6‴), 128.5 (C3‴ and C5‴), 137.0 (C1″ and C1′), 142.1 (C3″), 144.8 (C3′), 144.9 (C4′), 149.1 (C1‴ and C4″). HR-MS Calcd for $C_{27}H_{31}NO_7$: 481.2100. Found: 481.2032. *Anal.* Calcd for $C_{27}H_{31}NO_7$: C, 67.34; H, 6.49; N, 2.90. Found: C, 67.33; H, 6.49; N, 2.91.

2-*tert*-Butyldimethylsilyloxy-1-(3-*tert*-butyldimethylsilyloxy-4-methoxy-2,6-dimethylphenyl)-3-nitropropane (7a) TBDMSCl (148 mg, 0.98 mmol) and DBU (95 mg, 0.78 mmol) were added to a solution of **5a** (64 mg, 0.25 mmol) in anhydrous benzene (2 ml) and the whole was stirred for 1 min. The white precipitates were separated from the solution by filtration and the filtrate was washed with H_2O, then dried and concentrated. The residue was subjected to silica gel chromatography. The eluate with benzene–acetone (20 : 1, v/v) gave 79.5 mg (65.5%) of **7a**, as colorless crystals, mp 137—138 °C (hexane). IR (KBr) cm^{-1}: 1557, 1254. ^{1}H-NMR ($CDCl_3$) δ: −0.10, −0.02 (6H, each s, C2-$SiMe_2$), 0.15, 1.00 (9H, s, C3′-OSi-*tert*-Bu), 0.16 (6H, each s, C3′-$OSiMe_2$), 0.84 (9H, s, C2-OSi-*tert*-Bu), 2.23 (3H, s, C2′-Me), 2.27 (3H, s, C6′-Me), 2.76 (1H, dd, J=14.0, 7.9 Hz, C3-H), 2.94 (1H, dd, J=14.0, 7.3 Hz, C3-H), 3.75 (3H, s, Ar-OMe), 4.17 (1H, dd, J=11.9, 3.4 Hz, C1-H), 4.43 (1H, dd, J=11.9, 8.9 Hz, C1-H), 4.57—4.62 (1H, m, C2-H), 6.52 (1H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.4 and −4.7 (C2-OSiMe), −4.0 and −3.9 (C3′-OSiMe), 14.0 (C2′-Me), 17.8 (C2-OSi-C), 18.9 (C3′-Si-C), 20.7 (C6′-Me), 25.7 (C2-OSi-*tert*-Bu), 26.6 (C3′-OSi-*tert*-Bu), 35.5 (C1), 54.8 (Ar-OMe), 70.2 (C2), 81.0 (C3), 111.5 (C5′), 125.8 (C2′), 128.4 (C6′), 129.0 (C1′), 141.5 (C3′), 148.4 (C4′). HR-MS Calcd for $C_{24}H_{45}NO_5Si_2$: 483.2836. Found: 483.2854. MS *m/z*: 483 (M^+). *Anal.* Calcd for $C_{24}H_{45}NO_5Si_2$: C, 59.58; H, 9.38; N, 2.91. Found: C, 59.60; H, 9.37; N, 2.90.

***erythro*-4-(3-Benzyloxy-4-methoxyphenyl)-2-*tert*-butyldimethylsilyloxy-1-(3-*tert*-butyldimethylsilyloxy-4-methoxy-2,6-dimethylphenyl)-3-nitrobutane (E-7b)** E-**7b** was synthesized from E-**5b** in 78.5% yield by a procedure similar to that used for **7a**. E-**7b**: Colorless prisms, mp 122.5—123.5 °C (hexane). IR (KBr) cm^{-1}: 1590, 1549, 1253. ^{1}H-NMR ($CDCl_3$) δ: −0.59, −0.52 (6H, each s, C2-$OSiMe_2$), 0.13, 0.15 (6H, each s, C3′-OSiMe), 0.82, 0.83 (9H, each s, C2-OSi-*tert*-Bu), 1.00 (9H, s, C3′-OSi-*tert*-Bu), 2.20 (3H, s, C2′-Me), 2.24 (3H, s, C6′-Me), 2.73 (1H, dd, J=14.3, 4.0 Hz, C1-H), 3.01 (1H, dd, J=14.3, 10.1 Hz, C1-H), 3.09 (1H, dd, J=15.0, 3.7 Hz, C4-H), 3.36 (1H, dd, J=15.0, 10.5 Hz, C4-H), 3.73, 3.85 (6H, each s, 2×Ar-OMe), 4.33—4.36 (1H, m, C2-H), 4.60—4.64 (1H, m, C3-H), 5.11 (2H, s, OCH_2-Ar), 6.51 (1H, s, C5′-H), 6.71 (1H, d, J=2.1 Hz, C2″-H), 6.74 (1H, dd, J=8.6, 2.1 Hz, C6″-H), 6.81 (1H, d, J=8.6 Hz, C5″-H), 7.29—7.44 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.3 and −5.4 (C2-OSi-Me_2), −4.01 and −3.98 (C3′-OSiMe_2), 14.0 (C3-Me), 17.9 (C2-Si-C), 18.9 (C3′-OSi-C), 20.8 (C2-Me), 25.8 (C2-OSi-*tert*-Bu), 26.1 (C3′-OSi-*tert*-Bu), 33.5 (C4), 33.9 (C1), 54.8 and 56.0 (Ar-OMe), 71.2 (OCH_2-Ar), 73.1 (C2), 94.2 (C3), 111.4 (C5‴), 112.1 (C5′), 114.9 (C2′), 121.5 (C6′), 126.5 (C2″), 127.3 (C6‴), 127.5 (C2‴ and C6‴), 127.9 (C4‴), 128.6 (C3‴ and C5‴), 137.0 (C1″ and C1′), 141.4 (C3″), 148.3 (C3′), 148.4 (C4′), 149.0 (C1‴ and C4″). HR-MS Calcd for $C_{39}H_{59}NO_7Si_2$: 709.3829. Found: 709.3774. *Anal.* Calcd for $C_{39}H_{59}NO_7Si_2$: C, 65.97; H, 8.38; N, 1.97. Found: C, 65.95; H, 8.37; N, 1.96.

2-*tert*-Butyldimethylsilyloxy-1-(3-hydroxy-4-methoxy-2,6-dimethylphenyl)-3-nitropropane (6a) A 1.0 M solution of n-$Bu_4N^+F^-$ in THF (207 ml, 0.21 mmol) was added under a nitrogen atmosphere to a solution of **7a** (101 mg, 0.21 mmol) in anhydrous THF (5.0 ml) at −10 °C and the whole was stirred for 5 min. The reaction was quenched with saturated ammonium chloride and the whole was extracted 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 : 1, v/v) gave 50.5 mg (65.4%) of **6a** as a colorless oil. IR (oil) cm^{-1}: 3584, 1555, 1492. ^{1}H-NMR ($CDCl_3$) δ: −0.09, −0.01 (6H, each s, C2-$OSiMe_2$), 0.84 (9H, s, C2-OSi-*tert*-Bu), 2.23 (3H, s, C2′-Me), 2.28 (3H, s, C6′-Me), 2.76 (1H, dd, J=14.4, 8.2 Hz, C3-H), 2.95 (1H, dd, J=14.0, 7.0 Hz, C3-H), 3.75 (3H, s, Ar-OMe), 4.18 (1H, dd, J=11.6, 3.1 Hz, C1-H), 4.43 (1H, dd, J=11.6, 8.5 Hz, C1-H), 4.55—4.65 (1H, m, C2-H), 5.60 (1H, s, C3″-OH), 6.55 (1H, s, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.4 and −4.8 (C2-OSi-Me), 12.4 (C2′-Me), 17.8 (C2-OSi-C), 20.5 (C6′-Me), 25.6 (C2-OSi-*tert*-Bu), 35.5 (C1), 55.9 (Ar-OMe), 70.1 (C2), 80.9 (C3), 110.5 (C5′), 122.8 (C2′), 126.2 (C6′), 127.4 (C1′), 142.1 (C3′), 144.7 (C4′). HR-MS Calcd for $C_{18}H_{31}NO_5Si$: 369.1971. Found: 369.2016. MS *m/z*: 369 (M^+).

***erythro*-4-(3-Benzyloxy-4-methoxyphenyl)-2-*tert*-butyldimethylsilyloxy-1-(3-hydroxy-4-methoxy-2,6-dimethylphenyl)-3-nitrobutane (E-6b)** E-**6b** was synthesized from E-**7b** in 97% yield by a procedure similar to that used for **6a**. E-**6b**: Colorless prisms, mp 91—92 °C (hexane). IR (KBr) cm^{-1}: 3538, 1608, 1549, 1256. ^{1}H-NMR ($CDCl_3$) δ: −0.58, −0.51 (6H, each s, C2-$OSiMe_2$), 0.82, 0.83 (9H, each s, C2-OSi-*tert*-Bu), 2.21 (3H, s, C2′-Me), 2.25 (3H, s, C6′-Me), 2.76 (1H, dd, J=14.4, 4.0 Hz, C1-H), 3.04 (1H, dd, J=14.4, 10.1 Hz, C1-H), 3.10 (1H, dd, J=15.0, 3.7 Hz, C4-H), 3.37 (1H, dd, J=15.0, 10.4 Hz, C4-H), 3.84, 3.86 (6H, each s, 2×Ar-OMe), 4.33—4.37 (1H, m, C2-H), 4.61—4.64 (1H, m, C3-H), 5.10 (2H, s, OCH_2-Ar), 5.57 (1H, s, Ar-OH), 6.53 (1H, s, C5′-H), 6.69 (1H, d, J=2.1 Hz, C2″-H), 6.75 (1H, dd, J=8.2, 2.1 Hz, C6″-H), 6.81 (1H, d, J=8.2 Hz, C5″-H), 7.28—7.44 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.3 and −5.4 (C2-OSiMe_2), 12.4 (C3-Me), 17.9 (C2-OSi-C), 20.6 (C2-Me), 25.8 (C2-OSi-*tert*-Bu), 33.1 (C4), 33.8 (C1), 56.1 and 56.04 (Ar-OMe), 71.2 (OCH_2-Ar), 73.0 (C2), 94.1 (C3), 110.5 (C5‴), 112.1 (C5′), 114.8 (C2′), 121.6 (C6′), 127.0 (C2″), 127.5 (C2‴), 127.9 (C4‴),128.5 (C6‴), 128.6 (C3‴ and C5‴), 137.0 (C1′ and C1″), 142.1 (C3″), 144.7 (C3′ and C4′), 149.0 (C1‴ and C4″). HR-MS Calcd for $C_{33}H_{45}NO_7Si$: 595.2964. Found: 595.2888. MS *m/z*: 595 (M^+). *Anal.* Calcd for $C_{33}H_{45}NO_7Si$: C, 66.52; H, 7.61; N; 2.35. Found: C, 66.54; H, 7.60; N, 2.34.

Oxidation of the Phenol (5a) Method A: With BAHA (Reagent A, Run 1): Anhydrous Na_2CO_3 (1.25 g, 11.8 mmol), followed by BAHA (352 mg, 0.43 mmol), was added to a solution of **5a** (51 mg, 0.20 mmol) in anhydrous THF (20 ml) under a nitrogen atmosphere at 0 °C. The mixture was stirred for 10 min, then passed through a short column of silica gel with AcOEt–hexane (1 : 3, v/v). The eluate was concentrated, and the residue was subjected to silica gel chromatography. The eluate with benzene–acetone (20 : 1, v/v) gave 36.4 mg (72%) of a mixture of **8a** and **9a**. The mixture was further subjected to preparative HPLC with MeOH–H_2O (80 : 20, v/v). The first eluate gave 20 mg (40%) of 2,3-dihydro-6-methoxy-4,7aβ-dimethyl-2β-nitromethyl-5(7a*H*)-benzo[*b*]furanone (**8a**) as a colorless oil. IR (oil) cm^{-1}: 1660, 1629, 1552. ^{1}H-NMR ($CDCl_3$) δ: 1.47 (3H, s, C7-Me), 1.88 (3H, d, J=1.8 Hz, C4-Me), 2.68 (1H, dd, J=17.3, 4.3 Hz, C3-H_α), 3.24 (1H, ddq, J=17.3, 8.5, 1.8 Hz, C3-H_β), 3.67 (3H, s, C6-OMe), 4.42 (1H, dd, J=12.6, 5.4 Hz, –CH–NO_2), 4.49 (1H, dd, J=12.6, 6.6 Hz, –CH–NO_2), 4.95—5.05 (1H, m, C2-H_β), 5.95 (1H, s, C7-H). HR-MS Calcd for $C_{12}H_{15}NO_5$: 253.0950. Found: 253.0992. MS *m/z*: 253 (M^+). The second eluate gave 15.9 mg (32%) of 2,3-dihydro-6-methoxy-4,7aα-dimethyl-2β-nitromethyl-5(7a*H*)-benzo[*b*]furanone (**9a**) as a colorless oil. IR (oil) cm^{-1}: 1659, 1628, 1551. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (3H, s, C7a-Me), 1.91 (3H, d, J=1.8 Hz, C4-Me), 2.86 (1H, ddq, J=15.6, 8.5, 1.8 Hz, C3-H_α), 3.09 (1H, dd, J=15.6, 6.7 Hz, C3-H_β), 3.66 (3H, s, C6-OMe), 4.59 (1H, dd, J=12.5, 5.2 Hz, –CH–NO_2), 4.67 (1H, dd, J=12.5, 7.3 Hz, –CH–NO_2), 4.82—4.93 (1H, m, C2-H_β), 5.95 (1H, s, C7-H). HR-MS Calcd for $C_{12}H_{15}NO_5$: 253.0950. Found: 253.0957. MS *m/z*: 253 (M^+).

Method B: With $Fe(bpy)_3(ClO_4)_3$ (Reagent B, Run 2): $Fe(bpy)_3(ClO_4)_3$ (380 mg, 0.43 mmol) was added under a nitrogen atmosphere to a solution of **5a** (51 mg, 0.2 mmol) in anhydrous CH_2Cl_2 (5 ml), and the whole was stirred at 0 °C for 30 min. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed with H_2O, then dried and concentrated. The residue was purified as described in method A to give 16 mg (32%) of **8a** and 4 mg (8.0%) of **9a**.

Oxidation of the Phenol (E-5b) Method A: With BAHA (Reagent

A, Run 3): Reaction of E-**5b** (48 mg, 0.1 mmol) was carried out at −20 °C for 5 min by the procedure described for the reaction of **5a** with BAHA (method A) to give a crude product (containing **8b**, and **9b**). This was further subjected to preparative HPLC with MeOH–H_2O (52 : 48, v/v). The first eluate gave 9.7 mg (20.3%) of 2,3-dihydro-6-methoxy-4,7aβ-dimethyl-2β-[1-nitro-2-(3-benzyloxy-4-methoxyphenyl)ethyl]-5(7a*H*)-benzo[*b*]furanone (**8b**) as a colorless oil. IR (oil) cm^{-1}: 1663, 1630, 1550, 1516. ^{1}H-NMR ($CDCl_3$) δ: 1.45 (3H, s, C7a-Me), 1.88 (3H, d, J = 1.5 Hz, C4-Me), 2.92 (1H, dd, J = 6.4, 15.6 Hz, C3-H$_\beta$), 3.02 (1H, ddq, J = 1.8, 9.2, 13.7 Hz, C3-H$_\alpha$), 3.22 (2H, d, J = 8.9 Hz, –C$\underline{H}_2$–CH–NO_2), 3.67 (3H, s, C6-OMe), 3.86 (3H, s, C4-OMe), 4.38—4.43 (1H, m, –CH–NO_2), 4.72—4.77 (1H, m, C2-H$_\beta$), 5.12 (2H, s, C$\underline{H}_2$–Ar), 5.94 (1H, s, C7-H), 6.69 (1H, d, J = 2.1 Hz, C2′-H), 6.72 (1H, dd, J = 2.1, 8.2 Hz, C6′-H), 6.83 (1H, d, J = 8.2 Hz, C5′-H), 7.28—7.43 (5H, m, Ar-H). HR-MS Calcd for $C_{27}H_{29}NO_7$: 479.1944. Found: 479.1374. MS *m/z*: 479 (M^+). The second eluate gave 8 mg (16.2%) of 2,3-dihydro-6-methoxy-4,7aα-dimethyl-2β-[1-nitro-2-(3-benzyloxy-4-methoxyphenyl)ethyl]-5(7a*H*)-benzobenzo[*b*]furanone (**9b**) as a colorless oil. IR (oil) cm^{-1}: 1661, 1630, 1591, 1553. ^{1}H-NMR ($CDCl_3$) δ: 1.43 (3H, s, C7a-Me), 1.84 (3H, d, J = 1.2 Hz, C4-Me), 2.72 (1H, dd, J = 4.0, 17.1 Hz, C3-H$_\alpha$), 3.02 (1H, m, C3-H$_\beta$), 3.18 (2H, d, J = 8.2 Hz, –C$\underline{H}_2$–CH–NO_2), 3.69, 3.85 (6H, each s, 2 × ArOMe), 4.52—4.60 (2H, m, C2-H$_\beta$ and –CH–NO_2), 5.11 (2H, s, C$\underline{H}_2$-Ar), 5.95 (1H, s, C7-H), 6.68 (1H, d, J = 2.1 Hz, C2′-H), 6.70 (1H, dd, J = 2.1, 7.9 Hz, C6′-H), 6.80 (1H, d, J = 7.9 Hz, C5′-H), 7.28—7.43 (5H, m, Ar-H). HR-MS Calcd for $C_{27}H_{29}NO_7$: 479.1944. Found: 479.1954. MS *m/z*: 479 (M^+).

Method B: With $Fe(bpy)_3(ClO_4)_3$ (Reagent B, Run 4): Reaction of E-**5b** (48 mg, 0.1 mmol) was carried out at 0 °C for 30 min by the procedure described for the reaction of **7a** with $Fe(bpy)_3(ClO_4)_3$ (method B) to give a crude product (containing **8b**, and **9b**). This was purified as described in method A above to give 6.2 mg (13%) of **8b** and 3 mg (6%) of **9b**.

Oxidation of the Phenol (6a) Method A: With BAHA (Reagent A, Run 5): Reaction of **6a** (25 mg, 0.14 mmol) was carried out at 0 °C for 30 min by the procedure described for the reaction of **5a** with BAHA (method A) to give a crude product. The crude product was purified by column chromatography on silica gel using AcOEt–hexane (1 : 4, v/v) as an eluent to give 35 mg (71.3%) of 2-*tert*-butyldimethylsilyloxy-1-(3,4-dihydro-3,4-dioxo-2,6-dimethylphenyl)-3-nitropropane (**10a**) as a yellow oil. IR (oil) cm^{-1}: 1680, 1656, 1555. ^{1}H-NMR ($CDCl_3$) δ: −0.06 and 0.06 (6H, each s, Si-Me_2), 0.83 (9H, s, Si-*tert*-Bu), 2.05 (3H, s, C2′-Me), 2.21 (1H, d, J = 1.5 Hz, C6′-Me), 2.71 (1H, dd, J = 14.7, 3.7 Hz, C1-H), 2.90 (1H, dd, J = 9.5, 14.7 Hz, C1-H), 4.40—4.46 (1H, m, C2-H), 4.48—4.53 (2H, m, C3-H), 6.22 (1H, s, C5′-H). MS *m/z*: 353 (M^+).

Method B: With $Fe(byp)_3(ClO_4)_3$ (Reagent B, Run 6): When **6a** was subjected to the procedure described for the reaction of **5a** with $Fe(bpy)_3(ClO_4)_3$ (method B) at 0 °C for 30 min, no reaction took place.

Oxidation of the Phenol (E-6b) Method A: With BAHA (Reagent A, Run 7): Reaction of E-**6b** (83 mg, 0.14 mmol) was carried out at 0 °C for 15 min by the procedure described for the reaction of **5a** with BAHA (method A) to give a crude product. Purification of the crude product by column chromatography on silica gel using AcOEt–hexane (1 : 5, v/v) as an eluent gave 22.7 mg (28%) of *erythro*-4-(3-benzyloxy-4-methoxyphenyl)-2-*tert*-butyldimethylsilyloxy-1-(3,4-dihydro-3,4-dioxo-2,6-dimethylphenyl)-3-nitropropane, (**10b**) as a yellow oil. IR (oil) cm^{-1}: 1680, 1654, 1550. ^{1}H-NMR ($CDCl_3$) δ: −0.19 and 0.02 (6H, each s, Si-Me_2), 0.83 (9H, s, Si-*tert*-Bu), 1.92 (3H, s, C2′-Me), 2.11 (3H, s, C6′-Me), 2.56—3.63 (4H, m, C1 and C4-H), 3.87 (3H, s, Ar-OMe), 4.12—4.25 (1H, m, C2-H), 4.69—4.84 (1H, m, C3-H), 5.13 (2H, s, C$\underline{H}_2$-Ar), 6.17 (1H, s, C5′-H), 6.69—6.82 (3H, m, Ar-H), 7.28—7.55 (5H, m, Ar-H). MS *m/z*: 579 (M^+)

Oxidation of the Phenolic Silyl Ether (7a) Method A: With BAHA (Reagent A, Run 8): Reaction of **7a** (48 mg, 0.10 mmol) was carried out at −20 °C for 5 min by the procedure described for the reaction of **5a** with BAHA (method A) to give 27 mg (76.7%) of **10a** and a trace of 2β-*tert*-butyldimethylsilyloxy-6-hydroxy-4,7aβ-dimethyl-1β-nitro-5(7a*H*)-indanone (**11**), as colorless crystals, mp 100.5—101.0 °C (ether–hexane). IR (KBr) cm^{-1}: 3404, 1665, 1635, 1549. ^{1}H-NMR ($CDCl_3$) δ: 0.12, (6H, s, Si-Me_2), 0.91 (9H, s, Si-*tert*-Bu), 1.59 (3H, s, C7a-Me), 1.92 (1H, d, J = 1.3 Hz, C4-Me), 2.78 (1H, ddq, J = 18.0, 3.3, 1.5 Hz, C3-H$_\alpha$), 3.38 (1H, dd, J = 18.0, 7.9 Hz, C3-H$_\beta$), 4.72 (1H, s, C1-H$_\alpha$), 4.82 (1H, dd, J = 3.6, 7.9 Hz, C2-H$_\beta$), 6.06 (1H, s, C7-H), 6.50 (1H, s, C6-OH). ^{13}C-NMR ($CDCl_3$) δ: −5.4 and −4.8 (OSi$\underline{Me}_2$), 17.8 (OSi-$\underline{C}$), 17.9 (C4-Me), 25.6 (OSi-*tert*-Bu), 28.0 (C7a-Me), 39.5 (C3), 50.0 (C7a), 75.1 (C2), 98.8 (C1), 114.1 (C7), 127.8 (C4), 147.4 (C3a), 164.7 (C6), 181.1 (C5). MS *m/z*: 353 (M^+). *Anal.* Calcd for $C_{17}H_{27}NO_5Si$: C, 57.76; H, 7.70; N, 3.96. Found: C, 57.78; H, 7.68; N, 3.98.

Method B: With $Fe(bpy)_3(ClO_4)_3$ (Reagent B, Run 9): When **7a** was subjected to the procedure described for the reaction of **5a** with $Fe(bpy)_3(ClO_4)_3$ (method B), no reaction took place.

Synthesis of 11 from 10a Silica gel powder (50 mg) from a TLC plate (Merck Kieselgel 60 F_{254}) was added to a solution of **10a** (25 mg, 0.071 mmol) in anhydrous benzene (5 ml), and the mixture was stirred at room temperature for 1 h. The precipitates were separated from the solution by filtration and the filtrate was concentrated. The residue was subjected to silica gel chromatography. The eluate with AcOEt–hexane (1 : 6, v/v) gave 17.8 mg (71.1%) of **11**.

Oxidation of the Phenolic Silyl Ether (E-7b) Method A: With BAHA in THF (Reagent A, Run 10): Reaction of E-**7b** (28 mg, 0.04 mmol) was carried out at −20 °C for 5 min by the procedure described for the reaction of **5a** with BAHA (method A) to give 18 mg (78.4%) of **10b**.

Method B: With $Fe(bpy)_3(ClO_4)_3$ in CH_2Cl_2 (Reagent B, Run 11): When E-**7b** was was subjected to the procedure described for the reaction of **5a** with $Fe(bpy)_3(ClO_4)_3$ (method B) for 20 h, no reaction took place.

Method C: With BAHA in CH_2Cl_2 (Reagent A, Run 12): Reaction of E-**7b** (50 mg, 0.07 mmol) in anhydrous CH_2Cl_2 instead of THF was carried out at −20 °C for 30 min by the procedure described for the reaction of **5a** with BAHA (method A) to give a crude product. Purification of the crude product by column chromatography on silica gel using benzene–acetone (10 : 1, v/v) as an eluent gave 7 mg (17%) of *cis*-10-benzyloxy-6-*tert*-butyldimethylsilyloxy-5,6,7,8-tetrahydro-3-hydroxy-4-methyl-2,11-dimethoxy-4-methyl-7-nitro-13*H*-dibenzo[*a*,*d*]-cyclononanene (**12**) as colorless crystals (ether–hexane), mp 181.0—181.5 °C. IR (KBr) cm^{-1}: 3534, 1547. ^{1}H-NMR ($CDCl_3$) δ: 0.04, 0.19 (6H, each s, Si-Me_2), 0.91 (9H, s, Si-*tert*-Bu), 2.31 (3H, s, C4-Me), 3.09 (1H, dd, J = 14.4, 6.1 Hz, C5-H$_\beta$), 3.36 (1H, dd, J = 14.4, 11.6 Hz, C5-H$_\alpha$), 3.49 (1H, dd, J = 16.8, 5.8 Hz, C8-H$_\alpha$), 3.54 (1H, d, J = 14.0 Hz, C13-H$_\alpha$), 3.61 (1H, d, J = 16.8 Hz, C8-H$_\beta$), 3.69—3.75 (1H, m, C6-H$_\alpha$), 3.83 (3H, s, C2-OMe), 3.92 (3H, s, C11-OMe), 4.30 (1H, d, J = 14.0 Hz, C13-H$_\beta$), 4.83 (1H, dd, J = 11.6, 5.8 Hz, C7-H$_\alpha$), 5.06 (2H, s, C$\underline{H}_2$-Ar), 5.62 (1H, s, Ar-OH), 6.71 (1H, s, C1-H), 6.82 (1H, s, C9-H), 6.95 (1H, s, C12-H), 7.27—7.43 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.3 and −4.3 (Si-$\underline{Me}_2$), 12.3 (C4-$\underline{Me}$), 17.9 (Si-$\underline{C}$), 25.6 (Si-*tert*-$\underline{Bu}$), 27.9 (C8), 35.1 (C5), 36.7 (C13), 55.6 (C2-O$\underline{Me}$, 56.6 (C11-O$\underline{Me}$), 71.0 (C$\underline{H}_2$-Ar), 74.3 (C3), 91.9 (C7), 109.8 (C1), 114.8 (C12), 116.0 (C9), 122.3, 125.0, 127.9, 128.5, 130.0, 130.5, 133.2, 136.9, 142.6, 145.2, 146.9 and 148.6 (each Ar-$\underline{C}$). HR-MS Calcd for $C_{33}H_{43}NO_7Si$: 593.2808. Found: 593.2815. MS *m/z*: 593 (M^+). *Anal.* Calcd for $C_{33}H_{43}NO_7Si$: C, 66.75; H, 7.30; N, 2.36. Found: C, 66.77; H, 7.30; N, 2.37.

Method D: With $Fe(bpy)_3(ClO_4)_3$ in MeOH (Reagent B, Run 13): Reaction of E-**7b** (7 mmg, 0.1 mmol) in anhydrous MeOH instead of CH_2Cl_2 was carried out at room temperature for 15 min by the procedure described for the reaction of **5a** with $Fe(bpy)_3(ClO_4)_3$ (method B) to give a crude product (containing **13**, and **14**). This was further subjected to preparative HPLC with MeOH–H_2O (40 : 60, v/v). The first eluate gave 20 mg (31.6%) of *erythro*-4-(3-benzyloxy-4-methoxyphenyl)-2-*tert*-butyldimethylsilyloxy-1-(3,6-dihydro-4-methoxy-2,6β-dimethyl-3-oxophenyl)-3-nitrobutane (**13**) as a colorless oil. IR (oil) cm^{-1}: 1653, 1623, 1549. ^{1}H-NMR ($CDCl_3$) δ: −0.12, 0.01 (6H, each s, Si-$\underline{Me}_2$), 0.88 (9H, s, Si-*tert*-Bu), 1.47 (3H, s, C6′-Me), 1.96 (3H, s, C2′-Me), 2.56 (1H, dd, J = 14.4, 4.6 Hz, C1-H), 2.86 (1H, dd, J = 14.4, 9.5 Hz, C1-H), 3.03 (1H, s, C6′-OMe), 3.05 (1H, dd, J = 14.9, 4.3 Hz, C4-H), 3.34 (1H, dd, J = 14.9, 10.1 Hz, C4-H), 3.70 (3H, s, C4″-OMe), 3.87 (3H, s, C4′-OMe), 4.53—4.57 (1H, m, C2-H), 4.67—4.71 (1H, m, C3-H), 5.13 (2H, s, C$\underline{H}_2$-Ar), 5.65 (1H, s, C5′-H), 6.73 (1H, d, J = 1.7 Hz, C2″-H), 6.76 (1H, dd, J = 8.2, 1.7 Hz, C6″-H), 6.83 (1H, d, J = 8.2 Hz, C5″-H), 7.29—7.44 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.1 and −3.8 (Si-$\underline{Me}_2$), 12.8 (C2′-$\underline{Me}$), 18.0 (Si-$\underline{C}$), 25.9 (Si-*tert*-$\underline{Bu}$), 27.1 (C6′-$\underline{Me}$), 32.6 (C1), 33.9 (C4), 51.7 (C6′-O$\underline{Me}$), 55.0 (C4″-O$\underline{Me}$), 56.0 (C4′-O$\underline{Me}$), 71.1 (C$\underline{H}_2$-Ar), 71.7 (C2), 93.9 (C3), 112.0 (C5″), 114.8 (C2″), 117.2 (C5′), 121.5 (C6″), 127.3, 127.8, 128.0, 128.6, 148.3, 149.0, 150.5 and 152.1 (each Ar-$\underline{C}$), 180.8 (C′3). HR-MS Calcd for $C_{34}H_{47}NO_8Si$: 625.3070. Found: 625.3089. MS *m/z*: 625 (M^+).

The second eluate gave 21.4 mg (34.3%) of *erythro*-4-(3-benzyloxy-4-methoxyphenyl)-2-*tert*-butyldimethylsilyloxy-1-(3,6-dihydro-4-methoxy-2,6α-dimethyl-3-oxophenyl)-3-nitrobutane (**14**) as a colorless oil. IR (oil) cm^{-1}: 1653, 1620, 1549. ^{1}H-NMR ($CDCl_3$) δ: −0.01, 0.02 (6H, each s, Si-Me_2), 0.90 (9H, s, Si-*tert*-Bu), 1.44 (3H, s, C6′-Me), 1.97 (3H, s,

C2′-Me), 2.72 (1H, dd, J=14.0, 6.4 Hz, C4-H), 2.79 (1H, dd, J=14.0, 8.8 Hz, C4-H), 3.01 (1H, s, C6′-OMe), 3.04 (1H, dd, J=15.3, 4.9 Hz, C1-H), 3.40 (1H, dd, J=15.3, 10.1, Hz, C1-H), 3.70 (1H, s, C4″-OMe), 3.86 (3H, s, C4′-OMe), 4.48—4.52 (1H, m, C2-H), 4.62—4.64 (1H, m, C3-H), 5.13 (2H, s, C$\underline{H}_2$-Ar), 5.53 (1H, s, C5′-H), 6.71 (1H, d, J=2.1 Hz, C2″-H), 6.74 (1H, dd, J=8.2, 2.1 Hz, C6″-H), 6.83 (1H, d, J=8.2 Hz, C5″-H), 7.28—7.43 (5H, m, Ar-H). ^{13}C-NMR ($CDCl_3$) δ: −5.3 and −3.9 (Si-$\underline{Me}_2$), 13.2 (C2′-$\underline{Me}$), 18.0 (Si-$\underline{C}$), 25.9 (Si-*tert*-$\underline{Bu}$), 27.4 (C6′-$\underline{Me}$), 32.4 (C1), 33.5 (C4), 51.7 (C6′-O$\underline{Me}$), 55.0 (C4″-O$\underline{Me}$), 56.0 (C4′-O$\underline{Me}$), 71.1 ($\underline{C}H_2$-Ar), 72.7 (C2), 93.5 (C3), 112.1 (C5″), 114.8 (C2″), 117.2 (C5′), 121.4 (C6″), 127.3, 127.9, 128.6, 148.3, 149.0, 137.9, 148.3, 149.0, 149.7, 150.5 and 150.9 (each Ar-$\underline{C}$), 180.8 (C′3). HR-MS Calcd for $C_{34}H_{47}NO_8Si$: 625.3070. Found: 625.3114. MS m/z: 625 (M^+).

References

1) *a*) Fujita S., *Yuki Gosei Kagaku Kyokai Shi*, **40**, 307—320 (1982); *b*) Swenton J. S., *Acc. Chem. Res.*, **16**, 74—80 (1983).
2) Takeya T., Yamaki S., Itoh T., Hosogai H., Tobinaga S., *Chem. Pharm. Bull.*, **44**, 909—918 (1996).
3) *a*) Bell F. A., Ledwith A., Sherrington D. C., *J. Chem. Soc.*, (*C*), **1969**, 2719—2720; *b*) Kricka L., Ledwith A., *J. Chem. Soc., Perkin Trans. 1*, **1973**, 294—297; *c*) Schmidt W., Steckham E., *Angew. Chem. Int. Ed. Engl.*, **17**, 673—674 (1978); *d*) Bellville D. J., Wirth D. D., Bauld N. L., *ibid.*, **103**, 718—720 (1981); *e*) Pabon R. A., Bellville D. J., Bauld N. L., *ibid.*, **106**, 2730—2731 (1984); *f*) Kluge R., Sivilai L., Kamm B., *Tetrahedron*, **46**, 2371—2380 (1990); *g*) Bauld N. L., Mirafzal G. A., *J. Am. Chem. Soc.*, **113**, 3613—3614 (1991); *h*) Mirafzal H., Liu A., Bauld J. N. L., *ibid.*, **115**, 6072—6077 (1993); *i*) Schulz M., Dhanalekshmi S., Venkatachalam C. S., Balasubramanian K. K., *J. Chem. Soc., Chem. Commun.*, **1994**, 511—512; *j*) Takeya T., Ara Y., Tobinaga S., *Chem. Pharm. Bull.*, **43**, 1970—1976 (1995); *k*) *idem*, *ibid.*, **43**, 1977—1984 (1995).
4) *a*) Kupchan S. M., Britton R. W., Lacadie J. A., Ziegler M. F., Sigel C. W., *J. Org. Chem.*, **40**, 648—652 (1975); *b*) Polonsky J., "Progress in the Chemistry of Organic Natural Products," Vol. 47, ed. by Springer-Verlag, Berlin, 1985, pp. 221—264.
5) *a*) Zakharkin L. I., Khorlina I. M., *Tetrahedron Lett.*, **14**, 619—623 (1962); *b*) Mandel L., Lee D. E., Courtney L. F., *J. Org. Chem.*, **47**, 610—615 (1982).
6) *a*) Seebach D., Leher F., *Angew. Chem. Int. Ed. Engl.*, **15**, 505—511 (1976); *b*) Wollenberg R. H., Miller S. J., *Tetrahedron Lett.*, **35**, 3219—3223 (1976); *c*) Gilbert B. C., Norman R. O. C., *J. Chem. Soc.*, **60**, 1379—1385 (1982); *d*) Rosini G., Ballini R., *Synthesis*, **1988**, 833—847; *e*) Rosini G., Trost B. M., Fleming I., "Comprehensive Organic Synthesis," Vol. 2, ed. by Heathcock C. H., Pergamon Press, Oxford, 1991, pp. 239—275.
7) 1-(3-Benzyloxy-4-methoxyphenyl)-3-nitropropane was synthesized by reduction with $NaBH_4$ in the presence of silica gel from the corresponding nitrostyrene, which was prepared by the condensation of benzylisovanillin and nitroethane with ethylenediammonium diacetate.
8) T-**5b** was not purified from the mixture of E-**5b** and T-**5b**.
9) *a*) Collington E. W., Finch H., Smith I. J., *Tetrahedon Lett.*, **26**, 681—684 (1985); *b*) Schimittling E. A., Sawyer J. S., *Tetrahedon Lett.*, **32**, 7207—7210 (1991).
10) Murase M., Kotani E., Okazaki K., Tobinaga S., *Chem. Pharm. Bull.*, **31**, 3159—3162 (1986).
11) *a*) Yoshida J., Maekawa T., Murata T., Matsunaga S., *J. Am. Chem. Soc.*, **112**, 1962—1970 (1990); *b*) Yoshida J., *Yuki Gosei Kagaku Kyokai Shi*, **53**, 53—63 (1995).