SELECTIVE SYNTHESIS OF BENZYL ENOL ETHERS OF β-DICARBONYL COMPOUNDS IN BASIC CONDITION AND THE APPLICATION TOWARDS SYNTHESIS OF NAPHTHOQUINONES†

Kazuaki Katakawa, Dai Yonenaga, Tomoyo Terada, Naoya Aida, Airi Sakamoto, Keishi Hoshino, and Takuya Kumamoto*

Department of Organic Synthetic Chemistry, Research Institute of Pharmaceutical Sciences, Musashino University, 1-1-20, Shinmachi, Nishitokyo-city, Tokyo 202-8585, Japan. e-mail: t_kum632@musashino-u.ac.jp

Abstract – Selective synthesis of benzyl enol ether of β-tetronic acids and β-dicarbonyl compounds in basic condition was examined. Benzylation of α-methyl-β-tetronic acid with benzyl tosylate in the presence of potassium carbonate gave the corresponding benzyl enol ether exclusively. The reaction of β-tetronic acid and cyclic 1,3-diketones gave the O-benzyl adducts preferentially than the C,O-dibenzylated ones. Diels-Alder reaction of furan derived the benzyl enol ether of α-methyl-β-tetronic acid and benzyne furnished the functionalized napthoquinone derivatives.

Enol ethers of β-tetronic acids (4-O-alkyl β-tetronates) 1 are versatile building blocks in natural product synthesis and medicinal chemistry (Figure 1).1 Synthesis of these compounds is normally achieved by treating β-tetronic acids 2 and alcohols in the presence of acid catalyst.2 Mitsunobu reaction condition3 and alkylation in basic condition4 are another candidates and can be applicable to acid-sensitive substrates. The drawback of these conditions is the selectivity of C- / O-alkylation, in which C-alkylated 3 (or C,O-dialkylated 4) β-dicarbonyl compounds can be generated in this reaction system. For example, CsF-mediated O-selective alkylation of tetronic acid was achieved in high selectivity with alkyl halides with low reactivity such as ethyl iodide, however, low selectivity was observed when more reactive alkyl halide such as benzyl bromide was utilized.4b As a part of our projects of synthetic studies of natural products including naphthoquinones such as teretifoliones B (5),5 we have planned construction of oxygen-

† This article is dedicated to Professor Victor Snieckus on the occasion of his 77th birthday.
functionalized naphthoquinones via Diels-Alder reaction (DAR) of furans from enol ethers of β-tetronic acids and benzyne. In this report, we wish to report the selective synthesis of benzyl enol ethers of β-tetronic acids and some β-diketones in basic condition and the application of the benzyl enol ether to naphthoquinone synthesis via DAR with benzyne.

![Structures of β-tetronic acid derivatives 1-4 and teretifoliones B (5)](image)

Figure 1. Structures of β-tetronic acid derivatives 1-4 and teretifoliones B (5)

At first, benzylation of α-methyl-β-tetronic acid (6) was examined. Treatment of 6 and benzyl bromide in the presence of potassium carbonate as a base in N,N-dimethylformamide (DMF) gave a complex mixture including desired 7, which was isolated in 22% after purification (Table 1, run 1). Utilization of cesium carbonate instead of potassium carbonate gave similar result (run 2). Reactions with cesium fluoride and benzyl bromide or chloride afforded a mixture of 7 and undesired C-benzylated product 8.

### Table 1. Benzylation of α-methyl-β-tetronic acid (6) in basic condition

<table>
<thead>
<tr>
<th>run</th>
<th>X in BnX (eq)</th>
<th>base (eq)</th>
<th>7 : 8&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Isolated 7 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br (1.0)</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (2.0)</td>
<td>many spots</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Br (1.0)</td>
<td>Cs&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (2.0)</td>
<td>many spots</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>Br (1.0)</td>
<td>CsF (2.0)</td>
<td>1 : 2</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Cl (1.0)</td>
<td>CsF (2.0)</td>
<td>1 : 1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>OTs (1.0)</td>
<td>CsF (2.0)</td>
<td>3 : 1</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>OTs (1.0)</td>
<td>Cs&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (2.0)</td>
<td>1 : 0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>OTs (1.0)</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (2.0)</td>
<td>1 : 0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>OTs (1.5)</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt; (3.0)</td>
<td>1 : 0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>86</td>
</tr>
</tbody>
</table>

<sup>a</sup> Estimated from integration of <sup>1</sup>H-NMR of the crude products.  <sup>b</sup> 8 was not observed in <sup>1</sup>H-NMR of the crude products.
in low selectivity (runs 3 and 4). Benzyl tosylate (BnOTs, 9), prepared from benzyl alcohol and tosyl chloride in solvent-free condition\(^8\) was applied to this reaction and the ratio of 7 and 8 was improved to 3 : 1. 7 was isolated in 48% yield (run 5). Reaction with cesium and potassium carbonates gave 7 exclusively. 8 was not observed in \(^1\)H-NMR of crude product (runs 6 and 7). Reaction with increased amounts of both reagents benzyl tosylate and potassium carbonate gave 7 in 86% as isolated yield (run 8).

Benzylaion of other \(\beta\)-dicarboxyl compounds was examined. Benzylaion of \(\beta\)-tetronic acid (10a) gave the corresponding \(O\)-benzylated product 11a exclusively with small amount of \(C,O\)-dibenzylation one 12a, generated through the reaction of initial \(C\)-benzylation followed by \(O\)-benzylation. Generation of \(C,C\)-dibenzylation product 13 was not observed (Table 2, run 1). BnOTs (9) prepared in solution phase with modified reported procedure\(^9\) gave similar result (run 2). Reaction of cyclopentane-1,3-dione (10b) gave a mixture of \(O\)-benzylated 11b and \(C,O\)-dibenzylation products 12b in the same ratio as 10a (run 3), however, the selectivity was decreased to 5 : 1 in the case of cyclohexane-1,3-dione (10c) (run 4). Trial for the benzylaion of Merdrum’s acid (14) gave only \(C,C\)-dibenzylation product (data not shown).\(^{10}\)

Table 2. Benzylaion of \(\beta\)-dicarboxyl compounds 10 with BnOTs (9)\(^a\)

<table>
<thead>
<tr>
<th>run</th>
<th>substrate</th>
<th>11 : 12(^b)</th>
<th>Isolated 11 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10a</td>
<td>15 : 1</td>
<td>72</td>
</tr>
<tr>
<td>2(^c)</td>
<td>10a</td>
<td>15 : 1</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>10b</td>
<td>15 : 1</td>
<td>59</td>
</tr>
<tr>
<td>4</td>
<td>10c</td>
<td>5 : 1</td>
<td>52</td>
</tr>
</tbody>
</table>

\(^a\) 9 (1.5 eq) and \(K_2CO_3\) (3.0 eq) was used otherwise noted. \(^b\) Estimated from integration of \(^1\)H-NMR of the crude products. \(^c\) 9 (2.0 eq) prepared in solution phase was used.

Benzyl enol ether of \(\alpha\)-methyl-\(\beta\)-tetronic acid 7 was applied to naphthoquinone synthesis (Scheme 1). Furanone 7 was converted to furan 15,\(^{11}\) which were reacted with benzyne (17) in situ prepared from iodo triflate 14\(^{12}\) and \(n\)-butyllitium to give epoxynaphthalene 19, which has decomposed in the course of aqueous workup to give benzyloxynaphthoquinone 20\(^{13}\) in 32% yield from 7. DAR of furan 16 and benzyne (17) in the same manner gave naphthol 22 through epoxynaphthalene 21 in 46% isolated yield. Treatment of crude 22 with tetrabutylammonium fluoride (TBAF) gave 20 in 43% from 16. Oxidation of crude 22 with aqueous iron (III) chloride in methanol\(^{14}\) gave 20 and hydroxynaphthoquinone 23\(^{15}\) in 37% and 12% yields, respectively.
Scheme 1. Synthesis of napthoquinones 20 and 23. Conditions: (a) 1) n-BuLi, THF, -78 - -40 °C; 2) TMSCl, -40 - 0 °C, (b) TIPSOTf, Et3N, CH2Cl2, 0 °C, 1 h (62%), (c) n-BuLi, -78 C, 45 min, (d) workup (20: 32%); (e) TBAF, THF, 1 h, rt (20: 43%), (f) aq FeCl3, methanol, rt, 1.5 h (20: 37%, 23: 12%).

In summary, synthesis of benzyl enol ether of β-tetronic acids with O-selective benzyla- tion in basic condition was achieved by utilization of benzyl tosylate and potassium carbonate. Other β-dicarbonyl compounds were also O-benzylated selectively in this condition except Merdrum’s acid. Application of the enol ether of β-tetronic acid to DAR with bezyne gave desired functionalized naphthoquinones in moderate yield. Further research to improve the yield of DAR and synthetic studies towards naphthoquinone natural products with modified benzyne are now in progress.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point hot-stage instrument and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer with Attenuated Total Reflectance Unit ATR PRO450-S. 1H- (400 MHz) and 13C-NMR (100 MHz) spectra were recorded with JEOL JNM ECX 400 spectrometer with deuterated chloroform as a solvent and tetramethylsilane as an internal reference. EIMS was recorded on a JEOL GC-Mate II. Anhydrous CH2Cl2, DMF were purchased and THF was used as received as a gift from Wako Chemicals. TMSCl was used after distillation from CaH2.

Benzyl tosylate (9)

(Synthesis in solvent-free condition) A mixture of tosyl chloride (2.8 g, 15 mmol) and K2CO3 (9.2 g, 67 mmol) was ground in mortar under N2 atmosphere. Benzyl alcohol (2.8 g, 15 mmol) was added portionwise and the mixture was ground for further 1 h. Et2O (100 mL) was added and the mixture was filtered through a pad of Celite®. The filtrate was washed with ice-water (1 x 10 mL) and brine (1 x 10 mL) and dried over Na2SO4 in refrigerator. The solvent was evaporated in vacuo and the residue was
washed with hexane - Et2O (1 : 4) to give 9 (2.1 g, 54%) as colorless needles. 

mp 57-58 °C. IR no characteristic absorption. 1H-NMR δ (ppm) 2.44 (3H, s, CH3), 5.06 (2H, s, CH2), 7.23-7.30 (2H, m, Ar-H), 7.30-7.34 (5H, m, Ar-H), 7.80 (2H, d, J = 8.2 Hz, Ar-H).

(Synthesis in solution phase) To a solution of benzyl alcohol (0.1 mL, 1.00 mmol), Et3N (0.22 mL, 1.58 mmol), DMAP (30 mg, 0.25 mmol) in CH2Cl2 (5 mL), a solution of tosyl chloride (286 mg, 1.50 mmol) in CH2Cl2 (5 mL) was added at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was washed with H2O (1 x 10 mL), saturated aqueous NaHCO3 (2 x 10 mL), and brine (1 x 2 mL) and dried over Na2SO4. The solvent was evaporated in vacuo to give 9 (294 mg, 78%) as a colorless oil.

4-Benzylxylo-3-methyl-5H-furan-2-one (7)
Under N2 atmosphere, DMF (1.8 mL) was added to a mixture of 6 (101 mg, 0.88 mmol), 9 (345 mg, 1.31 mmol), prepared in solvent-free condition, and K2CO3 (365 mg, 2.64 mmol) at rt and the reaction mixture was stirred at rt for 24 h. H2O (1.0 mL) was added and the whole was extracted with AcOEt (3 x 10 mL). The combined organic layer was washed with saturated aqueous NH4Cl, H2O, saturated aqueous NaHCO3, and brine (each 1 x 1 mL), and dried over Na2SO4. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (CC) (SiO2, hexane – AcOEt 4 : 1) to give 7 as pale yellow solids (154 mg, 86%).

mp 111-112 °C (from hexane – AcOEt = 1 : 1). IR νmax (cm⁻¹) 1727, 1650. 1H-NMR δ (ppm) 1.86 (3H, t, J = 1.5 Hz, CH3), 4.63 (2H, q, J = 1.5 Hz, CH2), 5.22 (2H, s, CH2), 7.34-7.45 (5H, m, Ar-H). 13C-NMR δ (ppm) 7.4, 66.0, 72.3, 99.6, 127.3, 129.0, 135.0, 171.2, 175.2 (one C missing). HR-EIMS m/z 204.0773 (Calcd for C12H12O3: 204.0787).

3-Benzyl-3-methylfuran-2,4-dione (8)
A colorless oil. IR νmax (cm⁻¹) 1749. 1H-NMR δ (ppm) 1.43 (3H, s, CH3), 3.04 (1H, d, J = 13.1 Hz, CH2), 3.13 (1H, d, J = 13.1 Hz, CH2), 3.64 (1H, d, J = 17.2 Hz, CH2), 4.36 (1H, d, J = 17.2 Hz, CH2), 7.10-7.13 (2H, m, Ar-H), 7.23-7.30 (3H, m, Ar-H). 13C-NMR δ (ppm) 19.9, 43.0, 51.0, 72.7, 127.9, 128.9, 129.4, 134.3, 176.9, 210.6. HR-EIMS m/z 204.0809 (Calcd for C12H12O3: 204.0787).

4-Benzylxylo-5H-furan-2-one (11a)
Colorless powder. mp 110-111 °C (from hexane – AcOEt = 1 : 1) (lit2a 103-104 °C). IR νmax (cm⁻¹) 1739, 1615. 1H-NMR δ (ppm) 4.68 (2H, d, J = 1.1 Hz, CH2), 5.08 (2H, s, CH2), 5.19 (1H, t, J = 1.1 Hz, CH), 7.36-7.43 (5H, m, Ar-H).
3-Benzyl-4-benzyloxy-5H-furan-2-one (12a)
A colorless oil. IR v<sub>max</sub> (cm<sup>-1</sup>) 1745, 1666. <sup>1</sup>H-NMR δ (ppm) 3.62 (2H, s, CH<sub>2</sub>), 4.68 (2H, s, CH<sub>2</sub>), 5.13 (2H, s, CH<sub>2</sub>), 7.19-7.28 (8H, m, Ar-H), 7.37-7.40 (2H, m, Ar-H). <sup>13</sup>C-NMR δ (ppm) 28.1, 65.7, 72.2, 103.8, 126.4, 127.1, 128.4, 128.5, 129.0 (overlapped), 134.8, 139.0, 172.2, 174.4. HR-EIMS m/z 280.1093 (Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>3</sub>: 280.1100).

3-Benzyl-4-benzyloxy-5H-furan-2-one (12a)

3-Benzyloxycyclopent-2-en-1-one (11b)
Colorless solids. mp 47.5-49.5 °C. IR v<sub>max</sub> (cm<sup>-1</sup>) 1702, 1677. <sup>1</sup>H-NMR δ (ppm) 2.45-2.48 (2H, m, CH<sub>2</sub>), 2.66-2.69 (2H, m, CH<sub>2</sub>), 5.03 (2H, s, CH<sub>2</sub>), 5.41 (1H, t, J = 1.1 Hz, CH), 7.37-7.43 (5H, m, Ar-H). <sup>13</sup>C-NMR δ (ppm) 28.6, 34.0, 73.6, 105.5, 127.9, 128.76, 128.78, 134.5, 189.7, 205.8. HR-EIMS m/z 188.0841 (Calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>: 188.0837).

2-Benzyl-3-benzyloxycyclopent-2-en-1-one (12b)
A colorless oil. IR v<sub>max</sub> (cm<sup>-1</sup>) 1687, 1628. <sup>1</sup>H-NMR δ (ppm) 2.44-2.47 (2H, m, CH<sub>2</sub>), 2.68 (2H, t, J = 4.9 Hz, CH<sub>2</sub>), 3.51 (2H, s, CH<sub>2</sub>), 5.21 (2H, s, CH<sub>2</sub>), 7.14-7.18 (1H, m, Ar-H), 7.20-7.28 (6H, m, Ar-H), 7.32-7.38 (3H, m, Ar-H). <sup>13</sup>C-NMR δ (ppm) 25.1, 27.4, 33.6, 70.9, 120.8, 125.8, 126.9, 128.2, 128.5, 128.7, 128.8, 135.8, 140.1, 184.1, 204.1. HR-EIMS m/z 278.1313 (Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>: 278.1307).

3-Benzyloxycyclohex-2-en-1-one (11c)
Colorless solids. mp 64-65 °C (lit<sup>16</sup> 67 °C). IR v<sub>max</sub> (cm<sup>-1</sup>) 1648, 1602. <sup>1</sup>H-NMR δ (ppm) 2.01 (2H, quint., J = 6.5 Hz, CH<sub>2</sub>), 2.37 (2H, t, J = 6.6 Hz, CH<sub>2</sub>), 2.48 (2H, t, J = 6.3 Hz, CH<sub>2</sub>), 4.89 (2H, s, CH<sub>2</sub>), 5.49 (1H, s, CH), 7.34-7.42 (5H, m, Ar-H). <sup>13</sup>C-NMR δ (ppm) 21.2, 29.0, 36.7, 70.4, 103.4, 127.8, 128.5, 128.7, 135.0, 177.5, 199.7. HR-EIMS m/z 202.0997 (Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: 202.0994).

2-Benzyl-3-benzyloxycyclohex-2-en-1-one (12c)
A colorless oil. IR v<sub>max</sub> (cm<sup>-1</sup>) 1639, 1606. <sup>1</sup>H-NMR δ (ppm) 1.97 (2H, quint., J = 6.5 Hz, CH<sub>2</sub>), 2.37 (2H, t, J = 6.8 Hz, CH<sub>2</sub>), 2.60 (2H, t, J = 6.3 Hz, CH<sub>2</sub>), 3.67 (2H, s, CH<sub>2</sub>), 5.01 (2H, s, CH<sub>2</sub>), 6.95-7.14 (1H, m, Ar-H), 7.16-7.24 (6H, m, Ar-H), 7.30-7.38 (3H, m, Ar-H). <sup>13</sup>C-NMR δ (ppm) 20.9, 25.6, 27.9, 36.4, 69.5, 119.8, 125.3, 127.0, 127.9, 128.2, 128.7, 128.8, 136.2, 141.6, 171.6, 197.9. HR-EIMS m/z 292.1439 (Calcd for C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>: 292.1463).

2-Benzyl-3-benzyloxynaphthalene-1,4-dione (20)
To a solution of 7 (50 mg, 0.24 mmol) in THF (1.5 mL), n-BuLi (1.36 M in hexane, 0.18 mL, 0.25
mmoL) was added at -78 °C and the reaction mixture was stirred at -40 °C for 35 min. TMSCl (31 µL, 0.24 mmol) was added and the reaction mixture was stirred at -40 °C for 10 min and at 0 °C for 1 h. A solution of 18 (86 mg, 0.24 mmol) in THF (1.5 mL) and n-BuLi (1.36 M in hexane, 0.18 mL, 0.25 mmol) were added successively at -78 °C and the reaction mixture was stirred at -78 °C for 45 min. H2O (1 mL) was added and the whole was extracted with AcOEt (3 x 5 mL). The combined organic layer was washed with brine (1 x mL), dried over Na2SO4, and evaporated in vacuo. The residue was purified by CC (SiO2, hexane – AcOEt = 100 : 0 to 85 : 15) to give 20 as a brown oil (25 mg, 37%).

IR νmax (cm⁻¹) 1667, 1651, 1614, 1594. ¹H-NMR δ (ppm) 2.04 (3H, s, CH3), 5.42 (2H, s, CH2), 7.31-7.39 (3H, m, Ar-H), 7.41-7.45 (2H, m, Ar-H), 7.67-7.72 (2H, m, Ar-H), 8.05-8.08 (2H, m, Ar-H). ¹³C-NMR δ (ppm) 9.7, 75.1, 126.2, 128.3, 128.5, 128.6, 131.5, 132.0, 133.1, 133.3, 133.7, 136.7, 156.8, 181.4, 185.7 (one C missing). HR-EIMS m/z 278.0946 (Calcd for C18H14O3: 278.0943).

4-Benzylxy-3-methyl-2-triisopropoxyfuran (16)
According the reported procedure, to a solution of 7 (120 mg, 0.59 mmol) and Et3N (0.11 mL, 0.79 mmol) in CH2Cl2 (0.6 mL), TIPSOTf (0.17 mL, 0.63 mmol) was added at 0 °C and the whole was stirred at 0 °C for 1 h. The mixture was diluted with hexane (anhydrous, 3.0 mL), washed with ice-cooled aqueous half saturated NaHCO3 (2 x 1.2 mL) and ice-cooled brine (1 x 1.2 mL), and dried over MgSO4. The solvent was evaporated in vacuo and the residue was suspended in hexane (anhydrous, 1.2 mL) then filtered. The filtrate was concentrated in vacuo to give 16 as colorless solids (177 mg) as a mixture of 16, TIPSOH and 7 in 1 : 0.57 : 0.13 (74% w/w purity, 62% yield as 16). Colorless solids. ¹H-NMR δ (ppm) 1.08 (18H, d, J = 7.1 Hz, 6 x CH3), 1.19-1.28 (3H, m, 3 x CH), 1.80 (3H, s, CH3), 4.82 (2H, s, CH2), 6.45 (1H, s, CH), 7.29–7.42 (5H, m, Ar-H). ¹³C-NMR δ (ppm) 5.6, 12.3, 17.5, 71.7, 86.4, 111.7, 127.4, 127.9, 128.4, 137.1, 149.5, 151.5. HR-EIMS m/z 360.2146 (Calcd for C21H32O3Si: 360.2121).

2-Benzylxy-3-methyl-4-triisopropylsilyloxybenzalen-1-ol (22)
To a solution of 16 (149 mg, 74%, 0.31 mmol) and 18 (121 mg, 0.34 mmol) in THF (5 mL), n-BuLi (1.09 N in hexane, 0.63 mL, 0.69 mmol) was added at -78 °C for 15 min. H2O (5 mL) was added and the whole was extracted with AcOEt (3 x 10 mL). The combined organic layer was washed with H2O (1 x 3 mL) and brine (1 x 3 mL) and dried over Na2SO4. The solvent was evaporated in vacuo and the residue was purified by CC (SiO2, hexane – AcOEt = 95 : 5 – 91 : 9) to give 22 as a pale yellow oil (82 mg). After crystallization at -35 °C, an aliquot (62 mg) was washed with hexane to give 22 as colorless solids (46 mg, 46%).
mp 82-85 °C. IR ν\text{max} (cm\textsuperscript{-1}) 3372. ¹H-NMR δ (ppm) 1.12 (18H, d, J = 7.8 Hz, 6 x CH\textsubscript{3}), 1.40 (3H, sept., J = 7.6 Hz, 3 x CH), 2.44 (3H, s, CH\textsubscript{3}), 4.91 (2H, s, CH\textsubscript{2}), 5.52 (1H, s, OH), 7.37-7.47 (7H, m, Ar-H), 7.98-8.02 (1H, m, Ar-H), 8.04-8.08 (1H, m, Ar). ¹³C-NMR δ (ppm) 11.8, 14.2, 18.1, 75.8, 118.0, 121.6, 122.2, 122.9, 124.6, 124.7, 125.6, 128.2, 128.6, 128.9, 136.9, 138.1, 139.8, 143.9. HR-EIMS m/z 436.2440 (Calcd for C\textsubscript{27}H\textsubscript{36}O\textsubscript{3}Si: 436.2434).

Synthesis of naphthoquinones 20 and 23 from napthol 22.

(with TBAF) To a solution of crude 22 (182 mg, prepared from 7 (147 mg, 74%, 0.30 mmol) and 18 (120 mg, 0.34 mmol)) in THF (6.5 mL), TBAF (1 M solution in THF, 0.34 mL, 0.34 mmol) was added at rt and the reaction mixture was stirred at rt for 15 min. AcOEt (30 mL) was added and the whole was washed with saturated aqueous NH\textsubscript{4}Cl (1 x 3 mL) and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated in vacuo and the residue was purified by CC (SiO\textsubscript{2}, hexane – AcOEt = 95 : 5 to 50 : 50, CH\textsubscript{2}Cl\textsubscript{2} – hexane = 1 : 1) to give 20 as a pale brown oil (36 mg, 43%).

(with aq. FeCl\textsubscript{3}) To a solution of crude 22 (177 mg, prepared from 7 (146 mg, 81%, 0.33 mmol) and 18 (120 mg, 0.34 mmol)) in MeOH (6.8 mL), aqueous FeCl\textsubscript{3} (219 mg, 1.35 mmol in 1.9 mL) was added at rt and the reaction mixture was stirred at rt for 1.5 h. H\textsubscript{2}O (12 mL) was added and the mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (2 x 40 mL, 1 x 20 mL). The combined organic layer was washed with H\textsubscript{2}O (1 x 8 mL) and brine (1 x 8 mL) and dried over Na\textsubscript{2}SO\textsubscript{4}. The solvent was evaporated in vacuo and the residue was purified by CC (SiO\textsubscript{2}, hexane – AcOEt = 95 : 5, CH\textsubscript{2}Cl\textsubscript{2} – hexane = 1 : 1) to give 20 as a brown oil (34 mg, 37%) and 23 as pale yellow solids (8 mg, 12%).

2-Hydroxy-3-methylnaphthalene-1,4-dione (23) mp 167-169 °C (lit\textsuperscript{15} 172-173 °C). IR ν\text{max} (cm\textsuperscript{-1}) 3328, 1653. ¹H-NMR δ (ppm) 2.11 (3H, s, CH\textsubscript{3}), 7.69 (1H, td, J = 7.6 Hz, 1.4 Hz, Ar-H), 7.76 (1H, td, J = 7.5 Hz, 1.5 Hz, Ar-H), 8.09 (1H, dd, J = 7.6 Hz, 1.1 Hz, Ar-H), 8.13 (1H, dd, J = 7.7 Hz, 1.0 Hz, Ar-H). EIMS m/z 188 (M\textsuperscript{+}, 100%), 160 (69%), 132 (76%), 131 (79%), 105 (65%), 77 (65%).

ACKNOWLEDGEMENTS
This work was partially supported by The Uehara Memorial Foundation and a Grant from Musashino Joshi-Gakuin.

REFERENCES AND NOTES
1. (a) D. B. Ramachary and M. Kishor, Org. Biomol. Chem., 2010, 8, 2859 and references cited therein;


