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

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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 condition[3] and alkylation in basic condition[4] 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.[6] 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.

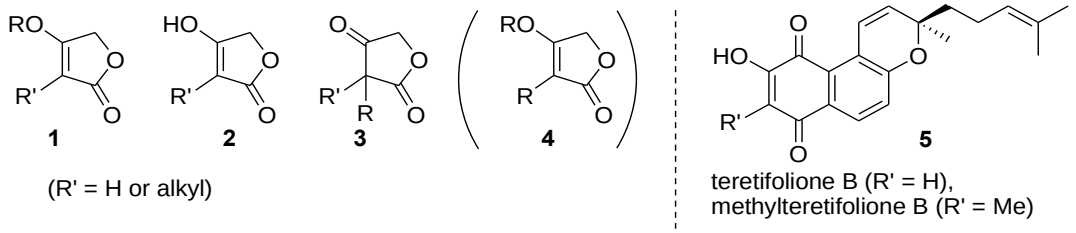
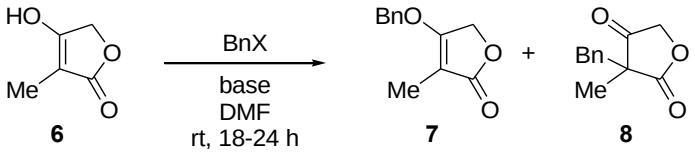


Figure 1. Structures of β-tetronic acid derivatives **1-4** and teretifoliones B (**5**)

At first, benzylation of α-methyl-β-tetronic acid (**6**)[7] was examined. Treatment of **6** and benzyl bromide in the presence of potassium carbonate as a base in *N*,*N*-dimethylformamide (DMF)[4c] 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[4a] 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 conidition

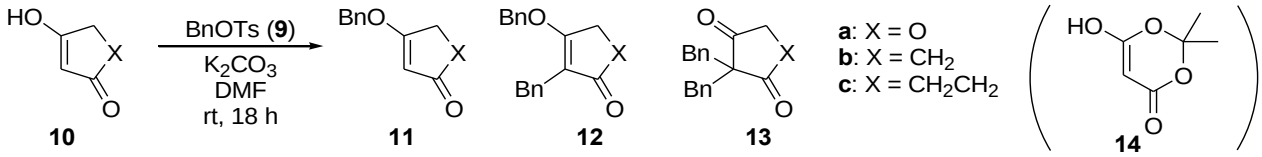


run	X in BnX (eq)	base (eq)	**7** : **8**[a]	Isolated **7** (%)
1	Br (1.0)	K_2CO_3 (2.0)	many spots	22
2	Br (1.0)	Cs_2CO_3 (2.0)	many spots	28
3	Br (1.0)	CsF (2.0)	1 : 2	-
4	Cl (1.0)	CsF (2.0)	1 : 1	-
5	OTs (1.0)	CsF (2.0)	3 : 1	48
6	OTs (1.0)	Cs_2CO_3 (2.0)	1 : 0[b]	68
7	OTs (1.0)	K_2CO_3 (2.0)	1 : 0[b]	60
8	OTs (1.5)	K_2CO_3 (3.0)	1 : 0[b]	86

[a] Estimated from integration of ^{1}H-NMR of the crude products. [b] **8** was not observed in ^{1}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). Benzylation of other β-dicarbonyl compounds was examined. Benzylation of β-tetronic acid (**10a**) gave the corresponding *O*-benzylated product **11a** exclusively with small amount of *C*,*O*-dibenzylated one **12a**, generated through the reaction of initial *C*-benzylation followed by *O*-benzylation. Generation of *C*,*C*-dibenzylated 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*-dibenzylated 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 benzylation of Merdrum's acid (**14**) gave only *C*,*C*-dibenzylated product (data not shown).[10]

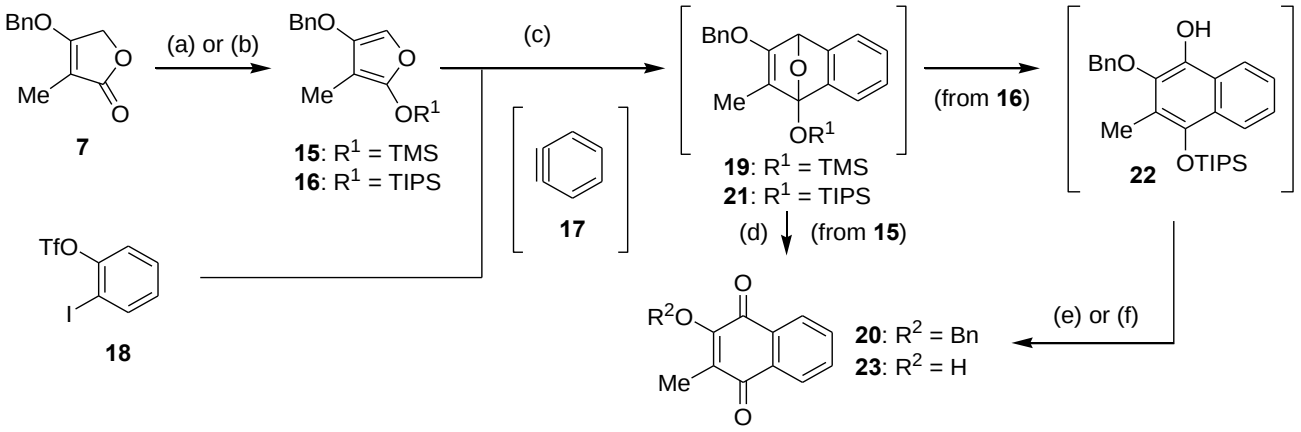
Table 2. Benzylation of β-dicarbonyl compounds **10** with BnOTs (**9**)[a]



run	substrate	**11** : **12**[b]	Isolated **11** (%)
1	**10a**	15 : 1	72
2[c]	**10a**	15 : 1	77
3	**10b**	15 : 1	59
4	**10c**	5 : 1	52

[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 α-methyl-β-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, Et_3N, CH_2Cl_2, 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 $FeCl_3$, methanol, rt, 1.5 h (**20**: 37%, **23**: 12%).

In summary, synthesis of benzyl enol ether of β-tetronic acids with *O*-selective benzylation 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 benzynes 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. ^{1}H- (400 MHz) and ^{13}C-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 CH_2Cl_2, DMF were purchased and THF was used as received as a gift from Wako Chemicals. TMSCl was used after distillation from CaH_2.

Benzyl tosylate (**9**)

(Synthesis in solvent-free condition) A mixture of tosyl chloride (2.8 g, 15 mmol) and K_2CO_3 (9.2 g, 67 mmol) was ground in mortar under N_2 atmosphere. Benzyl alcohol (2.8 g, 15 mmol) was added portionwise and the mixture was ground for further 1 h. Et_2O (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 Na_2SO_4 in refrigerator. The solvent was evaporated *in vacuo* and the residue was

washed with hexane - Et_2O (1 : 4) to give **9** (2.1 g, 54%) as colorless needles.
mp 57-58 °C. IR no characteristic absorption. ^{1}H-NMR δ (ppm) 2.44 (3H, s, CH_3), 5.06 (2H, s, CH_2), 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), Et_3N (0.22 mL, 1.58 mmol), DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (5 mL), a solution of tosyl chloride (286 mg, 1.50 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was washed with H_2O (1 x 10 mL), saturated aqueous $NaHCO_3$ (2 x 10 mL), and brine (1 x 2 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to give **9** (294 mg, 78%) as a colorless oil.

4-Benzyloxy-3-methyl-5*H*-furan-2-one (**7**)
Under N_2 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 K_2CO_3 (365 mg, 2.64 mmol) at rt and the reaction mixture was stirred at rt for 24 h. H_2O (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 NH_4Cl, H_2O, saturated aqueous $NaHCO_3$, and brine (each 1 x 1 mL), and dried over Na_2SO_4. The solvent was evaporated *in vacuo* to give a yellow oil, which was purified by column chromatography (CC) (SiO_2, hexane – AcOEt 4 : 1) to give **7** as pale yellow solids (154 mg, 86%).
mp 111-112 °C (from hexane – AcOEt = 1 : 1). IR ν_{max} (cm^{-1}) 1727, 1650. ^{1}H-NMR δ (ppm) 1.86 (3H, t, *J* = 1.5 Hz, CH_3), 4.63 (2H, q, *J* = 1.5 Hz, CH_2), 5.22 (2H, s, CH_2), 7.34-7.45 (5H, m, Ar-H). ^{13}C-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 $C_{12}H_{12}O_3$: 204.0787).

3-Benzyl-3-methylfuran-2,4-dione (**8**)
A colorless oil. IR ν_{max} (cm^{-1}) 1749. ^{1}H-NMR δ (ppm) 1.43 (3H, s, CH_3), 3.04 (1H, d, *J* = 13.1 Hz, CH_2), 3.13 (1H, d, *J* = 13.1 Hz, CH_2), 3.64 (1H, d, *J* = 17.2 Hz, CH_2), 4.36 (1H, d, *J* = 17.2 Hz, CH_2), 7.10-7.13 (2H, m, Ar-H), 7.23-7.30 (3H, m, Ar-H). ^{13}C-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 $C_{12}H_{12}O_3$: 204.0787).

4-Benzyloxy-5*H*-furan-2-one (**11a**)
Colorless powder. mp 110-111 °C (from hexane – AcOEt = 1 : 1) (lit[2a] 103-104 °C). IR ν_{max} (cm^{-1}) 1739, 1615. ^{1}H-NMR δ (ppm) 4.68 (2H, d, *J* = 1.1 Hz, CH_2), 5.08 (2H, s, CH_2), 5.19 (1H, t, *J* = 1.1 Hz, CH), 7.36-7.43 (5H, m, Ar-H).

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

A colorless oil. IR ν_{max} (cm^{-1}) 1745, 1666. ^{1}H-NMR δ (ppm) 3.62 (2H, s, CH_2), 4.68 (2H, s, CH_2), 5.13 (2H, s, CH_2), 7.19-7.28 (8H, m, Ar-H), 7.37-7.40 (2H, m, Ar-H). ^{13}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 $C_{18}H_{16}O_3$: 280.1100).

3-Benzyloxycyclopent-2-en-1-one (11b)

Colorless solids. mp 47.5-49.5 °C. IR ν_{max} (cm^{-1}) 1702, 1677. ^{1}H-NMR δ (ppm) 2.45-2.48 (2H, m, CH_2), 2.66-2.69 (2H, m, CH_2), 5.03 (2H, s, CH_2), 5.41 (1H, t, *J* = 1.1 Hz, CH), 7.37-7.43 (5H, m, Ar-H). ^{13}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 $C_{12}H_{12}O_2$: 188.0837).

2-Benzyl-3-benzyloxycyclopent-2-en-1-one (12b)

A colorless oil. IR ν_{max} (cm^{-1}) 1687, 1628. ^{1}H-NMR δ (ppm) 2.44-2.47 (2H, m, CH_2), 2.68 (2H, t, *J* = 4.9 Hz, CH_2), 3.51 (2H, s, CH_2), 5.21 (2H, s, CH_2), 7.14-7.18 (1H, m, Ar-H), 7.20-7.28 (6H, m, Ar-H), 7.32-7.38 (3H, m, Ar-H). ^{13}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 $C_{19}H_{18}O_2$: 278.1307).

3-Benzyloxycyclohex-2-en-1-one (11c)

Colorless solids. mp 64-65 °C (lit[16] 67 °C). IR ν_{max} (cm^{-1}) 1648, 1602. ^{1}H-NMR δ (ppm) 2.01 (2H, quint., *J* = 6.5 Hz, CH_2), 2.37 (2H, t, *J* = 6.6 Hz, CH_2), 2.48 (2H, t, *J* = 6.3 Hz, CH_2), 4.89 (2H, s, CH_2), 5.49 (1H, s, CH), 7.34-7.42 (5H, m, Ar-H). ^{13}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 $C_{13}H_{14}O_2$: 202.0994).

2-Benzyl-3-benzyloxycyclohex-2-en-1-one (12c)

A colorless oil. IR ν_{max} (cm^{-1}) 1639, 1606. ^{1}H-NMR δ (ppm) 1.97 (2H, quint., *J* = 6.5 Hz, CH_2), 2.37 (2H, t, *J* = 6.8 Hz, CH_2), 2.60 (2H, t, *J* = 6.3 Hz, CH_2), 3.67 (2H, s, CH_2), 5.01 (2H, s, CH_2), 6.95-7.14 (1H, m, Ar-H), 7.16-7.24 (6H, m, Ar-H), 7.30-7.38 (3H, m, Ar-H). ^{13}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 $C_{20}H_{20}O_2$: 292.1463).

2-Benzyloxy-3-methylnaphthalene-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. H_2O (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 Na_2SO_4, and evaporated *in vacuo*. The residue was purified by CC (SiO_2, hexane – AcOEt = 100 : 0 to 85 : 15) to give **20** as a brown oil (25 mg, 37%).

(lit[13a] mp 40-42 °C) IR ν_{max} (cm^{-1}) 1667, 1651, 1614, 1594. ^{1}H-NMR δ (ppm) 2.04 (3H, s, CH_3), 5.42 (2H, s, CH_2), 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). ^{13}C-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 $C_{18}H_{14}O_3$: 278.0943).

4-Benzyloxy-3-methyl-2-triisopropyloxyfuran (**16**)

According the reported procedure,[17] to a solution of **7** (120 mg, 0.59 mmol) and Et_3N (0.11 mL, 0.79 mmol) in CH_2Cl_2 (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 $NaHCO_3$ (2 x 1.2 mL) and ice-cooled brine (1 x 1.2 mL), and dried over $MgSO_4$. 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. ^{1}H-NMR δ (ppm) 1.08 (18H, d, J = 7.1 Hz, 6 x CH_3), 1.19-1.28 (3H, m, 3 x CH), 1.80 (3H, s, CH_3), 4.82 (2H, s, CH_2), 6.45 (1H, s, CH), 7.29–7.42 (5H, m, Ar-H). ^{13}C-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 $C_{21}H_{32}O_3Si$: 360.2121).

2-Benzyloxy-3-methyl-4-triisopropylsilyloxynaphthalen-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. H_2O (5 mL) was added and the whole was extracted with AcOEt (3 x 10 mL). The combined organic layer was washed with H_2O (1 x 3 mL) and brine (1 x 3 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by CC (SiO_2, 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_{max} (cm^{-1}) 3372. ^{1}H-NMR δ (ppm) 1.12 (18H, d, *J* = 7.8 Hz, 6 x CH_3), 1.40 (3H, sept., *J* = 7.6 Hz, 3 x CH), 2.44 (3H, s, CH_3), 4.91 (2H, s, CH_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). ^{13}C-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 $C_{27}H_{36}O_3Si$: 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_4Cl (1 x 3 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by CC (SiO_2, hexane – AcOEt = 95 : 5 to 50 : 50, CH_2Cl_2 – hexane = 1 : 1) to give **20** as a pale brown oil (36 mg, 43%).

(with aq. $FeCl_3$) 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 $FeCl_3$ (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_2O (12 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 40 mL, 1 x 20 mL). The combined organic layer was washed with H_2O (1 x 8 mL) and brine (1 x 8 mL) and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was purified by CC (SiO_2, hexane – AcOEt = 95 : 5, CH_2Cl_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[15] 172-173 °C). IR ν_{max} (cm^{-1}) 3328, 1653. ^{1}H-NMR δ (ppm) 2.11 (3H, s, CH_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^+, 100%), 160 (69%), 132 (76%), 131 (79%), 105 (65%), 77 (65%).

ACKNOWLEDGEMENTS

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