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 *Simaroubaceae* 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, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ [CAN], $\text{Pb}(\text{OAc})_4$, 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 oxygenated triterpenes which were isolated as bitter principles from *Simaroubaceae* 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. Diisobutylaluminum hydride (DIBAL) effected selective reduction of the ester group of **3** to afford the corresponding aldehyde **4** in 85% yield. The nitro-Aldol reaction⁶⁾ 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-nitropropane⁷⁾ 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 ₂ Cl ₂	0	8a (32%) + 9a (8%)
3	E-5b	A	THF	0	8b (20%) + 9b (16%)
4	E-5b	B	CH ₂ Cl ₂	0	8b (13%) + 9b (6%)
5	6a	A	THF	0	10a (71%)
6	6a	B	CH ₂ Cl 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 ₂ Cl ₂	0	No reaction
10	E-7b	A	THF	-20	10b (78%)
11	E-7b	B	CH ₂ Cl ₂	r.t.	No reaction
12	E-7b	A	CH ₂ Cl 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-5b⁸⁾ 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 C₆-OSi-*tert*-BuMe₂ (TBDMS) group and C₇-NO₂ 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*-Bu₄N⁺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 Na₂CO₃ 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:H₂O = 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, $Fe(bpy)_3(ClO_4)_3$, in methylene chloride (CH₂Cl₂)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 corresponding *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 F₂₅₄) 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 ¹H-NMR spectrum as compared with the signal of C₆-Me (δ 2.27) in **7a**. This suggests that C_{7a}-Me is the aliphatic-Me group. (iii) The signal of C₄-Me (δ 1.92) was observed as doublet because of homoallyl coupling (long-range coupling) between C₄-Me and C₃-H α . 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 C₃-H β was observed, but the proton signal of C₃-H α was not enhanced, (ii) similarly, when the signal of C₃-H β at δ 3.38 was irradiated, the signal of C₂-H β at δ 4.82 was increased by 6.9%, (iii) upon irradiation of the signal of C₇-H at δ 6.06, a 5.4% increment of C₁-H α 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(ClO₄)₃ using CH₂Cl₂ as the solvent, the corresponding *ortho*-quinones could not be obtained. Oxidation of E-**7b** with BAHA using CH₂Cl₂ 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(ClO₄)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 ¹H- and ¹³C-NMR spectra, with the aid of ¹H-¹³C shift correlation spectroscopy (¹H-¹³C 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 ¹H-NMR spectrum of **12**; (ii) the signal of C₆-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 C₁₃-H α and -H β 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 C₅-H α and C₆-H α , C₆-H β and C₇-H α , C₅-H β and C₆-H α , C₇-H α and C₈-H α , and C₇-H α and C₈-H β of **12** may be about 180°, 45°, 0°, 30°, and 90°, based on the values of the corresponding coupling constants, $J_{C_5-H\alpha, C_6-H\alpha} = 11.6$ Hz, $J_{C_5-H\beta, C_6-H\alpha} = 6.1$ Hz, $J_{C_6-H\alpha, C_7-H\alpha} = 11.6$ Hz, $J_{C_7-H\alpha, C_8-H\alpha} = 5.8$ Hz, and $J_{C_7-H\alpha, C_8-H\beta} = 0$ 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 C₇-OSi-*tert*-BuMe₂ group and C₈-NO₂ group adopt *cis* relative configuration.

The formations of **10b**, **12**, **13**, and **14** from E-**7b** by oxidation with BAHA or Fe(bipy)₃(ClO₄)₃ can be explained as follows (Chart 3): Compound E-**7b** undergoes one-electron oxidation with BAHA or Fe(byp)₃(ClO₄)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 (H₂O) 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 CH₂Cl₂ 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 $\text{Fe}(\text{bipy})_3(\text{ClO}_4)_3$ 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 ^1H - 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 $\times$ 4.6 mm i.d. for analytical scale or 25 cm $\times$ 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. ^1H -NMR (CDCl_3) δ : 0.15 (6H, s, Si-Me₂), 1.00 (9H, s, Si-*tert*-Bu), 2.20, 2.26 (6H, each s, 2 $\times$ Ar-Me), 3.61 (2H, s, Ar-CH₂), 3.66 (3H, s, CO₂Me), 3.75 (3H, s, OMe), 6.54 (1H, s, Ar-H). HR-MS Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4\text{Si}$: 338.1913. Found: 338.1924. Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{O}_4\text{Si}$: 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 ammonium 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. ^1H -NMR (CDCl_3) δ : 0.16 (6H, s, Si-Me₂), 1.00 (9H, s, Si-*tert*-Bu), 2.17, 2.87 (6H, each s, 2 $\times$ Ar-Me), 3.65 (2H, d, $J=2.2$ Hz, Ar-CH₂), 3.76 (3H, s, Ar-OMe), 6.58 (1H, s, Ar-H), 9.59 (1H, t, $J=2.2$ Hz, ArCH₂–CHO). HR-MS Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{Si}$: 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. ^1H -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 recrystallized 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. 1H -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, $2 \times$ Ar-OMe), 4.21–4.17 (1H, m, C2-H), 4.67–4.72 (1H, m, C3-H), 5.12 (2H, s, OCH_2 -Ar), 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 (C2'), 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. 1H -NMR ($CDCl_3$) δ : -0.10, -0.02 (6H, each s, C2-SiMe₂), 0.15, 1.00 (9H, s, C3'-OSi-*tert*-Bu), 0.16 (6H, each s, C3'-OSiMe₂), 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-OSiMe₂), -4.0 and -3.9 (C3'-OSiMe₂), 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. 1H -NMR ($CDCl_3$) δ : -0.59, -0.52 (6H, each s, C2-OSiMe₂), 0.13, 0.15 (6H, each s, C3'-OSiMe₂), 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, $2 \times$ 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-OSiMe₂), -4.01 and -3.98 (C3'-OSiMe₂), 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. 1H -NMR ($CDCl_3$) δ : -0.09, -0.01 (6H, each s, C2-OSiMe₂), 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-OSiMe₂), 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. 1H -NMR ($CDCl_3$) δ : -0.58, -0.51 (6H, each s, C2-OSiMe₂), 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, $2 \times$ 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-OSiMe₂), 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-4,7a β -dimethyl-2 β -nitromethyl-5(7aH)-benzo[b]furanone (**8a**) as a colorless oil. IR (oil) cm^{-1} : 1660, 1629, 1552. 1H -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_a), 3.24 (1H, ddq, $J=17.3$, 8.5, 1.8 Hz, C3-H_b), 3.67 (3H, s, C6-OMe), 4.42 (1H, dd, $J=12.6$, 5.4 Hz, -CH-NO₂), 4.49 (1H, dd, $J=12.6$, 6.6 Hz, -CH-NO₂), 4.95–5.05 (1H, m, C2-H_a), 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-4,7a α -dimethyl-2 β -nitromethyl-5(7aH)-benzo[b]furanone (**9a**) as a colorless oil. IR (oil) cm^{-1} : 1659, 1628, 1551. 1H -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_a), 3.09 (1H, dd, $J=15.6$, 6.7 Hz, C3-H_b), 3.66 (3H, s, C6-OMe), 4.59 (1H, dd, $J=12.5$, 5.2 Hz, -CH-NO₂), 4.67 (1H, dd, $J=12.5$, 7.3 Hz, -CH-NO₂), 4.82–4.93 (1H, m, C2-H_a), 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(ClO₄)₃ (Reagent B, Run 2): Fe(bpy)₃(ClO₄)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–H₂O (52:48, v/v). The first eluate gave 9.7 mg (20.3%) of 2,3-dihydro-6-methoxy-4,7a β -dimethyl-2 β -[1-nitro-2-(3-benzyloxy-4-methoxyphenyl)ethyl]-5(7aH)-benzo[*b*]furanone (**8b**) as a colorless oil. IR (oil) cm^{-1} : 1663, 1630, 1550, 1516. $^1\text{H-NMR}$ (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, $-\text{CH}_2-\text{CH}-\text{NO}_2$), 3.67 (3H, s, C6-OMe), 3.86 (3H, s, C4-OMe), 4.38–4.43 (1H, m, $-\text{CH}-\text{NO}_2$), 4.72–4.77 (1H, m, C2-H $_{\beta}$), 5.12 (2H, s, CH_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 C₂₇H₂₉NO₇: 479.1944. Found: 479.1374. MS m/z : 479 (M^+). The second eluate gave 8 mg (16.2%) of 2,3-dihydro-6-methoxy-4,7a α -dimethyl-2 β -[1-nitro-2-(3-benzyloxy-4-methoxyphenyl)ethyl]-5(7aH)-benzobenzofuranone (**9b**) as a colorless oil. IR (oil) cm^{-1} : 1661, 1630, 1591, 1553. $^1\text{H-NMR}$ (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, $-\text{CH}_2-\text{CH}-\text{NO}_2$), 3.69, 3.85 (6H, each s, 2 $\times$ ArOMe), 4.52–4.60 (2H, m, C2-H $_{\beta}$ and $-\text{CH}-\text{NO}_2$), 5.11 (2H, s, CH_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 C₂₇H₂₉NO₇: 479.1944. Found: 479.1954. MS m/z : 479 (M^+).

Method B: With Fe(bpy)₃(ClO₄)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(ClO₄)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. $^1\text{H-NMR}$ (CDCl_3) δ : -0.06 and 0.06 (6H, each s, Si-Me₂), 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(bpy)₃(ClO₄)₃ (Reagent B, Run 6): When **6a** was subjected to the procedure described for the reaction of **5a** with Fe(bpy)₃(ClO₄)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. $^1\text{H-NMR}$ (CDCl_3) δ : -0.19 and 0.02 (6H, each s, Si-Me₂), 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, CH_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 2 β -*tert*-butyldimethylsilyloxy-6-hydroxy-4,7a β -dimethyl-1 β -nitro-5(7aH)-indanone (**11**), as colorless crystals, mp 100.5 – 101.0°C (ether–hexane). IR (KBr) cm^{-1} : 3404, 1665, 1635, 1549. $^1\text{H-NMR}$ (CDCl_3) δ : 0.12, (6H, s, Si-Me₂), 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). $^{13}\text{C-NMR}$ (CDCl_3) δ : -5.4 and -4.8 (OSi-Me₂), 17.8 (OSi-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 C₁₇H₂₇NO₅Si: 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(ClO₄)₃ (Reagent B, Run 9): When **7a** was subjected to the procedure described for the reaction of **5a** with Fe(bpy)₃(ClO₄)₃ (method B), no reaction took place.

Synthesis of 11 from 10a Silica gel powder (50 mg) from a TLC plate (Merck Kieselgel 60 F₂₅₄) 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(ClO₄)₃ in CH₂Cl₂ (Reagent B, Run 11): When E-**7b** was subjected to the procedure described for the reaction of **5a** with Fe(bpy)₃(ClO₄)₃ (method B) for 20 h, no reaction took place.

Method C: With BAHA in CH₂Cl₂ (Reagent A, Run 12): Reaction of E-**7b** (50 mg, 0.07 mmol) in anhydrous CH₂Cl₂ 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-13H-dibenzo[*a, d*]-cyclononane (**12**) as colorless crystals (ether–hexane), mp 181.0 – 181.5°C . IR (KBr) cm^{-1} : 3534, 1547. $^1\text{H-NMR}$ (CDCl_3) δ : 0.04, 0.19 (6H, each s, Si-Me₂), 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, CH_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). $^{13}\text{C-NMR}$ (CDCl_3) δ : -5.3 and -4.3 (Si-Me₂), 12.3 (C4-Me), 17.9 (Si-C), 25.6 (Si-*tert*-Bu), 27.9 (C8), 35.1 (C5), 36.7 (C13), 55.6 (C2-OMe), 56.6 (C11-OMe), 71.0 (CH_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-C). HR-MS Calcd for C₃₃H₄₃NO₇Si: 593.2808. Found: 593.2815. MS m/z : 593 (M^+). Anal. Calcd for C₃₃H₄₃NO₇Si: 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(ClO₄)₃ in MeOH (Reagent B, Run 13): Reaction of E-**7b** (7 mmg, 0.1 mmol) in anhydrous MeOH instead of CH₂Cl₂ was carried out at room temperature for 15 min by the procedure described for the reaction of **5a** with Fe(bpy)₃(ClO₄)₃ (method B) to give a crude product (containing **13**, and **14**). This was further subjected to preparative HPLC with MeOH–H₂O (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-2,6 β -dimethyl-3-oxophenyl)-3-nitrobutane (**13**) as a colorless oil. IR (oil) cm^{-1} : 1653, 1623, 1549. $^1\text{H-NMR}$ (CDCl_3) δ : -0.12 , 0.01 (6H, each s, Si-Me₂), 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, CH_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). $^{13}\text{C-NMR}$ (CDCl_3) δ : -5.1 and -3.8 (Si-Me₂), 12.8 (C2'-Me), 18.0 (Si-C), 25.9 (Si-*tert*-Bu), 27.1 (C6'-Me), 32.6 (C1), 33.9 (C4), 51.7 (C6'-OMe), 55.0 (C4'-OMe), 56.0 (C4'-OMe), 71.1 (CH_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-C). HR-MS Calcd for C₃₄H₄₇NO₈Si: 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-2,6 α -dimethyl-3-oxophenyl)-3-nitrobutane (**14**) as a colorless oil. IR (oil) cm^{-1} : 1653, 1620, 1549. $^1\text{H-NMR}$ (CDCl_3) δ : -0.01 , 0.02 (6H, each s, Si-Me₂), 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, CH₂-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). ¹³C-NMR (CDCl₃) δ : -5.3 and -3.9 (Si-Me₂), 13.2 (C2'-Me), 18.0 (Si-C), 25.9 (Si-tert-Bu), 27.4 (C6'-Me), 32.4 (C1), 33.5 (C4), 51.7 (C6'-OMe), 55.0 (C4''-OMe), 56.0 (C4'-OMe), 71.1 (CH₂-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-C), 180.8 (C'3). HR-MS Calcd for C₃₄H₄₇NO₈Si: 625.3070. Found: 625.3114. MS m/z : 625 (M⁺).

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