Novel Pd(II)- and Pt(II)-Catalyzed Regio- and Stereoselective *trans*-Hydroarylation of Alkynes by Simple Arenes

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Abstract: Efficient *trans*-hydroarylation of alkynes by simple arenes has been realized regio- and stereoselectively at room temperature in the presence of Pd(II) or Pt(II) catalysts and a mixed solvent containing trifluoroacetic acid (TFA). Various arenes undergo *trans*-hydroarylation selectively across terminal and internal C−C triple bonds—including those conjugated to CHO, COMe, CO_2H, and CO_2Et groups, affording kinetically controlled *cis*-arylalkenes predominantly in most cases, especially, in good yields for electron-rich arenes and activated alkynes. The formation of arene/alkyne 1/2 or 2/1 adducts as side products is dependent on the arenes' and alkynes' substituents, which can be suppressed in some cases by changing the catalyst, catalyst concentration, and reaction time. The Pt(II) system, $PtCl_2$/2AgOAc/TFA, shows lower catalytic activity than $Pd(OAc)_2$/TFA, but higher selectivity, giving higher yields of adducts at the same conversion. On the basis of several isotope experiments and control reactions, a possible mechanism involving electrophilic metalation of aromatic C−H bonds by in-situ-generated cationic Pd(II) and Pt(II) species leading to intermolecular *trans*-arylpalladation to alkynes has been discussed.

Introduction

Catalytic activation of aromatic C−H bonds leading to useful organic reactions such as new C−C bond formation is of considerable interest for the chemical and pharmaceutical industries, and remains a challenge to chemists.[1] It would provide simple, clean, and economic methods for making aryl-substituted compounds directly from simple arenes since no prefunctionalization such as halogenation is involved. The catalytic systems for such a purpose have been sought for many years, although there are many examples of stoichiometric reaction of aromatic C−H bonds with transition metal compounds.[1b] The few available catalytic systems[1−3] based on transition metals activate aromatic C−H bonds mainly through the following routes:

(I) Chelation-assisted insertion of low-valent metals such as Ru(0)[2a] into aromatic C−H bonds in hydroarylation of C−C triple bonds. This involves the coordination of an arene's substituent to a transition metal complex followed by oxidative insertion into an *ortho*-aromatic C−H bond, resulting in the addition to multiple C−C bonds (Scheme 1).[2a] These systems are very useful in the activation of aromatic C−H bonds; however, they are apparently limited to functionalized arenes such as aromatic ketones at high reaction temperatures.

(II) Electrophilic metalation of aromatic C−H bonds by Pd(II) complexes to give σ-aryl-Pd complexes (**A** in Scheme 2) in oxidative coupling of arenes with olefins in acetic acid.[3] The σ-aryl-Pd complexes undergo *cis*-arylpalladation to C−C double bonds followed by Pd β-hydride elimination to give *trans*-arylalkenes in acetic acid (route a in Scheme 2). For this system, in situ regeneration of Pd(II) from Pd(0) by oxidants is the crucial step for the efficient catalysis, and turnover number (TON) is still not high enough for possible industrial applications.

On continuing our search for efficient catalytic systems for aromatic C−H bond activation and extending our coupling reaction of arenes with olefins[3] to the coupling with terminal alkynes, we found the reaction of arenes with alkynes in the presence of TFA as a solvent gives addition products instead of the expected coupling product.[3i]

We report herein that efficient addition of arenes to terminal and internal alkynes (route b in Scheme 2) has been realized regio- and stereoselectively at room temperature in the presence of Pd(II) or Pt(II) catalysts, and affording thermodynamically unfavorable *cis*-arylalkenes predominantly in most cases. The reaction may involve the formation of σ-aryl-Pd complexes through metalation of aromatic C−H bonds by in-situ-generated highly electrophilic Pd(II) and Pt(II) cationic species[3,4] (possibly as **C** in Scheme 2) in TFA. The reaction represents a useful synthetic protocol to form *cis*-arylalkenes from simple electron-rich arenes and alkynes in one step.

(1) (a) Shilov, E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Kakiuchi, F.; Murai, S. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 47−79. (c) Fujiwara, Y.; Jintoku, T.; Takaki, K. *CHEMTECH* **1990**, 636. (d) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (e) Trost, B. M. *Science* **1991**, *278*, 1471.

(2) (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 681. (c) Hong, P.; Cho, B.; Yamazaki, H. *Chem. Lett*. **1980**, 507. (d) Hong, P.; Cho, B.; Yamazaki, H.; *Chem. Lett.* **1979**, 339. (e) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782 (f) Christian, P. L.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 6616.

(3) (a) Moritani, I.; Fujiwara, Y. *Tetrahedron Lett*. **1967**, 1119. (b) Fujiwara, Y.; Moritani, I.; Danno, S.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166. (c) Asano, R.; Moritani, I.; Fujiwara, Y.; Teranishi, S. *Chem. Commun.* **1970**, 1293. (d) Fujiwara, Y.; Asano, R.; Moritani, I.; Teranishi, S. J. *J. Org. Chem.* **1976**, *41*, 1681. (e) Fujiwara, Y.; Takaki, K.; Taniguchi, Y. *Synlett* **1996**, 591. (f) Fuchita, Y.; Hiraki, K.; Kamogawa, Y.; Suenaga, M.; Toggoh, K.; Fujiwara, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1081. (g) Lu, W.; Yamaoka, Y.; Taniguchi, Y.; Kitamura, T.; Fujiwara, Y. *J. Organomet. Chem*. **1999**, *586*, 290. (h) Jia, C.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Org. Lett*. **1999**, *1*, 2097. (i) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992.

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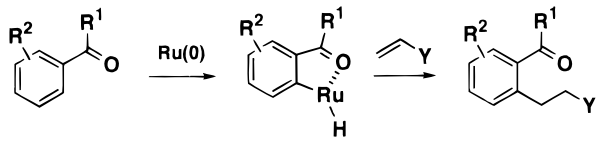
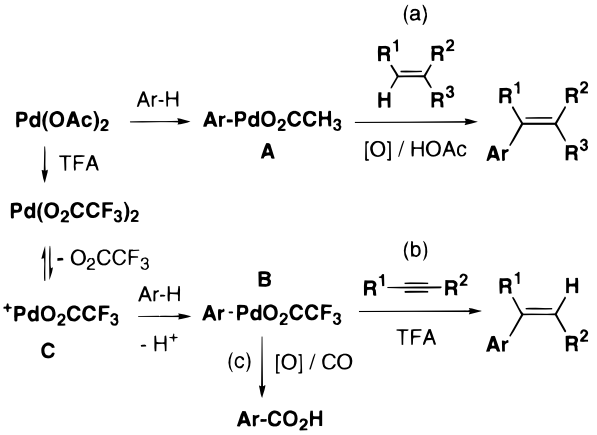
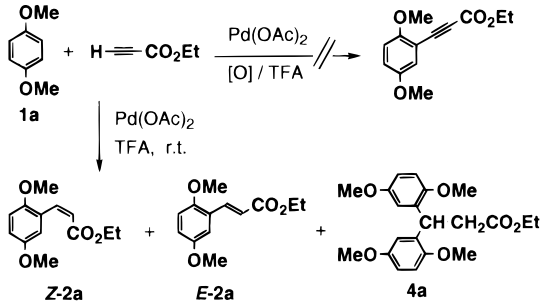
Scheme 1. Chelation-Assisted Ru(0)-Catalyzed Addition



Scheme 2. Pd-Catalyzed C−C Bond Formation Reactions Involving Electrophilic Metalation of Aromatic C−H Bonds



Scheme 3. Pd-Catalyzed Reaction of *p*-Dimethoxybenzene **1a** with Ethyl Propiolate in TFA



Results and Discussion

In the course of our studies of oxidative coupling of arenes with olefins, the possibility to extend the coupling reaction to terminal alkynes was investigated by reacting *p*-dimethoxybenzene (**1a**) with ethyl propiolate in the presence of an oxidant and a catalytic amount of $Pd(OAc)_2$ in TFA (Scheme 3). Instead of the expected coupling product ethyl 3-(2,5-dimethoxyphenyl)-propiolate, the reaction gave (2*Z*)-ethyl 3-(2,5-dimethoxyphenyl)-2-propenoate (*Z*-**2a**) (J_{H-H} = 12.3 Hz) as the main product, together with small amounts of the corresponding *E*-isomer (*E*-**2a**) (J_{H-H} = 16.2 Hz) and an arene/alkyne 2/1 adduct, ethyl 3-bis(2,5-dimethoxyphenyl)propionate (**4a**). Apparently, the compounds *Z*-**2a** and *E*-**2a** (1/1 adducts) resulted from monoaddition of the arene to the alkyne, and **4a** resulted from subsequent addition of another molecular arene to **2a** (this has been confirmed by addition reaction of arenes to alkenes in Table 5). The addtion reaction proceeds smoothly regardless of whether oxidants such as *t*-BuOOH and benzoquinone were employed. However, the reaction did not occur without either TFA or $Pd(OAc)_2$.

(4) (a) Brainard, M. W.; Nutt, W. R.; Lee, T. R.; Whitesides, G. M. *Organometallics* **1988**, *7*, 2379. (b) Clark, F. R. S.; Norman, R. O. C.; Thommas, C. B.; Willson, J. S. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1289. (c) White, S.; Bennett, B. L.; Roddick, D. M. *Organometallics* **1999**, *18*, 2536. (d) Peters, R. G.; Shannon, S.; Roddick, D. M. *Organometallics* **1998**, *17*, 4493. (e) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (f) Swang, O.; Blom, R.; Ryan, O.; Faegri, K. *J. Phys. Chem.* **1996**, *100*, 17334.

Table 1. Pd-Catalyzed Addition of **1a** to Ethyl Propiolate[a]

			yield (%)[b]		
entry	catalyst (mol %)	time (h)	(*Z*)-**2a**	(*E*)-**2a**	**4a**
1	$Pd(OAc)_2$ (0.1)	180	68	4	7
2	$Pd(OAc)_2$ (1)	45	72(56)	6	5
3	$Pd(OAc)_2$ (5)	27	26	15	2
4	$Pd(OAc)_2$ (5)	70	<3	5	(31)
5[c]	$Pd(OAc)_2$ (1)	48	58	3	3
6	$Pd(OAc)_2$ (1) + $P[C_6H_3(OMe)_2]_3$ (1)	45	70	5	6
7[c]	$Pd(OAc)_2$ (1) + PPh_3 (4)	45	41	trace	
8	$Pd(PPh_3)_4$ (2)	48	5	trace	
9	Pd (5%)/carbon (5)	48	8	trace	
10	$Pd(acac)_2$ (1)	48	68	3	2
11	$PdCl_2$ (1)	48	36	3	<1
12	$Pd(O_2CCF_3)_2(PPh_3)_2$ (1)	48	69	5	6
13[d]	$Pd(O_2CCF_3)_2(PPh_3)_2$ (1)	48	<3	trace	
14[e]	$PdCl_2$ (1) + AgO_3SCF_3 (2)	48	10	trace	
15	none	60	trace		

[a] Reaction conditions: **1a** (30 mmol), ethyl propiolate (5 mmol), TFA (4 mL), rt. [b] GC yield (isolated yields in parentheses) based on the alkyne. [c] 10 mmol of the arene employed. [d] AcOH (4 mL) + TFA (0.5 mL) used as the solvent and CF_3CO_2Na (0.025 mmol) added. [e] CH_2Cl_2 (4 mL) + CF_3SO_3H (0.5 mL) used as the solvent.

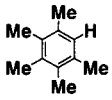
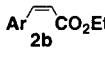
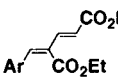
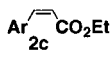
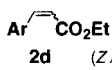
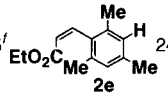
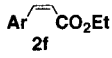
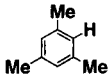
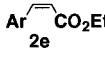
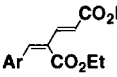
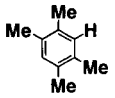
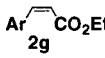
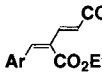
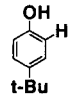
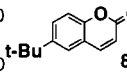
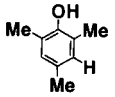
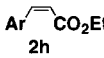
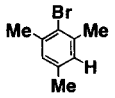
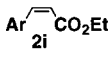
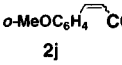
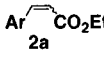
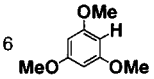
Optimization of Reaction Conditions. Prior to surveying the scope of this addition reaction, the reaction conditions were optimized and results are listed in Table 1. Pd(II) catalysts such as $Pd(OAc)_2$, $Pd(O_2CCF_3)(PPh_3)_2$, and $Pd(acac)_2$ showed higher catalytic activity than Pd(0) catalysts such as Pd/carbon and $Pd(PPh_3)_4$ (see entries 2, 8, 9, 10, and 12 in Table 1). The reaction was enhanced greatly by increasing the amount of $Pd(OAc)_2$, (from 0.1% to 1%, entries 1 and 2 in Table 1). When it was increased to 5%, the 2/1 adduct **4a** was obtained as the main product (entry 4). This means whether the reaction gives 1/1 or 2/1 adducts as the main product can be controlled by the concentration of $Pd(OAc)_2$. Higher concentration of Pd(II) facilitates the overall reaction. The tris(2,6-dimethoxyphenyl)-phosphine was added (1 equiv to Pd, entry 6) to the system in order to improve the addition reaction,[5c,6] but very little effect was found. However, adding more phosphine (4 equiv to Pd, entry 7) decreased the catalytic activity of the system, presumably because of blocking of the coordination sites of Pd(II). The best results were obtained with $Pd(OAc)_2$/TFA and $Pd(O_2CCF_3)_2(PPh_3)_2$/TFA systems (entries 2 and 12). The attempts to reduce the amount of TFA used in the reaction or to use other Pd(II) cationic system such as $PdCl_2/CF_3SO_3Ag$ only resulted in low yields (entries 13 and 14). Addition of a small amount of CH_2Cl_2 (one-fourth to TFA by volume) to the reaction system to improve the solubility of reactants had no detrimental effect on the reaction.

Hydroarylation of Terminal Acetylenes. The scope and generality of this reaction have been explored first using various commercially available arenes and several terminal acetylenes (Scheme 4, Tables 2 and 3). The addition of the arenes to ethyl

(5) (a) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: New York, 1995; pp 1−18. (b) Carri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (c) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (d) Little, A. F.; Fu, G. C. *J. Org. Chem.* **1998**, *64*, 10. (e) Tao, W.; Nesbitt, S.; Heck, R. F. *J. Org. Chem.* **1990**, *55*, 66.

(6) (a) Zeijden, A.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563. (b) Zargarrian, D.; Alper, H. *Organometallics* **1993**, *12*, 712. (c) Cacchi S.; Fabrizi, G.; Marinelli F.; Moro L.; Pace P. *Tetrahedron* **1996**, 10225. (d) Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* **1984**, *25*, 3137. (e) Cacchi, S.; Fabrizi, G.; Marinelli, F.; Moro, L.; Pace, P. *Synlett* **1997**, 1367. (f) Yanagihara, N.; Lambert, C.; Iritani, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2753. (g) Lu, X.; Zhu, G.; Ma, S. *Tetrahedron Lett.* **1992,** *33*, 7205.

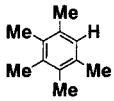
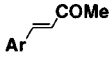
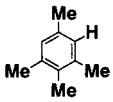
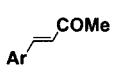
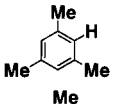
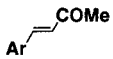
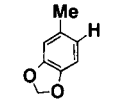
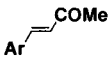
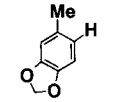
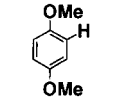
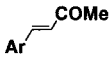
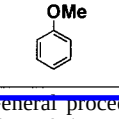
Table 2. Pd- and Pt-Catalyzed Addition of Arenes to Ethyl Propiolate[a]

Entry	Ar-H	Time (h)	Product and yield[b]
1		2	 85%  6%
2[c]		24	2b 95% 3a 0%[d]
3		48	 (45%)
4		24	 (45%) 2d (Z / E = 2)
5[f]		24	 62% 2f
6[e]		24	 49%  8%
7[f]		24	2e (63%) 2f (5%) 3b (11%)
8[g]		29	2e (13%) 2f (44%) 3b (10%)
9		20	 45%  12%
10		40	 51%
11[e]		40	8 (71%)
12		48	 57% 2h
13		48	 (46%) 2i
14		12	 10% (Z / E = 4) (p-MeOC$_6$H$_4$)$_2$CHCH$_2$CO$_2$Et 4b 38%
15[e]		45	 (78%) (Z / E = 8) Ar$_2$CHCH$_2$CO$_2$Et 4a (7%)
16		2	Ar$_2$CHCH$_2$CO$_2$Et 4c 30%

[a] General procedure was followed: arene (10 mmol), ethyl propiolate (5 mmol), $Pd(OAc)_2$ (0.05 mmol), TFA (4 mL), and CH_2Cl_2 (1 mL) at room temperature. [b] Isolated yield (GC yield in parentheses) based on the acetylene. [c] $PtCl_2$ (0.25 mmol) + AgOAc (0.5 mmol) used as catalyst. [d] Yield determined by ^{1}H NMR spectrum. [e] Arene (30 mmol) added. [f] Arene (3.4 mmol) and alkyne (5 mmol) used, and the yield based on the arene. [g] Arene (3.4 mmol) and alkyne (10 mmol) used, and the yield based on the arene.

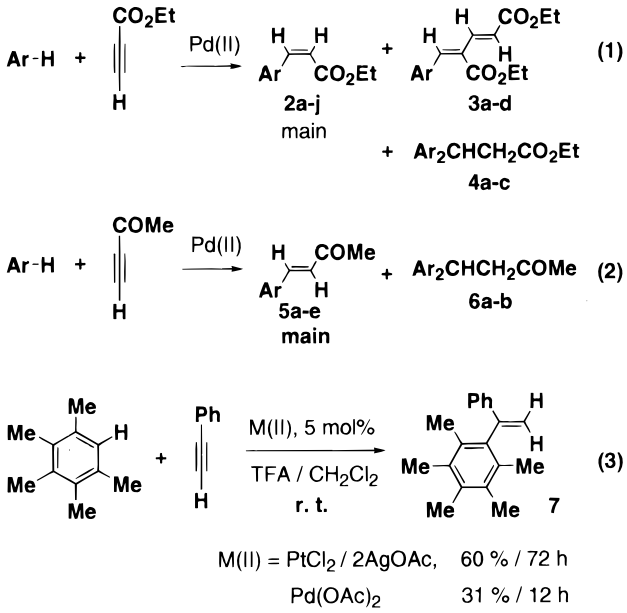
propiolate gave *cis*-adducts, (2*Z*)-ethyl 3-aryl-2-propenoates **2a**−**c**,**e**−**i** (J_{H-H} = 11.7 ± 0.6 Hz), predominantly in most cases (entries 1−15 in Table 2). The corresponding *trans*-isomers as the minor product were isolated (entry 15 in Table 2) or identified in the mixture of adducts by ^{1}H NMR (J_{H-H} = 15.9−16.5 Hz) in some cases (entries 4 and 14 in Table 2). Arene/alkyne 1/2 adducts, (2*E*,4*Z*)-4-(ethoxycarbonyl)-5-aryl-2,4-pentadienoates such as **3a**−**c,** as the minor products were observed in the reaction (e.g., entries 1, 6−9 in Table 2), and also arene/alkyne 2/1 adducts, ethyl 3-bisarylpropionates **4b**,**c**, were found to be the main products in some cases (entries 14 and 16 in Table 2).

Table 3. Pd-Catalyzed Addition of Arenes to 3-Butyne-2-one[a]

Entry	Ar-H	$Pd(OAc)_2$, mol % / Time (h)	Product and yield[b]
1		1% / 2 h	 5a 92%
2[c]		0.05% / 51h	5a (85%)
3[c]		0.02% / 96 h	5a (90%) (TON=4500)
4		1% / 2.5 h	 5b 72%
5[d]		1% / 27 h	5b 86%
6		1% / 24 h	 5c 65%
7[e]		1% / 5 h	5c 80%
8		1% /1 h	 5d 40% (65%) Ar$_2$CHCH$_2$COMe 6a (6%)
9		1% / 15 h	5d (5%) 6a (45%)
10		1% / 24 h	 5e 36%
11		1% / 12 h	(MeO-C$_6$H$_4$-)$_2$CHCH$_2$COMe 6b 27%

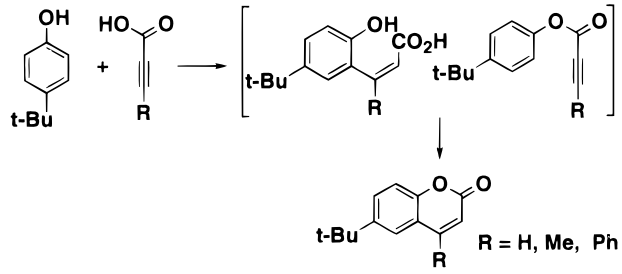
[a] General procedure was followed: arenes (10 mmol), alkyne (5 mmol), TFA (4 mL), and CH_2Cl_2 (1 mL), rt. [b] Isolated yield (GC yield in parentheses) based on acetylene. [c] Five times of reactants and solvents employed except the catalyst. [d] Arene (5 mmol) and alkyne (10 mmol) used, and the yield determined by ^{1}H NMR and based on arene. [e] Arene (5 mmol) and alkyne (7 mmol) used, and the yield based on arene was determined by ^{1}H NMR.

Scheme 4. Hydroarylation of Terminal Alkynes

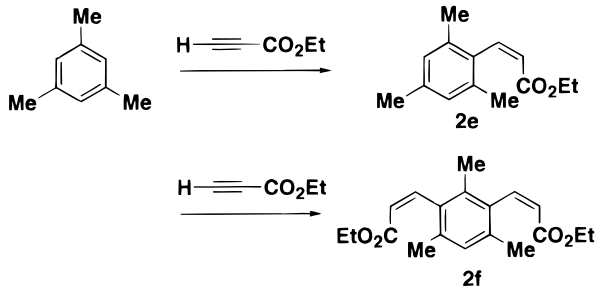


The reaction exhibited very good chemiselectivity with unprotected OH and Br substituents in arenes, all proving to be compatible (entries 10−13). A coumarin was obtained from the reaction of *p-tert*-butyl phenol with ethyl propiolate (entries 10

Scheme 5. Formation of Coumarins



Scheme 6. Formation of Dienes



and 11 in Table 2), apparently resulting from first addition of the phenol to the alkyne followed by cyclization via ester exchange (Scheme 5).[7] When the *ortho*-positions of a phenol were occupied by two methyl groups, the reactions gave a 1/1 adduct such as **2h** (entry 12 in Table 2). The reaction of mesityl bromide with ethyl propiolate afforded 1/1 adduct (2*Z*)-ethyl 3-(2,4,6-trimethyl-3-bromophenyl)-2-propenoate (entry 13 in Table 2). No corresponding debrominated adduct or debrominated arene was isolated or observed by ^{1}H NMR from the reaction mixture, suggesting that the catalytic cycle may not involve Pd(0) species.

A diene, (2*Z*)-ethyl 3-{2,4,6-trimethyl-3-[(*Z*)-2-ethoxycarbonylethylenyl)]phenyl]}propenoate (**2f**), was obtained from the reaction of (2*Z*)-ethyl 3-mesitylpropenoate (**2e**) with 1.5 equiv of ethyl propiolate (entry 5 in Table 2) or directly from the reaction of mesitylene with ethyl propiolate (entry 8 in Table 2). This provides a new and simple route to the aryldienes from simple arenes and alkynes (Scheme 6), and similar compounds could be prepared from diiodoarenes by the Heck reaction.[5e]

The reaction of the arenes with 3-butyn-2-one afforded exclusively *trans*-adducts, (3*E*)-4-aryl-3-buten-2-ones **5a**−**e** (J_{H-H} = 16.5 ± 0.3 Hz), as the only products in most cases (entries 1−8 and 10 in Table 3 and eq 2 in Scheme 4). The arene/alkyne 2/1 adducts, 4-bisaryl-butan-2-ones **6a**,**b**, were found in the cases where alkoxyarenes were used (entries 8, 9, and 11). The formation of arene/alkyne 1/1 to 2/1 adducts occurred in a sequential fashion; further addition of the arene to 1/1 adducts gave the 2/1 adducts as shown in Figure 1.

A close comparison of the adducts (in Tables 2 and 3) and the related arenes and alkynes reveals that whether the reaction gives 1/1 or 2/1 adducts as the main products depends mainly on the arenes' substituents. The arenes having alkoxyl substituents generally tend to proceed to 2/1 arene/acetylene adducts, especially for less hindered arenes such as anisole. The reaction of anisole with either ethyl propiolate or 3-butyn-2-one affords mainly the 2/1 arene/alkyne adducts with methoxyl in the *para*-

(7) For related catalytic C−H bond activation reactions involving phenolic functions as a directing group, see: (a) Kokubo, K.; Matsumasa, K.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 4564. (b) Trost, B. M.; Toste F. D. *J. Am. Chem. Soc*. **1996**, *118*, 6305.

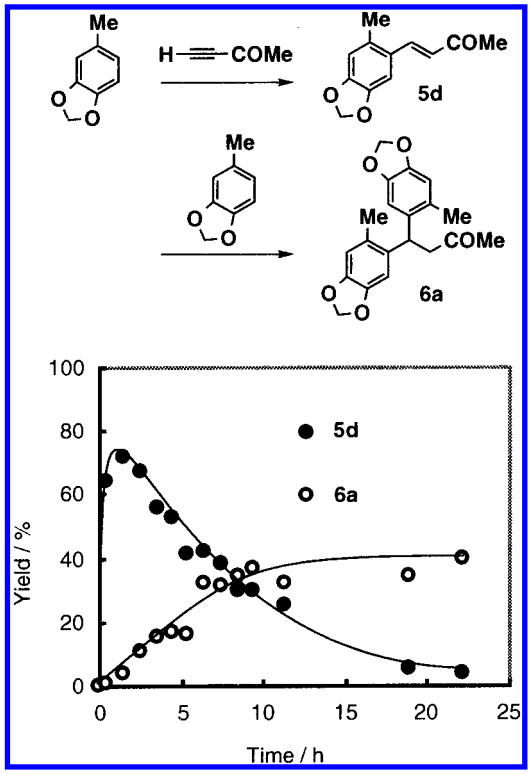


Figure 1. Time dependence of monoaddition vs diaddition in the reaction of 3,4-methylenedioxytoluene (2 equiv) with 3-butyn-2-one in the presence of 1% $Pd(OAc)_2$ in TFA at room temperature (GC yield based on the alkyne).

substitution (*para* >75%): ethyl 3-bis(4-methoxyphenyl)propionate (**4b**) or 4-bis(4-methoxyphenyl)butan-2-one (**6b**), respectively (entry 14 of Table 2 and entry 11 of Table 3).

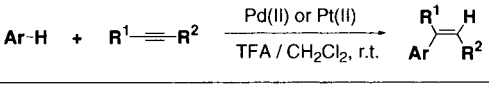
In some cases, the reaction can be switched from giving mainly 1/1 to 2/1 arene/alkyne adducts by controlling the reaction time (entries 8 and 9 in Table 3) and the concentration of $Pd(OAc)_2$ (entries 2 and 4 in Table 1). Also the formation of 1/2 adduct such as **3a** can be totally suppressed by employing $PtCl_2$/2AgOAc as catalyst (entry 2 in Table 2). The Pt(II) catalyst showed lower activity compared with Pd(II) catalysts, but better selectivity.

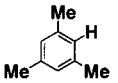
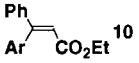
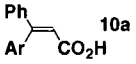
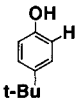
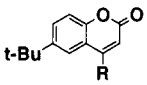
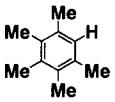
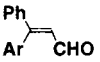
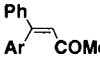
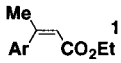
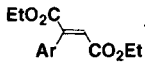
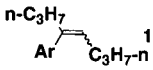
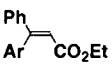
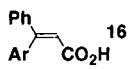
The reactions of pentamethylbenzene with phenylacetylene gave a Markovnikov-type adduct 1-pentamethylphenyl-1-phenylethylene **7** as the only isolated product (eq 3 in Scheme 4). No any other isomer was observed by analysis of the reaction mixture with GC and ^{1}H NMR.

From the results shown in Tables 2 and 3, one can see that the present reaction gives low to high yields of alkyne hydroarylation products, depending on the reactivity of arenes—the yield increases with increasing number of electron-donating groups (e.g., compare entries 1−8 in Table 3). The electron-rich arenes (having more than two electron-donating substituents) give good yields in general, showing characteristics of electrophilic substitution.[2,3,8] Also, the yield of 1/1 adducts can be improved by using an excess of alkynes (entry 7 in Table 2, and entries 5 and 7 in Table 3). It is also very interesting to find that the steric hindrance of arenes is not a problem for this reaction; therefore, the reaction of pentamethylbenzene is very fast, affording adducts in the highest yield (entries 1−4 of Table 2 and entries 1−3 of Table 3). This is in marked contrast to other Pd-catalyzed reactions such as the Heck reaction in which the steric hindrance is a big obstacle.[5a,d] The present reaction is

(8) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 501−521.

Table 4. Transition Metal-Catalyzed Addition of Arenes to Internal Alkynes [a]



Entry	Ar-H	Alkyne	Catalyst / Time (h)	Product and Yield [b]
1		Ph—≡—Ph	Pd / 42 h	 **9** (36%)
2		Ph—≡—Ph	Pt / 42 h	(56%)
3		Ph—≡—CO_2Et	Pd / 48 h	 **10** 11%  **10a** 42%
4		Ph—≡—CO_2H	Pd / 48 h	 R = Me **8a** (62%) [c]
5		Me—≡—CO_2H	Pd / 48 h	R = Ph **8b** (56%) [c]
6		Me—≡—CO_2H	Pd / 48 h	R = Ph **8b** (13%)
7		Ph—≡—CHO	Pd / 24 h	 **11** (8%)
8		Ph—≡—CHO	Pt / 48 h	60%
9		Ph—≡—Ph	Pd / 24 h	 **12** (58%)
10		Ph—≡—Ph	Pt / 24 h	63% (70%)
11		Ph—≡—Me	Pt / 24 h	 **13** 50% (61%)
12		Ph—≡—COMe	Pd / 24 h	 **14** 15%
13		Ph—≡—COMe	Pt / 72 h	(72%)
14		Me—≡—CO_2Et	Pd / 46 h	 **15** 78%
15		Ph—≡—CO_2H	Pd / 48 h	 **16** (40%)
16		Ph—≡—CO_2H	Pt / 48 h	71%
17		EtO_2C—≡—CO_2Et	Pd / 48 h	 **17** 60%
18		n-C_3H_7—≡—C_3H_7-n	Pd / 40 h	 **18** 60% (Z/E = 1)
19		Ph—≡—CO_2Et	Pd / 5 h	 **19** 71%  **16** 5%
20		Ph—≡—CO_2Et	Pd / 12 h	 **16** (98%)
21		Ph—≡—CO_2Et	Pt / 24 h	**16** 95% (98%)
22		Ph—≡—CO_2Et	$PtCl_2$ / 24 h	**16** (78%)
23 - 26		Ph—≡—CO_2Et	Rh > Ir > Ni, Ru / 140 h	**16** (46 ~ 22%)

[a] General procedure is followed: Arene (10 mmol), alkyne (5 mmol), TFA (4 mL), CH_2Cl_2 (1 mL), r.t. Pd, Pt, Rh, Ir, Ni, and Ru refer to $Pd(OAc)_2$, $PtCl_2$/2AgOAc, $Rh_2(OAc)_4$, $IrCl_3$/3AgOAc, $Ni(OAc)_2$, and $RuCl_3$/3AgOAc, all 0.25 mmol, respectively. [b] Isolated yield (GC yield in parentheses) based on the alkyne. [c] Trifluoroacetic anhydride (5 mmol) was added.

dictated by electronic effects of the substituents in arene rather than steric effects.

The efficiency of this reaction can be seen from the reaction of pentamethylbenzene with 3-butyn-2-one in the presence of 0.02 mol % $Pd(OAc)_2$ (entry 3 in Table 3). This reaction gave (3*E*)-4-(pentamethylphenyl)-3-buten-2-one (**5a**) in 90% GC yield, with a 4500 TON, in 96 h.

Hydroarylation of Internal Alkynes. The scope and generality of this reaction also have been explored by the reaction of various commercially available internal alkynes with several arenes (Table 4). Here we focus on the variety of alkynes which bear functional groups such as CHO, COMe, CO_2H, etc., all proving to be compatible. The reaction affords thermodynamically unfavorable *cis*-arylalkenes predominantly in most cases (entries 3−17, 19−26), giving good yields of adducts especially over the $PtCl_2$/2AgOAc system.

Inspired by the higher selectivity of the $PtCl_2$/2AgOAc system (entries 1 and 2 of Table 2 and also entries 1−16 in Table 4), we tested several other transition metals such as Rh(III), Ir(III), Ru(III), and Ni(II) in the reaction of pentamethylbenzene with ethyl phenylpropiolate in order to screen catalytic systems by comparison with Pd(II) and Pt(II) system (entries 19−26 in Table 4). (2*Z*)-Ethyl 3-(pentamethylphenyl)cinnamate (**19**) and corresponding hydrolyzed (2*Z*)-3-(pentamethylphenyl)cinnamic acid (**16**) were isolated upon usual workup (entry 19 in Table 4). Compound **19** was hydrolyzed completely to **16** with prolonged reaction time (entry 20 in Table 4). The results summarized in Table 4 indicate that $Pd(OAc)_2$ and $PtCl_2$/AgOAc as catalysts are superior to other transition metal systems (entries 19−26 in Table 4). $Pd(OAc)_2$ has been found to be the most active catalyst. The reaction with $PtCl_2$/AgOAc is slower (slower conversion of alkynes) than that with $Pd(OAc)_2$ (entries 20 and 21), but gave higher yields at the same conversion levels (entries 7−16 in Table 4). The catalytic activity of the transition metals decreases in the order Pd(II) > Pt(II) ≫ Rh(III) > Ir(III) >

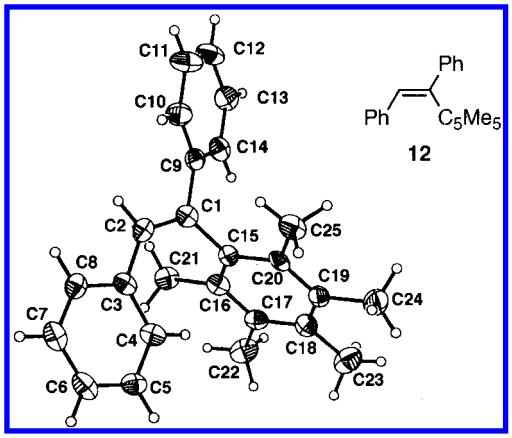


Figure 2. Crystal structure of **12**. Selected bond length (Å) and angles (deg): C1−C2 1.341(5), C1−C9 1.491(5), C1−C15 1.496(5), C2−C3 1.468(5), C9−C1−C2 120.7(3), C9−C1−C15 116.0(3), C2−C1−C15 123.3(3), C1−C2−C3 131.3(4).

Ni(II), Ru (III), in accordance with the activity difference in electrophilic metalation of aromatic C−H bonds by theses metal ions.[1a,9]

The regio- and stereochemistry of all adducts (in Tables 2−4) were unambiguously established on the basis of chemical shifts and coupling constants in ^{1}H NMR spectra, and *differential NOE* experiments. The structures of 1-(pentamethylphenyl)-1-phenyl-2-phenylethylene **12** (Figure 2) and 1-(pentamethylphenyl)-1-phenylpropene **13** (see Supporting Information) were further confirmed to be in the (*Z*)-configuration by X-ray crystal structure analysis.

A close examination of all the results listed in Tables 2−4 reveals that the nature of the substituents in alkyne has a considerable effect on the regiochemistry of the reaction products and also on the reactivity of alkynes. The alkynes conjugated to an electron-withdrawing group such as CHO, CO_2H, COMe, or CO_2Et act as good acceptors of aryl nucleophiles, providing β-aryl-substituted alkenes exclusively and being *cis*-alkenes predominantly in most cases. The reaction of the alkynes conjugated to a phenyl group provides the 1-arylalkenes with the aryl group substituted at the 1-position selectively (eq 3 in Scheme 4 and entry 11 in Table 4). No other stereo- or regioisomers were isolated or observed from the reaction mixture. The regiochemistry of this reaction is dominated by electronic effects of the substituents in alkyne rather than steric effects, and similar to the effect of the substituents in arenes. The reaction with internal alkynes is slower than that with terminal alkynes. For instance, the reactivity of acetylenes RC≡CCO_2Et decreases with the substituent R in the order R = H > Ph > Me.

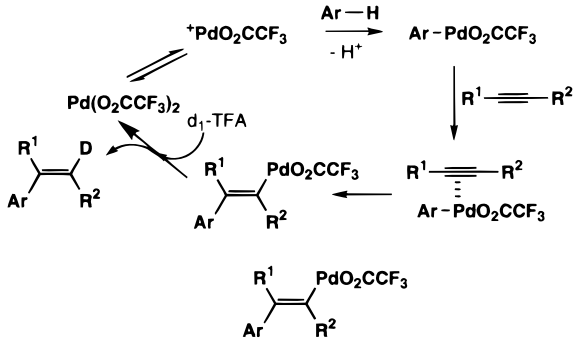
A possible side reaction is the addition of trifluoroacetic acid to C−C triple bonds of alkynes followed by hydrolysis to give ketones.[6g,10] This has been also observed in a few cases under our reaction conditions, especially in the absence of the arene or in the presence of inactive arenes, while in the absence of the Pd catalyst no such side reaction occurs.

Pd(0)-catalyzed hydroarylation of alkynes with aryl halides in the presence of reductants such as sodium formate reported by Cacchi et al.[6c−e] provides a mixture of regio- and stereoisomers in general. The present catalytic hydroarylation of terminal or internal alkynes by simple arenes in a highly regio- and stereoselective fashion offers a valuable and unique method for the preparation of *cis*-arylalkene, which cannot be easily accessed by other reactions. The understanding of the effectiveness of this reaction requires an understanding of the mechanism.

(9) Shul'pin, G. B. *Organic Reactions Catalyzed by Metal Complexes*; Nauka: Moscow, 1988.

(10) Simonetta, M.; Gavezzotti, A. In *The Chemistry of the Carbon−Carbon Triple Bond*; Patai, S., Ed.; John Wiley & Sons: New York, 1978; Part 1, pp 1−73.

Scheme 7. The Possible Mechanism



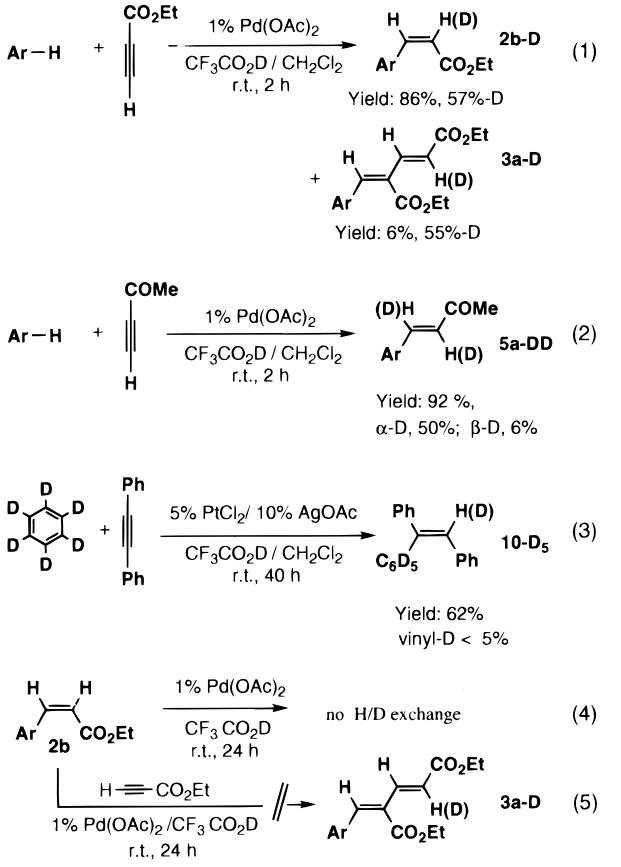
Mechanistic Considerations. The experimental findings and their implications discussed already give us some information about the possible mechanism of this reaction, which has been outlined in Scheme 7.

(A) Formation of σ-Aryl-Pd Complexes via Electrophilic Metalation of Aromatic C−H Bonds. It seems reasonable for σ-arylpalladium complexes to be involved in the present reaction on the basis of the reactivity order of both transition metals and arenes in the present reaction (Tables 2−4). As mentioned already, the reactivity order of transition metals in the present reaction is consistent with the reactivity order of electrophilic metalation of aromatic C−H bonds by these metal ions.[1a,9] Formation of such σ-arylpalladium complexes also has been partially confirmed by ^{1}H NMR spectra with the disappearance of the aryl hydrogen of pentamethylbenzene in the reaction with 1 equiv of $Pd(OAc)_2$ in TFA in a few minutes at room temperature. Such aryl-Pd(II) complexes have been known as intermediates in the coupling of arenes with olefins, and in the coupling of arenes with arenes.[3f] Similar aryl-Pt(II) complexes have been synthesized from cationic Pt(II) complexes.[4a,d] The facile formation of such Pd-aryl complexes (such as **B** in Scheme 2) in TFA has been demonstrated by the coupling reaction of arenes with arenes,[4b] and also by formation of aromatic acid from simple arenes with carbon monoxide (route c in Scheme 2),[3g] both at room temperature. Unfortunately, the attempt to obtain the isotope effect in the reaction of mesitylene plus mesitylene-d_{12} with 3-butyn-2-one in TFA was thwarted by a rapid aryl H/D exchange, even in the absence of Pd(II) catalysts. [8]

The present hydroarylation reaction fails in a hydrocarbon solvent (hexane), ethereal solvent (THF), halogenated solvent (CH_2Cl_2), or acetic acid, even in the presence of catalytic amounts of TFA and $Pd(O_2CCF_3)_2$. A reasonable explanation is that the reaction requires highly cationic Pd(II) species to facilitate the formation of stable σ-aryl-Pd complexes.[4] It has been proved that the acid loss from Pd or Pt trifluoroacetate complexes is irreversible under the neutral or less acidic conditions;[4c] thus, the presence of a large excess of TFA is necessary to keep cationic Pd(II) species. The loose interaction of labile trifluoroacetate anion with Pd(II) makes it highly cationic and therefore highly active in the electrophilic substitution of arenes. Also, a strong acid like TFA would facilitate the hydrolysis of vinyl−M complexes to give the final products.[6a]

(B) Formation of Vinyl-Pd(II) Species. The reaction of pentamethylbenzene with two alkynes carried out in CF_3CO_2D as the solvent (eqs 1 and 2 in Scheme 8) indicates that deuterium atoms have been incorporated into adducts as vinyl atoms at

Scheme 8. Isotope Experiments (Ar = Pentamethylphenyl)



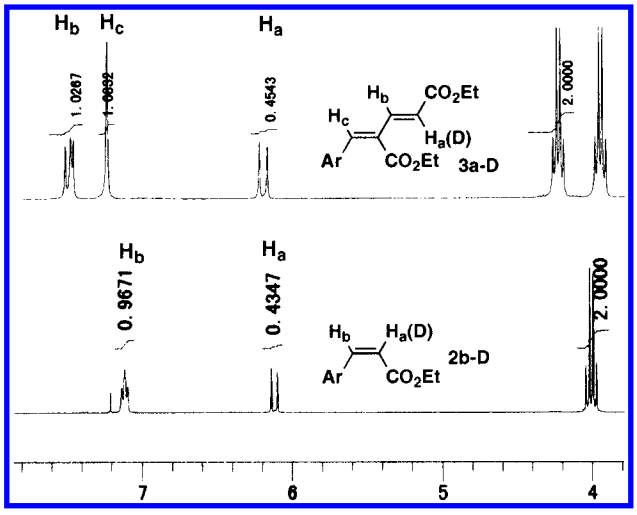
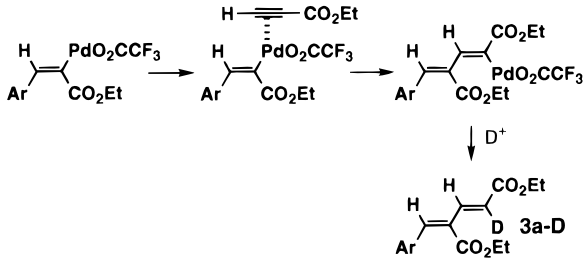


Figure 3. Part of ^{1}H NMR spectra of **2b-D** and **3a-D** (Ar = pentamethylphenyl).

the α positions predominantly, on the basis of ^{1}H NMR and GC/MS spectra of the adducts by comparison with those of the adducts from TFA (undeuterated) as the solvent. Only traces of the *β*-deuterium-incorporated adducts were detected in the reaction of pentamethylbenzene with ethyl propiolate by GC/MS. Two typical ^{1}H NMR spectra for deuterium-containing adducts **2b-D** and **3a-D** in eq 1 are shown in Figure 3. The adduct **5a-DD** (from the reaction of pentamethylbenzene with 3-butyn-2-one in CF_3CO_2D) with deuteriums incorporated at α and *β* vinylic positions at different extents has been observed, being 50% at α and 6% at *β* (eq 2 in Scheme 8). The GC/MS spectra confirmed the formation of one- and two-deuterium-incorporated adducts (*m*/*z* $M^{+\bullet}$ = 217, 218). The deuterium

Scheme 9. Formation of the Arene/Alkyne 1/2 Adducts



incorporation at the *β* position may originate from the H/D exchange of the terminal alkyne in CF_3CO_2D, indicating that such an exchange reaction is very slow compared with the hydroarylation reaction under the present reaction conditions. This also implies that the present catalytic reaction does not involve the insertion of Pd(II) into the C−H bonds of terminal alkynes. Furthermore, the involvement of vinylidene Pd complexes is not the case in the present reaction.[5,13]

The reaction of benzene-d_6 with an internal alkyne (diphenylacetylene) in TFA (undeuterated) gave the adduct **10-D$_5$** with almost no deuterium atoms incorporated in the vinyl positions and almost 100% deuterium substitution at a phenyl group (*m*/*z* $M^{+\bullet}$ = 261) (eq 3 in Scheme 8). This reveals that the vinyl hydrogens originate completely from the solvent TFA.

It may also be possible that the vinyl deuteriums of **2b-D** could result from H/D-exchange of the vinyl hydrogens of **2b** in CF_3CO_2D in the presence of Pd(II) catalysts. The vinyl H/D exchange has been excluded by a control reaction (eq 4 in Scheme 8), which was carried out by stirring a solution of **2b** in CF_3CO_2D in the presence of 5% $Pd(OAc)_2$ at room temperature for 24 h, since no vinyl H/D exchange was observed by ^{1}H NMR.

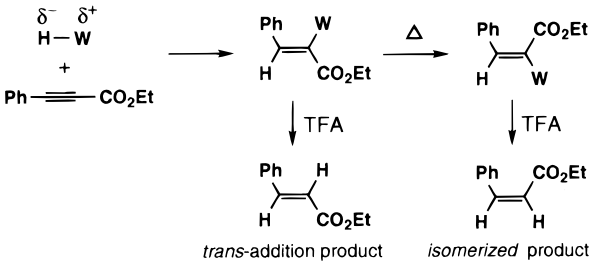
All these results provide very strong evidence for formation of the vinyl-Pd(II) complexes. Further very strong evidence for such vinyl-Pd(II) complexes is the formation of the 1/2 arene/alkyne adducts such as **3a-D** as a side product (eq 1 in Scheme 8). The impossiblity of the formation of **3a-D** from **2b** has been proved by another control reaction, shown as eq 5 in Scheme 8. The only possible route to **3a-D** is *cis*-addition of the vinyl-Pd intermediate to another molecular alkyne, affording the adduct **3a-D** (J_{H-H} = 16.5 Hz) after hydrolysis by TFA (Scheme 9).

(C) *trans*-Addition of Aryl-Pd Complexes across the C−C Triple Bond. On the basis of the generally accepted concept, most transition metal-mediated carbometalation to C−C multiple bonds proceeds in a *cis*-fashion, giving *trans*-adducts,[5] but still there are some reports of net *trans*-additions of M−H or M−R across C−C triple bonds.[2d,6] In some cases, *trans*-addition is the preferred mode.[6a] Also, Pd(II)-catalyzed predominant *trans*-addition of carboxylic acids to alkynes has been reported in an inter- or intramolecular fashion.[6f,g] The occurrence of *trans*-addition is not well understood, while the *cis*-addition is believed to occur by a concerted process where the M−R bond approaches the alkyne in a coplanar manner.[11] The present hydroarylation affords *cis*-arylalkene predominantly in most cases, indicating the addition of aryl and hydrogen groups across C−C triple bonds in a *trans*-fashion.

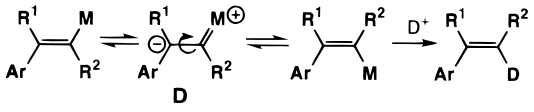
The striking resemblance between our present *trans*-hydroarylation of alkynes and the stoichiometric *trans*-addition of $(CO)_2(NO)(PMe_3)_2W$−H to the same alkynes (Scheme 10)

(11) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.
(12) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.
(13) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

Scheme 10. The *Trans*-Addition of the Tungsten Hydride to Ethyl Phenylpropiolate and Thermal Isomerization[6a]



Scheme 11. Possible Route for Formation of *Trans*-Alkenes



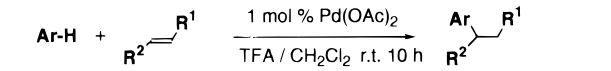
reported by Berke et al.,[6a] from the reactivity order of different alkynes to the regio- and stereochemistry of final products, suggests that the arylpalladium complexes may undergo *trans*-arylpalladation across C−C triple bonds to give the vinyl-Pd-(II) complexes in a way similar to the *trans*-hydrotungstenation in Scheme 10. The protonation of these vinyl-Pd(II) complexes by TFA gives the final adducts. An overall possible mechanism is shown in Scheme 7.

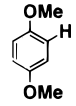
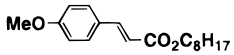
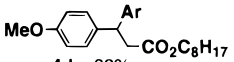
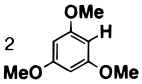
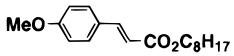
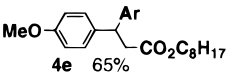
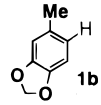
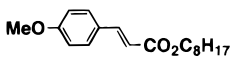
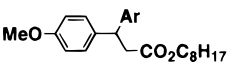
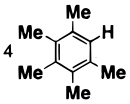
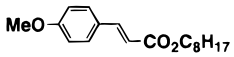
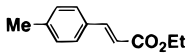
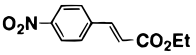
The *cis*-arylalkenes offered by the present reaction are thermodynamically unfavorable; they are formed through *trans*-hydroarylation of alkynes preferentially under kinetically controlled conditions. They may undergo thermal isomerization through a dipolar Pd intermediate **D** as suggested by Alper et al.[6] to give *trans*-arylalkenes in some cases (Scheme 11); this may be the case in the reaction of arenes with 3-butyn-2-one. This is the possible reason why the reactions of pentamethylbenzene with 4-phenyl-3-butyn-2-one and 3-butyn-2-one give the *cis*-adduct **14** (entries 12 and 13 in Table 4) and the *trans*-adduct **5a** (entries 1−3 in Table 3), respectively. *trans*-Arylpalladation of alkynes followed by thermal isomerization may give thermodynamically favorable *trans*-arylalkenes such as **5a**.

(D) The Formation of 2/1 Arene/Alkyne Adducts. As mentioned already, the arenes having only alkoxyl substituents tend to give 2/1 arene/alkyne adducts (see Tables 2 and 3). To clarify the possible reasons for this, several reactions of substituted cinnamates with arenes have been performed in order to see the effects of the substituents in both arenes and alkenes (Table 5). The addition of arenes to alkenes occurs only when both arenes and cinnamates have alkoxyl substituents (entries 1−3 in Table 5), indicating that the presence of an alkyloxyl in arenes and phenylethylenyl moiety of alkenes is critical to the success of the reaction (Table 5). These results suggest the possible involvement of carbocations in the reactions (Scheme 2). The electron-rich alkoxylphenyl group provides resonance stabilization of the positive charge at the cations.[12]

Therefore, the possible mechanism has been outlined in Scheme 7. The formation of σ-aryl-Pd complexes from electrophilic metalation of aromatic C−H bonds by cationic Pd(II) species would be followed by coordination of alkynes to Pd. Also it is possible that the formation of σ-arylpalladium complexes and the coordination of alkynes to Pd could occur at the same time. *trans*-Insertion of C−C triple bonds to the σ-aryl-Pd bonds would result in the vinyl-Pd complexes, and the arene/alkyne 1/1 adduct would be released upon protonation of the vinyl-Pd complexes. The possible involvement of Pd-(II)-vinylidene and Pd(II)-allenyl complexes could be excluded

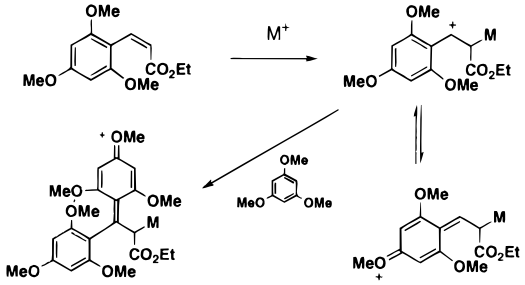
Table 5. Pd-catalyzed Addition of Arenes to Alkenes[a]



Entry	Ar-H	Alkene	Product and yield[b]
1			 **4d** 83%
2			 **4e** 65%
3	 **1b**		 **4f** 86%
4			no reaction
5	**1b**		no reaction
6	**1b**		no reaction

[a] General procedure was followed: arene (5 mmol), alkene (5 mmol), $Pd(OAc)_2$ (0.05 mmol), TFA (3.5 mL), and CH_2Cl_2 (1.5 mL), at rt for 10 h. [b] Isolated yield based on the alkene.

Scheme 12. Possible Involvement of Carbocations in the Addition of Alkoxyarenes to Alkenes



because of the nature of the adducts.[13,14] The possible involvement of the vinylcarbocations from alkynes (and subsequent electrophilic substitution of arenes) in the present reaction cannot be excluded, although we did not have enough evidence to confirm it.

In summary, we have found a selective addition reaction of simple arenes to the activated carbon−carbon triple bonds with selective aromatic C−H bond cleavage in the presence of catalytic amounts of palladium, platinum, or other transition metal catalysts under mild conditions. A valuable and unique character of the present reaction is the *trans*-addition of aryl and hydrogen groups across C−C triple bonds (although the specific mechanism of such addition is not necessarily clear), giving predominantly *cis*-3-aryl-α,β-unsaturated acids, esters, ketones, and aldehydes, since the known catalytic reactions normally provide thermodynamically favorable *trans*-isomers.[5,10] The present reaction constitutes a convenient and useful method for the synthesis of *cis*-arylalkenes in one step from commercially available alkynes and electron-rich arenes, and should find wide applications in organic synthesis.

(14) Chen, J. T.; Hsu, R. H.; Chen, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 3243.

Experimental Section

General. All the reactions were performed in dry Pyrex tubes, and only under argon atmosphere when Pd(0) catalysts were used. All starting materials and solvents were used as received without further purification unless otherwise indicated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR (300 MHz) in $CDCl_3$ solution (TMS as an internal standard). The methyl protons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate in a sealed tube containing D_2O were used as an internal standard when the reaction mixture (containing TFA) was directly subjected to ^{1}H NMR analysis. IR spectra were recorded either neat or as a film on sodium chloride plates or as KBr pellets on a HORIBA FT-200 spectrophotometer. Melting points were measured with YANACO micro melting apparatus and are uncorrected. The GC analysis was performed on a Shimadzu GC-8A using a 2.0-m × 3-mm-diameter stainless steel column packed with Unisole 10T + H_3PO_4 (5 + 0.5)% on 80−100 mesh Uniport HP with a flame ionization detector. For thin-layer chromatography (TLC), Merck precoated aluminum plates were used and detection was accomplished with an UV lamp. Flash column chromatography employed Wako silica gel, Wakogel C-300, 45−75 μm with a mixed solvent of hexane/EtOAc (3/1 to 12/1, depending on the polarity of the reaction products) as eluent. The elemental analysis and GC/MS were performed at the Faculty of Science and at the Institute of Fundamental Research of Organic Chemistry of Kyushu University, respectively.

The regio- and stereochemistry of all adducts (in Tables 2−5) were unambiguously established on the basis of chemical shifts and coupling constants in ^{1}H NMR spectra, and differential NOE experiments. Notably, the absorption of the α- and β-vinylic hydrogens for adducts having vinylcarbonyl groups occurs at 6.0 ± 0.6 and 7.3 ± 0.7 ppm, respectively. The coupling constants $J_{H\alpha-H\beta}$ for *cis*- and *trans*-alkenes are around 11.7 ± 0.6 and 16.5 ± 0.3 Hz, respectively. The vinyl hydrogens of compounds **10**, **10a**, **11**, **12**, **13**, **14**, **16**, **19**, and **15** (Table 3) were assigned to be *cis* with phenyl and methyl groups respectively by differential NOE study of the ^{1}H NMR spectrum (irradiation of the vinyl proton led to the respective enhancement of the signals of phenyl and methyl groups). The vinyl protons at the 5-position of **3a**, **3b**, and **3c** (singlet in ^{1}H NMR spectra) were assigned to be *cis* with the vinyl protons at the 3-position (doublet, J = 15.9 Hz) also by differential NOE of the ^{1}H NMR spectrum.

General Procedure for Alkyne Hydroarylation. To a cold mixture of the arene (10 mmol), the transition metal catalyst (0.02−5 mol %), TFA (4 mL), and CH_2Cl_2 (1 mL) on an ice−water bath was added the alkyne (5 mmol) with stirring. After continuous stirring at the same temperature for 5 min, the mixture was warmed to room temperature. Stirring continued until no further increase of the reaction products or the disappearance of one starting material as monitored by GC, TLC, or ^{1}H NMR. When the yield was determined by GC, diethyl phthalate was added to reaction mixture as an internal standard. The reaction mixture was poured into a saturated NaCl aqueous solution and extracted with ether. The ethereal layer was washed with saturated NaCl, neutralized with Na_2CO_3 solution, and dried over anhydrous Na_2SO_4. The solvent was removed in a vacuum, and the products were separated by flash column chromatography.

A Specific Example. Pentamethylbenzene (1.51 g, 10.2 mmol), Pd(OAc)$_2$ (10 mg, 0.045 mmol), TFA (4 mL), and CH_2Cl_2 (1 mL) were mixed in a 25-mL dry Pyrex tube on an ice−water bath, and then ethyl propiolate (0.475 g, 4.9 mmol) was added to this mixture and the mixture was stirred for 5 min. Then the mixture was warmed to room temperature and stirred for 3 h. After workup according to the general procedure and column chromatography with 8/1 hexane/EtOAc as eluent, two compounds were isolated as white crystals: (2*Z*)-ethyl 3-(pentamethylphenyl)propenoate (**2b**) (1.05 g) in 88% yield and ethyl (2*E*,4*Z*)-4-(ethoxycarbonyl)-5-(pentamethylphenyl)-2,4-pentadienoate (**3a**) (0.05 g) in 6% yield, respectively.

Characterization Data. (2*Z*)-Ethyl 3-(2,5-Dimethoxyphenyl)-propenoate (*Z*-2a). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, J = 7.2 Hz, 3H, CH_3), 3.76 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 4.14 (q, J = 7.2 Hz, 2H, OCH_2), 5.97 (d, J = 12.3 Hz, 1H, vinyl), 6.80 (d, J = 8.7 Hz, 1H, aryl), 6.87 (dd, J = 3.0 and 8.7 Hz, 1H, aryl), 7.12 (d, J = 12.3 Hz, 1H, vinyl), 7.24 (d, J = 3.0 Hz, 1H, aryl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.01, 55.66, 55.95, 60.06, 111.25, 115.53, 115.97, 120.18, 124.63, 138.33, 151.50, 152.72, 166.19. IR (neat, cm^{-1}): 1710 (C═O). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.84. Found: C, 65.84; H, 6.78.

(2*E*)-Ethyl 3-(2,5-Dimethoxyphenyl)propenoate (*E*-2a). Light pink oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (t, J = 7.2 Hz, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.25 (q, J = 7.2 Hz, OCH_2), 6.49 (d, J = 16.2 Hz, 1H, vinyl), 6.9 (m, 2H, aryl), 7.16 (d, J = 2.7 Hz, 1H, aryl), 7.96 (d, J = 16.2, 1H, vinyl). ^{13}C NMR: δ 14.19, 55.53, 55.84, 60.19, 112.24, 113.06, 116.85, 118.78, 123.78, 139.56, 152.62, 153.33, 167.16. ^{1}H NMR and ^{13}C NMR spectra are in good agreement with the reported values of chemical shifts and coupling constants.[15a,d]

(2*Z*)-Ethyl 3-(Pentamethylphenyl)propenoate (2b). White crystals, mp 71.8−72.3 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, J = 7.2 Hz, 3H, CH_3), 2.14 (s, 6H, $2CH_3$), 2.19 (s, 6H, $2CH_3$), 2.22 (s, 3H, CH_3), 4.01 (q, J = 7.2 Hz, 2H, OCH_2), 6.12 (d, J = 12.0 Hz, 1H, vinyl), 7.12 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.84, 16.22, 16.60, 17.46, 59.61, 122.01, 129.61, 131,72, 133.11, 133.79, 146.32, 165.23. IR ($CHCl_3$, cm^{-1}): 1724 (C═O). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.89; H, 9.01.

(2*E*)-Ethyl 3-(1-Naphthyl)propenoate (2c). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7.2 Hz, 3H, CH_3), 3.96 (q, J = 7.2 Hz, 2H, OCH_2), 6.19 (d, J = 12.3 Hz, 1H, vinyl), 7.42 (m, 4H, aryl), 7.48 (d, J = 12.3 Hz, 1H, vinyl), 7.8 (m, 3H, aryl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.64, 59.95, 122.61, 124.22, 124.81, 125.65, 126.05, 126.38, 128.35, 128.53, 130.91, 132.85, 133.08, 141.63, 165.69. IR (neat, cm^{-1}): 1712 (C═O). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.45; H, 6.26.

Ethyl 3-(2,5-Dimethylphenyl)-2-propenoate (2d). Colorless oil as an inseparable mixture of (*Z*,*E*)-isomers (*Z*/*E* = 2:1). The (*Z*)-**2d** and (*E*)-**2d** have different coupling constants for their vinyl hydrogens and are easily discernible from each other. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, J = 7.2 Hz, 3H, CH_3), 1.29 (t, J = 7.2 Hz, 1.5H, CH_3), 2.19 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.27 (s, 1.5H, CH_3), 2.34 (s, 1.5H, CH_3), 4.05 (q, J = 7.2 Hz, 2H, OCH_2), 4.22 (q, J = 7.2 Hz, 1H, OCH_2), 5.96 (d, J = 12.3 Hz, 1H, vinyl), 6.32 (d, J = 15.9 Hz, 0.5H, vinyl), 6.98 (s, 1H, aryl), 7.02 (m, 3H, aryl), 7.07 (d, J = 12.3 Hz, 1H, vinyl), 7.32 (s, 1H, 0.5H, aryl), 7.93 (d, J = 15.9 Hz, 0.5H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.74, 14.12, 19.03, 19.11, 20.67, 20.70, 59.79, 60.15, 118.71, 120.74, 126.70, 128.35, 128.91, 129.10 129.33, 130.48, 130.62, 132.38, 134.18, 134.38, 134.64, 135.43, 142.17, 142.68, 165.79, 166.83. IR (neat, cm^{-1}): 1712 (C═O). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.52; H, 7.92.

(2*Z*)-Ethyl 3-Mesitylpropenoate (2e). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08 (t, J = 6.9 Hz, 3H, CH_3), 2.14 (s, 6H, $2CH_3$), 3.25 (s, 3H, CH_3), 4.01 (q, J = 6.9 Hz, OCH_2), 6.10 (d, J = 12.0 Hz, 1H, vinyl), 6.82 (s, 2H, aryl), 7.00 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.77, 19.93, 20.83, 59.70, 122.59, 127.62, 132.62, 134.24, 136.43, 143.93, 165.22. IR ($CHCl_3$, cm^{-1}): 1729 (C═O). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.84; H, 8.39.

(2*Z*)-Ethyl 3-{2,4,6-Trimethyl-3-[(1*Z*)-2-ethoxycarbonylethylenyl)]-phenyl}propenoate (2f). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, J = 7.2 Hz, 6H, $2CH_3$), 2.05 (s, 3H, CH_3), 2.15 (s, 6H, $2CH_3$), 4.03 (q, J = 7.2 Hz, 4H, $2OCH_2$), 6.12 (d, J = 11.7 Hz, 2H, vinyl), 6.88 (s, 1H, aryl), 7.03 (d, J = 11.7 Hz, 2H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.82, 17.57, 20.08, 59.76, 122.60, 128.26, 130.87, 132.89, 133.35, 144.24, 165.24. IR (neat, cm^{-1}): 1718 (C═O). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.02; H, 7.60.

(2*Z*)-Ethyl 3-(2,3,5,6-Tetramethylphenyl)-2-propenoate (2g). Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (t, J = 6.9 Hz, 3H, CH_3), 1.97 (s, 6H, $2CH_3$), 2.10 (S, 6H, $2CH_3$), 3.88 (q, J = 6.9 Hz, 2H, OCH_2), 6.01 (d, J = 11.7 Hz, 1H, vinyl), 6.77 (s, 1H, aryl), 6.94 (d, J = 11.7 Hz, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.63, 16.20, 19.66, 59.50, 122.27, 129.95, 130.31, 132.72, 135.49, 145.23, 165.10.

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IR (neat, cm^{-1}): 1714 (C═O). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 76.28; H, 8.68.

(2Z)-Ethyl (2,4,6-Trimethyl-3-hydroxyphenyl)propenoate (2h). White crystals, mp 58.7−59.6 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, J = 6.9 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 4.03 (q, J = 6.9 Hz, 2H, OCH_2), 5.20 (s, 1H, OH), 6.11 (d, J = 11.7 Hz, 1H, vinyl), 6.73 (s, 1H, aryl), 6.97 (d, J = 11.7 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.79, 13.70, 15.65, 19.27, 59.90, 120.48, 122.23, 122.34, 125.56, 128.84, 133.81, 144.20, 149.84, 165.54. IR ($CHCl_3$, cm^{-1}): 3485 (OH), 1714 (C═O). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.70; H, 7.70.

(2Z)-Ethyl 3-(2,4,6-Trimethyl-3-bromophenyl)propenoate (2i). A waxy solid, mp 29.5−30.6 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, J = 7.2 Hz, 3H, CH_3), 2.11(s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.02 (q, J = 7.2 Hz, 2H, OCH_2), 6.13 (d, J = 12.0 Hz, 1H, vinyl), 6.93 (s, 1H, aryl), 7.02 (d, J = 12.0 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.85, 19.88, 21.21, 23.87, 60.04, 123.21, 124.99, 129.24, 133.14, 134.30, 134.55, 136.88, 143. 56, 165.14. IR ($CHCl_3$, cm^{-1}): 1729 (C═O). Anal. Calcd for $C_{14}H_{17}O_2Br$: C, 56.58; H, 5.77. Found: C, 56.87; H, 5.81.

Ethyl 3-(2-Methoxyphenyl)-2-propenoate (2j). Light yellow oil as an inseparable *Z*,*E*-mixture (*Z*:*E* = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11 (t, J = 7.2 Hz, 3H, CH_3), 1.24 (t, J = 6.9 Hz, 0.8H, CH_3), 3.70 (s, 0.8H, OCH_3), 3.73 (s, 3H, OCH_3), 4.04 (q, J = 7.2 Hz, 2H, OCH_2), 4.17 (q, J = 6.9 Hz, 0.5H, OCH_2), 5.87 (d, J = 12.6 Hz, 1H, vinyl), 6.45 (d, J = 15.9 Hz, 0.25H, vinyl), 6.83 (m, 2.5 H, aryl), 7.08 (d, 1H, J = 12.6 Hz, 1H, vinyl), 7.20 (m, 1.25 H, aryl), 7.41 (dd, J = 1.8 and 7.5 Hz, 0.25H, aryl), 7.46 (dd, J = 1.5 and 7.8 Hz, 1H, aryl), 7.91 (d, J = 15.9 Hz, 0.25H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.98, 14.26, 55.08, 55.29, 59.97, 60.22, 111.12, 111.01, 118.67, 119.76, 119.88, 129.57, 123.32, 123.99, 128.80, 130.08, 130.62, 131.30, 138.90, 139.90, 156.99, 158.21, 166.25, 167.39. IR ($CHCl_3$, cm^{-1}): 1721 (C═O). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.70; H, 6.89.

(2*E*,4*Z*)-Ethyl 4-(Ethoxycarbonyl)-5-(pentamethylpenyl)-2,4-pentadienoate (3a). Colorless crystals, mp 60.8−62.0 (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 6.9 Hz, 3H, CH_3), 1.32 (t, J = 6.9 Hz, 3H, CH_3), 2.12 (s, 6H, $2CH_3$), 2.18 (s, 6H, $2CH_3$), 2.22 (s, 3H, CH_3), 3.97 (q, J = 6.9 Hz, 2H, OCH_2), 4.25 (q, J = 6.9 Hz, 2H, OCH_2), 6.17 (d, J = 15.9 Hz, 1H, vinyl), 7.25 (s, 1H, vinyl), 7.50 (d, J = 15.9 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.40, 14.26, 16.19, 16.67, 17.78, 60.47, 60.53, 120.41, 130.37, 132.04, 132.44, 133.98, 134.44, 141.48, 145.25, 166.01, 166.84. IR ($CHCl_3$, cm^{-1}): 1734 (C═O), 1716 (C═O). Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.35; H, 8.16.

(2*E*,4*Z*)-Ethyl 4-(Ethoxycarbonyl)-5-mesityl-2,4-pentadienoate (3b). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (t, J = 6.9 Hz, 3H, CH_3), 1.22 (t, J = 6.9 Hz, 3H, CH_3), 2.05 (s, 6H, $2CH_3$), 2.16 (s, 3H, CH3), 3.90 (q, J = 6.9 Hz, 2H, OCH_2), 4.15 (q, J = 6.9 Hz, 2H, OCH_2), 6.15 (d, J = 15.9 Hz, 1H, vinyl), 6.73 (s, 2H, aryl), 7.04 (s, 1H, vinyl), 7.37 (d, J = 15.9 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.28, 14.09, 19.93, 20.78, 60.30, 60.52, 120.55, 127.66, 131.93, 134.27, 134.96, 137.09, 141.20, 142.93, 165.86, 166.58. IR ($CHCl_3$, cm^{-1}): 1730 (C═O), 1722 (C═O). Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.40; H, 7.72.

(2*E*,4*Z*)-Ethyl 4-Ethoxycarbonyl-5-(2,3,5,6-tetramethylphenyl)-2,4-pentadienoate (3c). Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84 (t, J = 6.9 Hz, 3H, CH_3), 1.32 (t, J = 6.9 Hz, 3H, CH_3), 2.06 (s, 6H, $2CH_3$), 2.20 (s, 6H, $2CH_3$), 3.95 (q, J = 6.9 Hz, 2H, OCH_2), 4.25 (q, J = 6.9 Hz, 2H, OCH_2), 6.22 (d, J = 15.9 Hz, 1H, vinyl), 6.90 (s, 1H, aryl), 7.22 (s, 1H, vinyl), 7.48 (d, J = 15.9 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.35, 14.26, 16.63, 19.78, 60.51, 60.55, 120.64, 130.88, 130.93, 133.27, 134.19, 134.95, 141.35, 144.42, 165.99, 166.84. IR (cm^{-1}, neat): 1714 (C═O). Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.77; H 7.93. Found: C, 73.58; H, 8.22.

Ethyl 3-Bis(2,5-dimethoxyphenyl)propionate (4a). Yellow crystals, mp 88.3−89.5 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, J = 6.9 Hz, 3H, CH_3), 3.00 (d, J = 8.4 Hz, 2H, CH_2), 3.70 (s, 6H, $2OCH_3$), 3.71 (s, 6H, $2OCH_3$), 4.01 (q, J = 6.9 Hz, 2H, OCH_2), 5.15 (t, J = 8.4 Hz, 1H, CH), 6.65 (dd, J = 2.7 and 9.0 Hz, 2H, aryl), 6.74 (d, J = 9.0 Hz, 2H, aryl), 6.76 (d, J = 2.7 Hz, 2H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.94, 35.32, 38.32, 55.42, 56.06, 59.98, 110.98, 111.76, 115.25, 132.47, 151.47, 153.28, 172.06. IR ($CHCl_3$, cm^{-1}): 1729 (C═O). Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.43; H, 7.10.

Ethyl 3-Bis(4-methoxyphenyl)propionate (4b). Colorless oil (>90% of di-*para*-substitution as determined by GC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, J = 6.9 Hz, 3H, CH_3), 2.98 (d, J = 8.1 Hz, 2H, OCH_2), 3.73 (s, 6H, $2OCH_3$), 4.01 (q, J = 6.9 Hz, 2H, OCH_2), 4.50 (t, J = 8.1 Hz, 1H, CH), 6.80 (d, J = 9.0 Hz, 2H, aryl), 7.13 (d, J = 9.0 Hz, 2H, aryl). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98, 41.11, 45.36, 55.01, 60.21, 113.73, 128.40, 135.90, 157.94, 171.79. IR ($CHCl_3$, cm^{-1}): 1733 (C═O). Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.49; H, 7.07.

Ethyl 3-Bis(2,4,6-trimethoxyphenyl)propionate (4c). Colorless crystals, mp 106.4−107.3 °C (hexane/EtOAc = 4). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.16 (t, J = 7.2 Hz, 3H, CH_3), 3.05 (d, J = 8.4 Hz, 2H, CH_2), 3.67 (s, 12H, $4OCH_3$), 3.75 (s, 6H, $2OCH_3$), 4.05 (q, J = 7.2 Hz, 2H, OCH_2), 5.18 (t, J = 8.4 Hz, 1H, CH), 6.05 (s, 4H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.25, 29.95, 37.80, 55.07, 55.67, 59.41, 91.06, 113.83, 158.72, 159.29, 173.58. IR (KBr, cm^{-1}): 1735 (C═O). Anal. Calcd for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96. Found: C, 63.56; H, 6.92.

2′-Ethylhexyl 3-(2,5-Dimethoxyphenyl)-3-(4-methoxyphenyl)propionate (4d). Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.79 (t, J = 7.2 Hz, 3H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3), 1.18−1.35 (m, 9H, alkyl), 2.99 (m, 2H, CH_2C═O), 3.69 (s, 3H, CH_3O), 3.70 (s, 3H, CH_3O), 3.71 (s, 3H, CH_3O), 3.88 (d, J = 5.4 Hz, 2H, CH_2O), 4.86 (t, J = 7.8 Hz, 1H, CH), 6.64 (dd, J = 2.7, 9.0 Hz, 1H, aryl), 6.72 (s, 1H, aryl), 6.73 (d, J = 8.7 Hz, 1H, aryl), 6.77 (d, J = 8.7 Hz, 2H, aryl), 7.17 (d, J = 8.7 Hz, 2H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.76, 13.88, 22.81, 23.48, 28.78, 30.16, 38.59, 39.62, 39.84, 54.97, 55.41, 55.90, 66.45, 110.81, 111.62, 113.55, 114.56, 128.69, 133.57, 134.92, 151.00, 153.44, 157.88, 172.07. IR (neat, cm^{-1}): 1737 (C═O). Anal. Calcd for $C_{26}H_{36}O_5$: C, 72.87; H, 8.47. Found: C, 73.13; H, 8.42.

2′-Ethylhexyl 3-(2,4,6-Trimethoxyphenyl)-3-(4-methoxyphenyl)-propionate (4e). Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80 (t, J = 7.2 Hz, 3H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3), 1.16−1.45 (m, 9H, alkyl), 3.18 (m, 2H, CH_2C═O), 3.62 (s, 3H, CH_3O), 3.65 (s, 3H, CH_3O), 3.67 (s, 6H, CH_3O), 3.87 (m, 2H, CH_2O), 5.11 (t, J = 7.5 Hz, 1H, CH), 6.06 (s, 2H, aryl), 6.70 (d, J = 8.4 Hz, 2H, aryl), 7.22 (d, J = 8.4 Hz, 2H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.50. 13.65, 22.56, 23.22, 28.54, 29.88, 31.19, 34.86, 37.77, 38.41, 54.44, 55.05, 65.74, 90.74, 112.51, 112.71, 128.05, 135.96, 157.15, 158.53, 159.43, 172.71. IR (neat, cm^{-1}): 1729 (C═O). Anal. Calcd for $C_{27}H_{38}O_6$: C, 70.95; H, 8.48. Found: C, 70.72; H, 8.45.

2′-Ethylhexyl 3-(2-Methyl-4,5-methylenedioxyphenyl)-3-(4-methoxyphenyl)propionate (4f). Light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.80 (t, J = 7.2 Hz, 3H, CH_3), 0.87 (t, J = 7.2 Hz, 3H, CH_3), 1.10−1.45 (m, 9H, alkyl), 2.22 (s, 3H, CH_3), 2.92 (dd, J = 1.2 and 7.8 Hz, 2H, CH_2C═O) 3.74 (s, 3H, OCH_3), 3.90 (d, J = 5.4 Hz, 2H, OCH_2), 4.61 (t, J = 7.8 Hz, 1H, CH), 5.86 (q, J = 2.4 Hz, 2H, CH_2O_2), 6.73 (s, 1H, aryl), 6.60 (s, 1H, aryl), 6.78 (d, J = 9.0 Hz, 2H, aryl), 7.08 (d, J = 9.0 Hz, 2H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.82, 14.03, 19.61, 22.87, 23.58, 28.83, 30.23, 38.65, 41.39, 42.01, 55.10, 66.68, 100.67, 106.81, 110.74, 113.82, 128.58, 129.10, 134.68, 135.26, 145.58, 145.83, 158.02, 171.99. IR (neat, cm^{-1}): 1734 (C═O). Anal. Calcd for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03. Found: C, 73.42; H, 8.05.

(3*E*)-4-(Pentamethylphenyl)-3-buten-2-one (5a). Light yellow crystals, mp 78.3−80.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.20 (s, 12H, $4CH_3$), 2.23 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.16 (d, J = 16.5 Hz, 1H, vinyl), 7.71 (d, J = 16.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.24, 16.66, 17.71, 27.14, 130.85, 132.42, 132.59, 133.65, 135.07, 144.86, 197.94. IR ($CHCl_3$, cm^{-1}): 1685 (C═O). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H 9.32. Found: C, 83.26; H, 9.32.

(3*E*)-4-(2,4,5,6-Tetramethylphenyl)-3-buten-2-one (5b). Colorless crystals, mp 77.4−78.1 °C (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.24 (d, J = 16.5 Hz, 1H, vinyl), 6.90

(s, 1H, aryl), 7.69 (d, J = 16.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.63, 17.53, 20.55, 20.58, 27.34, 129.63, 132.16, 132.96, 133.13, 133.18, 134.58, 136.83, 143.49, 198.39. IR (cm^{-1}): 1662 (C═O). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.25; H, 9.03.

(3*E*)-4-Mesityl-3-buten-2-one (5c). Light yellow crystals, mp 64.5−65.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H, CH_3), 2.29 (s, 6H, $2CH_3$), 2.35 (s, 3H, CH_3), 6.30 (d, J = 16.5 Hz, 1H, vinyl), 6.86 (s, 2H, aryl), 7.64 (d, J = 16.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.70, 20.73, 27.04, 128.96, 130.52, 131.99, 136.41, 138.11, 141.54, 197.89. The structure of this compound was confirmed by converting it to (*Z*)-[(2*E*)-3-mesitylprop-2-enylidene]succinic anhydride,[15e] mp 159.6−162 °C (160.0−161 °C).[15e]

(3*E*)-4-(2-Methyl-4,5-methylenedioxyphenyl)-3-buten-2-one (5d). Colorless crystals, mp 112.4−114.3 °C (hexane/EtOAc = 3). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 5.96 (s, 2H, O−CH_2−O), 6.51 (d, J = 15.9 Hz, 1H, vinyl), 6.68 (s, 1H, aryl), 7.05 (s, 1H, aryl), 7.75 (d, J = 15.9 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.63, 27.76, 101.32, 105.43, 110.72, 125.68, 126.40, 133.45, 140.21, 146.48, 149.53, 198.14. IR (KBr, cm^{-1}): 1664 (C═O). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.54; H, 5.95.

(3*E*)-4-(2,5-Dimethoxyphenyl)-3-buten-2-one (5e). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.71 (d, J = 16.5 Hz, 1H, vinyl), 6.85 (d, J = 9.0 Hz, aryl), 6.94 (dd, J = 2.7 and 9.0 Hz, 1H, aryl), 7.07 (d, J = 2.7 Hz, 1H, aryl), 7.86 (d, J = 16.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.97, 55.61, 55.93, 112.29, 112.44, 117.43, 123.71, 127.71, 138.36, 152.63, 153.43, 198.89. IR ($CHCl_3$, cm^{-1}): 1675 (C═O). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.84; H, 6.84. Found: C, 69.65; H, 6.76.

4-Bis(2-methyl-4,5-methylenedioxyphenyl)-2-butanone (6a). Colorless crystals, mp 131.8−133.6 °C (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.11 (s, 3H, CH_3), 2.20 (s, 6H, $2CH_3$), 2.92 (d, J = 7.8 Hz, 2H, CH_2−C═O), 4.69 (t, J = 7.8 Hz, 1H, CH), 5.87 (s, 4H, 2O−CH_2O−), 6.56 (s, 2H, aryl), 6.62 (s, 2H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.28, 30.30, 38.22, 49.02, 100.72, 107.06, 110.72, 128.91, 134.33, 145.59, 145.83, 206.67. IR (KBr, cm^{-1}): 1720 (C═O). Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.33; H, 5.92.

4-Bis(4-methoxylphenyl)-2-butanone (6b). Yellow oil (75% di-*para*-substitution as determined by GC in three isomers of *p*-, *o*-, *m*-). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.04 (s, 3H, CH_3), 3.09 (d, J = 7.5 Hz, 2H, CH_3), 3.73 (s, 6H, $2OCH_3$), 4.47 (t, J = 7.5 Hz, 1H, CH), 6.80 (d, J = 8.4 Hz, 4H, aryl), 7.11 (d, J = 8.4 Hz, 4H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.53, 44.47, 49.99, 55.10, 113.84, 128.44, 136.26, 157.94, 207.09. IR (neat, cm^{-1}): 1714 (C═O). GC/MS: m/z M^+ for $C_{18}H_{20}O_3$, 284. A small amount of the other two isomers in this mixture is difficult to recognize, but GC/MS spectra show their presence. GC/MS: m/z M^+, 284.

1-Pentamethylphenyl-1-phenylethylene (7). Colorless crystals, mp 66.5−67.2 °C (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.10 (s, 6H, $2CH_3$), 2.23 (s, 6H, $2CH_3$), 2.28 (s, 3H, CH_3), 5.06 (d, J = 1.5 Hz, 1H, vinyl), 5.96 (d, J = 1.5 Hz, 1H, vinyl), 7.23−7.28 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.54, 16.75, 17.83, 114.29, 126.00, 127.42, 128.35, 131.56, 132.33, 133.70, 138.71, 140.02, 148.65. Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H 8.86. Found: C, 90.99; H, 8.85.

6-*tert*-Butylcoumarin (8). Light yellow crystals, mp 76.4−78.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (s, 9H, 3 CH_3), 6.41 (d, J = 9.6 Hz, 1H, vinyl), 7.27 (d, J = 8.7 Hz, 1H, aryl), 7.45 (d, J = 2.7 Hz, 1H, aryl), 7.60 (dd, J = 2.7 and 8.7 Hz, 1H, aryl), 7.71 (d, J = 9.6 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.27, 34.46, 116.31, 116.36, 118.21, 124.08, 129.45, 143.87, 147.53, 151.99, 161.14. IR ($CHCl_3$, cm^{-1}): 1721 (CO). Anal. Calcd for $C_{13}H_{14}O_2$; C, 77.20; H, 6.98. Found: C, 77.05; H, 7.11.

4-Phenyl-6-*tert*-butylcoumarin (8a). Colorless crystals, mp 108.3−109.0 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.27 (s, 9H, *tert*-butyl), 6.36 (s, 1H, vinyl), 7.35 (d, J = 8.4 Hz, 1H, aryl), 7.54 (m, 6H, aryl), 7.60 (dd, J = 2.4, 8.4 Hz, 1H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 31.2, 34.6, 115.0, 116.8, 118.2, 123.1, 128.4, 128.8, 129.5, 129.6, 135.4, 147.2, 152.2, 155.9, 161.0. IR ($CHCl_3$, cm^{-1}): 1726 (C═O). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.94; H, 6.55.

4-Methyl-6-*tert*-butylcoumarin (8b). Light yellow crystals, mp 123.5−124.0 °C (hexane/EtOAc) (123 °C).[15b] ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H, $3CH_3$), 2.46 (d, J = 1.5 Hz, 3H, CH_3), 6.28 (d, J = 1.5 Hz, vinyl), 7.27 (d, J = 8.7 Hz, 1H, aryl), 7.57 (s, 1H, aryl), 7.60 (d, J = 8.7 Hz, 1H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.59, 31.33, 34.59, 114.84, 116.55, 119.20, 120.51, 129.33, 147.17, 151.46, 152.59, 161.01. IR ($CHCl_3$, cm^{-1}): 1729 (C═O).

(2*Z*)-Ethyl 3-Mesitylcinnamate (10). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.10 (t, J = 6.9 Hz, 3H, CH_3), 2.03 (s, 6H, $2CH_3$), 2.32 (s, 3H, CH_3), 4.02 (q, J = 6.9 Hz, 2H, OCH_2), 6.61 (s, 1H, vinyl), 6.90 (s, 2H, aryl), 7.33 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.99, 19.74, 21.15, 59.85, 117.54, 126.94, 127.99, 128.64, 129.46, 134.62, 135.22, 136.68, 138.35, 155.06, 165.67. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.44; H, 7.55.

(2*Z*)-3-Mesitylcinnamic Acid (10a). Colorless crystals, mp 195.0−195.6 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.02 (s, 6H, $2CH_3$), 2.31 (s, 3H, CH_3), 6.59 (s, 1H, vinyl), 6.89 (s, 2H, aryl), 7.30 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.71, 21.12, 116.94, 127.10, 128.19, 128.72, 129.84, 134.44, 134.68, 137.07, 138.19, 157.13, 169.75. IR ($CHCl_3$, cm^{-1}): 3010 (wide and broad, COOH), 1697 (C═O). Anal. Calcd for C $_{18}H_{18}O_2$: C, 81.87; H, 6.81. Found: C, 81.68; H, 6.66.

(2*Z*)-3-Pentamethylphenylcinnamaldehyde (11). Gray solid, mp 114.0−115.2 °C ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.04 (s, 6H, $2CH_3$), 2.23 (s, 6H, $2CH_3$), 2.29 (s, 3H, CH_3), 6.81 (d, J = 7.2 Hz, 1H, vinyl), 7.32−7.40 (m, 5H, aryl), 9.30 (d, J = 7.2 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.35, 16.70, 17.87, 126.24, 127.13, 128.77, 130.45, 131.12, 132.62, 132.85, 134.99, 137.74, 162.88, 194.10. IR ($CHCl_3$, cm^{-1}): 1670 (C═O). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.76; H, 7.53.

(2*Z*)-1-Pentamethylphenyl-1,2-bisphenylethylene (12). Colorless crystals, mp 114.6−115.8 °C (hexane/EtOAc). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.01 (s, 6H, $2CH_3$), 2.21 (s, 6H, $2CH_3$), 2.30 (s, 3H, CH_3), 6.90−7.10 (m, 5H, aryl), 7.14 (s, 1H, vinyl), 7.18−7.36 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.62, 16.86, 17.18, 126.18, 126.71, 127.09, 127.82, 128.12, 128.35, 128.59, 131.11, 132.72, 133.90, 136.28, 137.63, 141.70, 142.18. Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03. Found: C, 91.82; H, 8.03.

(2*Z*)-1-Pentamethylphenyl-1-phenylpropene (13). Colorless crystals, mp 98.0−98.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.49 (d, J = 6.9 Hz, 3H, CH_3), 2.04 (s, 6H, $2CH_3$), 2.23 (s, 6H, $2CH_3$), 2.27 (s, 3H, CH_3), 6.35 (q, J = 6.9 Hz, 1H, vinyl), 7.20 (s, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.15, 16.63, 16.75, 17.17, 123.24, 125.73, 126.42, 128.22, 131.52, 132.19, 133.32, 135.96, 141.19, 141.79. Anal. Calcd for C_{20} H_{24}: C, 90.85; H, 9.15. Found: C, 90.58; H, 9.18.

(3*Z*)-4-(Pentamethylphenyl)-4-phenyl-3-buten-2-one (14). Brown crystals, mp 49.2−50.5 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.69 (s, 1H, CH_3), 2.04 (s, 6H, $2CH_3$), 2.23 (s, 6H, $2CH_3$), 2.29 (s, 3H, CH_3), 6.83 (s, 1H, vinyl), 7.33 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.46, 16.83, 17.67, 29.29, 127.30, 128.03, 128.65, 129.47, 130.37, 132.85, 134.84, 135.19, 139.18, 154.80, 200.18. IR ($CHCl_3$, cm^{-1}): 1654 (C═O). Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 85.90; H, 8.30.

(2*E*)-Ethyl 3-(Pentamethylphenyl)-2-butenoate (15). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, J = 6.9 Hz, 3H, CH_3), 2.04 (d, J = 1.5 Hz, 3H, CH_3), 2.09 (s, 6H, $2CH_3$), 2.19 (s, 6H, $2CH_3$), 2.22 (s, 3H, CH_3), 3.95 (q, J = 6.9 Hz, 2H, OCH_2), 6.04 (q, J = 1.5 Hz, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.92, 16.33, 16.63, 16.93, 26.58, 59.31, 118.88, 127.90, 132.05, 133.30, 137.99, 158.08, 165.23. IR ($CHCl_3$, cm^{-1}): 1733 (C═O). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.43; H, 9.34.

(2*Z*)-3-(Pentamethylphenyl)cinnamic Acid (16). White crystals, mp 240.2−241.4 °C (hexane/EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 6H, $2CH_3$), 2.20 (s, 6H, 2 CH_3), 2.27 (s, 3H, CH_3), 6.62 (s, 1H, vinyl), 7.30 (m, 5H, aryl), 10.13 (br, 1H, COOH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.47, 16.84, 17.52, 117.13, 127.27, 128.66, 129.70, 130.13, 132.52, 134.26, 134.64, 138.78, 158.49, 169.51. IR ($CHCl_3$, cm^{-1}): 3000 (wide and broad, COOH), 1697 (C═O). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H 7.53. Found: C, 81.28; H, 7.65.

Diethyl 2-Pentamethylphenylfumarate (17). White crystals, mp 54.0−55.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (t, J = 7.2 Hz, 3H, CH_3), 1.25 (t, J = 6.9 Hz, 3H, CH_3), 2.03 (s, 6H, $2CH_3$), 2.17 (s,

6H, $2CH_3$), 2.21 (s, 3H, CH_3), 3.98 (q, $J = 7.2$ Hz, 2H, CH_2O), 4.24 (q, $J = 6,9$ Hz, 2H, CH_2O), 7.08 (s, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.73, 14.13, 16.40, 16.87, 17.66, 60.44, 61.65, 129.06, 130.38, 131.18, 131.82, 134.58, 146.33, 164.93, 166.46. IR ($CHCl_3$, cm^{-1}): 1728 (C═O). Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.93; H, 8.28.

4-(Pentamethylphenyl)-4-octene (*Z*/*E* = 1/1) (18). An inseparable mixture of 4-(pentamethylphenyl)-4-octene (*Z*/*E* = 1/1) and pentamethylbenzene, as identified by GC/MS, ^1H NMR, and ^{13}C NMR analyses. ^1H NMR (300 MHz, $CDCl_3$): δ 0.7−1.7 (m, 14 H), 2.18 (m, 15H), 5.48 (m, 1H, vinyl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.65, 13.94, 14.05, 14.27, 15.21, 16.52, 16.58, 17.40, 20.73, 22.40, 22.94, 24.88, 29.70, 30.6, 31.11, 32.25, 38.40, 41.14, 126.29, 127.63, 129.62, 130.47, 131.25, 132.08, 132.61, 136.71, 138.74, 138.80, 140.25, 140.76. GC/MS: *m*/*z* M^+ for **20**, 258, calcd 258.

(2*Z*)-Ethyl 3-(Pentamethylphenyl)cinnamate (19). A colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.07 (t, $J = 7.2$ Hz, 3H, CH_3), 2.01 (s, 6H, $2CH_3$), 2.21 (s, 6H, $2CH_3$), 2.26 (s, 3H, CH_3), 4.01 (q, $J = 7.2$ Hz, 2H, CH_2O), 6.62 (s, 1H, vinyl), 7.33 (m, 5H, aryl). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.89, 16.44, 16.79, 17.44, 59.65, 117.37, 127.09, 128.53, 129.24, 129.86, 131.89, 133.75, 135.47, 139.05, 156.88, 165.68. IR (neat, cm^{-1}): 1737 (C═O). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.61; H, 7.95.

Reaction of Pentamethylbenzene with Ethyl Propiolate in CF_3CO_2D. The general procedure was followed using $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), HC≡CCO_2Et (0.15 g, 1.5 mmol), Me_5C_6H (0.45 g, 3.0 mmol), CF_3CO_2D (1.5 mL), and CH_2Cl_2 (0.5 mL) with stirring for 2 h at room temperature. Standard workup gave two white crystals as **2b-D** (0.326 g in 86% yield) and **3a-D** (18 mg in 6% yield). The ^1H NMR spectrum of **2b-D** is similar to that of **2b** except for the occurrence of a singlet vinylic resonance at 7.12 ppm and the unequal intensities of the vinylic resonances based on the integration of protons in the ester group (Figure 3): δ 7.12 (s + d, $J = 12.0$ Hz, 1H), 6.12 (d, $J = 12.0$ Hz, 0.43H, 57% of D incorporation). GC/MS: *m*/*z* $M^{+\bullet}$ for **2b-D**, 247; for **2b**, 246, and a small amount of **2b-D$_2$**, 248. The ^1H NMR spectrum of **3a-D** is similar to that of **3a** except for the occurrence of a singlet vinylic resonance at 7.50 ppm and the unequal intensities of the vinylic resonances based on the integration of protons in the ester group (Figure 3): δ 7.50 (s + d, $J = 15.9$ Hz, 1H), 7.25 (s, $J = 15.9$ Hz, 1H), 6.17 (d, $J = 15.9$ Hz, 0.45H, 55% of D incorporation). GC/MS: *m*/*z* $M^{+\bullet}$ for **3a-D**, 345; for **3a**, 344; and for a small amount of **3a-D$_2$**, 346.

Reaction of Pentamethylbenzene with 3-Butyn-2-one in CF_3CO_2D. The general procedure was followed using $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), HC≡CCOMe (0.10 g, 1.5 mmol), Me_5C_6H (0.45 g, 3.0 mmol), CF_3CO_2D (1.5 mL), and CH_2Cl_2 (0.5 mL) for 2 h at room temperature. Standard workup gave 0.305 g of white crystals (in 92% % yield) as **5a-DD**. The ^1H NMR spectrum of **5a-DD** is similar to that of **5a**, except for the occurrence of a singlet vinylic resonance at 7.71 ppm and the unequal intensities of the vinylic resonances based on the integration of protons in the methyl group connected to the carbonyl: δ 7.71 (s + d, $J = 16.5$ Hz, 0.94 H, 6% of D incorporation), 6.16 (d, $J = 16.5$ Hz, 0.50H, 50% of D incorporation). GC/MS: *m*/*z* $M^{+\bullet}$ for **5a-DD**, 217 and 218; for **5a**, 216.

Reaction of Benzene-d_6 with Diphenylacetylene in TFA. The general procedure was followed using $PtCl_2$ (13.3 mg, 0.05 mmol), AgOAc (16.6 mg, 0.10 mmol), PhC≡CPh (0.18 g, 1 mmol), C_6D_6 (0.42 g, 5.0 mmol), CF_3CO_2H (2 mL), and CH_2Cl_2 (0.5 mL) with stirring for 40 h at room temperature. Standard workup gave 0.16 g of colorless oil (in 62% % yield) as **10-D$_5$**. The ^1H NMR spectrum of **10-D$_5$** indicated that the intensities of the vinyl proton (at 6.94 ppm as a singlet) and aryl protons (at 7.05 ppm, multiplet, 5H and at 7.26, multiplet, 5H) are in a ratio of 1:10. GC/MS: *m*/*z* $M^{+\bullet}$ for **10-D$_5$**, 261. All these data suggest that there are five D's in **10-D$_5$**, but no D has been incorporated into the vinylic proton (TFA does not contain D).

H/D Exchange Reaction of (2*Z*)-Ethyl 3-(Pentamethylphenyl)-propenoate (2b) in CF_3CO_2D. 2b (25 mg, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and CF_3CO_2D (0.5 mL) were mixed in an NMR tube, and then a sealed capillary tube containing sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O was inserted into the mixture. It is concluded that no vinylic proton H/D exchange was found since no decrease in the intensity of any peak in the ^1H NMR spectrum was observed. In fact, the spectrum of the reaction mixture was the same as that of **2b** in TFA.

Reaction of (2*Z*)-Ethyl 3-(Pentamethylphenyl)propenoate (2b) and Ethyl Propiolate in CF_3CO_2D. 2b (25 mg, 0.1 mmol), HC≡CCO_2Et (20 mg, 0.2 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), and CF_3CO_2D (0.5 mL) were mixed in an NMR tube, and then a sealed capillary tube containing sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O was inserted into the mixture. It is concluded that no reaction took place after 24 h since no decrease in the intensity of any peak in the ^1H NMR spectrum was observed.

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Supporting Information Available: Details of the X-ray structure determinations of compounds **12** and **13** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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