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Palladium charcoal-catalyzed deprotection of *O*-allylphenols

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Abstract—Allyl aryl ethers can be easily cleaved by the use of 10% Pd/C under mild and basic conditions. The present reaction would involve a SET process rather than a π-allyl-palladium complex. The scope and limitation of this new deprotective methodology is also described.

1. Introduction

The phenolic hydroxyl group exists in various types of chemical compounds as demonstrated by the vast number of natural products in plant and animal life. The functional group plays a very important role in increasing biological activities in many cases. In developing a synthesis of any phenol-containing products, protection is often mandatory to prevent reaction with oxidizing agents and electrophiles or reaction of the nucleophilic phenoxide ion with even mild alkylating and acylating agents. Thus, many of the protective groups have been developed for phenol protection.[1] Allyl ether is known as one of the useful protective groups because of its stability in hydrolysis towards both acidic and basic conditions. Also, facile preparation of allyl ethers from a phenol with an allyl halide in the presence of a base is quite advantageous. Therefore, several one-step deprotective methods among them have appeared,[1] of which Pd-catalyzed deprotection was one of the most interesting features. In fact, combinations of $Pd(PPh_3)_4$ and reducing agents such as $NaBH_4$,[2] $LiBH_4$,[3] Bu_3SnH,[4] $PhSiH_3$,[5] morphorine,[6] $ZnCl_2$-polymethylhydrosiloxane,[7] or $TolSO_2H$[8] were reported. Also, electrochemical cleavage using $PdCl_2$[9] was investigated. As an alternative catalyst, Boss and Scheffold reported a reaction using 10% Pd/C with *p*-TsOH[10] under reflux conditions. During our synthetic studies[11] on host compounds combined with a crown ether and two orthocyclophanes, we unexpectedly found deprotection of the phenolic allyl ether of tetra(*O*-allyl-6-bromoisovanillyl)dibenzo-18-crown-6 (**1**) which gave a tetraphenol (**2a**) instead of a propyl ether (**2b**) under reductive conditions (H_2, 10% Pd/C in 10% KOH–MeOH) (Scheme 1). The structure of **2a** was determined as the corresponding acetate (**2c**), because the high polarity of **2a** prevented extraction into organic solvents. This result indicated that **1** suffered not only debromination but also deallylation. We envisaged that the present reaction could be applied to the cleavage of *O*-allylphenols. Here, we wish to describe a facile and mild reaction for deprotection of *O*-allylphenols using 10% Pd/C in 10% KOH–MeOH at ambient temperature[12] and discuss the reaction mechanism (Scheme 2).

2. Results and discussion

At first, the essential conditions for this facile reaction were investigated by the use of *O*-allylvanillin (**3**)[13] as a model compound (Scheme 3, Table 1). Without either a Pd catalyst or base, the reaction did not occur at room temperature (entries 1 and 3). The crown ether part was not necessary for the reaction (entries 2 and 5). Although the reaction proceeded in the absence of KOH under reflux, it was sluggish and isomerized enol ethers (**5a**,**b**) were formed (entry 4).[14] As a base, NaOMe was also efficient (entry 6), however, eventually, it was verified to be a simple combination of reagents (10% Pd/C and 10% KOH–MeOH) for cleavage of the allyl ether (entry 5).

Next, we applied the present reaction to various types of mono-substituted *O*-allylphenols (**6a**–**o**) for confirmation of scope and limitation (Scheme 4, Table 2). *O*-Allylphenols (**6a**–**h**), which have an electron-withdrawing or weak

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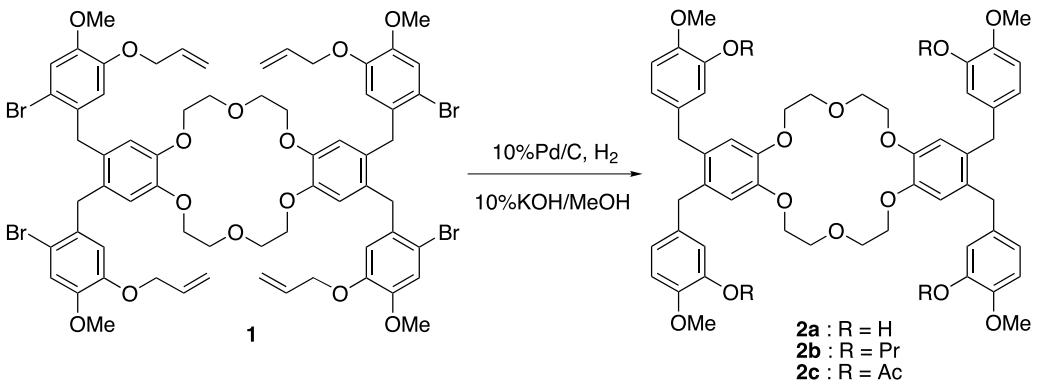
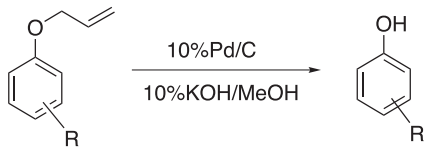
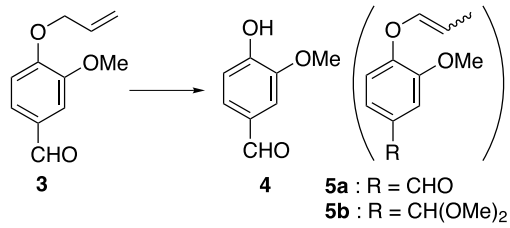


Scheme 1.



Scheme 2.



Scheme 3.

group, such as the methoxy or hydroxyl group, were lower compared with those of **6a**–**h** because of the formation of the corresponding propyl ethers (**8j**–**o**) by reduction and enol ethers (**9j**,**k**) by isomerization (entries 10–15).[14] Interestingly, although the reason was not clear, a substituted pattern on the benzene ring markedly affected the reaction. For example, deallylation of 2-methoxyallylphenol (**6l**) was faster than that of 3- and 4-methoxyallylphenols (**6j**,**k**) to yield 2-methoxyphenol (**7l**) in 76% yield (entries 10–12)

The reaction of more complex substrates (**6p**–**y**) also proceeded to afford the corresponding phenols (**7p**–**u**) in good to high yields (Table 3). Deprotection of *O*-allylphenols (**6s**,**t**), bearing an acid labile benzyl ether or acetal group, gave the corresponding phenols (**7s**,**t**) keeping another protective group (entries 4 and 5). Interestingly, in the reaction of the diether (**6u**), which has two kinds of allyl

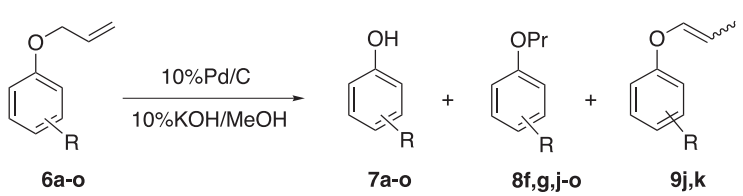
Table 1. Deallylation of *O*-allylvanillin (**3**)

Entry	Conditions	Yield (%)
1	10% KOH–MeOH, rt 24 h then reflux 24 h	0
2	10% KOH–MeOH, dibenzo-18-crown-6 (1 equiv), rt 24 h then reflux 24 h	0
3	10% Pd/C, MeOH, rt 72 h	0
4	10% Pd/C, MeOH, reflux 24 h	28[a]
5	10% Pd/C, 10% KOH–MeOH, rt 8 h	96
6	10% Pd/C, NaOMe (10 equiv), MeOH, rt 5 h	54

[a] Starting material (**3**; 49%) and enol ethers (**5a**; 9%, **5b**; 5%) were also obtained.

electron-donating group on the benzene ring, were readily deprotected to give the corresponding phenols (**7a**–**h**) in high yields (82–98%) (entries 1–8). It is noteworthy that the amido, cyano and nitro groups in the substrates remained intact during the reaction. In the case of *O*-allyl-4-bromophenol (**6i**), many by-products were observed on TLC to result in the formation of **7i** in moderate yield (entry 9). On the other hand, yields of deprotection for *O*-allylphenols (**6j**–**o**) bearing a strong electron-donating ethers, the allyl aryl ether bond was selectively cleaved to give phenol **7u** (81%) along with a small amount of benzyl propyl ether (**8u**) (10%) (entry 6). Moreover, the present reaction could apply to the substrates (**6v**–**y**), which have a variety of allyl ether moieties, to furnish *p*-nitrophenol (**7a**) in high yields (entries 7–10).

During the investigation of the present reaction, we found that the choice of the palladium catalyst was quite



Scheme 4.

Table 2. Deallylation of various *O*-allylphenols (**6a–o**)

Entry	Substrate	R	Time (h)	**7** (%)	**8** (%)	(*E*)-**9** (%)	(*Z*)-**9** (%)
1	**6a**	*p*-NO_2	9	94			
2	**6b**	*m*-NO_2	9	97			
3	**6c**	*o*-NO_2	8	96			
4	**6d**	*p*-CN	10	98			
5	**6e**	*p*-CO_2Me	10	44 (44)[a]			
6	**6f**	*p*-CO_2H	10	82	3		
7	**6g**	*p*-*t*-Bu	24	86	12		
8	**6h**	*p*-NHAc	48	86			
9	**6i**	*p*-Br	7	49			
10	**6j**	*p*-OMe	96	17	20	4[b]	20[b]
11	**6k**	*m*-OMe	48	45	23[b]	12[b]	4[b]
12	**6l**	*o*-OMe	24	76	6		
13	**6m**	*p*-OH	96	10	53		
14	**6n**	*m*-OH	96	0 (45)[b,c]	15[b]		
15	**6o**	*o*-OH	96	0 (43)[c]	21		

[a] Value in parenthesis is yield of *p*-hydroxybenzoic acid.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Value in parenthesis is recovery of starting material.

important. Although the reason was not clear, different activity in this system was observed by the use of Pd catalysts, which were purchased from four different suppliers, in the reaction of **7a** and **7h**. (Scheme 4, Table 4).[15]

Next, we turned our attention to clarify the reaction mechanism. As mentioned above, *O*-allylphenols were easily cleaved to give the corresponding phenols in good to high yields except for the substrates bearing a strong electron-donating group. To compare the reactivity of the

Table 3. Deallylation of various *O*-allylphenols (**6p–y**)

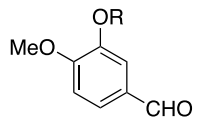
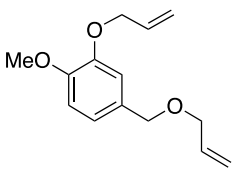
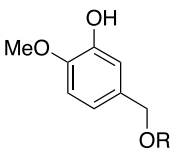
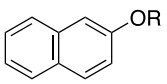
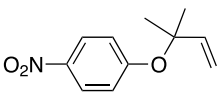
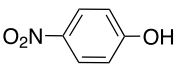
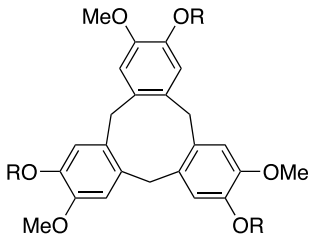
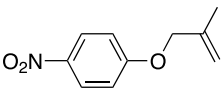
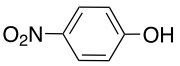
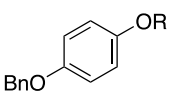
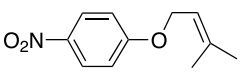
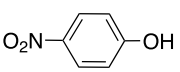
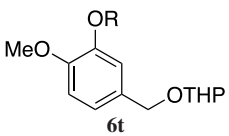
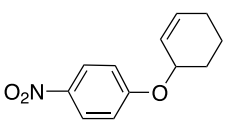
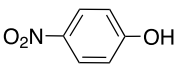
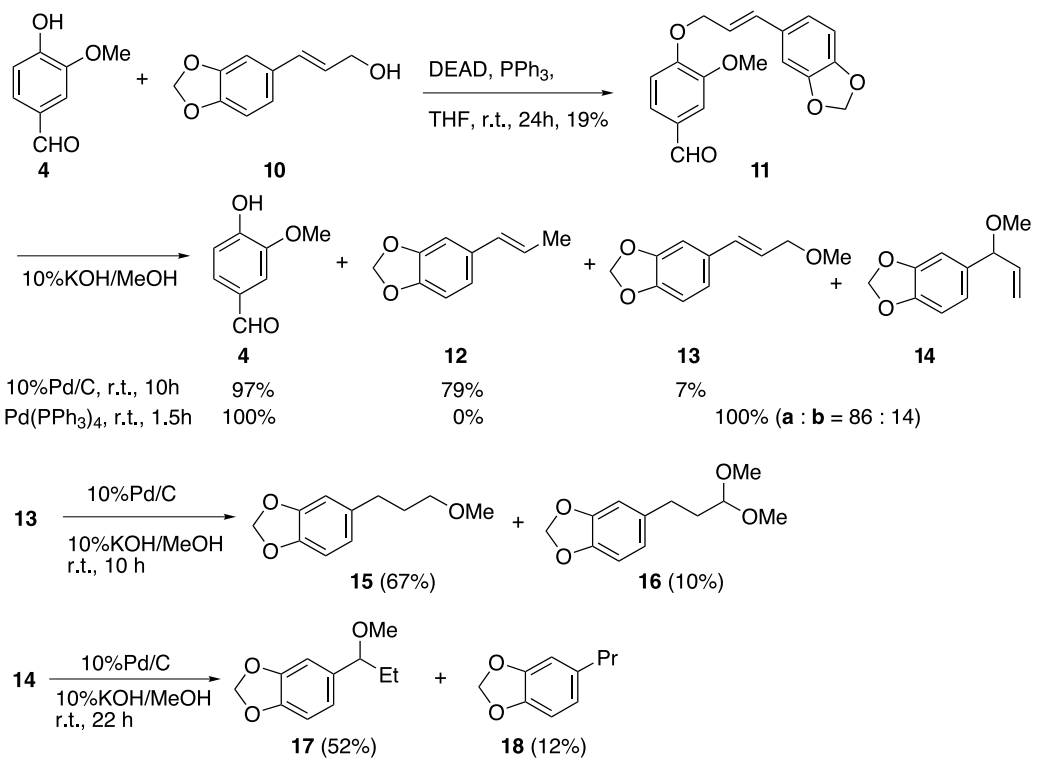
Entry	Substrate (R=allyl)	Time (h)	Product (%) (R=H)	Entry	Substrate	Time (h)	Product (%)
1	 **6p**	5	**7p** (87%)	6	 **6u**	7	 **7u**: R=Allyl (81%) **8u**: R=Pr (10%)
2	 **6q**	4	**7q** (75%)	7	 **6v**	24	 **7a** (100%)
3	 **6r**	13	**7r** (71%)	8	 **6w**	24	 **7a** (97%)
4	 **6s**	8	**7s** (95%)	9	 **6x**	30	 **7a** (96%)
5	 **6t**	7	**7t** (65%)	10	 **6y**	24	 **7a** (95%)

Table 4. Effect of Pd catalyst[a]

Entry	Substrate	Supplier of Pd	Time (h)	Product (%)	Lot. No.
1	**6a**	Kojima	9	**7a** (94)	206047
2	**6a**	Aldrich	7	**7a** (96)	07617PI
3	**6a**	Nacalai	10	**7a** (95)	V2P1618
4	**6a**	Merck	99	**7a** (68)	S37269
5	**6h**	Kojima	48	**7h** (86)	206047
6	**6h**	Aldrich	9	**7h** (87)	07617PI
7	**6h**	Nacalai	5d	**7h** (89)	V2P1618
8	**6h**	Merck	7d	**7h** (2)	S37269

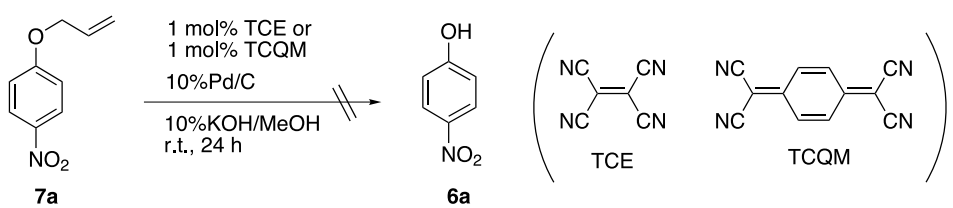
[a] The reaction was performed using substrate (100 mg) and 10% Pd/C (20 mg).

When the deallylation reaction was performed with $Pd(PPh_3)_4$, vanillin (**4**) and allyl methyl ethers (**13**, **14**) were obtained in quantitative yields via the formation of π-allyl-Pd(II) complexes. The ratio (**13**/**14**=86/14) of the ethers was determined by ^1H NMR spectroscopy. However, the reaction of **11** with 10% Pd/C under similar conditions as noted above afforded vanillin (**4**), 4-(1-propenyl)-1,2-methylenedioxybenzene (**12**), and 4-(3-methoxy-1-propenyl)-1,2-methylenedioxybenzene (**13**). With Pd/C, transformation of **13** and **14** into **12** during the reaction could not be excluded. Thus, the reaction of **13** and **14** was carried out under similar conditions in 10% KOH–MeOH. However, the reaction of both **13** and **14** did not give **12** at all and unexpected products (**15**–**18**) were produced. These results clearly indicated that the reaction involved an oxidation–reduction process by the single-electron transfer (SET) process.[15,17–19] To confirm the SET process, the reaction of **7a** with Pd/C was performed in the presence of tetracyanoethylene (TCE)[20a,b] or tetracyanoquinodimethane (TCQM),[20c,d] which are known as electron-capture reagents. As expected, the reaction of *O*-allyl-*p*-nitrophenol (**7a**) with a catalytic amount of TCE or TCQM did not form *p*-nitrophenol (**6a**) even after 24 h and the starting material (**7a**) was recovered in quantitative yield in each case (Scheme 6).

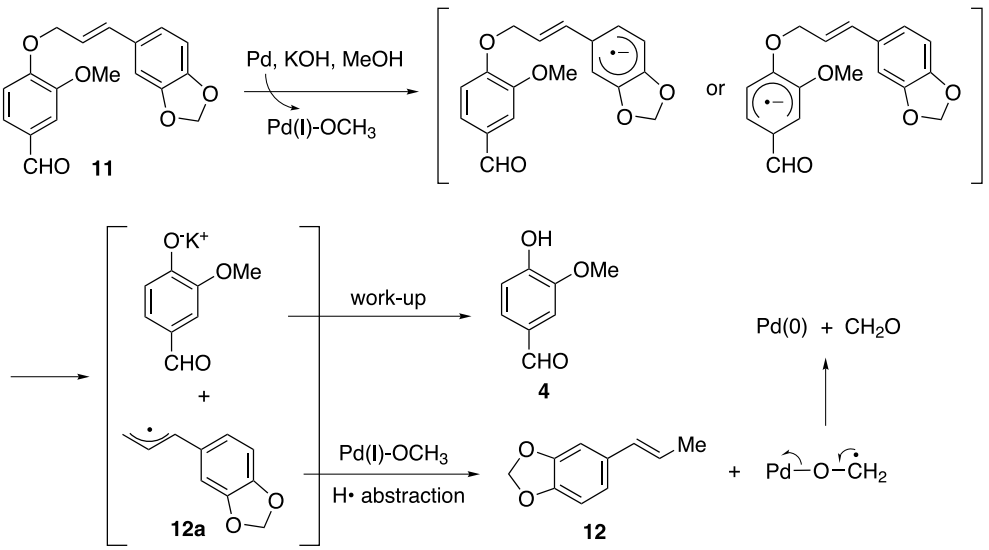


Scheme 5.

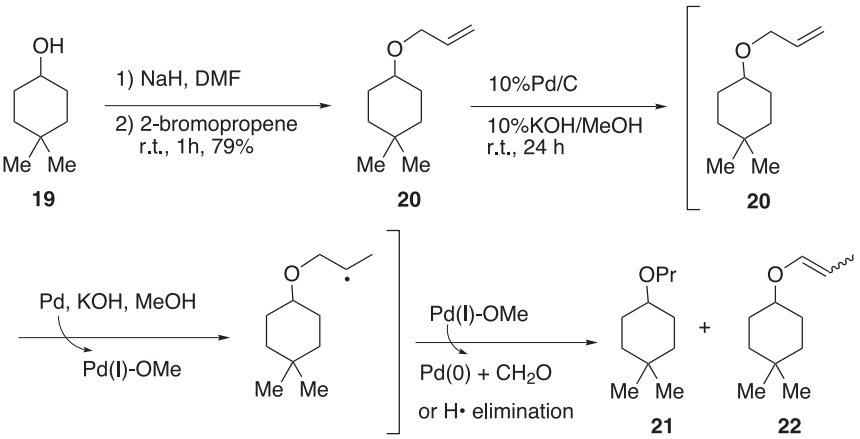
Pd catalyst in the present system, the reaction of **6m** with $Pd(PPh_3)_4$ in 10% KOH/MeOH was performed at rt for 5 h to give *p*-hydroquinone (**7m**) in 88% yield without the formation of **8** and **9**. The result suggested that the 10% Pd/C- and $Pd(PPh_3)_4$-catalyzed reaction would proceed by a different mechanism. With $Pd(PPh_3)_4$, deallylation of allyl ethers usually occurs via the formation of π-allyl-Pd(II) complexes followed by the reaction with nucleophiles.[16] To investigate the fate of an allyl moiety, the reaction of styryl ether (**11**) was carried out with Pd/C and $Pd(PPh_3)_4$ (Scheme 5).



Scheme 6.



Scheme 7.



Scheme 8.

As a result, we proposed a plausible pathway of the present deallylation as shown in Scheme 7. Namely, the coordination of the Pd atom on the aromatic ring facilitated the SET process and the resulting radical anion formed a phenoxide ion and a radical species (**12a**), which would abstract the hydrogen atom from PdOMe to give **12**.[21]

Finally, the reaction of an aliphatic allyl ether (**20**), which was obtained by allylation of **19**,[22] was investigated (Scheme 8). As expected, no deallylation product (**19**) was produced, and an inseparable mixture of a propyl ether (**21**) and an enol ether (**22**) was obtained by reduction and isomerization. The result is compatible with involving the SET process in this reaction.

3. Conclusion

In summary, we have investigated the deprotection of various *O*-allylphenols to give the corresponding phenols. The reaction of *O*-allylphenols bearing electron-withdrawing and weak electron-donating groups on the benzene ring proceeded smoothly, whereas the reaction of *O*-allylphenols having strong electron-donating groups gave phenols in nil to moderate yields. Moreover, we revealed that the present reaction proceeded via the SET process. Because 10% Pd/C was a heterogeneous catalyst, the deprotected phenol was obtained in essentially pure form by simple filtration and extraction procedure. We believe that the present reaction provides a new, convenient deprotective method for *O*-allylphenols due to its mild conditions and simple procedure.

4. Experimental

4.1. General

All melting and boiling points were measured on a Büchi or a Yanagimoto (hot plate) melting point apparatus and by a bulb-to-bulb distillation 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).

4.1.1. 11,12,24,25-Tetra(5-allyloxy-2-bromo-4-methoxybenzyl)-2,5,8,15,18,21-hexaoxatricyclo[2-.4.0.0$^{9.4}$]heoctahydro-5,8,11,16,19,22-hexaoxa-dibenzo[*a*,*j*]cyclooctadecene 9,11,13,21,23,25-hexaene (1).[23] Mp 176–177 °C (benzene–EtOH); ^{1}H NMR δ 6.39, 6.54, 7.02 (each 4H, s), 5.86–6.00 (8H, m), J=17.8 Hz), 5.19 (4H, d, J=10.5 Hz), 4,37 (8H, d, J=5.4 Hz), 4.05 (8H, m), 3.96 (8H, m), 3,84 (12H, s), 3.82 (8H, s); MS m/z 1380 (M^+), 1382 (M^++2); HRMS m/z calcd for $C_{64}H_{68}Br_4O_{14}$ (M^+) 1380.1928, found: 1380. 1957.

4.1.2. 11,12,24,25-Tetra(5-allyloxy-2-bromo-4-methoxybenzyl)-2,5,8,15,18,21-hexaoxatricyclo[2-.4.0.0$^{9.4}$]heoctahydro-5,8,11,16,19,22-hexaoxadibenzo[*a*,*j*]cyclooctadecene 9,11,13,21,23,25-hexaene (2c). A mixture of **1** (0.050 g, 0.04 mmol) and 10% Pd/C (0.017 g) in 10% KOH–MeOH (13 mL) was stirred at rt for 30 h. The mixture was filtered by suction and the filtrate was evaporated under reduced pressure. Then, acetic anhydride was added to the residue and the mixture was stirred for 5 h. The reaction was quenched with a $NaHCO_3$ solution and the mixture was extracted with $CHCl_3$. The organic extracts were washed with brine, then dried and evaporated under reduced pressure to give a residue, which was purified by TLC ($CHCl_3$–MeOH=100:1) to afford **2c** (0.009 g, 24%) as pale yellow crystals; mp 165–166 °C ($CHCl_3$–MeOH); ^{1}H NMR δ 6.86 (8H, s), 6.64, 6.65 (each 4H, s), 4.10 (8H, brs), 3.99 (8H, brs), 3.80 (12H, s), 3.76 (8H, s), 2.29 (12H, s); MS m/z 1072 (M^+); HRMS m/z calcd for $C_{60}H_{64}O_{18}$ (M^+) 1072.4093, found: 1072.4109.

4.1.3. Deallylation of *O*-allylvanillin (3) (Table 1, entry 4). A mixture of **3** (0.100 g, 0.52 mmol) and 10% Pd/C (0.020 g) in MeOH (10 mL) was refluxed for 24 h. The mixture was filtered by suction and the filtrate was evaporated under reduced pressure. Purification of the residue on preparative TLC (hexane/AcOEt=3:1) afforded vanilline (0.022 g, 28%), **5a**[24] (0.009 g, 9%), **5b** (0.007 g, 5%) and **3** (0.049 g, 49%).

4.1.4. 4-Dimethoxymethyl-2-methoxy-1-propenyloxybenzene (5b). Oil; ^{1}H NMR δ 7.04 (1H, d, J=1.5 Hz), 6.95–6.96 (2H, m), 6.29 (1H, dq, J=12.9, 1.7 Hz), 5.34 (1H, s), 4.91 (1H, dt, J=12.9, 6.9 Hz), 3.90 (3H, s), 3.33 (6H, s), 1.74 (3H, dd, J=1.7, 6.9 Hz); MS m/z 208 (M^+); HRMS m/z calcd for $C_{13}H_{18}O_4$ (M^+) 238.1205, found: 238.1202.

4.1.5. Deallylation of *O*-allylvanillin (3) (Table 1, entry 5). A mixture of **3** (0.100 g, 0.52 mmol) and 10% Pd/C (0.020 g) in 10% KOH–MeOH (10 mL) was stirred at rt for 8 h. The mixture was filtered by suction and the filtrate was evaporated under reduced pressure. Water was added to the residue and the mixture was washed with ether. After the aqueous layer was acidified with 1 M HCl, the mixture was extracted with AcOEt. The organic extracts were washed with brine and dried. The solvent was evaporated under reduced pressure to give vanillin (**4**) (0.076 g, 96%), of which the ^{1}H NMR spectrum was identical with that of an authentic sample.

4.2. General procedure for synthesis of *O*-allylphenols (6a–r and 6v–y)

A suspension of a phenol (**6a**–**r**) (1 equiv), K_2CO_3 (1.5 equiv), and 3-bromopropene (1.15 equiv) in dry DMF (1 mL per 1 mmol of **6**) was stirred at rt for 1–18 h. The mixture was filtered by suction and water was added to the filtrate. The aqueous layer was extracted with Et_2O. The organic extracts were washed with brine, then dried and evaporated under reduced pressure to give a residue, which was purified by column chromatography to afford **6a**–**r**[25a–l] and **6v**–**y**.[25m–p]

4.2.1. 1-Allyloxy-4-benzyloxybenzene (6s). A suspension of 4-benzyloxyphenol (1.0 g, 5.0 mmol), 3-bromopopene (0.43 mL, 5.0 mmol), and K_2CO_3 (0.828 g, 6.0 mmol) in acetone (10 mL) was refluxed for 20 h. Then, a saturated aqueous NH_4Cl solution was added and the mixture was extracted with Et_2O. The organic extracts were washed with brine, dried and evaporated under reduced pressure to give a solid, which was recrystallized from Et_2O–hexane to afford **6s** (0.850 g, 71%) as colorless crystals; mp 57–58 °C (Et_2O–hexane); ^{1}H NMR δ 7.28–7.44 (5H, m), 6.83–6.92 (4H, m), 5.97–6.13 (1H, m), 5.24–5.43 (1H, m), 5.01 (2H, s), 4.48 (2H, dt, J=5.1 Hz, 1.5 Hz); MS m/z 240 (M^+); HRMS m/z calcd for $C_{16}H_{16}O_2$ (M^+) 240.1152, found: 240.1145.

4.2.2. 2-Allyloxy-4-(2-tetrahydropyranyloxy)methyl-1-methoxybenzene (6t). A solution of *O*-allylisovanillyl alcohol (3.0 g, 15.5 mmol), 3,4-dihydro-2*H*-pyrane (1.68 mL, 18.4 mmol), and *p*-TsOH (0.060 g, 3.1 mmol) in CH_2Cl_2 (40 mL) was stirred at rt for 20 h. The mixture was washed with a saturated aqueous $NaHCO_3$ solution and brine, successively, then dried and evaporated under reduced pressure to give an oily residue, which was purified by column chromatography (hexane/AcOEt=6:1) to give **6t** (1.56 g, 36%) as a colorless oil; ^{1}H NMR δ 6.83–6.94 (3H, m), 6.02–6.17 (1H, m), 5.25–5.45 (2H, m), 4.70, 4.02 (each 1H, d, J=11.8 Hz), 4.60–4.63 (3H, m), 3.89–3.96 (1H, m), 3.87 (3H, s), 3.50–3.58 (1H, m), 1.50–1.91 (6H, m); MS m/z 278 (M^+); HRMS m/z calcd for $C_{16}H_{22}O_4$ (M^+) 278.1516, found: 278.1511.

4.2.3. 2-Allyloxy-4-allyloxymethyl-1-methoxybenzene (6u). To a suspension of *O*-allylisovanillyl alcohol (1.0 g, 5.2 mmol) and 60% NaH (0.424 g, 10.6 mmol) in DMF (10 mL) at 0 °C was added 2-bromopropene (0.45 mL, 5.15 mmol) over a period of 10 min. After being stirred at rt for 18 h, the reaction was quenched with a saturated aqueous NH_4Cl solution. The mixture was extracted with a mixture of AcOEt and benzene. The organic extracts were washed with brine, then dried and evaporated in vacuo to give an oily residue, which was purified by distillation under reduced pressure (150 °C/4 mm Hg) to afford **6u** (0.950 g, 79%) as a colorless oil; ^{1}H NMR δ 6.81–6.92 (3H, m), 5.87–6.16 (2H, m), 5.16–5.44 (4H, m) 4.61 (2H, dt, J=5.4, 1.6 Hz), 4.43 (2H, s), 3.99 (2H, dt, J=5.7, 1.4 Hz), 3.85 (3H, s); MS m/z 234 (M^+); HRMS m/z calcd for $C_{14}H_{18}O_3$ (M^+) 234.1254, found: 234.1248.

4.3. General procedure for deallylation of *O*-allylphenols (6a–y)

A mixture of an *O*-allylphenol (100 mg) and 10% Pd/C (20 mg) in 10% KOH–MeOH (10 mL) was stirred at rt for an appropriate time. After the catalyst was filtered out, the filtrate was concentrated in vacuo. Water was added to the residue and the mixture was washed with ether. After the aqueous layer was acidified with 1 M HCl, the mixture was extracted with AcOEt. The organic extracts were washed with brine and dried. The solvent was evaporated under reduced pressure to give the corresponding phenol (**7a**–**q**,[26] **r**,[25l] **s**,[26] **t**, **u**). The ether layer was washed with brine, then dried and evaporated in vacuo to give a residue, which was purified by preparative TLC to afford the enol ethers (**8f**,[26]**g**,[26] **j**,[27a] **k**,[26] **l**,[27a] **m**,[26] **n**,[27b] **o**,[27c] **u**) and/or propyl ethers (**9j**,[28a] **k**[28b]).

4.3.1. 5-(Tetrahydropyran-2-yloxymethyl)-2-methoxyphenol (7t). Oil; ^{1}H NMR δ 6.92 (1H, d, J=1.3 Hz), 6.80 (1H, dd, J=1.3, 8.3 Hz), 6.76 (1H, d, J=8.3 Hz), 5.71 (1H, s), 4.65, 4.36 (each 1H, d, J=11.6 Hz), 4.63–4.68 (1H, m), 3.86–3.93 (1H, m), 3.79 (3H, s), 3.48–3.56 (1H, m), 1.48–1.86 (6H, m); MS m/z 238 (M^+); HRMS m/z calcd for $C_{13}H_{18}O_4$ (M^+) 238.1203, found: 238.1198.

4.3.2. 5-Allyloxymethyl-2-methoxyphenol (7u). Oil; ^{1}H NMR δ 6.93 (1H, s), 6.83 (2H, s), 5.59–6.01 (1H, m), 5.59 (1H, s), 5.20–5.33 (2H, m), 4.43 (2H, s), 4.00 (2H, dt, J=4.3, 1.5 Hz), 3.89 (3H, s); MS m/z 194 (M^+); HRMS m/z calcd for $C_{11}H_{14}O_3$ (M^+) 194.0942, found: 194.0940.

4.3.3. 2-Methoxy-5-propoxymethylphenol (8u). Oil; ^{1}H NMR δ 6.93 (1H, s), 6.82 (2H, s), 5.71 (1H, s), 4.40 (2H, s), 3.86 (3H, s), 3.40 (2H, t, J=6.6 Hz), 1.56–1.66 (2H, m), 0.93 (3H, t, J=7.4 Hz); m/z 196 (M^+).

4.3.4. *O*-[3-(3,4-Methylenedioxyphenyl)-2-propenyl]-vanillin (11). To a solution of vanillin (0.456 g, 3.0 mmol), **10**[29] (0.535 g, 3.0 mmol), and PPh_3 (0.790 g, 3.0 mmol) in THF (15 mL) at 0 °C was added DEAD (1.312 g, 3.0 mmol). After being stirred for 2 h, PPh_3 (0.395 g, 1.5 mmol) and DEAD (0.656 g, 1.5 mmol) were added and the mixture was stirred for an additional 24 h. Then, the solvent was evaporated under reduced pressure to give an oily residue. Ether was added to the mixture and the precipitates were filtered. Evaporation of the filtrate in vacuo gave a residue, which was purified by column chromatography (hexane/benzene/AcOEt=5:5:1) to give **11** (0.426 g, 46%) as colorless crystals; mp 130–131 °C (AcOEt–hexane); ^{1}H NMR δ 9.82 (1H, s), 7.44 (1H, dd, J=1.7, 8.0 Hz), 7.42 (1H, d, J=8.0 Hz), 7.00 (1H, d, J=8.0 Hz), 6.93 (1H, d, J=1.5 Hz), 6.82 (1H, dd, J=1.2, 8.1 Hz), 6.74 (1H, d, J=8.1 Hz), 6.64 (1H, d, J=15.8 Hz), 6.26 (1H, dt, J=6.0, 15.8 Hz), 5.93 (2H, s), 4.79 (2H, d, J=6.0 Hz), 3.93 (3H, s); MS m/z 312 (M^+); HRMS m/z calcd for $C_{18}H_{16}O_5$ (M^+) 312.0998, found: 312.0990.

4.3.5. Deallylation of 11. (a) With 10% Pd/C; a mixture of **11** (0.050 g, 0.16 mmol) and 10% Pd/C (0.010 g) in 10% KOH–MeOH (15 mL) was stirred at rt for 10 h. The usual work-up gave a residue, which was purified by preparative TLC (hexane/AcOEt=10:1) to yield vanillin (0.024 g, 97%), **12**[26] (0.021 g, 79%) and **13**[30a] (0.002 g, 7%). (b) With $Pd(PPh_3)_4$; a solution of **11** (0.050 g, 0.16 mmol) and $Pd(PPh_3)_4$ (0.001 g) in 10% KOH–MeOH (15 mL) was stirred at rt for 1.5 h. Evaporation of the solvent afforded a residue, which was partitioned into a mixture of ether and water. The organic layer was washed with brine, then dried and evaporated in vacuo to give an inseparable mixture of **13**[30a] and **14**[30b] (0.031 g, 100%, **13/14**=86/14). The aqueous layer was acidified with 3 M HCl and extracted with AcOEt. The organic extracts were washed with brine, then dried and evaporated in vacuo to give vanillin (0.024 g, 100%). The ratio of **13** to **14** was determined by integration of the peaks due to the methoxyl groups in ^{1}H NMR spectroscopy.

4.3.6. Reaction of 13 with 10% Pd/C. A mixture of **13** (0.040 g, 0.21 mmol) and 10% Pd/C (0.008 g) in 10% KOH–MeOH (5 mL) was stirred at rt for 10 h. The usual work-up gave a residue, which was purified by preparative TLC (hexane/AcOEt=5:1) to yield **15**[31a] (0.034 g, 67%) and **16**[31b] (0.006 g, 10%).

4.3.7. Reaction of 14 with 10% Pd/C. A mixture of **14** (0.100 g, 0.52 mmol) and 10% Pd/C (0.020 g) in 10% KOH–MeOH (10 mL) was stirred at rt for 22 h. The usual work-up gave a residue, which was purified by preparative TLC (benzene) to yield **17**[32] (0.052 g, 52%) and **18**[26] (0.011 g, 12%).

4.3.8. 4-Allyloxy-1,1-dimethylcyclohexane (20). To a suspension of 4,4-dimethylcyclohexanol (**19**, 0.640 g, 5.0 mmol) and 55% NaH (0.262 g, 6.0 mmol) in DMF (25 mL) at rt was added 2-bromopropene (0.52 mL, 6.0 mmol) over a period of 5 min. After being stirred for 1 h, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O. The organic extracts were washed with brine, then dried and evaporated in vacuo to give an oily residue, which was purified by bulb-to-bulb distillation (130 °C/40 mm Hg) to afford **20** (0.662 g, 79%) as a colorless oil; ^{1}H NMR δ 5.93 (1H, ddt, J=17.1 Hz, 10.2, 5.5 Hz), 5.27(1H, ddd, J=1.5, 3.3, 17.1. Hz), 5.15 (1H, ddd, J=1.5, 3.3, 10.2 Hz), 4.00 (2H, dt, J=5.5, 1.5 Hz), 3.22–3.31 (1H, m), 1.72–1.83 (2H, m), 1.39–1.54 (4H, m), 1.12–1.22 (2H, m), 0.92, 0.90 (each 3H, s); MS m/z 168 (M^+); HRMS m/z calcd for $C_{11}H_{20}O$ (M^+) 168.1512, found: 168.1505.

4.3.9. Deallylation of 20. A mixture of **20** (0.100 g, 0.60 mmol) and 10% Pd/C (0.020 g) in 10% KOH–MeOH (10 mL) was stirred at rt for 24 h. The usual work-up gave an inseparable mixture of **21** and **22**. (0.096 g, 95%, (*E*)-**21**/(*Z*)-**21**/**22**=14/36/50). The ratio of (*E*)-**21** to (*Z*)-**21** was determined by integration of the peaks due to the olefinic protons in ^{1}H NMR spectroscopy. The ratio of **21** and **22** was determined by integration of the peaks due to C_1 protons in ^{1}H NMR spectroscopy.

Compound **21**. ^{1}H NMR δ 6.08 (0.28H, brd, J=12.3 Hz), 5.98 (0.72H, brd, J=6.5 Hz), 4.88 (0.28H, dq, J=6.4, 12.3 Hz), 4.38 (0.72H, qui, J=6.5 Hz), 3.52–3.62 (1H, m), 1.40–1.82 (9H, m), 1.14–1.28 (2H, m), 0.87–0.98 (6H, m).

Compound **22**. ^{1}H NMR δ 3.89 (2H, t, J=6.8 Hz),

3.15–3.41 (1H, m), 1.73–1.79 (2H, m), 1.38–1.64 (6H, m), 1.17 (2H, brt, J=13.3 Hz), 0.92 (3H, t, J=6.3 Hz), 0.92, 0.91 (each 3H, s).

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