Role of Halide Ions in Divalent Palladium-Mediated Reactions: Competition between β-Heteroatom Elimination and β-Hydride Elimination of a Carbon−Palladium Bond

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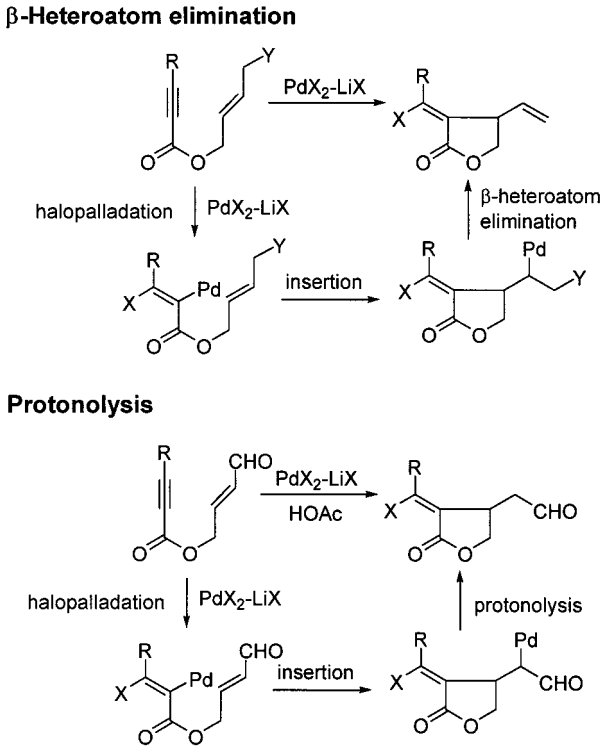
The integral role of halide ions as a ligand in the reactions of stoichiometric arylpalladium reagents and Pd(II)-catalyzed reaction of phenylmercuric acetate with various allylic compounds were studied. The halide ion was found to inhibit β-H elimination and promote β-heteroatom elimination in acidic media. In this reaction, a C−Pd intermediate with a β-heteroatom (including halogen, acetoxy, alkoxy, and hydroxyl groups) gives only β-heteroatom elimination product in the presence of halide ions, while β-H elimination is effectively blocked.

Introduction

Although the Pd(II) species is the most common active species in palladium-catalyzed carbon−carbon bond forming reactions, most of the carbon−carbon coupling reactions initially mediated by Pd(II) species are stoichiometric.[1] The main reason is that methods of quenching the carbon−palladium bond to regenerate the divalent palladium species are rarely reported,[2] and the carbon−palladium bond is easily quenched by β-hydride elimination or reductive elimination, which in general generates the Pd(0) species, making the catalytic cycle impossible. Thus, oxidizing agents are necessary to regenerate the divalent palladium catalyst.[1b,f,g] In our previous work in the cyclization reaction of allylic alkynoates to α-alkylidene-γ-butyrolactones, we explored the β-heteroatom elimination[2f,g] (intramolecular version of Kaneda's work[2c]) and protonolysis reaction[3] to quench the carbon−palladium bond in the presence of halide ions and regenerate the divalent palladium species (Scheme 1).[2c] In both reactions, halide ions were found to be necessary for the catalytic cycle and high yield of the reactions.

Scheme 1



A number of research studies addressed the importance of halide ligands in reactions normally catalyzed by Pd(0).[4] Also the role of halide ions as a ligand has been considered in divalent palladium-catalyzed reactions.[5]

Palladium(II)-catalyzed reactions in the presence of halide ions were developed in early works.[1] Chloropal-

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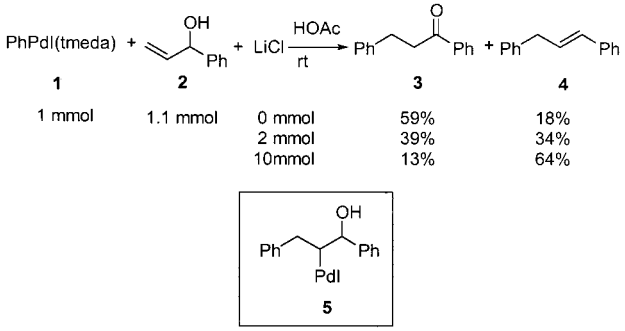
ladate compounds are widely used as homogeneous catalysts because of their good solubilities in water and other polar solvents.[6] Recent studies revealed that halopalladate complexes can be generated in situ from various catalyst precursors and act as the actual catalytic species in a much wider range of Pd(II)-catalyzed reactions, e.g., $Pd(OAc)_2$−benzoquinone−LiCl-promoted 1,4-difunctionalization of 1,3-dienes,[1g,7] and $Pd(OAc)_2$−LiBr-mediated heteroatom addition to carbon−carbon multiple bonds.[8] In the former case, it was shown that the regio- and stereoselectivities of the reaction depend on the presence or absence of LiCl.[7] In addition, the dependence of the β-H elimination reaction of a carbon−palladium species on the LiCl concentration has also been reported.[5c−e]

While studying the mechanism and trying to optimize these divalent palladium-catalyzed cyclization reactions, we found that halide ion concentration significantly influences the *Z*/*E* selectivity of the exocyclic double bond (Scheme 1).[2f,g,3] Recently, we reported the role of halide ion in the tandem halopalladation−insertion−protonolysis reaction and found that the halide ion could inhibit the β-H elimination but promote the protonolysis reaction in acidic media.[3e] In this paper, we wish to report our result of the role of halide ions in the competition between β-heteroatom elimination and β-hydride elimination of a carbon−palladium intermediate with both β-heteroatom and β-hydrogen.

Results and Discussion

In the synthesis of α-haloalkylidene-β-vinyl-γ-butyrolactone derivatives from the enyne coupling of 4′-halo-2′-alkenyl alkynoates, excess halide salts were used to obtain high *Z* stereoselectivity of the exocyclic double bond in the lactone products.[9] A study on the stereochemistry of the β-heteroatom elimination in these systems revealed that the β-heteroatom elimination

Scheme 2



proceeds through *trans* elimination with the rates in the following order: β-halide > β-OAc > β-OR > β-OH ~ β-H in acid medium.[10] The slow rate of β-H elimination observed in our experiments was unexpected in light of the many facile β-H eliminations reported in the literature.[11] This led us to analyze these results with more discretion. In the studies of the role of halide ions in protonolysis reactions, it is clear that halide ions can inhibit β-H elimination and promote protonolysis of the C−Pd bond. This result stimulated us to study the effect of halide ions in the β-heteroatom elimination processes; we conducted this study with the stoichiometric model reactions.

Stoichiometric Reaction of PhPdI(tmeda) (1) with Allylic Alcohol. The reaction of complex **1** (tmeda = tetramethylethylenediamine)[12] with 1-phenyl-2-propenol (**2**) was conducted in HOAc at room temperature with different amounts of LiCl (Scheme 2).

The insertion of **2** to **1** first gives intermediate **5**. From **5**, β-H elimination gives ketone **3**, while β-heteroatom elimination furnishes olefin **4**. In the absence of LiCl, the reaction gave ketone **3** as the major product (β-H elimination pathway), while the olefin **4** was isolated as the minor product (β-OH elimination pathway). In the presence of 2 equiv of LiCl, β-H elimination and β-heteratom elimnination products were comparable. However, in the presence of 10 equiv of LiCl, the reaction gave predominantly the β-heteroatom elimination product. These results suggest that β-H elimination is suppressed in the presence of excess chloride ion.

Stoichiometric Reaction of 6 with Different Allylic Compounds. It should be noted that 1 equiv of iodide is present in complexes **1**. So all these reactions were carried out in the presence of at least 1 equiv of halide ligand. To obtain accurate results, a halide-free palladium complex **6**[13] was chosen to study the reaction (Scheme 3). The results of the reactions of complex **6** with allylic compounds (including halides, acetate, ether, and alcohol) in HOAc in the presence of different amounts of LiCl were given in Table 1.

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Scheme 3

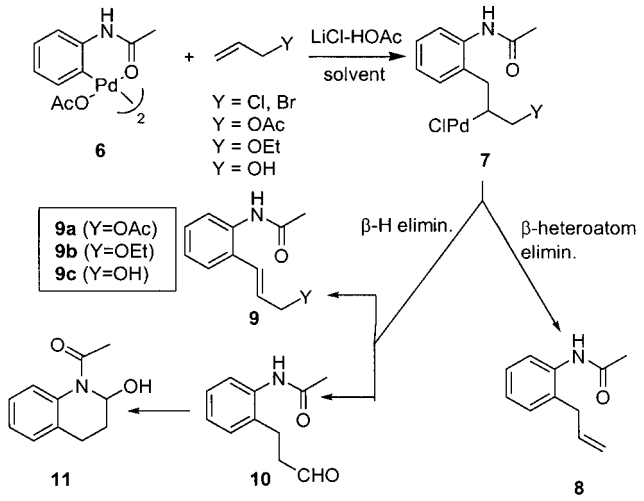
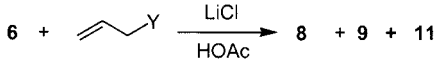


Table 1. Role of Chloride Ion in the Reaction of Complex 6 with Allylic Compounds



	reactants[a]		yield of product (%)[b]		
			β-heteroatom elimination	β-H elimination	
entry	Y	LiCl (equiv)	**8**	**9**	**11**
1	Cl	10	81		
2	Cl	0	61		
3	OAc	10	75		
4	OAc	0		66 (**9a**)	
5	OEt	10	60		
6	OEt	0		69 (**9b**)	
7	OH	10	64		
8	OH	0		39 (**9c**)	30

[a] Reaction conditions: Complex **6**: LiCl/allylic compounds = 1:20:10, HOAc, rt. [b] Isolated yield based on **6**.

In the absence of chloride ion, reactions of allyl acetate and allyl ether with **6** in HOAc all gave products **9a** (Y = OAc) and **9b** (Y = OEt), respectively, while the reactions with allyl alcohol gave products **9c** (Y = OH) and **11**. Both **9** and **11** were formed from β-H elimination of the intermediate **7** (Table 1, entries 4, 6, and 8). Product **11** has a cyclic lactol-like structure, presumably formed by the interaction between the amide N-H group and the aldehyde group of **10** (Scheme 3).[14] When the reactions were carried out with excess LiCl (10 equiv) in HOAc, all the allylic compounds yield **8** as the only product, and no trace of **9** or **11** was detected (Table 1, entries 1, 3, 5, and 7). LiBr and LiI gave similar results. However, in some cases, a small amount of acetanilide was isolated. For example, when allyl alcohol reacted with **6** in the presence of 10 equiv of LiBr or LiI, apart from **8**, acetanilide was also isolated in 7% and 11%, respectively. That the presence of excess halide may facilitate the protonolysis of an aryl−pallalium bond has previously been reported.[15]

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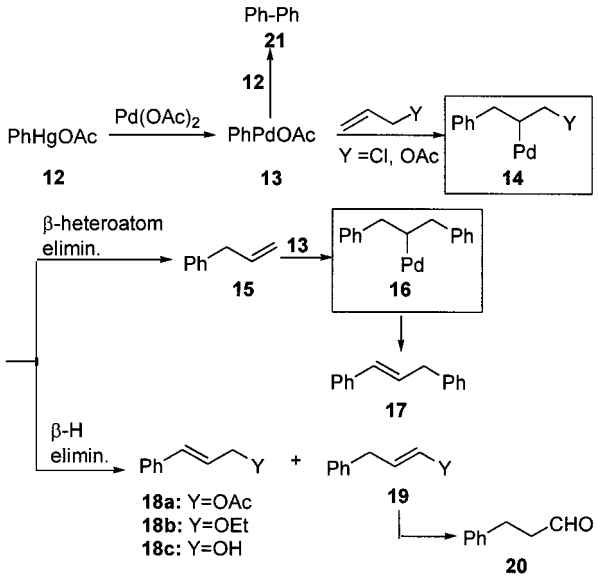
Scheme 4

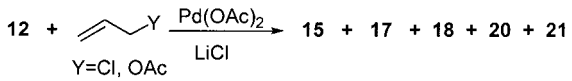


When allyl chloride (similarly allyl bromide) was reacted with complex **6** in HOAc at room temperature, either in the absence or in the presence of LiCl, the reaction gave **8** as the sole product, implying that only β-heteroatom elimination occurred in the quenching of the C−Pd bond (Table 1, entries 1 and 2). The same product was produced with no influence from the amount of LiCl present in the reaction system. This might be due to (1) the good leaving ability of chloride or (2) that the chloride ion produced from the reaction further inhibits β-H elimination.

The results of the stoichiometric reaction of complexes **1** and **6** indicate that the halide ions play an important role in the competition between β-heteroatom elimination and β-H elimination of the C−Pd bond. The halide ions serve a similar role to that in the protonolysis reaction.[3e] Thus, in the presence of excess halide ions, β-heteroatom elimination reaction was promoted with complete suppression of the β-H elimination.

Catalytic Reactions of Phenylmercuric Acetate with Allylic Compounds. The above conclusion can be further verified by catalytic reactions. The reactions of phenylmercuric acetate (3 mmol) with an allylic compound (Y = Cl, OAc, OEt, OH; 9 mmol) were tested in HOAc (15 mL) using a catalytic amount of $Pd(OAc)_2$ (5 mol % based on PhHgOAc) at room temperature (Scheme 4). When an excess of LiCl (30 mmol) was used, the reaction gave products **15** and **17**, suggesting that only β-heteroatom elimination occurred from the intermediate **14**. Compound **17** might be produced from further insertion of **15** with **13** followed by β-H elimination of **16** (Scheme 4; Table 2, entries 1, 3, and 5). For allyl chloride, a small amount of coupling product **21** was also formed. For allyl ether, β-H elimination products were also formed in comparative amount. The reaction is disordered for allyl alcohol. While the reaction was carried out in the absence of LiCl, it yields only a small amount of products **18** and **20**, mainly derived from the β-H elimination of the intermediate **14**. The low yield might be due to the formation of a [PdH] species from β-H elimination, which made the catalytic cycle impossible. Product **18a** was also formed from allyl chloride and allyl alcohol, which may be due to the

Table 2. Pd(II)-Catalyzed Reaction of Phenylmercuric Acetate with Allylic Compounds[a]

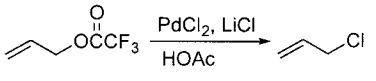


	reactants			ratio of products[c]				
				β-heteroatom elimination		β-H elimination		
entry	Y	LiBr (equiv)	yield, %[b]	**15**	**17**	**18**	**20**	**21**
1	Cl	10	77	25	4			1
2	Cl	0	16	1	3	3 (**18a**)		
3	OAc	10	76	5	2			
4	OAc	0	3			**18a**[d]		
5	OEt	10	48	13	1	5.3 (**18b**)	10	
6	OEt	0	4.5			**18b**[e]		
7	OH	10	disordered reaction					
8	OH	0	4			2 (**18a**) 5 (**18c**)	2	

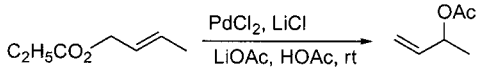
[a] Phenylmercuric acetate (**12**, 1 equiv), $Pd(OAc)_2$ (0.05 equiv), allylic compound (5 equiv). [b] Isolated yield based on **12**. [c] The ratio was determined from ^1H NMR spectra. [d] Only **18a** was obtained. [e] Only **18b** was obtained.

exchange of acetate with the chloride and hydroxyl group,[16] while for allyl chloride, besides **18**, compounds **15** and **17** were also formed probably due to the presence of chloride ion originated from the substrate. The formation of **15** occurred from β-heteroatom elimination promoted by the presence of chloride ion. Compound **20** was formed from allyl ether and allyl alcohol, indicating that β-H elimination can occur from both β-positions.

Two reports by Henry described that allylic esters could undergo exchange reactions in the presence of $PdCl_2$ and LiCl in HOAc, e.g., allyl trifloroacetate to chloride exchange (eq 1) and crotyl ester exchange−isomerization (eq 2):[17]



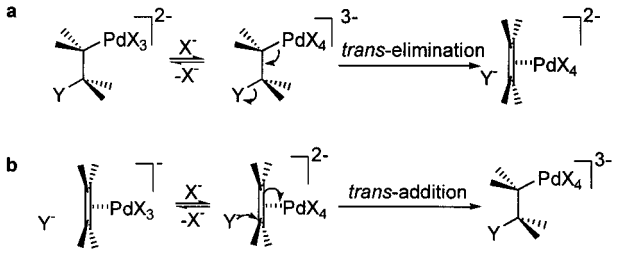
(eq 1)



(eq 2)

In our experiments, we found that in the presence of excess halide ions both allyl chloride and allyl acetate gave β-elimination products. The question arises whether the allyl acetate is first transformed to an allyl chloride, which then takes part in the coupling reaction. To clarify this issue, allyl acetate was subjected to a $Pd(OAc)_2$−LiBr mixture in CD_3CO_2D and monitored by ^1H NMR spectroscopy. No change was detected after 72 h. It appeared that allyl acetate is not transformed to allyl bromide under our reaction conditions; we thus conclude that the reactions did proceed through allyl acetate.

Scheme 5



Both stoichiometric and catalytic reactions revealed that excess chloride ion would inhibit β-H elimination and promote β-heteroatom elimination. This might be ascribed to the following: (a) the presence of excess halide ion makes the Pd coordinatively saturated and the β-H elimination not so feasible; (b) the coordination of halide ion to Pd increases the electron density of Pd, resulting in the weakening of the C−Pd bond.[12,15]

We have previously established that β-heteroatom eliminations proceed through a *trans* elimination mechanism.[10] Combined with the new observation that an excess of halide ions assists this process, we propose an E2-like mechanism for the β-heteroatom elimination (Scheme 5, a). The halide ion first coordinates to Pd, forming a highly electron-rich pentacoordinated Pd center. This weakens the C−Pd bond and is followed by simultaneous C−Pd bond cleavage and elimination of the leaving group from the opposite side to yield the alkene. β-Heteroatom elimination is the reverse process of nucleophilic addition to a Pd(II)-coordinated C=C double bond. We wish to note that Bäckvall et al.[7b,18] studied such addition processes and found they proceed via *trans* addition in the presence of a high concentration of halide ions (Scheme 5, b), which is in agreement with our results.

From the systematic studies of the integral role of halide ions as a ligand in the reactions of stoichiometric arylpalladium reagents and the Pd(II)-catalyzed reactions of phenylmericuric acetate with various allylic compounds, we have established that an excess of halide ions can block β-H elimination while promote β-heteroatom elimination. These reactions cannot be achieved with phosphine ligands because under similar conditions excess phosphine shuts down the reaction completely by blocking the coordination of the olefinic substrate. This unique advantage of halide may result from the facile ligand exchange from a halide to an olefin, as opposed to the sluggish and unfavorable exchange from a phosphine to an olefin.

It is significant that by simply applying metal halides, the reaction pathway of an alkylpalladium intermediate can be easily switched from the normal β-H elimination (Heck-type reaction) to β-heteroatom elimination, while the β-position possesses a leaving group. Unlike β-H elimination, which normally leads to formation of Pd(0), β-heteroatom elimination regenerates divalent palladium as the active species. On the basis of these findings and the many well-established Pd(II)-initiated C−Pd formation reactions,[19] an array of divalent palladium-catalyzed reactions can be designed.[3e]

(16) A control experiment showed that allyl chloride did react with $Hg(OAc)_2$ with the formation of allyl acetate.

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In conclusion, halide ions play an important role in the studied Pd(II)-catalyzed reactions. The halide ion could inhibit β-H eilmination and promote β-heteroatom elimination in acidic media similar to protonolysis.[3e] For the reaction of a C−Pd intermediate with a β-heteroatom (including halogen, acetoxy, alkoxy, and hydroxyl groups), only the β-heteroatom elimination product was obtained, while the β-H elimination is effectively blocked. It is significant that halide ions in these reactions do not inhibit the insertion of the double bond as phosphines usually do, but only inhibit the β-H elimination step. This important finding is expected to have a broad impact on the studies of Pd(II)-catalyzed reactions and lead to rational design of efficient catalytic systems.

Experimental Section

General Procedures. Spectral data were obtained by the use of the following instruments: Bruker AM-300 (^{1}H NMR), Bruker AM-360 (^{13}C NMR), Shimadzu IR-440 (IR), Finnigan 4021 (MS), and Finnigan MAT8430 (HRMS). Complexes **1**[12] and **6**[13] were prepared according to the literature procedure.

Reaction of Phenylpalladium Iodide Tetramethlethylenediamine Complex 1 with 1-Phenylprop-2-enol. A mixture of complex **1** (426 mg, 1 mmol), 1-phenylprop-2-enol (146 mg, 1.1 mmol), HOAc (5 mL), and LiCl (in different amounts) in a Schlenk tube was stirred at room temperature under argon. After the reaction was completed, ether (100 mL) was added. The ether layer was washed with water (10 mL × 2) and brine (10 mL × 2) and dried (Na_2SO_4). The residue was chromatographed on silica gel (eluent: petroleum ether/ethyl acetate = 20:1), giving **3** and **4** (Scheme 2). Data for **3**: ^{1}H NMR ($CDCl_3$) δ 8.00−7.20 (m, 10H), 3.21−2.85 (m, 4H); IR (KCl) 3050, 2940, 1690, 1600, 1590, 1500, 1460, 1420, 1370, 1080, 980, 755, 710, 700, 565 cm^{-1}.[20] Data for **4**: ^{1}H NMR ($CDCl_3$) δ 7.94−7.10 (m, 10H), 6.52−6.20 (m, 2H), 3.50 (d, J = 7 Hz, 2H); IR (neat) 3050, 3010, 1600, 1490, 1450, 960, 740, 695 cm^{-1}.[21]

Reaction of Di-μ-acetatobis(2-acetaminophenyl-2C,O)-dipalladium(II) (6) with Allyl Compounds. General Procedure. To a suspension of complex **6** (80 mg, 0.13 mmol) in HOAc (2 mL) was added allyl compounds (allyl chloride, allyl acetate, allyl ethyl ether, or allyl alcohol, 1.34 mmol). The mixture was stirred at room temperature for 5−20 min. After separation of the palladium by filtration through a short column of silica gel, the filtrate was concentrated under vacuum and the residue was chromatographed on silica gel (petroleum ether/ethyl acetate = 2:1) to afford products **8**, **9a**, **9b**, **9c**, and **11** as shown in Table 1.

8: mp 87−89 °C (lit.[22] 94−95.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.45−7.10 (m, 4H), 6.05−5.90 (m, 1H), 5.20 (d, J = 9.9 Hz, 1H), 5.05 (d, J = 16 Hz, 1H), 3.40 (d, J = 6.1 Hz, 2H), 2.14 (s, 3H); IR (KCl) 3286, 1657, 1587, 1536, 1482, 1371, 1298, 994, 970, 916, 753 cm^{-1}; MS (m/z) 176 (M^+ + 1), 175 (M^+), 160, 132 (100), 118, 91, 77; HRMS calcd For $C_{11}H_{13}NO$, 175.0997; found, 175.1007.

9a: mp 97−98 °C; ^{1}H NMR ($CDCl_3$) δ 7.64−7.04 (m, 5H), 6.66 (d, J = 15.8 Hz, 1H), 6.11 (dt, J = 15.8, 6.3 Hz, 1H), 4.65 (dd, J = 6.3, 1.4 Hz, 2H), 2.11 (s, 3H), 2.03 (s, 3H); IR (KBr) 3240, 1736, 1652, 1239 cm^{-1}; MS (m/z) 233 (M^+); 191, 173, 130 (100). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.73; H, 6.45; N, 5.82.

9b: mp 102−103 °C; ^{1}H NMR ($CDCl_3$) δ 7.73−7.03 (m, 4H), 6.62 (d, J = 15.6 Hz, 1H), 6.15 (dt, J = 15.6, 5.7 Hz, 1H), 4.08 (dd, J = 5.7, 1.5 Hz, 2H), 3.51 (q, J = 7.0 Hz, 2H), 2.15 (s, 3H), 1.19 (t, J = 7.0 Hz, 3H); IR (KBr) 3269, 1658 cm^{-1}; MS (m/z) 219 (M^+), 190, 176, 130 (100). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.98; H, 7.75; N, 6.30.

9c: mp 108−109 °C; ^{1}H NMR ($CDCl_3$) δ 7.68−7.06 (m, 5H), 6.63 (d, J = 16.1 Hz, 1H), 6.20 (dt, J = 16.1, 5.2 Hz, 1H), 4.27 (dd, J = 5.2, 1.2 Hz, 2H), 2.13 (s, 3H); IR (KBr) 3263, 1660 cm^{-1}; MS (m/z) 191 (M^+), 174, 148, 130 (100). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.91; H, 6.87; N, 7.30.

11:[3e] oil; ^{1}H NMR ($CDCl_3$) δ 7.18−7.04 (m, 4H), 5.95 (t, J = 7.6 Hz, 1H), 4.31 (br, 1H), 2.55−2.52 (m, 1H), 2.46−2.38 (m, 2H), 2.20 (s, 3H), 1.59−1.57 (m, 1H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 172.6, 136.6, 134.6, 127.1, 126.5, 125.3, 124.4, 78.7, 31.8, 25.1, 23.2; ^{13}C NMR DEPT 135 spectra (90 MHz) δ 127.1, 126.6, 125.3, 124.4, 78.7, 31.8(−), 25.1(−), 23.2; IR (neat) ν 3394, 1647, 1584, 1493, 1373, 1334, 956, 789, 761 cm^{-1}; MS (m/z) 192 (M^+ + 1), 191 (M^+), 174, 163, 149, 148, 132, 130, 106(100), 93, 91, 77; HRMS calcd for $C_{11}H_{13}NO_2$, 191.0946; found, 191.0938.

Palladium-Catalyzed Reaction of Phenylmercuric Acetate with Allyl Compounds. General Procedure. To a mixture of phenylmercuric acetate (1.14 g, 3 mmol) and LiCl (1.28 g, 30 mmol) in HOAc (15 mL) was added allyl compounds (15 mmol) and $Pd(OAc)_2$ (34 mg, 5 mol %). After stirring at room temperature for 26 h, the mixture was poured into water (50 mL) and extracted with pentane (200 mL). The organic layer was washed with saturated $NaHCO_3$ solution and brine and dried (Na_2SO_4). After removing the solvent, the residue was purified by column chromatography on silica gel (pentane) to obtain products **15**, **17**, **18a**, **18b**, **18c**, **20**, and **21** as shown in Table 2.

15: oil; ^{1}H NMR ($CDCl_3$) δ 7.38−7.33 (m, 2H), 7.29−7.24 (m, 3H), 6.10−5.97 (m, 1H), 5.17−5.11 (m, 2H), 3.45 (d, J = 6.6 Hz, 2H); IR (KBr) 3027, 2923, 1638, 1602, 1495, 1452, 1433, 997, 917, 743, 702 cm^{-1}.

17: oil;[21] ^{1}H NMR ($CDCl_3$) δ 7.35−7.10 (m, 10H), 6.40 (d, J = 15.9 Hz, 1H), 6.35 (dt, J = 15.9 Hz, 6.4 Hz, 1H), 3.40 (d, J = 6.4 Hz, 2H); IR (KBr) 3084, 3028, 1947, 1653, 1601, 1496, 1452, 965, 740, 694.

18a: oil;[23a] ^{1}H NMR ($CDCl_3$) δ 7.43−7.28 (m, 5H), 6.67 (d, J = 15.9 Hz, 1H), 6.31 (dt, J = 15.9, 6.4 Hz, 1H), 4.75 (d, J = 6.4 Hz, 2H), 2.12 (s, 3H); IR (KBr) 3027, 2942, 1733, 1494, 1450, 1381, 1364, 1236, 1029, 970, 750, 696 cm^{-1}.

18b: oil;[23b] ^{1}H NMR ($CDCl_3$) δ 7.50−7.15 (m, 5H), 6.60 (d, J = 15.9 Hz, 1H), 6.35 (dt, J = 15.9, 6.0 Hz, 1H), 4.15 (d, J = 6.0 Hz, 2H), 3.60 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H).

18c: oil;[23c] ^{1}H NMR ($CDCl_3$) δ 7.34−7.15 (m, 5H), 6.55 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 5.7 Hz, 1H), 4.26 (dd, J = 5.7, 1.2 Hz, 2H); IR (KBr) 3350, 3061, 3027, 2925, 2859, 1494, 1450, 1094, 1011, 968, 747, 693 cm^{-1}.

20: oil;[23d] ^{1}H NMR ($CDCl_3$) δ 9.76 (t, J = 1.3 Hz, 1H), 7.28−7.14 (m, 5H), 2.91 (t, J = 7.5 Hz, 2H), 2.75−2.69 (m, 2H); IR (KBr) 3027, 2929, 2722, 1723, 1495, 1452, 1245, 1139, 1056, 750, 704 cm^{-1}.

21: mp 70−71 °C (lit.[24] 70 °C); ^{1}H NMR ($CDCl_3$) δ 7.53−7.42 (m, 10H); IR (KCl) 1479, 1429, 1344, 1170, 903, 728, 695 cm^{-1}.

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