Palladium- and Platinum-Catalyzed Addition of Aldehydes and Imines with Allylstannanes. Chemoselective Allylation of Imines in the Presence of Aldehydes

Hiroyuki Nakamura,[†] Hideki Iwama,[‡] and Yoshinori Yamamoto*,[‡]

Contribution from the Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812, Japan, and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77, Japan

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Abstract: The reaction of allylstannanes **1** with aldehydes **2** in THF was catalyzed by Pd(II) or Pt(II) complexes (10 mol %) either at room temperature or at reflux, giving the corresponding homoallylic alcohols **3** in high to good yields. Among the catalysts examined, $PtCl_2(PPh_3)_2$ gave the best result. No only allyltribitylstannane but also methallyl- and crotyltributylstannane could be utilized in this transition metal catalyzed reaction. Detailed mechanistic studies of the Pd(II)-catalyzed allylation, using NMR spectroscopy, revealed that the bis-π-allylpalladium complex is a key intermediate for the catalytic cycle and it exhibits nucleophilic reactivity. The nucleophilic reactivity of the intermediate is in marked contrast to the electrophilic reactivity of ordinary π-allylpalladium complexes (π-allylPdX, X = OAc, halogen, OCO_2R, etc.). The addition of allyl-, crotyl-, and methallylstannanes to various imines **4** proceeded very smoothly to give the corresponding allylated products (homoallylic amines **5**) in good to high yields. *The reactivities of allylstannanes to imines were higher than those to aldehydes under the catalytic conditions*, although it is known that the reactivity of allylstannanes to aldehydes is higher than that to imines under the Lewis acid promoted condition. Imines were chemoselectively allylated in the presence of aldehydes and the highest selectivities were obtained using π-allylpalladium chloride dimer **11** as a catalyst.

Introduction

The allylation of aldehydes and imines with allylstannanes has emerged as an important reaction type and has seen extensive development and applications in synthesis.[1] The reaction of aldehydes with allyltrialkylstannanes takes place in the presence of Lewis acids,[2] at high pressures,[3] or at high temperatures.[4] The Lewis acid promoted reaction of allyltrialkylstannanes is the most commonly used reaction conditions.[5] A little is known about the allylic stannane−aldehyde condensa-

tion reactions *catalyzed by* Lewis acids[6] or *by* transition metal complexes.[7] In this paper we report that the reaction of allylstannanes **1** with aldehydes **2** in THF is catalyzed by Pd(II) or Pt(II) complexes (eq 1).[8a] Further studies reveal that palladium- and platinum-catalyzed allylation can be applied to imines **4**, which affords the corresponding homoallylic amines **5** in high yields (eq 2).[8b] Moreover, we have found that imines are chemoselectively allylated in the presence of aldehydes by using π-allylpalladium chloride dimer catalyst. This finding was rather surprising to us, because it is widely accepted by organometallic and organic chemists that an aldehyde is more reactive toward carbanionic organometallics, such as allyl Grignard and allyllithium reagents, than the corresponding imine (eqs 3 and 4). Higher reactivity of aldehydes is also the case

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[†] Kyushu University.
[‡] Tohoku University.
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(4) (a) Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1972,** *35,* C20. (b) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* **1989,** *45,* 1007. (c) Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989,** 1521. (d) Jephcoto, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989,** 1529.
(5) Many of these reactions have been referred to as "Lewis acid catalyzed". However, this is not accurate. In general, an equivalent (or excess) amount of a Lewis acid has been used.

(6) Lewis acid catalyzed allylation of aldehydes with allyltrimethylsilane has been reported. (a) Davis, A. P.; Jaspars, M. *J. Chem. Soc., Chem. Commun.* **1990,** 1176. (b) Davis, A. P.; Jaspars, M. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 470. (c) Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993,** *115,* 11490. Brønsted acid catalyzed allylation of aldehydes with allyltributylstannane. (d) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* **1993,** *34,* 1313. Lewis acid catalyzed asymmetric allylation of aldehydes with allylstannanes. (e) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993,** *115,* 7001. (f) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993,** *115,* 8467. (g) Keck, G. E.; Krishnamurthy, D.; Grier, M. C. *J. Org. Chem.* **1993,** *58,* 6543.
(7) (a) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983,** *48,* 4634. (b) Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* **1990,** *112,* 408. They suggested that Pd(II) complexes might act as a Lewis acid or nucleophilic π-allylpalladium complexes might be involved. (c) Masuyama, Y. In *Advances in Metal−Organic Chemistry*; JAI Press: London, 1994; Vol. 3, p 255. Masuyama, Y.; Takahara, J. P.; Kurusu, Y. *J. Am. Chem. Soc.* **1988,** *110,* 4473. Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992,** *114,* 2577. π-Allylpalladium complexes are converted in situ to allyltrichlorostannanes in the presence of $SnCl_2$.
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Table 1. Transition Metal Catalyzed Allylation of Aldehydes (and a Ketone) with Allylstannanes[a]

entry	allylstannane **1**	aldehyde **2**	catalyst (10 mol %)	reaction temp/time	product	yield (%)
1	**1a**	**2a**	PtCl$_2$(PPh$_3$)$_2$	r.t./4 days	**3a**	90
2	**1a**	**2a**	PdCl$_2$(PPh$_3$)$_2$	r.t./4 days	**3a**	64
3	**1a**	**2a**	PdCl$_2$(dppf)	r.t./4 days	**3a**	59
4	**1a**	**2a**	Pd(PPh$_3$)$_4$	r.t./4 days	**3a**	40
5	**1a**	**2b**	PtCl$_2$(PPh$_3$)$_2$	reflux/11 h	**3b**	83
6	**1a**	**2c**	PtCl$_2$(PPh$_3$)$_2$	reflux/8 h	**3c**	94
7	**1a**	**2d**	PtCl$_2$(PPh$_3$)$_2$	reflux/8 h	**3d**	70
8	**1a**	**2e**	PtCl$_2$(PPh$_3$)$_2$	reflux/10 h	**3e**	99
9	**1a**	**2f**	PtCl$_2$(PPh$_3$)$_2$	50 °C/1 day	**3f**	40
10	**1a**	**2g**	PtCl$_2$(PPh$_3$)$_2$	reflux/8 h	**3g**	58
11	**1a**	**2h**	PtCl$_2$(PPh$_3$)$_2$	reflux/1 day	**3h**	81
12	**1a**	**2i**	PtCl$_2$(PPh$_3$)$_2$	reflux/12 h	**3i**	43
13	**1b**[b]	**2a**	PtCl$_2$(PPh$_3$)$_2$	r.t./4 day	**3j**	37
14	**1b**[b]	**2b**	PtCl$_2$(PPh$_3$)$_2$	reflux/1 h	**3k**	48
15	**1b**[b]	**2d**	PtCl$_2$(PPh$_3$)$_2$	reflux/8 day	**3l**	65
16	**1c**	**2a**	PtCl$_2$(PPh$_3$)$_2$	50 °C/1 day	**3m**	~100
17	**1c**	**2b**	PtCl$_2$(PPh$_3$)$_2$	reflux/10 h	**3n**	63
18	**1c**	**2d**	PtCl$_2$(PPh$_3$)$_2$	reflux/14 h	**3o**	71
19	**1c**	**2e**	PtCl$_2$(PPh$_3$)$_2$	reflux/14 h	**3p**	67
20	**1c**	**2f**	PtCl$_2$(PPh$_3$)$_2$	reflux/16 h	**3q**	49

[a] The reaction was monitored by TLC and quenched, after an appropriate period, by filtrating the reaction mixture through a short silica-gel column chromatograph. In the case of the reaction which gave **3** in low yields, the starting aldehyde was recovered. [b] (Z)-Crotylstannane was used. [c] r.t. = room temperature.
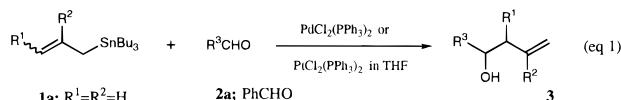

1a; R^1=R^2=H
b; R^1=CH$_3$, R^2=H
c; R^1=H, R^2=CH$_3$
d; R^1=H, R^2=OCH$_3$

2a; PhCHO
b; p-BrC$_6$H$_4$CHO
c; o-BrC$_6$H$_4$CHO
d; p-(NO$_2$)C$_6$H$_4$CHO
e; c-C$_6$H$_{11}$CHO
f; n-C$_5$H$_{11}$CHO
g; PhCH$_2$CH$_2$CHO
h; trans-PhCH=CHCHO
i; cyclohexanone
j; p-MeOC$_6$H$_4$CHO
k; p-MeC$_6$H$_4$CHO
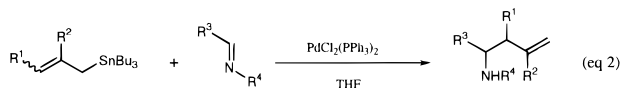
4a; R^3=p-(NO$_2$)C$_6$H$_4$, R^4=p-(CO$_2$Me)C$_6$H$_4$
b; R^3=p-(NO$_2$)C$_6$H$_4$, R^4=Ph
c; R^3=p-(NO$_2$)C$_6$H$_4$, R^4=Bn
d; R^3=Ph, R^4=p-(CO$_2$Me)C$_6$H$_4$
e; R^3=p-(OMe)C$_6$H$_4$, R^4=p-(CO$_2$Me)C$_6$H$_4$
f; R^3=PhCH=CH, R^4=p-(CO$_2$Me)C$_6$H$_4$
g; R^3=i-Pr, R^4=p-(CO$_2$Me)C$_6$H$_4$
h; R^3=c-Hex, R^4=p-(OMe)C$_6$H$_4$
i; R^3=p-MeC$_6$H$_4$, R^4=p-(CO$_2$Me)C$_6$H$_4$
j; R^3=c-Hex, R^4=p-(CO$_2$Me)C$_6$H$_4$

in the Lewis acid mediated allylation with allylstannanes and allylsilanes.[1]
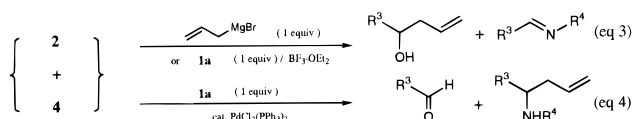
Results and Discussion

Allylation of Aldehydes with Allylstannanes. The reaction of allylstannanes **1** with aldehydes **2** in THF was catalyzed by Pd(II) or Pt(II) complexes (10 mol %) either at room temperature or at reflux, giving the corresponding homoallylic alcohols **3** in high to good yields. The results are summarized in Table 1. The addition of allyltributylstannane **1a** to benzaldehyde proceeded very smoothly even at room temperature in the presence of PtCl$_2$(PPh$_3$)$_2$ (10 mol %) (entry 1). The use of PdCl$_2$(PPh$_3$)$_2$ or PdCl$_2$(dppf) gave lower chemical yields (entries

2 and 3). Recently, we have found that the addition of 1-carboranyltributylstannane to aldehydes is catalyzed by a palladium(0) complex such as Pd$_2$(dba)$_3$·CHCl$_3$/dppe to afford, after hydrolysis, the corresponding adduct, 1-carboranyl-carbinols, in good to high yields.[9] Accordingly, we examined Pd(0) catalysts such as Pd$_2$(dba)$_3$·CHCl$_3$/dppe and Pd(PPh$_3$)$_4$ (entry 4), but the allylation product was obtained in lower yield. The use of other transition metal complexes, such as Rh(H)-(CO)(PPh$_3$)$_3$, RuCl$_2$(PPh$_3$)$_3$, and NiCl$_2$(PPh$_3$)$_2$, afforded the adduct in 10−30% yields. Therefore the Pd(II) complex is a more suitable catalyst for the allylation of aldehydes in comparison with the Pd(0) complexes, and the Pt(II) catalyst is the best one among the catalysts examined. Aromatic, α,β-unsaturated, and aliphatic aldehydes underwent the allylation reaction in the presence of PtCl$_2$(PPh$_3$)$_2$ catalyst (10 mol %) in THF under reflux to give the corresponding allylation products in high to good yields (entries 5−11). Even cyclohexanone reacted with allyltributylstannane under similar conditions to afford the adduct (43%) along with recovered cyclohexanone (entry 12). The reactions of (Z)-crotyltributylstannane **1b** were slower than those of **1a** (entries 13−15), presumably due to the γ-methyl substituent of **1b**. The syn/anti diastereomer ratios of the adducts were nearly 1:1, and the allylation products at the α-position were not detected.[10] In general, the reaction with methallyltributylstannane **1c** proceeded smoothly in the presence of PtCl$_2$(PPh$_3$)$_2$ catalyst in THF at reflux (entries 16−20). Needless to say, the allylation did not take place *in the absence of PtCl$_2$(PPh$_3$)$_2$* in THF at reflux.

Reaction Mechanism. In order to clarify the mechanism of the allylation reaction catalyzed by PtCl$_2$(PPh$_3$)$_2$ and PdCl$_2$-(PPh$_3$)$_2$, we investigated an intermediate produced from a stoichiometric reaction between allylstannane **1a** and PdCl$_2$-(PPh$_3$)$_2$ in THF-d_8 (Scheme 1). A 1:1 mixture of **1a** and PdCl$_2$-(PPh$_3$)$_2$ was refluxed for 1 h under Ar. The ^{1}H NMR spectra of this mixture at 25 °C (Figure 1A) indicated formation of the π-allylpalladium chloride complex **6**, PPh$_3$, and tributylstannyl chloride: a sharp quintet (δ 5.61, 1 H, $J = 10$ Hz) and a broad

(9) Nakamura, H.; Sadayori, N.; Sekido, M.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun*. **1994**, 2581.

(10) The diastereoisomer ratio and the γ/α adduct ratio were determined by comparison with the ^{1}H NMR spectra of authentic samples; see ref 1c and the following: Yamamoto, Y.; Yatagai, H.; Ichihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239.
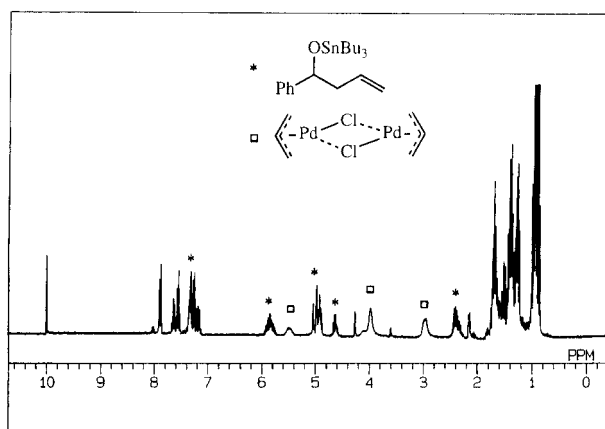
Figure 1. (A) The ^{1}H-NMR spectra of a 1:1 mixture of **1a** and PdCl$_2$-(PPh$_3$)$_2$ at 25 °C in THF-d_8. There is a rapid equilibrium between σ- and π-allylpalladium complexes (*). (B) The ^{1}H-NMR spectra of the π-allylpalladium chloride complex **6** (*) in CDCl$_3$ which was isolated from the mixture of (A) by column chromatography on silica gel. Ethyl acetate (▲), used as an eluant, could not be removed completely.

Figure 2. Temperature-dependent ^{1}H-NMR spectra of bis-π-allylpalladium complex **7** at (a) 25, (b) 0, (c), −20, (d), −40, and (e) −60 °C, respectively, prepared from π-allylpalladium chloride dimer (1 equiv) and **1a** (2 equiv) in THF-d_8. At 25 °C, there is a rapid equilibrium between the syn and anti bis-π-allylpalladium complex. At −20 °C, both syn and anti isomers appeared, and the spectra of these isomers (○ and ●) were separated clearly at −60 °C. At −60 °C, the signals of π-allylpalladium chloride dimer appeared around 3.2, 4.3, and 5.6 ppm (□). It is indicated that the exchange of allyl ligand between unreacted π-allylpalladium chloride dimer **11** and bis-π-allylpalladium **7** could occur rapidly at higher temperatures and that the exchange became slow at −60 °C.

doublet (δ 3.51, 4 H, $J = 7$ Hz) were in good agreement with the signals previously observed by Kurosawa for an equilibrium mixture between π- and σ-allyl (cis and trans) palladium species.[11] The π-allylpalladium chloride complex **6** was isolated from a mixture of **6**, PPh$_3$, and Bu$_3$SnCl through a short silica gel column chromatography (Figure 1B). Very curiously, **6** itself or a mixture of **6**, PPh$_3$, and Bu$_3$SnCl did not react with benzaldehyde at all. However, if allylstannane **1a** was added to a mixture of benzaldehyde and **6** (or **6** including PPh$_3$ and Bu$_3$SnCl), the allylation took place immediately. We thought that bis-π-allylpalladium complex **7** would be a key intermediate for the allylation. Triphenylphosphine free bis-π-allylpalladium complex **7** was prepared from the reaction of π-allylpalladium chloride dimer (1 equiv) and allylstannane **1a** (2 equiv) (Figure 2). The ^{1}H NMR spectra of **7** was in good agreement with the reported spectra.[12] The addition of benzaldehyde to **7** (including Bu$_3$SnCl) gave the corresponding homoallyl alcohol after hydrolysis. This process was followed by ^{1}H NMR (Figure 3). When benzaldehyde was added to **7** in THF-d_8 at room temperature, the signals due to **7** disappeared and those ascribed to ((1-phenyl-3-butenyl)oxy)tributylstannane and π-allylpalla-

dium chloride dimer appeared. Perhaps **7** would react with benzaldehyde to give a π-allyl(alkoxy)palladium complex which would afford the (butenyloxy)stannane via redistribution with tributylstannyl chloride (eq 5).

The catalytic cycle proceeds most probably as shown in Scheme 1.[13] The cycle may start from **8** instead of **7**, since triphenylphosphine is involved in the reaction system. The

(11) Numata, S.; Okawara, R.; Kurosawa, H. *Inorg. Chem.* **1977**, *16*, 1737. See also: Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839.

(12) (a) Becconsall, J. K.; Job, B. E.; O'Brien, S. *J. Chem. Soc. A* **1967**, 423. (b) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425. Henc, B.; Jolly, P. W.; Saltz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449.

Figure 3. ^{1}H-NMR spectra of the mixture, obtained from **2a** and **7** (which was prepared from **1a** and π-allylpalladium chloride dimer **11** as mentioned in Figure 2). The spectrum was measured in THF-d_8 at room temperature after 1 h of mixing. The signals (*) around 2.4, 4.6, 5.0, 5.8, and 7.3 ppm are due to ((1-phenyl-3-butenyl)oxy)-tributylstannane, and those (□) around 3.0, 4.0, and 5.5 ppm are ascribed to π-allylpalladium chloride dimer. A small excess of benzaldehyde was added, and therefore the signals due to benzaldehyde can been seen in the figure.

Scheme 1
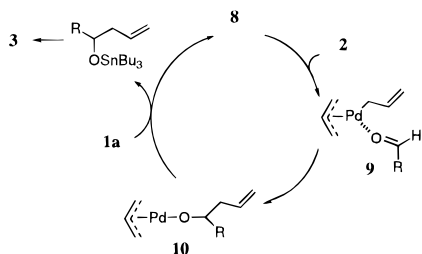
π-allyl–σ-allyl palladium complex **9** may produce the homo-allyloxy palladium **10**, which would react with allylstannane **1a** to give **8** and the homoallyloxystannane derivative. It is clear that the only species which reacts with an aldehyde without any additive is **7**; no reaction takes place between **6** and an aldehyde (even in the presence of Bu$_3$SnCl);[14] π-allylpalladium chloride dimer does not react with aldehydes in the presence of additives.

Reactivity of Unsymmetrical Bis-π-allylpalladium Complexes. Since it became clear that symmetrical bis-π-allyl-palladium complex **7** is a key intermediate and exhibits nucleophilic reactivity in contrast with π-allylpalladium chloride complex **11** which exhibits electrophilic reactivity, we next investigated the reactivity order of π-allyl ligands of unsym-metrical π-allyl complexes. The stoichiometric reaction between 1 equiv of π-allylpalladium chloride dimer **11** and 2 equiv of methallyltributylstannane **1c** gave π-allyl-π-methallylpalladium complex **12a** in quantitative yield. Although ^{1}H-NMR inves-tigation of the reaction mixture clearly indicated disappearance of **1c** and formation of the unsymmetrical complex **12a**, it was not clear whether **12a** consisted of a single complex or of an equilibrium mixture of three complexes (bis-π-allylpalladium **7**, **12a**, and bis-π-methallylpalladium **13**). Treatment of this complex **12a** (or the mixture of three complexes) with 2 equiv of benzaldehyde afforded a 31:69 mixture of the allylation **3a**

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(13) Tsuji et al. reported a bis-π-allylpalladium intermediate, generated by palladium-catalyzed dimerization of butadiene, reacted with aldehydes: Ohno, K.; Mitsuya, T.; Tsuji, J. *Tetrahedron* **1972**, *28*, 3705 and references cited therein.

(14) A possibility that the reaction of **5** with an aldehyde may be assisted by the presence of Bu$_3$SnCl cannot be completely excluded.

**Table 2.** Reactivity of Unsymmetrical Bis-π-allylpalladium Complexes

entry	allylstannane **1**	conversion yield (%)	yield of **3** (%)	adducts	ratio
1	**1c**	90	64	**3a/3m**	31:69
2	**1d**	69	49	**3a/3r**	10:90
3	**1b**	68	46	**3a/3j**	68:32

Table 3. Palladium-Catalyzed Allylation of Allylic Stannanes with Imines[a]

entry	allylstannane **1**	imines **4**	reaction time	product **5**	yield (%)
1	**1a**	**4a**	1 day	**5a**	77
2	**1a**	**4b**	14 h	**5b**	91
3	**1a**	**4c**	1 day	**5c**	98
4	**1a**	**4d**	2 days	**5d**	98
5	**1a**	**4e**	2 days	**5e**	82
6	**1a**	**4f**	20 h	**5f**	90
7	**1a**	**4g**	14 h	**5g**	81
8	**1a**	**4h**	2 days	**5h**	72
9	**1b**[b]	**4a**	1 day	**5i**	96 (6/4)[c]
10	**1b**[b]	**4b**	18 h	**5j**	76 (1/1)
11	**1c**	**4g**	20 h	**5k**	80

[a] A mixture of **1** (0.6 mmol), **4** (0.5 mmol), PdCl$_2$(PPh$_3$)$_2$ (0.05 mmol), and THF (5 mL) was stirred at 50 °C for the indicated period. [b] Crotylstannane, whose *E/Z* ratio was 76/24, was used. [c] Syn/anti ratio was shown in parentheses. Crotylstannane, whose *E/Z* ratio was 60/40, also produced the adduct in 94% yield with the same syn/anti ratio.

and methallylation product **3m**. The reaction of 1 equiv of π-allylpalladium chloride dimer, 2 equiv of methoxyallyltri-butylstannane **1d**, followed by addition of 2 equiv of benzal-dehyde gave a 10:90 mixture of **3a** and **3r**. It is clear that the methoxyallyl ligand of the palladium complex (or complexes) is more reactive toward benzaldehyde than allyl ligand, and therefore, an electron-donating substituent at the β-position of the allyl ligand enhances its transfer ability to electrophiles. The similar reaction as above using crotyltributylstannane gave a 68:32 mixture of **3a** and **3j**. These results are summarized in Table 2. It is apparent that the crotyl ligand of the π-allyl-π-crotylpalladium complex (or complexes) is less reactive than the π-allyl ligand. Very interestingly, only branched alcohol was obtained from the crotyl complex (see also Table 1, entires 13–15).
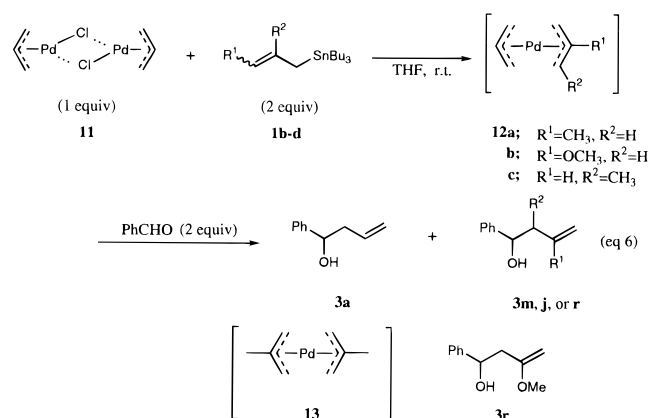
Allylation of Imines with Allylstannanes. We next inves-tigated the palladium-catalyzed allylation of imines **4** and the results are summarized in Table 3. The aromatic imines derived from *p*-nitrobenzladehyde, **4a**, **4b**, and **4c**, reacted very smoothly with allyltributylstannane **1a** to give the corresponding homo-allylamines, **5a**, **5b**, and **5c**, respectively, in high yields (entries

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(15) Although π-allyl–π-methallyl complex is shown in eq 3, interven-tion of bis-π-allyl and bis-π-methallyl complexes cannot be ruled out completely.
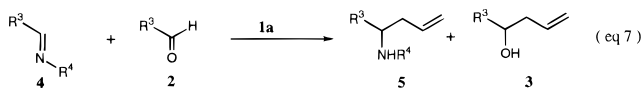
Table 4. Chemoselective Allylation to Imines in the Presence of Aldehydes

entry	imine 4	aldehyde 2	condition[a]	combined yield (%)	adducts 5/3	ratio of 5/3[b]
1	4a	2d	A	90	5a/3d	90:10
2			B	95		10:90
3	4b	2d	A	84	5b/3d	83:17
4			B	91		19:81
5	4e	2j	A	99	5e/3s	97:3
6			B	96		1:>99
7	4i	2k	A	86	5k/3t	94:6
8			B	99		5:95
9	4f	2h	A	99	5f/3h	>99:1
10			B	98		1:>99
11	4h	2e	A	80	5h/3e	91:9
12			C	60		1:>99
13	4j	2e	A	99	5l/3e	>99:1
14			C	60		1:>99

[a] Method A: A mixture of **4** (0.2 mmol), **2** (0.2 mmol), and allyltributylstannane (0.2 mmol) was dissolved in 5 mL of THF. (η^3-C$_3$H$_5$PdCl)$_2$ (0.02 mmol, 10 mol %) was added to this mixture at room temperature and the mixture was stirred until the solution turned to black suspension. Methods B and C: A mixture of **4** (0.2 mmol), **2** (0.2 mmol), and allyltributylstannane (0.2 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$. To this mixture was added 0.8 mmol of BF$_3$·OEt$_2$ (method B) or SnCl$_4$ (method C) at −78 °C and the mixture was stirred for 1 h. [b] Ratios were determined by ^{1}H NMR.

1−3). The aromatic imines **4d** and **4e**, derived from benzaldehyde and *p*-anisaldehyde, also produced the corresponding homoallylamines **5d** and **5e**, respectively, in high yields (entries 4 and 5). The use of methyl *p*-aminobenzoate as the imine component gave, in general, better results than the use of aniline itself (however see entry 2 as an exception). The reactions of the imine **4f** derived from cinnamaldehyde and of aliphatic imine **4g** derived from isobutyraldehyde proceeded also very smoothly (entries 6 and 7). The use of *p*-methoxyaniline, instead of methyl *p*-aminobenzoate, as an imine component was examined in the case of aliphatic aldehydes such as cyclohexylcarboxaldehyde and the allylation product **5h** was obtained in good yield (entry 8). Not only allyltributylstannane **1a**, but also methallyl-(**1b**) and crotyl- (**1c**) tributylstannane could be utilized and the corresponding allylation products (**5i−k**) were obtained in good to high yields (entries 9−11). Here again, only branched homoallylamines **5i** and **5j** were obtained (entries 9 and 10). We had a very interesting observation on the reaction of crotylstannane: the reaction to imines **4a** and **4b** was faster than that to the corresponding aldehydes (entries 9 and 10).[8,16] Accordingly, we next examined the palladium-catalyzed allylation in the presence of both aldehydes and imines.

Chemoselective Allylation of Imines in the Presence of Aldehydes. The results of chemoselective allylation are shown in Table 4 (see also eq 7). Generally speaking, the reactivity

$$R^3 \underset{R^4}{\overset{N}{\diagdown}} \quad + \quad R^3 \overset{O}{\diagdown} H \quad \xrightarrow{1a} \quad R^3 \underset{NHR^4}{\diagdown} + \quad R^3 \underset{OH}{\diagdown} \qquad (eq\ 7)$$

4   2   5   3

of allylstannanes to aldehydes is higher than that to imines under the Lewis acid promoted conditions (methods B and C).[1] However, chemoselectivity of the allylation under the palladium-catalyzed conditions was completely reversed; especially the highest selectivities were obtained using π-allylpalladium

Scheme 2

chloride dimer as a catalyst (method A).[17] Reasonably high chemoselectivity was obtained in the allylation of *p*-nitrobenzaldehyde **2d** and its imine partner **4a**, derived from methyl *p*-aminobenzoate (the Ciufolini imine[18]) (entries 1 and 2). The use of imine derived from aniline decreased the chemoselectivity (entries 3 and 4). Very high chemoselectivities were produced in the allylation of other aromatic, aliphatic, and cinnamic aldehydes and their imine partners (entries 5−14). The use of the Ciufolini imine was essential to obtain such high chemoselectivities. We also examined the allylation with allylmagnesium bromide in the presence of *p*-nitrobenzaldehyde and **4b** (1:1) to elucidate chemoselectivity in a carbanionic allylation; the ratio of **5b:3d** was 1:>99 (cf. entries 3 and 4).

This unprecedented chemoselectivity can be explained by the difference of the coordination ability between N and O atoms to the transition metal (Scheme 2). In general, the N atom can coordinate to a transition metal more strongly than the O atom. *Catalytic amounts of the bis-π-allylpalladium* intermediate **7** would react with imines more predominantly than with aldehydes to give **14**, which would afford **5** via **15**. The key intermediate **7** is regenerated by the reaction of **15** and **1a**. On the other hand, *excess amounts of Lewis acid* (>2 equiv) can coordinate to both aldehyde and imines, activating both electrophiles in the same manner; the resulting aldehyde−Lewis acid complex is more electrophilic than the imine complex. The use of 1 equiv of BF$_3$·OEt$_2$ in the reaction between **4a** and **2d** gave an ca. 50:50 ratio of **5a** to **3d** and the use of catalytic (10 mol %) BF$_3$·OEt$_2$ did not give the allylation products at all.[19] The regeneration of **7** via the catalytic process in addition to the strong coordinative preference of the N atom becomes a key to this unusual chemoselectivity; the Lewis acid promoted reaction never proceeds via a catalytic process.

Conclusion

The catalytic reaction enables the allylation to be carried out under essentially neutral conditions either at room temperature or at ∼65 °C. The present findings clarify that bis-π-allylpalladium complexes exhibit nucleophilic reactivity although it is widely accepted that mono-(π-allyl)PdX-type complexes, where X is an electron-withdrawing group such as Cl, OAc, etc., exhibit electrophilic reactivity.

Further, the reactivities of allylstannanes to imines under the catalytic conditions were higher than those to aldehydes. Both

(16) The reactivity of crotylstannane **1b** was typical. The reaction of **1b** with benzaldehyde gave the adduct in only 37% yield after 4 days at room temperature, whereas the reaction with the corresponding imine afforded the allylated amine in essentially quantitative yield.

(17) PdCl$_2$(PPh$_3$)$_2$, which was used in the allylation shown in Table 1, also worked in the chemoselective allylation, but (η^3-C$_3$H$_5$PdCl)$_2$ gave better results.

(18) Ciuforini, M. A.; Spencer, G. O. *J. Org. Chem.* **1989**, *54*, 4739. For transition metal catalyzed addition of pronucleophiles to the imines, see: Yamamoto, Y.; Kubota, Y.; Honda, Y.; Fukui, H.; Asao, N.; Nemoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 3161.

(19) Normally, more than 1 equiv of Lewis acid is needed for the allylation of aldehydes or imines using allylstannanes and silanes.[1] Quite recently, catalytic allylation of imines promoted by lanthanide triflates has been reported: Bellucci, C.; Cozzi, P.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7289. However, the chemical yields (30−70%) were generally low in the catalytic system.

6646   *J. Am. Chem. Soc., Vol. 118, No. 28, 1996*

Nakamura et al.

the palladium coordination characteristic and catalytic cycle are presumably the origin of the present unusual chemoselectivity. Not only the allylation of aldehydes and imines under neutral and catalytic conditions but also the unprecedented chemoselective allylation of imines in the presence of aldehydes provide another synthetically useful methodology for allylation in addition to the exiting excellent methods.[1]

Experimental Section

General. Spectral data were obtained by use of the following instruments: JEOL GSX-270 (NMR), SHIMADZU FTIR-8200A (FT-IR), and JEOL JMS-HX-110 (MS).

Allylation of Aldehydes. A typical procedure for the PtCl$_2$(PPh$_3$)$_2$-catalyzed allylation is as follows. A mixture of 0.2 mmol of aldehyde **2**, 0.22 mmol of allyltributylstannane **1**, and 0.02 mmol of PtCl$_2$(PPh$_3$)$_2$ (10 mol %) is dissolved in 1 mL of dried THF under Ar atmosphere. The mixture was stirred either at room temperature or at reflux for an appropriate period of time. The reaction was monitored by TLC. The reaction was quenched by filtrating the mixture through a short silica gel column chromatography. The NMR examination the reaction mixture prior to column chromatography indicated the formation of the corresponding stannyloxy derivative. Therefore, the hydrolysis of the Sn–O bond would take place during silica gel column chromatography. The structures of the resulting homoallyl alcohols were determined unambiguously by comparison with authentic samples, prepared by the literature procedure.[20]

Allylation of Imines. A typical procedure for the PdCl$_2$(PPh$_3$)$_2$-catalyzed allylation is as follows. A mixture of 0.5 mmol of imine **4**, 0.6 mmol of allyltributylstannane **1**, and 0.05 mmol of PdCl$_2$(PPh$_3$)$_2$ (10 mol %) is dissolved in 1 mL of dried THF under Ar atmosphere. The mixture was stirred at 50 °C for an appropriate period of time. The reaction was monitored by TLC. The reaction was quenched by filtrating the mixture through a short florisil column chromatography. The resulting homoallylamine **5** was purified by silica gel column chromatography.

Chemoselective Allylation of Imines in the Presence of Aldehydes. Method A. A mixture of **4** (0.2 mmol), **2** (0.2 mmol), and allyltributylstannane (0.2 mmol) was dissolved in 5 mL of THF. (η^3-C$_3$H$_5$PdCl)$_2$ (0.02 mmol, 10 mol %) was added to this mixture at room temperature and the mixture was stirred until the solution turned to a black suspension. The reaction was quenched by filtrating the mixture through a short florisil column chromatography. Ratios of **4** to **2** were determined by ^{1}H-NMR.

Methods B and C. A mixture of **4** (0.2 mmol), **2** (0.2 mmol), and allyltributylstannane (0.2 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$. To this mixture was added 0.8 mmol of BF$_3$·OEt$_2$ (method B) or SnCl$_4$ (method C) at −78 °C and the mixture was stirred for 1 h. The reaction was quenched by saturated NaHCO$_3$ aqueous solution. The mixture was extracted with ether, dried with MgSO$_4$, and condensed in vacuo. Ratios of **4** to **2** were determined by ^{1}H NMR.

N-(4-(Methoxycarbonyl)phenyl)-1-(4-nitrophenyl)buten-3-ylamine (5a). Yellow solid: IR (KBr) 3369, 1703, 1604, 1519, 1344, 1275, 1174 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 5.72 (m, 1H), 5.24 (bd, *J* = 8.0 Hz, 2H), 4.60 (bs, 2H), 3.82 (s, 3H), 2.64 (m, 1H), 2.57 (m, 1H). ^{13}C NMR (CDCl$_3$) δ 166.99, 150.26, 150.20, 147.26, 132.87, 131.37, 127.12, 124.03, 119.68, 119.36, 112.42, 56.27, 51.52, 42.47. HRMS (EI) Calcd for C$_{18}$H$_{18}$N$_2$O$_4$: *m/z* 326.1267. Found: *m/z* 326.1268.

N-Phenyl-1-(4-nitrophenyl)buten-3-ylamine (5b). Liquid: IR (neat) 3600−3200, 3078, 3053, 1639, 1602, 1520, 1430, 1344, 1317, 1288, 1269 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 8.19 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.55 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.09 (ddt, *J* = 8.5 Hz, 2H), 6.68 (ddt, *J* = 7.5, 7.5, 2.0 Hz, 1H), 6.43 (ddt, *J* = 8.5, 8.5, 2.0 Hz, 2H), 5.74

(20) **3a**, **3b**, **3h**, and **3k**: Chen, C.; Shen, Y.; Huang, Y. *Tetrahedron Lett.* **1988**, *29*, 1395. **3c**: see ref 2a. **3d**, **3l**, and **3q**: Nishigaichi, Y.; Nakao, N.; Takuwa, A. *J. Chem. Soc., Perkin Trans. 1* **1993**, *11*, 1203. **3e**, **3j**, **3m**, **3n**, **3o**, and **3p**: Boldrini, G. P.; Lodi, L.; Tagliavini, E.; Tarasco, C.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1987**, *52*, 5447. **3f**, **3i**, and **3q**: Shono, T.; Ishifune, M.; Kashimura, S. *Chem. Lett.* **1990**, 449. **3g**: see ref 2b.

(m, 1H), 5.21 (m, 2H), 4.47 (dd, 8.0, 5.0 Hz, 1H), 4.21 (bs, 1H), 2.69−2.39 (m, 2H). HRMS (EI) Calcd for C$_{16}$H$_{16}$N$_2$O$_2$: *m/z* 268.1212. Found: *m/z* 268.1220.

N-Benzyl-1-(4-nitrophenyl)buten-3-ylamine (5c). Liquid: IR (neat) 3600−3200, 3076, 3028, 2978, 2840, 1640, 1519, 1434, 1346, 1317, 1109 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 8.21 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.55 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.26 (m, 5H), 5.68 (m, 1H), 5.08 (m, 2H), 3.82 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 1H), 3.51 (d, *J* = 13.5 Hz, 1H), 2.69−2.39 (m, 2H). ^{13}C NMR (CDCl$_3$) δ 151.70, 139.81, 134.16, 128.46, 128.37, 128.14, 128.00, 127.12, 123.71, 118.58, 61.13, 51.54, 42.82.

N-(4-(Methoxycarbonyl)phenyl)-1-phenylbuten-3-ylamine (5d). Liquid: IR (neat) 3381, 1686, 1654, 1600, 1281, 1172, 836 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.76 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.20−7.34 (m, 5H), 6.45 (dt, *J* = 8.5 Hz, 2H), 5.75 (ddd, *J* = 16.5, 10, 8.0 Hz, 1H), 5.25−5.13 (m, 2H), 4.57 (bd, *J* = 5.0 Hz, 1H), 4.48 (m, 2H), 3.8 (s, 3H), 2.57 (m, 1H). ^{13}C NMR (CDCl$_3$) δ 167.19, 150.92, 142.37, 134.02, 131.31, 128.66, 127.22, 126.13, 118.64, 118.55, 112.33, 56.55, 51.43, 42.88. HRMS (EI) Calcd for C$_{18}$H$_{19}$NO$_2$: *m/z* 281.1416. Found: *m/z* 281.1416.

N-(4-(Methoxycarbonyl)phenyl)-1-(4-methoxyphenyl)buten-3-ylamine (5e). White solid: IR (KBr) 3377, 1680, 1654, 1602, 1534, 1510, 1437, 1348, 1294, 1175, 1032, 833 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 8.5 Hz, 2H), 5.74 (m, 1H), 5.18 (m, 2H), 4.53 (bd, *J* = 5.0 Hz, 1H), 4.43 (dt, *J* = 7.0, 5.0 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.55 (m, 2H). ^{13}C NMR (CDCl$_3$) δ 167.1, 158.75, 150.98, 134.33, 134.13, 131.31, 127.22, 118.55, 114.09, 112.36, 56.01, 55.23, 51.43, 42.96. Anal. Calcd for C$_{19}$H$_{21}$NO$_3$: C, 72.3; H, 6.80; N, 4.50. Found: C, 72.6; H, 6.91; N, 4.51. HRMS (EI) Calcd for C$_{19}$H$_{21}$NO$_3$: *m/z* 311.1522. Found: *m/z* 311.1535.

N-(4-(Methoxycarbonyl)phenyl)-1-phenyl-1,5-hexadien-3-ylamine (5f). Liquid: IR (neat) 3367, 3026, 2947, 1700, 1604, 1521, 1434, 1338, 1276, 1174, 1109, 968 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.84 (d, *J* = 9.0 Hz, 2H), 7.28 (m, 5H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 15.0 Hz, 1H), 6.17 (dd, *J* = 15.0, 5.0 Hz, 1H), 5.84 (m, 1H), 5.20 (m, 2H), 4.28 (d, *J* = 6.0 Hz, 1H), 4.28 (d, *J* = 6.0 Hz, 1H), 4.15 (m, 1H), 3.83 (s, 3H), 2.51 (m, 2H). ^{13}C NMR (CDCl$_3$) δ 167.25, 151.12, 136.55, 133.82, 131.45, 130.76, 130.13, 128.55, 127.60, 126.39, 118.73, 112.25, 54.12, 51.49, 40.26. HRMS (EI) Calcd for C$_{20}$H$_{21}$NO$_2$: *m/z* 307.1572. Found: *m/z* 307.1573.

N-(4-(Methoxycarbonyl)phenyl)-2-methyl-5-hexen-3-ylamine (5g). Liquid: IR (neat) 3371, 3076, 2958, 1699, 1639, 1606, 1522, 1491, 1434, 1340, 1313, 1273, 1174, 1109 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.83 (dt, *J* = 9.0, 2.0 Hz, 2H), 6.53 (dt, *J* = 9.0, 2.0 Hz, 2H), 5.78 (m, 1H), 5.07 (bd, 5 Hz, 1H), 5.02 (bs, 1H), 3.84 (s, 3H), 3.35 (m, 1H), 2.14−2.42 (m, 2H), 1.90 (m, 1H), 0.96 (t, *J* = 6.0 Hz, 6H). Anal. Calcd for C$_{15}$H$_{21}$NO$_2$: C, 72.7; H, 8.56; N, 5.66. Found: C, 72.3; H, 8.59; N, 5.53.

N-(4-Methoxyphenyl)-1-cyclohexylbuten-3-ylamine (5h). Liquid: IR (neat) 3500, 2924, 2851, 1638, 1617, 1511, 1449, 1239, 1179, 1041, 912, 817 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.75 (dt, *J* = 9.0, 2.5 Hz, 2H), 6.53 (dt, *J* = 9.0, 2.5 Hz, 2H), 5.80 (m, 1H), 5.07 (bd, 5 Hz, 1H), 5.02 bs, 1H), 3.14 (dt, *J* = 7.0 5.5 Hz, 1H), 2.12−2.40 (m, 2H), 1.05−1.85 (m, 11H). ^{13}C NMR (CDCl$_3$) δ 135.80, 116.94, 114.95, 114.46, 90.07, 58.57, 55.86, 41.26, 35.91, 29.46, 29.17, 26.64, 26.43. HRMS (EI) Calcd for C$_{17}$H$_{25}$NO: *m/z* 259.1936. Found: *m/z* 259.1936.

N-(4-(Methoxycarbonyl)phenyl)-2-methyl-1-(4-nitrophenyl)buten-3-ylamine (5i). Liquid: IR (neat) 3400, 2975, 1706, 1521, 1345, 1279, 1176, 1109 cm^{-1}. ^{1}H NMR (CDCl$_3$): major isomer δ 8.18 (dt, *J* = 11.5, 2.5 Hz, 2H), 7.76 (dt, *J* = 11.5, 2.5 Hz, 2H), 7.45 (dt, *J* = 11.5, 2.5 Hz, 2H), 6.40 (dt, *J* = 11.5, 2.5 Hz, 2H), 5.65 (m, 1H), 5.23 (m, 2H), 4.64 (bd, *J* = 7.0 Hz, 1H), 4.50 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 2.74 (m, 1H), 1.03 (d, *J* = 9.0 Hz, 3H); minor isomer δ 8.20 (dt, *J* = 11.5, 2.5 Hz, 2H), 7.75 (dt, *J* = 11.5, 2.5 Hz, 2H), 7.56 (dt, *J* = 11.5, 2.5 Hz, 2H), 6.39 (dt, *J* = 11.5, 2.5 Hz, 2H), 5.71 (m, 1H), 5.23 (m, 2H), 4.64 (bd, *J* = 7.0 Hz, 1H), 4.30 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.80 (s, 3H), 2.59 (m, 1H), 1.09 (d, *J* = 9.0 Hz, 3H). ^{13}C NMR (CDCl$_3$): major isomer δ 166.93, 150.20, 149.53, 138.63, 131.25, 128.12, 123.45, 118.99, 117.09, 112.25, 60.59, 51.37, 43.45, 30.72, 15.43; minor isomer δ 166.93, 150.40, 148.27, 138.54, 131.25, 127.88, 123.68, 118.99,

117.09, 112.19, 61.31, 51.37, 44.43, 30.72, 16.90. HRMS (EI) Calcd for $C_{19}H_{20}N_2O_4$: *m/z* 340.1423. Found: *m/z* 340.1420.

N-Phenyl-2-methyl-1-(4-nitrophenyl)buten-3-ylamine   (5j).
Liquid: IR (neat) 3411, 3053, 2970, 2929, 1706, 1600, 1530, 1506, 1429, 1344, 1197, 1109 cm^{-1}. ^{1}H NMR (CDCl$_3$): major isomer δ 8.18 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.54 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.07 (dt, *J* = 8.5, 2H), 6.66 (t, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 8.5 Hz, 2H), 5.70 (m, 1H), 5.19 (m, 2H), 4.43 (m, 1H), 4.19 (m, 1H), 2.71 (q, *J* = 7.0 Hz, 1H), 1.01 (d, *J* = 7.0 Hz, 3H); minor isomer δ 8.17 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.48 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.04 (dt, *J* = 8.5 Hz, 2H), 6.66 (t, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 8.5 Hz, 2H), 5.70 (m, 1H), 5.19 (m, 2H), 4.25 (m, 1H), 4.19 (m, 1H), 2.54 (q, *J* = 7.0 Hz, 1H), 1.05 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (CDCl$_3$): major isomer δ 157.31, 150.69, 146.77, 139.23, 129.30, 129.15, 128.26, 123.48, 117.92, 113.40, 61.13, 44.89, 15.09; minor isomer δ 157.3, 149.40, 146.49, 139.17, 129.38, 129.15, 128.09, 123.48, 117.20, 113.31, 62.00, 43.65, 17.13. ^{1}HRMS (EI) Calcd for $C_{17}H_{18}N_2O_2$: *m/z* 282.1368. Found: *m/z* 282.1373.

N-(4-(Methoxycarbonyl)phenyl)-2,5-dimethyl-5-hexen-3-ylamine (5k). Liquid: IR (neat) 3700−2800, 2605, 2361, 2340, 1645, 1433 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.82 (dt, *J* = 8.0, 2.0 Hz, 2H), 6.54 (dt, *J* = 8.0, 2.0 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 2H), 3.84 (s, 3H), 3.50 (m, 1H), 2.35−2.05 (m, 2H), 1.99 (m, 1H), 1.69 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ 152.16, 142.77, 131.60, 113.05, 11.50, 55.37, 51.43, 39.54, 30.93, 22.14, 18.26, 17.85. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.5; H, 8.87; N, 5.36. Found: C, 73.1; H, 8.80; N, 5.30. MS (EI) *m/z*. HRMS (EI) Calcd for $C_{16}H_{23}NO_2$: *m/z* 261.1729. Found: *m/z* 261.1733.

N-(4-(Methoxycarbonyl)phenyl)-1-cyclohexylbuten-3-ylamine (5l). Liquid: IR (neat) 3371, 3074, 2925, 2852, 1695, 1604, 1525, 1435, 1344, 1281, 1174, 1109 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 2H), 5.78 (m, 1H), 5.08 (bd, *J* = 5.5 Hz, 1H), 5.03 (bs, 1H), 3.97 (bd, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.35 (m, 1H), 2.43−2.15 (m, 2H), 1.86−1.60 (m, 5H), 1.50 (m, 1H), 1.32−0.94 (m, 5H). ^{13}C NMR (CDCl$_3$) δ 152.13, 134.94, 131.57, 117.55, 117.43, 111.59, 56.90, 51.37, 41.49, 35.99, 29.49, 28.94, 26.40, 26.23. HRMS (EI) Calcd for $C_{18}H_{25}NO_2$: *m/z* 287.1885. Found: *m/z* 287.1883.