Investigation of Selective Mono-deallylation of *O*,*O*′-Diallylcatechols and 3-Methylene-1,5-benzodioxepanes

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Selective mono-deallylation of *O*,*O*′-diallylcatechols using 10% Pd/C was investigated to give the corresponding allylphenols. A similar reaction of 3-methylene-1,5-benzodioxepanes afforded *O*-methacryl catecohols. When substrates bearing various substituents on the benzene ring were subjected to the reaction, regioselective cleavage of an ether bond occurred at the side of *para* position to an electron-withdrawing group on the aromatic ring. On the other hand, an electron-donating group did not cause any selectivity.

Key words deallylation; palladium charcoal; *O*,*O*′-diallylcatechol; 3-methylene-1,5-benzodioxepane

Protective groups play an important role in organic synthesis.[2)] Allyl ether is known as one of the useful protective groups because of its stability in hydrolysis towards both acidic and basic conditions. Recently, we reported a novel procedure for the deallylation of various allyl aryl ethers with 10% Pd/C in 10% KOH–MeOH.[3—5)] However, in the reaction, *O*-allylphenol, having a strong electron-donating group such as a hydroxy group, gave poor results (Chart 1). Thus, when this reaction is applied to *O*,*O*′-diallylcatechols, *O*-allylphenol, which has an electron-donating hydroxyl group, would be formed by selective mono-deallylation.[6—9)] Because the product is a mono *O*-protected catechol, it would be a useful intermediate in organic synthesis. In this paper, we describe regioselective mono-deallylation of *O*,*O*′-diallylcatechols and 3-methylene-1,5-benzodioxepanes (Chart 2).

Results and Discussion

At first, the reaction of various *O*,*O*′-diallylcatechols was examined (Chart 3). The reaction of *O*,*O*′-diallylcatechol (**1**)[10)] with 10% Pd/C in 10% KOH–MeOH[3)] for 4 d gave the expected *O*-allylphenol (**2**)[11)] in 72% yield along with unchanged **1** (12%). A similar reaction of 2,3-diallyloxynapthalene (**3**)[12)] afforded naphthalenol (**4**) in 65% yield. In each case, no further deallylation product from **2** or **4** was produced, as expected. Unfortunately, the reaction of 1,2-diallyloxynapthalene (**5**) failed to give a complex mixture. As a result, the deallylation reaction of *O*,*O*′-diallylcatechols required a long time, or unexpected degradation of the starting material occurred.

Next, we turned our attention to the reaction of 3-methylene-1,5-benzodioxepanes, because the strain due to the 7-membered ring would facilitate a ring cleavage compared to the cleavage of the allyl moiety in *O*,*O*′-diallylcatechols. Thus, the reaction of 3-methylene-1,5-benzodioxepane (**6**),[13)] which was obtained from catechol and 3-chloro-2-methylpropene, was performed for 7 h to give *O*-methacrylphenol (**7**)[14)] in 73% yield. Interestingly, a similar reaction of **6** using $Pd(PPh_3)_4$ instead of Pd/C was sluggish and afforded **8** (61%) by mono-deprotection after 24 h along with unchanged **6** (24%).

The Pd/C-mediated reaction of the naphthalene derivative (**9**) furnished **10** in 84% yield. In the case of **11**, which has a similar 1,2-diallyloxy moiety in **5**, **12** was produced regioselectively. The structure of **12** was determined as follows. Methylation of **12**, and subsequently the Claisen rearrangement, proceeded to give **14**. Because it is known that the Claisen rearrangement of 1-substitued naphthalene having an allyloxy moiety at C-2 does not produce 3-allyl-2-naphthalenol,[15)] **12** was determined as 2-naphthalenol. As a result, it was confirmed that 3-methylene-1,5-benzodioxepanes are superior to *O*,*O*′-diallylcatechols in the present reaction at the point of reaction time and yield of the product.

We next investigated the regioselective ring cleavage of substituted 3-methylene-1,5-benzodioxepanes. When the reaction of substrates (**15a**, **b**)[9)] having an electron-withdrawing group was performed, a regioselective cleavage of an ether bond occurred to furnish **16a**, **b**. However, low regioselectiv-

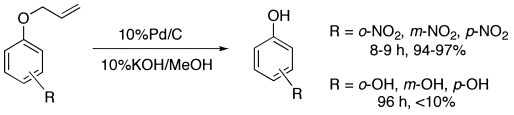

Chart 1

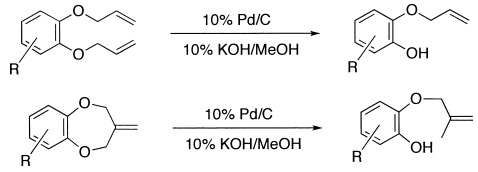

Chart 2

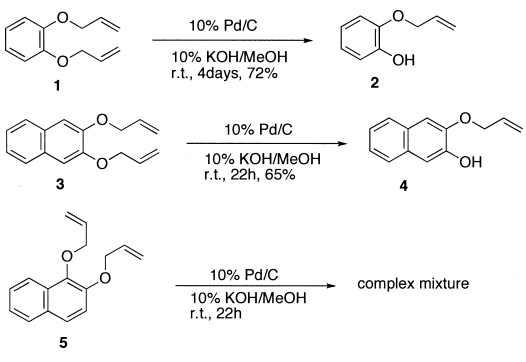

Chart 3

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ity was observed in the reaction of substrates (**15c**, **d**)[9] bearing an electron-donating group.

The structure of the products (**16a**, **b**, **d** and **17d**) was determined by their conversion to the corresponding acetates. In ^{1}H-NMR, chemical shifts (δ 7.19, 7.22, 6.81) of the C6 proton of acetylated products (**18**, **19**, **22**) were observed at a lower field than those (δ 7.00, 7.06, 6.47) of the deallylation products (**16a**, **b**, **d**). In the case of **16c** and **17c**, one of the catalytic hydrogenation products was identical with the product (**20**) obtained from **16b** by catalytic hydrogenation.

Interestingly, a similar deallylation of *O*,*O*′-diallyl protocatechoaldehyde (**24**), which has the same electron-withdrawing group as in **15b**, resulted in the formation of two regioisomers (**25**, **26**), the structures of which were determined by conversion to known compounds (**27**, **28**).[4]

Conclusion

In summary, Pd/C-mediated mono-deallylation of various *O*,*O*′-diallylcatechols and 3-methylene-1,5-benzodioxepanes was investigated to give the expected monophenols. It was found that 3-methylene-1,5-benzodioxepanes were superior to *O*,*O*′-diallylcatechols in the present reaction at the point of reaction time and yield of product. A regioselective cleavage of an ether bond occurred in the reaction of 3-methylene-1,5-benzodioxepanes having an electron-withdrawing group, whereas low regioselectivity was observed in the substrates bearing an electron-donating group. The present reaction offers a convenient synthesis of mono *O*-protected catechols, which are thought to be important intermediates for access to drugs and natural products.

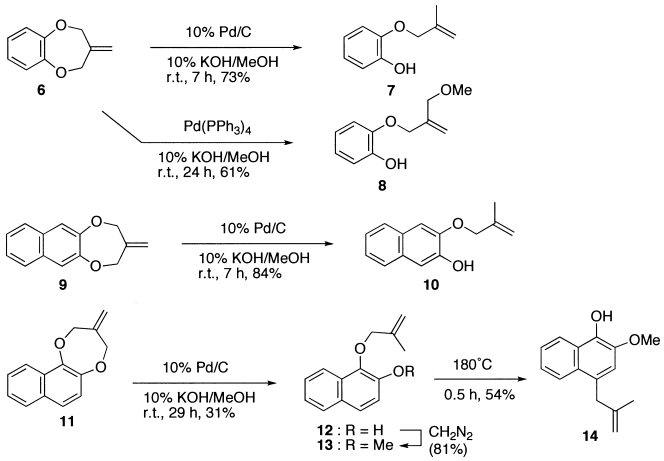

Chart 4

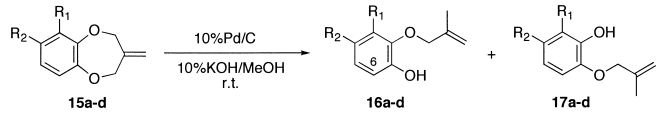

Chart 5

Experimental

General All melting points were measured on a Yanagimoto (hot plate) melting point apparatus and are uncorrected. ^{1}H-NMR spectra were taken with a JEOL JNM AL-300 (300 MHz) spectrometer in a $CDCl_3$ solution with tetramethylsilane as the internal standard. Mass spectra were measured on a Hitachi M-80 or a JEOL JMS D-300 spectrometer. Column chromatography was performed over silica gel (Merck Kiegelsel 60). Preparative TLCs were run on Merck 5744, or Merck 5715 plates. Organic extracts were dried over $MgSO_4$. Ten percent Pd/C was purchased from Kojima Co. and used as received (Lot. No. 206047).

General Procedure for the Preparation of *O*,*O*′-Diallylcatechols A mixture of dihydroxyarene (1 eq), 3-bromopropene (2.5 eq), NaI (0.1 eq) and K_2CO_3 (3 eq) in DMF was stirred at r.t. for 1 h. Then, the solid mass was fil-

Table 1. Regioselective Deallylation of Various 3-Methylene-1,5-benzodioxepanes (**15a**—**d**)

Entry	Substrates	R_1	R_2	**16** (%)[a]	**17** (%)[a]
1	**15a**	H	NO_2	86	0
2	**15b**	H	CHO	62	0
3	**15c**	H	Me	32[b]	61[b]
4	**15d**	OMe	H	21	54

a) Isolated yield. *b*) Determined by ^{1}H-NMR.

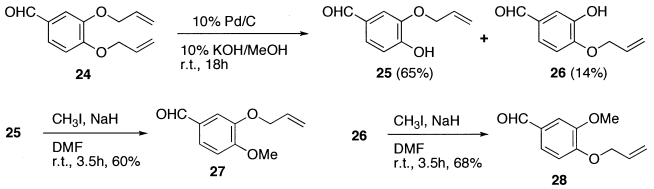

Chart 7

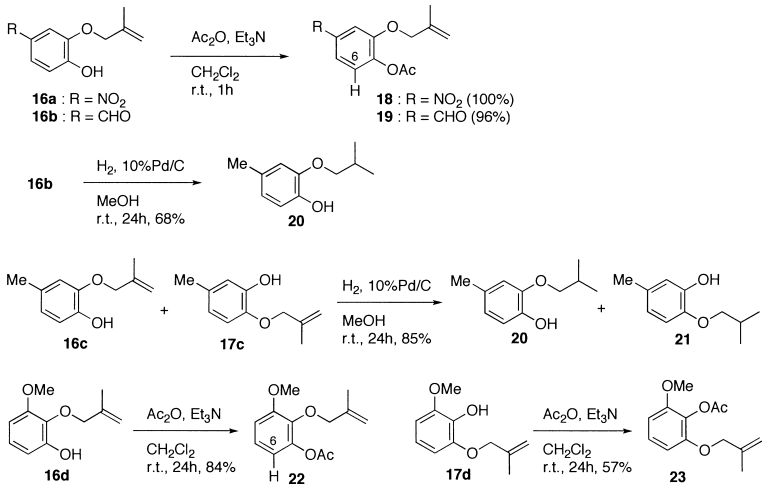

Chart 6

tered off. The filtrate was diluted with water and extracted with ether. The organic extracts were washed with water and brine, dried and evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography (hexane : AcOEt=10—30 : 1) to give *O,O′*-diallylcatechols.

1,2-Bis(2-propenyloxy)benzene (1) From catechol (1.009 g, 9.17 mmol), **1** (1.649 g, 95%) was obtained as a colorless oil. ^{1}H-NMR δ: 4.60 (4H, dt, J=5.3, 1.6 Hz, OCH_2), 5.26 (2H, dq, J=10.5, 1.6 Hz, C=CH_2), 5.41 (2H, dq, J=17.2, 1.6 Hz, C=CH_2), 6.08 (2H, ddq, J=17.2, 10.5, 5.3 Hz, C$\underline{H}$=CH_2), 6.90 (4H, s, aromatic H). MS m/z 190 (M^+). HR-MS m/z Calcd for $C_{12}H_{14}O_2$ (M^+): 190.0993. Found: 190.1001.

2,3-Bis(2-propenyloxy)benzene (3) From 2,3-dihydroxynaphthalene (1.004 g, 6.27 mmol), **3** (1.0502 g, 70%) was obtained as colorless crystals. mp 59—60 °C (hexane). ^{1}H-NMR δ: 4.70 (4H, dt, J=5.3, 1.5 Hz, OCH_2), 5.31 (2H, dq, J=10.6, 1.5 Hz, C=C$\underline{H}$H), 5.48 (2H, dq, J=17.2, 1.5 Hz, C=CH$\underline{H}$), 6.08—6.21 (2H, ddq, J=17.2, 10.6, 5.3 Hz, C$\underline{H}$=CH_2), 7.12 (2H, s, aromatic H), 7.31, 7.65 (each 2H, dd, J=6.1, 3.3 Hz, aromatic H). MS m/z 240 (M^+). HR-MS m/z Calcd for $C_{16}H_{16}O_2$ (M^+): 240.1150. Found: 240.1141.

1,2-Bis(2-propenyloxy)naphthalene (5) From 1,2-dihydroxynaphthalene (0.499 g, 3.11 mmol), **5** (0.552 g, 74%) was obtained as a colorless oil. ^{1}H-NMR δ: 4.68—4.73 (4H, m, OCH_2), 5.23—5.31 (2H, m, C=C$\underline{H}$H), 5.41—5.49 (2H, m, C=CH$\underline{H}$), 6.06—6.26 (2H, m, C$\underline{H}$=CH_2), 7.26, 7.57 (each 1H, d, J=9 Hz, aromatic H), 7.36, 7.46 (each 1H, dd, J=6.8, 1.3 Hz, aromatic H), 7.75—7.78 (each 1H, m, aromatic H), 8.13—8.17 (each 1H, m, aromatic H). MS m/z 240 (M^+). HR-MS m/z Calcd for $C_{16}H_{16}O_2$ (M^+): 240.1150. Found: 240.1149.

3,4-Bis(2-propenyloxy)benzaldehyde (24) From 3,4-dihydroxybenzaldehyde (1.269 g, 9.19 mmol), **24** (2.011 g, 100%) was obtained as a colorless oil. ^{1}H-NMR δ: 4.66, 4.70 (each 2H, dt, J=5.0, 1.5 Hz, OCH_2), 5.30, 5.34 (each 1H, dq, J=8.1, 1.3 Hz, C=CH$\underline{H}$), 5.45 (2H, dq, J=18.2, 1.3 Hz, C=C$\underline{H}$H), 6.02—6.16 (2H, m, C$\underline{H}$=CH_2), 6.98 (1H, d, J=7.4 Hz, aromatic H), 7.41—7.45 (2H, m, aromatic H), 9.83 (1H, s, CHO). MS m/z 218 (M^+). HR-MS m/z Calcd for $C_{13}H_{14}O_3$ (M^+): 218.0943. Found: 218.0943.

General Procedure for the Preparation of 3-Methylene-1,5-benzodioxepanes A mixture of catechol (1 eq), 3-chloro-2-methylpropene (1 eq) and K_2CO_3 (2 eq) in 2-butanone and DMF (5 : 2) was heated at 80 °C. After completion of the reaction, the solid mass was filtered. The filtrate was diluted with water and extracted with ether. The organic extracts were washed with water and brine, dried and evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography (hexane : AcOEt=10 : 1) to give 3-methylene-1,5-benzodioxepanes.

3-Methylene-1,5-benzodioxepane (6) From catechol (0.554 g, 5.03 mmol), **6** (0.521 g, 64%) was obtained as a colorless oil. ^{1}H-NMR δ: 4.76 (4H, s, OCH_2), 5.06 (2H, s, C=CH_2), 6.87—6.96 (4H, m, aromatic H). MS m/z 162 (M^+). HR-MS m/z Calcd for $C_{10}H_{10}O_2$ (M^+): 162.0680. Found: 168.0675.

3,4-Dihydro-3-methylene-2*H*-naphtho[2,3-*b*][1,4]dioxepin (9) From 2,3-dihydroxynaphthalene (1.014 g, 6.33 mmol), **8** (0.701 g, 52%) was obtained as colorless crystals. mp 77—78 °C (hexane). ^{1}H-NMR δ: 4.79 (4H, t, J=1.1 Hz, OCH_2), 5.11 (2H, t, J=1.1 Hz, C=CH_2), 7.32, 7.65 (each 2H, dd, J=6.2, 3.3 Hz, aromatic H), 7.37 (2H, s, aromatic H). MS m/z 212 (M^+). HR-MS m/z Calcd for $C_{14}H_{12}O_2$ (M^+): 212.0837. Found: 212.0832.

3,4-Dihydro-3-methylene-2*H*-naphtho[1,2-*b*][1,4]dioxepin (11) From 1,2-dihydroxynaphthalene (0.500 g, 3.13 mmol), **11** (0.367 g, 55%) was obtained as colorless crystals. ^{1}H-NMR δ: 4.90, 4.97 (each 2H, s, OCH_2), 5.12 (2H, t, J=1.1 Hz, C=CH_2), 7.12 (1H, d, J=8.8 Hz, aromatic H), 7.34—7.48 (3H, m, aromatic H), 7.73, 8.15 (each 1H, dd, J=8.3, 0.6 Hz, aromatic H). MS m/z 212 (M^+). HR-MS m/z Calcd for $C_{14}H_{12}O_2$ (M^+): 212.0837. Found: 212.0831.

3-Methylene-7-nitro-1,5-benzodioxepane (15a) From 4-nitrocatechol (3.011 g, 19.4 mmol), **15a** (3.521 g, 86%) was obtained as yellow crystals. mp 87—88 °C (2-propanol). ^{1}H-NMR δ: 4.83, 4.89 (each 2H, s, OCH_2), 5.15, 5.17 (each 1H, s, C=CH_2), 6.99—7.00 (1H, m, aromatic H), 7.80—7.85 (2H, m, aromatic H). MS m/z 207 (M^+). HR-MS m/z Calcd for $C_{10}H_9O_4N$ (M^+): 207.0531. Found: 207.0534.

3-Methylene-1,5-benzodioxepane-7-carbaldehyde (15b) From 3,4-dihydroxybenzaldehyde (0.996 g, 7.21 mmol), **15b** (0.8331 g, 61%) was obtained as a colorless oil. ^{1}H-NMR δ: 4.79, 4.86 (each 2H, s, OCH_2), 5.09, 5.13 (each 1H, s, C=CH_2), 7.01 (1H, d, J=8.8 Hz, aromatic H), 7.45—7.47 (2H, m, aromatic H), 9.82 (1H, s, CHO). MS m/z 190 (M^+). HR-MS (EI) m/z Calcd for $C_{11}H_{10}O_3$ (M^+) 190.0629. Found: 190.0629.

7-Methyl-3-methylene-1,5-benzodioxepane (15c) From 4-methylcatechol (1.007 g, 8.12 mmol), **15c** (0.872 g, 61%) was obtained as a colorless oil. ^{1}H-NMR δ: 2.20 (3H, s, CH_3), 4.67, 4.69 (each 2H, s, OCH_2), 5.00—5.02 (2H, m, C=CH_2), 6.63—6.69 (2H, m, aromatic H), 6.77 (1H, d, J=8.1 Hz, aromatic H). MS m/z 176 (M^+). HR-MS m/z Calcd for $C_{11}H_{12}O_2$ (M^+): 176.0836. Found: 176.0837.

6-Methoxy-3-methylene-1,5-benzodioxepane (15d) From 3-methoxycatechol (3.009 g, 21.5 mmol), **15d** (3.422 g, 83%) was obtained as a colorless oil. ^{1}H-NMR δ: 3.84 (3H, s, OCH_3), 4.77, 4.83 (each 2H, s, OCH_2), 5.06 (2H, s, C=CH_2), 6.54—6.58 (2H, m, aromatic H), 6.83 (1H, t, J=7.6 Hz, aromatic H). MS m/z 192 (M^+). HR-MS m/z Calcd for $C_{11}H_{12}O_3$ (M^+): 192.0786. Found: 192.0786.

General Procedure for the Deallylation Reaction of *O,O′*-Diallylcatechols and 3-Methylene-1,5-benzodioxepanes A mixture of *O,O′*-diallylcatechol (100 mg) or 3-methylene-1,5-benzodioxepanes (100 mg) with 10% Pd/C (20 mg) in 10% KOH–MeOH (10 ml) was stirred at ambient temperature for an appropriate time. After the catalyst was filtered, the filtrate was concentrated *in vacuo*. A one-molar aqueous HCl solution was added to the residue and the mixture was extracted with AcOEt. The organic extracts were washed with brine and dried. The solvent was evaporated under reduced pressure to give a residue, which was purified by silica gel TLC to afford the corresponding phenol.

2-(2-Propenyloxy)phenol (2) Colorless oil. ^{1}H-NMR δ: 4.61 (2H, dt, J=4.9, 1.3 Hz, OCH_2), 5.32 (1H, ddd, J=11.7, 2.3, 1.2 Hz, C=CH$\underline{H}$), 5.41 (1H, ddd, J=16.8, 2.6, 1.2 Hz, C=C$\underline{H}$H), 5.66 (1H, br, OH), 6.07 (1H, ddt, J=17.2, 10.5, 5.5 Hz, C$\underline{H}$=CH_2), 6.78—6.97 (4H, m, aromatic H). MS m/z 150 (M^+). HR-MS m/z Calcd for $C_9H_{10}O_2$ (M^+) 150.0681. Found: 150.0688.

3-(2-Propenyloxy)naphthalen-2-ol (4) Colorless crystals. mp 39—39.5 °C. ^{1}H-NMR δ: 4.71 (2H, ddd, J=5.5, 1.5, 1.3 Hz, OCH_2), 5.36 (1H, dq, J=10.5, 1.3 Hz, C=CH$\underline{H}$), 5.46 (1H, dq, J=17.2, 1.3 Hz, C=C$\underline{H}$H), 5.97 (1H, br, OH), 6.12 (1H, ddt, J=17.2, 10.5, 5.5 Hz, C$\underline{H}$=CH_2), 7.11 (1H, s, aromatic H), 7.28—7.33 (3H, m, aromatic H), 7.63—7.66 (2H, m, aromatic H). MS m/z 200 (M^+). HR-MS m/z Calcd for $C_{13}H_{12}O_2$ (M^+): 200.0836. Found: 200.0835.

2-(2-Methyl-2-propenyloxy)phenol (7) Colorless oil. ^{1}H-NMR δ: 1.84 (3H, d, J=0.6 Hz, CH_3), 4.50 (2H, s, OCH_2), 5.02 (1H, dd, J=0.9, 0.6 Hz, C=CH$\underline{H}$), 5.08 (1H, dd, J=0.9, 0.6 Hz, C=C$\underline{H}$H), 5.67 (1H, s, OH), 6.79—6.96 (4H, m, aromatic H). MS m/z 164 (M^+). HR-MS m/z Calcd for $C_{10}H_{12}O_2$ (M^+): 164.0837. Found: 164.0831.

3-(2-Methyl-2-propenyloxy)naphthalen-2-ol (10) Colorless crystals. mp 39 °C. ^{1}H-NMR δ: 1.87 (3H, s, CH_3), 4.62 (2H, s, OCH_2), 5.06 (1H, s, C=CH$\underline{H}$), 5.14 (1H, s, C=C$\underline{H}$H), 5.97 (1H, s, OH), 7.11 (1H, s, aromatic H), 7.23—7.34 (3H, m, aromatic H), 7.63—7.66 (2H, m, aromatic H). MS m/z 214 (M^+). HR-MS m/z Calcd for $C_{14}H_{14}O_2$ (M^+): 214.0993. Found: 214.0999.

1-(2-Methyl-2-propenyloxy)naphthalen-2-ol (12) Colorless crystals. ^{1}H-NMR δ: 1.94 (3H, s, CH_3), 4.43 (2H, s, OCH_2), 5.09 (1H, s, C=CH$\underline{H}$), 5.30 (1H, s, C=C$\underline{H}$H), 5.84 (1H, s, OH), 7.22 (1H, d, J=8.8 Hz, aromatic H), 7.33 (1H, ddd, J=8.3, 8.1, 1.3 Hz, aromatic H), 7.47 (1H, ddd, J=8.4, 8.3, 1.3 Hz, aromatic H), 7.55 (1H, d, J=8.8 Hz, aromatic H), 7.77 (1H, d, J=8.3 Hz, aromatic H), 7.94 (1H, d, J=8.4 Hz, aromatic H). MS m/z 214 (M^+). HR-MS m/z Calcd for $C_{14}H_{14}O_2$ (M^+): 214.0993. Found: 214.0990.

2-(2-Methyl-2-propenyloxy)-4-nitrophenol (16a) Yellow crystals. mp 170—171 °C (MeOH–iPr$_2$O). ^{1}H-NMR δ: 1.85 (3H, s, CH_3), 4.61 (2H, s, OCH_2), 5.09 (1H, d, J=1.0 Hz, C=CH$\underline{H}$), 5.12 (1H, d, J=1.0 Hz, C=C$\underline{H}$H), 6.24 (1H, s, OH), 7.00 (1H, d, J=8.8 Hz, aromatic H), 7.76 (1H, d, J=2.6 Hz, aromatic H), 7.88 (1H, dd, J=8.8, 2.6 Hz, aromatic H). MS m/z 209 (M^+). HR-MS m/z Calcd for $C_{10}H_{12}O_4N$ (M^+): 209.0688. Found: 209.0695.

4-Hydroxy-3-(2-methyl-2-propenyloxy)benzaldehyde (16b) Colorless oil. ^{1}H-NMR δ: 1.85 (3H, d, J=0.6 Hz, CH_3), 4.59 (2H, s, OCH_2), 5.06 (1H, dd, J=0.9, 0.6 Hz, C=CH$\underline{H}$), 5.10 (1H, dd, J=0.9, 0.6 Hz, C=C$\underline{H}$H), 6.28 (1H, s, OH), 7.06, 7.42 (each 1H, d, J=7.7 Hz, aromatic H), 7.44 (1H, dd, J=1.7, 0.7 Hz, aromatic H), 9.81 (1H, d, J=0.7 Hz, CHO). MS m/z 192 (M^+). HR-MS m/z Calcd for $C_{11}H_{12}O_3$ (M^+): 192.0786. Found: 192.0790.

4-Methyl-2-(2-methyl-2-propenyloxy)phenol (16c) and 5-Methyl-2-(2-methyl-2-propenyloxy)phenol (17c) An inseparable mixture of **16c** and **17c** (93%) was obtained as a colorless oil. The ratio of **16c** and **17c** was determined to be *ca.* 1 : 2 by ^{1}H-NMR analysis. ^{1}H-NMR δ: 1.82, 1.83 (together 3H, each s, CH_3), 2.35, 2.27 (together 3H, each s, aromatic CH_3), 4.44, 4.45 (together 2H, each s, OCH_2), 5.00 (1H, s, =CH_2), 5.07 (1H, s, =CH_2), 5.50 (0.66H, s, OH), 5.62 (0.34H, s, OH), 6.59—6.83 (3H, m, aromatic H). MS m/z 178 (M^+). HR-MS m/z Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994. Found: 178.0990.

3-Methoxy-2-(2-methyl-2-propenyloxy)phenol (16d) Colorless oil. ^{1}H-NMR δ: 1.87 (3H, s, CH_3), 3.85 (3H, s, OCH_3), 4.47 (2H, s, OCH_2), 4.99

(1H, s, C=CHH), 5.11 (1H, s, C=CHH), 5.83 (1H, s, OH), 6.47 (1H, dd, J=8.3, 1.4 Hz, aromatic H), 6.61 (1H, dd, J=8.3, 1.4 Hz, aromatic H), 6.93 (1H, t, J=8.3 Hz, aromatic H). MS m/z 194 (M^+). HR-MS m/z Calcd for $C_{11}H_{14}O_3$ (M^+): 194.0941. Found: 194.0935.

2-Methoxy-6-(2-methyl-2-propenyloxy)phenol (17d) Colorless oil. ^{1}H-NMR δ: 1.83 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 4.51 (2H, s, OCH_2) 4.99 (1H, s, C=CHH), 5.08 (1H, s, C=CHH), 5.58 (1H, s, OH), 6.57 (1H, t, J=8.6 Hz, aromatic H), 6.76 (2H, d, J=8.6 Hz, aromatic H). MS m/z 194 (M^+). HR-MS m/z Calcd for $C_{11}H_{14}O_3$ (M^+): 194.0941. Found: 194.0940.

2-(2-Methoxyallyloxy)phenol (8) A mixture of an **6** (0.100 g) and $Pd(PPh_3)_4$ (2 mg) in 10% KOH–MeOH (10 ml) was stirred at r.t. for 24 h. After the solvent was concentrated *in vacuo*, the residue was purified by silica gel TLC (hexane : AcOEt=10 : 1) to afford **8** (0.073 g, 61%) as a colorless oil. ^{1}H-NMR δ: 3.39 (3H, s, OCH_3), 4.08 (2H, s, OCH_2), 4.59 (2H, s, CH_2OCH_3), 5.28 (1H, s, C=CHH), 5.29 (1H, s, C=CHH), 6.47 (1H, br s, OH), 6.80—6.92 (4H, m, aromatic H). MS m/z 178 (M^+). HR-MS m/z Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994. Found: 178.0991.

2-Methoxy-1-(2-methyl-2-propenyloxy)naphthalene (13) To a suspension of **12** (0.029 g, 0.14 mmol) in MeOH (3 ml) was added an ethereal solution of diazomethane (15 ml). Then the solvent was reduced under reduced pressure to give a residue, which was purified by preparative TLC (hexane : AcOEt=5 : 1) to afford **13** (0.025 g, 81%) as a colorless oil. ^{1}H-NMR δ: 1.96 (3H, s, CH_3), 3.97 (3H, s, OCH_3), 4.50 (2H, s, OCH_2), 5.01 (1H, s, C=CHH), 5.23 (1H, s, C=CHH), 7.28 (1H, d, J=9.0 Hz, aromatic H), 7.35 (1H, ddd, J=8.3, 8.1, 1.3 Hz, aromatic H), 7.46 (1H, ddd, J=8.4, 8.3, 1.3 Hz, aromatic H), 7.59 (1H, d, J=9.0 Hz, aromatic H), 7.77 (1H, d, J=8.1 Hz, aromatic H), 8.15 (1H, d, J=8.4 Hz, aromatic H). MS m/z 228 (M^+). HR-MS m/z Calcd for $C_{15}H_{16}O_2$ (M^+): 228.1149. Found: 228.1141.

2-Methoxy-4-(2-methyl-2-propenyl)naphthalen-1-ol (14) After **13** (0.025 g, 0.11 mmol) was heated at 180 °C for 0.5 h, purification by preparative TLC (hexane : AcOEt=5 : 1) gave **14** (0.014 g, 54%) as a pale yellow oil. ^{1}H-NMR δ: 1.77 (3H, s, CH_3), 3.71 (2H, s, CH_2), 3.98 (3H, s, OCH_3), 4.60 (1H, s, C=CHH), 4.84 (1H, s, C=CHH), 5.92 (1H, s, OH), 7.11 (1H, s, aromatic H), 7.35 (1H, ddd, J=8.4, 8.3, 1.5 Hz, aromatic H), 7.43 (1H, ddd, J=8.3, 8.3, 1.5 Hz, aromatic H), 7.88 (1H, d, J=8.4 Hz, aromatic H), 8.17 (1H, dd, J=8.3, 1.5 Hz, aromatic H). MS m/z 228 (M^+). HR-MS m/z Calcd for $C_{15}H_{16}O_2$ (M^+): 228.1149. Found: 228.1155.

1-Acetoxy-2-(2-methyl-2-propenyl)-4-nitrobenzene (18) A mixture of **16a** (0.054 g, 0.26 mmol), Et_3N (0.060 g, 0.60 mmol), and acetic anhydride (0.053 g, 0.52 mmol) in 3 ml of $CHCl_3$ was stirred at r.t. for 1 h. After the reaction was quenched with water, the mixture was extracted with $CHCl_3$. The organic extracts were washed with brine, dried, and evaporated under reduced pressure to give a residue, which was purified by recrystallization to afford **18** (0.076 g, 100%) as colorless crystals. mp 74.5—75 °C (2-propanol). ^{1}H-NMR δ: 1.82 (3H, s, CH_3), 2.35 (3H, s, $COCH_3$), 4.54 (2H, s, OCH_2), 5.04 (1H, s, C=CHH), 5.10 (1H, s, C=CHH), 7.19 (1H, d, J=8.8 Hz, aromatic H), 7.82 (1H, d, J=2.6 Hz, aromatic H), 7.87 (1H, dd, J=8.8, 2.6 Hz, aromatic H). MS m/z 251 (M^+). HR-MS m/z Calcd for $C_{12}H_{13}NO_5$ (M^+): 251.0792. Found: 251.0787.

1-Acetoxy-2-(2-methyl-2-propenyl)-4-nitrobenzene (19) After acetylation of **16b** (0.040 g, 0.21 mmol) similar to that described for **16a**, **19** (0.048 g, 96%) was obtained as a colorless oil. ^{1}H-NMR δ: 1.81 (3H, d, J=0.6 Hz, CH_3), 2.34 (3H, s, $COCH_3$), 4.52 (2H, s, OCH_2), 5.00 (1H, d, J=0.9 Hz, C=CHH), 5.08 (1H, d, J=0.9 Hz, C=CHH), 7.22 (1H, d, J=8.3 Hz, aromatic H), 7.46—7.49 (2H, m, aromatic H), 9.93 (1H, s, CHO). MS m/z 234 (M^+). HR-MS m/z Calcd for $C_{13}H_{14}O_4$ (M^+): 234.0892. Found: 234.0897.

2-Isobutoxy-4-methylphenol (20) Catalytic hydrogenation of **16b** (0.030 g, 0.16 mmol) with 10% Pd/C (6.0 mg) in MeOH (2 ml) was performed at r.t. for 24 h. After filtration of the catalyst, evaporation of the filtrate gave **20** (0.021 g, 68%) as a colorless oil. ^{1}H-NMR δ: 1.03 (6H, d, J=6.8 Hz, CH_3), 2.12 (1H, tq, J=6.8, 6.6 Hz, $CH(CH_3)_2$), 2.27 (3H, s, $ArCH_3$), 3.78 (2H, d, J=6.6 Hz, OCH_2), 5.49 (1H, br, OH), 6.63—6.65 (2H, m, aromatic H), 6.81 (1H, d, J=8.1 Hz, aromatic H). MS m/z 180 (M^+). HR-MS m/z Calcd for $C_{11}H_{16}O_2$ (M^+): 180.1149. Found: 180.1148.

2-Isobutoxy-4-methylphenol (20) and 2-Isobutoxy-5-methylphenol (21) A mixture of phenols (**16c**, **17c**) (0.029 g, 0.16 mmol) and 10% Pd/C (6.5 mg) in MeOH (2 ml) was stirred at r.t. for 24 h. After filtration of the catalyst, the filtrate was evaporated under reduced pressure to give an inseparable mixture of **20** and **21** (0.025 g, 85%). The ratio (1 : 2) of **20** and **21** was determined by ^{1}H-NMR analysis. The ^{1}H-NMR spectrum of the former product (**20**) was identical with that obtained by the reduction of **16b**.

21: ^{1}H-NMR δ: 1.02 (6H, d, J=6.8 Hz, CH_3), 2.03—2.18 (1H, m, $CH(CH_3)_2$), 2.25 (3H, s, $ArCH_3$), 3.76 (2H, d, J=6.4 Hz, OCH_2), 5.60 (1H, s, OH), 6.59—6.75 (2H, m, aromatic H), 6.72 (1H, d, J=8.1 Hz, aromatic H). MS m/z 180 (M^+). HR-MS m/z Calcd for $C_{11}H_{16}O_2$ (M^+): 180.1149. Found: 180.1145.

2-Acetoxy-1-methoxy-3-(2-methyl-2-propenyloxy)benzene (22) Acetylation of **15d** (0.042 g, 0.22 mmol) similar to that described for **16a** afforded **22** (0.043 g, 84%) as a colorless oil. ^{1}H-NMR δ: 1.84 (3H, s, CH_3), 2.29 (3H, s, $COCH_3$), 3.86 (3H, s, OCH_3), 4.41 (2H, s, OCH_2), 4.93 (1H, s, C=CHH), 5.07 (1H, s, C=CHH), 6.68 (1H, dd, J=8.3, 1.5 Hz, aromatic H), 6.81 (1H, dd, J=8.3, 1.5 Hz, aromatic H), 7.02 (1H, d, J=8.3 Hz, aromatic H). MS m/z 236 (M^+). HR-MS m/z Calcd for $C_{13}H_{16}O_4$ (M^+): 236.1047. Found: 236.1042.

1-Acetoxy-3-methoxy-2-(2-methyl-2-propenyloxy)benzene (23) Acetylation of **17d** (0.049 g, 0.25 mmol) similar to that described for **16a** afforded **23** (0.034 g, 57%) as a colorless oil. ^{1}H-NMR δ: 1.79 (3H, s, CH_3), 2.33 (3H, s, $COCH_3$), 3.82 (3H, s, OCH_3), 4.43 (2H, s, OCH_2), 4.96 (1H, s, C=CHH), 5.05 (1H, s, C=CHH), 6.59 (1H, dd, J=8.4, 0.9 Hz, aromatic H), 6.60 (1H, dd, J=8.4, 0.9 Hz, aromatic H), 7.09 (1H, d, J=8.4 Hz, aromatic H). MS m/ 236 (M^+). HR-MS m/z Calcd for $C_{13}H_{16}O_4$ (M^+): 236.1047. Found: 236.1047.

4-Hydroxy-3-(2-propenyloxy)benzaldehyde (25) and 3-Hydroxy-4-(2-propenyloxy)benzaldehyde (26) From **24** (51.7 mg, 0.237 mmol), **25** (34 mg, 65%) and **26** (7.2 mg, 14%) were obtained as colorless crystals.

25: mp 64.5—65.5 °C (iPr$_2$O). ^{1}H-NMR δ: 4.69 (2H, dt, J=5.5, 1.5 Hz, OCH_2), 5.36 (1H, dq, C=CHH), 5.44 (1H, dq, C=CHH), 6.00—6.13 (1H, m, CH=CH_2), 6.29 (1H, s, OH), 7.06 (1H, dd, J=7.2, 1.1 Hz aromatic H), 7.41—7.44 (2H, m, aromatic H), 9.82 (1H, s, CHO). MS m/z 178 (M^+). HR-MS m/z Calcd for $C_{10}H_{10}O_3$ (M^+): 178.0630. Found: 178.0621.

26: ^{1}H-NMR δ: 4.70 (2H, dt, J=5.5, 1.5 Hz, OCH_2), 5.40 (1H, dq, C=CHH), 5.44 (1H, dq, C=CHH), 5.80 (1H, s, OH), 6.00—6.13 (1H, m, CH=CH_2), 6.97 (1H, d, J=8.3 Hz aromatic H), 7.41 (1H, dd, J=8.3, 2.0 Hz, aromatic H), 7.45 (1H, d, J=2.0 Hz, aromatic H), 9.84 (1H, s, CHO). MS m/z 178 (M^+). HR-MS m/z Calcd for $C_{10}H_{10}O_3$ (M^+) 178.0630. Found: 178.0623.

4-Methoxy-3-(2-propenyloxy)benzaldehyde (27) A mixture of **25** (0.051 g, 0.28 mmol) and NaH (0.020 mg, 0.53 mmol) in DMF (2 ml) was stirred at r.t. for 5 min. After MeI (0.057 g, 0.40 mmol) was added to the mixture, the mixture was stirred for 3.5 h. Then, the reaction was quenched with water. The mixture was extracted with Et_2O. The organic extracts were washed with brine, dried and evaporated under reduced pressure to give a residue, which was purified by preparative TLC (hexane : AcOEt=5 : 1) to afford **27** (0.033 g, 60%) as a colorless oil. ^{1}H-NMR δ: 3.96 (3H, s, OCH_3), 4.67 (2H, ddd, J=5.5, 1.5, 1.3 Hz, OCH_2), 5.33 (1H, dq, J=10.5, 1.3 Hz, C=CHH), 5.45 (1H, dq, J=17.2, 1.5 Hz, C=CHH), 6.10 (1H, ddt, J=17.2, 10.5, 5.5 Hz, CH=CH_2), 6.99 (1H, d, J=8.3 Hz, aromatic H), 7.41 (1H, d, J=1.8 Hz, aromatic H), 7.46 (1H, dd, J=8.3, 1.8 Hz, aromatic H), 9.84 (1H, s, CHO). MS m/z 192 (M^+). HR-MS m/z Calcd for $C_{11}H_{12}O_3$ (M^+): 192.0785. Found: 192.0784.

3-Methoxy-4-(2-propenyloxy)benzaldehyde (28) After the reaction of **26** (0.040 g, 0.23 mmol) similar to that described for **27**, **28** (0.029 g, 68%) was obtained as a colorless oil. ^{1}H-NMR δ: 3.94 (3H, s, OCH_3), 4.71 (2H, ddd, J=5.3, 1.5, 1.3 Hz, OCH_2), 5.35 (1H, dq, J=10.5, 1.3 Hz, C=CHH), 5.44 (1H, dq, J=17.2, 1.5 Hz, C=CHH), 6.09 (1H, ddt, J=17.2, 10.5, 5.3 Hz, CH=CH_2), 6.98 (1H, d, J=8.8 Hz, aromatic H), 7.42—7.45 (2H, m, aromatic H), 9.85 (1H, s, CHO). MS m/z 192 (M^+). HR-MS m/z Calcd for $C_{11}H_{12}O_3$ (M^+) 192.0785. Found: 192.0779.

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References and Notes

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