# *Ortho*-Vinylation Reaction of Phenols with Ethyne

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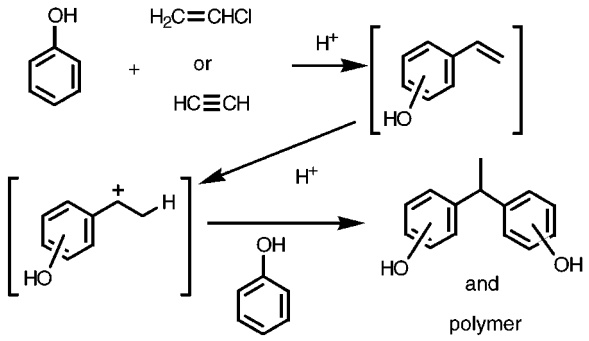
Phenols were vinylated at the *ortho*-position with ethyne in the presence of $SnCl_4$−$Bu_3N$ reagent. The reaction was applicable to phenols possessing either electron-donating or electron-withdrawing groups. 2,6-Divinylphenols were synthesized under modified conditions. A reaction mechanism involving carbostannylation of alkynyltin and phenoxytin was discussed.

In 1908, pure *o*-vinylphenol was synthesized for the first time by decarboxylation of *o*-hydroxycinnamic acid.[1] Since then, a number of methods were developed for the synthesis of vinylphenols. Electrophilic acylation of phenol followed by reduction and dehydration was employed in the commercial production of *p*-vinylphenol by Maruzen Petrochemicals Co.[2] Another method which utilized benzylic oxidation of ethylphenol was reported.[3] Halophenol derivatives could be vinylated by the Heck reaction.[4] Pyrolysis of heterocyclic compounds was reported.[5] All these syntheses, however, employed stepwise transformations starting from phenol.

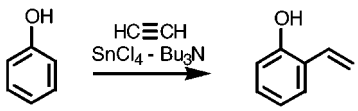
The direct vinylation of phenol with ethyne, vinyl halides, oxirane, vinyl acetate, etc., is potentially the most straightforward method. However, many attempts of the electrophilic substitution failed giving 1,1-diarylethanes as well as mixtures of oligomeric and polymeric substances (Scheme 1).[6] Although some reports claimed formation of vinylphenols,[7] these results could not be reproduced.[8] Formation of 1,1-diarylethane suggested the generation of the vinylphenol in the reaction mixture which appeared not to be stable under the reaction conditions. Rapid protonation takes place giving benzylic cation, which reacts with another molecule of phenol. Protonation of vinylphenol must be much faster than the protonation of the vinylating reagents such as ethyne or vinyl halide. Attempts at phenol vinylation under basic conditions also gave polymeric substances.[9]

**Scheme 1**




Poly(vinylphenol)s are attracting much attention in the field of material sciences.[10] Many applications were examined including photoresist, antibacterial polymer, nonlinear optic material, liquid crystal, cross-linking agent, etc. It should be emphasized that the protected poly(*p*-vinylphenol) is the photoresist material for the production of the next generation DRAM (dynamic random access memory). Despite such importance, a very small amount of work has been done on the chemistry of hydroxystyrenes other than the three isomers of vinylphenol, which may be due to their unavailability. The conventional synthesis of vinylphenols as mentioned above required multistep transformations from phenol, which were not suitable for the preparation of functionalized derivatives. We previously reported a novel method which converts phenols to *o*-vinylphenols using ethyne as the vinylating reagent (Scheme 2).[11] Described here are the details of this reaction.

**Scheme 2**




† Department of Chemistry, Tohoku University.
‡ MITI.

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(9) Karpukhin, P. P.; Slachinskaya, A. I.; Sergeeva, L. I.; Spengler, V. M. *Vestn. Khar'kov. Politekh. Inst.* **1971**, *60*, 50; *Chem Abstr.* **1973**, *79*, 115905x. Reppe, W. *Ann.* **1956**, *601*, 81. Karpukhin reported the synthesis of vinylphenol under basic conditions using pressurized ethyne, while Reppe reported polymerization.
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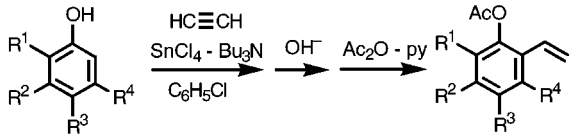
**Table 1. Vinylation of Phenols with Ethyne**




| | | | | | conditions | | | |
|---|---|---|---|---|---|---|---|---|
| entry | $R^1$ | $R^2$ | $R^3$ | $R^4$ | vinylation[a] | workup[b] | yield/% | ratio[c] |
| 1 | H | H | H | H | A | I | 80 | |
| 2 | H | H | Me | H | A | I | 83 | |
| 3 | H | H | *t*-Bu | H | A | I | 83 | |
| 4 | H | H | Ph | H | A | I | 83 | |
| 5 | Me | H | H | H | A | I | 90 | |
| 6 | *t*-Bu | H | H | H | A | I | 91 | |
| 7 | H | Me | H | H | A | I | 75 | 1:1 |
| 8 | H | *t*-Bu | H | H | A | I | 78 | 1:1 |
| 9 | H | CH=CHCH=CH | | H | A | I | 38 | |
| 10 | H | H | MeO | H | A | II | 83 | |
| 11 | H | H | *t*-$BuMe_2SiO$ | H | A | II | 79 | |
| 12 | H | H | $Et_3SiO$ | H | A | II | 66 | |
| 13 | H | H | $CH_3COO$ | H | A | II | 83 | |
| 14 | H | H | *t*-BuCOO | H | A | II | 76 | |
| 15 | H | H | $PhCH_2OCOO$ | H | A | II | 87 | |
| 16 | H | H | *p*-$TolSO_3$ | H | A | II | 86 | |
| 17 | H | H | $CF_3SO_3$ | H | A | II | 76 | |
| 18 | MeO | H | H | H | A | II | 81 | |
| 19 | *t*-$BuMe_2SiO$ | H | H | H | A | II | 62 | |
| 20 | H | MeO | H | H | C | II | 48 | 3:1 |
| 21 | H | *t*-$BuPh_2SiO$ | H | H | A | II | 92 | 3:1 |
| 22 | H | $CH_3COO$ | H | H | A | II | 71 | 3:1 |
| 23 | H | *t*-BuCOO | H | H | A | II | 86 | 3:1 |
| 24 | H | $CF_3SO_3$ | H | H | A | II | 76 | 3:1 |
| 25 | H | *t*-BuCOO | H | *t*-BuCOO | A | II | 90 | |
| 26 | H | *t*-$BuMe_2SiO$ | H | *t*-$BuMe_2SiO$ | A | II | 69 | |
| 27 | H | $Et_3SiO$ | H | $Et_3SiO$ | A | III | 58 | |
| 28 | H | H | $NO_2$ | H | B | I | 41[d] | |
| 29 | H | H | F | H | A | I | 74 | |
| 30 | H | H | $CF_3$ | H | A | III | 73 | |
| 31 | H | H | CN | H | A | III | 67 | |
| 32 | CN | H | H | H | A | III | 79 | |
| 33 | F | H | H | H | B | I | 82 | |
| 34 | $CF_3$ | H | H | H | A | III | 52 | |
| 35 | H | $NO_2$ | H | H | B | I | 41[d] | 2:1 |
| 36 | H | F | H | H | A | I | 68 | 4:1 |
| 37 | H | $CF_3$ | H | H | A | III | 78 | 1:1 |

[a] Conditions of vinylation: A: 60 °C, 1 h. B: 90 °C, 30 min. C: 60 °C, 30 min. [b] Basic workup conditions. I: 2 M NaOH aq, reflux, 1 h. II: $K_2CO_3$, methanol, reflux 30 min. III: $K_2CO_3$, methanol, room temperature, 1 h. [c] Ratio of 6-vinylated and 2-vinylated products formed in the reaction of 3-substituted phenol. [d] Isolated without acetylation.

The following procedures were employed for the vinylation of phenol with gaseous ethyne giving *o*-vinylphenol. $SnCl_4$ and $Bu_3N$ were added to a chlorobenzene solution of ethyne to generate stannylacetylene, which was the active vinylating species of the present reaction. Then, another portion of $SnCl_4$ and $Bu_3N$ was added followed by phenol. The second tin reagent was used to generate phenoxytin, the other species responsible for the C−C bond formation. Then, the mixture was heated at 60 °C for 1 h to couple the organotin compounds. The new organotin thus generated was treated with aqueous NaOH or $K_2CO_3$ in methanol at reflux for protodestannylation. If the alkaline treatment was not sufficiently done, the yield decreased. Since *o*-vinylphenol was relatively unstable especially in the presence of small amounts of acid, the product was isolated after acetylation (Table 1, entry 1). Introduction of the electron-withdrawing protecting group improved the stability. Acetylated *o*-vinylphenol was distilled in the presence of radical inhibitor. The vinylation reaction could be conducted in 10-g scale using these protocols. There are several notable aspects in the reaction procedures. The ethyne was introduced to chlorobenzene at −50 °C before the addition of the tin reagent and was then stopped. The gas need not be bubbled throughout the reaction due to the high efficiency of the C−C bond formation. The vinylation proceeded rapidly at 60 °C in solvents such as chlorobenzene or 1,2-dichloroethane.

Vinylation of the three isomers of cresol and *tert*-butylphenol represents the reaction of alkyl-substituted phenols. *Ortho*- and *para*-substituted phenols gave expected mono-vinylated products in high yields (entries 2−6). As for the *meta*-substituted phenols, a mixture of regioisomers was obtained in comparable amounts, which was more easily separated by chromatography after deacetylation (entries 7 and 8). Notably, the bulky *ortho*-substituent did not interfere with the vinylation as indicated by the reaction of *o*-*tert*-butylphenol (entry 6). Furthermore, a considerable amount of vinylation took place at the sterically congested 2-position of *m*-*tert*-

(11) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1995**, *117*, 1151.

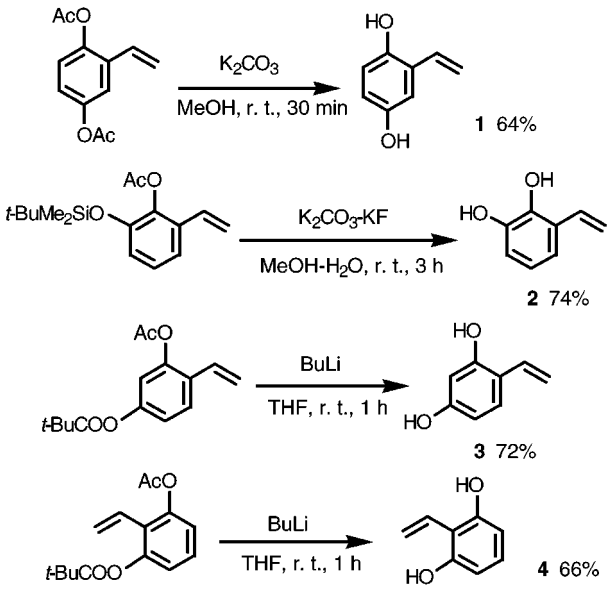
butylphenol (entry 8). A polycyclic aromatic compound such as 2-naphthol was also vinylated, although with lower yield because of decomposition (entry 9).

Styrenes possessing electron-donating groups, especially at the *ortho*- and *para*-position, were known to be sensitive to acid and oxygen and to polymerize readily.[12] The vinylation reaction of benzenepolyol derivatives therefore could reveal the scope and the limitation of the present method. Various monoprotected 1,4-benzenediols were subjected to vinylation (entries 10−17). Methoxy, *tert*-butyldimethylsilyloxy, benzyloxycarbonyloxy, pivaloyloxy, and sufonyloxy groups were unaffected, and 2-ethenyl-1,4-benzenediols with two hydroxy groups differentiated were obtained in high yields. The reactions were worked up with $K_2CO_3$ in methanol at reflux to avoid deprotection. Although acetate survived the vinylation reaction conditions, deacetylation took place during the alkaline workup (entry 13). The diacetylated product was obtained by the reacetylation of 2-ethenyl-1,4-benzenediol. Thus, the present vinylation tolerated various functionalities, and $SnCl_4$−$Bu_3N$ conditions turned out to be fairly mild. However, trityl and 2*H*-tetrahydropyran-2-yl derivatives decomposed during the vinylation. Vinylation of 1,2-benzenediol derivatives also took place (entries 18 and 19). Attempted vinylation of 1,4-benzenediol and 1,3-benzenediol failed, giving polymeric substances.

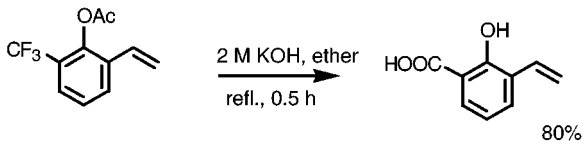
Vinylphenols synthesized from monoprotected 1,3-benzenediol were expected to be less stable compared to the vinylated 1,4- and 1,2-benzenediol derivatives, since the former compounds possessed electron-donating groups at both *ortho*- and *para*-positions of the vinyl group. We were therefore pleased to find that *m*-methoxyphenol could be vinylated by the present methodology (entry 20). The reaction, however, competed with the decomposition reaction and must be stopped before the consumption of the starting material. The yield was improved by changing the protecting group to an acyl, silyl, or sulfonyl group (entries 21−24). Irrespective of the protecting groups, approximately 3:1 mixtures of the regioisomers were obtained. The vinylation took place at the less-hindered site predominantly. Even bis-silylated and bis-pivalated 1,3,5-benzenetriols could be vinylated successfully (entries 25−27).

The protecting groups were next removed from these polyhydroxystyrene derivatives (Scheme 3). 2-Ethenyl-1,4-benzenediol (**1**) was synthesized by deprotection of the diacetate with $K_2CO_3$-methanol. *tert*-Butyldimethylsilyl and acetate groups were removed simultaneously with $K_2CO_3$−KF as shown in the synthesis of 3-ethenyl-1,2-benzenediol (**2**). Two isomers formed by the reaction of *m*-pivaloxyphenols were separated by chromatography and were subjected to the deprotection with butyllithium in THF at room temperature. 4-Ethenyl-1,3-benzenediol (**3**) and 2-ethenyl-1,3-benzenediol (**4**) were more sensitive than **1** and **2** to acid and oxygen. These reactions therefore were conducted using the freeze-evacuated solvents and were quenched with buffer. Since contact of **3** and **4** with silica gel caused polymerization, they were purified by reverse phase chromatography. While dihydroxystyrenes **1**−**3** were obtained in crystalline form,

**Scheme 3**




**Scheme 4**




the aqueous solution of **4** could not be concentrated to dryness without polymerization even using freeze-drying techniques. Synthesis of **1** was previously reported which used decarboxylation of the corresponding hydroxycinnamic acid.[13] It employed a lengthy transformation from chromone and suffered from low yields at the final stages. Compounds **2**,[14] **3**,[15] and **4** have not been prepared chemically, making this new methodology useful.

The present vinylation was next applied to phenols with electron-withdrawing groups (Table 1, entries 28−37). Phenols possessing a fluoro, trifluoromethyl, and cyano group were converted to the corresponding vinylphenols in satisfactory yields. A higher reaction temperature was required for nitrophenols, and vinylated products could be isolated without acetylation (entries 28 and 35). Vinylated products obtained from *o*- and *p*-(trifluoromethyl)phenol decomposed when treated with aqueous NaOH under reflux, giving carboxylic acid derivatives, while the *meta*-derivative was not affected. It may be due to the $\beta$-elimination reaction that generates quinoid compounds. To avoid such decomposition, the reactions of trifluoromethylphenols and cyanophenols were worked up with $K_2CO_3$ in methanol at room temperature (entries 30−32, 34, and 37). The vinylation and hydrolysis of *o*-(trifluoromethyl)phenol gave vinylsalicylic acid (Scheme 4). It is interesting from a synthetic point of view, since the compound could not be obtained by the

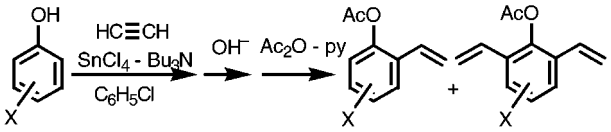
(12) Overberger, C. G.; Arond, L. H.; Tanner, D.; Taylor, J. J.; Alfrey, T., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 4848. Okamoto, Y.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 485. Mayen, M.; Marechal, E. *Bull. Soc. Chim. Fr.* **1972**, 4662.

(13) Updegraff, I. H.; Cassidy, H. G. *J. Am. Chem. Soc.* **1949**, *71*, 407. Iwabuchi, S.; Ueda, M.; Kobayashi, M.; Kojima, K. *Polymer J.* **1974**, *6*, 185.

(14) 3-Ethenyl-1,2-benzenediol was obtained as a microbial metabolite of styrene. Warhurst, A. M.; Clarke, K. F.; Hill, R. A.; Holt, R. A.; Fewson, C. A. *Appl. Environ. Microbiol.* **1994**, *60*, 1137.

(15) Synthesis of 4-ethenyl-1,3-benzenediol was noted without structure determination in ref 7. It may be unlikely if one looks at the results of many attempted Friedel−Crafts vinylation of phenol.

**Table 2. 2,6-Divinylation of Phenols with Ethyne**




| entry | X | conditions[a] | yield/% | ratio[b] divinyl:monovinyl |
|---|---|---|---|---|
| 1 | H | I | 66 | 5:1 |
| 2 | 4-Me | I | 69 | 5:1 |
| 3 | 4-(*t*-Bu) | I | 71 | 5:1 |
| 4 | 4-MeO | I | 77 | ≥10:1 |
| 5 | 4-(*t*-BuMe$_2$SiO) | II | 73 | 6:1 |
| 6 | 4-(*t*-BuPh$_2$SiO) | II | 72 | ≥10:1 |
| 7 | 4-Ph | I | 80 | 1:1 |
| 8 | 4-(*t*-BuCOO) | II | 87 | 1:3 |
| 9 | 3-Me | I | 75 | 4:1[c] |
| 10 | 3-MeO | I | 25 | ≥10:1 |
| 11 | 3-(*t*-BuMe$_2$SiO) | III | 48 | ≥10:1 |
| 12 | 3-(*t*-BuPh$_2$SiO) | III | 49 | ≥10:1 |
| 13 | 3,5-bis(*t*-BuMe$_2$SiO) | III | 41 | 8:1 |

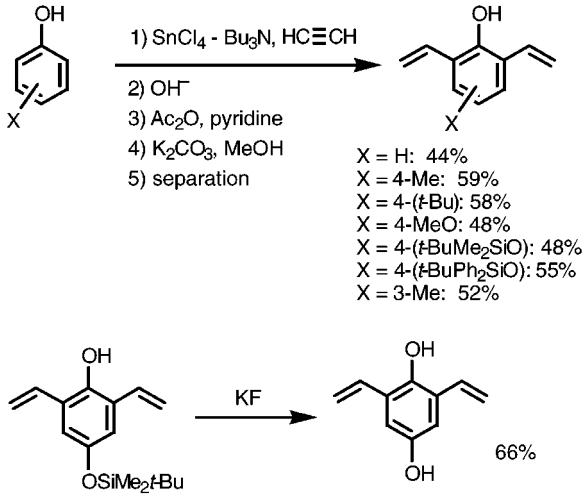
[a] Conditions of workup. I: 2 M aq NaOH, ethanol, 100 °C, 2 h. II: $K_2CO_3$, methanol, room temperature, 1 h. III: $K_2CO_3$, THF water, room temperature, 1 h. [b] Ratio of mono-vinylated phenol and divinylated phenol. [c] Mono-vinylated product is a 1:1 mixture of 2-vinyl-5-methylphenyl acetate and 2-vinyl-3-methylphenyl acetate.

vinylation of the salicylic acid ester. Hydrogen bonding to the phenolic hydroxy group appeared to reduce the reactivity.

It was found that the modifications of the reaction conditions gave 2,6-divinylphenols (Table 2).[16] Divinylbenzenes are an important class of chemicals in polymer synthesis and organic synthesis.[17,18] Their chemistry, however, has been limited to the three isomers of divinylbenzene,[19] and very few functionalized derivatives have been known. Divinylbenzenes were synthesized by stepwise transformations from benzene via diethylbenzene, dihalobenzene, diformylbenzene, etc.,[20] which were not suitable for the preparation of functionalized derivatives. This synthesis therefore provided an easy access to functionalized *m*-divinylbenzenes.

A reaction temperature of 100 °C was necessary to allow the bis-vinylation to occur. A lower temperature gave mainly mono-vinylation, and decomposition took place at temperatures exceeding 100 °C. As mentioned previously, sequential addition is important, and the amount of the tin reagent (5 + 2 mol equiv) was also critical to obtain the divinylphenol predominantly. When it was changed, for example, to 2 + 2, 2 + 5, 5 + 5, or 5 + 0 mol equiv, 1:1 mixtures of mono- and divinylated products were formed. Addition of an excess of tin reagent and ethyne to these reaction mixtures did not improve the ratio. Use of a large excess of reagent (12 + 0 mol equiv) gave mono-vinylated product predominantly in a ratio of 1:6. Treatment of isolated 4-*tert*-butyl-2-vinylphenol with ethyne under these conditions resulted in decomposition. The first and the second vinylation apparently are not independent chemical processes, and the reaction mechanism of the divinylation is rather complex.

**Scheme 5**




Several *para*- and *meta*-substituted phenols and phenol itself were treated with ethyne under these conditions. Alkoxy and alkyl derivatives gave divinylphenol predominantly to exclusively. Although the reaction of *m*-methoxyphenol competed with decomposition, the divinylated product could still be obtained (entry 10). *p*-Pivaloxyphenol and *p*-phenylphenol gave comparable amounts of monovinyl and divinyl derivatives (entries 7 and 8). The divinylation was facilitated by the electron-donating substituents on the aromatic ring. Even 3,5-bis(silyloxy)phenol was divinylated, giving a protected 2,6-diethenyl-1,3,5-benzenetriol (entries 13). To avoid deprotection, the reactions of silyloxyphenols and acyloxyphenols were quenched with either $K_2CO_3$ in methanol or $K_2CO_3$ in THF−water at room temperature. The latter conditions were employed in the reaction of *m*-(silyloxy)phenols, since alcohol addition took place to the reactive olefin when the workup was conducted in the presence of methanol.

Mixtures of divinylphenyl acetate and monovinylphenyl acetate were treated with $K_2CO_3$ in methanol to give 2,6-divinylphenol and 2-vinylphenol, which were readily separable by silica gel chromatography. Thus, divinylphenols were obtained from phenol, alkylphenols, and alkoxyphenols in overall yields ranging from 40 to 60% (Scheme 5). Treatment of 4-(*tert*-butyldimethylsilyloxy)phenol with KF in methanol gave 2,6-divinyl-1,4-benzenediol, which can be an interesting building block for redox polymers. Despite the simple molecular structure, most divinylphenols synthesized here, including the parent 2,6-divinylphenol itself, were new compounds.[21]

(16) Preliminary report. Yamaguchi, M.; Arisawa, M.; Hirama, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1663.

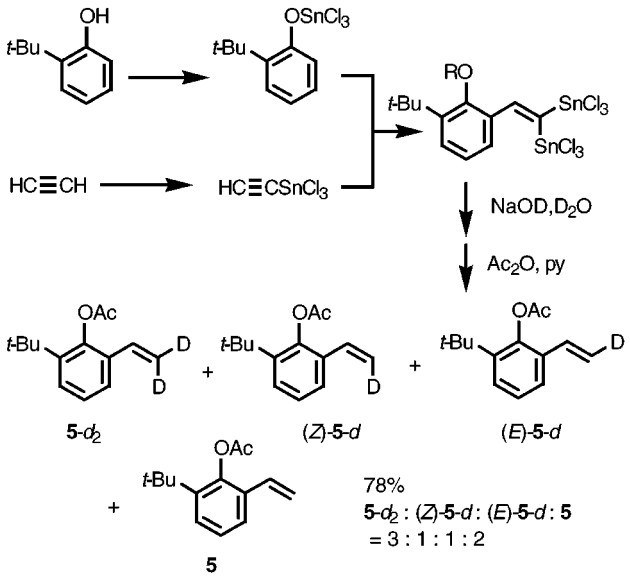
(17) For examples, see: Suzuki, M.; Lim, J.-C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574. Kumar, A.; Eichinger, B. E. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 311. Chujo, Y.; Tomita, I.; Kozawa, Y.; Saegusa, T. *Macromolecules* **1993**, *26*, 2643. Thorn-Csányi, E.; Pflug, K. P. *J. Mol. Cat.* **1994**, *90*, 69.

(18) For examples, see: Liu, L.; J. Katz, T. *Tetrahedron Lett.* **1990**, *31*, 3983. Hamana, H.; Horiguchi, K.; Hagiwara, T.; Narita, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1884. Padias, A. B.; Tien, T.-P.; Hall, H. K., Jr. *J. Org. Chem.* **1991**, *56*, 5540. Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. *J. Am. Chem. Soc.* **1991**, *113*, 3485. Suzuki, T.; Fukushima, T.; Yamashita, Y.; Miyashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2793.

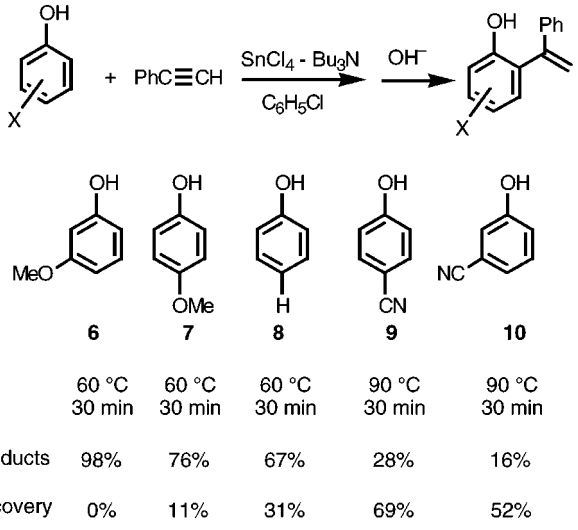
(19) Separation of isomeric divinylbenzenes. Storey, B. T. *J. Polym. Sci., Part A* **1965**, *3*, 265. Wiley, R. H.; Jin, J. I.; Kamath, Y. *J. Polym. Sci., Part A-1* **1968**, *6*, 1065.

(20) For examples, see: Johnston, H. W.; Williams, J. L. R. *J. Am. Chem. Soc.* **1947**, *69*, 2065. Mitchell, R. H.; Ghose, B. N.; Williams, M. E. *Can. J. Chem.* **1977**, *55*, 210. Plevyak, J. E.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2454. McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. Nuyken, O.; Siebzehnrübl, F. *Makromol. Chem.* **1988**, *189*, 541.

**Scheme 6**




**Scheme 7**




| | 60 °C 30 min | 60 °C 30 min | 60 °C 30 min | 90 °C 30 min | 90 °C 30 min |
|---|---|---|---|---|---|
| products | 98% | 76% | 67% | 28% | 16% |
| recovery | 0% | 11% | 31% | 69% | 52% |

The mechanism of the phenol vinylation would be analogous to the alkenylation reaction, which we previously reported.[11,22] Ethyne and phenol are converted to trichlorostannylethyne and phenoxytin, respectively, and the carbostannylation reaction between the organotin compounds gives the 2-[$\beta$,$\beta$-bis(trichlorostannyl)vinyl]-phenol derivative (Scheme 6). The reactive olefins of the vinylphenols may be protected from oligomerization and polymerization by bis-stannylation. Involvement of such an intermediate was validated by deuteration experiments. When the vinylation reaction of *o*-*tert*-butylphenol was quenched with NaOD in $D_2O$, both olefinic protons were deuterated. Control experiments showed no deuterium exchange at vinyl protons of the ethenylphenol in NaOD−$D_2O$. The alkaline workup conducted in the present reaction protonated the carbon−tin bond of the bis-stannyl intermediates. Relatively facile protonation of the vinylstannane may be partly due to the

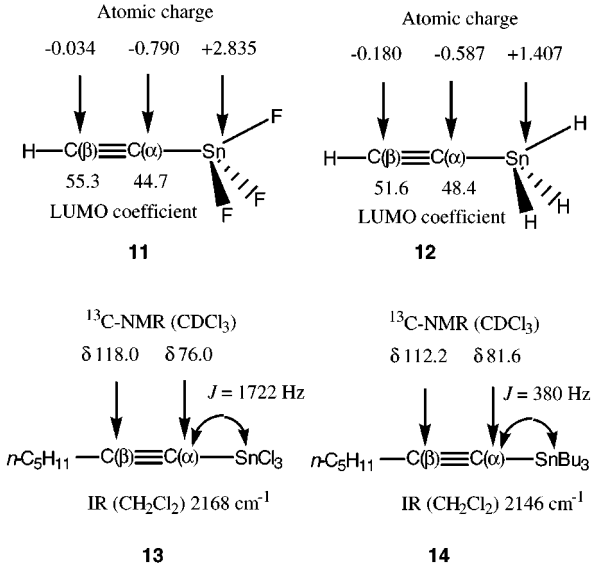



**Figure 1.**

presence of the ethenylphenol keto form, which can possess allyltin structure.

To gain additional information on the carbostannylation reaction, the reactivity of substituted phenols was compared. The rate difference was pronounced in alkenylation compared to vinylation probably because of the steric reasons. *m*-Methoxyphenol (**6**), *p*-methoxyphenol (**7**), phenol (**8**), *p*-cyanophenol (**9**), and *m*-cyanophenol (**10**) were reacted with phenylacetylene (Scheme 7). Alkenylation of **6** and **7** for 30 min at 60 °C gave mixtures of mono- and divinylated products in 98% and 76% yields, respectively. While no starting material was recovered in the former reaction, 11% of **7** was recovered in the latter. The vinylation rate of **8** was slightly lower than that of **7**. The vinylation of **9** and **10** did not proceed at 60 °C, and a higher temperature of 90 °C was required. Under the same reaction conditions, the conversion was greater for **9** than for **10**. The reactivity order then was summarized as **6** > **7** ≥ **8** > **9** > **10** and qualitatively correlated with the electron density at the *ortho*-carbon atom. The phenol, or more precisely the phenoxytin, appeared to behave as a nucleophile.

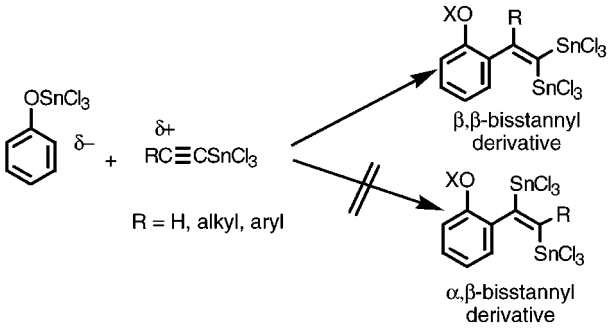
As for the alkynyltin, ab initio calculations[23] of HC≡$CSnF_3$ (**11**) showed that the $\beta$-carbon atom was less negatively charged than the α-carbon atom (Figure 1). In addition, the coefficients of $\pi^*$ orbitals of C—C triple bond were larger at the $\beta$-carbon atom. These tendencies were more prominent with **11** than with HC≡$CSnH_3$ (**12**), which were consistent with $^{13}$C NMR chemical shifts of the stannylated 1-alkyne. The acetylenic $\beta$-carbon of alkynyltrichlorotin **13** derived from 1-heptyne appeared at considerably lower field than the corresponding tributyltin derivative **14**. Experimentally, trialkylalkynyltin and trialkylphenoxytin did not undergo carbostannylation. Thus, the electrophilic alkynyltin turned out to

(21) A patent of 4-methyl-2,6-divinylphenol appeared. Kitano, H. Japan Pat. 74 14,319, 1974; *Chem. Abstr.* **1975**, *82*, 114031j.

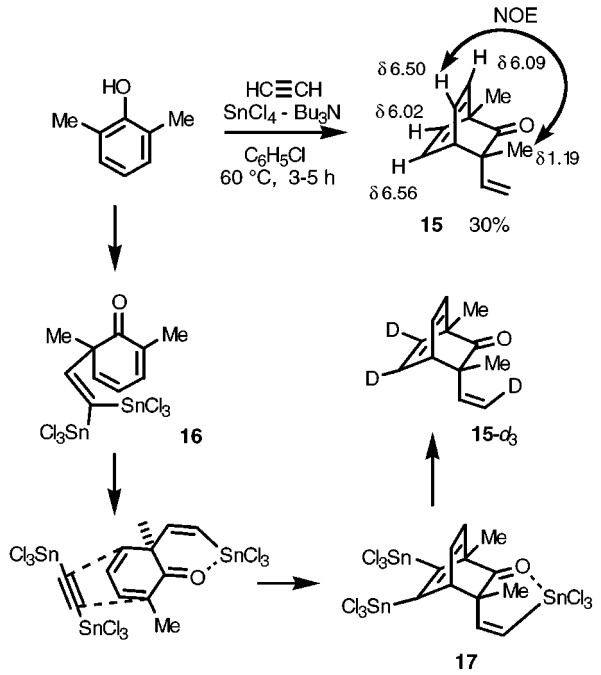
(22) Also see, Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1993**, *115*, 3362. Hayashi, A.; Yamaguchi, M.; Hirama, M.; Kabuto, C.; Ueno, M. *Chem. Lett.* **1994**, 1881.

(23) All calculations were carried out at RHF/LANL1MB level by using *Gaussian* 92. The NBO analyses were made with respect to the fully optimized geometries. We evaluated atomic charges and orbital coefficients based on the NBO analyses. *Gaussian* 92, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

**Scheme 8**




**Scheme 9**




be more reactive toward carbostannylation. This electrophilic property is due to the inductive effect of $SnCl_3$ group rather than the mesomeric effect since the IR absorption of **13** appeared at a higher wavenumber than **14**.

The carbostannylation seems to be controlled by the electronic nature of each tin reagent and can be envisaged as the reaction of nucleophilic phenoxytin and electrophilic stannylacetylenes. The regioselective *β,β*-bis-stannyl olefin formation therefore could be explained as the nucleophilic attack of phenoxytin at the electrophilic *β*-carbon atom of the stannylacetylene (Scheme 8). We, however, are not yet able to present the precise transition structure of the carbostannylation reaction.

All of the above reactions took place at the *ortho*-position of phenolic hydroxy group. To explore the possibility of *para*-vinylation, 2,6-dimethylphenol was vinylated using our standard conditions, which gave the relatively unstable bicyclo[2.2.2]octane derivative **15** (Scheme 9). The structure, consisting of one molecule of phenol and two molecules of ethyne, was determined by 2D-NMR including NOE studies, and all of the protons were assigned unambiguously. When the reaction was worked up with $NaOD-D_2O$, **15**-$d_3$ was obtained, indicating the presence of tris-stannylated intermediate **17**. Thus, the formation of **15** should have taken place via **16** by the *ortho*-vinylation of dimethylphenol with concomitant dearomatization. The vinylating reagent appears to be strongly directed to the *ortho*-position. Two possibilities were considered for the introduction of the other ethyne unit: The Diels−Alder reaction of stannylated ethyne with **16**, or the intramolecular conjugate addition of vinyltin. Since both protons at the bridged position of **17** were stannylated (deuterated), the former mechanism appeared likely. The conjugate addition of **16** should give the mono-stannylated intermediate.

To summarize, various functionalized phenols were converted to *o*-vinylphenol by treating with ethyne in the presence of the $SnCl_4-Bu_3N$ reagent. This reaction and the new products obtained may find various applications in organic chemistry and polymer chemistry.

## Experimental Section

**4-Methoxy-2-ethenyl-1-phenyl Acetate** (synthesis in 20 mmol scale). Under an argon atmosphere, ethyne was bubbled into a a stirred chlorobenzene (100 mL) solution of $SnCl_4$ (9.7 mL, 80 mmol) and $Bu_3N$ (20 mL, 80 mmol) at −50 °C for 30 min. Then, *p*-methoxyphenol (**7**, 2.49 g, 20 mmol) in chlorobenzene (2 mL) was added, and the mixture was heated at 60 °C for 1 h. $K_2CO_3$ (13.8 g) and methanol (100 mL) were added, and refluxing was continued for another 30 min. After being cooled to room temperature, the contents were poured into a mixture of ether and saturated aq $KHSO_4$. The precipitate formed was filtered through Celite, and the organic materials were extracted twice with ether. The combined organic layers were washed with brine and dried over $Na_2SO_4$. Ether was removed under reduced pressure, and acetic anhydride (20 mL) and pyridine (20 mL) were added to the resulting chlorobenzene solution. After the mixture was stirred for 8 h at room temperature, saturated aq $KHSO_4$ was added. The organic materials were extracted twice with ethyl acetate, washed with saturated aq $NaHCO_3$ and brine, dried over $Na_2SO_4$, and concentrated in vacuo. 4-Methoxy-2-vinylphenyl acetate (3.14 g, 82%) was obtained by flash chromatography (hexane:ethyl acetate = 50:1 to 20:1) over silica gel. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 2.31 (3H, s), 3.81 (3H, s), 5.33 (1H, brd, $J$ = 11.0 Hz), 5.74 (1H, brd, $J$ = 17.6 Hz), 6.70 (1H, dd, $J$ = 17.6, 11.0 Hz), 6.82 (1H, dd, $J$ = 8.8, 2.9 Hz), 6.95 (1H, d, $J$ = 8.9 Hz), 7.06 (1H, d, $J$ = 2.9 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 20.8, 55.5, 110.9, 114.3, 116.5, 123.2, 130.3, 130.8, 141.7, 157.4, 169.7. IR (neat) 1763, 922, 899, 826 cm$^{-1}$. MS (EI, 70 eV) *m*/*z* (%) 192 ($M^+$, 37), 150 ($M^+ - CH_3$, 100), 135 ($M^+ - CH_2CO - CH_3$, 26). HRMS (EI, 70 eV) calcd for $C_{11}H_{12}O_3$: 192.0787. Found: 192.0789 ($M^+$).

**2-Ethenyl-1-phenyl Acetate** (synthesis in 120 mmol scale). An oven-dried, 1-L, three-necked, round-bottomed flask fitted with a gas inlet was placed under an argon atmosphere and charged with 1,2-dichloroethane (600 mL). After it was cooled to −50 °C in a methanol bath, $SnCl_4$ (30 mL, 250 mmol) and $Bu_3N$ (60 mL, 250 mmol) were added, and acetylene gas was introduced at −40 °C (methanol bath) for 2.5−3 h. After bubbling was stopped, the methanol bath was removed, and the mixture was stirred at room temperature for 30 min. Phenol (11.8 g, 125 mmol) in 1,2-dichloroethane (20 mL), $SnCl_4$ (30 mL), and $Bu_3N$ (60 mL) were added successively, and the mixture was heated at 60 °C for 6 h. After being cooled to room temperature, the mixture was poured into a 3-L, round-bottomed flask, and stirred with aqueous 4 N sodium hydroxide (1 L) and ethanol (500 mL) at room temperature overnight. Then the reaction mixture was poured into a 5-L separating funnel and extracted twice with diethyl ether. The organic phase was washed twice with aqueous 2 N hydrochloric acid (1 L). The aqueous phase was acidified by addition of aqueous 2 N hydrochloric acid (ca. 3 L) and extracted twice with diethyl ether. The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated to about 500 mL under reduced pressure. Then, pyridine (60 mL) was added to precipitate tin salts, which were filtered through a Celite pad (No. 545) and washed sufficiently with diethyl ether. The

combined organic layers were again concentrated to about 500 mL under reduced pressure. Acetic anhydride (120 mL) and a catalytic amount of 4-(dimethylamino)pyridine were added, and the mixture was stirred at room temperature overnight. Then, the mixture was poured into a 1-L separating funnel, washed with a saturated solution of $KHSO_4$ and $NaHCO_3$, dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure. Flash short-column chromatography with hexane:ethyl acetate = 20:1 gave crude acetate (16 g, 80%). Then, *tert*-butylhydroquinone (10 mg) was added, and distillation under reduced pressure gave 2-ethenylphenyl acetate (12−14 g, 60−70%) as a pale-yellow liquid, bp 55−65 °C/0.8 mmHg (lit.[24] 85 °C/1 mmHg). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 2.33 (3H, s), 5.33 (1H, dd, $J$ = 1.2, 11.1 Hz), 5.75 (1H, dd, $J$ = 1.1, 17.6 Hz), 6.75 (1H, dd, $J$ = 11.1, 17.6 Hz), 7.04 (1H, dd, $J$ = 1.8, 7.5 Hz), 7.21 (1H, dt, $J$ = 1.8, 7.5 Hz), 7.29 (1H, dt, $J$ = 2.0, 7.4 Hz), 7.57 (1H, dd, $J$ = 2.0, 7.4 Hz). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 20.8, 116.3, 122.5, 126.1, 126.4, 128.6, 130.1, 130.3, 147.9, 169.2. IR (neat) 1765, 1632, 915, 714 cm$^{-1}$. HRMS $C_{10}H_{10}O_2$: calcd 162.0681. Found: 162.0669.

**2-Ethenyl-6-*tert*-butylphenyl Acetate (5).** $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.35 (9H, s), 2.35 (3H, s), 5.30 (1H, dd, $J$ = 1.6, 11.2 Hz), 5.70 (1H, dd, $J$ = 1.6, 17.6 Hz), 6.60 (1H, dd, $J$ = 11.2, 17.6 Hz), 7.16 (1H, t, $J$ = 8.0 Hz), 7.33 (1H, dd, $J$ = 1.6, 8.0 Hz), 7.42 (1H, dd, $J$ = 1.6, 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 21.5, 30.6, 34.7, 116.5, 124.7, 125.8, 126.7, 131.3, 131.8, 141.5, 146.7, 169.0. IR (neat) 1767 cm$^{-1}$. MS $m/z$ 218 ($M^+$, 8), 176 ($M^+ - CH_2CO$, 63), 161 ($M^+ - C_4H_9$, 100). HRMS calcd for $C_{14}H_{18}O_2$: 218.1306. Found: 218.1298. A deuteration experiment was conducted using 2-*tert*-butylphenol except that the reaction was worked up with 2 M NaOD in $D_2O$. Deuterated **5** was obtained in 78% yield. By $^1$H NMR the product contained 30% of **5**, 15% of (*Z*)-**5**-*d*, and 15% of (*E*)-**5**-*d*. $^1$H NMR ($CDCl_3$) $\delta$ 5.29 (1H, d, $J$ = 11.2 Hz). (*E*)-**5**-*d*. $^1$H NMR ($CDCl_3$) $\delta$ 5.69 (1H, d, $J$ = 17.6 Hz). No deuteration was observed at the aromatic proton. Treatment of **5** with 2 M NaOD in $D_2O$ at 90 °C for 1 h resulted in no deuteration at the aromatic and vinyl protons.

**3-Ethenyl-1,2-benzenediol (2).** Under a nitrogen atmosphere, a solution of 2-(*tert*-butyldimethylsilyloxy)-6-vinylphenyl acetate (154 mg, 0.5 mmol) in methanol (5 mL) and water (1 mL) was freeze-evacuated. After addition of $K_2CO_3$ (69 mg, 0.5 mmol) and KF (29 mg, 0.5 mmol), the mixture was freeze-evacuated again and stirred for 6 h at room temperature. Then, 0.1 M phosphate buffer (pH 7.2, 10 mL) and brine were added, and the organic materials were extracted twice with ethyl acetate. The combined extracts were dried over $Na_2SO_4$, concentrated, and flash chromatographed over silica gel, giving **2** (50 mg, 74%). Mp 26.6−27.8 °C (benzene−hexane). $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 5.15 (1H, dd, $J$ = 1.7, 11.3 Hz), 5.69 (1H, dd, $J$ = 1.7, 17.8 Hz), 6.61 (1H, t, $J$ = 7.8 Hz), 6.67 (1H, dd, $J$ = 1.7, 7.5 Hz), 6.91 (1H, dd, $J$ = 1.7, 7.5 Hz), 7.00 (1H, dd, $J$ = 11.2, 17.8 Hz). $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 113.6, 115.1, 118.1, 120.3, 126.3, 133.1, 144.3, 146.4. IR (KBr) 3350, 1618 790, 736 cm$^{-1}$. MS (EI, 70 eV) $m/z$ 135 ($M^+$, 100), 110 ($M^+ - C_2H_2$, 78). HRMS (EI, 70 eV) calcd for $C_8H_8O_2$: 136.0525. Found: 136.0529. $^1$H NMR spectral data in acetone-$d_6$ agreed with the reported values.[14]

**2-Ethenyl-1,4-benzenediol (1).** The same procedures were employed except that KF was not added. Mp 107.8−108.4 °C (AcOEt−MeOH) (lit.[13] mp 111 °C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.47 (1H, brs), 4.66 (1H, brs), 5.35 (1H, dd, $J$ = 11.0, 1.2 Hz), 5.71 (1H, dd, $J$ = 17.8, 1.2 Hz), 6.64, (1H, dd, $J$ = 8.5, 3.0 Hz), 6.69 (1H, d, $J$ = 8.3 Hz), 6.88 (1H, d, $J$ = 3.0 Hz), 6.89 (1H, dd, $J$ = 18.1, 11.7 Hz). $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 5.13 (1H, dd, $J$ = 1.6, 11.0 Hz), 5.64 (1H, dd, $J$ = 1.6, 17.9 Hz), 6.54 (1H, dd, $J$ = 3.0, 8.6 Hz), 6.61 (1H, d, $J$ = 8.4 Hz), 6.86 (1H, d, $J$ = 3.0 Hz), 6.95 (1H, dd, $J$ = 11.0, 17.9 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 113.3, 115.7, 116.0, 116.9, 125.7, 131.1, 146.9, 149.4. $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 113.0, 113.3, 116.7, 117.5, 126.6, 133.1, 149.0, 151.2. IR (KBr) 3250, 1626, 1612, 916 cm$^{-1}$.

(24) Dhekne, V. V.; Rao, A. S. *Synthesis* **1980**, 58.

**4-Ethenyl-1,3-benzenediol (3).** Under a nitrogen atmosphere, butyllithium in hexane (0.5 mL, 0.8 mmol) was added to a freeze-evacuated THF (2 mL) solution of 3-acetoxy-4-vinylphenyl pivalate (52 mg, 0.2 mmol) at room temperature. The mixture was freeze-evacuated and stirred at room temperature for 1 h. Then, the reaction was quenched by adding 0.1 M phosphate buffer (pH 7.2, 10 mL). After addition of brine, the organic materials were extracted twice with ethyl acetate. The aqueous layer was acidified to pH 5 by addition of sat. aq $KHSO_4$ and extracted with ethyl acetate. The combined extracts were washed with brine, dried over $Na_2SO_4$, and concentrated to a small volume (ca. 0.2 mL) in vacuo. The solvents must not be removed to dryness, otherwise polymerization will take place. A trace amount of ethyl acetate was removed by repeated addition and evaporation of methanol. After performing reverse phase chromatography (Lobar column, ODS, $H_2O$:MeOH = 1:1), fractions containing **3** were collected, and methanol was removed in vacuo. The organic materials were extracted with ethyl acetate, washed with brine, and dried over $Na_2SO_4$. The solution was concentrated to a small volume, and NMR spectra were obtained by solvent exchange to $CD_3OD$. The yield (72%) was estimated by NMR with an internal standard dioxane. MS spectra were recorded as a solution. $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 4.97 (1H, dd, $J$ = 1.7, 11.2 Hz), 5.53 (1H, dd, $J$ = 1.9, 17.8 Hz), 6.26 (1H, dd, $J$ = 2.4, 9.0 Hz), 6.26 (1H, d, $J$ = 2.0 Hz), 6.88 (1H, dd, $J$ = 11.2, 17.9 Hz), 7.22 (1H, d, $J$ = 9.0 Hz). $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 103.4, 108.0, 110.5, 118.3, 128.2, 132.9, 157.0, 159.1. MS (EI, 70 eV) $m/z$ 136 ($M^+$, 100), 121 ($M^+$ − Me, 11). HRMS (EI, 70 eV) calcd for $C_8H_8O_2$: 136.0525. Found: 136.0529. Pyridine (1 mL) was added to the $CD_3OD$ solution, and $CD_3OD$ was evaporated. Then, acetic anhydride (1 mL) was added, and the mixture was stirred for 5 h at room temperature. Saturated aq $KHSO_4$ was added, and the organic materials were extracted with ether. After being dried over $Na_2SO_4$, the solvents were removed, and silica gel chromatography gave 4-ethenyl-1,3-benzenediol diacetate (18 mg, 48%). The NMR spectra coincided with the authentic sample.

**2-Ethenyl-1,3-benzenediol (4).** Mp 73.8−74.5 °C (AcOEt−MeOH). $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 5.27 (1H, dd, $J$ = 2.9, 12.2 Hz), 6.07 (1H, dd, $J$ = 3.0, 17.9 Hz), 6.29 (2H, d, $J$ = 8.1 Hz), 6.81 (1H, t, $J$ = 8.1 Hz), 6.92 (1H, dd, $J$ = 12.0, 17.9 Hz). $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 107.8, 113.5, 117.2, 128.8, 129.4, 157.9. IR (KBr) 3468, 3404, 1635, 1626, 792, 785, 754 cm$^{-1}$. MS (EI, 70 eV) $m/z$ 136 ($M^+$, 100), 118 ($M^+$ − Me, 6), 107 ($M^+$ − CHO, 12). HRMS (EI, 70 eV) calcd for $C_8H_8O_2$: 136.0524. Found: 136.0526.

**3-Ethenyl-2-hydroxybenzoic Acid.** A mixture of 2-(trifluoromethyl)-6-ethenylphenyl acetate (117 mg, 0.51 mmol), ether (10 mL), and 2 M KOH (20 mL) was heated at reflux for 30 min. The cooled solution was then acidified with 2 M HCl and extracted with ether. The organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo. Flash chromatography on silica gel with ethyl acetate−hexane (1:1) gave the product (68 mg, 80%). Mp 124.2−125.5 °C (EtOH−$Et_2O$) (lit.[25] 131−133 °C). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.36 (1H, dd, $J$ = 10.4, 1.6 Hz), 5.82 (1H, dd, $J$ = 17.6, 1.6 Hz), 6.92 (1H, t, $J$ = 8.4 Hz), 7.07 (1H, dd, $J$ = 17.6, 11.2 Hz), 7.71 (1H, dd, $J$ = 7.6, 1.6 Hz), 7.87 (1H, dd, $J$ = 8.0, 1.6 Hz), 10.87 (2H, brs). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 111.2, 115.5, 119.1, 126.7, 130.1, 130.2, 133.4, 159.4, 174.0. IR ($CHCl_3$) 3250−2700, 1659 cm$^{-1}$. MS (EI, 70 eV) $m/z$ 164 ($M^+$, 58), 146 ($M^+ - H_2O$, 52), 118 ($M^+ - H_2CO_2$, 100). HRMS (EI, 70 eV) calcd for $C_9H_8O_3$: 164.0473. Found: 164.0473.

**2,6-Diethenyl-4-methoxyphenyl Acetate.** Ethyne was bubbled into chlorobenzene (170 mL) at −50 °C for 1 h. Bubbling was stopped, and $SnCl_4$ (5.9 mL, 50 mmol) and $Bu_3N$ (11.9 mL, 50 mmol) were added. The mixture was stirred at room temperature for 1 h under an argon atmosphere, and then *p*-methoxyphenol (**7**, 1.24 g, 10 mmol) in chlorobenzene (30 mL), $SnCl_4$ (2.3 mL, 20 mmol), and $Bu_3N$ (4.8 mL, 20 mmol)

(25) Iwasaki, M.; Tirrell, D.; Vogl, O. *J. Polym. Sci., Polym. Chem.* **1980**, *18*, 2755.

were added successively. After the mixture was heated at 100 °C for 1 h, 2 M NaOH (400 mL) and ethanol (150 mL) were added, and heating was continued for another 2 h at 100 °C. The mixture was cooled and acidified with 2 M HCl. The organic materials were extracted with ether, washed with brine, dried over $MgSO_4$, and filtered. After removal of ether under reduced pressure, pyridine (8.1 mL) and acetic anhydride (4.7 mL) were added to the resulting chlorobenzene solution, and the products were acetylated by stirring at room temperature for 12 h. The mixture was poured into water, and the organic materials were extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (hexane:ethyl acetate = 100:1) over silica gel gave 2,6-diethenyl-4-methoxyphenyl acetate (1.49 g, 77%). It contained about 5% of 2-ethenyl-4-methoxyphenyl acetate as indicated by $^1$H NMR. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 2.33 (3H, s), 3.83 (3H, s), 5.34 (2H, dd, $J$ = 11.0, 1.0 Hz), 5.73 (2H, dd, $J$ = 17.5, 1.1 Hz), 6.66 (2H, dd, $J$ = 17.5, 11.0 Hz), 7.00 (2H, s). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 20.4, 55.4, 110.7, 116.7, 130.3, 131.5, 139.3, 157.1, 169.1. IR (neat) 1767, 1597, 1031, 920, 756 cm$^{-1}$. MS (EI) *m*/*z* 218 ($M^+$, 12), 176 (100). HRMS calcd for $C_{13}H_{14}O_3$: 218.0943. Found: 218.0966.

**2,6-Diethenyl-4-*tert*-butylphenol.** A 5:1 mixture of 2,6-diethenyl-4-*tert*-butylphenyl acetate and 2-ethenyl-4-*tert*-butylphenyl acetate (171 mg, 0.71 mmol) was obtained from 4-*tert*-butylphenol (150 mg, 1.0 mmol). Under an argon atmosphere, $K_2CO_3$ (98 mg, 0.71 mmol) was added to a methanol (10 mL) solution of the above mixture. After stirring for 1 h, water was added, and the organic materials were extracted twice with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. 2,6-Diethenyl-4-*tert*-butylphenol (118 mg, 58% yield from 4-*tert*-butylphenol) was obtained as a colorless oil by flash chromatography (hexane:ethyl acetate = 30:1) over silica gel. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.33 (9H, s), 5.31 (1H, s), 5.42 (2H, dd, $J$ = 11.2, 1.4 Hz), 5.73 (2H, dd, $J$ = 17.7, 1.4 Hz), 6.94 (2H, dd, $J$ = 17.7, 11.3 Hz), 7.30 (2H, s). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 31.4, 34.1, 116.3, 123.8, 124.5, 132.3, 143.0, 148.0. IR (neat) 3544, 1630, 996, 911, 882 cm$^{-1}$. MS (EI) *m*/*z* 202 ($M^+$, 33), 187 ($M^+ - Me$, 100). HRMS calcd for $C_{14}H_{18}O$: 202.1356. Found: 202.1355.

**2,6-Diethenyl-1,4-benzenediol.** Under an argon atmosphere, KF (77 mg, 1.32 mmol) was added to a freeze-evacuated methanol solution (10 mL) of 2,6-diethenyl-4-(*tert*-butyldimethylsilyloxy)phenol (182 mg, 0.66 mmol). The mixture was stirred for 1 h, and then water was added. The organic materials were extracted twice with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. 2,6-Diethenyl-1,4-benzenediol (71 mg, 66%) was obtained by flash chromatography over silica gel (hexane:ethyl acetate = 2.5:1). Mp 131−132 °C (toluene). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.19 (2H, dd, $J$ = 11.1, 0.8 Hz), 5.62 (2H, dd, $J$ = 17.7, 0.8 Hz), 6.83 (2H, s), 7.02 (2H, dd, $J$ = 17.7, 11.1 Hz). $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 112.9, 114.3, 129.3, 133.0, 145.7, 151.9. IR (KBr) 3260, 1450, 1415, 1361, 1201, 1000, 962, 920, 862, 787 cm$^{-1}$. MS (EI) *m*/*z* 162 ($M^+$, 100), 147 ($M^+ - Me$, 48). HRMS calcd for $C_{10}H_{10}O_2$: 162.0680. Found: 162.0681. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06%; H, 6.21%. Found: C, 74.15%; H, 6.32%.

**4-Methoxy-2-(1-phenylethenyl)phenol.** Under an argon atmosphere, a mixture of *p*-methoxyphenol (**7**, 124 mg, 1 mmol), phenylacetylene (100 mg, 1.0 mmol), $SnCl_4$ (0.48 mL, 4 mmol), and $Bu_3N$ (1.0 mL, 4 mmol) in chlorobenzene (20 mL) was heated at 60 °C for 30 min. 2 M KOH (40 mL) and ethanol (10 mL) were added, and refluxing was continued for another 1 h. After being cooled to room temperature, the contents were poured into a mixture of ether and 2 M HCl, and the organic materials were extracted with ether. The organic layer was dried over $Na_2SO_4$ and concentrated. 4-Methoxy-2-(1-phenylethenyl)phenol (130 mg, 57%) and 4-methoxy-2,6-bis(1-phenylethenyl)phenol (63 mg, 19%) were obtained along with the recovered **7** (14 mg, 11%) by flash chromatography over silica gel. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.75 (3H, s), 4.77 (1H, s), 5.42 (1H, d, $J$ = 1.6 Hz), 5.86 (1H, d, $J$ = 1.6 Hz), 6.69 (1H, d, $J$ = 2.8 Hz), 6.83 (1H, dd, $J$ = 8.4, 2.8 Hz), 6.88 (1H, d, $J$ = 8.8 Hz), 7.36 (5H, m). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 55.8, 115.0, 115.2, 116.4, 116.6, 126.8, 128.0, 128.4, 128.6, 139.0, 145.1, 146.9, 153.1. IR (neat) 3526, 1488 cm$^{-1}$. MS (EI) *m*/*z* 226 ($M^+$, 67), 225 ($M^+ - H$, 100), 211 ($M^+ - Me$, 29). HRMS calcd for $C_{15}H_{14}O_2$: 226.0994. Found: 226.1000.

**4,7-Dimethyl-7-ethenyl-2,5-bicyclo[2.2.2]octadien-8-one (15).** 2,6-Dimethylphenol (122 mg, 1.0 mmol) was vinylated with ethyne by standard procedures, and the reaction was worked up by adding 2 M NaOH and heating at 90 °C for 1 h. After being cooled to room temperature, the organic layer was separated, washed twice with 2 M HCl, and dried over $Na_2SO_4$. Chlorobenzene was removed in vacuo, and NMR analysis of the crude product indicated the formation of **15** in 60% yield. Very rapid flash chromatography on silica gel gave pure **15** (52 mg, 30%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 1.19 (3H, s), 1.56 (3H, s), 3.67 (1H, m), 4.99 (1H, d, $J$ = 11.6 Hz), 5.09 (1H, d, $J$ = 17.6 Hz), 5.71 (1H, dd, $J$ = 16.8, 10.0 Hz), 6.02 (1H, d, $J$ = 6.4 Hz), 6.09 (1H, d, $J$ = 6.4 Hz), 6.50 (1H, t, $J$ = 6.4 Hz), 6.56 (1H, t, $J$ = 6.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 15.7, 27.1, 47.4, 48.2, 58.2, 114.0, 133.5, 135.1, 135.8, 136.4, 143.0, 206.6. IR (neat) 2972, 2931, 1716, 1454, 995, 917 cm$^{-1}$. Deuteration experiments were conducted using 2 M NaOD in $D_2O$ giving **15**-$d_3$ in 30% isolated yield. $^1$H NMR absorptions at $\delta$ 6.56, 6.02, and 4.99 disappeared, indicating >95% deuteration.

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**Supporting Information Available:** Spectral data of the vinylphenol derivatives described in the present study. $^1$H NMR and $^{13}$C NMR spectra of vinylphenols are also included (86 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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