Preparation of N-Diprotected Allylic Amines via Palladium(0)-Catalyzed Coupling Reactions

Robert O. Hutchins,* Jia Wei, and Samala J. Rao

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received November 15, 1993

Introduction

Considerable effort has been expended toward the development of methodologies for the synthesis of allylic amines because of their importance as synthetic intermediates and as functional groups in many natural and bioactive compounds.[1] Of various available methods, palladium(0)-catalyzed allylic amination reactions have been extensively investigated[2,3] in which nitrogen nucleophiles and π-allylpalladium complexes are employed. The π-allylpalladium complexes can be generated from a variety of allylic derivatives[3] with allylic acetates reportedly the best substrates and tetrakis(triphenylphosphine)palladium the catalyst of choice.[4] Although secondary amines are often excellent nucleophiles for palladium(0)-catalyzed allylic aminations, use of primary amines has found limited success, with diallylation often a problem.[3j,5] In order to circumvent this complication, several protected primary amine nucleophiles or amine precursors, such as 4,4'-dimethoxybenzhydrylamine (DMB-NH_2),[6] phthalimide and succinimide,[7] sodium *p*-toluenesulfonamide,[8] sodium azide,[9] and di-*tert*-butyl iminodicarbonate (DBIC),[10] have been introduced with various degrees of success.

Results and Discussion

As part of our continuous interest in palladium(0)-catalyzed allylic substitution reactions,[11] this report describes the utility of diethyl *N*-sodio-*N*-(*tert*-butoxycarbonyl)phosphoramide (**1**, Scheme 1) as a convenient aminating reagent for palladium(0)-catalyzed couplings with allylic acetates to afford primary allylic amines protected as the diethyl *N*-(*tert*-butoxycarbonyl)phosphoramide (DBCP) derivatives. Amidate **1** is a readily-prepared, nonhygroscopic solid introduced by Zwierzak[12] for Gabriel-type synthesis of amines. Since the nitrogen atom in **2** bears two different protecting groups, this reagent offers an advantage of selective deprotection to afford either a primary allylic amine hydrochloride **3** or a diethyl *N*-allyl-*N*-phosphoramidate (**4**),[12] which is in turn a useful precurser for the preparation of secondary amines (Scheme 1).[13]

The allylic amination process is straightforward and is presented in Scheme 2. Thus, equal molar quantities of an allylic acetate **5a–i** and **1** are refluxed in THF with a catalytic amount of $[(C_6H_5)_3P]_4Pd^0$. After consumption of the acetate (monitored by GC), the reaction products **7a–i** were isolated by preparative TLC, flash chromatography, or flash distillation. Results for a variety of structural types are presented in Table 1 and illustrate pertinent features of the protocol. Thus, while allylic acetates devoid of further substitution (entries 1–3) afford excellent yields of aminated DBCP products **7** in 2.5–4.5 h, further substitution (entries 4–9) gave diminished yields and required longer reaction periods (28–72 h). The trisubstituted geranyl and neryl acetates (entries 4, 5) were particularly sluggish and both afforded low yields of the *E* allylic stereoisomer **7d** (along with mixtures of trienes). The loss of alkene geometry obtained with **5e** in Pd(0)-catalyzed aminations has also been observed with DMB-NH_2 and attributed to a π-allylpalladium–amine complex which facilitates alkene isomerization,[6] with the product *E* alkene arising from the more thermodynamically stable syn π-allyl complex.[2c,4,6] With the unsymmetrical 1 and 3 allylic acetates **5a–f,h** (entries 1–6, 8), the products obtained resulted from approach of **1** at the less-hindered primary site with only traces of other isomers of **7** detected (TLC, ^1H and ^{31}P NMR). This, along with the diminished yields with substituted acetates, presumably reflects the steric bulkiness of **1** imparted by the large diethyl phosphoramide fragment.[14]

In summary, reaction of allylic acetates and **1** catalyzed by palladium(0) provided useful yields of N-diprotected allylic amines **7**. Because of the mildness of the condition for selective deprotection, this method is of value for the synthesis of both primary and secondary allylic amines.

Experimental Section

General Information. Mass spectra were performed on a Finnigan 4000 instrument at 70 eV and were recorded as *m/e*. Proton and carbon-13 NMR spectra were recorded in $CDCl_3$ on

(1) (a) Malek, N. J.; Moormann, A. E. *J. Org. Chem.* **1982**, *47*, 5395. (b) Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685.

(2) For reviews, see: (a) Heck, R. F. *Palladium Reagents in Organic Chemistry*; Academic Press: London, 1985. (b) Trost, B. M. *Angew. Chem. Int. Ed. Engl.* 1989, *28*, 1173. (c) Trost, B. M; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982, Vol. 8, p 799. (d) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1981. (e) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (f) Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357.

(3) (a) Nikado, N.; Aslanian, R.; Scavo, F.; Helquist, P.; Akermark, B.; Backvall, J. E. *J. Org. Chem.* **1984**, *49*, 4738. (b) Godleski, S. A.; Heacock, D. J.; Meinhart, J. D.; Van Wallendael, S. *J. Org. Chem.* **1983**, *48*, 2101. (c) Godleski, S. A.; Meinhart, J. D.; Miller, D. J.; Van Wallendael, S. *Tetrahedron Lett.* **1981**, *22*, 2247. (d) Baer, H. H., Hanna, Z. S. *Can. J. Chem.* **1981**, *59*, 889. (e) Andriamialisoa, R. Z.; Langlois, N.; Langlois, Y. *Heterocycles* **1980**, *14*, 1457. (f) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1980**, *45*, 2741. (g) Trost, B. M.; Godleski, S. A.; Belletire, J. L. *J. Org. Chem.* **1979**, *44*, 2052. (h) Trost, B. M.; Godleski, S. A.; Genet, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 3930. (i) Nordberg, R. E.; Backvall, J.-E. *J. Organomet. Chem.* **1985**, *285*, C24. (j) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, 3821. (k) Safi, M.; Sinou, D. *Tetrahedron Lett.* **1991**, 2025.

(4) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.

(5) (a) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 3727. (b) Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559.

(6) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451.

(7) Inoue, Y.; Taguchi, M.; Toyofuku, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3021.

(8) Bystrom, S. E.; Aslanian, R.; Backvall, J.-E. *Tetrahedron Lett.* **1985**, *26*, 1749.

(9) Murahashi, S.-I.; Tanigawa, Y.; Imada, Y.; Taniguchi, Y. *Tetrahedron Lett.* **1986**, *27*, 227.

(10) Connel, R. D.; Rein, T.; Akermark, B.; Helquist, P. *J. Org. Chem.* **1988**, *53*, 3845, and references cited therein.

(11) The reductive replacement of allylic oxygen, sulfur, and selenium functional groups by hydride has been previously reported. See: (a) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380. (b) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* **1980**, *21*, 27.

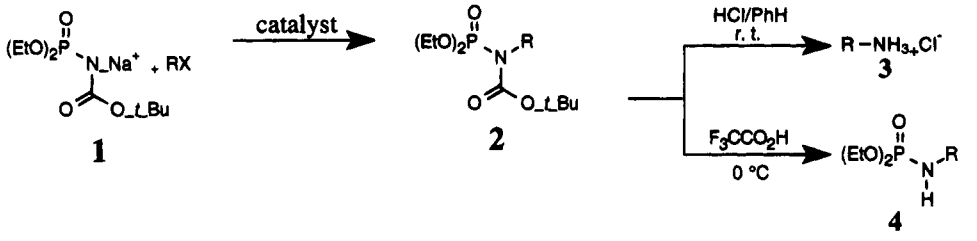
(12) For preparation and reaction of diethyl *N*-sodio-N-(*tert*-butoxycarbonyl)phosphoramidate (**1**) and also partial and total cleavage of the amidate products **7**, see: Zwierzak, A.; Pilichowska, S. *Synthesis* **1982**, 922.

(13) Zwierzak, A.; Brylikowska-Piotrowicz, J. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 107; Zwierzak, A. *Synthesis* **1984**, 332.

(14) The diethyl phosphoramide moiety apparently introduces much more steric congestion than a *tert*-butoxycarbonyl group since the related reagent DBIC often affords considerably more secondary amide product (ref 10).

0022-3263/94/1959-4007$04.50/0

Scheme 1



Scheme 2

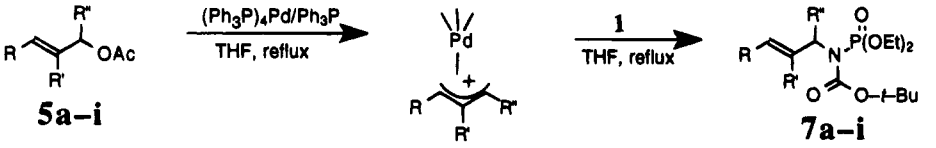
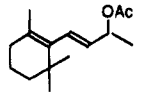
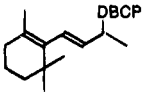
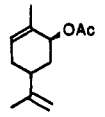
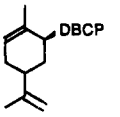


Table 1. Palladium-Catalyzed Allylic Amination of Allyl Acetates 5 and Diethyl *N*-Sodio-*N*-(*tert*-butoxycarbonylphosphoramidate (1) to Diethyl *N*-(*tert*-Butoxycarbonyl)phosphoramidates 7

entry	allylic esters 5	product 7	yield (%)[a]
1	(*E*)-PhCH=CHCH$_2$OAc (**5a**)	(*E*)-PhCH=CHCH$_2$(DBCP)[b] **7a**	93
2	(*E*)-Me(CH$_2$)$_6$CH=CHCH$_2$OAc (**5b**)	(*E*)-Me(CH$_2$)$_6$CH=CHCH$_2$(DBCP) **7b**	98
3	Me(CH$_2$)$_6$CH(OAc)CH=CH$_2$ (**5c**)	**7b**	91
4	(2*E*)-MeC=CH(CH$_2$)$_2$CMe=CHCH$_2$OAc (**5d**)	(2*E*)-MeC=CH(CH$_2$)$_2$CMe=CHCH$_2$(DBCP) **7d**	21[c]
5	(2*Z*)-MeC=CH(CH$_2$)$_2$CMe=CHCH$_2$OAc (**5e**)	**7d**	19[c]
6	(*E*)-PhCH=CHCHMeOAc (**5f**)	(*E*)-PhCH=CHCHMe(DBCP) (**7f**)	56
7	(*E*)-Me(CH$_2$)$_3$CH(OAc)CH=CHMe (**5g**)	(*E*)-Me(CH$_2$)$_3$CH(DBCP)CH=CHMe (**7g**) and (*E*)-Me(CH$_2$)$_3$CH=CHCH(DBPC)Me **7g′**	67[d]
8	 **5h**	 **7h**	52
9	 **5i**	 **7i**	53

[a] Isolated yields of purified products. [b] DBCP = Diethyl *N*-(*tert*-butoxycarbonyl)phosphoramide. [c] ca. 25% of mixtures of trienes also obtained. [d] Ratio **7g**:**7g′** = 4:1.

a Bruker 250 FT-NMR spectrometer. ^{31}P NMR spectra were taken on a JEOL-FX90Q multinuclear NMR spectrometer with 85% H_3PO_4 as external reference. IR spectra were recorded on a Perkin-Elmer 1600 series instrument. Gas chromatography was performed on a Varian-3700 model instrument equipped with flame detector and a 15 × 1/8 ft, 3% OV-17 on 100% Supelcoport column. Silica gel (~400 mesh) was used in flash chromatography. Analytical and preparative TLC were performed using Analtech brand silica gel plates. Diethyl *N*-sodio-*N*-(*tert*-butoxycarbonyl)phosphoramidate[12] and tetrakis(triphenylphosphine)palladium(0)[15] were prepared as described. The acetates used were either obtained commercially or prepared from the alcohols by standard methods. Unless otherwise indicated, reagents purchased commercially were used without further purification. All reactions were carried out under an argon atmosphere. Dry THF was obtained by distillation from sodium–benzophenone ketyl under a nitrogen atmosphere. Organic solutions were dried over anhydrous magnesium sulfate.

General Procedure: Preparation of Diethyl *N*-*trans*-Cinnamyl-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7a). In a 50-mL two-necked round-bottomed flask, equipped with a magnetic stirring bar, a rubber septum, and a reflux condenser, was placed tetrakis(triphenylphosphine)palladium (69 mg; 0.06 mmol), triphenylphosphine (46 mg; 0.18 mmol), *trans*-cinnamyl acetate (**5a**) (350 mg 2.00 mmol) and 15 mL of freshly distilled THF. The contents of the flask was stirred at room temperature for 15 min and powdered diethyl *N*-sodio-*N*-(*tert*-butoxycarbonyl)phosphoramidate (1) (550 mg (2.00 mmol) was added in one portion. The reaction was then refluxed for 2.5 h, cooled to room temperature, diluted with 15 mL of ether, and washed with 5 mL of brine. The brine wash was extracted with ether and the combined organic phase was dried and concentrated on a rotary evaporator. The product **7a** was isolated by flash column chromatography (silica gel, 9:1 diethyl ether:pentane) to give 640 mg of clear oil (93% yield): ^{1}H NMR δ 7.34 (m, 5H, Ph), 6.62 (d, J = 15.8 Hz, 1H), 6.26 (m, 1H), 4.28 (q, J = 6.5 Hz), 4.13 (q, J = 7.5 Hz, 4H), 1.50 (s, 9H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ 152.8, 136.6, 132.4, 128.0, 127.1, 125.9, 125.0, 81.8, 62.9, 47.7, 27.7, 15.8, 15.7; ^{31}P NMR δ 0 (overlapping with H_3PO_4 reference peak); IR (film) 1700 (s, C=O) cm^{-1}; MS (*m/e*) 371 (M + 1), 370 (M$^+$), 314, 313, 269, 240, 212, 155, 130, 117. Anal. Calcd for $C_{18}H_{28}NPO_5$: C, 58.53; H, 7.64. Found: C, 58.16; H, 7.32.

Diethyl *N*-*trans*-2-Decenyl-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7b). Using the procedure described above, 750 mg (98%) of pure product **7b** was obtained from *trans*-2-decenyl acetate **5b** (400 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), and tetrakis(triphenylphosphine)palladium (690 mg; 0.06 mmol) and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 4.5 h and the product isolated by Kugelrohr distillation (0.12 mmHg/140–160 °C) as a colorless oil: ^{1}H NMR δ 5.70 (m, 1H), 5.53 (m, 1H), 4.09 (m, 4H), 2.01 (m, 2H), 1.49 (s, 9H), 1.34 (t, J = 1 Hz, 6H), 1.26 (m, 10H), 0.87 (t, 3H); ^{13}C NMR δ 152.9 (C=O), 134.2, 125.6, 81.9, 63.1, 48.0, 32.2, 31.8, 29.1, 28.0, 22.6, 16.1, 14.0; ^{31}P NMR δ 2.02; IR (film) 1720 (s, C=O) cm^{-1}; MS (*m/e*) 392 (M + 1), 391 (M$^+$), 336, 335, 291, 198, 192, 180, 155, 138. Anal. Calcd for $C_{19}H_{38}NPO_5$: C, 58.29; H, 9.78. Found: C, 58.26; H, 10.22.

Using the procedure described above, 690 mg (91%) of pure

(15) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

product **7b** was also obtained from 1-decen-3-ylacetate (**5c**) (0.40 g; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 4 h and the product isolated by Kugelrohr distillation (0.4 mmHg/120–145 °C bath) as a colorless oil. Spectral data indicated the product to be identical to that obtained above.

Diethyl *N*-Geranyl-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7d). Using the procedure described above, 160 mg (21%) of pure product **7d** was obtained from geranyl acetate (**5d**)-(390 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis-(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 24 h and stirred at room temperature for 3 days. The product was isolated by Kugelrohr distillation (0.4 mmHg/100–170 °C) to give a colorless oil: ^{1}H NMR δ 5.26 (m, 1H), 5.08 (m, 1H), 4.12 (m, 1H), 2.03 (m, 4H), 1.73 (s, 3H), 1.67 (s, 3H), 1.60 (2, 3H), 1.49 (s, 9H), 1.34 (m, 6H); ^{13}C NMR δ 153.2 (C=O), 138.1, 131.1, 123.7, 120.9, 81.7, 62.9, 44.2, 39.4, 31.9, 28.0, 26.3, 25.5, 23.3, 17.5, 16.2, 16.0, 15.9; ^{31}P NMR δ 2.32; IR (film) 1721 (s, C=O) cm^{-1}; MS (*m/e*) 391 (M + 1), 390 (M$^+$), 334, 333, 289, 279, 262, 220, 198, 155, 136. Anal. Calcd for $C_{19}H_{36}NPO_5$: C, 58.59; H, 9.32. Found: C, 58.27; H, 9.36.

Using the procedure described above, 150 mg (19%) of pure product **7d** was also obtained from neryl acetate (**5e**) (390 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 24 h and stirred at room temperature for 3 days. The product was isolated by Kugelrohr distillation (0.4 mmHg/100–170 °C) to give a colorless oil. Spectral data indicated the product to be identical to that obtained above. With both **5d** and **5e**, triene mixtures (*ca.* 25%) were detected by GC along with small amounts of the starting acetates.

Diethyl *N-trans*-(1-Phenyl-3-butenyl)-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7f). Using the procedure described above, 430 mg (56%) of pure product **7f** was obtained from *trans*-1-phenyl-3-buten-2-yl acetate (**5f**) (380 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 28 h and the product isolated by Kugelrohr distillation (0.4 mmHg/110–150 °C) to give a colorless oil: ^{1}H NMR δ 7.32 (m, 5H), 6.57 (dd, J = 5.9 Hz, J = 2.3 Hz, 2H), 4.95 (m, J = 6.6 Hz, 1H), 4.12 (m, 4H), 1.57 (d, J = 6.9 Hz, 3H), 1.49 (s, 9H), 1.34 (m, 6H); ^{13}C NMR δ 152.7 (C=O), 136.7, 130.8, 130.7, 128.2, 127.2, 126.1, 82.1, 63.1, 63.0, 55.7, 55.1, 28.0, 20.0, 16.1, 16.0; ^{31}P NMR δ 2.39; IR (film) 1716 (s, C=O) cm^{-1}; MS (*m/e*) 385 (M + 1), 384 (M$^+$) 328, 327, 283, 254, 198, 155, 131. Anal. Calcd for $C_{19}H_{30}NPO_5$: C, 59.52; H, 7.89. Found: C, 59.11; H, 7.95.

Diethyl *N*-[4-(2-Octenyl)]-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7g). Using the procedure described above, 490 mg (67%) of a 4:1 mixture of **7g** and **7g′** (determined by NMR) was obtained from 4-acetoxy-2-octene (**5g**) (340 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis(triphenylphosphine)-palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 28 h and the product isolated by flash column chromatography (silica gel, 10% diethyl ether in pentane) to give a colorless oil: ^{1}H NMR δ 5.82 (q, J = 7.2 Hz, 1H), 5.63 (m, 1H), 4.73 (m, 1H), 4.08 (m, 4H), 2.01 (q, J = 6.5 Hz, 2H), 1.48 (s, 9H), 1.44 (d, J = 7.0 Hz, 3H), 1.32 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR δ 152.5, 131.8, 130.8, 81.3, 62.4, 54.8, 31.4, 30.9, 27.7, 21.7, 19.7, 15.7, 13.3; ^{31}P NMR δ 2.53. IR (film) 1720 (s, C=O) cm^{-1}; MS (*m/e*) 364 (M + 1), 363 (M$^+$), 307, 263, 206, 155. Anal. Calcd for $C_{17}H_{34}NPO_5$: C, 56.18; H, 9.43. Found: C, 56.45; H, 9.35.

Diethyl *N*-(2-β-Ionyl)-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7h). Using the procedure described above, 450 mg (52%) of pure product **7h** was obtained from β-ionol acetate (**5h**)-(470 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis-(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 31 h and the product was isolated by Kugelrohr distillation (0.4 mmHg/110–155 °C) to give a colorless oil: ^{1}H NMR δ 6.07 (d, J = 15.9 Hz, 1H), 5.80 (dd, J = 7.5, 15.9 Hz, 1H), 4.81 (m, J = 7.0 Hz, 1H), 4.10 (m, 4H), 1.96 (t, 2H), 1.66 (s, 3H), 1.57 (m, 2H), 1.52 (d, J = 7.0 Hz, 3H), 1.48 (s, 9H), 1.42 (m, 2H), 1.34 (m, 6H), 0.97 (s, 6H); ^{13}C NMR δ 152.3 (C=O), 136.3, 134.1, 131.4, 128.9, 127.9, 81.3, 62.4, 55.3, 39.0, 33.5, 32.2, 28.2, 27.7, 20.9, 19.9, 18.9, 15.8; ^{31}P NMR δ 0 (overlapping with H_3PO_4 reference peak); IR (film) 1720 (s, C=O) cm^{-1}; MS (*m/e*) 430 (M + 1), 429 (M$^+$), 373, 329, 254, 198, 193, 176, 154. Anal. Calcd for $C_{22}H_{40}NPO_5$: C, 61.52; H, 9.39. Found: C, 61.75; H, 9.06.

Diethyl *N*-Carvyl-*N*-(*tert*-butoxycarbonyl)phosphoramidate (7i). Using the procedure described above, 350 mg (45%) of pure product **7i** was obtained from *cis*-carvyl acetate (**5i**) (390 mg; 2 mmol), amidate **1** (550 mg; 2 mmol), tetrakis-(triphenylphosphine)palladium (69 mg; 0.06 mmol), and triphenylphosphine (46 mg; 0.18 mmol). The reaction was refluxed for 72 h, and the product was isolated by flash column chromatography (silica gel, 10% diethyl ether in pentane) to give a colorless oil: ^{1}H NMR δ 5.49 (s, 1H), 4.18 (m, 2H), 4.12 (m, 4H), 2.48 (m, 1H), 2.24 (m, 2H), 2.02 (m, 3H), 1.76 (d, J = 13.4 Hz, 3H), 1.65 (m, 4H), 1.47 (s, 9H), 1.35 (m, 6H); ^{13} C NMR δ 152.2 (C=O), 148.8, 133.7, 122.6, 109.4, 81.8, 63.1, 58.8, 55.4, 41.7, 38.2, 33.5, 30.4, 27.9, 21.6, 20.5, 20.3, 19.9, 16.1; ^{31}P NMR δ 3.23; IR (film) 1723 (s, C=O) cm^{-1}; MS (*m/e*) Anal. Calcd for $C_{19}H_{34}NPO_5$: C, 58.90; H, 8.85. Found: C, 58.53; H, 9.40.