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Highly selective hydroarylation of propiolic acid derivatives using a $PtCl_2$/AgOTf catalytic system

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Abstract—Hydroarylation of propiolic acid derivatives with arenes in trifluoroacetic acid efficiently proceeded in the presence of $PtCl_2$/AgOTf catalyst to give *cis*-cinnamic acid derivatives in good to high yields. This $PtCl_2$/AgOTf-catalyzed reaction did not afford any 4-arylbuta-1,3-diene-1,3-dicarboxylic acid derivatives formed by $Pd(OAc)_2$-catalyzed hydroarylation. The specific optimization of the catalytic hydroarylation and application to electron-rich arenes are reported.

1. Introduction

Direct C–H bond functionalization has several advantages compared to conventional synthetic methods. This method does not require prefunctionalization because it uses only C–H bonds instead of reactive groups as the reaction site for the functionalization. It not only reduces the reaction steps but also avoids use of toxic halogenated compounds. In other words, simple and cheap organic hydrocarbons can be used as starting materials. Furthermore, the C–H functionalization method is also favorable from the viewpoint of atom economy because some functional groups are used as leaving groups that are not incorporated into the products. Therefore, direct C–H bond functionalization would provide an ideal transformation process that is clean, simple, and cheap. Direct C–H functionalization using transition metal catalysts is of increasing interest in organic chemistry.[1]

Styrene and its derivatives are versatile intermediates in organic synthesis and various synthetic methods have been reported. Representative reactions of catalytic reactions involve a transition metal-catalyzed coupling reaction using organometallic compounds[2] and a coupling reaction of organic halides or triflates with alkenes (Mizoroki–Heck reaction).[3,4]

Recently, many synthetic methods for hydroarylation of alkynes using transition metal catalysts have been reported.[5] Several transition metal compounds catalyze the hydroarylation of alkynes with arenes and heteroarenes.[6–16] Transition metal-catalyzed addition reactions of arenes having directing groups such as carbonyl, imino, and nitrile groups via chelation-assisted C–H bond activation have been extensively studied by Murai, Kakiuchi, and Chatani.[1h,i] A chelation-assisted reaction of arenes to alkynes is catalyzed by several transition metal compounds to afford *ortho*-alkenylation products.[17–21] Similarly, intramolecular hydroarylation of alkynes catalyzed by transition metal compounds proceeds to give cyclic aromatics and heterocycles.[22–27]

Although we have reported that the $Pd(OAc)_2$-catalyzed hydroarylation of alkynes proceeds under very mild conditions to afford *cis*-aryl substituted alkenes with high regio- and stereoselectivity,[8a,b,d] the reaction in the case of ethyl propiolate gives diethyl (1*E*,3*Z*)-4-arylbuta-1,3-diene-1,3-dicarboxylates along with the desired product, ethyl (2*Z*)-cinnamates, resulting in low selectivity and yield of the desired product. On the other hand, we preliminarily found that the hydroarylation of ethyl propiolate proceeded selectively to give cinnamates without the formation of buta-1,3-diene-1,3-dicarboxylates when a Pt(II) catalyst, $PtCl_2$/AgOAc, was used instead of $Pd(OAc)_2$.[8b] However, the activity of the $PtCl_2$/AgOAc catalyst was still low and required improvement. Thus, we studied the $PtCl_2$ catalyst in detail to improve the activity of the Pt catalyst and to discover better catalytic systems.[28]

A more strong cationic Pt catalyst is required to improve the activity because the hydroarylation is considered to proceed by electrophilic aromatic substitution. Silver compounds like AgOAc are thought to react with $PtCl_2$ and exchange

Keywords: Hydroarylation; Propiolic acid derivatives; Platinum chloride; Silver triflate; Cinnamic acid derivatives.
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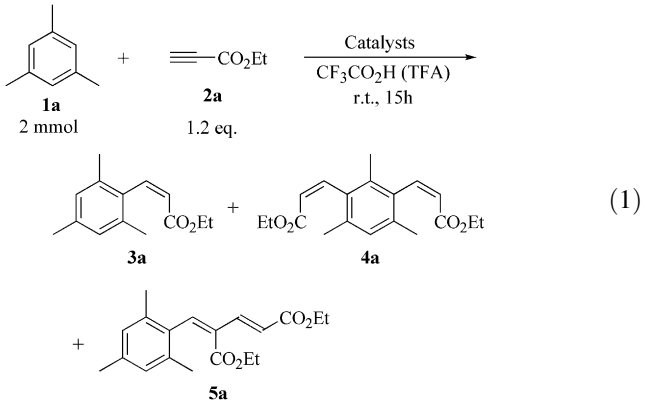
ligands to afford a more cationic and active Pt species. The formation of a more active Pt catalyst than $PtCl_2$/AgOAc is expected when silver compounds having less basic anions such as ^{-}OTf, BF_4^-, and PF_6^- are used. Therefore, the effects of silver compounds as additives for $PtCl_2$-catalyzed hydroarylation were investigated.

2. Results and discussion

2.1. Effect of silver compounds as additives

The reaction of ethyl propiolate (**2a**) with mesitylene (**1a**) was chosen for the present investigation because it gave ethyl (2*Z*)-3-(2,4,6-trimethylphenyl)propenoate (**3a**), ethyl (2*Z*)-3-{3-[(1*Z*)-2-(ethoxycarbonyl)ethenyl]-2,4,6-trimethylphenyl}propenoate (**4a**), and diethyl (1*E*,3*Z*)-4-(2,4,6-trimethylphenyl)buta-1,3-diene-1,3-dicarboxylate (**5a**) in moderate yields in the case of the $Pd(OAc)_2$ catalyst (Eq. 1), as shown in Table 1. Table 1 indicates that the percentage of **5a** is almost constant (ca. 15%) even when the molar ratio of **2a** to **1a** was changed from 0.75 to 2.0.



(1)

Table 1. $Pd(OAc)_2$-catalyzed hydroarylation of **2a** with **1a**[a]

Entry	**2a** (equiv)	Time (h)	Conversion of **1a** (%)	Yields[b] (%)			Selectivity (%)		
				3a	**4a**	**5a**	**3a**	**4a**	**5a**
1	2.0	25	100	52	19	13	61	23	16
2	1.5	15	86	58	5	12	78	7	16
3	1.5	25	87	60	6	13	76	7	17
4	1.2	15	73	51	2	10	81	3	15
5	1.2	25	76	55	2	10	81	4	15
6	1.2	45	77	55	2	11	81	3	16
7	1.2	15	74[c]	48	2	8	84	3	13
8	0.75	15	50	37	Trace	6	85	1	14

[a] Reaction conditions: **1a** (2 mmol), **2a**, $Pd(OAc)_2$ (0.05 mmol), TFA (1 mL) at room temperature.
[b] GC yields based on **1a**.
[c] The reaction was conducted at 70 °C.

The reaction was carried out with $PtCl_2$ (0.05 mmol), the silver compound (0.1 mmol), **1a** (2 mmol), and **2a** (2.4 mmol) in trifluoroacetic acid (TFA) (1 mL) at room temperature for 15 h. The results are given in Table 2. The $PtCl_2$/AgOAc-catalyzed reaction gave **3a** and **4a** in 36 and 1% yields, respectively (entry 2), while the reaction did not proceed in the absence of the catalyst (entry 11). The reaction did not give **5a**. However, the yield and the conversion were low and almost identical to those obtained when only $PtCl_2$ was used (entry 1). Addition of $AgOCOCF_3$ did not affect the reaction (entry 3). Ag_2CO_3 slightly improved the yield and the conversion (entry 4). Increasing the amount of Ag_2CO_3 did not improve the yields (entry 5). $AgBF_4$ and $AgPF_6$ were effective (entries 6 and 7), but AgOTf was the best additive among the Ag compounds tested (entry 8). A $PtCl_2$/AgOTf catalyst gave the highest conversion and yield among the Pd and Pt catalysts employed, showing that the $PtCl_2$/AgOTf catalyst is effective. Addition of triflic acid (TfOH) in place of AgOTf resulted in low yields (entry 9). The reaction also proceeded by using only AgOTf in the absence of $PtCl_2$, but the yield was very low (entry 10). This result suggests that the active catalyst is the Pt species generated from the reaction of AgOTf and $PtCl_2$. It is considered that the role of AgOTf is to transform insoluble $PtCl_2$ into a soluble, cationic, and active Pt species.

Table 2. $PtCl_2$-catalyzed hydroarylation of **2a** with **1a**[a]

Entry	Catalysts (mol %)	Conversion of **1a** (%)	Yields[b] (%)		
			3a	**4a**	**5a**
1	$PtCl_2$ (2.5)	43	39	2	0
2	$PtCl_2$/AgOAc (2.5/5)	41	36	1	0
3	$PtCl_2$/$AgOCOCF_3$ (2.5/5)	44	40	1	0
4	$PtCl_2$/Ag_2CO_3 (2.5/2.5)	51	44	2	0
5	$PtCl_2$/Ag_2CO_3 (2.5/5)	52	44	2	0
6	$PtCl_2$/$AgBF_4$ (2.5/5)	78	66	11	0
7	$PtCl_2$/$AgPF_6$ (2.5/5)	76	64	9	0
8	$PtCl_2$/AgOTf (2.5/5)	84	67	16	0
9	$PtCl_2$/TfOH (2.5/30)	68	23	1	0
10	AgOTf (5)	20	13	0	0
11	None	1	0	0	0

[a] Reaction conditions: **1a** (2 mmol), **2a** (2.4 mmol), catalysts, and TFA (1 mL) at room temperature for 15 h.
[b] GC yields based on **1a**.

2.2. Optimization of reaction conditions

The reaction using $PtCl_2$/AgOTf catalyst was then investigated to optimize the reaction conditions (Table 3). Extension of the reaction time from 15 to 45 h improved the conversion of **1a** to give a higher yield of **4a** (entry 2). Higher temperature also increased the conversion of **1a**, but the yields of **3a** and **4a** decreased (entries 3 and 4). This observation can be explained by hydrolysis of the ester products **3a** and **4a** to the corresponding acid forms at higher temperature in TFA. Using an excess amount of **1a** is effective for the selective formation of **3a**. When the reaction of **1a** (4 mmol) with **2a** (2 mmol) was conducted under the same conditions, **3a** and **4a** were formed in 86 and 12% yields, respectively (entry 5).

Table 3. Optimization of reaction conditions[a]

Entry	Time (h)	Temp (°C)	Conversion of **1a** (%)	Yields[b] (%)		
				3a	**4a**	**5a**
1	15	rt	84	67	16	0
2	45	rt	94	64	28	0
3	15	50	92	57	24	0
4	15	70	92	19	10	0
5	15[c]	rt	50	44 (84)[d]	3 (12)[d]	0 (0)[d]

[a] Reaction conditions: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **1a** (2 mmol), **2a** (2.4 mmol), catalysts, TFA (1 mL).
[b] GC yields based on **1a**.
[c] Compounds **1a** (4 mmol) and **2a** (2 mmol) were used.
[d] The yields in parentheses were based on **2a**.

Table 4. Effect of temperature on the $PtCl_2$/AgOTf-catalyzed hydroarylation[a]

Entry	Temp (°C)	Yields[b] (%)			
		3a (*Z*/*E*)[c]	**4a**	**5a**	**6a** (*Z*/*E*)[c,d]
1	30	81 (100/0)	9	0	—
2	40	83 (>99/1)	10	0	—
3	50	75 (99/1)	10	0	7 (78/22)
4	60	60 (98/2)	10	0	11 (86/14)
5	70	32 (97/3)	6	0	39 (94/6)

[a] Reaction conditions: **1a** (4 mmol), **2a** (2 mmol), $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), TFA (1 mL), 8 h.
[b] GC yields based on **2a**.
[c] *Z*/*E* ratio was determined by ^{1}H NMR.
[d] Isolated yields.

2.3. Effect of temperature on hydroarylation

Next, we investigated the effect of temperature using an excess amount of **1a** (Table 4). The reaction almost completed in 8 h even at room temperature (entry 1). The reaction at 40 °C improved the yields of **3a** and **4a** slightly, but further elevation of temperature decreased their yields (entries 2–5). Instead, 3-(2,4,6-trimethylphenyl)propenoic acid (**6a**), which is derived from the hydrolysis of **3a**, was obtained at higher temperature. The amount of **6a** increased when the temperature was increased. The isomerization of the *Z*- to *E*-isomer also took place at higher temperature.

The time dependence of **3a** under the reaction conditions at 70 °C clearly shows the hydrolysis and isomerization of **3a** (Fig. 1). From these results, a lower reaction temperature is preferred because the hydroarylation competes with the hydrolysis of the ester and isomerization at higher temperature.

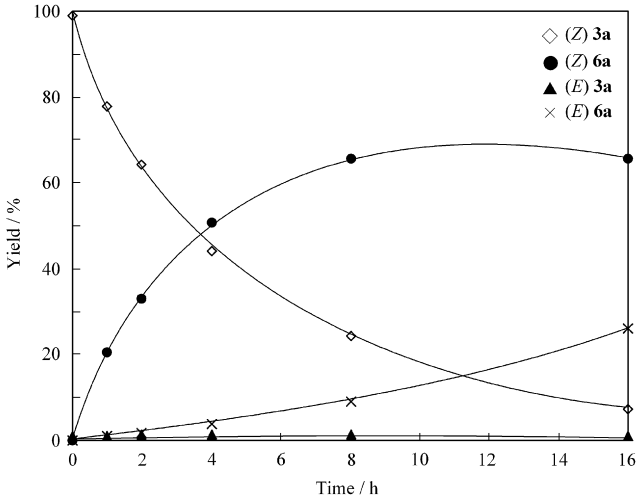
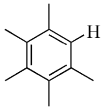
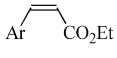
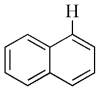
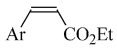
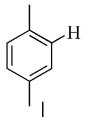
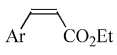
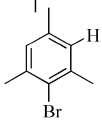
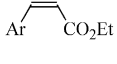
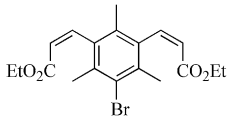
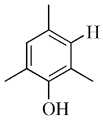
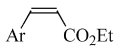
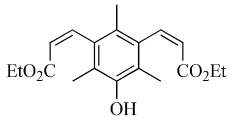


Figure 1. Time dependence of **3a** under the reaction conditions. [Reaction conditions: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **3a** (1.5 mmol), heptadecane (10 mg, as internal standard), TFA (1 mL), 70 °C. The yields were determined by ^{1}H NMR].

2.4. Scope of the reaction

Next, the reaction of **2a** with various arenes was examined (Table 5). The result shows that the reaction gave the hydroarylated products in good to excellent yields. Especially, the

Table 5. $PtCl_2$/AgOTf-catalyzed hydroarylation of **2a** with various arenes[a]

Entry	Ar–H	Temp (°C)	Time (h)	Products and yields[b] (%)				
1	 **1b**	rt	15		**3b**	91 (95)[c]		
2		rt	3		**3b**	(31)[c]		
3		rt	2		**3b**	(67)[c,d]		
4	 **1c**	rt	35		**3c**	65[e]		
5	 **1d**	rt	40		**3d**	61 (62) (*Z*/*E*=99/<1)		
6		50	15		**3d**	(34) (*Z*/*E*=91/9)		
7	 **1e**	rt	48		**3e**	30[f]		**4b** 1[f]
8		40	48		**3e**	64 (65)[g,h]		**4b** 5[g,h]
9		50	48		**3e**	(63)[g,i]		
10	 **1f**	rt	48		**3f**	76		**4c** 14

[a] Reaction conditions: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene (4 mmol), **2a** (2 mmol), TFA (1 mL).
[b] Isolated yields based on **2a**. The yields in parentheses were determined by GC.
[c] CH_2Cl_2 (0.25 mL) was used.
[d] $Pd(OAc)_2$ (0.02 mmol, 1 mol %) was used instead of $PtCl_2$/AgOTf. Compound **5b** was obtained in 20% yield.
[e] CH_2Cl_2 (0.5 mL) was used. Compound **6c** was obtained in <8% yield.
[f] CH_2Cl_2 (0.5 mL) was used.
[g] CH_2Cl_2 (0.5 mL) and $Cl(CH_2)_2Cl$ (0.5 mL) were used.
[h] Compound **6e** was isolated in 13% yield.
[i] Compound **6e** was isolated in 15% yield.

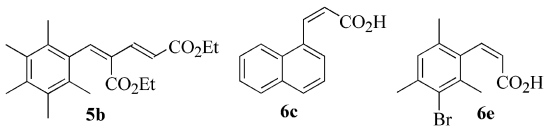


Figure 2.

electron-rich arene, pentamethylbenzene (**1b**), gave the product **3b** in high yield (entry 1). The reaction of **1b** resulted in a low conversion after 3 h, while the reaction using the $Pd(OAc)_2$ catalyst completed in 2 h to give **3b** and **5b** (Fig. 2) in 67 and 20% yields, respectively (entries 2 and 3). However, prolonging the reaction time improved the yield of **3b**. As a result, the yield was higher than that obtained by the reaction using $Pd(OAc)_2$ because of the higher selectivity of the Pt catalyst. A slower reaction rate was also observed during the course of the reaction of **1b** (Fig. 3). The slower rate with Pt catalysis may be due to a lower activity or lower solubility of the Pt catalyst than that of the Pd catalyst. The reactions of naphthalene (**1c**) and *p*-xylene (**1d**) also gave adducts **3c** and **3d** in good yields, respectively (entries 4 and 5). In the case of **1c**, hydroarylation occurred selectively at the α-position of **1c**. Increasing temperature in the reaction of **1d** resulted in a low yield of **3d** (entry 6). This reaction is tolerant to unprotected OH and Br groups. The reaction of 1-bromo-2,4,6-trimethylbenzene (**1e**) and 2,4,6-trimethylphenol (**1f**) gave adducts **3e** and **3f** in good yields, together with the bis-alkenylated products **4b** and **4c** (entries 7–10). In the case of **1e**, higher temperature was required to improve the yield because of the low reactivity of **1e** (entry 8). In the case of **1c** and **1e**, the hydrolyzed products **6c** and **6e** (Fig. 2) were observed (entries 4, 8, and 9). The yields of **3** in the $PtCl_2$/AgOTf-catalyzed reaction were generally higher than those in the $Pd(OAc)_2$-catalyzed reaction.

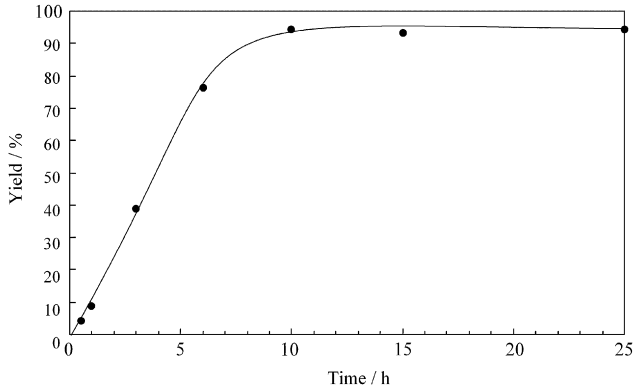
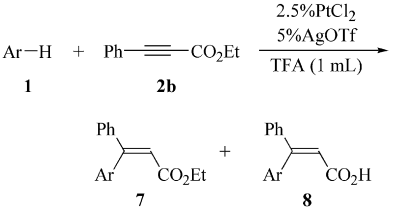


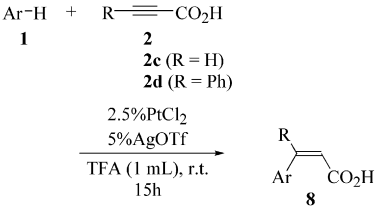
Figure 3. Time course of hydroarylation of **2a** with **1b**. [Reaction condition: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **1b** (4 mmol), **2a** (2 mmol), pentadecane (0.2 g, as internal standard), TFA (1 mL), CH_2Cl_2 (0.5 mL) at rt. GC yield based on **2a**.]

This reaction was also applied to the reaction of an internal alkyne, ethyl phenylpropiolate (**2b**) (Eq. 2, Table 6). The reaction of **2b** was slower than that of **2a** and a longer reaction time was required for high conversion of **2b**. The reaction mainly gave products **8**, which were formed by hydrolysis of esters **7** during the reaction, along with **7**. In the case of **1a**, higher temperature is required for good yield because the reaction was slower. The reaction gave a small amount of a decarboxylated product **9**, together with **7a** and **8a** (entry 2). On the other hand, the reaction of **1b** proceeded smoothly at room temperature but gave **8b** in high yield (entry 3).



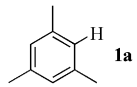
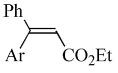
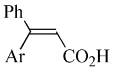
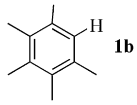
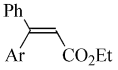
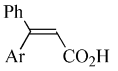
(2)

Hydroarylation of propiolic acids was also conducted because the prolonged reaction of ethyl propiolates mainly gave the hydrolyzed products **6** or **8**. This catalytic system was found to be effective for the reaction of propiolic acids (Eq. 3, Table 7). The reactions of propiolic acid (**2c**) gave the corresponding cinnamic acids **6** in good to high yields. The reactions of **1a** and **1b** gave **6a** and **6b** in 94 and 96% yields, respectively (entries 1 and 2). In the case of **1a**, 3 equiv of **1a** was used to increase the selectivity of **6a**. The reaction of **1c** at 40 °C gave **6c** in 77% yield (entry 3). The reaction of phenylpropiolic acid (**2d**) gave **8b** in moderate yield, probably due to the low solubility (entry 4).



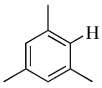
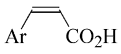
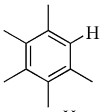
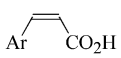
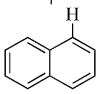
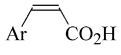
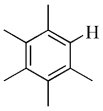
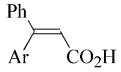
(3)

Table 6. $PtCl_2$/AgOTf-catalyzed hydroarylation of **2b**[a]

Entry	Ar–H	Temp	Time (h)	Products and isolated yields[b] (%)								
1	 **1a**	rt	50		**7a**	20[c]		**8a**	22			
2		40 °C	48		**7a**	14		**8a**	59		**9**	7
3	 **1b**	rt	50		**7b**	14[d]		**8b**	80[d]			

[a] Reaction conditions: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene (4 mmol), **2b** (Ph—≡—CO_2Et, 2 mmol), TFA (1 mL).
[b] The yields are based on **2b**.
[c] Crude yield determined by ^1H NMR; 43% of **2b** was remained.
[d] CH_2Cl_2 (0.25 mL) was used.

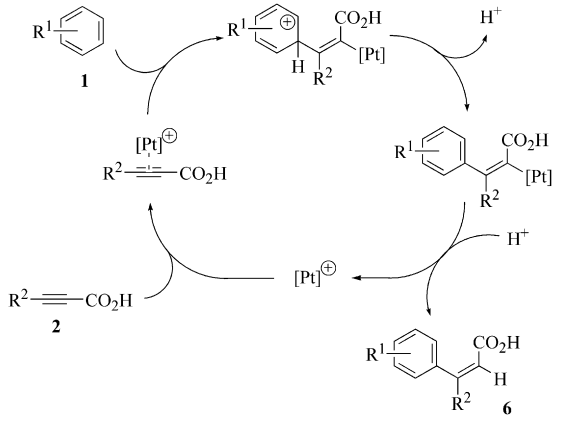
Table 7. $PtCl_2$/AgOTf-catalyzed hydroarylation of propiolic acids[a]

Entry	Ar–H		R	Temp (°C)	Time (h)	Products and yields[b] (%)		
1		**1a**	H **2c**	rt	15		**6a**	94[c]
2		**1b**	H **2c**	rt	15		**6b**	96[d]
3		**1c**	H **2c**	40	45		**6c**	77[e]
4		**1b**	Ph **2d**	rt	48		**8b**	48[f]

[a] Reaction conditions: $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene **1** (4 mmol), propiolic acids **2** (2 mmol), TFA (1 mL).
[b] Isolated yields based on **2**.
[c] Compound **1a** (6 mmol) was used.
[d] CH_2Cl_2 (0.25 mL) was used.
[e] $Cl(CH_2)_2Cl$ (0.75 mL) was used.
[f] CH_2Cl_2 (0.5 mL) was used.

2.5. Discussion of reaction mechanism

A recent report by Tunge and Foresee suggested that the $Pd(OAc)_2$-catalyzed hydroarylation of alkyne proceeds via electrophilic aromatic substitution.[9] Because Pd- and Pt-catalyzed hydroarylation proceeds under similar reaction conditions, the Pt-catalyzed hydroarylation is also considered to proceed via an electrophilic aromatic substitution mechanism. The electrophilic aromatic substitution mechanism is depicted in Scheme 1. The cationic Pt species, which is generated from $PtCl_2$ and an Ag compound initiate the reaction by coordination to a propiolic acid. The resulting activated propiolic acid complex attacks an arene electrophilically to form a Wheland intermediate. Proton release followed by protonolysis of a platinum-vinyl species results in the formation of a cinnamic acid with concomitant regeneration of an active Pt species, which completes the catalytic cycle.



Scheme 1. Plausible reaction mechanism of Pt-catalyzed hydroarylation.

3. Conclusion

It was found that AgOTf was an effective additive for $PtCl_2$-catalyzed hydroarylation of ethyl propiolate. It was also demonstrated that hydroarylation of ethyl propiolate catalyzed by $PtCl_2$/AgOTf proceeded smoothly to afford cinnamates selectively and efficiently. In the case of ethyl propiolate, the $PtCl_2$/AgOTf-catalyzed hydroarylation gave cinnamates in higher yields compared to the $Pd(OAc)_2$-catalyzed reaction because of higher selectivity of the Pt catalyst. This catalyst, especially, was the most effective for the reaction of propiolic acids.

4. Experimental

4.1. General

All solvents and reagents were commercially available and used as-received without further purification. All reactions were conducted in a dry Pyrex tube with a rubber septum. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR (300 MHz) using TMS as internal standard. Melting points were measured with a YANACO micromelting apparatus and are uncorrected. The GC analyses were performed on a Shimadzu GC-14B using a capillary column DB-1 (15 m×0.53 mm internal diameter×1.5 μm film thickness, J&W Scientific) with a flame ionization detector. The GC yield was determined by the internal standard method using *n*-pentadecane or *n*-heptadecane as internal standard. Mass spectra were measured on a Shimadzu GC/MS 5020A. Elemental analyses were performed by the Service Center for the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

4.2. General procedure for $Pd(OAc)_2$-catalyzed hydroarylation of 2a by 1a

After a mixture of $Pd(OAc)_2$ (0.05 mmol), mesitylene (**1a**) (2 mmol), and CF_3CO_2H (TFA) (1 mL) was stirred for 5 min on an ice/water bath, ethyl propiolate (**2a**) was added to the cold mixture. The mixture was then stirred at the desired temperature. After the reaction, *n*-heptadecane (0.2 g) as internal standard was added to the reaction mixture. The mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was analyzed by GC. The yields of the products and the conversion of **1a** were determined by using the internal standard method. The results are given in Table 1.

4.3. General procedure for investigation of silver additives and optimization of reaction conditions

After a mixture of $PtCl_2$ (0.05 mmol), an Ag compound, mesitylene (**1a**) (2 mmol), and CF_3CO_2H (TFA) (1 mL) was stirred for 5 min at room temperature, ethyl propiolate (**2a**) (2.4 mmol) was added. The reaction mixture was stirred at room temperature (25–30 °C) for 15 h. After the reaction, *n*-heptadecane (0.2 g) as internal standard was added. The mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was analyzed by GC. The yields of the products

and the conversion of **1a** were determined by using the internal standard method. The results are given in Tables 2 and 3.

4.4. General procedure for studying the effect of reaction temperature

After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **1a** (4 mmol), and TFA (1 mL) was stirred for 5 min at room temperature, **2a** (2 mmol) was added. The reaction mixture was stirred at the desired temperature for 8 h. After the reaction, *n*-heptadecane (0.2 g) as internal standard was added. The mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was analyzed by GC. The yields of the products were determined by using the internal standard method. After the ethereal layer was dried over anhydrous Na_2SO_4 and concentrated, the mixture was analyzed by ^1H NMR to determine the *Z*/*E* ratio of the products. The aqueous layer was acidified by aqueous HCl (ca. 36%) and extracted with diethyl ether (20 mL×3). The ethereal layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give **6a**. The *Z*/*E* ratio of **6a** was determined by ^1H NMR. The results are given in Table 4.

4.5. Procedure for studying the time dependence of 3a under the reaction conditions

A mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **3a** (1.5 mmol), heptadecane (12.3 mg, as internal standard), and TFA (1 mL) was stirred for 5 min at room temperature. After a portion of the reaction mixture was analyzed by ^1H NMR, the reaction mixture was stirred at 70 °C. After a certain period, a portion of the reaction mixture was analyzed by ^1H NMR. The yields of the products and the conversion of **3a** were determined by the internal standard method. The results are shown in Figure 1.

4.6. General procedure for $PtCl_2$/AgOTf-catalyzed hydroarylation of 2a with various arenes

After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene (4 mmol), and TFA (1 mL) was stirred for 5 min at room temperature, **2a** (2 mmol) was added. The mixture was stirred at the desired temperature. After the reaction, the reaction mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent. To obtain the GC yield, an internal standard, *n*-pentadecane or *n*-heptadecane, was added to the mixture after the reaction. The mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was analyzed by GC. The results are given in Table 5.

4.6.1. Typical example: hydroarylation of 2a with 1d (entry 5, Table 5). After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.10 mmol), **1d** (4 mmol), and TFA (1 mL) was stirred for 5 min at room temperature (25–30 °C), **2a** (2 mmol) was added. The mixture was continuously stirred at room temperature. After 40 h, the reaction mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of ethyl acetate/hexane (1/40 to 1/20) as eluent. (*Z*)-Ethyl 3-(2,5-dimethylphenyl)propenoate (**3d**) (1.26 mmol, 61%) was isolated as a colorless liquid and was confirmed by NMR.

4.7. Procedure for studying the time course of hydroarylation of 2a with 1b (Fig. 3)

After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), **1b** (4 mmol), pentadecane (0.2 g, as an internal standard), CH_2Cl_2 (0.5 mL), and TFA (1 mL) was stirred for 5 min at room temperature, **2a** (2 mmol) was added. The reaction mixture was stirred at room temperature. After a certain period, a portion of the reaction mixture (ca. 0.1 g) was poured into saturated $NaHCO_3$ aqueous solution (1.5 mL) and extracted with CH_2Cl_2 (2 mL). The organic layer was analyzed by GC. The yields of the products were determined by using the internal standard method.

4.8. General procedure for studying the $PtCl_2$/AgOTf-catalyzed hydroarylation of 2b

After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene (4 mmol), and TFA (1 mL) was stirred for 5 min at room temperature, **2b** (2 mmol) was added. The mixture was then stirred at the desired temperature. After the reaction, the reaction mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL×3). The ethereal layer was washed with aqueous 2 N NaOH (20 mL) and water (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as eluent, affording **7**. The combined aqueous layer was acidified by aqueous HCl (ca. 36%) and extracted with diethyl ether (20 mL×3). The ethereal layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give cinnamic acid, **8**. The results are given in Table 6.

4.9. General procedure for $PtCl_2$/AgOTf-catalyzed hydroarylation of propiolic acids

After a mixture of $PtCl_2$ (0.05 mmol), AgOTf (0.1 mmol), arene (4 mmol), and TFA (1 mL) was stirred for 5 min at room temperature, propiolic acid **2c** or **2d** (2 mmol) was added. The mixture was then stirred at the desired temperature. After the reaction, the reaction mixture was poured into water (20 mL), neutralized by $NaHCO_3$, and extracted with diethyl ether (20 mL). The ethereal layer was extracted with aqueous 2 N NaOH (10 mL×3). The combined aqueous layer was washed with diethyl ether (20 mL), acidified by aqueous HCl (ca. 36%), and extracted with CH_2Cl_2 (20 mL×3). The CH_2Cl_2 layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford cinnamic acid. The results are given in Table 7.

4.10. Products

4.10.1. Ethyl (2*Z*)-3-(2,4,6-trimethylphenyl)propenoate (3a).[8b,12,13a] Colorless liquid. ^1H NMR (300 MHz, $CDCl_3$)

δ 1.10 (t, J=7.1 Hz, 3H, CH_3), 2.16 (s, 6H, aryl–CH_3), 2.27 (s, 3H, aryl–CH_3), 4.03 (q, J=7.1 Hz, 2H, OCH_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. Ethyl (2*E*)-3-(2,4,6-trimethylphenyl)propenoate[29] was observed with the isomers of **3a** and **6a** in the mixture obtained from the reaction of **3a** at 70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, J=7.2 Hz, 3H, CH_3), 2.26 (s, 3H, aryl–CH_3), 2.33 (s, 6H, aryl–CH_3), 4.27 (q, J=7.2 Hz, 2H, OCH_2), 6.05 (d, J=16.2 Hz, 1H, vinyl), 6.89 (s, 2H, aryl), 7.84 (d, J=16.2 Hz, 1H, vinyl).

4.10.2. Ethyl (2*Z*)-3-(pentamethylphenyl)propenoate (3b).[8b,12,13a] Colorless crystals. Mp 72–74 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J=7.1 Hz, 3H, CH_3), 2.14 (s, 6H, aryl–CH_3), 2.20 (s, 6H, aryl–CH_3), 2.22 (s, 3H, aryl–CH_3), 4.01 (q, J=7.1 Hz, 2H, OCH_2), 6.13 (d, J=12.0 Hz, 1H, vinyl), 7.12 (d, J=12.0 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.96, 16.36, 16.74, 17.59, 59.78, 122.13, 129.76, 131.89, 133.23, 133.95, 146.46, 165.42.

4.10.3. Ethyl (2*Z*)-3-(1-naphthyl)propenoate (3c).[8b,13a] Slightly yellow 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, OCH_2), 6.24 (d, J=12.0 Hz, 1H, vinyl), 7.41–7.50 (m, 4H, naphthyl), 7.55 (d, J=12.0 Hz, 1H, vinyl), 7.80–7.91 (m, 3H, naphthyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.79, 60.11, 122.82, 124.39, 124.96, 125.81, 126.20, 126.49, 128.50, 128.67, 131.07, 133.04, 133.25, 141.79, 165.89.

4.10.4. Ethyl (2*Z*)-3-(2,5-dimethylphenyl)propenoate (3d).[8b,12] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, J=7.1 Hz, 3H, CH_3), 2.23 (s, 3H, aryl–CH_3), 2.29 (s, 3H, aryl–CH_3), 4.09 (q, J=7.1 Hz, 2H, OCH_2), 6.00 (d, J=12.0 Hz, 1H, vinyl), 6.98–7.08 (m, 2H, aryl), 7.08 (d, J=12.0 Hz, 1H, vinyl), 7.11 (s, 1H, aryl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.94, 19.33, 20.88, 60.06, 120.99, 129.09, 129.26, 129.53, 132.61, 134.46, 134.87, 142.86, 166.09.

4.10.5. Ethyl (2*Z*)-3-(3-bromo-2,4,6-trimethylphenyl)-propenoate (3e).[8b,13a] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (t, J=7.1 Hz, 3H, CH_3), 2.11 (s, 3H, aryl–CH_3), 2.30 (s, 3H, aryl–CH_3), 2.37 (s, 3H, aryl–CH_3), 4.02 (q, J=7.1 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 (75 MHz, $CDCl_3$) δ 13.89, 19.92, 21.25, 23.92, 60.09, 123.27, 125.03, 129.29, 133.19, 134.36, 134.60, 136.94, 143.59, 165.19.

4.10.6. Ethyl (2*Z*)-3-(3-hydroxy-2,4,6-trimethylphenyl)-propenoate (3f).[8b,12] Colorless crystals. Mp 59–60 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, J=7.1 Hz, 3H, CH_3), 2.10 (s, 6H, aryl–CH_3), 2.20 (s, 3H, aryl–CH_3), 4.03 (q, J=7.1 Hz, 2H, OCH_2), 4.49 (s, 1H, OH), 6.13 (d, J=12.0 Hz, 1H, vinyl), 6.80 (s, 1H, aryl), 7.00 (d, J=12.0 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.97, 13.96, 15.85, 19.54, 59.97, 120.18, 121.86, 122.86, 126.17, 129.15, 134.31, 143.94, 149.77, 165.39.

4.10.7. Ethyl (2*Z*)-3-{3-[(1*Z*)-2-ethoxycarbonylethenyl]-2,4,6-trimethylphenyl}propenoate (4a).[8b,12] Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (t, J=7.1 Hz, 6H, CH_3), 2.05 (s, 3H, aryl–CH_3), 2.15 (s, 6H, aryl–CH_3), 4.03 (q, J=7.1 Hz, 4H, OCH_2), 6.12 (d, J=11.7 Hz, 2H, vinyl), 6.88 (s, 1H, aryl), 7.04 (d, J=11.7 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.

4.10.8. Ethyl (2*Z*)-3-{3-bromo-5-[(1*Z*)-2-ethoxycarbonylethenyl]-2,4,6-trimethylphenyl}propenoate (4b). Slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (t, J=7.1 Hz, 6H, CH_3), 2.02 (s, 3H, aryl–CH_3), 2.32 (s, 6H, aryl–CH_3), 4.02 (q, J=7.1 Hz, 4H, OCH_2), 6.14 (d, J=11.7 Hz, 2H, vinyl), 7.04 (d, J=11.7 Hz, 2H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.92, 17.82, 21.76, 60.06, 123.24, 125.87, 129.91, 133.52, 134.37, 144.04, 165.11. MS (EI, *m*/*z*) 396, 394 (M^+).

4.10.9. Ethyl (2*Z*)-3-{5-[(1*Z*)-2-ethoxycarbonylethenyl]-3-hydroxy-2,4,6-trimethylphenyl}propenoate (4c). Colorless crystals. Mp 109–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (t, J=7.1 Hz, 6H, CH_3), 1.99 (s, 3H, aryl–CH_3), 2.10 (s, 6H, aryl–CH_3), 4.03 (q, J=7.1 Hz, 4H, OCH_2), 4.53 (s, 1H, OH), 6.14 (d, J=12.0 Hz, 2H, vinyl), 7.02 (d, J=12.0 Hz, 2H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.20, 13.98, 17.33, 59.95, 119.42, 122.87 (two peaks overlapped), 133.85, 144.24, 149.44, 165.33. MS (EI, *m*/*z*) 332 (M^+). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 68.86; H, 7.27.

4.10.10. Diethyl (1*E*,3*Z*)-4-(2,4,6-trimethylphenyl)buta-1,3-diene-1,3-dicarboxylate (5a).[8b] Slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J=7.1 Hz, 3H, CH_3), 1.31 (t, J=7.1 Hz, 3H, CH_3), 2.15 (s, 6H, aryl–CH_3), 2.26 (s, 3H, aryl–CH_3), 3.99 (q, J=7.1 Hz, 2H, OCH_2), 4.24 (q, J=7.1 Hz, 2H, OCH_2), 6.23 (d, J=15.9 Hz, 1H, vinyl), 6.82 (s, 2H, aryl), 7.15 (s, 1H, vinyl), 7.46 (d, J=15.9 Hz, 1H, vinyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.43, 14.24, 20.08, 20.93, 60.48, 60.69, 120.70, 127.79, 132.04, 134.39, 135.13, 137.28, 141.35, 143.07, 166.02, 166.79.

4.10.11. Diethyl (1*E*,3*Z*)-4-(pentamethylphenyl)buta-1,3-diene-1,3-dicarboxylate (5b).[8b] Slightly yellow crystals. ^{1}H 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, aryl–CH_3), 2.18 (s, 6H, aryl–CH_3), 2.22 (s, 3H, aryl–CH_3), 3.97 (q, J=7.1 Hz, 2H, OCH_2), 4.25 (q, J=7.1 Hz, 2H, OCH_2), 6.20 (d, J=15.9 Hz, 1H, vinyl), 7.26 (s, 1H, vinyl), 7.49 (d, J=15.9 Hz, 1H, vinyl).

4.10.12. (2*Z*)-3-(2,4,6-Trimethylphenyl)propenoic acid (6a). Colorless crystals. Mp 144–146 °C (EtOH/hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 6H, aryl–CH_3), 2.27 (s, 3H, aryl–CH_3), 6.10 (d, J=12.0 Hz, 1H, vinyl), 6.84 (s, 2H, aryl), 7.11 (d, J=12.0 Hz, 1H, vinyl), 11.00 (s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.00, 20.89, 122.07, 127.89, 131.99, 134.44, 136.92, 146.28, 171.10. MS (EI, *m*/*z*) 190 (M^+). Compound **6a** was confirmed by converting it to its ethyl ester **3a** using DMAP/DCC method[30] and comparing ^{1}H and ^{13}C NMR spectra. (2*E*)-3-(2,4,6-Trimethylphenyl)propenoic acid was observed in the reaction of ethyl propiolate (**2a**) with mesitylene (**1a**) at higher temperature and obtained as a mixture of *Z*- and

E-isomer of **6a**, but was not isolated. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H, aryl–CH_3), 2.32 (s, 6H, aryl–CH_3), 6.04 (d, J=16.2 Hz, 1H, vinyl), 6.89 (s, 2H, aryl), 7.91 (d, J=16.2 Hz, 1H, vinyl).

4.10.13. (2*Z*)-3-(Pentamethylphenyl)propenoic acid (6b). Colorless crystals. Mp 218–219 °C (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 6H, aryl–CH_3), 2.19 (s, 6H, aryl–CH_3), 2.22 (s, 3H, aryl–CH_3), 6.12 (d, J=12.0 Hz, 1H, vinyl), 7.20 (d, J=12.0 Hz, 1H, vinyl), 10.42 (br s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.35, 16.76, 17.62, 121.72, 129.87, 132.22, 132.38, 134.51, 148.28, 170.38. Compound **6b** was confirmed by converting it to its ethyl ester **3b** using DMAP/DCC method[30] and comparing ^{1}H and ^{13}C NMR spectra.

4.10.14. (2*Z*)-3-(1-Naphthyl)propenoic acid (6c). Slightly yellow solid. Mp 157–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (d, J=12.0 Hz, 1H, vinyl) 7.39–7.53 (m, 4H, naphthyl), 7.66 (d, J=12.0 Hz, 1H, vinyl), 7.81–7.87 (m, 3H, naphthyl), 9.80 (br s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.37, 124.18, 125.08, 125.97, 126.44, 126.92, 128.62, 129.15, 130.91, 132.27, 133.22, 144.66, 170.30. MS (EI, *m*/*z*) 198 (M^+). Compound **6b** was confirmed by converting it to its ethyl ester **3c** using DMAP/DCC method[30] and comparing ^{1}H and ^{13}C NMR spectra.

4.10.15. (2*Z*)-3-(3-Bromo-2,4,6-trimethylphenyl)propenoic acid (6e). Colorless powder. Mp 148–149 °C (EtOAc/hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H, aryl–CH_3), 2.28 (s, 3H, aryl–CH_3), 2.36 (s, 3H, aryl–CH_3), 6.11 (d, J=12.0 Hz, 1H, vinyl), 6.91 (s, 1H, aryl), 7.09 (d, J=12.0 Hz, 1H, vinyl), 9.86 (br s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.89, 21.25, 23.93, 122.48, 125.14, 129.44, 133.16, 133.83, 134.30, 137.28, 145.97, 170.35. Compound **6c** was confirmed by comparing ^{1}H and ^{13}C NMR spectra of the compound that was prepared by hydrolysis of **3e** by aqueous NaOH solution.

4.10.16. Ethyl (2*Z*)-3-(2,4,6-trimethylphenyl)-3-phenylpropenoate (7a).[8b] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J=7.1 Hz, 3H, CH_3), 2.03 (s, 6H, aryl–CH_3), 2.32 (s, 3H, aryl–CH_3), 4.03 (q, J=7.1 Hz, 2H, OCH_2), 6.61 (s, 1H, vinyl), 6.90 (s, 2H, aryl), 7.30–7.35 (m, 5H, phenyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.98, 19.73, 21.14, 59.83, 117.54, 126.93, 127.98, 128.63, 129.45, 134.61, 135.21, 136.67, 138.35, 155.03, 165.66.

4.10.17. Ethyl (2*Z*)-3-(pentamethylphenyl)-3-phenylpropenoate (7b).[8b] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, J=7.1 Hz, 3H, CH_3), 2.01 (s, 6H, aryl–CH_3), 2.21 (s, 6H, aryl–CH_3), 2.27 (s, 3H, aryl–CH_3), 4.00 (q, J=7.1 Hz, 2H, OCH_2), 6.62 (s, 1H, vinyl), 7.28–7.37 (m, 5H, phenyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.96, 16.47, 16.82, 17.49, 59.69, 117.43, 127.14, 128.57, 129.26, 129.92, 131.93, 133.79, 135.52, 139.12, 156.87, 165.75.

4.10.18. (2*Z*)-3-(2,4,6-Trimethylphenyl)-3-phenylpropenoic acid (8a).[8b] Colorless crystals. Mp 195–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 6H, aryl–CH_3), 2.32 (s, 3H, aryl–CH_3), 6.59 (s, 1H, vinyl), 6.89 (s, 2H, aryl), 7.30–7.33 (m, 5H, phenyl), 10.86 (br s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.71, 21.11, 117.00, 127.11, 128.16, 128.71, 129.83, 134.50, 134.63, 137.01, 138.23, 157.22, 170.18.

4.10.19. (2*Z*)-3-(Pentamethylphenyl)-3-phenylpropenoic acid (8b).[8b] Colorless crystals. Mp 238–240 °C (AcOEt/hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 6H, aryl–CH_3), 2.18 (s, 6H, aryl–CH_3), 2.24 (s, 3H, aryl–CH_3), 6.61 (s, 1H, vinyl), 7.27–7.29 (m, 5H, phenyl), 9.50 (br s, 1H, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.52, 16.90, 17.55, 117.14, 127.28, 128.73, 129.80, 130.37, 132.85, 133.87, 135.06, 138.60, 158.08, 168.33.

4.10.20. 1-Phenyl-1-(2,4,6-trimethylphenyl)ethene (9).[12] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 6H, aryl–CH_3), 2.32 (s, 3H, aryl–CH_3), 5.09 (d, J=1.5 Hz, 1H, vinyl), 5.95 (d, J=1.5 Hz, 1H, vinyl), 6.91 (s, 2H, aryl), 7.23–7.28 (m, 5H, phenyl). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.07, 21.03, 114.52, 125.82, 127.51, 128.09, 128.39, 136.13, 136.41, 138.16, 139.56, 146.86.

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