Regio- and Stereocontrolled Reaction of Arenes with Ethyl Propiolate Catalyzed by Palladium or Platinum Complexes with a Bidentate Phosphine Ligand. An Efficient and Straightforward Synthesis of (1*Z*,3*E*)-1-Aryl-1,3-butadienes

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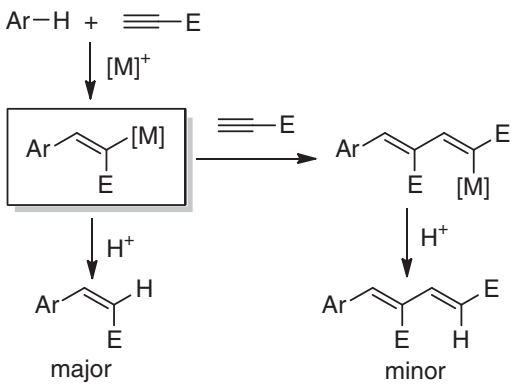
The reaction of mesitylene with ethyl propiolate in the presence of [Pd(dppe)$(OAc)_2$] in TFA at 30 °C for 5 h gave diethyl (2*E*,4*Z*)-4-[(2,4,6-trimethylphenyl)methylene]-2-pentenedioate selectively. Screening several bidentate phosphines ligands showed that dppe and dppm ligands are good for the arylbutadiene formation. This reaction was applied to other electron-rich arenes and found to be effective for synthesis of arylbutadienes and extended π-conjugated molecules. The regio- and stereoselective addition of an arene to propiolate was confirmed by NMR and single-crystal X-ray structural analyses of the products, suggesting that the arylbutadiene formation consisted of *anti* addition of an arene and a metal to the triple bond of ethyl propiolate, followed by *syn* addition to another molecule of ethyl propiolate. Similarly, the reaction of various arenes with ethyl propiolate in the presence of [Pt(dppe)$(OTf)_2$] catalyst gave arylbutadienes selectively. In the Pd- or Pt-catalyzed reaction of arenes with ethyl propiolate, it was found that a bidentate ligand controlled the reaction to lead the formation of arylbutadienes.

Generally C–H bonds are low in reactivity because of their nonpolar and strong nature. Introduction of functional groups into such C–H bonds requires prefunctionalization and therefore results in increasing reaction processes. However, if direct functionalization of the C–H bonds can be conveniently utilized for many synthetic processes, it will be a more efficient process without prefunctionalization and reduce the reaction steps and chemicals. From the viewpoint of green chemistry, such direct functionalization of the C–H bonds attracts much attention to many chemists and has been studied extensively.[1]

Hydroarylation of alkynes can formally be regarded as a reaction in which both aryl and hydrogen moieties of an aromatic compound add across a triple bond.[2] Therefore, hydroarylation of alkynes is one of the most effective methods for direct C–H bond functionalization that provides a convenient, clean, atom-economic and environmentally benign methodology to aryl-substituted alkenes without requiring prefunctionalization of arenes such as halogenation. We have found that the hydroarylation of propiolic acids or propiolates in trifluoroacetic acid (TFA) as solvent proceeds efficiently in the presence of $Pd(OAc)_2$, $PtCl_2$/AgOTf, or $K_2[PtCl_4]$/AgOTf as a catalyst to give *cis*-cinnamic acids or cinnamates regio- and stereoselectively.[3] As shown in Scheme 1, in the hydroarylation reaction, the cationic metal activates the alkyne to give an arylvinyl metal complex via electrophilic aromatic substitution.[4] The vinyl metal complex undergoes protonation to afford a *cis*-arylalkene as a major product. In the $Pd(OAc)_2$-catalyzed hydroarylation reaction, the vinyl palladium complex can add another alkyne to produce an arylbutadiene but this is a minor process.



Scheme 1. Hydroarylation reaction of alkynes.

The formation of the arylbutadiene results in low selectivity of hydroarylation and decreases the yield of hydroarylation products. However, we disclosed that the hydroarylation using a palladium complex with a bidentate phosphine ligand, [Pd(dppe)$(OAc)_2$] (dppe: 1,2-bis(diphenylphosphino)ethane), yielded the arylbutadiene predominantly.[5] Inspired by this result, we have considered the presence of *cis*- and *trans*-forms of the arylvinyl metal complex with an alkyne ligand, where the *trans*-form is considered to be more stable than the *cis*-form due to the steric hindrance according to the experimental results,[3] as shown in Scheme 2. A larger population of the *trans*-form gives the arylalkene by protonation, whereas only the *cis*-form can undergo the alkyne addition leading to the arylbutadiene. We imagined that the presence of the bidentate phosphine ligand controls the equilibrium between the *cis*- and

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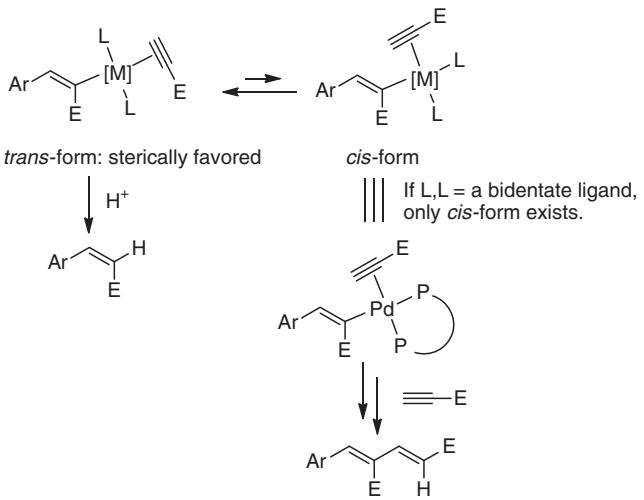
trans-forms and the desirable *cis*-form of the vinyl metal complex is fixed by the bidentate ligand. Addition of the vinyl–metal bond to the alkyne triple bond then takes place to give the arylbutadiene selectively. As a result, double insertion of the alkyne into the aryl–hydrogen bond is achieved.

To verify the ligand effect of bidentate phosphine compounds on the arylbutadiene formation, we examined in detail the reaction of ethyl propiolate with arenes in the presence of Pd or Pt complexes bearing a bidentate phosphine ligand. We herein report our findings concerning the direct formation of arylbutadienes from arenes and ethyl propiolate controlled by Pd or Pt complexes with bidentate phosphines.

Results and Discussion

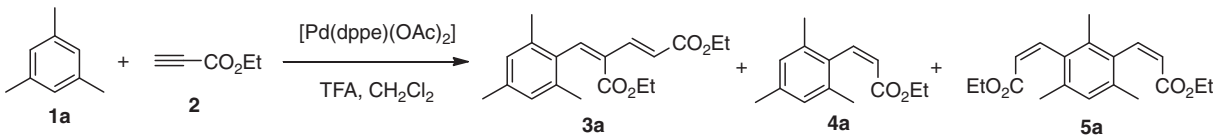
Effect of Bidentate Phosphine Ligands on Pd-Catalyzed Reaction. First, we studied the reaction of mesitylene (**1a**) with ethyl propiolate (**2**) in the presence of $[Pd(dppe)(OAc)_2]$ as a catalyst. TFA was used as a solvent for this reaction because we observed that TFA was effective for the hydroarylation reaction of **2** with arenes.[3] The results are summarized in Table 1. When the reaction of **1a** (1 mmol) and **2** (2 mmol) was conducted in the presence of $[Pd(dppe)(OAc)_2]$ (0.005 mmol) in TFA (1 mL) at 30 °C for 5 h, the desired arylbutadiene **3a** was formed in 68% yield, together with hydroarylation product **4a** (14%) and bis-hydroarylation product **5a** (4%) (Entry 1). As the amount of **1a** was increased to 2 and 3 mmoles, the yield of **3a** increased to 83% (Entries 2 and 3). However, increasing the amount of **2** did not improve the yield of **3a** (Entry 4). Use of an excess amount of **1a** inhibited the formation of **5a** to give higher yields of **3a** and **4a**. The amount of TFA in a mixed solvent of TFA and CH_2Cl_2 also affected the selectivity of **3a** (Entries 5–7). A small amount of TFA was favorable for selective formation of **3a** although the reaction did not proceed in the absence of TFA. As a result, the best result was obtained when 0.25 mL of TFA was used together with 0.75 mL of CH_2Cl_2 (Entry 6). The reactions at 0 and 50 °C gave similar results (Entries 8–10).

Next, we examined the palladium complexes with different ligands using the best reaction conditions described in Entry 6, Table 1. The results are given in Table 2. Bis(diphenylphosphino)methane (dppm) showed a similar effect of the ligand with a high selectivity of **3a** although the yield was not high (Entry 1). Increasing the ratio of TFA improved the yield of **3a** (Entries 2 and 3). Longer alkyl-chained ligands, 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb), resulted in a low selectivity of **3a** (Entries 4 and 5). This result suggests that a ridged structure of the palladium complex is suitable for the formation of arylbutadiene **3a**. 2,2′-Bipyridine (bpy) interrupted the reaction (Entry 6). A combined catalyst of $[Pd(dppm)Cl_2]$ and AgOAc showed the same results as $[Pd(dppm)(OAc)_2]$ (Entries 7–9), while $[Pd(dppm)Cl_2]$ itself reduced the reactivity (Entry 10). The reactions with $[Pd(dppe)Cl_2]$/AgOAc and $[Pd(dppe)(OTf)_2]$ catalysts did not improved the yield of **3a** (Entries 11 and 12). Interestingly, $Pd(OAc)_2$ itself did not show product selectivity in this solvent system (Entry 13) and a mono-



Scheme 2. Effect of bidentate ligand in the hydroarylation reaction.

Table 1. Optimization of Reaction Conditions[a)]



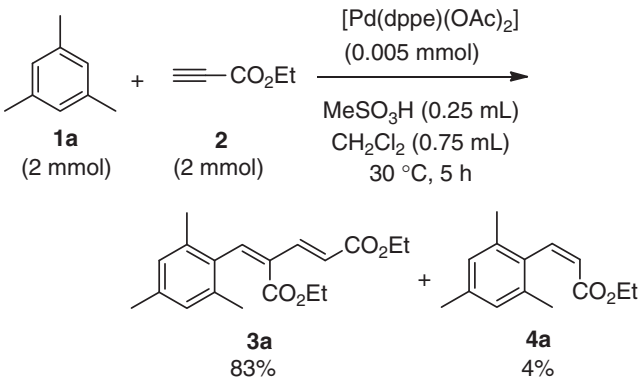
Entry	**1a** /mmol	**2** /mmol	TFA /mL	CH_2Cl_2 /mL	Temp /°C	Time /h	Yield/%[b)]		
							3a	**4a**	**5a**
1	1	2	1	0	30	5	68	14	4
2	2	2	1	0	30	5	83	17	0
3	3	2	1	0	30	5	83	17	0
4	1	3	1	0	30	5	37	0	2
5	2	2	0.5	0.5	30	5	83	16	0
6	2	2	0.25	0.75	30	5	91	9	0
7	2	2	0.1	0.9	30	5	55	2	2
8	2	2	1	0	0	5	86	14	0
9	2	2	1	0	50	2.5	83	17	0
10	2	2	0.25	0.75	0	5	91	5	0

a) Reaction conditions: $[Pd(dppe)(OAc)_2]$ (0.005 mmol), **1a**, **2**, and solvent. b) Yields were determined by GC and based on the least amount of the substrate.

Table 2. Effect of Ligands[a)]

Entry	Catalyst	TFA /mL	CH_2Cl_2 /mL	Yield/%		
				3a	**4a**	**5a**
1	$[Pd(dppm)(OAc)_2]$	0.25	0.75	53	5	2
2	$[Pd(dppm)(OAc)_2]$	0.5	0.5	84	5	0
3	$[Pd(dppm)(OAc)_2]$	1	0	86	6	0
4	$[Pd(dppp)(OAc)_2]$	0.25	0.75	57	23	1
5	$[Pd(dppb)(OAc)_2]$	0.25	0.75	19	29	1
6	$[Pd(bpy)(OAc)_2]$	0.25	0.75	1	3	0
7	$[Pd(dppm)Cl_2]$/AgOAc	0.25	0.75	54	2	3
8	$[Pd(dppm)Cl_2]$/AgOAc	0.5	0.5	81	3	1
9	$[Pd(dppm)Cl_2]$/AgOAc	1	0	85	4	1
10	$[Pd(dppm)Cl_2]$	0.25	0.75	47	1	0
11	$[Pd(dppe)Cl_2]$/AgOAc	0.25	0.75	71	8	0
12	$[Pd(dppe)(OTf)_2]$	0.25	0.75	81	9	0
13	$Pd(OAc)_2$	0.25	0.75	20	37	3
14	$[Pd(PPh_3)_2(OAc)_2]$	0.25	0.75	18	36	3
15	$[Pd(dppe)_2(OAc)_2]$	0.25	0.75	1	0	0

a) Reaction conditions: Pd catalyst (0.005 mmol), mesitylene (2 mmol), ethyl propiolate (2 mmol), TFA, and CH_2Cl_2 at 30 °C for 5 h.



Scheme 3. Hydroarylation in the presence of methanesulfonic acid.

dentate phosphine ligand, PPh_3, was not effective for the formation of **3a** (Entry 14). A palladium complex, $[Pd(dppe)_2(OAc)_2]$, doubly coordinated with dppe inhibited the reaction (Entry 15).

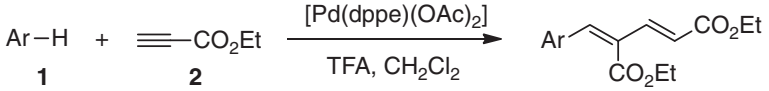
The presence of TFA is essential for this reaction. To verify the effect of the acid, we examined the reaction in the presence of other organic acids such as acetic acid, formic acid, and methanesulfonic acid. Among the acids examined, methanesulfonic acid promoted the reaction (Scheme 3). When the reaction of **1a** with **2** was conducted in the presence of $[Pd(dppe)(OAc)_2]$ in $MeSO_3H$ and CH_2Cl_2 at 30 °C for 5 h, **3a** and **4a** were formed in 83 and 4% yields, respectively.

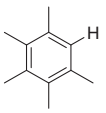
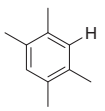
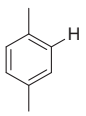
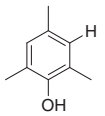
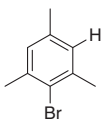
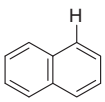
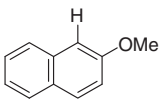
With the optimized reaction conditions in hand, we applied this reaction to other arenes (Table 3). In all cases, the reactions gave arylbutadienes **3** regio- and stereoselectively. In the presence of $[Pd(dppe)(OAc)_2]$, pentamethylbenzene (**1b**) and 1,2,4,5-tetramethylbenzene (**1c**) gave the corresponding arylbutadienes **3** in good to high yields along with a small amount of cinnamates **4** (Entries 1 and 2). In the case of *p*-xylene (**1d**) (Entries 3 and 4), $[Pd(dppm)Cl_2]$/AgOAc gave the better yield of arylbutadine **3d**. 2,4,6-Trimethylphenol (**1e**) and 2-bromomesitylene (**1f**) also gave the corresponding arylbutadines **3e** and **3f** in good yields although a larger amount of TFA was required in the case of **1f** because of lower reactivity of **1f** (Entries 5 and 6). Use of $[Pd(dppm)(OAc)_2]$ improved the selectivity but the yield of **3f** was similar (Entry 7). The same result was observed in the case of naphthalene (**1g**) (Entries 8 and 9). In the case of 2-methoxynaphthalene (**1h**), $[Pd(dppe)(OAc)_2]$ gave **3h** in good yield (Entry 10). In the case of naphthalene (**1g**) and *p*-xylene (**1d**), a larger amount of TFA was required to complete the reaction because of their low reactivity. When a larger amount of TFA was used, $[Pd(dppe)(OAc)_2]$ showed low selectivity while $[Pd(dppm)(OAc)_2]$ did good selectivity. These results indicate that $[Pd(dppm)(OAc)_2]$ is an effective catalyst for less reactive arenes which require a large amount of TFA. In the case of arenes with an electron-withdrawing group, arylbutadienes were not formed since hydroarylation reaction did not take place due to low reactivity. Although the hydroarylation reaction of propiolic acid with benzene or toluene occurred under catalytic conditions using a $K_2[PtCl_4]$/AgOTf catalytic system,[6b,6e] the reactions of **2** with *tert*-butylbenzene did not proceed under the conditions shown in the Entries 3 and 4 of Table 3. This result indicates that the reactivity of Pd falls with the coordination of dppe. In addition, substituted propiolates such as ethyl phenylpropiolate were not effective in the present reaction.

Since this hydroarylation with a bidentate phosphine ligand provides an arylbutadiene, this methodology can be applied to an extended π-conjugated molecule. The products **3a** and **4a** obtained from the reaction of **1a** with **2** also participated in this reaction and afforded **3i** and **3j** in good yields, respectively (Scheme 4). The reaction of **4a** explains clearly that an excess amount of **1a** is required in the reaction of **1a** with **2** to prevent further reaction of **4a**.

Regio- and Stereoselective Formation of Arylbutadienes. The addition of arenes to propiolate **2** under the reaction conditions proceeded regio- and stereoselectively. This fact is

Table 3. The Reaction of **2** with Various Arenes **1** in the Presence of [Pd(dppe)(OAc)$_2$] Catalyst[a)]



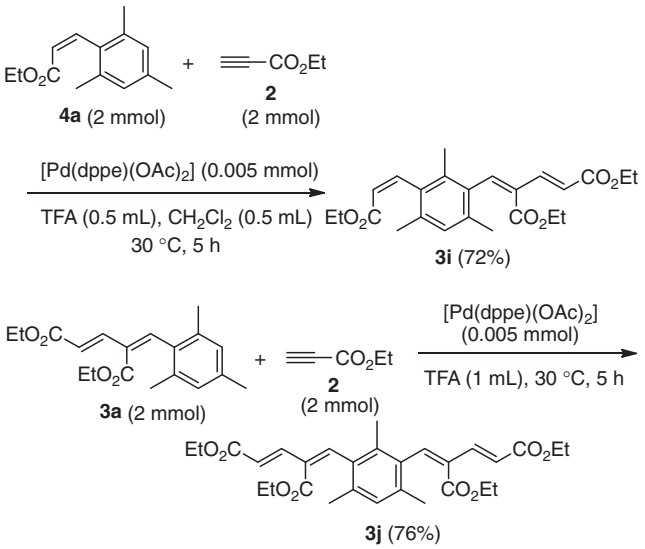
Entry	Arene Ar–H	Solvent/mL		Product and isolated yield/%[b)]			
		TFA	CH_2Cl_2	**3**		**4**	
1[c)]	 **1b**	0.25	0.75	**3b**	82	**4b**	9
2	 **1c**	0.25	0.75	**3c**	76	**4c**	7
3	 **1d**	0.5	0.5	**3d**	40	**4d**	16
4[d),e)]	**1d**	1	0	**3d**	75	**4d**	7
5	 **1e**	0.25	0.75	**3e**	73	**4e**	5
6	 **1f**	1	0.5	**3f**	66	**4f**	12
7[d)]	**1f**	1	0.5	**3f**	69	**4f**	2
8	 **1g**	0.5	0.5	**3g**	53	**4g**	18
9[d),f)]	**1g**	1	0.5	**3g**	67	**4g**	8
10	 **1h**	0.25	0.75	**3h**	70	**4h**	11

a) Reaction conditions: [Pd(dppe)(OAc)$_2$] (0.005 mmol), arene **1** (2 mmol), **2** (2 mmol), TFA, and CH_2Cl_2 at 30 °C for 5 h. b) Yields are based on **2**. c) Pentamethylbenzene (1.1 mmol) was used. d) [Pd(dppm)Cl$_2$] (0.005 mmol) and AgOAc (0.02 mmol) were used. e) *p*-Xylene (3 mmol) was used. f) 10 h.

understood by clarifying the stereochemistry and absolute structure of arylbutadienes **3**. In the ^{1}H NMR spectra of 1-aryl-1,3-butadienes, the coupling constant J value is 15.8–15.9 Hz for vicinal hydrogens of one olefinic double bond, showing that this structure is *trans* configuration, as shown in Figure 1. Concerning another double bond, differential NOE experiments were conducted to determine the stereochemistry. Irradiation of the hydrogen on the 4 position showed 16–20% enhancement in intensity of the vinylic proton at the 2 position, indicating that the hydrogens at the 2 and 4 positions are spatially close (Figure 1). These results show that all arylbutadienes obtained by this study have a (1*E*,3*Z*)-butadiene structure. Furthermore, a single-crystal X-ray structural analysis was conducted. Although most arylbutadienes were oil, fortunately arylbutadiene **3b** from pentamethylbenzene was crystal. A single crystal suitable for an X-ray analysis was obtained by slow evaporation from a solution of arylbutadiene **3b** in EtOH. The ORTEP structure obtained by a single X-ray structural analysis is depicted in Figure 2. From this result, it is clear that **3b** has the (1*E*,3*Z*)-1,3-butadiene structure.

The above structural analyses suggest that the arylbutadiene formation consists of the initial *anti* addition of an arene and a metal to the triple bond of ethyl propiolate and the subsequent *syn* addition to another molecule of ethyl propiolate followed by protonation.

Effect of Bidentate Phosphine Ligands on Pt-Catalyzed Reaction. Since a cationic platinum catalyst showed a high selectivity toward hydroarylation of alkynes compared with a cationic palladium catalyst, arylbutadienes were hardly formed in the Pt-catalyzed hydroarylation reaction.[6] Then, to evaluate the effect of a bidentate phosphine ligand on the arylbutadiene formation, we examined the reaction of arenes and ethyl propiolate in the presence of a platinum catalyst with a bidentate phosphine ligand.



Scheme 4. Application to extended π-conjugated molecules.

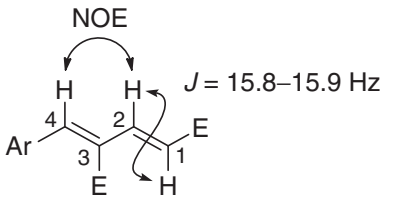


Figure 1. Stereochemistry of 1-aryl-1,3-butadienes.

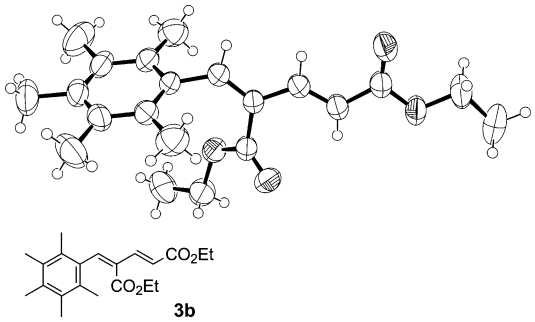
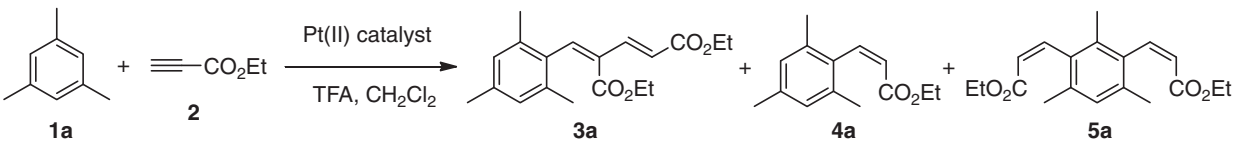


Figure 2. ORTEP representation of **3b**.

Table 4. Optimization of Reaction Conditions for Pt-Catalyzed Reaction of **1a** with **2**[a)]



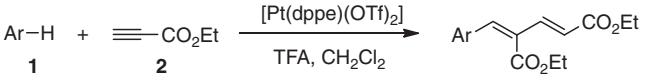
Entry	Catalyst	TFA /mL	CH_2Cl_2 /mL	Yield/%[b)]		
				3a	**4a**	**5a**
1	[Pt(dppm)$(OTf)_2$]	1	0	31	13	15
2	[Pt(dppm)$(OTf)_2$]	0.5	0.5	25	8	15
3	[Pt(dppe)$(OTf)_2$]	0.25	0.75	45	3	3
4	[Pt(dppe)$(OTf)_2$]	1	0	75	12	2
5	[Pt(dppp)$(OTf)_2$]	1	0	73	10	0
6	[Pt(dppp)$(OTf)_2$]	0.5	0.5	66	6	1
7	[Pt(*R*-BINAP)$(OTf)_2$]	1	0	79	16	0
8	[Pt(*R*-BINAP)$(OTf)_2$]	0.5	0.5	84	8	0
9	[Pt(*R*-BINAP)$(OTf)_2$]	0.25	0.75	79	2	0
10	[Pt(COD)Cl_2]/2AgOTf	1	0	0	13	0

a) Reaction conditions: Pt catalyst (0.005 mmol), mesitylene (2 mmol), ethyl propiolate (2 mmol), TFA, and CH_2Cl_2 at 30 °C for 5 h. b) Yields were determined by GC and based on the least amount of the substrate.

To determine optimum conditions, we first examined the reaction of mesitylene and ethyl propiolate in the presence of $Pt(OTf)_2$ complex with bidentate ligands such as dppm, dppe, dppp, and BINAP. The results are given in Table 4. In the case of the dppm ligand, the yields of arylbutadiene **3a** were only 31% and 25%, in TFA solvent and in a mixed solvent of TFA and dichloromethane, respectively (Entries 1 and 2). Although the reaction with the dppe ligand under the same conditions as the Pd-catalyzed reaction did not give a good result (Entry 3), the same reaction in TFA only afforded arylbutadiene **3a** in 75% yield (Entry 4). The dppp ligand showed a similar effect to the dppe ligand to give arylbutadiene **3a** in 73% yield (Entry 5), but use of a mixed solvent of TFA and dichloromethane decreased the yield to 66% (Entry 6). The BINAP ligand as the bidentate ligand gave an excellent effect (Entries 7–9), but the COD ligand did not show a good effect due to its loose coordination (Entry 10).

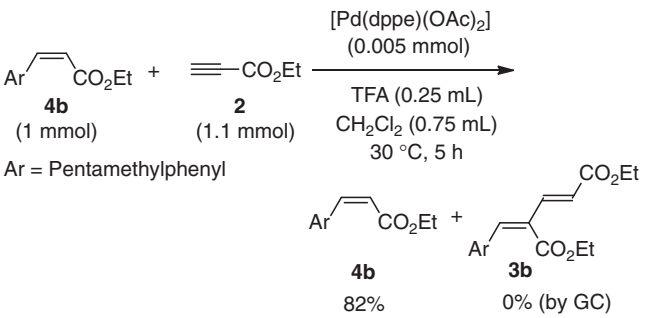
Using the [Pt(dppe)$(OTf)_2$] catalyst which gave good results, we examined the reaction of various aromatic substrates and ethyl propiolate. The results are given in Table 5. Arylbutadiene **3a** was isolated in 72–79% yield in the reactions of mesitylene **1a** with [Pt(dppe)$(OTf)_2$], [Pt(dppp)$(OTf)_2$], and [Pt(*R*-BINAP)$(OTf)_2$] catalysts under conditions similar to mentioning above (Entries 1–3). In the case of pentamethylbenzene (**1b**), the reaction was conducted in a mixed solvent of TFA and dichlorometane due to its low solubility. In any cases of [Pt(dppe)$(OTf)_2$], [Pt(dppp)$(OTf)_2$], and [Pt(*R*-BINAP)$(OTf)_2$] catalysts, arylbutadiene **3b** was obtained in 74–79% yield (Entries 4–6). The reaction with 1,2,4,5-tetramethylbenzene (**1c**) gave arylbutadiene **3c** in 74% yield

Table 5. The Reaction of **2** with Various Arenes **1** in the Presence of $[Pt(dppe)(OTf)_2]$[a)]



Entry	Arene	TFA /mL	CH_2Cl_2 /mL	Product	Yield /%[b)]
1[c)]	**1a**	1	0	**3a**	73
2[c),d)]	**1a**	1	0	**3a**	72
3[c),e)]	**1a**	1	0	**3a**	79
4[f)]	**1b**	1	0.25	**3b**	74
5[d),f)]	**1b**	1	0.25	**3b**	74
6[e)]	**1b**	1	0.25	**3b**	79
7	**1c**	1	0.35	**3c**	74
8[c)]	**1d**	1	0.5	**3d**	32[g)]
9	**1e**	1	0	**3e**	75
10	**1f**	1	0.5	**3f**	75
11	**1g**	1	0.5	**3g**	37

a) Reaction conditions: $[Pt(dppe)(OTf)_2]$ (0.005 mmol), arene **1** (2 mmol), **2** (2 mmol), TFA, and CH_2Cl_2 at 30 °C for 5 h. b) Isolated yields based on **2**. c) An arene **1** (3 mmol) was used. d) $[Pt(dppp)(OTf)_2]$ was used instead of $[Pt(dppe)(OTf)_2]$. e) [Pt(*R*-BINAP)$(OTf)_2$] was used instead of $[Pt(dppe)(OTf)_2]$. f) Pentamethylbenzene (1.1 mmol) was used. g) GC yield.



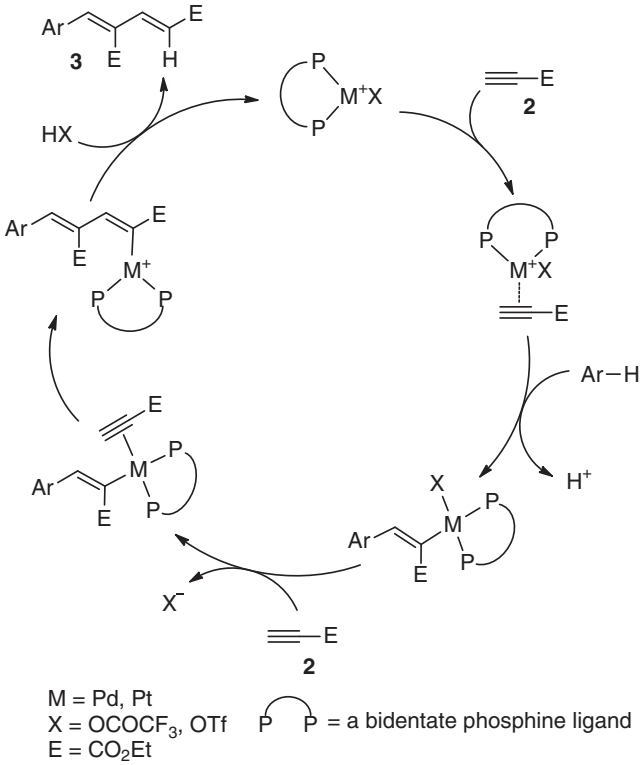
Scheme 5. Attempted reaction of **4b** with **2**.

(Entry 7), but the reaction with *p*-xylene (**1d**) decreased in the yield of arylbutadiene **3d** to 32%, because of its low reactivity (Entry 8). 2,4,6-Trimethylphenol (**1e**) and 2-bromomesitylene (**1f**) also reacted effectively to give arylbutadienes **3e** and **3f** in good yields, respectively (Entries 9 and 10). The reaction with naphthalene (**1b**) resulted in a low yield (Entry 11).

Although the platinum catalyst causes the hydroarylation reaction preferentially as compared with the palladium catalyst, the above-mentioned results show that the formation of arylbutadiene occurs preferentially when the platinum catalyst has a suitable bidentate ligand.

Reaction Mechanism. To check a possibility for the formation of arylbutadienes **3** from hydroarylation products **4**, we examined the reaction of **4b** with **2** (Scheme 5). However, we could not detect the formation of **3b** but found that the starting material **4b** remained unchanged. Therefore, this result suggests that hydroarylation products **4** are not the intermediates for arylbutadienes **3**.

Since arylbutadienes **3** are also generated in low yield in the Pd-catalyzed hydroarylation of **2** without a bidentate ligand,[3,4]



Scheme 6. Possible mechanism for arylbutadiene formation.

it is thought that a similar mechanism holds even in the present reaction. A possible mechanism concerning generation of arylbutadienes **3** is shown in Scheme 6. First, a cationic Pd or Pt catalyst with a bidentate ligand coordinates with ethyl propiolate (**2**) and forms a highly electrophilic alkyne complex, which undergoes aromatic electrophilic substitution with an aromatic compound to give an arylvinylmetal intermediate. If this intermediate causes protonation, hydroarylation product **4** will be generated, but the present reaction affords arylbutadiene **3** predominantly. Therefore, it is thought that the bidentate ligand has two roles: control of protonation and promotion of alkyne insertion. In this vinylmetal intermediate then, ligand exchange with ethyl propiolate occurs to form an alkyne-coordinated intermediate. In this intermediate, since the alkyne and the arylvinyl group exist close due to the presence of the bidentate ligand, insertion of the alkyne to the vinyl–metal bond takes place easily in the *syn* manner. The resulting arylbutadienylmetal intermediate undergoes protonation to generate arylbutadiene **3** with concomitant regeneration of the catalyst. Thus, the stereocontrolled arylbutadiene **3** is formed by the anti addition and the *syn* addition to alkyne **2**.

Conclusion

In conclusion, we have demonstrated that the reaction of arenes with ethyl propiolate in the presence of palladium or platinum catalyst could be controlled by a bidentate phosphine ligand. The bidentate phosphine ligand controls the reaction regio- and stereoselectively to give the arylbutadienes by successive reactions consisting of *anti* addition of an arene and a metal to the triple bond of ethyl propiolate and *syn* addition to another molecule of ethyl propiolate followed by protonation.

Since this reaction provides arylbutadienes as well as π-conjugated aromatic olefins, this methodology will be useful for organic synthesis directed to biological and material science.

Experimental

All chemicals and solvents used in the reaction were commercially available and used as received without further purification. $[Pd(dppe)(OAc)_2]$,[7] $[Pd(dppp)(OAc)_2]$,[8] $[Pd(PPh_3)_2(OAc)_2]$,[9] and $[Pd(dppe)_2(OAc)_2]$[10] were prepared from $Pd(OAc)_2$ and the corresponding phosphine according to the literature. $[PdCl_2(PhCN)_2]$ was prepared from $PdCl_2$ and benzonitrile according to the literature.[11] $[Pd(dppm)Cl_2]$ was prepared from $[PdCl_2(PhCN)_2]$ and dppm according to a reported method.[12] Thin layer chromatography (TLC) analyses were carried out using TLC aluminum sheets (Silica gel 60 F_{254}). Silica gel column chromatography was carried out using Silica Gel 60 (spherical, 63–210 μm). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR using tetramethylsilane (TMS) as an internal standard. Melting points were measured with a YANACO micro melting apparatus and are not corrected. GC analyses were performed on a Shimadzu GC-14B equipped with a flame ionization detector using capillary column (DB-1, 15 m × 0.53 mm i.d. × 1.5 mm film thickness). GC yields were determined using *n*-heptadecane or *n*-pentadecane as an internal standard. Elemental analyses were performed by the Service Center of the Elemental Analysis of Organic Compounds, Faculty of Science, Kyushu University.

Reaction of Mesitylene (1a) with Ethyl Propiolate (2) in the Presence of a Pd or Pt Catalyst. To a Pyrex tube equipped with a magnetic stirring bar were added a Pd or Pt catalyst (0.005 mmol), mesitylene (**1a**), TFA and CH_2Cl_2, and then capped with a septum rubber. After the mixture was stirred on an ice/water bath for 10 min, ethyl propiolate (**2**) was added to the cold mixture (the amounts of starting materials and solvents are described in Tables 1 and 4). Again, the mixture was stirred on an ice/water bath for 5 min and then stirred at 30 °C. After 5 h, *n*-heptadecane (ca. 0.15 g) as an internal standard was added to the reaction mixture. The mixture was poured into water (20 mL), neutralized with $NaHCO_3$, and extracted with Et_2O (20 mL, 10 mL × 2). The ethereal layer was analyzed by GC to determine the yields of the products **3a**, **4a**, and **5a**. These products were isolated and purified by column chromatography on silica gel with EtOAc/hexane as eluent.

In the case of $[Pd(dppm)(OAc)_2]$, the catalyst was prepared in situ from $[Pd(dppm)Cl_2]$ and AgOAc. The effect of the acids was examined by the same conditions as above, except for TFA.

Diethyl (2*E*,4*Z*)-4-[(2,4,6-Trimethylphenyl)methylene]-2-pentenedioate (3a):[3b] Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.15 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 3.99 (q, $J = 7.1$ Hz, 2H, CH_2), 4.25 (q, $J = 7.1$ Hz, 2H, CH_2), 6.22 (d, $J = 15.9$ Hz, 1H, vinyl), 6.83 (s, 2H, aryl), 7.15 (s, 1H, vinyl), 7.46 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.44, 14.24, 20.08, 20.94, 60.49, 60.70, 120.72, 127.81, 132.05, 134.40, 135.15, 137.29, 141.36, 143.06, 166.03, 166.80.

Ethyl (2*Z*)-3-(2,4,6-Trimethylphenyl)-2-propenoate (4a):[3b] Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, $J = 7.1$ Hz, 3H, CH_3), 2.16 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 4.03 (q, $J = 7.1$ Hz, 2H, CH_2), 6.11 (d, $J = 12.0$ Hz, 1H, vinyl), 6.84 (s, 2H, aryl), 7.02 (d, $J = 12.0$ Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.94, 20.11, 21.01, 59.92, 122.77, 127.78, 132.77, 134.44, 136.65, 144.13, 165.47.

Diethyl 2,4,6-Trimethylbenzene-1,3-di[(2*Z*)-2-propenonate] (5a):[3b] Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 1.12 (t, $J = 7.1$ Hz, 6H, CH_3), 2.05 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.03 (q, $J = 7.1$ Hz, 4H, CH_2), 6.12 (d, $J = 11.9$ Hz, 2H, vinyl), 6.88 (s, 1H, aryl), 7.03 (d, $J = 11.9$ Hz, 2H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 17.66, 20.17, 59.90, 122.68, 128.36, 130.97, 132.98, 133.46, 144.40, 165.38.

Genaral Procedure for $[Pd(dppe)(OAc)_2]$- or $[Pt(dppe)(OTf)_2]$-Catalyzed Reaction of an Arene with Ethyl Propiolate (2). After a mixture of $[Pd(dppe)(OAc)_2]$ or $[Pt(dppe)(OTf)_2]$ (0.005 mmol), an arene (2 mmol), TFA, and CH_2Cl_2 was stirred on an ice/water bath for 10 min, ethyl propiolate (**2**) (2 mmol) was added to the cold mixture (the amounts of solvents are described in Tables 3 and 5). Again, the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30 °C. After the reaction, the mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with CH_2Cl_2 (20 mL + 10 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using EtOAc/hexane as eluent, affording arylbutadienes **3**. In the reaction using $[Pd(dppm)Cl_2]$ and AgOAc as the catalyst, the catalyst was prepared by stirring a mixture of $[Pd(dppm)Cl_2]$ (0.005 mmol) and AgOAc (0.02 mmol) in TFA and CH_2Cl_2 at room temperature for 30 min. Then, an arene (2 mmol) was added and the mixture was stirred on an ice/water bath for 10 min. After addition of ethyl propiolate (2 mmol), the mixture was stirred on an ice/water bath for 5 min. Then, the mixture was stirred at 30 °C.

All products were characterized by ^1H and ^{13}C NMR. The stereochemistry of arylbutadiene **3** was determined by coupling constant in ^1H NMR spectra and differential NOE experiments.

Diethyl (2*E*,4*Z*)-4-[(Pentamethylphenyl)methylene]-2-pentenedioate (3b):[3b] Colorless crystals. Mp 79–81 °C (MeOH). ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.12 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 3.97 (q, $J = 7.1$ Hz, 2H, CH_2), 4.25 (q, $J = 7.1$ Hz, 2H, CH_2), 6.20 (d, $J = 15.8$ Hz, 1H, vinyl), 7.26 (s, 1H, vinyl), 7.49 (d, $J = 15.8$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.40, 14.26, 16.19, 16.66, 17.78, 60.47, 60.52, 120.41, 130.36, 132.04, 132.44, 133.98, 134.44, 141.47, 145.25, 166.01, 166.83.

Diethyl (2*E*,4*Z*)-4-[(2,3,5,6-Tetramethylphenyl)methylene]-2-pentenedioate (3c):[3b] Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.06 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 3.95 (q, $J = 7.1$ Hz, 2H, CH_2), 4.25 (q, $J = 7.1$ Hz, 2H, CH_2), 6.22 (d, $J = 15.9$ Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.22 (s, 1H, vinyl), 7.49 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.34, 14.26, 16.63, 19.78, 60.51, 60.54, 120.62, 130.86, 130.92, 133.27, 134.18, 134.93, 141.34, 144.42, 165.99, 166.83.

Diethyl (2*E*,4*Z*)-4-[(2,5-Dimethylphenyl)methylene]-2-pentenedioate (3d):[5] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.17 (q, $J = 7.1$ Hz, 2H, CH_2), 4.24 (q, $J = 7.1$ Hz, 2H, CH_2), 6.08 (d, $J = 15.9$ Hz, 1H, vinyl), 7.02–7.09 (m, 3H, aryl), 7.14 (s, 1H, vinyl), 7.42 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.70, 14.25, 19.34, 20.79, 60.52, 61.17, 120.23, 128.28, 129.94, 130.08, 132.51, 133.74, 133.93, 135.09, 139.90, 142.32, 166.73, 167.29.

Diethyl (2*E*,4*Z*)-4-[(3-Hydroxy-2,4,6-trimethylphenyl)-methylene]-2-pentenedioate (3e):[5] Yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.08 (s, 6H, CH_3), 2.20 (s, 3H, CH_3), 4.00 (q, $J = 7.1$ Hz, 2H, CH_2), 4.25 (q, $J = 7.1$ Hz, 2H, CH_2), 4.77 (br s, 1H, OH), 6.23 (d, $J = 15.9$ Hz, 1H, vinyl), 6.79 (s, 1H, aryl), 7.12 (s, 1H, vinyl), 7.47 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.16, 13.47, 14.23, 15.84, 19.45, 60.58, 60.76, 120.72, 120.79, 122.53, 126.78, 129.20, 133.49, 134.44, 141.37, 142.88, 149.89, 165.99, 166.87.

Diethyl (2*E*,4*Z*)-4-[(3-Bromo-2,4,6-trimethylphenyl)-methylene]-2-pentenedioate (3f):[5] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.99 (q, $J = 7.1$ Hz, 2H, CH_2), 4.24 (q, $J = 7.1$ Hz, 2H, CH_2), 6.25 (d, $J = 15.9$ Hz, 1H, vinyl), 6.92 (s, 1H, aryl), 7.13 (s, 1H, vinyl), 7.46 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.46, 14.26, 19.89, 21.50, 23.88, 60.61, 60.85, 121.44, 125.03, 129.33, 133.84, 133.93, 134.77, 135.06, 137.58, 140.89, 142.10, 165.64, 166.67.

Diethyl (2*E*,4*Z*)-4-(1-Naphthylmethylidene)-2-pentenedioate (3g):[5] Yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, $J = 7.1$ Hz, 3H, CH_3), 1.33 (t, $J = 7.1$ Hz, 3H, CH_3), 4.05 (q, $J = 7.1$ Hz, 2H, CH_2), 4.26 (q, $J = 7.1$ Hz, 2H, CH_2), 6.18 (d, $J = 15.8$ Hz, 1H, vinyl), 7.38–7.58 (m, 5H, naphthyl and vinyl), 7.65 (s, 1H, vinyl), 7.82–7.96 (m, 3H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.56, 14.27, 60.59, 61.14, 120.96, 124.09, 125.07, 126.08, 126.23, 126.69, 128.58, 129.57, 131.20, 132.45, 133.32, 134.25, 138.97, 141.90, 166.67, 167.02.

Diethyl (2*E*,4*Z*)-4-(2-Methoxy-1-naphthylmethylidene)-2-pentenedioate (3h):[5] Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75 (t, $J = 7.1$ Hz, 3H, CH_3), 1.33 (t, $J = 7.1$ Hz, 3H, CH_3), 3.90 (s, 3H, OCH_3), 3.91 (q, $J = 7.1$ Hz, 2H, CH_2), 4.26 (d, $J = 7.1$ Hz, 2H, CH_2), 6.39 (d, $J = 15.8$ Hz, 1H, vinyl), 7.24 (d, $J = 9.2$ Hz, 1H, aryl), 7.35 (dd, $J = 6.9$, 8.1 Hz, 1H, aryl), 7.47 (dd, $J = 6.9$, 8.4 Hz, 1H, aryl), 7.50 (s, 1H, vinyl), 7.59 (d, $J = 15.8$ Hz, 1H, vinyl), 7.78 (d, $J = 8.1$ Hz, 1H, aryl), 7.79 (d, $J = 8.4$ Hz, 1H, aryl), 7.84 (d, $J = 9.2$ Hz, 1H, aryl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.28, 14.23, 56.00, 60.35, 60.41, 112.50, 118.20, 120.29, 123.59, 123.80, 127.04, 128.28, 128.59, 130.73, 132.09, 133.86, 137.64, 142.51, 154.22, 166.18, 166.98.

Diethyl (2*E*,4*Z*)-4-{3-[(1*Z*)-2-(Ethoxycarbonyl)ethenyl]-2,4,6-trimethylbenzylidene}-2-pentenedioate (3i):[5] Colorless viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, $J = 7.1$ Hz, 3H, CH_3), 1.14 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (t, $J = 7.1$ Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.01 (q, $J = 7.1$ Hz, 2H, CH_2), 4.03 (q, $J = 7.1$ Hz, 2H, CH_2), 4.24 (q, $J = 7.1$ Hz, 2H, CH_2), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 6.22 (d, $J = 15.9$ Hz, 1H, vinyl), 6.87 (s, 1H, aryl), 6.99 (d, $J = 11.9$ Hz, 1H, vinyl), 7.15 (s, 1H, vinyl), 7.46 (d, $J = 15.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.54, 13.99, 14.24, 17.77, 20.10, 59.86, 60.49, 60.76, 120.71, 122.89, 128.40, 131.71, 132.27, 133.18, 134.16, 134.18, 134.44, 141.38, 143.11, 143.78, 165.10, 165.96, 166.78.

Tetraethyl 2,4,6-Trimethylbenzene-1,3-bis[(2*E*,4*Z*)-4-(ethoxycarbonyl)-2,4-pentadienoate] (3j):[5] Light yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, $J = 7.1$ Hz, 6H, CH_3), 1.32 (t, $J = 7.1$ Hz, 6H, CH_3), 2.04 (s, 3H, CH_3), 2.15 (s, 6H, CH_3), 4.03 (q, $J = 7.1$ Hz, 4H, CH_2), 4.25 (q, $J = 7.1$ Hz, 4H, CH_2), 6.21 (d, $J = 15.9$ Hz, 2H, vinyl), 6.86 (s, 1H, aryl), 7.11 (s, 2H, vinyl), 7.46 (d, $J = 15.9$ Hz, 2H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.64, 14.25, 17.92, 20.12, 60.56, 60.79, 120.93, 128.53, 132.45, 132.48, 134.62, 134.89, 141.27, 142.47, 165.75, 166.73.

Ethyl (2*Z*)-3-(Pentamethylphenyl)-2-propenoate (4b):[3b] Colorless crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, $J = 7.1$ Hz, 3H, CH_3), 2.14 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.22 (s, 3H, CH_3), 4.02 (q, $J = 7.1$ Hz, 2H, CH_2), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 7.13 (d, $J = 11.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.95, 16.35, 16.74, 17.59, 59.76, 122.09, 129.73, 131.87, 133.20, 133.93, 146.48, 165.39.

Ethyl (2*Z*)-3-(2,3,5,6-Tetramethylphenyl)-2-propenoate (4c):[3b] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (t, $J = 7.1$ Hz, 3H, CH_3), 2.08 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 4.00 (q, $J = 7.1$ Hz, 2H, CH_2), 6.14 (d, $J = 11.9$ Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.09 (d, $J = 11.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.86, 16.47, 19.93, 59.80, 122.44, 130.21, 130.51, 133.02, 135.69, 145.59, 165.43.

Ethyl (2*Z*)-3-(2,5-Dimethylphenyl)-2-propenoate (4d):[3b] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, $J = 7.1$ Hz, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.09 (q, $J = 7.1$ Hz, 2H, CH_2), 6.00 (d, $J = 12.1$ Hz, 1H, vinyl), 7.00–7.07 (m, 2H, aryl), 7.08 (d, $J = 12.1$ Hz, 1H, vinyl), 7.12 (s, 1H, aryl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.92, 19.29, 20.85, 60.02, 120.99, 129.06, 129.24, 129.52, 132.59, 134.44, 134.86, 142.81, 166.07.

Ethyl (2*Z*)-3-(3-Hydroxy-2,4,6-trimethylphenyl)-2-propenoate (4e):[3b] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (t, $J = 7.1$ Hz, 3H, CH_3), 2.09 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 4.04 (q, $J = 7.1$ Hz, 2H, CH_2), 4.65 (br s, 1H, OH), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 6.79 (s, 1H, aryl), 7.00 (d, $J = 11.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 12.95, 13.93, 15.84, 19.51, 59.99, 120.23, 121.93, 122.72, 126.03, 129.09, 134.20, 144.07, 149.77, 165.42.

Ethyl (2*Z*)-3-(3-Bromo-2,4,6-trimethylphenyl)-2-propenoate (4f):[3b] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, $J = 7.1$ Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.02 (q, $J = 7.1$ Hz, 2H, CH_2), 6.13 (d, $J = 11.9$ Hz, 1H, vinyl), 6.93 (s, 1H, aryl), 7.02 (d, $J = 11.9$ Hz, 1H, vinyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.88, 19.91, 21.24, 23.91, 60.07, 123.24, 125.02, 129.27, 133.18, 134.34, 134.58, 136.92, 143.59, 165.17.

Ethyl (2*Z*)-3-(1-Naphthyl)-2-propenoate (4g):[3b] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, $J = 7.1$ Hz, 3H,

CH_3), 4.00 (q, $J = 7.1$ Hz, 2H, CH_2), 6.23 (d, $J = 12.1$ Hz, 1H, vinyl), 7.41–7.50 (m, 4H, naphthyl), 7.54 (d, $J = 12.1$ Hz, 1H, vinyl), 7.80–7.90 (m, 3H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.77, 60.09, 122.77, 124.36, 124.95, 125.79, 126.19, 126.48, 128.49, 128.66, 131.04, 133.00, 133.22, 141.80, 165.88.

Ethyl (2*Z*)-3-(2-Methoxy-1-naphthyl)-2-propenoate (4h): Light yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 7.1$ Hz, 3H, CH_3), 3.90 (q, $J = 7.1$ Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 6.32 (d, $J = 11.9$ Hz, 1H, vinyl), 7.26 (d, $J = 9.0$ Hz, 1H, naphthyl), 7.26 (d, $J = 11.9$ Hz, 1H, vinyl), 7.32 (dd, $J = 6.9$, 8.1 Hz, 1H, naphthyl), 7.42 (dd, $J = 6.9$, 8.4 Hz, 1H, naphthyl), 7.77 (d, $J = 8.1$ Hz, 1H, naphthyl), 7.77 (d, $J = 8.4$ Hz, 1H, naphthyl), 7.81 (d, $J = 9.0$ Hz, 1H, naphthyl). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.62, 56.27, 59.84, 112.77, 119.19, 123.51, 123.94, 124.28, 126.53, 128.16, 128.63, 129.68, 131.91, 137.44, 153.52, 165.94. MS (EI, *m*/*z*): 256 (M^+, 40), 225 (15), 211 (15), 197 (33), 183 (100), 168 (38), 153 (29), 139 (44). IR (neat, cm^{-1}): 3058 (w), 2980 (m), 2840 (w), 1725 (n (C=O), s), 1623 (m), 1592 (m), 1510 (m), 1466 (m), 1268 (s), 1184 (s), 1086 (m), 1025 (m), 808 (m), 749 (m). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%. Found: C, 75.00; H, 6.30%.

A Single-Crystal X-ray Anaylsis of 3b. A suitable single crystal of **3b** for an X-ray analysis was obtained by slow evaporation of a solution of **3b** in EtOH. Data were collected on a Rigaku Saturn724 diffractometer using multilayer mirror monochromated Mo Kα radiation. All diagrams and calculations were performed using the CrystalStructure[13] crystallographic software package except for refinement, which was performed using SHELXL-97.[14] Crystal data: $C_{21}H_{28}O_4$, $M_r = 344.45$, triclinic, space group $P\bar{1}$ (#2), $a = 8.178(3)$ Å, $b = 11.007(5)$ Å, $c = 11.659(5)$ Å, $\alpha = 103.952(6)°$, $\beta = 92.334(5)°$, $\gamma = 98.757(7)°$, $V = 1003.4(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.140$ g cm^{-3}, Mo Kα radiation $\mu = 0.774$ cm^{-1}, 4505 reflections measured [($I > 2.00\sigma(I)$), 226 variables, $R1$ ($I > 2.00\sigma(I)$) = 0.0687, R (all reflections) = 0.1015, $wR2$ (all reflections) = 0.2436, goodness of fit indicator = 1.058. The details of the X-ray structure determination is described in Supporting Information. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 902760 for compound **3b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

NOE difference spectra of **3b–3j** and details of the X-ray structure determination of **3b**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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