Palladium(II)-Catalyzed Conjugate Addition of Aromatics to α,β-Unsaturated Ketones and Aldehydes with Arylantimony Compounds

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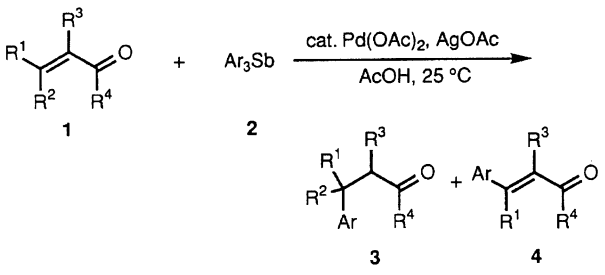
Triarylstibines react with α,β-unsaturated ketones and aldehydes in acetic acid at room temperature in the presence of AgOAc and a catalytic amount of $Pd(OAc)_2$ to afford the conjugate addition products (the formal hydroarylated compounds to an olefinic part) in good yields. In contrast, diarylantimony chlorides, arylantimony dichlorides, and diphenylantimony acetate react with the enones and enals even in the absence of AgOAc to afford the same products in higher yields compared with those from triarylstibines. These are new C–C bond-forming reactions using arylantimony(III) compounds in which the formation of a palladium enolate or a trivalent antimony enolate is proposed as an intermediate.

The chemistry of organic and inorganic antimony compounds has recently received considerable attention.[1] From the viewpoint of a carbon–carbon bond-forming reaction using organoantimony compounds, Malinovsky and Olifirenko's original work on $AlCl_3$-catalyzed reactions of acyl chlorides and alkyl bromides with arylstibines giving aryl ketones and alkylated arenes, respectively, should be cited first.[2] Arylstibines were also employed for several organic reactions by using a palladium(II) catalyst; i.e., the self-coupling of Ar_3Sb,[3] a Fujiwara–Heck coupling between Ph_3Sb and alkenes[4] or alkenylsilanes,[5] and the carbonylation of Ar_3Sb with CO[6a,7] or CO_2.[6b] We reported recently in a communication form[8] that triarylstibines reacted with α,β-unsaturated ketones and aldehydes in the presence of AgOAc and a catalytic amount of $Pd(OAc)_2$ to give products due to the conjugate addition of aromatics (the formal hydroarylated compounds to an olefinic part). During a continuation of this work to clarify the reaction pathway and to look for the actual role of AgOAc, we disclosed that diarylantimony chlorides, arylantimony dichlorides, and diphenylantimony acetate reacted efficiently with those ketones and aldehydes, even in the absence of AgOAc, to afford the same products. We report here on the details of these new C–C bond-forming reactions together with some mechanistic considerations.

Results and Discussion

The treatment of 4-phenylbut-3-en-2-one (**1a**) with an equimolar amount of triphenylstibine (**2k**) in acetic acid in the presence of a catalytic amount of $Pd(OAc)_2$ (0.1 molar amount) and AgOAc (2 equimolar amounts) at 25 °C for 24 h afforded 4,4-diphenylbutan-2-one (**3ak**; conjugate addition product[9]) in 42% yield (on the basis of **1a**) together with biphenyl (40%; 1.5 equimolar amounts of biphenyl to **2k** correspond to 100%), whereas 4,4-diphenylbut-3-en-2-one (**4ak**; Fujiwara–Heck coupling product[10]) was not produced. Without the addition of AgOAc, although biphenyl was formed in 6—25%, **3ak** was scarcely produced. A similar catalytic reaction using crotonaldehyde (**1g**) in place of 4-phenylbut-3-en-2-one also afforded the conjugate addition product, 3-phenylbutanal (**3gk**), in 61% yield (Scheme 1). The reaction did not occur at all with other compounds of group-15 elements, such as triphenylphosphine (Ph_3P) and triphenylarsine (Ph_3As), while from triphenylbismuthine (Ph_3Bi) the conjugate addition product was obtained in 5% yield using either **1a** or **1g** under similar conditions.

Reactions using **2k** were then carried out under a variety



a: R^1=Ph; R^2,R^3=H; R^4=Me
b: R^1,R^4=Me; R^2,R^3=H
c: R^1=n-C_5H_{11}; R^2,R^3=H; R^4=Me
d: R^1,R^2,R^3=H; R^4=Me
e: R^1,R^2,R^4=Me; R^3=H
f: R^1,R^4=$(CH_2)_3$; R^2,R^3=H
g: R^1=Me; R^2,R^3,R^4=H
h: R^1=n-C_3H_7; R^2,R^3,R^4=H
i: R^1,R^2,R^3,R^4=H
j: R^1,R^2,R^4=H; R^3=Me
k: Ar = Ph
l: Ar = 4-MeC_6H_4
m: Ar = 3-MeC_6H_4
n: Ar = 4-$MeOC_6H_4$
o: Ar = 4-ClC_6H_4
p: Ar = 3-ClC_6H_4
q: Ar = 4-$CF_3C_6H_4$
r: Ar = 1-naphthyl

Scheme 1.

Table 1. Palladium(II)-Catalyzed Reactions of Alkenes with Ph_3Sb (**2k**)[a]

Run	Alkene	Palladium salt	Additive	Yield/%[b]	
			mmol	**3**	**4** (*E*/*Z*)
1	**1a**	$Pd(OAc)_2$	AgOAc (2)	42	0
2	**1a**	$PdCl_2$	AgOAc (2)	Trace	0
3	**1a**	$[PdCl_2(PPh_3)_2]$	AgOAc (2)	0	0
4	**1a**	$Na_2[PdCl_4]$	AgOAc (2)	2	0
5	**1a**	$Pd(NO_3)_2$	AgOAc (2)	3	15
6	**1g**	$Pd(OAc)_2$	AgOAc (2)	61 (50)[c]	0
7	**1g**	$Pd(OAc)_2$	AgOAc (1)	28	0
8	**1g**	$Pd(OAc)_2$	Ag_2O (1)	13	0
9	**1g**	$Pd(OAc)_2$[d]	—	63	27
10	Methyl acrylate	$Pd(OAc)_2$	AgOAc (2)	4[e]	53[f] (100/0)
11	Methyl cinnamate	$Pd(OAc)_2$	AgOAc (2)	2[e]	83[g] (100/0)
12	Acrylonitrile	$Pd(OAc)_2$	AgOAc (2)	0	86[h] (67/33)
13	Styrene	$Pd(OAc)_2$	AgOAc (2)	0	99[i] (84/16)
14	Allyl acetate	$Pd(OAc)_2$	AgOAc (2)	0	36[j] (100/0)

a) All the reactions were carried out with alkene (1 mmol), Ph_3Sb (1 mmol), and palladium(II) salt (0.1 mmol) in AcOH (20 mL) at 25 °C for 24 h unless otherwise stated. b) GLC yield on the basis of alkene. Biphenyl was always produced in variable amounts (10—63% yields; 1.5 equimolar amounts of biphenyl to Ph_3Sb correspond to 100% yield). c) Isolated yield. d) $Pd(OAc)_2$ (1 mmol) was used. e) Methyl 3,3-diphenylpropanoate. f) Methyl cinnamate: other product, methyl 3,3-diphenylprop-2-enoate (35%). g) Methyl 3,3-diphenylprop-2-enoate. h) Cinnamonitrile. i) Stilbene. j) Cinnamyl acetate.

of reaction conditions with **1a** and **1g** used as substrates. The typical results are shown in Table 1. Although it scarcely proceeded upon using other palladium(II) salts, such as $PdCl_2$, $[PdCl_2(PPh_3)_2]$, and $Na_2[PdCl_4]$, in place of $Pd(OAc)_2$ (Runs 2—4), with $Pd(NO_3)_2$ the Fujiwara–Heck coupling product (**4ak**) was mainly obtained in low yield. It did not proceed upon using other silver (I) salts, such as AgCl, $AgNO_3$, and Ag_2SO_4 and $Cu(OAc)_2$, in place of AgOAc, though Ag_2O was slightly effective (Run 8). Although a similar reaction between **2k** and **1a** using a stoichiometric amount of $Pd(OAc)_2$ in the absence of AgOAc gave the conjugate addition product **3ak** in 63% yield, **4ak** was also obtained in 27% yield (Run 9). Thus, the presence of both $Pd(OAc)_2$ (catalytic) and AgOAc (stoichiometric) was revealed to be inevitable for a selective conjugate addition to give **3**. Interestingly, under completely the same reaction conditions as those in Runs 1 and 6, the Fujiwara–Heck coupling leading to phenylated alkenes occurred almost exclusively with α,β-unsaturated esters such as methyl acrylate and methyl cinnamate, and some alkenes such as acrylonitrile, styrene and allyl acetate (Runs 10—14).

From other easily available α,β-unsaturated ketones and aldehydes the corresponding conjugate addition products were also formed in good yields. Further, this reaction system could be applied to various triarylstibines. Representative results are shown in Table 2. The product yield was greatly dependent on the nature of the substrates. In all cases, biaryl was formed in considerable amount (25—40% yield) as a side product. The effect of substituents of triarylstibines **2** upon this conjugate addition was examined by using pent-3-en-2-one (**1b**) as a substrate. As shown in Table 2, the presence of an electron-withdrawing group, such as Cl and CF_3, on the aromatic ring of **2** increased the

Table 2. Palladium(II)-Catalyzed Reactions of Enones and Enals with Ar_3Sb (**2**)[a]

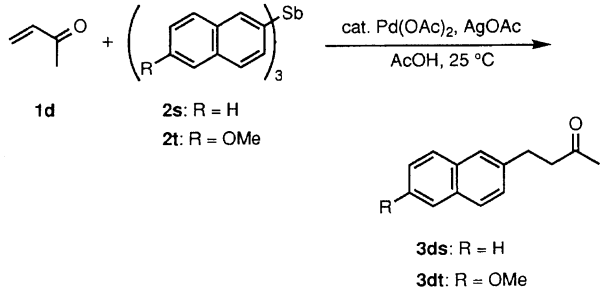
Enone or enal **1**	Triarylstibine **2**		Yield/%[b]
1b	**2k**	**3bk**	41
1b	**2l**	**3bl**	44
1b	**2m**	**3bm**	59
1b	**2n**	**3bn**	57
1b	**2o**	**3bo**	68
1b	**2p**	**3bp**	74
1b	**2q**	**3bq**	72[c]
1b	**2r**	**3br**	49
1c	**2k**	**3ck**	40
1d	**2k**	**3dk**	80[d]
1d	**2o**	**3do**	67
1d	**2r**	**3dr**	53
1d[e]	**2s**	**3ds**	95[f]
1d[e]	**2t**	**3dt**	99[f]
1e	**2k**	**3ek**	14
1f	**2k**	**3fk**	43
1g	**2l**	**3gl**	46
1h	**2k**	**3hk**	55
1i	**2k**	**3ik**	100[d]
1j	**2k**	**3jk**	35

a) All the reactions were carried out with **1** (1 mmol), **2** (1 mmol), $Pd(OAc)_2$ (0.1 mmol), and AgOAc (2 mmol) in AcOH (20 mL) at 25 °C for 24 h unless otherwise stated. b) Isolated yield on the basis of **1** unless otherwise stated. Biaryl was always produced (25—40% yield; 1.5 equimolar amounts of biaryl to Ar_3Sb correspond to 100% yield). c) Other product; (*E*)- and (*Z*)-4-[4-(trifluoromethyl)phenyl]pent-3-en-2-one (12%, *E*/*Z*=56/44). d) GLC yield. e) The reaction was carried out with **1** (1 mmol), **2** (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), and AgOAc (1 mmol) in AcOH (10 mL). f) Isolated yield on the basis of **2**.

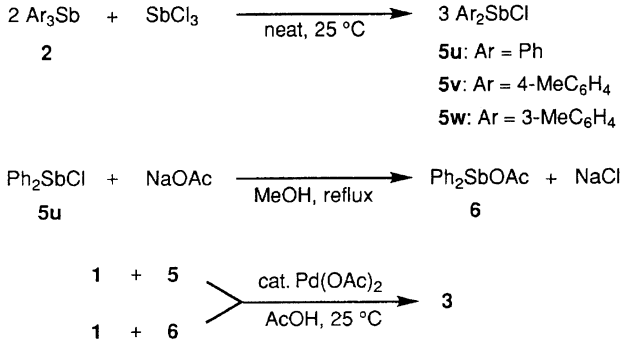
product yield. The Fujiwara–Heck coupling product was scarcely formed, except for the case of tris[4-(trifluoromethyl)phenyl]stibine (**2q**). Similar reactions between methyl vinyl ketone (**1d**) and tris(2-naphthyl)stibine (**2s**) or tris(6-methoxy-2-naphthyl)stibine (**2t**) afforded the corresponding conjugate addition products, **3ds** and **3dt**, in high yields, respectively, in which **3dt** is known as an antiinflammatory agent, called nabumetone (Scheme 2).[11]

We then examined the reactivity of diarylantimony chlorides and arylantimony dichlorides for this reaction, which are readily available by a redistribution of the triarylstibines and $SbCl_3$ (Schemes 3 and 4).[12] When **1a** (1 mmol) was treated with diphenylantimony chloride (1.2 mmol) (**5u**), prepared in situ from 2 molar amounts of **2k** and 1 equiv. $SbCl_3$, in acetic acid in the presence of a catalytic amount of $Pd(OAc)_2$ (0.1 molar amount) at 25 °C for 24 h, the conjugate addition product, 4,4-diphenylbutan-2-one (**3ak**), was obtained quantitatively together with a 12% yield of biphenyl (Scheme 3). From various enones or enals the corresponding conjugate addition products were produced in high yields; further, the reaction system could also be applied to other diarylantimony chlorides, such as **5v** and **5w**. Typical results are shown in Table 3. Although the reaction could also be carried out in wet tetrahydrofuran (THF) in place of acetic acid as a solvent, when completely dry THF was employed it scarcely occurred. The reactivity of diphenylantimony acetate was then examined.[13] The treatment of **1b** (0.5 mmol) with diphenylantimony acetate (0.5 mmol) (**6**) in acetic acid in the presence of a catalytic amount of $Pd(OAc)_2$ (0.1 molar amount) at 25 °C for 24 h afforded the conjugate addition product, 4-phenylpentan-2-one (**3bk**), in 81% yield together with a 16% yield of biphenyl (Scheme 3). From various enones or enals the corresponding conjugate addition products were also formed in high yields. Typical results are given in Table 3. Quite interestingly, the addition of AgOAc was not necessary for all these cases.

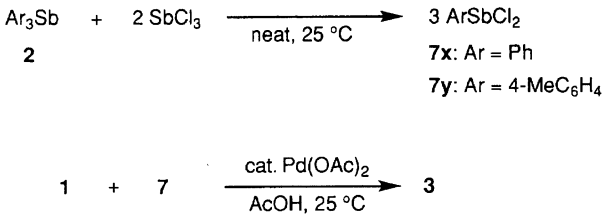
The treatment of **1a** (1 mmol) with phenylantimony dichloride (1.2 mmol) (**7x**), prepared in situ from an equimolar amount of **2k** and 2 molar amounts of $SbCl_3$, in acetic acid in the presence of a catalytic amount of $Pd(OAc)_2$ (0.1 molar amount) at 25 °C for 24 h, afforded the conjugate addition product, 4,4-diphenylbutan-2-one (**3ak**) quantitatively, together with a 4% yield of biphenyl (Scheme 4). From various enones or enals as well as another arylantimony dichloride **7y** the corresponding conjugate addition products were also produced in high yields (Table 4). In these cases, again, the addition of AgOAc was not necessary. Typical results are given in Table 4. The reactivity of diarylantimony salts (**5** and **6**) and arylantimony dichlorides (**7**) for this conjugate addition was generally higher than that of triarylstibines (**2**); furthermore, biaryl formation was greatly decreased in the



Scheme 2.



Scheme 3.



Scheme 4.

Table 3. Palladium(II)-Catalyzed Reactions of Enones or Enals with Ar_2SbCl (**5**)[a] and Ph_2SbOAc (**6**)[b]

Enone or enal **1**	Diarylantimony salts **5** or **6**		Yield/%[c]
1a	**5u**	**3ak**	100(87)
1a	**5v**	**3al**	81
1b	**5u**	**3bk**	100
1b	**5v**	**3bl**	(84)
1b	**5w**	**3bm**	(80)
1c	**5u**	**3ck**	86
1c	**5v**	**3cl**	75(65)
1c	**5w**	**3cm**	75(66)
1d	**5u**	**3dk**	88
1e	**5u**	**3ek**	Trace
1f	**5u**	**3fk**	89
1g	**5u**	**3gk**	98—100[d]
1h	**5u**	**3hk**	91
1i	**5u**	**3ik**	62
1a	**6**	**3ak**	70[e]
1b	**6**	**3bk**	81
1d	**6**	**3dk**	98
1g	**6**	**3gk**	75
1i	**6**	**3ik**	82

a) All the reactions were carried out with **1** (1 mmol), **5** (1.2 mmol), and $Pd(OAc)_2$ (0.1 mmol) in AcOH (10 mL) at 25 °C for 24 h. b) All the reactions were carried out with **1** (0.5 mmol), **6** (0.5 mmol), and $Pd(OAc)_2$ (0.05 mmol) in AcOH (10 mL) at 25 °C for 24—28 h. c) GLC yield on the basis of enone or enal. Isolated yield is shown in parentheses. d) Several runs. e) Other product; 4,4-diphenylbut-3-en-2-one (16%).

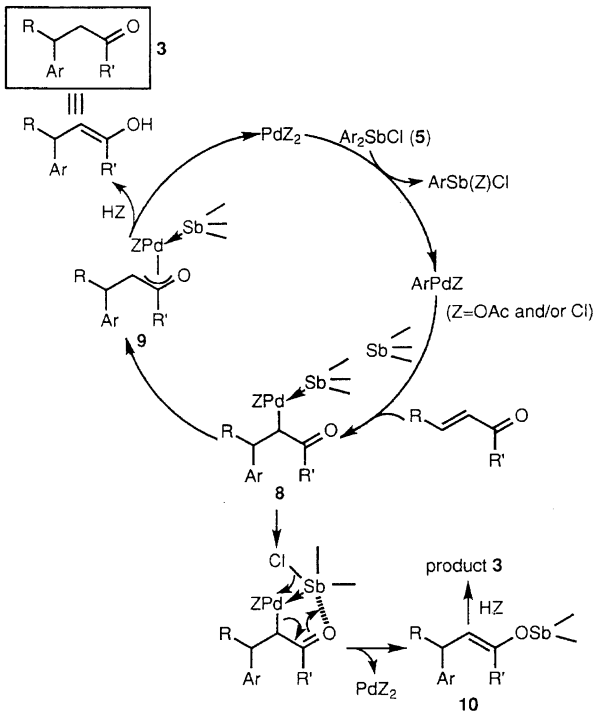
Table 4. Palladium(II)-Catalyzed Reactions of Enones or Enals with $ArSbCl_2$ (**7**)[a]

Enone or enal **1**	Arylantimony dichloride **7**		Yield/%[b]
1a	**7x**	**3ak**	100
1a	**7y**	**3al**	(89)
1b	**7x**	**3bk**	100(88)
1c	**7x**	**3ck**	83
1d	**7x**	**3dk**	99
1e	**7x**	**3ek**	25
1f	**7x**	**3fk**	90
1g	**7x**	**3gk**	74—78[c]
1i	**7x**	**3ik**	66

a) All the reactions were carried out with **1** (1 mmol), **7** (1.2 mmol), and $Pd(OAc)_2$ (0.1 mmol) in AcOH (10 mL) at 25 °C for 24 h. b) GLC yield on the basis of enone or enal. Isolated yield is shown in parentheses. c) Several runs.

former two cases.

A plausible catalytic reaction pathway for the conjugate addition is presented in Scheme 5 by choosing diarylantimony chloride (**5**) as an arylating reagent in which the presence of either a palladium enolate or an antimony enolate is assumed as an intermediate. Arylpalladium species [ArPdZ], produced by transmetallation between **5** and $Pd(OAc)_2$, adds to enones and enals to produce an alkylpalladium species **8**. This species may be converted to η^3-type palladium enolate (**9**), followed by protonolysis to give the conjugate addition product **3**.[15] The antimony of organoantimony(III) compounds, present in excess in the reaction system, may coordinate to the palladium to prevent a β-hydride elimination process, giving a Fujiwara–Heck coupling product **4**. In fact, we confirmed separately that, in $Pd(OAc)_2$ mediated reactions between **1a** and Ph_2SbCl (**5u**), the amount of **3** increased and that of **4** decreased by increasing the amount of **5u** (Scheme 6). This assumption is also in accord with the report by Cacchi et al.,[16] in which the addition of tertiary amines accelerated the heterolytic fission of the C–Pd bond of the intermediate σ-alkylpalladium species to give the conjugate addition product in the palladium-catalyzed reaction between 4-phenylbut-3-en-2-one and iodobenzene. In contrast to enals and enones, methyl acrylate afforded solely **4**. This is probably because the presence of an electron-withdrawing nature of a methoxy group (R′ = OMe) makes the intermediate **9** unfavorable, and accelerates β-hydride elimination from **8**. Although the details are not yet known, another pathway for **3** via an antimony enolate **10**[17] can not be excluded, where organoantimony(III) compounds may also coordinate to the carbonyl oxygen of the intermediate **8**, and a concerted elimination of the palladium(II) species gives the enolate **10**.

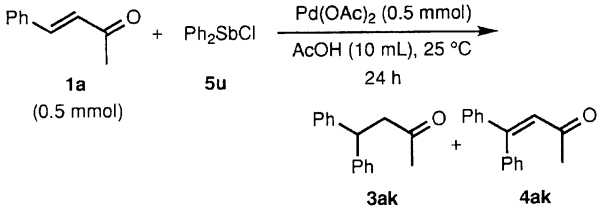


Scheme 5.

Although the addition of AgOAc was necessary in the case of triarylstibines **2**, the reaction pathway seemed to be intrinsically the same as those of diarylantimony and arylantimony salts. The actual role of AgOAc might be merely a reoxidant of zerovalent palladium, because a large amount of palladium(II) was consumed for ready homo- or cross-coupling of arylpalladium(II) acetate to produce biaryl (10—63% yield). The combination of $Pd(OAc)_2$ (catalyst) and AgOAc (reoxidant) has long been known for various palladium(II)-catalyzed reactions.[18]

Conclusion

Triarylstibines reacted with α,β-unsaturated ketones and aldehydes in acetic acid at room temperature in the presence of AgOAc and a catalytic amount of $Pd(OAc)_2$ to afford the conjugate addition products in good yields without the expected Fujiwara–Heck coupling products. On the other hand, diarylantimony chlorides, diphenylantimony acetate and arylantimony dichlorides reacted with the enones or enals, even in the absence of AgOAc, to afford the same products in higher yields compared with those from triaryl-



5u (mmol)	Yield/%[a] **3ak**	**4ak**
0.6	26	18
1.2	49	13
2.4	100	0

[a] GLC yield on the basis of **1a**.

Scheme 6.

stibines. These new reactions represented another example of C–C bond-forming reactions using arylantimony(III) compounds in which the formation of a palladium or antimony enolate was proposed as an intermediate.

Experimental

General Procedure. ^{1}H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL GSX-270 spectrometer using Me_4Si as an internal standard in $CDCl_3$. The chemical shifts are reported in δ units downfield from Me_4Si. Infrared spectra were obtained on a Hitachi EPI-G2 spectrophotometer. The melting points were determined on a Yanaco MP-J3 micro-melting-point apparatus and were uncorrected. Mass spectra were obtained on a Shimadzu QP-5000S spectrometer at an ionizing voltage of 70 eV. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a CBP 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm×25 m, 5.0 μm film thickness) column using helium as a carrier gas. The GLC yields were determined using suitable hydrocarbons as internal standards. The isolation of pure products was carried out with column chromatography (Wakogel C-200, 100—200 mesh, Wako Pure Chemical Ind. Ltd.) or preparative thin-layer chromatography (silica gel 60 HF_{254}, Merck).

Materials. Commercially available organic and inorganic compounds were used without further purification. Except for commercial triphenylstibine (**2k**), triarylstibines such as **2l**,[19] **2m**,[20] **2n**,[21] **2o**,[22] **2p**,[22] **2q**,[20] **2r**,[23] **2s**,[24] and **2t**[7] were prepared following literature procedures. Diarylantimony chlorides (**5**) and arylantimony dichlorides (**7**) were prepared in situ by a known disproportionation method with triarylstibines and $SbCl_3$.[12] Diphenylantimony acetate (**6**) was prepared in a pure form by a known method from the corresponding chloride and NaOAc: mp 114—116 °C (from toluene and then benzene) lit,[25] 130 °C; ^{1}H NMR δ = 2.14 (3H, s), 7.39—7.47 (6H, m), and 7.60—7.64 (4H, m). Anal. Found: C, 50.14; H, 3.78%. Calcd for $C_{14}H_{13}O_2Sb$: C, 50.19; H, 3.91%. All enones and enals were commercial products, except for non-3-en-2-one (**1c**), which was synthesized by the known method:[26] ^{1}H NMR δ = 0.90 (3H, t, J = 7.0 Hz), 1.28—1.54 (6H, m), 2.18—2.27 (2H, m), 2.24 (3H, s), 6.07 (1H, dt, J = 15.8 and 1.5 Hz), and 6.81 (1H, dt, J = 15.8 and 7.0 Hz); ^{13}C NMR δ = 14.0, 22.4, 26.8, 27.8, 31.4, 32.5, 131.3, 148.6, and 198.7. 4,4-Diphenylbutan-2-one (**3ak**) and 4,4-diphenylbut-3-en-2-one (**4ak**) were prepared separately by the known method[16] and used as authentic samples for GLC determination.

3ak: IR (neat) 3080, 3060, 3025, 3000, 1720, 1600, 1490, 1445, 1355, 1155, 740, 730, 695, and 540 cm^{-1}; ^{1}H NMR δ = 2.06 (3H, s), 3.17 (2H, d, J = 7.7 Hz), 4.58 (1H, t, J = 7.7 Hz), and 7.13—7.30 (10H, m); ^{13}C NMR δ = 30.6, 46.0, 49.6, 126.4, 127.7, 128.6, 148.8, and 206.8; MS *m/z* (rel intensity) 224 (M^+; 38), 181 (29), 167 (100), 152 (20), 103 (41), 91 (6), and 77 (20).

4ak: ^{1}H NMR δ = 1.88 (3H, s), 6.58 (1H, s), and 7.20—7.42 (10H, m); ^{13}C NMR δ = 30.3, 127.7, 128.4, 128.4, 128.8, 129.5, 129.6, 139.0, 140.8, and 200.2; MS *m/z* (rel intensity) 222 (M^+; 56), 221 (100), 207 (50), 178 (77), 152 (15), 105 (28), 89 (17), 77 (18), and 51 (18). All transition-metal salts were commercial products, except for $[PdCl_2(PPh_3)_2]$, which was prepared by a known method.[27]

General Procedure for Pd(II)-Catalyzed Reactions of α,β-Unsaturated Ketones and Aldehydes with Triarylstibines. A mixture of triarylstibine (1 mmol), enone or enal (1 mmol), $Pd(OAc)_2$ (0.023 g, 0.1 mmol), and AgOAc (0.334 g, 2 mmol) was stirred in acetic acid (20 mL) at 25 °C for 24 h. The precipitated black solid was filtered off and the filtrate was poured into brine (100 mL), extracted with dichloromethane (30 mL×2), and washed with saturated aqueous $NaHCO_3$. The organic phase was washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure usually left a pale-yellow oil, which was separated and purified by column chromatography or preparative TLC using an ethyl acetate-hexane mixture as an eluent to give the conjugate addition product. For obtaining the GLC yield, a similar reaction was carried out in the presence of an appropriate amount of 1,2-diphenylethane as an internal standard. The products obtained by the above procedure were characterized spectroscopically as shown below. The elemental analytical data are also given for new compounds.

3-Phenylbutanal (3gk): 50% yield; an oil; IR (neat) 3095, 3070, 3040, 2975, 2940, 2890, 2830, 2725, 1730, 1600, 1495, 1450, 1075, 1050, 1025, 760, and 700 cm^{-1}; ^{1}H NMR δ = 1.31 (3H, d, J = 7.0 Hz), 2.59—2.79 (2H, m), 3.29—3.42 (1H, m), 7.17—7.34 (5H, m), and 9.69 (1H, t, J = 2.2 Hz); ^{13}C NMR δ = 22.2, 34.3, 51.7, 126.5, 126.8, 128.7, 145.5, and 201.8; MS *m/z* (rel intensity) 148 (M^+; 39), 133 (34), 105 (100), 91 (63), 77 (51), and 51 (33).

4-Phenylpentan-2-one (3bk): 41% yield; an oil; IR (neat) 3070, 3040, 2960, 1720, 1600, 1495, 1450, 1360, 1160, 1025, 755, 695, and 530 cm^{-1}; ^{1}H NMR δ = 1.26 (3H, d, J = 7.0 Hz), 2.05 (3H, s), 2.60—2.79 (2H, m), 3.23—3.37 (1H, m), and 7.15—7.32 (5H, m); ^{13}C NMR δ = 22.0, 30.5, 35.4, 52.0, 126.3, 126.8, 128.5, 146.2, and 207.8; MS *m/z* (rel intensity) 162 (M^+; 34), 147 (65), 119 (15), 105 (100), 91 (52), 77 (35), and 51 (21).

4-(4-Methylphenyl)pentan-2-one (3bl): 44% yield; an oil; ^{1}H NMR δ = 1.24 (3H, d, J = 7.0 Hz), 2.05 (3H, s), 2.30 (3H, s), 2.57—2.77 (2H, m), 3.20—3.33 (1H, m), and 7.09 (4H, s); ^{13}C NMR δ = 21.0, 22.1, 30.5, 35.1, 52.1, 126.6, 129.2, 135.8, 143.1, and 207.9; MS *m/z* (rel intensity) 176 (M^+; 31), 161 (40), 119 (100), 105 (25), 91 (27), 77 (13), 65 (9), and 51 (7).

4-(3-Methylphenyl)pentan-2-one (3bm): 59% yield; an oil; IR (neat) 2950, 2910, 1715, 1605, 1360, 1155, 780, and 700 cm^{-1}; ^{1}H NMR δ = 1.24 (3H, d, J = 7.0 Hz), 2.04 (3H, s), 2.32 (3H, s), 2.57—2.77 (2H, m), 3.19—3.32 (1H, m), 6.98—7.01 (3H, m), and 7.14—7.19 (3H, m); ^{13}C NMR δ = 21.5, 22.0, 30.5, 35.4, 52.0, 123.7, 127.1, 127.6, 128.4, 138.0, 146.2, and 207.8; MS *m/z* (rel intensity) 176 (M^+; 59), 161 (53), 133 (50), 119 (100), 105 (60), 91 (49), 77 (23), 65 (18), and 51 (13). Anal. Found: C, 81.85; H, 9.34%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

4-(4-Methoxylphenyl)pentan-2-one (3bn): 57% yield; an oil; IR (neat) 2950, 1710, 1610, 1510, 1360, 1250, 1175, 1025, and 825 cm^{-1}; ^{1}H NMR δ = 1.23 (3H, d, J = 7.0 Hz), 2.04 (3H, s), 2.57—2.76 (2H, m), 3.19—3.32 (1H, m), 3.77 (3H, s), 6.81—6.86 (2H, m), and 7.11—7.14 (2H, m); ^{13}C NMR δ = 22.2, 30.6, 34.7, 52.2, 55.2, 113.9, 127.7, 138.2, 158.0, and 208.0; MS *m/z* (rel intensity) 192 (M^+; 20), 177 (4), 135 (100), 105 (14), 91 (12), 77 (11), 65 (6), and 51 (4).

4-(4-Chlorophenyl)pentan-2-one (3bo): 68% yield; an oil; IR (neat) 2950, 1715, 1595, 1490, 1410, 1360, 1160, 1090, 1010, 820, and 530 cm^{-1}; ^{1}H NMR δ = 1.23 (3H, d, J = 7.0 Hz), 2.05 (3H, s), 2.59—2.77 (2H, m), 3.22—3.72 (1H, m), 7.11—7.16 (2H, m) and 7.22—7.27 (2H, m); ^{13}C NMR δ = 22.0, 30.5, 34.7, 51.7, 128.2, 128.6, 131.9, 144.7, and 207.3; MS *m/z* (rel intensity) 198 (M^+ + 2; 11), 196 (M^+; 32), 181 (66), 139 (100), 125 (25), 103 (53), 77 (40), and 51 (17).

4-(3-Chlorophenyl)pentan-2-one (3bp): 74% yield; an oil; IR (neat) 2940, 1710, 1590, 1355, 1155, 1070, 775, and 685 cm^{-1}; ^{1}H NMR δ = 1.24 (3H, d, J = 7.0 Hz), 2.07 (3H, s), 2.59—2.78 (2H, m), 3.25—3.33 (1H, m), and 7.07—7.24 (4H, m); ^{13}C NMR

δ = 21.8, 30.5, 35.0, 51.5, 125.2, 126.5, 126.9, 129.8, 134.2, 148.3, and 207.1; MS *m/z* (rel intensity) 198 (M^+ + 2; 20), 196 (M^+; 60), 181 (100), 153 (40), 139 (84), 125 (56), 103 (72), 77 (61), and 51 (30). Anal. Found: C, 67.46; H, 6.53. Cl, 18.27%. Calcd for $C_{11}H_{13}OCl$: C, 67.18; H, 6.66; Cl, 18.03%.

4-[4-(Trifluoromethyl)phenyl]pentan-2-one (3bq). By using the above-described procedure, **3bq** (72%) was isolated as an oil as a mixture with Fujiwara–Heck coupling products, (*E*)- and (*Z*)-4-[4-(trifluoromethyl)phenyl]pent-3-en-2-one (12%, *E*/*Z* = 56/44). The molar ratio was determined from the peak areas of the clearly separated protons. Typical spectroscopic data are as follows.

3bq: ^{1}H NMR δ = 1.27 (3H, d, *J* = 7.0 Hz), 2.07 (3H, s), 2.65—2.83 (2H, m), 3.32–3.45 (1H, m), 7.33 (2H, d, *J* = 8.1 Hz), and 7.54 (2H, d, *J* = 8.1 Hz); ^{13}C NMR δ = 21.8, 30.5, 35.2, 51.5, and 207.1; MS *m/z* (rel intensity) 230 (M^+; 26), 215 (100), 187 (5), 173 (44), 159 (32), 133 (23), 103 (9), 77 (10), and 58 (54).

(*E*)-4-[4-(Trifluoromethyl)phenyl]pent-3-en-2-one: ^{1}H NMR δ = 2.30 (3H, s) and 2.53 (3H, d, *J* = 1.5 Hz); MS *m/z* (rel intensity) 228 (M^+; 42), 227 (42), 213 (100), 165 (75), 159 (57), 145 (19), 115 (41), and 51 (13).

(*Z*)-4-[4-(Trifluoromethyl)phenyl]pent-3-en-2-one: ^{1}H NMR δ = 1.93 (3H, s) and 2.17 (3H, d, *J* = 1.5 Hz); MS *m/z* (rel intensity) 228 (M^+; 35), 227 (59), 213 (100), 165 (88), 159 (68), 145 (22), 115 (42), and 51 (16).

4-(1-Naphthyl)pentan-2-one (3br): 49% yield; an oil; ^{1}H NMR δ = 1.40 (3H, d, *J* = 7.0 Hz), 2.12 (3H, s), 2.72—2.95 (2H, m), 4.14—4.27 (1H, m), 7.35—7.56 (4H, m), 7.71 (1H, d, *J* = 8.1 Hz), 7.83—7.87 (1H, m), and 8.14 (1H, d, *J* = 8.4 Hz); ^{13}C NMR δ = 21.2, 29.4, 30.6, 51.6, 122.5, 123.0, 125.5, 126.1, 126.8, 129.0, 131.1, 134.0, 142.2, and 207.8; MS *m/z* (rel intensity) 212 (M^+; 45), 197 (10), 179 (20), 155 (100), 141 (15), 128 (14), and 115 (9). Anal. Found: C, 84.63; H, 7.43%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

4-Phenylnonan-2-one (3ck): 40% yield; an oil; IR (neat) 3020, 2920, 2850, 1720, 1600, 1495, 1450, 1360, 1155, 750, and 695 cm^{-1}; ^{1}H NMR δ = 0.82 (3H, t, *J* = 6.6 Hz), 1.12—1.23 (6H, m), 1.52—1.63 (2H, m), 1.99 (3H, s), 2.70 (2H, d, *J* = 7.3 Hz), 3.05—3.16 (1H, m), and 7.13—7.32 (5H, m); ^{13}C NMR δ = 14.0, 22.5, 27.0, 30.6, 31.7, 36.4, 41.3, 50.9, 126.3, 127.5, 128.4, 144.6, and 208.0; MS *m/z* (rel intensity) 218 (M^+; 3), 160 (94), 147 (77), 117 (42), 104 (76), 91 (100), 77 (14), and 55 (15).

4-(4-Chlorophenyl)butan-2-one (3do): 67% yield; an oil; IR (neat) 2920, 1710, 1490, 1405, 1360, 1160, 1090, 1010, 805, 660, and 520 cm^{-1}; ^{1}H NMR δ = 2.12 (3H, s), 2.73 (2H, t, *J* = 7.0 Hz), 2.85 (2H, t, *J* = 7.0 Hz), and 7.08—7.27 (4H, m); ^{13}C NMR δ = 29.0, 30.1, 44.9, 128.5, 129.7, 131.8, 139.5, and 207.5; MS *m/z* (rel intensity) 184 (M^+ + 2; 22), 182 (M^+; 77), 167 (20), 147 (36), 139 (37), 125 (100), 103 (49), 77 (45), and 51 (29).

4-(1-Naphthyl)butan-2-one (3dr): 53% yield; an oil; ^{1}H NMR δ = 2.15 (3H, s), 2.87 (2H, t, *J* = 7.3 Hz), 3.36 (2H, t, *J* = 7.3 Hz), 7.14 (1H, d, *J* = 7.7 Hz), 7.30—7.56 (4H, m), 7.83—7.87 (2H, m), and 7.97—8.00 (2H, m); ^{13}C NMR δ = 26.8, 30.1, 44.5, 123.4, 125.6, 125.6, 125.9, 126.0, 127.0, 128.9, 131.6, 133.9, 137.0, and 207.9; MS *m/z* (rel intensity) 198 (M^+; 67), 155 (63), 141 (100), 128 (21), 115 (28), and 77 (11).

4-Methyl-4-phenylpentan-2-one (3ek): 14% yield; an oil; IR (neat) 3050, 3020, 2950, 2870, 1700, 1590, 1490, 1435, 1355, 1130, 1095, 1070, 1025, 755, 695, and 530 cm^{-1}; ^{1}H NMR δ = 1.43 (6H, s), 1.79 (3H, s), 2.74 (2H, s), and 7.20—7.38 (5H, m); ^{13}C NMR δ = 28.9, 31.8, 37.3, 57.0, 125.5, 126.0, 128.3, 148.1, and 208.2; MS *m/z* (rel intensity) 176 (M^+; 12), 119 (100), 91 (68), 77 (14), and 51 (10).

3-Phenylcyclohexanone (3fk): 43% yield; an oil; IR (neat) 3065, 3030, 2950, 2870, 1710, 1600, 1495, 1445, 1255, 1225, 1030, 755, and 695 cm^{-1}; ^{1}H NMR δ = 1.69—1.87 (2H, m), 2.05—2.18 (2H, m), 2.30—2.63 (4H, m), 2.94—3.06 (1H, m), and 7.20—7.35 (5H, m); ^{13}C NMR δ = 25.5, 32.8, 41.2, 44.7, 48.9, 126.5, 126.7, 128.7, 144.3, and 211.0; MS *m/z* (rel intensity) 174 (M^+; 82), 131 (72), 117 (100), 104 (70), 91 (35), 77 (26), and 51 (23).

3-(4-Methylphenyl)butanal (3gl): 46% yield; an oil; IR (neat) 3095, 3050, 3020, 2960, 2925, 2875, 2825, 2720, 1730, 1510, 1450, 1305, 1105, 1050, 1015, 810, and 530 cm^{-1}; ^{1}H NMR δ = 1.29 (3H, d, *J* = 7.0 Hz), 2.31 (3H, s), 2.57—2.77 (2H, m), 3.28—3.36 (1H, m), 7.11 (4H, s), and 9.69 (1H, t, *J* = 2.2 Hz); ^{13}C NMR δ = 21.0, 22.3, 33.9, 51.8, 126.6, 129.3, 136.0, 142.4, and 202.0.

3-Phenylhexanal (3hk): 55% yield; an oil; IR (neat) 3100, 3075, 3050, 2975, 2950, 2890, 2830, 2725, 1730, 1605, 1500, 1455, 760, and 700 cm^{-1}; ^{1}H NMR δ = 0.86 (3H, t, *J* = 7.3 Hz), 1.12—1.26 (2H, m), 1.58—1.66 (2H, m), 2.69—2.72 (2H, m), 3.13—3.24 (1H, m), 7.16—7.33 (5H, m), and 9.66 (1H, t, *J* = 2.2 Hz); ^{13}C NMR δ = 13.9, 20.4, 38.8, 39.9, 50.6, 126.6, 127.5, 128.6, 143.9, and 202.1; MS *m/z* (rel intensity) 176 (M^+; 27), 133 (78), 117 (13), 105 (70), 91 (100), 77 (35), 65 (11), and 51 (16).

2-Methyl-3-phenylpropanal (3jk): 35% yield; an oil; IR (neat) 3100, 3075, 3040, 2980, 2945, 2885, 2870, 2825, 2720, 1730, 1605, 1500, 1455, 1280, 1030, 740, and 700 cm^{-1}; ^{1}H NMR δ = 1.09 (3H, d, *J* = 7.0 Hz), 2.56—2.71 (2H, m), 3.06—3.12 (1H, m), and 7.15—7.33 (5H, m); ^{13}C NMR δ = 16.5, 39.3, 41.2, 126.4, 128.4, 129.0, 139.0, and 201.0; MS *m/z* (rel intensity) 148 (M^+; 25), 105 (16), 91 (100), 77 (13), 65 (17), and 51 (12).

Typical Procedure for the Preparation of the Antiinflammatory Compounds. Methyl vinyl ketone (0.070 g, 1 mmol) was added by a syringe to a suspension of tri-2-naphthylstibine (**2s**) (0.252 g, 0.5 mmol), AgOAc (0.167 g, 1 mmol), and $Pd(OAc)_2$ (0.011g, 0.05 mmol) in AcOH (10 mL). After the mixture was stirred at 25 °C for 24 h, the precipitated solid was filtered off and the filtrate was poured into brine (100 mL), extracted with dichloromethane (30 mL×2), and washed with saturated aqueous $NaHCO_3$. The organic phase was washed with water and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a brown solid, which was purified by preparative TLC using ethyl acetate/hexane (1/10) mixture as an eluent to give 4-(2-naphthyl)-butan-2-one (**3ds**) (0.095 g, 95% on the basis of **2s**) as a white solid: mp 43—44 °C (lit,[11] 45—46 °C); ^{1}H NMR δ = 2.08 (3H, s), 2.76 (2H, t, *J* = 7.3 Hz), 3.01 (2H, t, *J* = 7.3 Hz), 7.27 (1H, dd, *J* = 8.4 and 1.8 Hz), 7.34—7.45 (2H, m), 7.57 (1H, s), and 7.71—7.78 (3H, m); ^{13}C NMR δ = 29.8, 30.0, 44.9, 125.3, 126.0, 126.3, 127.0, 127.4, 127.6, 128.1, 132.0, 133.6, 138.5, and 207.8; MS *m/z* (rel intensity) 198 (M^+; 60), 155 (100), 141 (57), 128 (16), 115 (23), and 77 (7).

4-(6-Methoxy-2-naphthyl)butan-2-one (3dt): 99% yield; a white solid; mp 78—79 °C (lit,[11] 80—81 °C); ^{1}H NMR δ = 2.13 (3H, s), 2.80 (2H, t, *J* = 7.3 Hz), 3.01 (2H, t, *J* = 7.3 Hz), 3.89 (3H, s), 7.09—7.14 (2H, m), 7.24—7.28 (1H, m), 7.53 (1H, s), and 7.65 (2H, d, *J* = 8.4 Hz); ^{13}C NMR δ = 29.7, 30.1, 45.2, 55.3, 105.6, 118.8, 126.2, 127.0, 127.5, 128.9, 129.1, 133.1, 136.1, 157.3, and 208.0; MS *m/z* (rel intensity) 228 (M^+; 51), 185 (13), 171 (100), 153 (4), 141 (9), 128 (15), and 115 (9).

General Procedure for Pd(II)-Catalyzed Reactions of α,β-Unsaturated Ketones and Aldehydes with Diarylantimony Chlorides. Diarylantimony chloride (1.2 mmol) was prepared by the redistribution of triarylstibine (0.8 mmol) with antimony(III) chloride (0.4 mmol) in the absence of a solvent for 5 h at 25 °C. Then, a solution of enone or enal (1 mmol) and palladium(II) acetate (0.023 g, 0.1 mmol) in acetic acid (10 mL) was added to the in situ

prepared redistribution product, and the mixture was stirred for 24 h at 25 °C. The precipitated solid was filtered off and the filtrate was poured into brine (100 mL), extracted with ether (30 mL×2), and washed with a saturated aqueous $NaHCO_3$. The organic phase was washed with water, dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure usually left an oil, which was separated and purified by preparative TLC using ethyl acetate–hexane mixture as an eluent to give the conjugate addition products. For obtaining the GLC yield, a similar reaction was carried out in the presence of an appropriate amount of 1,2-diphenylethane as an internal standard. The products obtained by the above procedure were characterized spectroscopically as shown below. Compounds **3cl** and **3cm** are new.

4-(4-Methylphenyl)nonan-2-one (3cl): 65% yield; an oil; ^{1}H NMR δ = 0.82 (3H, t, J = 6.6 Hz), 1.18—1.22 (6H, m), 1.50—1.58 (2H, m), 1.99 (3H, s), 2.30 (3H, s), 2.68 (2H, d, J = 7.3 Hz), 3.01—3.12 (1H, m), and 7.03—7.10 (4H, m); ^{13}C NMR δ = 14.0, 21.0, 22.5, 27.1, 30.6, 31.8, 36.5, 41.0, 51.1, 127.3, 129.1, 135.7, 141.5, and 208.1; MS *m/z* (rel intensity) 232 (M^+; 12), 174 (56), 161 (47), 131 (24), 118 (22), 105 (100), 91 (16), 77 (8), 65 (5), and 55 (10). Anal. Found: C, 82.61; H, 10.44%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

4-(3-Methylphenyl)nonan-2-one (3cm): 66% yield; an oil; ^{1}H NMR δ = 0.83 (3H, t, J = 6.6 Hz), 1.15—1.23 (6H, m), 1.51—1.57 (2H, m), 2.00 (3H, s), 2.32 (3H, s), 2.68 (2H, d, J = 7.3 Hz), 3.01—3.12 (1H, m), 6.94—7.00 (3H, m), and 7.13—7.19 (1H, m); ^{13}C NMR δ = 14.0, 21.5, 22.5, 27.1, 30.6, 31.8, 36.5, 41.3, 51.0, 124.4, 127.1, 128.3, 128.3, 137.9, 144.6, and 208.1; MS *m/z* (rel intensity) 232 (M^+; 11), 174 (81), 161 (68), 131 (32), 118 (40), 105 (100), 91 (21), 77 (12), 65 (6), and 55 (25). Anal. Found: C, 82.64; H, 10.50%. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%.

General Procedure for Pd(II)-Catalyzed Reactions of α,β-Unsaturated Ketones and Aldehydes with Arylantimony Dichlorides. Arylantimony dichloride (1.2 mmol) was prepared by the redistribution of triarylstibine (0.4 mmol) with antimony (III) chloride (0.8 mmol) in the absence of solvent for 5 h at 25 °C. Then, a solution of enone or enal (1 mmol) and palladium(II) acetate (0.023 g, 0.1 mmol) in acetic acid (10 mL) was added to the in situ prepared redistribution product and the mixture was stirred for 24 h at 25 °C. The procedures for the work-up and for isolating the pure product are the same as those described above. For obtaining the GLC yield, a similar reaction was carried out in the presence of an appropriate amount of 1,2-diphenylethane as an internal standard. The conjugate addition products prepared by the above procedure were characterized spectroscopically, as shown below.

4-(4-Methylphenyl)-4-phenylbutan-2-one (3al): 89% yield; an oil; ^{1}H NMR δ = 2.07 (3H, s), 2.29 (3H, s), 3.16 (2H, d, J = 7.3 Hz), 4.54 (1H, t, J=7.7 Hz), 7.06—7.29 (9H, m); ^{13}C NMR δ =20.9, 30.6, 45.7, 49.7, 126.3, 127.5, 127.6, 128.5, 129.2, 135.9, 140.8, 144.1, and 207.0; MS *m/z* (rel intensity) 238 (M^+; 21), 220 (4), 195 (13), 181 (91), 165 (31), 117 (15), 103 (26), 91 (9), 77 (15), 65 (7), and 43 (100).

General Procedure for Pd(II)-Catalyzed Reactions of α,β-Unsaturated Ketones and Aldehydes with Diphenylantimony Acetate. A mixture of diphenylantimony acetate (0.5 mmol), enone or enal (0.5 mmol) and palladium(II) acetate (0.011 g, 0.05 mmol) was stirred in acetic acid (10 mL) at 25 °C for an appropriate time. The work-up procedure was similar to that described above. For obtaining the GLC yield, a similar reaction was carried out in the presence of an appropriate amount of 1,2-diphenylethane as an internal standard.

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