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Non-Catalyzed Thermal Reactions of Acylquinones with Allylstannanes

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Thermal reactions of acylquinones with allylstannanes in benzene afforded several kinds of product after column chromatography on silica gel; acyl allyl quinones, acyl allyl epoxy quinones, cyclopentanoid compounds including stannyl moiety, allyl hydroxy quinones, acyl hydroquinones, and acyl allyl hydroquinones. The main product comprises cyclopentanoid compounds, which are novel [2+3] cyclo adducts with 1,2-migration of trialkylstannyl moiety. Spectroscopic examinations (^{1}H NMR and Vis-UV) enabled us to confirm the reaction pathways that four types of precursors were initially generated via polarized tight pair and inverted to isolated products during purification by column chromatography. Similar reactions in acetonitrile showed a remarkable difference in the reactivity, that is, acyl allyl quinones and the corresponding hydroquinones are obtained, but the [2+3] cyclo adducts are not produced at all. From ^{1}H NMR examination, it was confirmed that three types of precursor are generated via solvent separated ion pairs at the initial stage. The rather strong reactivity of acylquinones towards allylstannanes will be due to electron withdrawing ability of acyl group.

In recent years, organotin chemistry has been dramatically developed.[1] A variety of organotin compounds have been applied as reagents or catalysts in the field of synthetic organic chemistry.[2] Allylstannanes are the best reagents for allylation of electrophilic substrates, but, in general, activation of substrates or transmetallation of reagents by Lewis acid is necessary for smooth and selective allylation.[3] For example, Lewis acid such as BF_3 coordinates to the carbonyl oxygen and enhances the electrophilicity of the substrate.

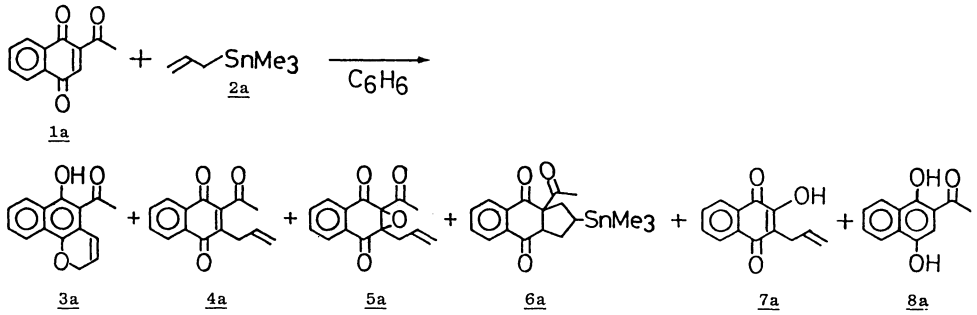
Electron deficient acylquinones exhibit unique reactivity, and several investigations relating to acylquinones have been reported by different groups.[4-7] We have reported Lewis acid catalyzed thermal reactions of acylquinones with allylstannanes, which are the key step of the total synthesis of antibiotics such as deoxyanthracyclinones[8] and pyranonaphthoquinones.[9] In these reactions, one or two allyl adducts are afforded in high yields. On the other hand, acylquinones react with allylstannanes even in the absence of Lewis acid, owing to both electron withdrawing ability and resonance efficiency.

In this paper, the thermal reactions of acylquinones with allylstannanes in the absence of catalyst will be discussed from products analyses, ^{1}H NMR, and Vis-UV. The characteristic diversity in the reactivity of acylquinones is considered from the steric and electronic nature of the relating reagents and polarity of solvents.

Results

Thermal Reactions of Acetylquinones with Allylstannanes. Thermal reactions of two kinds of acetylquinone (**1a,b**) with allylstannanes (**2a,b**) were investigated by examining the products and spectroscopic (^{1}H NMR and Vis-UV) analyses.

2-Acetyl-1,4-naphthoquinone **1a** (1 mmol) and allyltrimethylstannane **2a** (2 mmol) were dissolved in benzene (25 ml) and allowed to stand for 24 h under argon atmosphere. After treating the reaction mixture by column chromatography on silica gel, six compounds were isolated as the major products 5-acetyl-2*H*-benzo[*h*]chromene-6-ol **3a** (3%), 2-acetyl-3-allyl-1,4-naphthoquinone **4a** (20%), 2-acetyl-3-allyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone **5a** (20%), 3a-acetyl-2-trimethylstannyl-2,3,3a,4,9,9a-hexahydro-1*H*-cyclopenta[*b*]naphthalene-4,9-dione **6a** (32%), 3-allyl-2-hydroxy-1,4-naphthoquinone **7a** (3%), and 2-acetyl-1,4-naphthalenediol **8a** (20%) (Scheme 1). The identification of these isolated products was carried

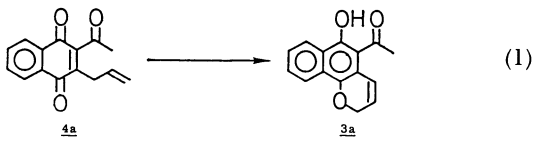


1a + 2a → 3a + 4a + 5a + 6a + 7a + 8a

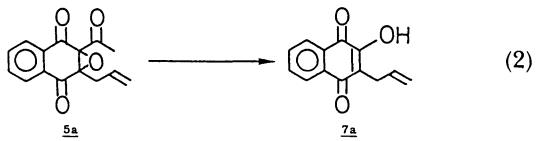
Scheme 1.

out on the basis of ^{1}H NMR, ^{13}C NMR, IR, mass spectroscopy, elementary analysis, and comparison with the authentic samples. Several spectral data which were characteristic of each product are described below. The IR spectrum of **3a** showed characteristic bands due to hydrogen bonded hydroxyl and carbonyl group at 3300 and 1600 cm^{-1}, respectively, and the allyl position methylene signal appeared at δ 4.77 as a doublet in its ^{1}H NMR spectrum. The IR spectrum of **4a** showed absorption bands due to carbonyl group at 1705 and 1665 cm^{-1}, and that of **5a** showed characteristic bands due to carbonyl group at 1710, 1695, and 1680 cm^{-1}. In their ^{1}H NMR spectra, the allyl methylene of **4a** appeared at δ 3.28 as a doublet (J=6 Hz), while that of **5a** showed diastereomeric peaks at δ 2.49 (dd, J=7, 15 Hz) and 3.00 (dd, J=7, 15 Hz). In the mass spectrum of **5a**, the parent peak and the ion peak arising from elimination of acetyl group appeared at m/z 256 (M^+) and 213 (M^+-43). All spectral data of **5a** was consistent with those of the authentic sample synthesized through another route.[6] The IR and ^{13}C NMR spectra of pale yellow compound **6a** showed characteristic bands due to carbonyl group at 1710, 1695, 1680 cm^{-1} and δ 203, 196, 194. Since ^{1}H NMR spectrum of **6a** showed only one peak due to trimethylstannyl group at δ 0.06, only one diastereomer was generated, and cis stereochemistry has been assigned to **6a** based upon analysis of the ^{13}C-^{119}Sn coupling constant.[10] In its mass spectrum, ion peaks arising from elimination of methyl group appeared at m/z 391 and 389 (M^+-15) along with those of tin isotopes ^{120}Sn and ^{118}Sn. Compound **7a** and **8a** were identified by comparison with the authentic samples.[6,11]

Of these isolated products, **3a** and **7a** were generated from **4a** and **5a**, respectively, during the treatment with silica gel. Furthermore, the generation of the cyclopentanoid adduct **6a** is worth mentioning, because it is a [2+3] cycloaddition product resulted via migration of trimethylstannyl moiety. A similar [2+3] cycloaddition reaction of allylstannanes was recently reported by Herndon.[12]



(1)



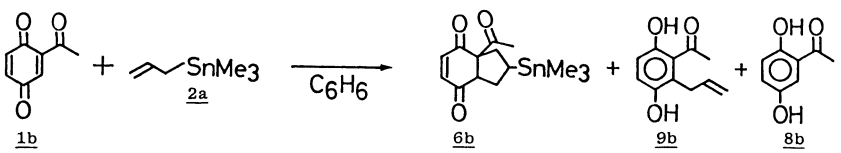
(2)

Although the thermal reaction between **1a** and **2a** in dichloromethane gave the same products as those obtained in benzene in a slightly different distribution, remarkable differences were observed in the reaction in acetonitrile. The color of an acetonitrile solution changed from yellow to dark green soon after mixing **1a** with **2a** and the reaction completed within 30 min. It seems interesting that compounds **3a**, **4a**, **5a**, **7a**, and **8a** were generated but the cyclopentanoid compound **6a** was not obtained at all.

Similarly, thermal reaction of **1b** with **2a** in benzene gave 3a-acetyl-2-trimethylstannyl-2,3,3a,4,7,7a-hexahydrindene-4,7-dione **6b** (23%), 2-acetyl-1,4-benzenediol **8b** (36%), and 2-acetyl-3-allyl-1,4-benzenediol **9b** (27%) as the major products after purification by column chromatography on silica gel (Scheme 2). On the contrary, in acetonitrile, a yellow solution changed to dark green immediately after mixing **1b** with **2a**, and the reaction completed within 10 min. After the usual examination, **8b** (18%) and **9b** (18%) were identified but the cyclopentanoid compound **6b** was not observed at all.

A similar reactivity of **1a,b** in the reaction with allyltributylstannane **2b** was recognized. The results are summarized in Table 1. Compared with other p-quinones such as non-substituted quinones, halogeno quinones, alkyl quinones, alkoxy quinones, and so on, the reactivity of 2-acetyl-1,4-quinones **1a,b** was quite specific in the aspects as follows. First, the reaction proceeds spontaneously without activation of reagents. In general, the reaction of p-benzoquinone with **2** does not proceed without irradiation or catalyst. Second, polarity of solvents strongly affects both the reaction rate and products distribution. Thus, in a nonpolar solvent such as benzene, the reaction proceeded relatively slowly, resulting in the formation of [2+3] cycloadducts **6a,b**. On the other hand, in a polar solvent such as acetonitrile, the reaction proceeded quickly, but **6a,b** were not given.

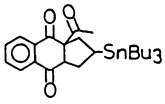
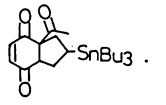
In order to clarify the reaction pathways, ^{1}H NMR measurement was carried out in the reaction of **1a** with **2a**. When a benzene-d_6 solution containing **1a** (ca. 10^{-2} M; 1 M=1 mol dm^{-3}) and **2a** (ca. 10^{-2} M) was allowed to stand in an NMR sample tube under argon atmosphere, many new peaks emerged stepwisely, but



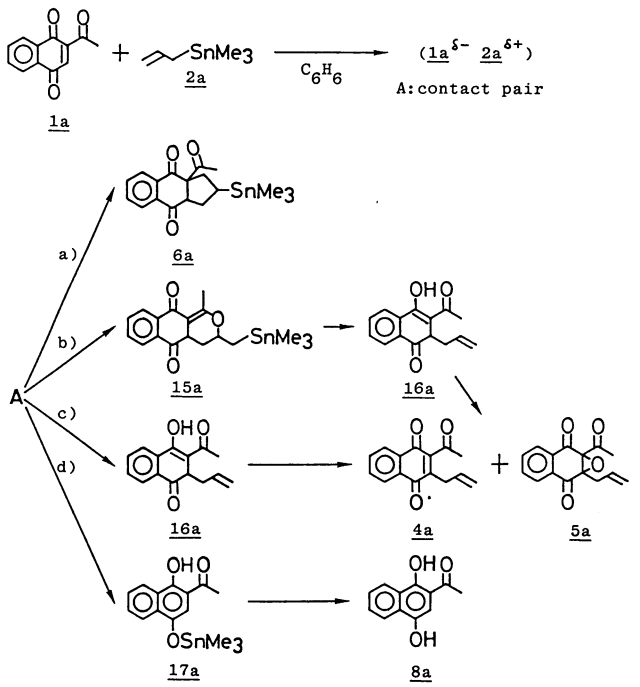
Scheme 2.

Table 1. Thermal Reactions of Acetylquinones (**1**) with Allylstannanes (**2**)

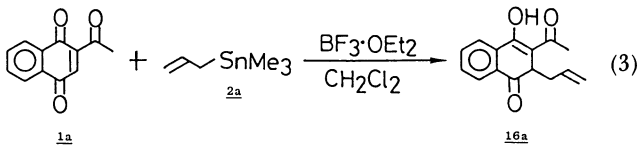
Quinone	Tin	Reaction Conditions		Isolated yields/%							
1a	**2a**	C_6H_6	21h	**3a**(3)	**4a**(20)	**5a**(12)	**6a**(32)	**7a**(3)	**8a**(21)		
1a	**2a**	CH_2Cl_2	20h	**3a**(2)	**4a**(23)	**5a**(12)	**6a**(41)	**7a**(3)	**8a**(3)		
1a	**2a**	CH_3CN	1h	**3a**(1)	**4a**(28)	**5a**(28)		**7a**(4)	**8a**(12)		
1a	**2b**	C_6H_6	20h	**3a**(2)	**4a**(18)	**5a**(10)		**7a**(2)	**8a**(15)		**10a**(35)[a]
1a	**2b**	CH_3CN	1h	**3a**(3)	**4a**(30)	**5a**(22)		**7a**(3)	**8a**(19)		
1b	**2a**	C_6H_6	5h				**6b**(23)		**8b**(36)	**9b**(27)	
1b	**2a**	CH_3CN	10min						**8b**(18)	**9b**(18)	
1b	**2b**	C_6H_6	1.5h						**8b**(10)	**9b**(29)	**10b**(10)[b]

a) **10a**:  . b) **10b**:  .

the peaks gradually disappeared due to the starting reagents. After standing for 24 h, trace amounts of **1a**, **2a**, and four main products were observed. Compared with the ^{1}H NMR spectra of the authentic samples and structurally related substrates, these four products were assigned to **6a** (40%), **15a** (40%), **16a** (10%), and **17a** (3%) as shown in Scheme 3. The assignments were accomplished by using (2-deuterioallyl)trimethylstannane **2c** instead of **2a**, but several unidentified peaks remained.[13] To our surprise, the isolated products **3a**, **4a**, **5a**, **7a**, and **8a** were not observed during this measurement. It was thus confirmed that these five isolated products were the resultants of **15a**, **16a**, and **17a**. The ^{1}H NMR spectrum of **15a** showed characteristic bands due to acetyl group and trimethylstannyl group at δ 2.42 (3H, d, J=2 Hz) and 1.12 (9H, s), respectively. In addition, similar resonances arising from the diastereomer of [4+2] cycloadduct **15a** were observed at δ 2.44 (3H, d, J=2 Hz) and 1.13 (9H, s). The relative ratio of diastereomers was estimated to be 6/1 from integral values of each peak at δ 2.42 and 2.44. The ^{1}H NMR spectrum of **17a** showed characteristic singlet peak due to trimethylstannyl group at δ 0.24 (9H, s). However, any attempts to isolate **15a** and **17a** have failed so far. Furthermore, the reaction mixture was passed through a very short silica-gel column after standing for 24 h, and then, all fractions were collected, concentrated, and measured similarly by ^{1}H NMR. Five compounds, **4a** (4%), **5a** (2%), **6a** (38%), **8a** (5%), and **16a** (45%) were observed, but **15a** and **17a** completely disappeared. The quantity of cyclopentanoid compound **6a** was little affected by treating with silica-gel column, but the quantity of **16a** slightly increased.[14] In the presence of Lewis acid such as BF_3, compound **16a** was given as the sole allyl adduct.



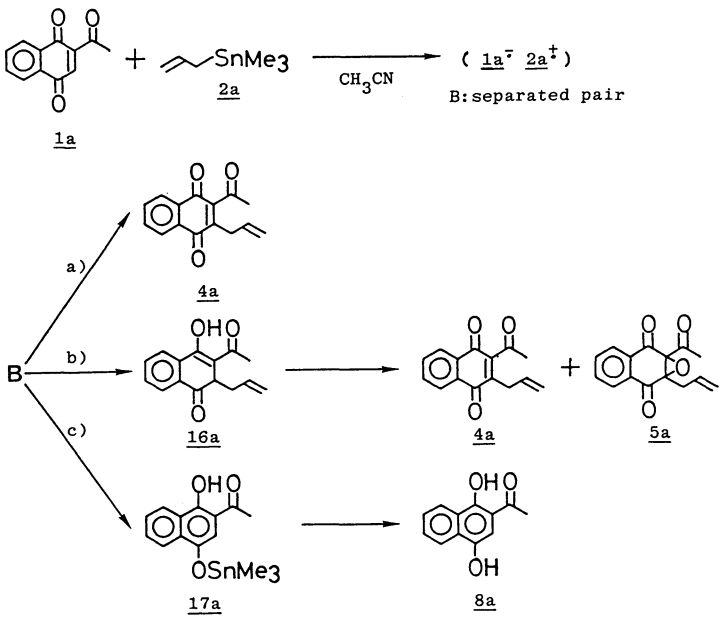
Scheme 3.



(3)

A similar ^{1}H NMR measurement in acetonitrile-d_3 was also undertaken. In this case, the color of a solution changed from yellow to green soon after mixing of **1a** with **2a**. The peak of the 3-position of **1a** broadened instantly and new peaks emerged quickly. The starting acylquinone **1a** was completely consumed within 30 min, and three products, **4a** (10%), **16a** (55%), and **17a** (17%) were observed. The cyclized products, **6a** and **15a**, involving trimethylstannyl moiety were not generated in this case. After treating the reaction mixture with silica gel, **4a** (9%), **5a** (2%), **8a** (15%), and **16a** (50%) were identified (Scheme 4).

Furthermore, we have applied Vis-UV absorption method to follow the reaction of **1a** with **2b** in benzene. Addition of **2b** to a benzene solution of **1a** resulted in a development of absorption bands corre-



Scheme 4.

sponding to each product with three isosbestic points at 328, 371, and 425 nm, which were not influenced by concentrations of two reagents (Fig. 1). These facts suggest that each product was generated via an identical intermediate. In other words, the rate determining step of the reaction seems to be the formation of the common intermediate.

Thermal Reactions of Related Acylquinones with Allylstannane. The thermal reactions of other acylquinones **1c—f** (1 mmol) with allyltrimethylstannane **2a** (2 mmol) were carried out in benzene (25 ml). By the reaction of 2-propionyl-1,4-naphthoquinone **1c** with **2a**, several kinds of product were given after purification by column chromatography on silica gel and spectroscopically identified; chromene **3c**, allyl quinone **4c**, allyl epoxy quinone **5c**, [2+3] cycloadduct **6c**, allyl hydroxy quinone **7a**, and hydroquinone **8c**. On the other hand, the thermal reactions of 2-pivaloyl-1,4-naphthoquinone **1d** and 2-acetyl-3-methyl-1,4-naphthoquinone **1e** with **2a** did not proceed at all.[15] The reaction of 2-acetyl-8-methoxy-1,4-naphthoquinone **1f**, in which electron donating methoxyl group was introduced to phenyl ring, with **2a** gave allyl quinone **4f**, [2+3] cycloadduct **6f**, and hydroquinone **8f**. The results are summarized in Scheme 5.

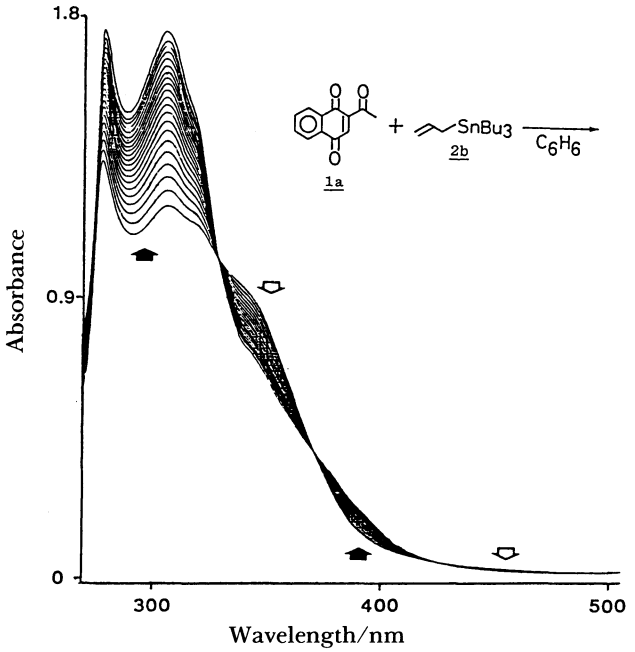
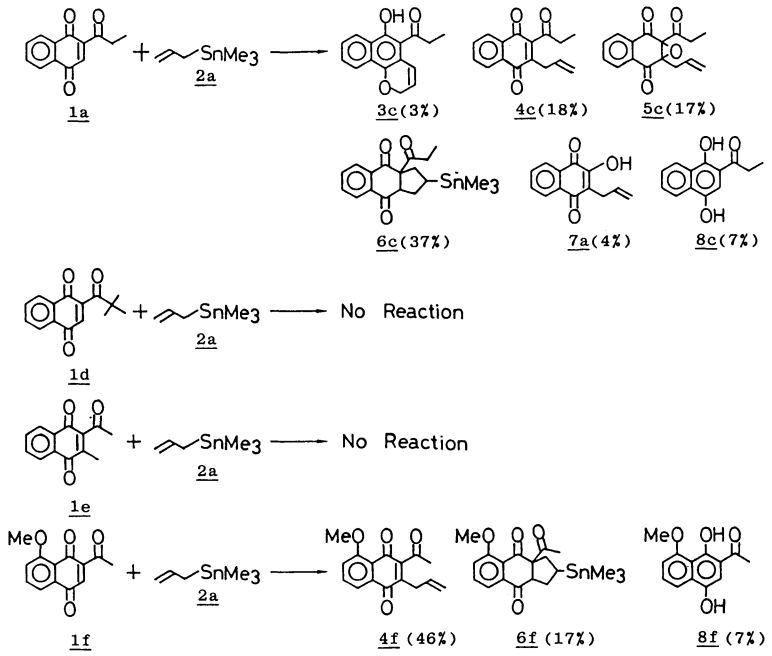


Fig. 1. Absorption spectral change observed during the reaction of **1a** with **2b** in benzene.

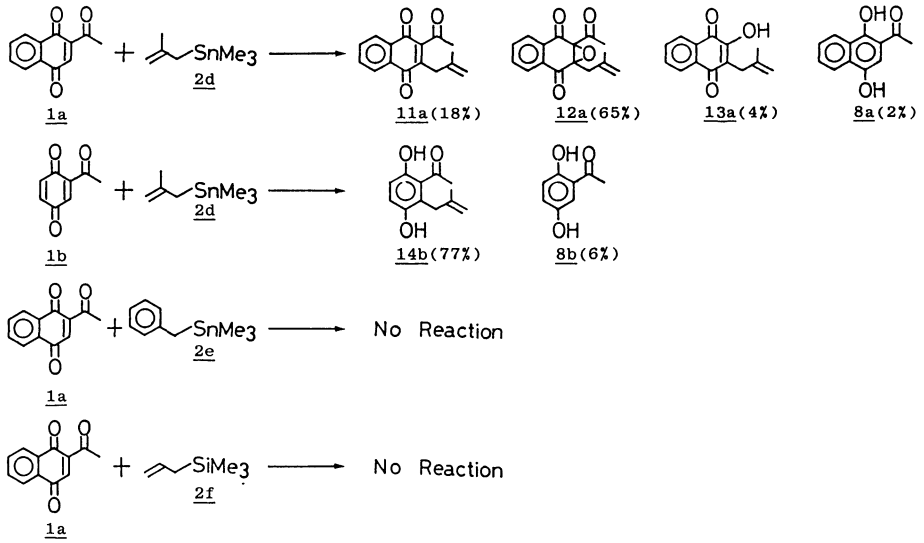
Thermal Reactions of Acetylquinones with Methallyl- or Benzylstannanes or Allylsilane. In the thermal reaction of 2-acetyl-1,4-naphthoquinone **1a** with (2-methylallyl)trimethylstannane **2d**, allylated products **11a** and **12a** were obtained as usual, but [2+3] cycloadduct like **6a** was not formed. In the thermal reaction of **1a** with benzyltrimethylstannane **2e** or with allyltrimethylsilane **2f** in benzene, no progress of reactions was recognized. The results are summarized in Scheme 6.

Discussion

The reactivity of acylquinones with allylstannanes was quite specific from two aspects: 1) thermal reaction proceeded spontaneously without activation of reactants and 2) solvent polarity strongly affected the distribution of product ratio. These characteristics seem to derive from both strong oxidizing power and resonance ability of acyl group under anionic state of acylquinones **1**, and from both mild reducing power and probable cleavage of carbon-tin bond under



Scheme 5.



Scheme 6.

cationic state of allylstannanes **2**. During these reactions, acylquinones **1** behave as electron acceptors and allylstannanes **2** behave as electron donors.

Based upon the above results, reaction pathways were proposed as given in Schemes 3 and 4. The reaction between **1a** and **2a** was selected as a representative.

In a nonpolar solvent such as benzene, polarized species are not stabilized by solvent molecules, and the charge transfer can therefore occur only in the case that two species are brought sufficiently close and the polarized two species $\mathbf{1a}^{\delta-}$ and $\mathbf{2a}^{\delta+}$ will be kept in a tightly contacted pair in solvent cage (intermediate pair **A**). In general, the 3-position of $\mathbf{1a}^-$ shows highly electrophilic reactivity toward electron rich reaction center and the negative charge is stabilized by resonance effect of acyl group. The following four pathways a—d) from tight pair **A** will be most reasonable. As for the generation of compound **6a**, since tin stabilizes its cationic β-position by hyperconjugative interaction, [2+3] cycloaddition between $\mathbf{1a}^-$ and $\mathbf{2a}^+$ will occur before C-Sn bond cleavage of $\mathbf{2a}^+$ with 1,2-migration of trimethylstannyl moiety.[16] Similarly to the path a), generation of compound **15a** will proceed by [4+2] cycloaddition before C-Sn bond cleavage of $\mathbf{2a}^+$. In this path, cationic β-carbon of $\mathbf{2a}^+$ will be trapped by resonant acetyl-carbonyl oxygen. Contrary to the cases a) and b), generation of compound **16a** will proceed by allylation of $\mathbf{1a}^-$ at the 3-position with C-Sn bond cleavage of $\mathbf{2a}^+$. The H

atom of hydroxyl group at the 1-position may be released from solvent molecules. As for the compound **17a**, escaped $\mathbf{1a}^-$ from solvent cage will abstract H atom from solvent molecules and remaining anionic oxygen atom may trap trimethylstannyl cation.

Probably, three compounds **15a**, **16a**, and **17a** convert to the corresponding isolated products during the usual working-up process such as silica-gel long column chromatography (Scheme 3). The six membered [4+2] cycloadduct **15a** generated via path b) has enol structure in its skeleton, and converts into **16a** with C-Sn bond cleavage under acidic condition followed by aromatization to 2-acetyl-3-allyl-1,4-naphthalenediol, which will be easily autoxidized to the corresponding quinone **4a** with air or remaining **1a**. Thus, both **15a** and **16a** are the precursors of **4a** and **5a**, and **17a** converts into **8a**.

On the other hand, in a polar solvent such as acetonitrile, polarized species can be stabilized by solvent molecules, and electron transfer will occur even in the case that two reactants are apart somewhat each other. From two facts that the color of the reacting solution turned from yellow to green soon after mixing the reagents and that the 3-position of **1a** broadened instantly in ^{1}H NMR examination, single electron transfer seems to occur from **2a** to **1a**, resulting in the formation of solvent separated loose radical ion pair between $\mathbf{1a}^{\cdot-}$ and $\mathbf{2a}^{\cdot+}$ (intermediate pair **B**). Owing to the high $\sigma_{C\text{-}Sn}$ bond orbital energy and to electropositive character of tin, $\mathbf{2a}^{\cdot+}$ tends to undergo rapid generation of allyl radical and trimethylstannyl cation, so C-C bond formation between $\mathbf{1a}^{\cdot-}$ and allyl radical will occur.[17] Therefore, the cyclized compounds having trimethylstannyl moiety such as **6a** and **15a** will not be obtained under these conditions. The remarkable difference between the reactivity of the reactions in benzene and that in acetonitrile should be ascribed to the difference in the activation energy of formation of the two intermediates **A** and **B**.

The results in the reactions of related acylquinones **1c—f** with **2a** in benzene provided information on steric and electronic effects for the reactivity. Thus, introduction of electron donating methoxyl group to phenyl ring or introduction of methyl group to acetyl group did not affect reactivity as a whole, that is, [2+3] cycloadducts and allylated quinones were obtained as the case of **1a**. On the other hand, introduction of *t*-butyl group as a part of acyl group (**1d**) or introduction of methyl group to the reacting 3-position (**1e**) diminished the reactivity completely. From these results, it is concluded that decreasing oxidizing power of acylquinones can not appreciably reduce the reactivity toward **2a**, but that increasing steric hindrance around the 3-position of acylquinone entirely reduces the reactivity.[18]

Thermal reactions of **1a,b** with methallylstannane **2d** in benzene afforded allylated products, but [2+3] cycloadduct such as **6a** was not obtained at all. This is due to the inductive effect of methyl group which stabilizes the intermediary cationic β-position of $\mathbf{2d}^+$ and the effect of the steric hindrance between methyl group and trimethylstannyl group. The 1,2-migration of the trimethylstannyl moiety was thus suppressed. Thermal reactions of **1a,b** with benzylstannane **2e** or allylsilane **2f** did not proceed at all, due to the lower electron donating ability of **2e** and **2f**.

Experimental

General Remarks. All melting points were determined on a Yanagimoto micro-melting point apparatus and uncorrected. Mass spectra were measured by a JEOL JMS-DX-300 mass spectrometer. ^{1}H NMR spectra were obtained by a JEOL JNM-PX-100 and a JEOL JNM-GX-400 spectrometers. ^{13}C NMR spectra were obtained by a JEOL JNM-GX-400 spectrometer. Chemical shifts were recorded as δ values in parts per million (ppm) from tetramethylsilane as an internal standard. IR spectra were obtained by a JASCO IRA-1 spectrometer for KBr pellets or neat oil on NaCl. The electronic spectra were obtained by a Shimadzu UV-3000 spectrometer. Column chromatography was done on Wakogel C-200 and Merck Kieselgel 60H for flash column chromatography. Elementary analyses were performed by the Microanalytical Laboratory of Kyoto University. Cyclic voltammetry was carried out by a PAR Model 174 with working electrodes of platinum wire.

Starting Materials. Benzene was used after distillation from sodium wire. Acetonitrile and dichloromethane were used after distillation from phosphorus pentaoxide. Benzene-d_6 and acetonitrile-d_3 were commercially available and used after distillation. 2-Acetyl-1,4-naphthoquinone **1a**, 2-acetyl-1,4-benzoquinone **1b**, 2-propionyl-1,4-naphthoquinone **1c**, 2-pivaloyl-1,4-naphthoquinone **1d**, 2-acetyl-3-methyl-1,4-naphthoquinone **1e**, and 2-acetyl-8-methoxy-1,4-naphthoquinone **1f** were synthesized by the previously reported methods.[6,19] All acylquinones were purified by recrystallization and sublimation. Allylic- and benzylstannanes **2a—e** were prepared by the reported methods.[20,21] All tin reagents were purified by distillation. Allyltrimethylsilane **2f** was commercially available and used without further purification.

General Procedures. Acylquinone (1 mmol) and allylstannane (2 mmol) were dissolved in benzene or acetonitrile (25 ml) and allowed to stand for suitable time under argon atmosphere. The reaction mixture was concentrated, subjected to column chromatography on silica gel, and eluted with hexane-ether.

Physical Properties of the Products. 5-Acetyl-2*H*-benzo[*h*]chromene-6-ol (**3a**): Yellow needles from hexane-chloroform; mp 119—123 °C. MS; *m/z* 240 (M^+). Found: C, 74.82; H, 4.82%. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%. IR (KBr); 3300 (OH), 1600 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=2.63 (3H, s), 4.77 (2H, d, *J*=4 Hz), 5.8 (1H, dt, *J*=9, 4 Hz), 6.75 (1H, d, *J*=9 Hz), 7.5—7.7 (2H, m), 8.12 (1H, d, *J*=8 Hz), 8.42 (1H, d, *J*=8 Hz), 13.8 (1H, s).

5-Propionyl-2*H*-benzo[*h*]chromene-6-ol (**3c**): Yellow needles from hexane-ether; mp 69—72 °C. MS; *m/z* 254 (M^+). High resolution MS; Found: *m/z* 254.0944. Calcd for $C_{16}H_{14}O_3$: M, 254.0944. IR (KBr); 3400 (OH), 1605 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$); δ=1.25 (3H, t, *J*=7 Hz), 2.94 (2H,

q, J=7 Hz), 4.78 (2H, d, J=4 Hz), 5.88 (1H, dt, J=9, 4 Hz), 6.74 (1H, d, J=9 Hz), 7.5—7.7 (2H, m), 8.11 (1H, d, J=8 Hz), 8.41 (1H, d, J=8 Hz), 13.66 (1H, s).

2-Acetyl-3-allyl-1,4-naphthoquinone (**4a**): Yellow needles from hexane-chloroform; mp 57—59 °C. MS; m/z 240 (M^+). High resolution MS; Found: m/z 240.0789. Calcd for $C_{15}H_{12}O_3$: M, 240.0785. IR (KBr); 1705 (C=O), 1665 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=2.50 (3H, s), 3.28 (2H, d, J=6 Hz), 5.1—5.3 (2H, m), 5.8—6.0 (1H, m), 7.8—7.9 (2H, m), 8.1—8.3 (2H, m).

2-Propionyl-3-allyl-1,4-naphthoquinone (**4c**): Yellow oil. MS; m/z 254 (M^+). High resolution MS; Found: m/z 254.0937. Calcd for $C_{16}H_{14}O_3$: M, 254.0944. IR (neat); 1705 (C=O), 1660 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=1.20 (3H, t, J=7 Hz), 2.76 (2H, q, J=7 Hz), 3.25 (2H, d, J=7 Hz), 5.1—5.2 (2H, m), 5.8—5.9 (1H, m), 7.75—7.85 (2H, m), 8.1—8.2 (2H, m).

3-Acetyl-2-allyl-5-methoxy-1,4-naphthoquinone (**4f**): Pale yellow crystals from hexane-ether; mp 127—129 °C. MS; m/z 270 (M^+). Found: C, 70.99; H, 5.10%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%. IR (KBr); 1705(C=O), 1650 (C=O), 1630 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=2.47 (3H, s), 3.23 (2H, d, J=7 Hz), 4.01 (3H, s), 5.12 (2H, m), 5.83 (1H, m), 7.2—7.4 (1H, m), 7.6—7.8 (2H, m).

2-Acetyl-3-allyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**5a**): Pale yellow needles from hexane-chloroform; mp 88—90 °C. MS; m/z 213 (M^+−43). Found: C, 70.23; H, 4.66%. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72%. IR (KBr); 1710 (C=O), 1695 (C=O), 1680 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=2.46 (3H, s), 2.49 (1H, dd, δ=7, 15 Hz), 3.00 (1H, dd, J=7, 15 Hz), 5.19 (2H, m), 5.85 (1H, m), 7.7—7.8 (2H, m), 8.0—8.1 (2H, m).

3-Allyl-2-propionyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**5c**): Yellow crystals from hexane-ether; mp 53—55 °C. MS; m/z 270 (M^+). High resolution MS; Found: m/z 270.0929. Calcd for $C_{16}H_{14}O_4$: M, 270.0892. IR (neat); 1725 (C=O), 1690 (C=O), 1680 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=1.16 (3H, t, J=7 Hz), 2.5—2.9 (4H, m), 5.1 (2H, m), 5.85 (1H, m), 7.7—7.9 (2H, m), 8.0—8.1 (2H, m).

3a-Acetyl-2-trimethylstannyl-2,3,3a,4,9,9a-hexahydro-1*H*-cyclopenta[*b*]naphthalene-4,9-dione (**6a**): Pale yellow crystals from hexane-ether; mp 93—95 °C. MS; m/z 391 (M^+−15, ^{120}Sn), 389 (M^+−15, ^{118}Sn). Found: C, 53.27; H, 5.39%. Calcd for $C_{18}H_{22}O_3Sn$: C, 53.37; H, 5.47%. IR (KBr); 1705 (C=O), 1680 (C=O), 1670 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=0.06 (9H, s), 1.50 (1H, m), 1.92 (1H, t, J=13 Hz), 2.0—2.2 (5H, m), 3.07 (1H, dd, J=8, 13 Hz), 3.62 (1H, dd, J=8, 11 Hz), 7.75—7.85 (2H, m), 8.05—8.15 (2H, m). ^{13}C NMR($CDCl_3$); δ=−11.2, 20.1, 26.6, 34.2, 39.6, 53.8, 77.6, 127.0, 133.8, 134.1, 134.8, 194.5, 196.2, 202.6.

3a-Acetyl-2-trimethylstannyl-2,3,3a,4,7,7a-hexahydrindene-4,7-dione (**6b**): Yellow crystals from hexane-chloroform; mp 45—47 °C. MS; m/z 341 (M^+−15, ^{120}Sn), 339 (M^+−15, ^{118}Sn). Found: C, 47.44; H, 5.64%. Calcd for $C_{14}H_{20}O_3Sn$: C, 47.37; H, 5.68%. IR (neat); 1700 (C=O), 1680 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=0.03 (9H, s), 1.32 (1H, m), 1.83 (1H, t, J=13 Hz), 2.0—2.2 (5H, m), 2.86 (1H, dd, J=7, 12 Hz), 3.45 (1H, dd, J=6, 10 Hz), 6.63 (1H, d, J=17 Hz), 6.67 (1H, d, J=17 Hz).

3a-Propionyl-2-trimethylstannyl-2,3,3a,4,9,9a-hexahydro-1*H*-cyclopenta[*b*]naphthalene-4,9-dione (**6c**): Pale yellow needles from hexane-ether; mp 59—62 °C. MS; m/z 405 (M^+−15, ^{120}Sn), 403 (M^+−15, ^{118}Sn). Found: C, 54.72; H, 5.78%. Calcd for $C_{19}H_{24}O_3Sn$: C, 54.45; H, 5.77%. IR (KBr); 1710 (C=O), 1680 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=−0.01 (9H, s), 0.85 (3H, t, J=7 Hz), 1.41 (1H, m), 1.85 (1H, t, J=12 Hz), 2.09 (2H, t, J=10 Hz), 2.46 (2H, q, J=7 Hz), 3.01 (1H, dd, J=7, 13 Hz), 3.54 (1H, dd, J=9, 10 Hz), 7.65 (2H, m), 7.9—8.0 (2H, m).

3a-Acetyl-2-trimethylstannyl-5-methoxy-2,3,3a,4,9,9a-hexahydro-1*H*-cyclopenta[*b*]naphthalene-4,9-dione (**6f**): Pale yellow crystals from hexane-ether; mp 113—115 °C. MS; m/z 421 (M^+−15, ^{120}Sn), 419 (M^+−15, ^{118}Sn). Found: C, 52.48; H, 5.59%. Calcd for $C_{19}H_{24}O_4Sn$: C, 52.45; H, 5.56%. IR (KBr); 1695 (C=O), 1680 (C=O), 1665 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=0.06 (9H, s), 1.47 (1H, m), 1.75 (1H, t, J=13 Hz), 2.10 (1H, m), 2.16 (3H, s), 2.23 (1H, m), 3.13 (1H, dd, J=7, 13 Hz), 3.71 (1H, dd, J=7, 10 Hz), 3.93 (3H, s), 7.15—7.25 (1H, m), 7.55—7.65 (2H, m).

2-Allyl-3-hydroxy-1,4-naphthoquinone (**7a**): Yellow crystals from hexane-ether; mp 113—116 °C. MS; m/z 214 (M^+). High resolution MS; Found: m/z 214.0626. Calcd for $C_{13}H_{10}O_3$: M, 214.0629. IR (KBr); 3350 (OH), 1655 (C=O), 1640 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=3.37 (2H, d, J=7 Hz), 5.10 (2H, m), 5.91 (1H, m), 7.35 (1H, s), 7.6—7.8 (2H, m), 8.0—8.2 (2H, m).

2-Acetyl-1,4-naphthalenediol (**8a**): Yellow powders from ethanol; mp 209—210 °C. MS; m/z 202 (M^+). IR (KBr); 3280 (OH), 1600 (C=O) cm^{-1}.

2-Acetyl-1,4-benzenediol (**8b**): Yellow crystals from ethanol; mp 201—203 °C. MS; m/z 152 (M^+). IR (KBr); 3220 (OH), 1600 (C=O) cm^{-1}.

2-Propionyl-1,4-naphthalenediol (**8c**): Yellow crystals from ethanol; mp 182—184 °C. MS; m/z 216 (M^+). High resolution MS; Found: m/z 216.0786. Calcd for $C_{13}H_{12}O_3$: M, 216.0786. IR (KBr); 3360 (OH), 1625 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=1.28 (3H, t, J=7 Hz), 3.03 (2H, q, J=7 Hz), 4.96 (1H, s), 7.55—7.70 (2H, m), 8.10 (1H, d, J=8 Hz), 8.46 (1H, d, J=8 Hz), 13.70 (1H, s).

2-Acetyl-8-methoxy-1,4-naphthalenediol (**8f**): Yellow crystals from ethanol; mp 153—155 °C. MS; m/z 232 (M^+). High resolution MS; Found: m/z 232.0741. Calcd for $C_{13}H_{12}O_4$: M, 232.0736. IR (KBr); 3500 (OH), 3220 (OH), 1620 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=2.66 (3H, s), 4.06 (3H, s), 5.21 (1H, s), 6.96 (1H, d, J=7 Hz), 7.10 (1H, s), 7.56 (1H, dd, J=7, 8 Hz), 7.75 (1H, d, J=8 Hz), 13.50 (1H, s).

2-Acetyl-3-allyl-1,4-benzenediol (**9b**): Pale yellow crystals from ethanol; mp 78—80 °C. MS; m/z 192 (M^+). IR (KBr); 3400 (OH), 1670 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=2.11 (3H, s), 2.93 (2H, d, J=6 Hz), 4.33 (1H, s), 4.5—4.6 (2H, m), 5.5—5.6 (1H, m), 6.2—6.3 (2H, m), 13.80 (1H, s).

3a-Acetyl-2-tributylstannyl-2,3,3a,4,9,9a-hexahydro-1*H*-cyclopenta[*b*]naphthalene-4,9-dione (**10a**): Pale yellow needles from hexane-ether; mp 48—49 °C. MS; m/z 475 (M^+−57, ^{120}Sn), 473 (M^+−57, ^{118}Sn). Found: C, 61.28; H, 7.53%. Calcd for $C_{27}H_{40}O_3Sn$: C, 61.04; H, 7.59%. IR (KBr); 1700 (C=O), 1670 (C=O) cm^{-1}. ^1H NMR($CDCl_3$); δ=0.6—0.8 (15H, m), 1.2—1.4 (6H, m), 1.5—1.6 (7H, m), 1.92 (1H, t, J=13 Hz), 2.1—2.3 (5H, m), 3.12 (1H, dd, J=8, 13 Hz), 3.66 (1H, dd, J=8, 10 Hz), 7.75—7.85 (2H, m), 8.05—8.15 (2H, m). ^{13}C NMR($CDCl_3$); δ=8.2, 13.5, 19.8, 26.5, 27.2, 29.0, 34.5, 40.0, 53.8, 77.7, 127.0, 127.1, 133.7, 134.1, 134.7, 194.3, 196.0, 202.5.

3a-Acetyl-2-tributylstannyl-2,3,3a,4,7,7a-hexahydrindene-4,7-dione (**10b**): Yellow oil. MS; m/z 483 ($M+H^+$, ^{120}Sn), 481 ($M+H^+$, ^{118}Sn). Found: C, 57.12; H, 8.15%. Calcd for

$C_{23}H_{38}O_3Sn$: C, 57.40; H, 7.96%. IR (neat); 1700 (C=O), 1680 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=0.7—0.9 (15H, m), 1.2—1.4 (6H, m), 1.5—1.6 (7H, m), 1.83 (1H, t, J=13 Hz), 2.1—2.3 (5H, m), 2.86 (1H, dd, J=7, 12 Hz), 3.45 (1H, dd, J=6, 10 Hz), 6.7 (2H, m).

2-Acetyl-3-(2-methylallyl)-1,4-naphthoquinone (**11a**): Yellow needles from hexane-ether; mp 53—55 °C. MS; m/z 254 (M^+). High resolution MS; Found: m/z 254.0948. Calcd for $C_{16}H_{14}O_3$: M, 254.0944. ^1H NMR ($CDCl_3$); δ=1.78 (3H, s), 2.45 (3H, s), 3.26 (2H, s), 4.62 (1H, s), 4.83 (1H, s), 7.75—7.85 (2H, m), 8.05—8.15 (2H, m).

2-Acetyl-3-(2-methylallyl)-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (**12a**): Pale yellow needles from hexane-ether; mp 72—74 °C. MS; m/z 227(M^+—43). Found: C, 71.02; H, 5.07%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%. IR (KBr); 1720 (C=O), 1690 (C=O), 1685 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=1.73 (3H, s), 2.37 (3H, s), 2.54 (1H, d, J=16 Hz), 2.75 (1H, d, J=16 Hz), 4.65 (1H, s), 4.81 (1H, s), 7.7—7.8 (2H, m), 7.9—8.0 (2H, m).

2-Hydroxy-3-(2-methylallyl)-1,4-naphthoquinone (**13a**): Yellow crystals from hexane-ether; mp 116—120 °C. MS; m/z 228 (M^+). High resolution MS; Found: m/z 228.0763. Calcd for $C_{14}H_{12}O_3$: M, 228.0786. IR (KBr); 3360 (OH), 1655 (C=O), 1640 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$); δ=1.80 (3H, s), 3.32 (2H, s), 4.73 (1H, s), 4.78 (1H, s), 7.35 (1H, s), 7.65—7.75 (2H, m), 8.05—8.15 (2H, m).

2-Acetyl-3-(2-methylallyl)-1,4-benzenediol (**14b**): Pale yellow crystals from ethanol; mp 78—80 °C. MS; m/z 206 (M^+). High resolution MS; Found: m/z 206.0943. Calcd for $C_{12}H_{14}O_3$: M, 206.0943. ^1H NMR ($CDCl_3$); δ=1.85 (3H, s), 2.58 (3H, s), 4.59 (1H, s), 4.94 (1H, s), 5.28 (1H, s), 6.76 (1H, d, J=8 Hz), 6.94 (1H, d, J=8 Hz), 10.28 (1H, s).

^1H NMR Measurements. 2-Acetyl-1,4-naphthoquinone **1a** (0.03 mmol) and allyltrimethylstannane **2a** (0.04 mmol) were dissolved in benzene-d_6 (0.5 ml) and allowed to stand for 24 h under argon atmosphere in an NMR sample tube. The ^1H NMR measurements were carried out several times during the reaction. Then, the reaction mixture was poured into silica-gel short column, and all fractions were concentrated, dissolved in benzene-d_6, and measured again.

^1H NMR Spectral Data of Products in Benzene-d_6. Compound **15a** (diastereomer A): δ=1.12 (9H, s), 0.93 (1H, dd, J=7, 12 Hz), 0.97 (1H, dd, J=9, 12 Hz), 2.05 (1H, m), 2.26 (1H, m), 2.42 (3H, d, J=2 Hz), 3.13 (1H, ddq, J=6, 11, 2 Hz), 3.74 (1H, m), 7.0—7.2 (2H, m), 8.03 (1H, d, J=7 Hz), 8.44 (1H, d, J=7 Hz).

Compound **15a** (diastereomer B): δ=1.13 (9H, s), 0.90—0.95 (2H, m), 2.44 (3H, d, J=2 Hz), 3.8 (1H, m). Other peaks overlapped and were unable to be analyzed. The ratio A/B was estimated to be 6/1 from integral values of each peak at δ=2.42 and 2.44. Compound **15a** was not isolated.

Compound **16a**: δ=1.66 (3H, s), 2.00 (1H, m), 2.20 (1H, m), 3.25 (1H, dd, J=5, 7 Hz), 4.6—4.7 (2H, m), 5.3—5.4 (1H, m), 7.0—7.2 (2H, m), 7.84 (1H, d, J=8 Hz), 7.96 (1H, d, J=8 Hz).

Compound **17a**: δ=0.24 (9H, s), 2.25 (3H, s), 6.67 (1H, s), 6.9—7.1 (2H, m), 7.95 (1H, d, J=7 Hz), 8.38 (1H, d, J=7 Hz).

Compound **4a**: δ=2.15 (3H, s), 3.14 (2H, d, J=7 Hz), 4.9—5.1 (2H, m), 5.7—5.9 (1H, m), 7.0—7.1 (2H, m), 7.8—7.9 (2H, m).

Compound **5a**: δ=2.09 (3H, s), 2.41 (1H, dd, J=7, 15 Hz), 2.88 (1H, dd, J=7, 15 Hz), 4.9—5.0 (2H, m), 5.8—5.9 (1H, m), 6.9—7.0 (2H, m), 7.7—7.8 (2H, m).

Compound **6a**: δ=—0.03 (9H, s), 1.26 (1H, m), 1.8—2.1 (6H, m), 2.89 (1H, dd, J=8, 13 Hz), 3.64 (1H, dd, J=8, 10 Hz), 7.0—7.1 (2H, m), 8.02 (1H, d, J=7 Hz), 8.15 (1H, d, J=7 Hz).

Compound **8a**: δ=0.95 (1H, s), 2.25 (3H, s), 6.18 (1H, s), 7.2—7.4 (2H, m), 8.21 (1H, d, J=8 Hz), 8.68 (1H, d, J=8 Hz).

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