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Reactivity of naphthol towards nucleophiles in anodic oxidation

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Abstract—Reactivity of the anodic oxidation of 4-methoxy-1-naphthol **1** in the presence of nucleophiles has been investigated. The reaction with electron-rich alkenic nucleophiles such as 1-methoxy-4-propenylbenzene **2** and isosafrole **3** gave a very high yield, whereas the reaction with dihydropyran **4** and dihydrofuran **5** gave a moderate yield, but with ethyl vinyl ether **6** gave a very low yield of the substituted dihydronaphthofuran derivatives **7**–**10** and **12**, respectively. Unexpectedly, the glycosyl derivative **11** was preferentially produced rather than naphthofuran **10** upon using **5** as a nucleophile. In addition, the dimers **15** and **16** were obtained in moderate yield without addition of nucleophile to **1**. The mechanism of the oxidation reactions including the [3+2] and [5+2] cycloaddition were discussed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Oxidation of phenol and its congeners has been used for the synthesis of the corresponding quinones and coupling products.[1] In particular, binaphthol derivatives are of interest, because of characteristic unit of biologically active natural products, as well as important chiral-auxiliary for asymmetric induction.[2] While a number of oxidants and their practical usage[3] have been developed to achieve the oxidation of naphthols, few electrochemical oxidations have been reported.[4,6b] The reason might be that considerable efforts were required to acquire optimized conditions by controlling such parameters as reaction cell (divided or undivided), solvent (neutral, acidic or basic conditions), supporting salts, and so on. Despite of such difficulties, electrochemical reaction would be an efficient methodology, from viewpoints of environmental consideration by employing clean electric energy to provide target molecules.

As part of our ongoing project for the anodic oxidation of phenol derivatives to generate key synthon towards complicated naturally occurring molecules,[5] this paper describes the oxidation of 4-methoxy-1-naphthol **1** in the presence of nucleophiles to study scope and limitation of the oxidation reaction.[6,7]

2. Results and discussion

To investigate the detailed profile of the oxidation of naphthols and compare its reactivity with those of phenol derivatives, 4-methoxy-1-naphthol **1** was subjected to anodic oxidation in the presence of alkenic nucleophiles **2**–**6**. As expected, the electrochemically generated cation was reacted with both styrene-(**2**,**3**) and vinyloxy-(**4**–**6**) type nucleophiles to construct naphthofurans. The results are summarized in Table 1 and Fig. 1.

Optimization of the conditions to obtain quantitative yield of the cycloadducts **7** and **8** using 1-methoxy-4-(1-propenyl)benzene **2** and isosafrole **3**, was achieved by employing CH_3CN as a solvent at constant current electrolysis (CCE) (entries 1 and 4). The acidic solvents e.g. CH_3CN–AcOH,[6b,c] Ac_2O,[6a] or CH_3NO_2–AcOH[6f] have been reported to give high yields of oxidation products in the case of phenol derivatives. In addition to the cycloadducts **7** and **8**, such solvents as Ac_2O or CH_3CN/Ac_2O, gave undesired acetate **13** and quinone **14** in moderate yields (entries 2, 3, 5 and 6).

Oxidation of **1** provided two kinds of the oxidized forms (**A** and **B**), depending on electrons and protons abstracted (Scheme 1). Both active species might be stabilized by the accompanied phenyl residue, which gave a similar effect to electron-donating substituents in the case of phenol derivatives. While **A** underwent a homogeneous coupling to give dimers **15** and **16**, the cation **B** reacted with nucleophiles existed to afford naphthofurans **7**–**10** and **12**, through the [3+2] cycloaddition reaction.

Anodic oxidation of **1** with **4** gave the corresponding cycloadduct **9** in moderate yields (entries 7 and 8), but still

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Table 1. The anodic oxidation of **1** with or without nucleophiles and the corresponding products

Entry	Nucleophiles	equiv. mol	mA (F/mol) mV	Solvents (ml)	Products (%)												
					7	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**19**	**21**
1	**2**	12	10 (2.2) 300–610	A (25)	96												
2		12	10 (2.4) 320–690	B (25)	44						50						
3		12	10 (2.4) 380–720	C (25)	28							68					
4	**3**	15	10 (2.2) 250–550	A (30)		95											
5		15	10 (2.2) 350–750	B (25)		48					50						
6		15	10 (2.2) 340–780	C (25)		36						55					
7	**4**	5	15 (2.6) 150–650	A (25)			45[a]								32		
8		25	10 (2.5) 180–630	A (25)			19[b]						22	5		6	
9	**5**	10	5 (2.1) 300–570	A (25)					79								
10		10	15 (2.5) 180–650	A (25)					70				17	2			
11		10	80–3[c] 1500	A (25)				39				17	11	6			
12[d]	**6**	20	10 (2.2) 180–750	A (35)						4[e]							71
13		20	13 (2.5) 170–760	A (25)						12[f]							65
14[d]			13 (2.6) 220–600	A (18)								52	45				
15[d]			50–3[c] 1500	A (15)								11	22	58			

[a] **1** was recovered in 20% yield.
[b] **1** was recovered in 31% yield.
[c] Electrolysis was performed under the CPE conditions, whereas CCE conditions were employed for others.
[d] A 0.33 mmol amount of **1** was used against 0.17 mmol for other entries.
[e] **1** was recovered in 17% yield.
[f] **1** was recovered in 17% yield. Solvents: A, CH_3CN; B, Ac_2O; C, CH_3CN-Ac_2O (1/1).

better than in the case of 4-methoxyphenol,[6a] which might be due to the stability effect, as mentioned above. On the other hand, unexpectedly, the anodic oxidation with **5** under the same CCE conditions as that of **4**, gave the C-glycoside **11**[8] in high yields (entries 9 and 10). The cycloadduct **10** was obtained under constant potential electrolysis (CPE) conditions (1500 mV vs. SCE, entry 11). A possible mechanism is that the acidity in the reaction generated the O-tetrahydrofuranylation of **1** to give **18**, followed by the O→C glycosyl migration (**20**) and the additional two-electron oxidation provided **11** (Scheme 2). Alternatively, the bicyclo[3.2.1]-type derivative **C** might be produced by the cationic [5+2] cycloaddition of the dienophile **5**, and the abstraction of the methyl group afforded the glycosyl product **11**. The CPE condition (1500 mV vs. SCE) in entry 11 might effect a quick generation of the cation **B**, leading to **10**, before the O-glycosylation of a phenol group, although a certain amount of **5** would be oxidized (the first oxidation potential: 1400 mV). To ascertain the O→C migration, **18** was submitted to the same oxidation reaction, which gave only a trace amount of **11** among the naphthoquinone **14** (58%) and the two dimmers, **15** (31%) and **16** (4%). Upon reaction of **1** with **5** in the presence of catalytic TsOH, a mixture of **18** (70%) and **20** (28%) was obtained after 14 h, while **18** was quantitatively produced after 1 h, which was a similar reaction time to that of electrolysis. In addition, upon monitoring the reaction of entry 9 every 10 min, **18** was not detected, but probably the migration and following oxidation were so fast as to observe neither **18** nor **20**. Although the O→C migration process might be plausible, the [5+2]-type process could not be excluded to explain the relatively high yield production of **11** within a short period. The efficient O→C glycosyl migration under Lewis acid conditions has been reported,[9] and the anodic oxidation provided an alternative methodology employing mild and safe conditions. In contrast to dihydrofuran **5**, its 6-membered derivative **4** gave preferably the cycloadduct **9**, and the corresponding C-glycoside **19** was isolated only in 6% yield under low current conditions (entry 8).[10] Further attempts of explanation of this reactivity difference are under way.

Anodic oxidation of **1** with ethyl vinyl ether **6** gave the naphthofuran derivative **12** in low yield, which could be improved slightly using a high electric current (entries 12 and 13). The undesired acetal **21** in considerable amount could not be avoided. This is due to the acid-sensitive character of **6**, which reacted with the phenol group of **1** faster than the cycloaddition to the cation, leading to acetal **21**.

In entries 8, 10 and 11, the dimers **15** and **16** were obtained through radical coupling of the one-electron oxidation product (**A** in Scheme 1) to give **15**, followed by the further oxidation to give **16**. On the other hand, chemical oxidation of naphthols usually produced benzoquinones (type **14**) or its dimer (type **16**), while binaphthol **15** was characteristically obtained under anodic oxidation conditions.[11] As shown in entries 14 and 15, the anodic oxidation without nucleophiles in concentrated solution provide the dimer **15** in moderate yield as well as **16**.[3h] While oxidative couplings by employing oxidants were known,[12] electrochemical conversion of 4-methoxyphenol into the corresponding biaryl was not accomplished, except the case of 2,3,5-tribromo-4-methoxyphenol.[13]

In conclusion, the anodic oxidation of 4-methoxy-1-naphthol **1** was undertaken to understand their scope and limitation as substrates in phenolic oxidations. The cation **B**, electrolytically generated, reacted with nucleophiles (**2**–**6**) presented to give the corresponding naphthofuran derivatives (**7**–**10** and **12**). Unexpectedly, upon using **5**,

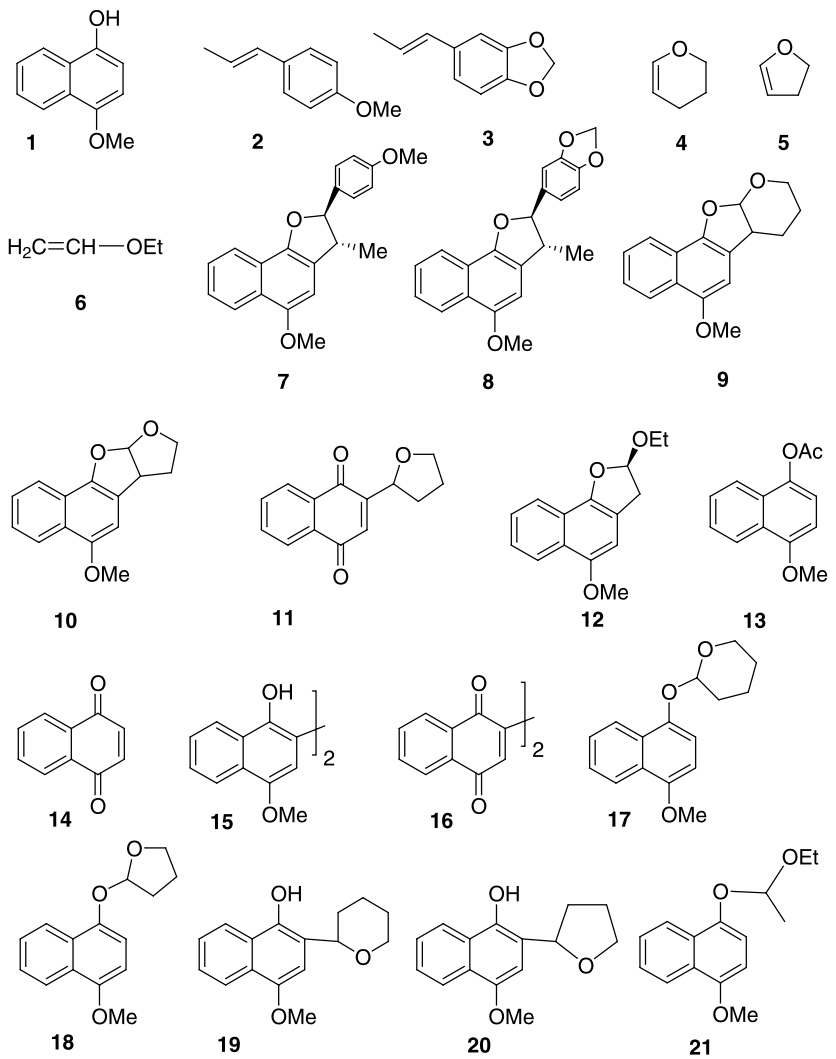
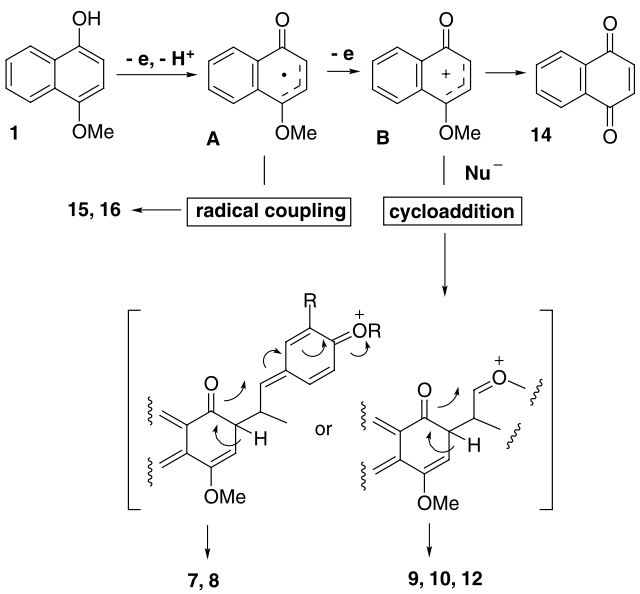
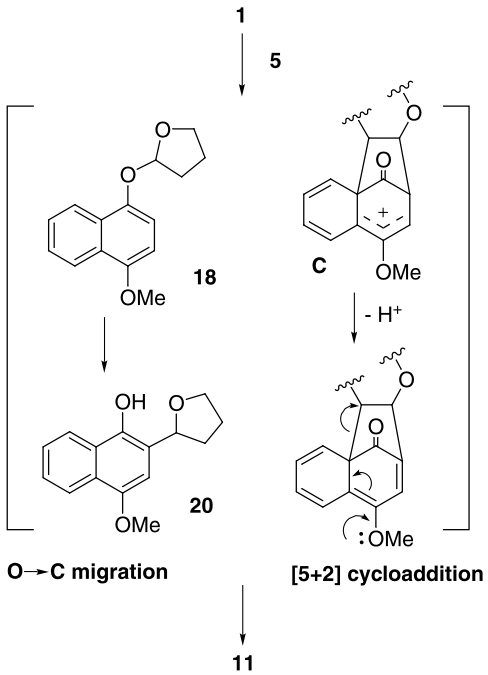


Figure 1.



Scheme 1.



Scheme 2.

the C-glycoside **11** was characteristically obtained which might adapt an entirely different mechanism. The dimers **15** and **16** were effectively produced by the appropriate oxidation conditions. In particular, binaphthol **15** was characteristically produced, different from usual chemical oxidation. Further electrochemical investigation of other naphthols[14] for a possibility to construct synthetic intermediates of naturally occurring complicated molecules, are extensively in progress in our laboratory.

3. Experimental

IR spectra were recorded on a JASCO Model A-202 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM EX-270, a JEOL JNM GX-400 NMR, or a JEOL JNM ALPHA-400 spectrometer in a deuteriochloroform ($CDCl_3$) solution using tetramethylsilane as an internal standard, unless otherwise stated. Low- and high-resolution mass spectra were obtained on a Hitachi M-80 B GC–MS spectrometer operating at the ionization energy of 70 eV or JEOL JMS-700 spectrometer. All melting points were obtained on a Yanaco MP-S3 and are uncorrected. Preparative and analytical TLC were carried out on silica-gel plates (Kieselgel 60 F_{254}, E. Merck A. G., Germany) using UV light, spraying with 5% phosphomolybdic acid in ethanol for detection. Katayama silica-gel (K 070) was used for column chromatography.

3.1. General procedure for anodic oxidation of 4-methoxy-1-naphthol 1

A solution of **1** in an appropriate solvent was electrolyzed in the presence of *n* Bu_4NBF_4 (180 mg) as supporting salts and appropriate alkenic nucleophiles such as 1-methoxy-4-propenylbenzene **2**, isosafrole **3**, dihydropyran **4**, dihydrofuran **5**, and ethyl vinyl ether **6** using a glassy carbon beaker as an anode and a platinum wire as a cathode, in a divided cell through glass-filters. Based on CV curves, oxidation potentials of **1** and the representative nucleophile **5** were 620 and 1400 mV vs. SCE (first peaks in CV), respectively. The nucleophiles were added to the reaction mixture all at once, since they would not be oxidized under CCE conditions. Under Ar atmosphere, the electrolysis was then performed at the oxidation potentials and current of the substrates given in Table 1. The reaction mixture was evaporated and purified by column chromatography and/or preparative TLC.

3.1.1. (2*R,3*R**)-2,3-Dihydro-5-methoxy-2-(4-methoxyphenyl)-3-methylnaphtho[1,2-*b*]furan 7.** Mp 90–91°C; IR and ^{1}H NMR agreed with Ref. 6b; ^{13}C NMR: δ 18.9, 47.3, 55.6, 56.3, 92.9, 100.7, 114.4, 121.4, 121.8, 122.9, 124.0, 125.5, 125.9, 126.5, 128.0, 133.9, 148.4, 150.8, and 160.1. EI-MS *m*/*z* 320 (37), 216 (7), 212 (43), 189 (33), 149 (42), 122 (100). Found: *m*/*z* 320.1183. Calcd for $C_{21}H_{20}O_3$: M, 320.1158.

3.1.2. 2-(2*H*-Benzo[*d*]1,3-dioxol-5-yl)-(2*R,3*R**)-2,3-dihydro 5-methoxy-3-methylnaphtho[1,2-*b*]furan 8.** IR (film) 3068, 1639, 1596, and 1488 cm^{-1}; ^{1}H NMR: δ 1.47 (3H, d, *J*=6.8 Hz), 3.54 (1H, dq, *J*=8, 6.8 Hz), 3.95 (3H, s), 5.19 (1H, d, *J*=8 Hz), 5.94 (2H, s), 6.60 (1H, s), 6.77 (1H, d, *J*=8 Hz), 6.90 (1H, dd, *J*=2, 8 Hz), 6.94 (1H, d, *J*=2 Hz), 7.43 (2H, complex), 7.91 (1H, dd, *J*=1.5, 7.2 Hz), and 8.17 (1H, dd, *J*=1.5, 7.2 Hz); ^{13}C NMR: δ 18.8, 47.1, 55.6, 92.2, 99.7, 100.7, 106.3, 107.8, 119.3, 120.7, 121.1, 122.3, 122.7, 124.7, 125.3, 125.7, 135.1, 147.2, 147.5, 147.7, and 150.1. EI-MS *m*/*z* 334 (45), 301 (21), 278 (19), 231 (16), 212 (41), 189 (32), 149 (42), 122 (100). Found: *m*/*z* 334.1218. Calcd for $C_{21}H_{18}O_4$: M, 334.1204.

3.1.3. 3,4,4a,11a-Tetrahydro-6-methoxynaphtho[2′,1′:4,5]furo[2,3-*b*]-2*H*-pyran 9. IR (film) 3062, 2930, 1594, and 1459 cm^{-1}; ^{1}H NMR: δ 1.56 (1H, m), 1.65 (1H, m), 1.91 (1H, m), 2.12 (1H, m), 3.49 (1H, dt, *J*=1.5, 6.4 Hz), 3.78 (2H, complex), 3.98 (3H, s), 6.11 (1H, d, *J*=6.8 Hz), 6.68 (1H, s), 7.47 (2H, dq, *J*=1.5, 6.8 Hz), 7.96 (1H, d, *J*=8 Hz), and 8.20 (1H, d, *J*=8 Hz); ^{13}C NMR: δ 19.9, 22.5, 40.1, 56.1, 60.5, 100.2, 104.5, 120.8, 121.2, 121.3, 122.4, 125.1, 125.4, 126.1, 147.2, and 150.4. EI-MS *m*/*z* 256 (100), 241 (18), 225 (22), 211 (13), 185 (11), 128 (11), and 83 (21). Found: *m*/*z* 242.0931. Calcd for $C_{15}H_{14}O_3$: (M−CH_2), 242.0941.

3.1.4. 2,3,3a,10a-Tetrahydro-5-methoxyfuro[2,3-*b*]-naphtho[2,1-*d*]furan 10. IR (film) 3070, 2928, 1592, and 1456 cm^{-1}; ^{1}H NMR: δ 2.18 (1H m), 2.34 (1H, m), 3.65 (1H, m), 3.97 (3H, s), 4.10 (1H, m), 4.13 (1H, m), 6.49 (1H, d, *J*=5.9 Hz), 6.68 (1H, s), 7.47 (2H, ddd, *J*=1.5, 4.8, 6.8 Hz), 7.95 (1H, d, *J*=8.0 Hz), and 8.20 (1H, d, *J*=8.0 Hz). EI-MS *m*/*z* 242 (100), 227 (43), 213 (8), 186 (11), 157 (13), and 115 (17). Found: *m*/*z* 242.0973. Calcd for $C_{15}H_{14}O_3$: M, 242.0943.

3.1.5. 2-Tetrahydrofuran-2-ylnaphthalene-1,4-dione 11.[8] Mp 95–96°C; IR (film) 3050, 2924, 1663, 1593, 1562, and 1455 cm^{-1}; ^{1}H NMR: δ 1.70 (1H, m), 1.98 (2H, complex), 2.52 (1H, m), 3.92 (1H, dq, *J*=6.8, 7.3 Hz), 4.04 (1H, dq, *J*=5.9, 7.3 Hz), 4.98 (1H, t, *J*=8.3 Hz), 7.01 (1H, s), 7.72 (2H, ddd, *J*=2.0, 4.9, 7.3 Hz), and 8.06 (2H, ddd, *J*=2.0, 2.4, 4.9 Hz). EI-MS *m*/*z* 228 (100), 200 (86), 172 (88), 158 (56), 144 (50), 130 (19), and 102 (37). Found: *m*/*z* 228.0814. Calcd for $C_{14}H_{12}O_3$: M, 228.0786.

3.1.6. 2-Ethoxy-5-methoxy-2,3-dihydronaphtho[1,2-*b*]furan 12. IR (film) 3065, 2932, 1590, 1554, and 1450 cm^{-1}; ^{1}H NMR: δ 1.25 (3H, t, *J*=7.5 Hz), 3.18 (1H, dd, *J*=2.2, 16.1 Hz), 3.52 (1H, dd, *J*=7.2, 16.1 Hz), 3.72 (1H, dq, *J*=6.8, 14 Hz), 3.96 (3H, s), 4.04 (1H, dq, *J*=6.8, 14 Hz), 5.91 (1H, dd, *J*=2.4, 6.8 Hz), 6.75 (1H, s), 7.46 (2H, ddd, *J*=2.0, 4.9, 7.3 Hz), 7.92 (1H, dd, *J*=1.5, 7.3 Hz), 8.18 (1H, dd, *J*=1.5, 7.3 Hz). Found: *m*/*z* 244.1070. Calcd for $C_{15}H_{16}O_3$: M, 244.1097.

3.1.7. 2-(1-Hydroxy-4-methoxy-(2-naphthyl))-4-methoxy-1-naphthol 15. IR (film) 3273, 1643, 1596, and 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD 3:1): δ 3.98 (6H, s), 6.71 (2H, s), 7.57 (4H, m), 8.18 (2H, dd, *J*=2.4, 7.3 Hz), and 8.28 (2H, dd, *J*=2.4, 7.3 Hz). EI-MS *m*/*z* 346 (30), 314 (10), 299 (13), 224 (32), 167 (37), 149 (100), 104 (16), and 71 (18). Found: *m*/*z* 346.1201. Calcd for $C_{22}H_{18}O_4$: M, 346.1204.

3.1.8. 4-Methoxy-2-(perhydro-2*H*-pyran-2-yl)-1-naphthol 19. IR (film) 3295, 3064, 2943, 1598, 1460, and

1404 cm^{-1}; ^1H NMR: δ 1.55 (2H, m), 1.63 (2H, m), 1.80 (1H, m), 2.00 (1H, m), 3.62 (1H, m), 3.89 (3H, s), 3.92 (1H, m), 4.58 (1H, dd, J=1.8, 7.8 Hz), 6.31 (1H, s), 7.40 (2H, ddd, J=2.0, 4.9, 7.3 Hz), 8.06 (1H, dd, J=1.5, 7.3 Hz), and 8.13 (1H, dd, J=1.5, 7.3 Hz). EI-MS m/z 258 (90), 225 (10), 211 (13), 187 (26), 167 (58), 149 (100), 129 (18), 105 (19), and 71 (40). Found: m/z 258.1221. Calcd for $C_{16}H_{18}O_3$: M, 258.1254.

3.2. Synthesis of 18 and 20

A mixture of **1** (29 mg, 0.17 mmol) and **5** (0.2 ml, 2.9 mmol) in the presence of catalytic amounts of TsOH in THF (20 ml) was stirred for 14 h under Ar atmosphere. The reaction mixture was evaporated and purified by column chromatography (CH_2Cl_2) to yield **18** (29 mg, 70%) and **20** (12 mg, 28%).

3.2.1. 4-Methoxy-2-tetrahydrofuran-2-yl-1-naphthol 20. IR (film) 3303, 3073, 2950, 1635, 1599, and 1457 cm^{-1}; ^1H NMR: δ 2.06 (3H, m), 2.45 (1H, m), 3.90 (3H, s), 4.01 (1H, m), 4.19 (1H, m), 5.14 (1H, dd, J=6.4, 6.8 Hz), 6.35 (1H, s), 7.48 (2H, ddd, J=2.0, 4.9, 7.3 Hz), 8.13 (1H, dd, J=1.5, 7.3 Hz), and 8.21 (1H, dd, J=1.5, 7.3 Hz); ^{13}C NMR: δ 22.5, 33.8, 55.7, 68.6, 83.0, 102.6, 116.1, 121.3, 121.7, 125.3, 125.4, 125.7, 126.1, 144.1, and 148.3. EI-MS m/z 244 (37), 216 (7), 202 (28), 187 (18), 159 (14), 120 (7), and 85 (100). Found: m/z 244.1053. Calcd for $C_{15}H_{16}O_3$: M, 244.1098.

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10. If not reduced in situ, **19** carrying a lower oxidation stage than that of **11**, could not be obtained by the [5+2] process (Scheme 2). At least, reaction with **6** might involve the O⟶C process.
11. Similar bisnaphthols were obtained by employing electron donor–acceptor complexes. See: Okamoto, I.; Doi, H.; Kotani, E.; Takeya, T. *Tetrahedron Lett.* **2001**, *42*, 2987–2989.
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14. From among several naphthol derivatives, only **1** satisfied the chemistry described in this article.