Lewis Acid Mediated Claisen-Type Rearrangement of Aryl Dienyl Ethers

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Rearrangement of aryl pentadienyl ethers in the presence of BF_3·OEt_2 affords pentadienyl phenols in good yields without formation of the corresponding [3,3] rearranged products. The mechanism of this rearrangement was studied by deuterium labeling and cross-coupling reactions. The scope and limitations of the rearrangement are discussed.

The Claisen rearrangement and its applications to organic synthesis have been studied for a long time.[1] In recent years, this rearrangement has been applied in stereocontrolled natural product synthesis[2] and asymmetric induction.[3] The term "Claisen rearrangement", which originally denoted the rearrangement of allyl aryl ethers to *o*- or *p*-allylphenols, has now been extended to analogous rearrangements of allyl vinyl ethers (Ireland–Claisen rearrangement),[3b,4] *N*-allylenamines and *N*-allylanilines (aza-Claisen rearrangement),[3a,5] and allyl vinyl sulfides (thio-Claisen rearrangement).[6] Experimental and theoretical studies of these reactions have been carried out.[7] Several methods have been used to induce these rearrangements, including thermal,[1] acid catalysis,[8] anion catalysis (especially for the Ireland–Claisen rearrangement),[4] and transition metal catalysis.[9]

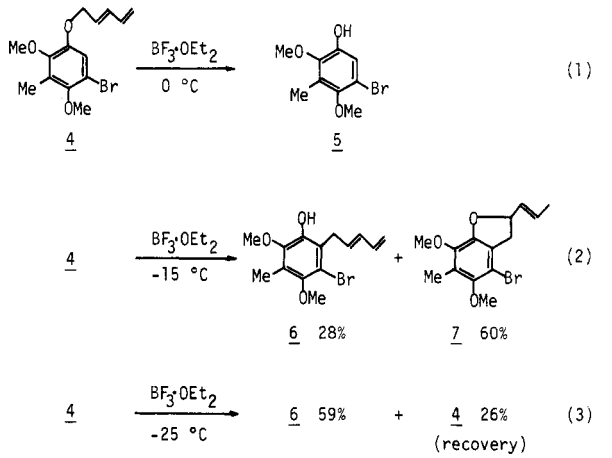
Only one example[10] of the thermal rearrangement of an aryl 2,4-pentadienyl ether has been reported, and with low selectivity, giving a mixture of [5,5] and [3,3] rearrangement products (Table I, entry 1). The regioselective dienylation of an aromatic ring could be very useful in organic synthesis,[11] and we have therefore explored the regioselectivity of the rearrangement of aryl 2,4-pentadienyl ethers in the presence of Lewis acids.

Results and Discussion

Lewis Acid. In contrast to the thermal reaction, the Lewis acid mediated Claisen-type rearrangement of 2,4-pentadienyl phenyl ether proceeded regioselectively to afford *p*-(2,4-pentadienyl)phenol (**2**) (Table I, entries 3–5). Among several Lewis acids, boron trifluoride etherate gave the best results. Diethylaluminum chloride, which is an efficient Lewis acid for the Claisen rearrangement of allyl aryl ethers, especially electron-deficient ones,[8b] was less effective. Titanium tetrachloride gave only phenol and no dienylated products, presumably because it broke the ether bond to give the titanium phenolate.[12]

Generality. The BF_3·OEt_2-mediated rearrangement was applied to a number of substituted phenyl 2,4-pentadienyl ethers. The generality of the reaction is obvious from Table II, and good yields were obtained in most of the reactions. Several characteristics of the rearrangement were observed. (1) In every case, exclusive α (and/or ϵ) rearrangement of the pentadienyl group was observed without any [3,3] rearrangement. (2) When the aryl ethers have no substituent in the para position (type A), the rearrangement occurred exclusively at this position (entries 6–11). (3) When the aryl ethers have a simple alkyl or an electron-donating group in the para position (type B), the rearrangement preferentially occurred at the meta position (entries 12–16). (4) When a bulky group blocks the para position and one of the ortho positions of the ethers is unsubstituted (type C), ortho rearrangement was observed, generally in lower yield than those of type A and B ethers (entries 17–27). These results indicate that the reaction mechanisms of type A and B ethers are different from those of type C ethers.

The rearrangements of polysubstituted phenols were complicated by several factors. For example, the rearrangement of **4** (entry **22**) was quite sensitive to the reaction temperature. At temperatures above 0 °C, the C–O



bond of **4** was cleaved to afford the corresponding phenol

(1) For example: (a) Tarbell, D. S. *Organic Reactions*; Wiley: New York, 1944; Vol. 2, p 1. (b) Rhoads, S. J.; Raulins, N. R., ref 1a, 1975; Vol. 22, p 1. (c) Bennett, G. B. *Synthesis* **1977**, 589.

(2) (a) Funk, R. L.; Munger, J. D., Jr. *J. Org. Chem.* **1985**, *50*, 707. (b) Kraus, G. A.; Fulton, B. S. *Tetrahedron* **1984**, *40*, 4777.

(3) (a) Kurth, M. J.; Decker, O. H. W.; Hope, H.; Yanuck, M. D. *J. Am. Chem. Soc.* **1985**, *107*, 443. (b) Nagatsuma, M.; Shirai, F.; Sayo, N.; Nakai, T. *Chem. Lett.* **1984**, 1393. (c) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668.

(4) (a) Cha, J. K.; Lewis, S. C. *Tetrahedron Lett.* **1984**, *25*, 5263. (b) Kurth, M. J.; Yu, C.-M. *Ibid.* **1984**, *25*, 5003. (c) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2.

(5) (a) Danishefsky, S. J.; Phillips, G. B. *Tetrahedron Lett.* **1984**, *25*, 3159. (b) Gilbert, J. C.; Senaratne, K. P. A. *Ibid.* **1984**, *25*, 2303.

(6) (a) Takada, S.; Makisumi, Y. *Chem. Pharm. Bull.* **1984**, *32*, 872. (b) Takada, S.; Ishizuka, N.; Sasatani, T.; Makisumi, Y.; Jyoyama, H.; Hatakeyama, H.; Asanuma, F.; Hirose, K. *Ibid.* **1984**, *32*, 877.

(7) (a) Dewar, M. J. S.; Healy, E. F. *J. Am. Chem. Soc.* **1984**, *106*, 7127. (b) Gajewski, J. J.; Emrani, J. *Ibid.* **1984**, *106*, 5733.

(8) (a) Borgulya, J.; Madeja, R.; Fahrni, P.; Hansen, H.-J.; Schmid, H.; Barner, R. *Helv. Chim. Acta* **1973**, *56*, 14. (b) Sonnenberg, F. M. *J. Org. Chem.* **1970**, *35*, 3166. (c) Narasaka, K.; Bald, E.; Mukaiyama, T. *Chem. Lett.* **1975**, 1041. (d) Yoshizawa, T.; Toyofuku, H.; Tachibana, K.; Kuroda, T. *Ibid.* **1982**, 1131.

(9) Schenck, T. G.; Bosnish, B. *J. Am. Chem. Soc.* **1985**, *107*, 2058.

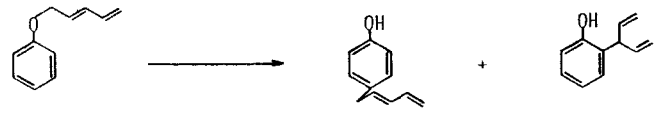
(10) Fráter, G. Y.; Schmid, H. *Helv. Chim. Acta* **1968**, *51*, 190; **1970**, *53*, 269.

(11) (a) For example: Naruta, Y.; Arita, Y.; Nagai, N.; Uno, H.; Maruyama, K. *Chem. Lett.* **1982**, 1859. (b) Naruta, Y.; Maruyama, K. *J. Synth. Org. Chem. Jpn.* **1984**, *12*, 41.

(12) Weidemann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31.

0022-3263/86/1951-5083$01.50/0

Table I. Claisen-Type Rearrangement of 2,4-Pentadienyl Phenyl Ether

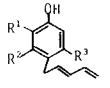
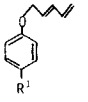
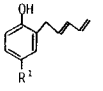
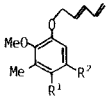
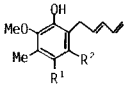
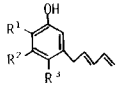


1 2 3

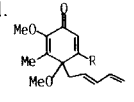
entry	conditions	isolated yield, % 2	3
1	*N,N*-diethylaniline, 186 °C, 5 h	37	24
2	$TiCl_4$ (2 equiv), *N,O*-BTSA[a] (0.5 equiv) CH_2Cl_2, −78 °C, 0.5 h	*b*	*b*
3	$TiCl_4$ (2 equiv), $Ti(OPr\text{-}i)_4$ (1 equiv) *N,O*-BTSA[a] (0.5 equiv), CH_2Cl_2, −78 °C, 0.5 h	35	
4	Et_2AlCl (1.2 equiv), CH_2Cl_2, −40 °C, 1 h	56	
5	$BF_3\text{-}OEt_2$ (1.2 equiv), CH_2Cl_2, −40 °C, 1 h	76	

[a] *N,O*-Bis(trimethylsilyl)acetamide which was added as a hydrogen chloride scavenger.[8c] [b] Phenol was obtained.

Table II. Lewis Acid Mediated Claisen-Type Rearrangement of Aryl 2,4-Pentadienyl Ethers[a]

entry	aryl dienyl[b] ether	R^1	R^2	R^3	product[b]	isol yield, %	entry	aryl dienyl[b] ether	R^1	R^2	R^3	product[b]	isol yield, %
6		Me	Me	H		94	17		*t*-Bu				62
7		Me	H	Me		91	18		Ph				43
8		MeO	H	H		84	19		NO_2				0
9		H	*t*-Bu	H		73	20		MeO	F			62[e]
10				H		80							
11		NO_2	H	H		0[c]							
12		Me	H	Me		70	21		MeO	Cl			76[f]
							22		MeO	Br			59[f]
13		MeO	Me	MeO		86	23		MeO	MeO			0[g]
14		BnO	Me	MeO		80	24		MeO	*i*-PrO			0[h]
15		MeO	Me	BnO		81	25		AcO	Br			25
16		H				39[d]	26			Br			27
							27		BnO	Br			9

[a] All reactions except entries 20, 21, and 22 were performed by the general procedure (see Experimental Section). [b] The stereochemistry of the starting 2,4-pentadienyl ethers (97% trans) was converted in the course of this rearrangement, and every product had 100% trans configuration as determined by 400-MHz ^1H NMR. [c] 2-Nitrophenol and the dienyl ether were obtained in 8% and 51% yields, respectively. [d] 1-Pentadienylnaphthol (26%) and the starting substrate (22%) were obtained. [e] $AlCl_3\text{-}OEt_2$ was used instead of $BF_3\text{-}OEt_2$. [f] This rearrangement was carried out at −25 °C for 1 h. [g] **8** (R = OMe) was obtained in 60% yield. [h] **9** (R = OPr-*i*) was obtained in 51% yield.



8 R=OMe
9 R=OPr^i

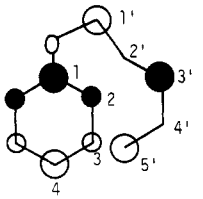
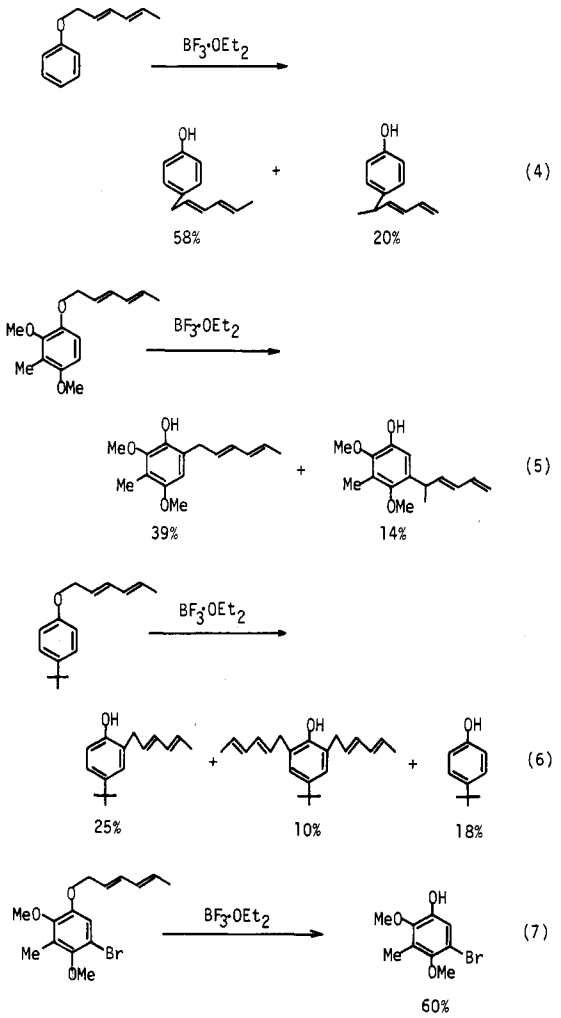


Figure 1.

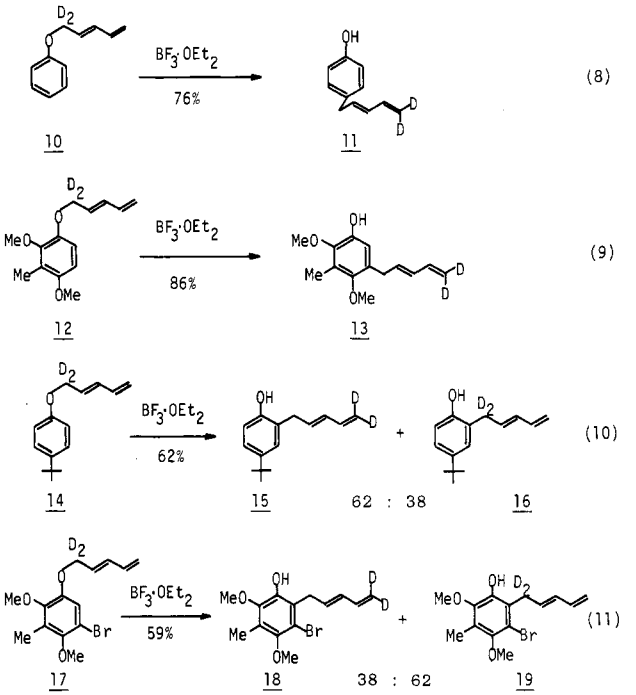
5. At −15 °C the ortho-rearranged phenol **6** (28%) was obtained, accompanied by the 2-vinyldihydrobenzofuran derivative **7** (60%). The optimum yield (59%) of the *o*-dienyl phenol **6** was obtained at −25 °C. Above −25 °C, most of the starting compound **4** was recovered with concomitant formation of **6**. When a substrate has a bulky substituent next to a vacant ortho position, ipso-rearrangement to the para position was observed (entries 23 and 24).

Aryl dienyl ethers with substituents labile to the Lewis acid did not undergo a clean rearrangement (entries 25 and 26). The ether **46** (R^1 = OH, R^2 = Br) gave a complex mixture in this reaction.

The rearrangement of the 2,4-hexadienyl group showed a very different reaction pattern from that of the pentadienyl group. Thus a type B hexadienyl ether rearranged to the ortho position (eq 5), one type C ether gave a bis-hexadienyl adduct (eq 6), and another type C ether afforded only the corresponding phenol (eq 7). This rearrangement of hexadienyl ethers proceeded in lower yields and with lower regioselectivity. These results suggest a different mechanism from that of the pentadienyl ethers.



Mechanism. To clarify the mode of rearrangement in the pentadienyl systems, ethers **10**, **12**, **14**, and **17**, with regioselectively 1-deuterated pentadienyl groups,[13] were synthesized and submitted to the Lewis acid mediated rearrangement. Type A and B ethers **10** and **12** gave exclusively the ϵ-deuterated products (eq 8, 9), while type



C ethers **14** and **17** gave the two regioisomers **15** + **16** and **18** + **19**, respectively (eq 10, 11). Especially in the latter two examples, deuterium scrambling at both α and ϵ positions in the products suggests a rearrangement mechanism other than intramolecular.

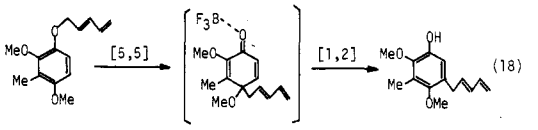
To determine whether an intermolecular reaction was occurring, these rearrangements were carried out in the presence of free phenol. Type A and B ethers gave no cross-coupling products (eq 12, 13), and the added phenol was recovered quantitatively. Type C ethers, however, gave some cross-coupling products (eq 14, 15). We conclude that the rearrangement of type A and B ethers proceeds via the concerted [5,5] and tandem [5,5]/[1,2][15,16] mechanisms, while that of type C involves both inter- and intramolecular processes.

Cross-coupling products were also observed with all three types of hexadienyl ethers (eq 16, 17, and 6), which suggests some participation of the intermolecular reaction.

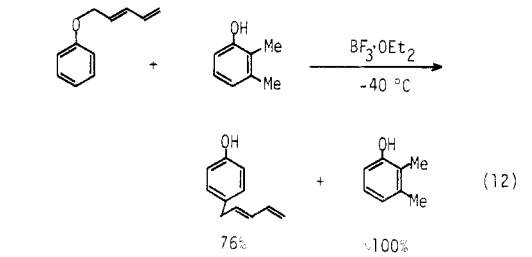
(13) Aryl 1-deuterated-2,4-pentadienyl ethers were synthesized by Mitsunobu reaction[14] of coupling phenols with 1-deuterated-2,4-pentadienol, which was produced from ethyl 2,4-pentadienoate with lithium aluminum deuteride.

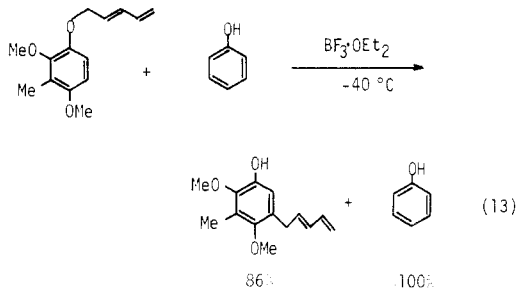
(14) Mitsunobu, O. *Synthesis* **1981**, 1.

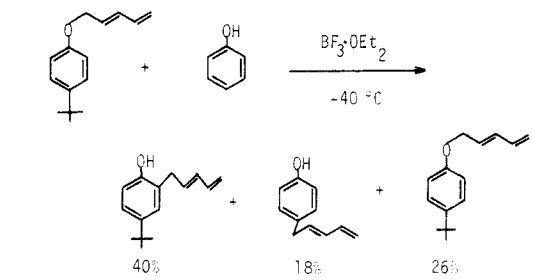
(15) The rearrangement of the phenol moiety to the meta position, i.e., apparent [4,5] rearrangement, would proceed via successive concerted migration, i.e., tandem [5,5]/[1,2] fashion (eq 18).

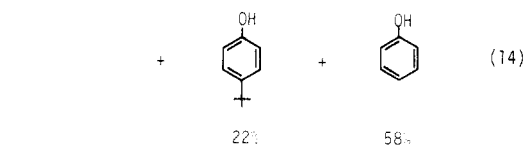


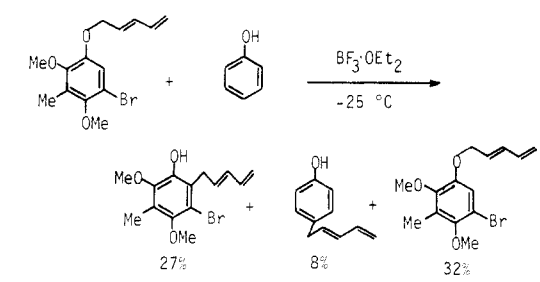
(16) (a) Miller, B. *J. Am. Chem. Soc.* **1970**, *92*, 6246 and 6252. (b) Miller, B. *Acc. Chem. Res.* **1975**, *8*, 245.

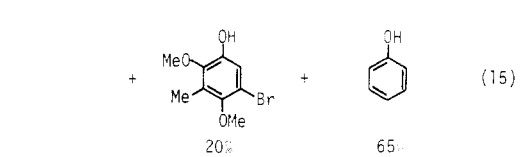




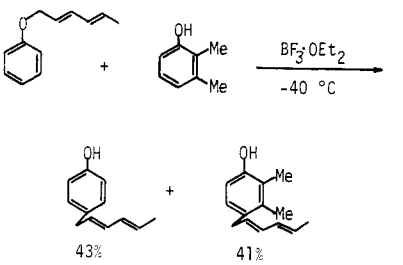


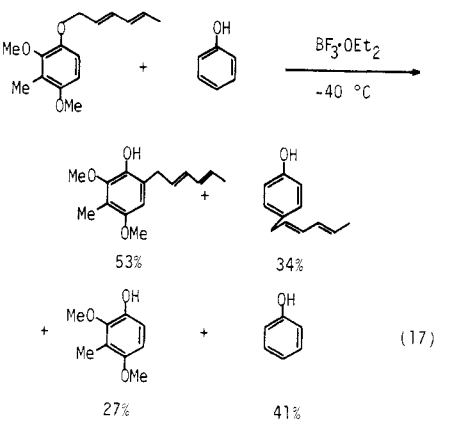






The questions of why these three reaction modes are involved in the rearrangement of pentadienyl ethers and why the thermally allowed [3,3] rearrangement[10] does not occur can be elucidated by orbital symmetry considerations.[16] The frontier orbital (SOMO) of the substrate is shown in Figure 1. The coordination of the Lewis acid as well as protonation[16] are predicted to take place on the nonbonded (n) electrons of the oxygen atom. By this perturbation, the effective electronegativity of the oxygen atom will be increased, and the coefficient of each atom will be affected, while the orbital symmetries will not be appreciably changed as shown in Figure 2. The difference in the rearranged modes between the Lewis acid mediated and the thermal reaction will be intensively correlated with the coefficients. From symmetry considerations, [5,5] rearrangement to C_4 and [3,3] rearrangement to C_2 would be allowed in both Lewis acid mediated (type A and B) and thermal rearrangements. Although the coefficients of the pentadienyl group are different from each other (Figure 2), because of the oxonium ion attached at 1′ position, the coefficients of the frontier orbital will be greater at C_5 than at C_3.[17] On the other hand (Figure 1), without this effect, the coefficients should be the same at C_5 and C_3. Therefore, [3,3] migration would be suppressed in the Lewis acid mediated system.





For the rearrangement of type C ethers, since normal coordination of BF_3 to the oxygen n-electron could not promote reaction, the Lewis acid might push out the dienyl radical (or cation) and the terminal carbon of this radical (or cation) might attack both intra- and intermolecularly at the vacant ortho position.

Experimental Section

General Methods. Melting points were measured with a micromelting point apparatus and are uncorrected. Proton magnetic resonance spectra were observed with JEOL PS-100 and JMN-FX400 spectrometers with tetramethylsilane as an internal standard. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Mass spectra were measured with a JEOL JMS-DX 300 mass spectrometer. Column chromatography was performed on Wako-gel C-200. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University. All solvents were freshly distilled and stored under a nitrogen atmosphere. Dichloromethane was distilled from calcium hydride. Ether and THF were distilled from benzophenone ketyl and stored over

(17) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; p 125. The expected oxonium ion, which was generated by coordination of Lewis acid to the aryl pentadienyl ether, can be approximated by an electron-withdrawing group. The LUMO coefficients of the resulted pentadienyl group show the largest value at the $C_{5'}$ position of the diene.

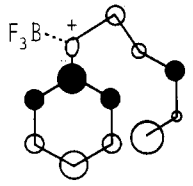


Figure 2.

sodium wire. Unless otherwise noted, other solvents were used after simple distillation. Lewis acids, i.e., BF_3·OEt_2, $TiCl_4$, and $AlCl_3$·OEt_2, were used without further purification.

1-Chloro-2,4-pentadiene. To a solution of 1,4-pentadien-3-ol (5 g, 60 mmol), which was prepared from vinylmagnesium bromide and acrolein in isopentane (12 mL), was added concentrated HCl (16.6 mL) at 0 °C. After stirring for 2 h, the organic layer was successively washed with water and dilute $NaHCO_3$ solution, dried over $MgSO_4$, concentrated (<60 °C bath temperature, >100 mmHg), and distilled (bp 57 °C/100 mmHg) twice to afford 5.4 g (52.2 mmol, 87%) of 1-chloro-2,4-pentadiene (97% trans configuration) as a colorless liquid. Satisfactory NMR, IR, and mass spectral data were obtained in comparison with those reported.[10]

2-Hydroxy-4-methoxy-3-methylbenzaldehyde (21). To a CH_2Cl_2 solution of 3-methoxy-2-methylphenol[18] (2.68 g, 19 mmol) was added Cl_2CHOCH_3 (2.1 mL, 23 mmol) and $TiCl_4$ (2.6 mL, 23 mmol) at 0 °C under nitrogen. After being stirred for 1 h at 0 °C, the mixture was poured into ice water and extracted with CH_2Cl_2, washed with water twice and then brine, dried over $MgSO_4$, and evaporated to give 3.07 g (18.5 mmL, 95%) of crude **21**: mp 62–63 °C; NMR (CCl_4) δ 2.04 (s, 3 H), 3.94 (s, 3 H), 6.45 (d, 1 H, J = 9 Hz), 7.26 (d, 1 H, J = 9 Hz), 9.67 (s, 1 H); MS, m/e (relative intensity) 166 (M^+, 57), 165 (100), 152 (57), 148 (20), 136 (30).

2-(Benzyloxy)-4-methoxy-3-methylphenol (22). To NaH (888 mg, 22.2 mmol) in DMF (20 mL) was added a DMF (20 mL) solution of **21** (3.07 g, 18.5 mmol) at 0 °C under nitrogen over 15 min. After stirring for 1 h at this temperature, benzyl bromide (3.8 g, 22.2 mmol) was added and the mixture was stirred for another 3 h. The mixture was poured into water and extracted with ether. The ethereal solution was washed with water three times and then brine, dried over $MgSO_4$, and evaporated. After purification by column chromatography on silica gel (hexane–ether as eluent) 3.55 g (14.8 mmol, 80%) of the benzyl ether of **21** was obtained. Then a CH_2Cl_2 solution of this benzyl ether was added to *m*-CPBA (3.82 g, 17.8 mmol) in CH_2Cl_2 (30 mL) at 0 °C and stirred for 3 h at room temperature. The mixture was washed with aqueous Na_2CO_3 solution three times and evaporated. The residue was dissolved in MeOH (20 mL) and added to a methanol solution of KOH (1.23 g, 22 mmol). The solution was stirred for 1 h at 0 °C and then evaporated to remove MeOH. To this residue was added ether and dilute HCl solution and the ethereal layer was washed with water twice and then brine, dried over $MgSO_4$, and evaporated. After chromatographic purification on silica gel, 2.53 g of **22** (11 mmol, 75%) was obtained. NMR (CCl_4) δ 2.10 (s, 3 H), 3.66 (s, 3 H), 4.75 (s, 3 H), 6.12 (br, 1 H, OH), 6.35 (d, 1 H, J = 8 Hz), 7.25 (m, 5 H); IR (NaCl) 3520 (m), 1485 (s), 1360 (m), 1260 (m), 1150 (m), 1105 (vs), 780 (m), 750 (m), 720 (m), 690 cm^{-1} (m); MS, m/e (relative intensity) 244 (M^+, 7), 153 (31), 125 (10), 91 (100). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6.75.

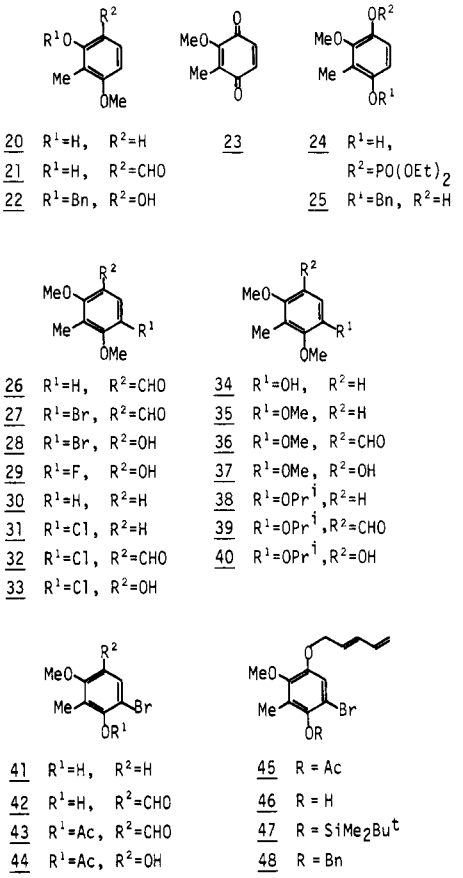
4-(Benzyloxy)-2-methoxy-3-methylphenol (25). A solution of 2-methoxy-3-methyl-1,4-benzoquinone[19] (342 mg, 2.1 mmol) in dry benzene (3 mL) and EtOH (0.6 mL) was stirred under nitrogen and cooled to −2 °C. A mixture of diethyl phosphite (0.4 mL, 3.2 mmol) and 0.4 mL of a solution of sodium (1 g) in absolute ethanol (40 mL) was added at such a rate that the temperature did not rise above 6 °C. After additional stirring for 10 min and neutralization with dilute HCl solution, the mixture was extracted with CH_2Cl_2. After usual workup and purification on silica gel (PLC), **24** (407 mg, 67%) was obtained: NMR (CCl_4) δ 1.37 (t, 6 H, J = 6 Hz), 2.07 (s, 3 H), 3.76 (s, 3 H), 4.22 (q, 4 H, J = 6 Hz), 6.23 (d, 1 H, J = 8 Hz), 6.74 (d, 1 H, J = 8 Hz), 8.20 (br, 1 H, OH); MS, m/e (relative intensity) 290 (M^+, 49), 153 (37), 139 (31), 127 (38), 109 (100). **24** was benzylated by the same procedure in 75% yield: NMR (CCl_4) δ 1.49 (t, 6 H, J = 8 Hz), 2.16 (s, 3 H), 3.80 (s, 3 H), 4.12 (q, 4 H, J = 8 Hz), 5.01 (s, 3 H), 6.55 (d, 1 H, J = 9 Hz), 7.08 (d, 1 H, J = 9 Hz), 7.32 (m, 5 H).

A MeOH (15 mL) solution of this benzyl ether was added to KOH (1.3 g, 23 mmol) in MeOH (15 mL) at 0 °C under nitrogen. After stirring for 1 h, MeOH was removed by evaporation, and water and ether were added to the residue. After usual workup, chromatographic purification gave 1.48 g (5.8 mmol, 50%) of **25**: NMR (CCl_4) δ 2.18 (s, 3 H), 3.68 (s, 3 H), 4.89 (s, 3 H), 5.60 (br, 1 H, OH), 6.47 (d, 1 H, J = 8 Hz), 6.67 (d, 1 H, J = 8 Hz), 7.31 (m, 5 H); IR (NaCl) 3400 (m), 1480 (s), 1460 (m), 1260 (m), 1230 (m), 1095 (s), 1020 (m), 780 (m), 750 (m), 730 cm^{-1} (m); MS, m/e (relative intensity) 244 (M^+, 38), 153 (88), 125 (33), 91 (100). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.67.

5-Bromo-2,4-dimethoxy-3-methylbenzaldehyde (27). An acetic acid solution (75 mL) of bromine (40.7 g, 0.25 mol) was added to a mixture of 2,4-dimethoxy-3-methylbenzaldehyde[19] (38.2 g, 0.12 mol), sodium acetate (42.4 g, 0.52 mol), and iodine (560 mg) in acetic acid (150 mL), and the resulting solution was stirred at 80 °C for 24 h. After removal of the solvent in vacuo and aqueous treatment, the mixture was extracted with ether. After usual workup, the crude product was chromatographed (hexane–ether as eluent) to give 40.5 g (0.147 mol, 69%) of 5-bromo-2,4-dimethoxy-3-methylbenzaldehyde (**27**) as colorless needles: mp 55–57 °C; NMR ($CDCl_3$) δ 2.24 (s, 3 H), 3.80 (s, 3 H), 3.84 (s, 3 H), 7.74 (s, 1 H), 10.04 (s, 1 H); IR (KBr) 1680 cm^{-1} (vs); MS, m/e (relative intensity) 258 (M^+, 100), 260 (98). Anal. Calcd for $C_{10}H_{11}O_3Br$: C, 46.36; H, 4.28; Br, 30.84. Found: C, 46.48; H, 4.21; Br, 30.89.

5-Bromo-2,4-dimethoxy-3-methylphenol (28) was produced from **27** in 86% yield by the same method as described for the synthesis of **22**: NMR (CCl_4) δ 2.22 (s, 3 H), 3.72 (s, 6 H), 5.94 (br, 1 H, OH), 6.94 (s, 1 H); IR (NaCl) 1240 (s), 890 cm^{-1} (m); MS, m/e (relative intensity) 248 (13), 246 (M^+, 15), 233 (18), 231 (20), 156 (100). Anal. Calcd for $C_9H_{11}O_3Br$: C, 43.75; H, 4.49; Br, 32.34.

Chart I



(18) Akiba, M.; Ikuta, S.; Takada, T. *J. Chem. Soc., Chem. Commun.* **1983**, 817.

(19) Luly, J. R.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 2745.

Found: C, 43.69; H, 4.52; Br, 32.39.

5-Fluoro-2,4-dimethoxy-3-methylphenol (29). To NaH (2.7 g, 68 mmol) in DMF (30 mL) was added **28** (14 g, 56 mmol) in DMF (30 mL) at 0 °C for 15 min. The mixture was stirred for 1 h, and $ClCH_2OCH_3$ (5.1 mL, 68 mmol) was added. After stirring for an additional hour, water was added, and the mixture was extracted with ether. After usual workup, the methoxymethyl ether of **28** was obtained. To this methoxymethyl ether (0.734 g, 2.5 mmol) in dry ether (5 mL) was added 1.8 mL of *n*-BuLi (1.5 M hexane solution) at −75 °C, and the mixture was stirred for 1 h at this temperature. $FClO_3$[20] was bubbled through this solution at −50 °C for 1 h, and the solution was quenched with water and extracted with ether. After usual workup, the fluorinated product was treated with 5% HCl solution (0.5 mL) in acetone (5 mL) and refluxed for 1 h. After usual workup and chromatographic purification on silica gel, 335 mg (1.8 mmol, 72%) of **29** was obtained as colorless plates: mp 85–87 °C; NMR (CCl_4) δ 2.18 (s, 3 H), 3.66 (s, 3 H), 3.74 (s, 3 H), 5.80 (br, 1 H, OH), 6.39 (d, 1 H, J = 11 Hz); IR (KBr) 3360 (vs), 1610 (s), 1590 (vs), 1450 (s), 1380 (w), 1250 (s), 1050 cm^{-1} (s); MS, m/e (relative intensity) 186 (M^+, 100), 168 (44). Anal. Calcd for $C_9H_{11}O_3F$: C, 58.06; H, 5.96; F, 10.2. Found: C, 58.14; H, 5.85; F, 10.11.

1-Chloro-2,4-dimethoxy-3-methylphenol (33). To 2,6-dimethoxytoluene (**30**)[19] (30.4 g, 0.2 mol) in CCl_4 (118 mL) was added *t*-BuOCl (19.7 mL, 0.2 mol), and the mixture was refluxed for 2 h. After usual workup, 34.5 g (0.186 mol) of crude **31** was obtained. This chloride (1.86 g, 10 mmol) was dissolved in CH_2Cl_2 (30 mL), Cl_2CHOCH_3 (1.1 mL, 12.1 mmol) and $TiCl_4$ (1.8 mL, 12.1 mmol) were added at 0 °C, and the mixture was stirred for 1 h at this temperature. Water was added, and the resulting solution was extracted with CH_2Cl_2. After usual workup, 1.38 g (6.5 mmol, 65%) of **32** was obtained. This aldehyde was converted to the corresponding phenol (**33**) in 76% yield as in the synthesis of **28**.

33: NMR (CCl_4) δ 2.19 (s, 3 H), 3.66 (s, 3 H), 3.70 (s, 3 H), 5.68 (br, 1 H, OH), 6.72 (s, 1 H); IR (NaCl) 3350 (m), 1600 (s), 1480 (s), 1220 (s), 1000 cm^{-1} (s); MS, m/e (relative intensity) 204 (34), 202 (M^+, 100), 187 (86), 167 (30). Anal. Calcd for $C_9H_{11}O_3Cl$: C, 53.35; H, 5.47; Cl, 17.50. Found: C, 53.29; H, 5.39; Cl, 17.55.

2,4,5-Trimethoxy-3-methylphenol (37). Phenol **34**[19] was converted to the corresponding methyl ether **35** in 98% yield by the alkylation technique used in the synthesis of **22**. The ether **35** was converted to **37** in 53% yield by the used method to convert **31** to **33**: NMR (CCl_4) δ 2.15 (s, 3 H), 3.69 (s, 3 H), 3.78 (s, 6 H), 5.50 (br, 1 H, OH), 6.32 (s, 1 H); MS, m/e (relative intensity) 198 (M^+, 65), 167 (100). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.64; H, 7.21.

5-Isopropoxy-2,4-dimethoxy-3-methylphenol (40). 40 (45% from **34**) was synthesized in the same way as **37**, using isopropyl bromide: NMR (CCl_4) δ 1.28 (d, 6 H, J = 6 Hz), 2.11 (s, 3 H), 3.80 (s, 3 H), 6.40 (s, 1 H); MS, m/e (relative intensity) 226 (M^+, 58), 183 (100). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.81; H, 8.21.

4-Acetoxy-5-bromo-2-methoxy-3-methylphenol (44). By the same method used for the synthesis of **32**, **41**[18] was converted to the aldehyde **42** in 75% yield: white solid, mp 110–112 °C; NMR (CCl_4) δ 2.26 (s, 3 H), 3.88 (s, 3 H), 7.84 (s, 1 H), 10.12 (s, 1 H); IR (KBr) 1660 (vs), 1240 (s), 880 cm^{-1} (m). **42** (3.7 g, 15 mmol) was acetylated with pyridine (2 mL) and acetic anhydride (5 mL) for 22 h at room temperature. The crude acetate was purified by column chromatography on silica gel (benzene as eluent) to give 3.37 g (11.1 mmol, 74%) of **43** as white needles: mp. 146–149 °C; NMR (CCl_4) δ 2.08 (s, 3 H), 2.30 (s, 3 H), 3.89 (s, 3 H), 7.78 (s, 1 H), 10.02 (s, 1 H); IR (KBr) 2920 (m), 1760 (s), 1680 (s), 1575 (s), 1450 (m), 1380 (s), 1180 (s), 1080 (s), 1000 cm^{-1} (m); MS, m/e (relative intensity) 288 (M^+, 25), 286 (24), 246 (83), 244 (89), 200 (40), 198 (34), 148 (100). This acetoxy aldehyde was converted to the corresponding phenol (**44**) in 87% yield by the same manner as in the synthesis of **28**: NMR (CCl_4) δ 2.04 (s, 3 H), 2.30 (s, 3 H), 3.60 (s, 3 H), 6.16 (br, 1 H), 6.82 (s, 1 H); IR (NaCl) 3400 (m), 1770 (vs), 1760 (vs), 1480 (s), 1420 (m), 1200 (s), 1080 (m), 780 cm^{-1} (s); MS, m/e (relative intensity) 276 (90), 274 (M^+, 100). Anal. Calcd for $C_{10}H_{11}O_4Br$: C, 43.66; H, 4.03; Br, 29.05. Found: C, 43.87; H, 4.27; Br, 29.11.

Preparation of Aryl 2,4-Penta- and 2,4-Hexadienyl Ethers. General Procedure. To a dry acetone solution (5 mL, dried over $CaSO_4$) of the phenol (3 mmol) and K_2CO_3 (4.5 mmol) was added 1-chloro-2,4-pentadiene (0.33 mL, 3.6 mmol) or 1-bromo-2,4-hexadiene[21] (0.53 mL, 3.6 mmol) at reflux temperature under nitrogen, and the resulting solution was refluxed for 16 h. After cooling to room temperature, the volatile material was removed by evaporation, water was added, and residue was extracted with ether. The ethereal layer was washed twice with 10% NaOH solution and then with water, dried over $MgSO_4$, and evaporated. The crude product was purified by column chromatography on silica gel (hexane–ether as eluant). All aryl dienyl ethers were prepared by this procedure except as noted. In the synthesis of hexadienyl ethers, the undesired regioisomers, aryl 1-methyl-2,4-pentadienyl ethers, were observed in the crude product in small amounts (<2%).

2,4-Pentadienyl phenyl ether (1) (62%): colorless oil; satisfactory NMR, IR, and mass spectral data were obtained in comparison with the literature.[10]

Entry 6. 2,3-Dimethylphenyl 2,4-pentadienyl ether (60%): colorless oil; NMR (CCl_4) δ 2.12 (s, 3 H), 2.22 (s, 3 H), 4.46 (d, 2 H, J = 5 Hz), 5.05 (d, 1 H, J = 10 Hz), 5.11 (d, 1 H, J = 14 Hz), 5.80 (m, 1 H), 6.20 (m, 2 H), 6.80 (m, 3 H); IR (NaCl) 1260 (vs), 1000 (vs), 950 (m), 900 (s), 760 cm^{-1} (s); MS, m/e (relative intensity) 188 (M^+, 28), 122 (100). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.79; H, 8.77.

Entry 7. 2,5-Dimethylphenyl 2,4-pentadienyl ether (64%): colorless oil; NMR (CCl_4) δ 2.14 (s, 3 H), 2.25 (s, 3 H), 4.44 (d, 2 H, J = 6 Hz), 5.02 (d, 1 H, J = 10 Hz), 5.14 (d, 1 H, J = 14 Hz), 5.76 (m, 1 H), 6.21 (m, 2 H), 6.45 (s, 1 H), 6.52 (d, 1 H, J = 7 Hz), 6.88 (d, 1 H, J = 7 Hz); IR (NaCl) 1260 (vs), 1020 (s), 1000 (s), 950 (m), 910 (s), 840 (m), 800 cm^{-1} (s); MS, m/e (relative intensity) 188 (M^+, 40), 122 (100). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.81; H, 8.69.

Entry 8. 2-Methoxyphenyl 2,4-pentadienyl ether (81%): colorless oil; NMR (CCl_4) δ 3.72 (s, 3 H), 4.44 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.22 (d, 1 H, J = 14 Hz), 5.73 (m, 1 H), 6.17 (m, 2 H), 6.75 (m, 4 H); IR (NaCl) 1250 (vs), 1220 (s), 1020 (s), 1000 (s), 960 (m), 900 (m), 750 cm^{-1} (s); MS, m/e (relative intensity) 190 (M^+, 80), 124 (100). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.54; H, 7.21.

Entry 9. 3-*tert*-Butylphenyl 2,4-pentadienyl ether (68%): NMR (CCl_4) δ 1.30 (s, 9 H), 4.44 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.04 (d, 1 H, J = 14 Hz), 5.74 (m, 1 H), 6.21 (m, 2 H), 6.57 (m, 1 H), 5.86 (m, 3 H); IR (NaCl) 1270 (s), 1210 (s), 1000 (s), 950 (m), 900 cm^{-1} (s); MS, m/e (relative intensity) 216 (M^+, 100), 159 (54), 150 (50). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.34; H, 9.21.

Entry 10. 1-Naphthyl 2,4-pentadienyl ether (59%): colorless oil; NMR (CCl_4) δ 4.86 (d, 2 H, J = 6 Hz), 4.99 (d, 1 H, J = 10 Hz), 5.06 (d, 1 H, J = 14 Hz), 5.44–6.40 (m, 3 H), 6.48–6.54 (m, 1 H), 7.06–7.36 (m, 4 H), 7.54–7.68 (m, 1 H), 8.20–8.28 (m, 1 H); IR (NaCl) 1260 (s), 1010 (s), 1000 (s), 940 (w), 900 (m), 780 (s), 760 cm^{-1} (s); MS, m/e (relative intensity) 210 (M^+, 46), 144 (100). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.88; H, 6.93.

Entry 11. 2-Nitrophenyl 2,4-pentadienyl ether (50%): colorless oil; NMR (CCl_4) δ 4.62 (d, 2 H, J = 6 Hz), 5.04 (d, 1 H, J = 10 Hz), 5.13 (d, 1 H, J = 14 Hz), 5.62–5.88 (m, 1 H), 6.01–6.46 (m, 2 H), 6.84–7.00 (m, 2 H), 7.22–7.46 (m, 1 H), 7.60–7.72 (m, 1 H); IR (NaCl) 1520 (s), 1250 (s), 1000 (s), 950 (m), 900 cm^{-1} (m); MS, m/e (relative intensity) 205 (M^+, 100), 139 (97). Anal. Calcd for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.53; H, 5.66; N, 6.79.

Entry 12. 2,4-Dimethylphenyl 2,4-pentadienyl ether (80%): colorless oil; NMR (CCl_4) δ 2.15 (s, 3 H), 2.18 (s, 3 H), 4.38 (d, 2 H, J = 6 Hz), 5.03 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 5.68 (m, 1 H), 6.28 (m, 2 H), 6.54 (d, 1 H, J = 7 Hz), 6.80 (d, 1 H, J = 7 Hz), 6.83 (s, 1 H); MS, m/e (relative intensity) 188 (M^+, 30), 122 (100). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.12; H, 8.77.

Entry 13. 2,4-Dimethoxy-3-methylphenyl 2,4-pentadienyl ether (70%): colorless oil; NMR (CCl_4) δ 2.09 (s, 3 H), 3.58 (s,

(20) Wehrenalp, G. B. *J. Inorg. Nucl. Chem.* **1956**, *2*, 266.

(21) Mori, K. *Tetrahedron* **1974**, *30*, 3807.

3 H), 3.71 (s, 3 H), 4.32 (d, 2 H, J = 6 Hz), 4.92 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 5.54–5.86 (m, 1 H), 6.00–6.30 (m, 2 H), 6.24 (d, 1 H, J = 9 Hz), 6.50 (d, 1 H, J = 9 Hz); IR (NaCl) 1250 (s), 1150 (s), 1000 (s), 950 (m), 900 cm^{-1} (m); MS, m/e (relative intensity) 234 (M^+, 100), 168 (76). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.56; H, 7.63.

Entry 14. 2-(Benzyloxy)-4-methoxy-3-methylphenyl 2,4-pentadienyl ether (85%): colorless oil; NMR (CCl_4) δ 2.04 (s, 3 H), 3.72 (s, 3 H), 4.44 (d, 2 H, J = 6 Hz), 4.91 (s, 2 H), 5.00 (d, 1 H, J = 10 Hz), 5.12 (d, 1 H, J = 14 Hz), 5.82 (m, 1 H), 6.30 (m, 2 H), 6.53 (d, 1 H, J = 8 Hz), 6.59 (d, 1 H, J = 8 Hz), 7.27 (m, 5 H); MS, m/e (relative intensity) 498 (M^+, 31), 432 (100). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.54; H, 7.32.

Entry 15. 4-(Benzyloxy)-2-methoxy-3-methylphenyl 2,4-pentadienyl ether (88%): colorless oil; NMR (CCl_4) δ 2.14 (s, 3 H), 3.77 (s, 3 H), 4.83 (d, 2 H, J = 6 Hz), 4.88 (s, 2 H), 5.06 (d, 1 H, J = 10 Hz), 5.18 (s, 1 H, J = 14 Hz), 5.90 (m, 1 H), 6.30 (m, 2 H), 6.39 (d, 1 H, J = 9 Hz), 6.59 (d, 1 H, J = 9 Hz), 7.30 (m, 5 H); MS, m/e (relative intensity) 498 (M^+, 47), 432 (100). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.43; H, 7.22.

Entry 16. 2-Naphthyl 2,4-pentadienyl ether (60%): colorless oil; NMR (CCl_4) δ 4.44 (d, 2 H, J = 5 Hz), 5.05 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 5.64–5.92 (m, 1 H), 6.08–6.40 (m, 2 H), 6.98–7.40 (m, 4 H), 7.58–7.68 (m, 3 H); IR (NaCl) 1260 (s), 1000 (s), 940 (m), 900 (m), 740 cm^{-1} (s); MS, m/e (relative intensity) 210 (M^+, 41), 144 (100). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.83; H, 6.43.

Entry 17. 4-*tert*-Butylphenyl 2,4-pentadienyl ether (86%): colorless oil; NMR (CCl_4) δ 1.25 (s, 9 H), 4.25 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.12 (d, 1 H, J = 14 Hz), 5.81 (m, 1 H), 6.25 (m, 2 H), 6.75 (d, 2 H, J = 9 Hz), 7.13 (d, 2 H, J = 9 Hz); MS, m/e (relative intensity) 216 (M^+, 36), 201 (36), 135 (100), 107 (24). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.42; H, 9.58.

Entry 18. 4-Biphenylyl 2,4-pentadienyl ether (84%): colorless oil; NMR (CCl_4) δ 4.45 (d, 2 H, J = 6 Hz), 5.03 (d, 1 H, J = 10 Hz), 5.14 (d, 1 H, J = 14 Hz), 5.78 (m, 1 H), 6.30 (m, 2 H), 6.80 (d, 2 H, J = 8 Hz), 7.22 (d, 2 H, J = 8 Hz), 7.30 (m, 5 H); MS, m/e (relative intensity) 236 (M^+, 75), 170 (100), 141 (39), 115 (40). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.62; H, 6.96.

Entry 19. 4-Nitrophenyl 2,4-pentadienyl ether (83%): colorless oil; NMR (CCl_4) δ 4.64 (d, 2 H, J = 6 Hz), 4.99 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 5.80 (m, 1 H), 6.30 (m, 2 H), 6.88 (d, 2 H, J = 8 Hz), 8.09 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{11}H_{11}O_3N$: C, 64.38; H, 5.40. Found: C, 64.57; H, 5.65.

Entry 20. 4-Fluoro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (87%): colorless oil; NMR (CCl_4) δ 2.12 (s, 3 H), 3.69 (s, 3 H), 3.75 (s, 3 H), 4.40 (d, 2 H, J = 6 Hz), 4.96 (d, 1 H, J = 10 Hz), 5.23 (d, 1 H, J = 14 Hz), 5.60–5.88 (m, 1 H), 6.02–6.40 (m, 2 H), 6.37 (d, 1 H, J = 12 Hz); IR (NaCl) 2940 (m), 1490 (s), 1460 (m), 1430 (m), 1225 (s), 1220 (m), 1180 (w), 1130 (m), 1100 (s), 1090 (s), 1000 (s), 900 cm^{-1} (m); MS, m/e (relative intensity) 252 (M^+, 10), 185 (100), 167 (71). Anal. Calcd for $C_{14}H_{17}O_3F$: C, 66.65; H, 6.79; F, 7.53. Found: C, 66.44; H, 6.88; F, 7.75.

Entry 21. 4-Chloro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (89%): colorless oil; NMR (CCl_4) δ 2.14 (s, 3 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 4.46 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.16 (d, 1 H, J = 14 Hz), 5.2 (m, 1 H), 6.20 (m, 2 H), 6.69 (s, 1 H); IR (NaCl) 1480 (s), 1210 (m), 1240 (s), 1100 (s), 1070 (s), 1000 (s), 900 (m), 810 cm^{-1} (w); MS, m/e (relative intensity) 268 (M^+, 14), 270 (5), 201 (100), 173 (32). Anal. Calcd for $C_{14}H_{17}O_3Cl$: C, 62.57; H, 6.38; Cl, 13.19. Found: C, 63.09; H, 6.51; Cl, 13.25.

Entry 22. 4-Bromo-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (78%): colorless oil; NMR (CCl_4) δ 2.12 (s, 3 H), 3.64 (s, 3 H), 3.68 (s, 3 H), 4.40 (d, 2 H, J = 6 Hz), 4.96 (d, 1 H, J = 10 Hz), 5.16 (d, 1 H, J = 14 Hz), 5.54–5.92 (m, 1 H), 6.00–6.40 (m, 2 H), 6.76 (s, 1 H); IR (NaCl) 1260 (s), 1240 (vs), 1000 (s), 950 (m), 900 cm^{-1} (m); MS, m/e (relative intensity) 314 (M^+, 54), 312 (60), 247 (86), 245 (90), 139 (100). Anal. Calcd for $C_{14}H_{17}O_3Br$: C, 53.69; H, 5.47; Br, 25.51. Found: C, 54.73; H, 5.48; Br, 25.89.

Entry 23. 3-Methyl-2,4,5-trimethoxyphenyl 2,4-pentadienyl ether (82%): colorless oil; NMR (CCl_4) δ 2.10 (s, 3 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 4.47 (d, 2 H, J = 6 Hz), 5.06 (d, 1 H, J = 10 Hz), 5.18 (d, 1 H, J = 14 Hz), 5.90 (m, 1 H), 6.30 (m, 2 H), 6.29 (s, 1 H); MS, m/e (relative intensity) 264 (M^+, 54), 198 (100). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.34; H, 7.75.

Entry 24. 5-Isopropoxy-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (83%): colorless oil; NMR (CCl_4) δ 1.28 (d, 6 H, J = 6 Hz), 2.16 (s, 3 H), 3.76 (s, 6 H), 4.55 (d, 2 H, J = 6 Hz), 5.10 (d, 1 H, J = 10 Hz), 5.24 (d, 1 H, J = 14 Hz), 5.77–6.10 (m, 1 H), 6.36–6.60 (m, 3 H); IR (NaCl) 1480 (s), 1410 (m), 1370 (m), 1230 (s), 1100 (s), 1000 (s), 900 (w), 770 (w); MS, m/e (relative intensity) 292 (M^+, 12), 225 (100), 183 (56), 155 (67). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.01; H, 8.32.

Entry 25. 4-Acetoxy-5-bromo-2-methoxy-3-methylphenyl 2,4-pentadienyl ether (56%): colorless oil; NMR (CCl_4) δ 2.12 (s, 3 H), 2.24 (s, 3 H), 3.74 (s, 3 H), 4.39 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 5.60–5.94 (m, 1 H), 6.02–6.34 (m, 2 H), 6.64 (s, 1 H); IR (NaCl) 2920 (m), 1760 (vs), 1460 (s), 1420 (s), 1365 (m), 1200 (vs), 1100 (s), 960 (w), 920 (w), 775 cm^{-1} (s); MS, m/e (relative intensity) 340 (M^+, 33), 342 (19), 300 (100), 298 (71), 271 (63), 269 (42). Anal. Calcd for $C_{15}H_{17}O_4Br$: C, 52.80; H, 5.02; Br, 23.42. Found: C, 52.97; H, 5.22; Br, 23.49.

Entry 26. A solution of 4-acetoxy-5-bromo-2-methoxy-3-methylphenyl 2,4-pentadienyl ether (**45**, 673 mg, 2 mmol) in MeOH (15 mL) was added at 0 °C to KOH (336 mg/15 mL) in MeOH, which was bubbled with nitrogen for 0.5 h prior to the addition. After stirring for 3 h at 0 °C under nitrogen, the reaction mixture was quenched with 10% HCl solution and extracted with ether three times. The organic phase was washed with water and brine and evaporated. The residue was purified through a short column of silica gel (hexane–ether as eluent) to give 390 mg (1.3 mmol, 65%) of 6-bromo-3-methoxy-2-methyl-4-[(2,4-pentadienyl)oxy]phenol (**46**) as a colorless oil: NMR (CCl_4) δ 2.16 (s, 3 H), 3.74 (s, 3 H), 4.80 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.13 (d, 1 H, J = 14 Hz), 5.18 (s, 1 H, OH), 5.62–5.94 (m, 1 H), 6.02–6.46 (m, 2 H), 6.54 (s, 1 H); IR (NaCl) 3500 (m), 2910 (m), 1460 (s), 1280 (s), 1220 (s), 1180 (s), 990 (m), 770 (s), 745 cm^{-1} (s); MS, m/e (relative intensity) 300 (12), 298 (12), 233 (93), 231 (100).

A solution of this phenol (**46**, 389 mg, 1.3 mmol), *tert*-butyldimethylsilyl chloride (235 mg, 1.6 mmL), and imidazole (221 mg, 3.3 mmol), in dry DMF (0.78 mL) was stirred overnight under nitrogen. The reaction mixture was quenched with water and extracted with ether. The organic phase was washed with water and brine, dried over $MgSO_4$, and evaporated. After chromatographic purification, 422 mg (1.0 mmol, 78%) of 5-bromo-4-[(*tert*-butyldimethylsilyl)oxy]-2-methoxy-3-methylphenyl 2,4-pentadienyl ether (**47**) was obtained as a colorless oil: NMR (CCl_4) δ 0.26 (s, 6 H), 1.10 (s, 9 H), 2.13 (s, 3 H), 3.80 (s, 3 H), 4.50 (d, 2 H, J = 6 Hz), 5.03 (d, 1 H, J = 10 Hz), 5.15 (d, 1 H, J = 14 Hz), 4.72–6.00 (m, 1 H), 6.24–6.47 (m, 2 H), 6.94 (s, 1 H); IR (NaCl) 2910 (m), 1460 (m), 1425 (m), 1250 (m), 1230 (m), 1100 (m), 845 (m), 825 (m), 770 cm^{-1} (m); MS, m/e (relative intensity) 414 (12), 412 (M^+, 11), 347 (88), 345 (100), 291 (79), 289 (84). Anal. Calcd for $C_{19}H_{29}O_3BrSi$: C, 55.20; H, 7.70; Br, 19.33; Si, 6.79. Found: C, 55.35; H, 7.18; Br, 19.08; Si, 6.87.

Entry 27. **46** was benzylated by the same method as in the synthesis of **22**: colorless oil; NMR (CCl_4) δ 2.18 (s, 3 H), 3.76 (s, 3 H), 4.51 (d, 2 H, J = 6 Hz), 4.80 (s, 2 H), 5.01 (d, 1 H, J = 10 Hz), 5.26 (d, 1 H, J = 14 Hz), 5.56–6.44 (m, 3 H), 6.88 (s, 1 H), 7.24–7.46 (m, 5 H); IR (KBr) 2920 (m), 1460 (m), 1370 (m), 1230 (s), 1160 (m), 1000 (m), 960 (w), 725 cm^{-1} (m); MS, m/e (relative intensity) 390 (76), 388 (M^+, 100), 291 (55), 289 (54), 243 (88). Anal. Calcd for $C_{20}H_{21}O_3Br$: C, 61.71; H, 5.44; Br, 20.53. Found: C, 61.55; H, 5.22; Br, 20.75.

Equation 4. 2,4-Hexadienyl phenyl ether (83%): colorless oil; NMR (CCl_4) δ 1.72 (d, 3 H, J = 6 Hz), 4.42 (d, 2 H, J = 6 Hz), 5.50–5.77 (m, 2 H), 5.86–6.52 (m, 2 H), 6.72–6.89 (m, 3 H), 7.06–7.22 (m, 2 H); IR (NaCl) 1595 (s), 1495 (s), 1380 (m), 1300 (m), 1235 (s), 1170 (m), 745 (s), 680 cm^{-1} (s); MS, m/e (relative intensity) 174 (M^+, 95), 159 (72), 145 (100), 131 (72). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.75; H, 8.89.

Equation 5. 2,4-Hexadienyl 2,4-dimethoxy-3-methylphenyl ether (88%): white solid, mp 28–30 °C; NMR (CCl_4) δ 1.72 (d, 3 H, J = 7 Hz), 2.05 (s, 3 H), 3.67 (s, 3 H), 3.73 (s, 3 H), 4.36 (d, 2 H, J = 6 Hz), 5.38–5.58 (m, 2 H), 5.58–6.22 (m, 2 H), 6.29 (d,

1 H, J = 8 Hz), 6.54 (d, 1 H, J = 8 Hz); IR (KBr) 1460 (s), 1250 (s), 1110 (s), 1050 (m), 990 (s), 780 cm^{-1} (m); MS, m/e (relative intensity) 248 (M^+, 88), 247 (100), 193 (81). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.75; H, 8.25.

Equation 6. 4-*tert*-Butylphenyl 2,4-hexadienyl ether (70%): colorless plates, mp 55–57 °C; NMR (CCl_4) δ 1.26 (s, 9 H), 1.69 (d, 3 H, J = 6 Hz), 4.44 (d, 2 H, J = 6 Hz), 5.40–5.80 (m, 2 H), 5.92–6.39 (m, 2 H), 6.76 (d, 2 H, J = 8 Hz), 7.22 (d, 2 H, J = 8 Hz). Anal. Calcd for $C_{16}H_{22}O$: C, 83.48; H, 9.63. Found: C, 83.34; H, 9.82.

Equation 7. 5-Bromo-2,4-dimethoxy-3-methylphenyl 2,4-hexadienyl ether (69%): white solid, mp 39–41 °C; NMR (CCl_4) δ 1.76 (d, 3 H, J = 7 Hz), 2.18 (s, 3 H), 3.69 (s, 3 H), 3.75 (s, 3 H), 4.44 (d, 2 H, J = 6 Hz), 5.44–5.84 (m, 2 H), 5.84–6.46 (m, 2 H), 6.83 (s, 1 H); IR (KBr) 1450 (s), 1370 (s), 1230 (s), 1100 (m), 1060 (s), 990 (s), 790 cm^{-1} (s); MS, m/e (relative intensity) 328 (M^+, 35), 326 (36), 247 (100), 246 (100). Anal. Calcd for $C_{15}H_{19}O_3Br$: C, 55.06; H, 5.85; Br, 24.42. Found: C, 55.23; H, 5.97; Br, 24.56.

Lewis Acid Mediated Claisen-Type Rearrangement of the Dienyl Group. General Procedure. A solution of aryl 2,4-penta- or 2,4-hexadienyl ether (1 mmol) in dry CH_2Cl_2 (10 mL) was cooled to −40 °C (CH_3CN–solid CO_2 bath). To the mixture was added $BF_3{\cdot}OEt_2$ (0.16 mL, 1.2 mmol), and it was stirred for 1 h at −40 °C. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic phase was washed with water and brine, dried over $MgSO_4$, and evaporated. The products were separated by PLC or column chromatography on silica gel (hexane–ether as eluent). All reactions except entries 20, 21, and 22 in Table II and eq 7 were performed according to this general procedure. The rearranged position of the dienyl group on aryl ring was confirmed by inspection of the shift value induced by $Eu(fod)_3$, after acetylation if necessary.

Table I, Entry 5. 4-(2,4-Pentadienyl)phenol (2) (76%): colorless oil; satisfactory NMR, IR, and mass spectral data were obtained in comparison with the literature.[10]

Table II, Entry 6. 2,3-Dimethyl-4-(2,4-pentadienyl)phenol (94%): colorless oil; NMR (CCl_4) δ 2.12 (s, 6 H), 3.32 (d, 2 H, J = 7 Hz), 4.76 (br, 1 H, OH), 4.88–5.10 (m, 2 H), 5.56–6.34 (m, 3 H), 6.49 (d, 1 H, J = 8 Hz), 6.78 (d, 1 H, J = 8 Hz); IR (NaCl) 1000 (s), 960 (m), 890 (s), 800 cm^{-1} (s); MS, m/e (relative intensity) 188 (M^+, 100), 122 (23). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.74; H, 8.77.

Entry 7. 2,5-Dimethyl-4-(2,4-pentadienyl)phenol (91%): colorless oil; NMR (CCl_4) δ 2.12 (s, 6 H), 3.22 (d, 2 H, J = 7 Hz), 4.84–5.08 (m, 2 H), 5.32–6.32 (m, 3 H), 6.40 (s, 1 H), 6.74 (s, 1 H); IR (NaCl) 1000 (s), 950 (m), 900 (s), 860 cm^{-1} (m); MS, m/e (relative intensity) 188 (M^+, 100), 122 (31). Anal. Calcd for $C_{13}H_{16}O$: C, 82.57; H, 8.50. Found: C, 83.08; H, 8.32.

Entry 8. 2-Methoxy-4-(2,4-pentadienyl)phenol (84%): colorless oil; NMR (CCl_4) δ 3.24 (d, 2 H, J = 7 Hz), 3.72 (s, 3 H), 4.88–5.12 (m, 2 H), 5.60 (br, 1 H, OH), 5.60–6.44 (m, 3 H), 6.52–6.80 (m, 3 H); IR (NaCl) 1270 (vs), 1030 (s), 1000 (s), 950 (m), 900 cm^{-1} (m); MS, m/e (relative intensity) 190 (M^+, 100), 125 (42). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.88; H, 7.75.

Entry 9. 3-*tert*-Butyl-4-(2,4-pentadienyl)phenol (60%): colorless oil; NMR (CCl_4) δ 1.32 (s, 9 H), 2.50 (br, 2 H), 4.84–5.08 (m, 2 H), 5.74–6.48 (m, 4 H), 6.64–6.92 (m, 2 H); IR, (NaCl) 1200 (s), 1000 (s), 780 (vs), 750 cm^{-1} (vs); MS, m/e (relative intensity) 216 (M^+, 100), 150 (37). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.42; H, 9.58.

Entry 10. 4-(2,4-Pentadienyl)-1-naphthol (80%): colorless oil; NMR (CCl_4) δ 3.66 (d, 2 H, J = 5 Hz), 4.82–5.04 (m, 2 H), 5.60–6.42 (m, 3 H), 6.54 (d, 1 H, J = 8 Hz), 6.96 (d, 1 H, J = 8 Hz), 7.24–7.38 (m, 2 H), 7.74–7.84 (m, 2 H); IR (NaCl) 1000 (s), 945 (w), 900 (m), 770 (vs), 750 cm^{-1} (vs); MS, m/e (relative intensity) 210 (M^+, 100), 144 (21). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.92; H, 6.54.

Entry 11. 2-Nitrophenol (8%) was obtained with the recovery (51%).

Entry 12. 2,4-Dimethyl-5-(2,4-pentadienyl)phenol (70%): colorless oil; NMR (CCl_4) δ 2.14 (s, 6 H), 3.23 (d, 2 H, J = 6 Hz), 4.44 (br, 1 H, OH), 4.93 (d, 1 H, J = 10 Hz), 5.04 (dd, 1 H, J = 14, 3 Hz), 5.76 (m, 3 H), 6.41 (s, 1 H), 6.80 (s, 1 H); MS, m/e (relative intensity) 188 (M^+, 100), 122 (39), 91 (61). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.84; H, 8.32.

Entry 13. 2,4-Dimethoxy-3-methyl-5-(2,4-pentadienyl)phenol (86%): colorless solid, mp 99–103 °C; 400-MHz ^1H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 3.37 (d, 2 H, J = 6.7 Hz), 3.67 (s, 3 H), 3.75 (s, 3 H), 4.98 (dd, 1 H, J = 10, 1.2 Hz), 5.06 (dd, 1 H, J = 17.1, 10.4 Hz), 5.76 (s, 1 H), 5.81 (dt, 1 H, J = 7.6, 15.2 Hz), 6.10 (dd, 1 H, J = 10, 15.2 Hz), 6.32 (ddd, 1 H, J = 17.1, 10.0, 10.4 Hz); IR (NaCl) 1010 (s), 1000 (s), 900 cm^{-1} (m); MS, m/e (relative intensity) 234 (M^+, 100), 187 (52), 131 (40), 91 (38). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.54; H, 7.86.

Entry 14. 2-(Benzyloxy)-4-methoxy-3-methyl-5-(2,4-pentadienyl)phenol (80%): colorless oil; NMR (CCl_4) δ 2.14 (s, 3 H), 3.33 (d, 2 H, J = 7 Hz), 3.25 (s, 3 H), 2.98 (s, 2 H), 4.90 (d, 1 H, J = 10 Hz), 5.07 (d, 1 H, J = 14 Hz), 6.00 (m, 3 H), 6.54 (s, 1 H), 7.32 (m, 5 H); MS, m/e (relative intensity) 310 (M^+, 24), 222 (100). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.52; H, 7.23.

Entry 15. 4-(Benzyloxy)-2-methoxy-3-methyl-5-(2,4-pentadienyl)phenol (81%): colorless oil; NMR (CCl_4) δ 2.18 (s, 3 H), 3.32 (d, 2 H, J = 7 Hz), 3.66 (s, 3 H), 4.70 (s, 2 H), 4.91 (d, 1 H, J = 10 Hz), 5.04 (d, 1 H, J = 4 Hz), 5.40 (br, 1 H, OH), 6.00 (m, 3 H), 6.58 (s, 1 H), 7.32 (m, 5 H); MS, m/e (relative intensity) 310 (M^+, 100), 244 (31). Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.21; H, 7.32.

Entry 16. The starting dienyl ether (22%) and an unseparable mixture of 4-(2,4-pentadienyl)-2-naphthol (39%) and 1-(2,4-pentadienyl)-2-naphthol (22%) were obtained.

4-(2,4-Pentadienyl)-2-naphthol: NMR (CCl_4) δ 3.50 (d, 2 H, J = 6 Hz), 4.82 (d, 1 H, J = 10 Hz), 5.00 (d, 1 H, J = 14 Hz), 5.60–6.32 (m, 3 H), 7.08 (s, 1 H), 7.09 (s, 1 H), 7.40–7.80 (m, 4 H).

1-(2,4-Pentadienyl)-2-naphthol: NMR (CCl_4) δ 3.70 (d, 2 H, J = 6 Hz), 4.82 (d, 1 H, J = 10 Hz), 5.10 (d, 1 H, J = 14 Hz), 5.60–6.32 (m, 3 H), 6.82–7.21 (m, 2 H), 7.40–7.81 (m, 4 H).

The mixture: IR (NaCl) 3400 (m), 1510 (m), 1260 (m), 1200 (m), 100 (s), 780 (vs), 750 cm^{-1} (vs). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.79; H, 6.94.

Entry 17. 4-*tert*-Butyl-2-(2,4-pentadienyl)phenol (62%): colorless oil; NMR (CCl_4) δ 1.25 (s, 9 H), 4.25 (d, 2 H, J = 6 Hz), 5.01 (d, 1 H, J = 10 Hz), 5.12 (d, 1 H, J = 14 Hz), 5.81 (m, 1 H), 6.25 (m, 2 H), 6.75 (d, 1 H, J = 9 Hz), 7.12 (s, 1 H), 7.13 (d, 1 H, J = 9 Hz); MS, m/e (relative intensity) 216 (M^+, 36), 201 (36), 135 (100), 107 (25). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.54; H, 9.55.

Entry 18. 4-Phenyl-2-(2,4-pentadienyl)phenol (43%): colorless oil; NMR (CCl_4) δ 3.45 (d, 2 H, J = 6 Hz), 4.94 (d, 1 H, J = 10 Hz), 5.10 (d, 1 H, J = 14 Hz), 6.00 (m, 3 H), 6.70 (d, 1 H, J = 8 Hz), 7.30 (m, 8 H); MS, m/e (relative intensity) 236 (M^+, 100), 221 (69), 207 (93), 195 (38), 182 (41). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.32; H, 6.99.

Entry 19. 4-Nitrophenol was obtained (60%).

Entry 20. 5-Fluoro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (151 mg, 0.6 mmol) in dry CH_2Cl_2 (6 mL) was treated with $AlCl_3{\cdot}OEt_2$ at −40 °C for 1 h under nitrogen. After the usual workup described in the general procedure, 94 mg (0.37 mmol, 62%) of 3-fluoro-4,6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol was obtained as a colorless oil: NMR (CCl_4) δ 2.13 (s, 3 H), 3.34 (d, 2 H, J = 7 Hz), 3.67 (s, 3 H), 3.73 (s, 3 H), 4.76–5.08 (m, 2 H), 5.43 (s, 1 H, OH), 5.32–6.32 (m, 3 H); MS, m/e (relative intensity) 252 (M^+, 30), 251 (70), 233 (41), 185 (100). Anal. Calcd for $C_{14}H_{17}O_3F$: C, 66.65; H, 6.79; F, 7.53. Found: C, 66.54; H, 6.99; F, 7.32.

Entry 21. 5-Chloro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether was rearranged according to the general procedure at −25 °C to give 3-chloro-4,6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol as a colorless oil: 76%; NMR (CCl_4) δ 2.17 (s, 3 H), 3.50 (d, 2 H, J = 7 Hz), 3.69 (s, 6 H), 5.00 (m, 2 H), 5.47 (br, 1 H, OH), 5.80 (m, 1 H), 6.06 (m, 2 H); IR (NaCl) 2940 (vs), 1450 (s), 1410 (s), 1345 (m), 1300 (m), 1225 (m), 1110 (s), 1090 (s), 1000 cm^{-1} (s); MS, m/e (relative intensity) 270 (36), 268 (M^+, 100), 216 (38), 214 (99). Anal. Calcd for $C_{14}H_{17}O_3Cl$: C, 62.57; H, 6.38; Cl, 13.19. Found: C, 62.75; H, 6.50; Cl, 13.09.

Entry 22. 5-Bromo-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether was reacted according to the general procedure at −15 °C to give a mixture of 3-bromo-4,6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol (**6**, 28%) and 4-bromo-5,7-dimethoxy-6-methyl-2-(*trans*-1-propenyl)-1-oxoindan (**7**, 60%).

6: white solid, mp 71–74 °C; NMR (CCl_4) δ 2.44 (s, 3 H), 3.60 (d, 2 H, J = 7 Hz), 3.74 (s, 3 H), 3.76 (s, 3 H), 4.94 (d, 1 H, J = 10 Hz), 5.05 (d, 1 H, J = 14 Hz), 5.68 (s, 1 H, OH), 5.48–5.92 (m, 1 H), 5.92–6.84 (m, 2 H); IR (KBr) 1000 (s), 950 (m), 890 cm^{-1} (s); MS, m/e (relative intensity) 312 (M^+, 100), 314 (84). Anal. Calcd for $C_{14}H_{17}O_3Br$: C, 53.69; H, 5.47; Br, 25.51. Found: C, 53.81; H, 5.47; Br, 25.25.

7: colorless oil; NMR (CCl_4) δ 1.72 (d, 3 H, J = 6 Hz), 2.08 (s, 3 H), 2.81 (dd, 1 H, J = 16, 8 Hz), 3.21 (dd, 1 H, J = 16, 8 Hz), 3.60 (s, 3 H), 3.80 (s, 3 H), 5.04 (dt, 1 H, J = 6, 8 Hz), 5.64 (m, 2 H); IR (NaCl) 960 cm^{-1} (m); MS, m/e (relative intensity) 312 (M^+, 100), 314 (94). Anal. Calcd for $C_{14}H_{17}O_3Br$: C, 53.69; H, 5.47; Br, 25.51. Found: C, 53.79; H, 5.32; Br, 25.31.

When **4** was treated with $BF_3{\cdot}OEt_2$ at −25 °C in CH_2Cl_2 for 1 h, the dienylated product (**6**, 59%) and starting ether (**4**, 26%) were obtained.

Entry 23. 2,4,5-Trimethoxy-3-methyl-4-(2,4-pentadienyl)-2,5-cyclohexadienone (**8**) was obtained as colorless oil (60%): NMR (CCl_4) δ 1.76 (s, 3 H), 2.55 (dd, 1 H, J = 8, 13 Hz), 2.76 (dd, 1 H, J = 8, 13 Hz), 3.01 (s, 3 H), 3.68 (s, 3 H), 3.77 (s, 3 H), 5.00 (d, 1 H, J = 10 Hz), 5.17 (d, 1 H, J = 14 Hz), 5.80–6.13 (m, 3 H), 5.60 (s, 1 H). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.11; H, 8.53.

Entry 24. As in the case of entry 18, 2,4-dimethoxy-3-methyl-5-isopropoxy-4-(2,4-pentadienyl)-2,5-cyclohexadienone was obtained as a colorless oil: 51%; 400-MHz ^1H NMR (CCl_4) δ 1.31 (d, 3 H, J = 6.1 Hz), 1.35 (d, 3 H, J = 6.1 Hz), 1.86 (s, 3 H), 2.51 (dd, 1 H, J = 7.6, 13.4 Hz), 2.72 (dd, 1 H, J = 7.3, 13.4 Hz), 3.00 (s, 3 H), 3.68 (s, 3 H), 4.43 (dt, 1 H, J = 6.1, 6.1 Hz), 4.94 (d, 1 H, J = 10.0 Hz), 5.04 (d, 1 H, J = 16.8 Hz), 5.14 (dt, 1 H, J = 7.3, 15.0 Hz), 5.59 (s, 1 H), 5.96 (dd, 1 H, J = 10.3, 15.0 Hz), 6.11 (ddd, 1 H, J = 16.8, 10.0, 10.3 Hz). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.95; H, 8.35.

Entry 25. 4-Acetoxy-3-bromo-6-methoxy-5-methyl-2-(2,4-pentadienyl)phenol (25%): colorless oil; NMR (CCl_4) δ 2.02 (s, 3 H), 2.44 (s, 3 H), 3.50 (d, 2 H, J = 7 Hz), 3.54 (s, 3 H), 4.74–5.06 (m, 2 H), 5.46–6.34 (m, 3 H), 6.10 (s, 1 H, OH); IR (NaCl) 2920 (m), 1760 (s), 1460 (m), 1420 cm^{-1} (m); MS, m/e (relative intensity) 340 (M^+, 45), 342 (44). Anal. Calcd for $C_{15}H_{17}O_4Br$: C, 52.80; H, 5.02; Br, 23.42. Found: C, 52.97; H, 5.33; Br, 23.65.

Entry 26. 3-Bromo-4-[(*tert*-butyldimethylsilyl)oxy]-6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol (27%): colorless oil; NMR (CCl_4) δ 0.26 (s, 6 H), 1.04 (s, 9 H), 2.14 (s, 3 H), 3.53 (d, 2 H, J = 7 Hz), 3.92 (s, 3 H), 4.80–5.20 (m, 2 H), 5.40–6.20 (m, 3 H); MS, m/e (relative intensity) 414 (M^+, 32), 412 (31), 333 (100). Anal. Calcd for $C_{19}H_{29}O_3BrSi$: C, 55.20; H, 7.07; Br, 19.33; Si, 6.79. Found: C, 55.32; H, 7.27; Br, 19.54; Si, 6.32.

Entry 27. 4-(Benzyloxy)-3-bromo-6-methoxy-5-methyl-2-(2,4-pentadienyl)phenol (9%): colorless oil; NMR (CCl_4) δ 2.15 (s, 3 H), 3.60 (d, 2 H, J = 7 Hz), 3.69 (s, 3 H), 4.80 (s, 2 H), 4.80–5.20 (m, 2 H), 5.60 (s, 1 H, OH), 5.56–6.40 (m, 3 H), 7.21–7.46 (m, 5 H); MS, m/e (relative intensity) 390 (32), 388 (M^+, 31), 309 (100). Anal. Calcd for $C_{20}H_{21}O_3Br$: C, 61.71; H, 5.44; Br, 20.53. Found: C, 61.97; H, 5.32; Br, 20.38.

Equation 4. 4-(2,4-Hexadienyl)phenol (58%) and 4-(1-methyl-2,4-pentadienyl)phenol (20%) were obtained as an inseparable mixture.

4-(2,4-Hexadienyl)phenol: 400-MHz ^1H NMR ($CDCl_3$) δ 1.73 (d, 3 H, J = 7.0 Hz), 3.32 (d, 2 H, J = 6.7 Hz), 5.60 (dt, 1 H, J = 6.7, 13.7 Hz), 5.66 (dq, 1 H, J = 7.0, 13.7 Hz), 6.05 (m, 2 H), J = 10.0, 13.7, Hz), 6.81 (d, 2 H, J = 7.9 Hz), 7.05 (d, 2 H, J = 7.9 Hz).

4-(1-Methyl-2,4-pentadienyl)phenol: 400-MHz ^1H NMR ($CDCl_3$) δ 1.35 (d, 3 H, J = 7.0 Hz), 3.43 (dq, 1 H, J = 7.0, 6.7 Hz), 4.99 (d, 1 H, J = 9.2 Hz), 5.12 (s, 1 H, J = 16.8 Hz), 5.84 (dd, 1 H, J = 6.7, 15.3 Hz), 6.05 (dd, 1 H, J = 15.3, 10.0 Hz), 6.30 (ddd, 1 H, J = 16.8, 9.2, 10.0 Hz), 6.83 (d, 2 H, J = 7.9 Hz), 7.08 (d, 2 H, J = 7.9 Hz).

The mixture: IR (NaCl) 2980 (m), 1650 (m), 1510 (s), 1440 (m), 1230 (s), 950 (m), 820 (m), 735 cm^{-1} (m); MS, m/e (relative intensity) 174 (M^+, 100), 159 (62), 145 (66), 133 (95). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.95; H, 8.32.

Equation 5. A mixture of 6-(2,4-hexadienyl)-2,4-dimethoxy-3-methylphenol and 5-(1-methyl-2,4-pentadienyl)-2,4-dimethoxy-3-methylphenol was obtained.

6-(2,4-Hexadienyl)-2,4-dimethoxy-3-methylphenol: NMR (CCl_4) δ 1.72 (d, 3 H, J = 7 Hz), 2.05 (s, 3 H), 3.26 (d, 2 H, J = 7 Hz), 3.65 (s, 6 H), 5.20–5.64 (m, 2 H), 5.66–6.00 (m, 2 H), 6.21 (s, 1 H).

5-(1-Methyl-2,4-pentadienyl)-2,4-dimethoxy-3-methylphenol: NMR (CCl_4) δ 1.28 (d, 3 H, J = 7 Hz), 2.05 (s, 3 H), 3.28 (t, 1 H, J = 7 Hz), 3.65 (s, 6 H), 4.98 (d, 1 H, J = 10 Hz), 5.12 (d, 1 H, J = 14 Hz), 5.50–5.80 (m, 1 H), 5.90–6.20 (m, 2 H), 6.47 (s, 1 H).

The mixture: IR (NaCl) 3400 (m), 2930 (m), 1460 (s), 1410 (m), 1120 (s), 770 (s), 750 cm^{-1} (s); MS, m/e (relative intensity) 248 (73), 247 (100), 205 (65), 181 (96). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.21; H, 8.07.

Equation 6. A mixture of 4-*tert*-butyl-2-(2,4-hexadienyl)phenol (25%), 4-*tert*-butyl-2,6-bis(2,4-hexadienyl)phenol (10%), and 4-*tert*-butylphenol (18%) was obtained.

4-*tert*-Butyl-2-(2,4-hexadienyl)phenol: NMR (CCl_4) δ 1.24 (s, 9 H), 1.74 (d, 3 H, J = 7 Hz), 3.38 (d, 2 H, J = 7 Hz), 4.67 (br, 1 H, OH), 5.32–6.14 (m, 4 H), 6.60 (d, 1 H, J = 8 Hz), 6.98 (s, 1 H), 7.00 (d, 1 H, J = 8 Hz); IR (NaCl) 3400 (m), 2960 (m), 1500 (w), 1360 (m), 1270 (s), 990 (m), 900 (w), 810 (m), 720 cm^{-1} (s). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.65; H, 9.89.

4-*tert*-Butyl-2,6-bis(2,4-hexadienyl)phenol: NMR (CCl_4) δ 1.28 (s, 9 H), 1.74 (d, 6 H, J = 7 Hz), 3.36 (d, 2 H, J = 7 Hz), 4.83 (br, 1 H, OH), 5.32–6.18 (m, 4 H), 6.90 (s, 2 H); IR (NaCl) 3400 (m), 2950 (m), 1480 (m), 1230 (m), 990 cm^{-1} (m). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74. Found: C, 85.28; H, 9.92.

Equation 7. The corresponding phenol was obtained (60%).

Preparation of Aryl [1,1-$^2H_2$]-2,4-Pentadienyl Ethers. [1,1-$^2H_2$]-2,4-Pentadienol. To lithium aluminum deuteride (666 mg, 16 mmol) was added ethyl 2,4-pentadienoate (2.0 g, 16 mmol) in dry ether (30 mL) at 0 °C under nitrogen. After stirring for 1 h at 0 °C, ice–water was added to decompose excess deuteride, and to the resulting mixture was added a 10% H_2SO_4 aqueous solution and ether. After the usual workup and distillation (bp 87 °C/66 mmHg), 1.1 g (12.8 mmol, 80%) of [1,1-$^2H_2$]-2,4-pentadienol was obtained as colorless liquid: NMR (CCl_4) δ 3.38 (br, 1 H, OH), 5.02 (d, 1 H, J = 10 Hz), 5.13 (d, 1 H, J = 15 Hz), 5.72 (d, 1 H, J = 15 Hz), 6.00–6.50 (m, 2 H).

General Method. A mixture of phenol (0.4 mmol), [1,1-$^2H_2$]-2,4-pentadienol (45 μL, 0.4 mmol), $EtO_2CN{=}NCO_2Et$ (61 μL, 0.4 mmol), and PPh_3 (105 mg, 0.4 mmol) in dry THF (4 mL) was stirred for 48 h at room temperature. Then the mixture was filtrated and evaporated. After purification by PLC, the aryl [1,1-$^2H_2$]-2,4-pentadienyl ether was obtained without contamination by [5,5-$^2H_2$] isomer.

Equation 8. [1,1-$^2H_2$]-2,4-Pentadienyl phenyl ether (10) (65%): colorless oil; NMR (CCl_4) δ 5.04 (d, 1 H, J = 10 Hz), 5.20 (d, 1 H, J = 15 Hz), 5.81 (d, 1 H, J = 15 Hz), 6.12–6.44 (m, 2 H), 6.68–6.92 (m, 3 H), 7.04–7.28 (m, 2 H).

Equation 9. [1,1-$^2H_2$]-2,4-Pentadienyl 2,4-dimethoxy-3-methylphenyl ether (12) (60): colorless oil; NMR (CCl_4) δ 2.06 (s, 3 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 5.07 (d, 1 H, J = 10 Hz), 5.18 (d, 1 H, J = 14 Hz), 5.89 (d, 1 H, J = 14 Hz), 6.32 (d, 1 H, J = 9 Hz), 6.40–6.48 (m, 2 H), 6.58 (d, 1 H, J = 9 Hz).

Equation 10. 4-*tert*-Butylphenyl [1,1-$^2H_2$]-2,4-pentadienyl ether (14) (70%): colorless oil; NMR (CCl_4) δ 1.29 (s, 9 H), 5.05 (d, 1 H, J = 10 Hz), 5.16 (d, 1 H, J = 14 Hz), 5.79 (d, 1 H, J = 14 Hz), 6.08–6.30 (m, 2 H), 6.68 (d, 2 H, J = 8 Hz), 7.14 (d, 2 H, J = 8 Hz).

Equation 11. 5-Bromo-2,4-dimethoxy-3-methylphenyl [1,1-$^2H_2$]-2,4-pentadienyl ether (17) (64%): colorless oil; NMR (CCl_4) δ 2.20 (s, 3 H), 3.73 (s, 3 H), 3.78 (s, 3 H), 5.12 (d, 1 H, J = 10 Hz), 5.22 (d, 1 H, J = 14 Hz), 5.84 (d, 1 H, J = 14 Hz), 6.24–6.42 (m, 2 H), 6.85 (s, 1 H).

Claisen-Type Rearrangement of Aryl [1,1-$^2H_2$]-2,4-Pentadienyl Ethers. This reaction was carried out by the general procedure described above.

Equation 8. 4-([5,5-$^2H_2$]-2,4-Pentadienyl)phenol (11) (76%): colorless oil; NMR (CCl_4) δ 3.34 (d, 2 H, J = 7 Hz), 4.60 (br, 1 H, OH), 5.64–6.00 (m, 2 H), 6.04–6.36 (m, 1 H), 6.64 (d, 2 H, J = 8 Hz), 6.96 (d, 2 H, J = 8 Hz); MS, m/e (relative intensity) 162 (M^+, 69), 149 (100), 107 (77).

Equation 9. [5,5-$^2H_2$]-5-(2,4-Pentadienyl)-2,4-dimethoxy-3-methylphenol (13) (86%): colorless oil; NMR (CCl_4) δ 2.23

(s, 3 H), 3.36 (d, 2 H, J = 7.0 Hz), 3.66 (s, 3 H), 3.76 (s, 3 H), 5.36 (br, 1 H, OH), 5.80 (dt, 1 H, J = 7.0, 14.6 Hz), 6.10 (ddt, 1 H, J = 14.6, 10.4, 1.5 Hz), 6.30 (d, 1 H, J = 10 Hz), 6.62 (s, 1 H); MS, m/e (relative intensity) 236 (M^+, 36), 189 (12), 161 (7), 133 (9), 86 (66), 84 (100).

Equation 10. A mixture of [5,5-$^2H_2$]-2-(2,4-pentadienyl)-4-*tert*-butylphenol (**15**) and [1,1-$^2H_2$]-2-(2,4-pentadienyl)-4-*tert*-butylphenol (**16**) was obtained in 62% yield. The isomeric ratio was determined to be **15**:**16** = 62:38 by 400-MHz ^1H NMR.

15: colorless oil; 400-MHz ^1H NMR (CCl_4) δ 1.29 (s, 9 H), 3.44 (d, 2 H, J = 7 Hz), 4.78 (s, 1 H, OH), 5.89 (dt, 1 H, J = 7, 16 Hz), 6.17 (dd, 1 H, J = 10.3, 15 Hz), 6.33 (d, 1 H, J = 10 Hz), 6.52 (d, 1 H, J = 8 Hz), 6.92 (s, 1 H), 6.96 (d, 1 H, J = 8 Hz).

16: colorless oil; 400-MHz ^1H NMR (CCl_4) δ 1.29 (s, 9 H), 4.78 (s, 1 H, OH), 5.03 (d, 1 H, J = 10 Hz), 5.17 (d, 1 H, J = 16 Hz), 5.89 (d, 1 H, J = 15 Hz), 6.17 (dd, 1 H, J = 10.3, 15 Hz), 6.33 (ddd, 1 H, J = 16, 10, 10 Hz), 6.52 (d, 1 H, J = 8 Hz), 6.92 (s, 1 H), 6.96 (d, 1 H, J = 8 Hz).

Equation 11. A mixture of [5,5-$^2H_2$]-2-(2,4-pentadienyl)-3-bromo-4,6-dimethoxy-5-methylphenol (**18**) and [1,1-$^2H_2$]-2-(2,4-pentadienyl)-3-bromo-4,6-dimethoxy-5-methylphenol (**19**) was obtained in 59% yield. The product ratio was determined to be **18**:**19** = 33:67 by 400-MHz ^1H NMR.

18: NMR (CCl_4) δ 2.26 (s, 3 H), 3.60 (d, 2 H, J = 7.0 Hz), 3.74 (s, 3 H), 3.77 (s, 3 H), 5.61 (dt, 1 H, J = 7.0, 15.0 Hz), 6.12 (dd, 1 H, J = 10.3, 15.0 Hz), 6.28 (d, 1 H, J = 10.3 Hz).

19: NMR (CCl_4) δ 2.26 (s, 3 H), 3.74 (s, 3 H), 3.77 (s, 3 H), 4.95 (d, 1 H, J = 10 Hz), 5.08 (d, 1 H, J = 17 Hz), 5.79 (d, 1 H, J = 15.0 Hz), 6.12 (dd, 1 H, J = 10.3, 15.0 Hz), 6.28 (ddd, 1 H, J = 17.0, 10.0, 10.3 Hz).

Cross-Coupling Reaction. General Procedure. To a dienyl ether (1 mmol) and phenol (1 mmol) (in eq 8, 2,3-dimethylphenol was used instead of phenol) in dry CH_2Cl_2 (10 mL) was added BF_3·OEt_2 (1.2 mmol) at −40 °C (in eq 11, −25 °C) under nitrogen. After 1 h, water and CH_2Cl_2 were added and after the usual workup, the products were analyzed by NMR and GC.

Equation 12. 4-(2,4-Pentadienyl)phenol (76%) and 2,3-dimethylphenol (100%) were obtained.

Equation 13. 2,4-Dimethoxy-3-methyl-5-(2,4-pentadienyl)-phenol (86%) and phenol (100%) were obtained.

Equation 14. 4-*tert*-Butyl-2-(2,4-pentadienyl)phenol (40%), 4-(2,4-pentadienyl)phenol (18%), 4-*tert*-butylphenyl 2,4-pentadienyl ether (26%), 4-*tert*-butylphenol (22%), and phenol (58%) were obtained.

Equation 15. 3-Bromo-4,6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol (27%), 4-(2,4-pentadienyl)phenol (8%), 5-bromo-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether (32%), 5-bromo-2,4-dimethoxy-3-methylphenol (20%), and phenol (65%) were obtained.

Equation 16. 4-(2,4-Hexadienyl)phenol (43%), 2,3-dimethoxy-4-(2,4-hexadienyl)phenol (41%), phenol (14%), and 2,3-dimethylphenol (29%) were obtained.

Equation 17. 2,4-Dimethoxy-3-methyl-6-(2,4-hexadienyl)-phenol (53%), 4-(2,4-hexadienyl)phenol (34%), 2,4-dimethoxy-3-methylphenol (27%), and phenol (41%) were obtained.

Registry No. **1**, 17270-06-3; **2**, 17270-08-5; **3**, 17270-07-4; **4**, 105103-86-4; **5**, 105103-87-5; **6**, 105103-88-6; **7**, 105103-89-7; **8**, 105103-90-0; **9**, 105103-91-1; **10**, 103993-11-9; **11**, 103993-14-2; **12**, 103993-12-0; **13**, 104016-73-1; **14**, 103993-13-1; **15**, 103993-15-3; **16**, 103993-16-4; **17**, 105103-92-2; **18**, 105103-93-3; **19**, 105103-94-4; **21**, 54700-36-6; **21** (benzyl ether), 105104-09-4; **22**, 105103-95-5; **24**, 105103-96-6; **24** (benzyl ether), 105104-10-7; **25**, 105104-12-9; **26**, 7149-92-0; **27**, 28006-93-1; **28** (methoxymethyl ether), 105104-11-8; **29**, 105103-97-7; **30**, 5673-07-4; **31**, 105103-98-8; **32**, 105103-99-9; **33**, 105104-00-5; **34**, 19676-67-6; **35**, 25576-97-0; **37**, 105104-01-6; **40**, 105104-02-7; **41**, 88010-46-2; **42**, 105104-03-8; **43**, 105104-04-9; **44**, 88088-57-7; **45**, 105104-05-0; **46**, 105104-06-1; **47**, 105104-07-2; **48**, 105104-08-3; Cl_2CHOCH_3, 4885-02-3; $TiCl_4$, 7550-45-0; $ClCH_2OCH_3$, 107-30-2; $FClO_3$, 7616-94-6; PhOH, 108-95-2; 2,3-$Me_2C_6H_3OH$, 526-75-0; 1-chloro-2,4-pentadiene, 40596-30-3; 1,4-pentadien-3-ol, 922-65-6; vinyl bromide, 593-60-2; acrolein, 107-02-8; 3-methoxy-2-methylphenol, 6971-52-4; benzyl bromide, 100-39-0; 2-methoxy-3-methyl-1,4-benzoquinone, 2207-57-0; isopropyl bromide, 75-26-3; 1-bromo-2,4-hexadiene, 63072-78-6; 2,3-dimethylphenyl 2,4-pentadienyl ether, 103992-92-3; 2,5-dimethylphenyl 2,4-pentadienyl ether, 105104-13-0; 2,5-dimethylphenol, 95-87-4; 2-methoxyphenyl 2,4-pentadienyl ether, 103992-93-4; 2-methoxyphenol, 90-05-1; 3-*tert*-butylphenyl 2,4-pentadienyl ether, 103992-94-5; 3-*tert*-butylphenol, 585-34-2; 1-naphthyl 2,4-pentadienyl ether, 103992-97-8; 1-naphthol, 90-15-3; 2-nitrophenyl 2,4-pentadienyl ether, 105104-14-1; 2-nitrophenol, 88-75-5; 2,4-dimethylphenyl 2,4-pentadienyl ether, 103992-95-6; 2,4-dimethylphenol, 105-67-9; 2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether, 103992-96-7; 2,4-dimethoxy-3-methylphenol, 19676-67-6; 2-(benzyloxy)-4-methoxy-3-methylphenyl 2,4-pentadienyl ether, 105104-15-2; 4-(benzyloxy)-2-methoxy-3-methylphenyl 2,4-pentadienyl ether, 105104-16-3; 2-naphthyl 2,4-pentadienyl ether, 103992-98-9; 2-naphthol, 135-19-3; 4-*tert*-butylphenyl 2,4-pentadienyl ether, 103992-99-0; 4-*tert*-butylphenol, 98-54-4; 4-biphenylyl 2,4-pentadienyl ether, 103993-00-6; 4-biphenylol, 92-69-3; 4-nitrophenyl 2,4-pentadienyl ether, 105104-17-4; 4-nitrophenol, 100-02-7; 5-fluoro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether, 105104-18-5; 5-chloro-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether, 105104-19-6; 3-methyl-2,4,5-trimethoxyphenyl 2,4-pentadienyl ether, 105104-20-9; 5-isopropoxy-2,4-dimethoxy-3-methylphenyl 2,4-pentadienyl ether, 105104-21-0; *tert*-butyldimethylsilyl chloride, 18162-48-6; 2,4-hexadienyl phenyl ether, 17270-09-6; 2,4-hexadienyl 2,4-dimethoxy-3-methylphenyl ether, 105104-23-2; 4-*tert*-butylphenyl 2,4-hexadienyl ether, 105104-24-3; 5-bromo-2,4-dimethoxy-3-methylphenyl 2,4-hexadienyl ether, 105104-25-4; 2,3-dimethyl-4-(2,4-pentadienyl)phenol, 103993-01-7; 2,5-dimethyl-4-(2,4-pentadienyl)phenol, 105104-22-1; 2-methoxy-4-(2,4-pentadienyl)-phenol, 103993-02-8; 3-*tert*-butyl-4-(2,4-pentadienyl)phenol, 103993-03-9; 4-(2,4-pentadienyl)-1-naphthol, 103993-06-2; 2,4-dimethyl-5-(2,4-pentadienyl)phenol, 103993-04-0; 2,4-dimethoxy-3-methyl-5-(2,4-pentadienyl)phenol, 103993-05-1; 2-(benzyloxy)-4-methoxy-3-methyl-5-(2,4-pentadienyl)phenol, 105104-26-5; 4-(benzyloxy)-2-methoxy-3-methyl-5-(2,4-pentadienyl)phenol, 105104-27-6; 4-(2,4-pentadienyl)-2-naphthol, 103993-08-4; 1-(2,4-pentadienyl)-2-naphthol, 103993-07-3; 4-*tert*-butyl-2-(2,4-pentadienyl)phenol, 103993-09-5; 4-phenyl-2-(2,4-pentadienyl)-phenol, 103993-10-8; 3-chloro-4,6-dimethoxy-5-methyl-2-(2,4-pentadienyl)phenol, 105104-28-7; 4-acetoxy-3-bromo-6-methoxy-5-methyl-2-(2,4-pentadienyl)phenol, 105104-29-8; 3-bromo-4[(*tert*-butyldimethylsilyl)oxy]-6-methoxy-5-methyl-2-(2,4-pentadienyl)phenol, 105104-30-1; 4-(benzyloxy)-3-bromo-6-methoxy-5-methyl-2-(2,4-pentadienyl)phenol, 105104-31-2; 4-(1-methyl-2,4-pentadienyl)phenol, 17277-04-2; 6-(2,4-hexadienyl)-2,4-dimethoxy-3-methylphenol, 105104-32-3; 5-(1-methyl-2,4-pentadienyl)-2,4-dimethoxy-3-methylphenol, 105104-33-4; 4-*tert*-butyl-2-(2,4-hexadienyl)phenol, 105104-34-5; 4-*tert*-butyl-2,6-bis(2,4-hexadienyl)phenol, 105104-35-6; ethyl 2,4-pentadienoate, 13038-12-5; [1,1-^2H]-2,4-pentadienol, 87020-69-7; 2,3-dimethyl-4-(2,4-hexadienyl)phenol, 105104-36-7.