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TETRAHEDRON

Palladium(0)-Catalyzed Coupling of Allenyl *N*-Tosylcarbamates with Hypervalent Iodonium Salts

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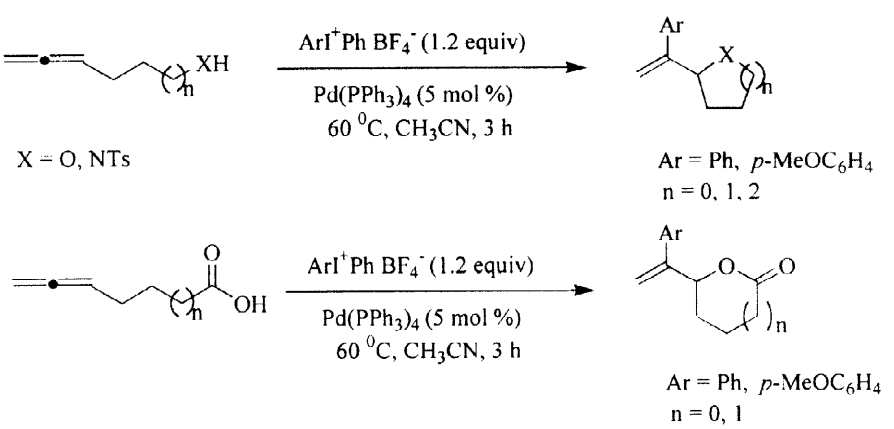
Abstract: The palladium $Pd(PPh_3)_4$-catalyzed coupling reaction of allenyl N-tosylcarbamates with hypervalent iodonium salts afforded the cyclized *trans*-5-substituted oxazolidinones, 3-oxazin-2-ones, and higher membered carbamates under mild conditions.

Introduction

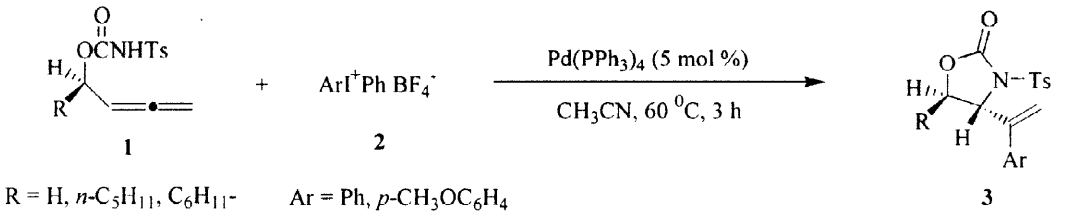
The substituted 1,3-oxazolidin-2-ones, 3-oxazin-2-one, and other higher membered carbamates which have allylic amine moiety are important structural units for amino sugars and rare amino acids. Recently, Tamaru et al. [1, 2] reported the palladium-catalyzed allylamination and the silver(I)-catalyzed aminocyclization of *O*-(2,3-butadienyl) *N*-tosylcarbamates to form 5-substituted *N*-tosyl-4-vinyl-2-oxazolidinones [3]. The palladium(II)-catalyzed aminocarbonylative coupling of *O*-(2,3-butadienyl) *N*-tosylcarbamates to give 2-oxazolidinones was also reported by Tamaru et al [4]. In connection with our projects utilizing hypervalent iodonium salts in palladium-catalyzed cyclization reaction, we have studied coupling-cyclization of allenylamines, allenyl alcohols, and allenylcarboxylic acid with hypervalent iodonium to form cyclized heterocyclic tetrahydrofurans, tetrahydropyrans, pyrrolidines, piperidines, or lactones [5].



Scheme 1

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00340-3

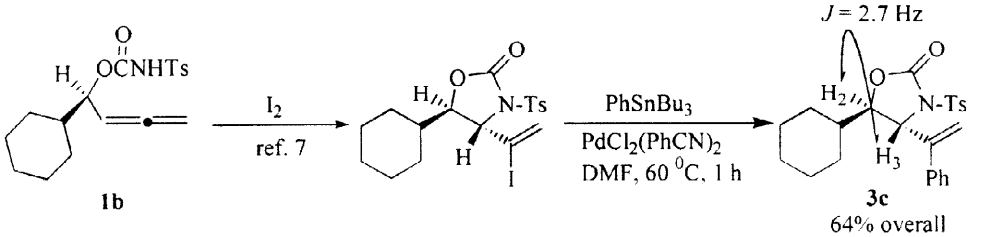
Alternatively we have investigated the palladium(0)-catalyzed coupling of hypervalent iodonium salts [6] with allenyl *N*-tosyl carbamates to form oxazolidin-2-ones, oxazin-2-ones (Scheme 2).



Scheme 2

Results and Discussion

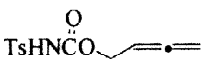
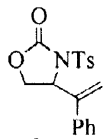
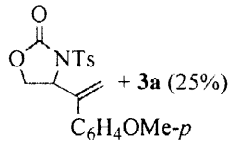
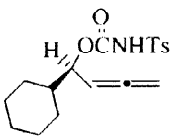
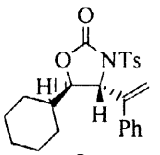
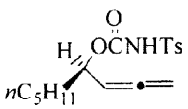
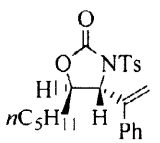
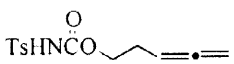
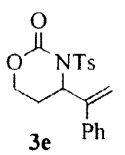
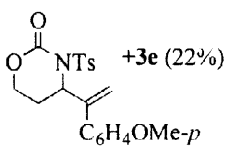
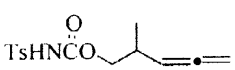
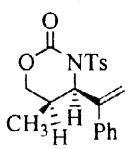
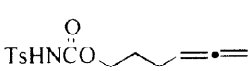
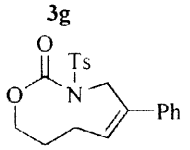
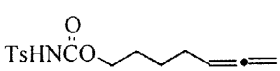
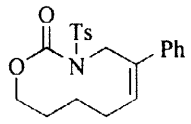
The results of regio- and stereoselective coupling and cyclization to form allylic amines are summarized in Table 1. To determine optimum reaction conditions, a series of experiments has been performed with the carbamate **1a** with diphenyliodonium tetrafluoroborate (**2a**). Of the calaysts tested $Pd(OAc)_2/Ph_3P$, $Pd_2(dba)_3{\cdot}CHCl_3/Ph_3P$, and $(Ph_3P)_4Pd$, $(Ph_3P)_4Pd$ was the best choice. As suitable solvent, CH_3CN and DMF were effective even if THF was not suitable. For the base, K_2CO_3 or Cs_2CO_3 was employed. The yields was improved when the reaction was run at 60 °C for 3 h than run the room temperature for 18 h. The *O*-(2,3-butadienyl)carbamate (**1a**) reacted with **2a** in the presence of $(Ph_3P)_4Pd$ in CH_3CN at 60 °C for 3 h to afford the oxazolidine **3a** in 71% yield (entry 1 in Table 1). Under the same conditions treatment of **1a** with *p*-methoxyphenyl(phenyl)iodonium tetrafluoroborate (**2b**) gave *p*-methoxyphenyl- or phenyl-substituted oxazolidine **3b** and **3a** in 47 and 25% yields, which were easily separable by column chromatography (entry 2). When cyclohexyl-substituted allenyl carbamate **1b** was coupled with diphenyliodonium tetrafluoroborate **2a**, *trans*-substituted oxazolidine **3c** was obtained in 74% yield (entry 3). The stereochemistry of the cyclized product **3c** was confirmed by comparison of the coupling constant (J = 2.7 Hz) in **3c** for the two protons (H_2 and H_3) in the ring system with the authentic compound (J = 2.7 Hz) which was synthesized by transformation of **1b** to **3c**. The carbamate **1b** was subjected to iodocyclization [7] followed by the Stille coupling to afford the authentic cyclic carbamate **3c** in 64% overall yield (Scheme 3).



Scheme 3

Similarly, *n*-pentyl-substituted allenyl carbamate **1c** reacted to provide the *trans*-**3d** in 71% yield (entry 4). When *O*-(3,4-pentadienyl) carbamate **1d** was coupled with **2a**, the carbamate **3e** was obtained in 63% yield

Table1. Palladium(0)-Catalyzed Coupling-Cyclization of Allenyl Carbamates with Hypervalent Iodonium Salts

Entry	Substrates	Iodonium Salts	Product	Yield(%)
1	 **1a**	$Ph_2I^+ BF_4^-$ **2a**	 **3a**	71
2	**1a**	p-$CH_3OC_6H_4I^+Ph\ BF_4^-$ **2b**	 + **3a** (25%) **3b** (47%)	72
3	 **1b**	**2a**	 **3c**	74
4	 **1c**	**2a**	 **3d**	71
5	 **1d**	**2a**	 **3e**	63
6	**1d**	**2b**	 +**3e** (22%) **3f** (43%)	65
7	 **1e**	**2a**	 **3g**	57
8	 **1f**	**2a**	 **3h**	65
9	 **1g**	**2a**	 **3i**	44

(entry 5). Treatment of 2-methyl-substituted carbamate **1e** [8] with **2a** under the same conditions afforded the *cis*-isomer **3g** [9] in 57% yield (entry 7).

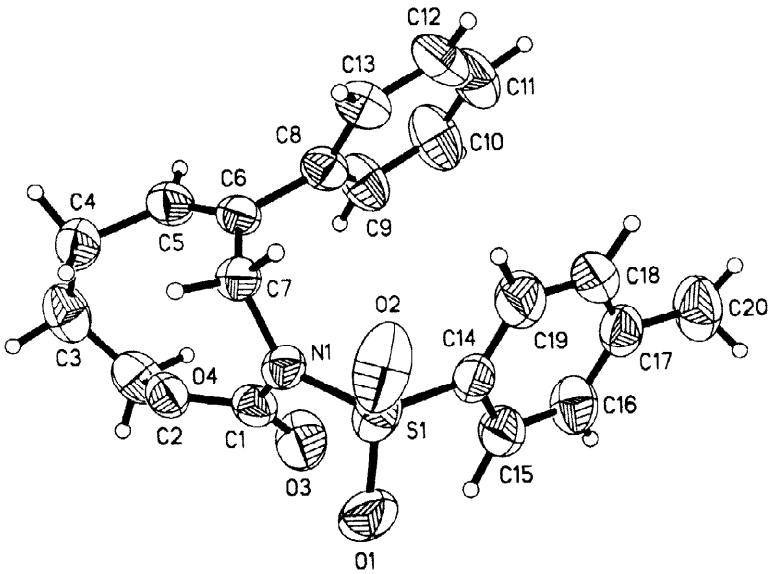


Fig 2. ORTEP drawing of **3h**

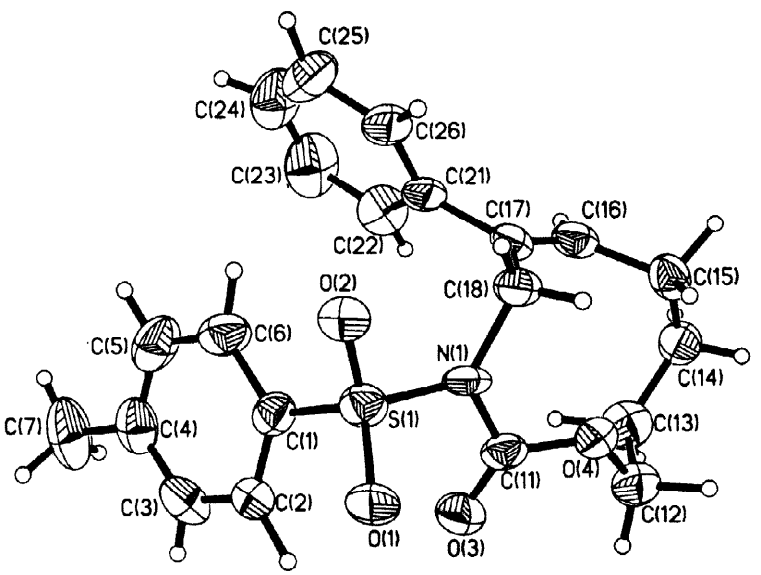
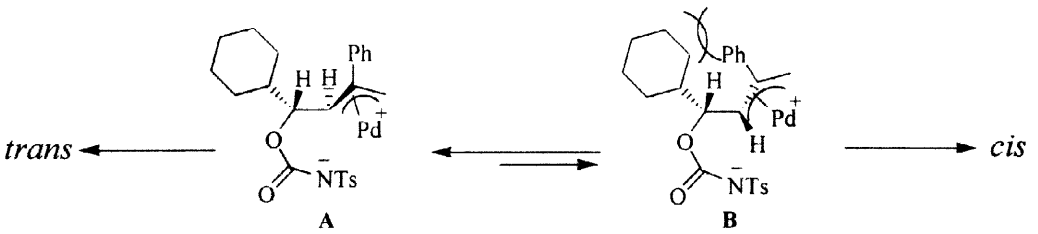


Fig 3. ORTEP drawing of **3i**

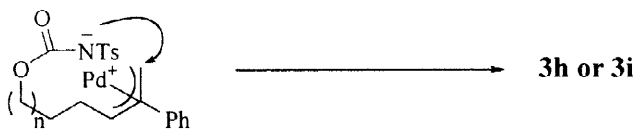
In considering plausible mechanism for the coupling and cyclization of allenyl carbamate **1b**, it is presumed that $PhPd^{+}$ BF_4^{-} from Ph_2I^{+} BF_4^{-} and Pd(0) *via* oxidative addition adds to the allene to form π–allylpalladium complex and undergo intramolecular nucleophilic addition to afford the cyclized product [10]. The formation of *trans*-isomer **3c** may be rationalized by a mechanism depicted below, where the transition state **A** leading to

trans-product is preferred over **B** (Scheme 4).



Scheme 4

However, when this method was extended to 4,5 hexa- and 5,6-hepatadienyl carbamates **1f** and **1g** with **2a**, nine- and ten-membered compounds **3h** and **3i** were afforded in 65 and 44% yields, respectively. The structures of **3h** and **3i** were confirmed unambigously by X-ray crystallography (Figs 2 and 3). The exclusive formation of *endo*-cyclized products may be rationalized by *endo*-cyclization of intermediate π–allylpalladium complex (Scheme 5) instead of *exo*-cyclization (entries 8 and 9) [11,12].



n = 1,2

Scheme 5

In summary the palladium-catalyzed coupling of allene carbamate to form 1,3-oxazolidin-2-ones, tetrahydro-1,3-oxazine-2-ones, and macrocyclic carbamates was achieved under mild conditions.

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Experimental

General. IR spectra were obtained on a Nicolet FT-IR 205 spectrometer. GC-MS spectra were measured on a Hewlett-Packard 5880 GC system. ^{1}H NMR spectra were obtained on a Bruker 400 (400 MHz). NMR spectra were recorded in ppm (δ) related to tetramethylsilane (δ = 0.00) as an internal standard unless stated otherwise and are reported as follows; chemical shift, multiplicity (br = broad, s = singlet, t = triplet, q = quartet, m = multiplet), coupling constants and integration.

All reactions involving organometallic reagents were carried out in an inert atmosphere of nitrogen. CH_3CN was freshly distilled from calcium hydride prior to use. Small and medium scale purification were performed by flash chromatography.

3-[(4-Methylphenyl)sulfonyl]-5-cyclohexyl-4-(1-phenylvinyl)-1,3-oxazolidin-2-one (3c).

Typical procedure: To a stirred solution of Ph_2I^+ BF_4^- (**2a**) (302 mg, 0.82 mmol) and K_2CO_3 (237 mg, 1.71 mmol) in CH_3CN (1 mL) was added $Pd(PPh_3)_4$ (47 mg, 5 mol%) followed by allenyl carbamate **1b** (237 mg, 0.68 mmol) in CH_3CN (1 mL). The reaction mixture was stirred at 60 °C for 3h, cooled to room temperature, and quenched with saturated NH_4Cl solution. The mixture was extracted with ether and the organic layer was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The crude product was separated by SiO_2 column chromatography (EtOAc/hexanes 1:20) to afford the oxazolidine **3c** (214 mg, 74%). TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.44. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.08-1.66 (m,11H), 2.43 (s, 3H), 3.92 (dd, 1H, *J* = 2.7, 5.8 Hz), 5.10 (d, 1H, *J* = 2.7 Hz), 5.14 (s, 1H), 5.34 (s, 1H), 7.26-7.37 (m, 7H), 7.93-7.95 (m, 2H). IR (neat) 2932, 1780, 1370, 1252, 1092 cm^{-1}. MS (m/e) 425 (M^+), 158, 155, 91 (base peak). HRMS calcd for $C_{24}H_{27}NO_4S$ 425.1660, found 425.1651

3-[(4-Methylphenyl)sulfonyl]-4-(1-phenylvinyl)-1,3-oxazolidin-2-one (3a).

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.49. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 4.03-4.06 (dd, 1H, *J* = 3.1, 8.5 Hz), 4.46-4.50 (t, 1H, *J* = 8.5 Hz), 5.19 (d, 1H, *J* = 0.6 Hz), 5.41(dd, 1H, *J* = 0.6, 5.4 Hz), 5.43 (d, 1H, *J* = 4.9Hz), 7.26-7.37 (m, 7H), 7.94-7.96 (m, 2H). IR (neat) 2926, 1785, 1376, 1188 cm^{-1}. MS (m/e) 343 (M^+), 176, 155, 108, 91 (base peak), 77, 65. HRMS calcd for $C_{18}H_{17}NO_4S$ 343.0878, found 343.0872.

3-[(4-Methylphenyl)sulfonyl]-4-(1-(4-methoxyphenylvinyl)-1,3-oxazolidin-2-one (3b).

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.51. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.45 (s, 3H), 3.81 (s, 3H), 4.03-4.06 (dd, 1H, *J* = 3.1, 8.5 Hz), 4.46-4.50 (t, 1H, *J* = 8.5 Hz), 5.10 (d, 1H, *J* = 0.6 Hz), 5.38(dd, 1H, *J* = 0.6, 5.4 Hz), 5.40 (d, 1H, *J* = 4.9Hz), 6.86-6.89 (m, 2H), 7.22-7.26 (m, 2H), 7.32 (m, 2H), 7.94 (m, 2H). IR (neat) 2926, 1779, 1370, 1100 cm^{-1}. MS (m/e) 373 (M^+), 133 (base peak), 91. HRMS calcd for $C_{19}H_{19}NO_5S$ 373.0983, found 373.0986.

3-[(4-Methylphenyl)sulfonyl]-5-pentyl-4-(1-phenylvinyl)-1,3-oxazolidin-2-one (3d).

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.42. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.11-1.60 (m,11H), 2.43 (s, 3H), 4.14 (m, 1H), 4.98 (dd, 1H, *J* = 0.6, 2.8 Hz), 5.19 (d, 1H, *J* = 0.7 Hz), 5.40(s, 1H), 7.26-7.42 (m, 7H), 7.92-7.94 (m, 2H). IR (neat) 2960, 1780, 1371, 1174 cm^{-1}. MS (m/e) 413 (M^+), 203, 122, 77 (base peak), 49. HRMS calcd for $C_{23}H_{27}NO_4S$ 413.1660, found 413.1657.

3-[(4-Methylphenyl)sulfonyl]-4-(1-phenylvinyl)-1,3-oxazinan-2-one (3e).

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.51. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.83 (dd,1H, *J* = 2.1, 14.3 Hz), 2.14 (m, 1H), 2.43 (s, 3H), 4.23 (ddd, 1H, *J* = 1.3, 2.9, 13.4 Hz), 4.36 (ddd, 1H, *J* = 2.9, 12.9, 13.4 Hz), , 5.11 (s, 1H), 5.22 (s, 1H), 5.73 (d, 1H, *J* = 4.6Hz), 7.26-7.37 (m, 7H), 7.93-7.95 (m, 2H). IR (neat) 2950, 1725, 1355, 1256, 1090 cm^{-1}. MS (m/e) 357 (M^+), 264, 189, 102, 91 (base peak), 82. HRMS calcd for $C_{19}H_{19}NO_4S$ $[M+H]^+$ 358.1113, found 358.1111.

3-[(4-Methylphenyl)sulfonyl]-4-(1-(4-methoxyphenylvinyl)-1,3-oxazinan-2-one (3f).

TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.53. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.83 (dd,1H, *J* = 2.1, 14.3 Hz), 2.14 (m, 1H), 2.43 (s, 3H), 3.38 (s, 3H), 4.23 (ddd, 1H, *J* = 1.3, 2.9, 13.4 Hz), 4.36 (ddd, 1H, *J* = 2.9, 12.9, 13.4 Hz),

5.11 (s, 1H), 5.22 (s, 1H), 5.73 (d, 1H, J = 4.6Hz), 6.93 (m, 2H), 7.29 (m, 2H), 7.53 (m, 2H), 7.96 (m, 2H). IR (neat) 2950, 1725, 1355, 1256, 1090 cm^{-1}. MS (m/e) 387 (M^+), 189, 160, 133(base peak), 91. HRMS calcd for $C_{20}H_{21}NO_5S$ $[M+H]^+$ 388.1174, found 388.1171.

3-[(4-Methylphenyl)sulfonyl]-5-methyl-4-(1-phenylvinyl)-1,3-oxazinan-2-one (3g).
TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.54 . ^1H NMR ($CDCl_3$, 400 MHz) δ 1.12 (d, 3H, J = 4.2 Hz), 1.98 (m, 1H), 2.43 (s, 3H), 3.90 (dd, 1H, J = 6.0, 13.4 Hz), 4.43 (dd, 1H, J = 6.6, 13.4 Hz), 5.16 (s, 1H), 5.34 (d, 1H, J = 6.0 Hz), 5.53 (s, 1H), 7.26-7.42 (m, 7H), 7.92-7.94 (m, 2H). IR (neat) 2960, 1780, 1371, 1174 cm^{-1}. MS (m/e) 371 (M^+), 216, 188, 174 (base peak), 118, 91, 71. HRMS calcd for $C_{20}H_{21}NO_4S$ $[M+H]^+$ 372.1261, found 372.1261.

3-[(4-Methylphenyl)sulfonyl]-5-phenyl-2,3,4,7,8,9-hexahydro-1,3-oxazonin-2-one (3h).
TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.64 . ^1H NMR ($CDCl_3$, 400 MHz) δ 1.97 (m, 2H), 1.98 (m, 1H), 2.31 (s, 3H), 2.50 (m, 2H), 4.24 (t, 2H, J = 5.20 Hz), 4.97 (s, 2H), 5.73 (t, 1H, J = 6.7 Hz), 6.90 (m, 2H), 7.10-7.28 (m, 7H). IR (neat) 2958, 1773, 1357, 1168 cm^{-1}. MS (m/e) 371 (M^+), 283, 216, 188, 174 (base peak), 118, 91, 71.

3-[(4-Methylphenyl)sulfonyl]-5-phenyl-3,4,7,8,9,10-hexahydro-2H-1,3-oxazecin-2-one (3i)
TLC; SiO_2, EtOAc/hexanes 1 : 1, R_f = 0.56. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.55-1.62 (m, 4H), 1.80 (m, 2H), 2.32 (s, 3H), 2.54 (br, 2H), 4.93 (br, 2H), 5.59 (t, 1H, J = 6.3 Hz), 7.00 (m, 2H), 7.06-7.34 (m, 7H). IR (neat) 2958, 1780, 1363, 1172 cm^{-1}. MS (m/e) 385 (M^+), 188, 144 (base peak), 129, 91, 85.

Reference and Notes

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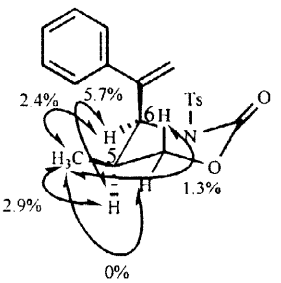
8. For the preparation of 3-methyl-substitute allenol. See, Konegawa T, Ohtsuka Y, Ikeda H, Sugai T, Ohta H. Synlett 1997;1297-1299.
9. The *cis*-stereochemistry was determined on the basis of NOE experiments in ^1H NMR spectrum (300 MHz).

Irradiation of C(5) proton (1.98 ppm) results in an NOE enhancement (5.7%) of the C(6) proton (5.34 ppm). The formation of *cis*-product is known. See, Trost BM, Sudhakar AR. J. Am. Chem. Soc. 1988;110:7933-7935.



NOE of **3g**

10. A different mechanism which involves the nucleophilic attack of the carbamate moiety to form vinylpalladium intermediate which is subsequently subjected to reductive elimination cannot be eliminated.
11. Recently Trost *et al.* reported the palladium-catalyzed carbocyclization of allenyl derivatives to form nine- and ten-membered rings. See, Trost BM, Michellys PY, Gerusz VJ. Angew. Chem. Int. Ed. Engl. 1997;1750-1753.
12. In our experiments, the reaction of **1f** with iodobenzene (4 equiv) in the presence of $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (4 equiv), $n$$Bu_4NCl$ (1.6 equiv) in CH_3CN at reflux for 3 h by the procedure of Walkup and Gallagher gave a complex mixture of products, which were separated to afford the product **3h** in a low (27%) yield.