JOC Article

Studies on Pd(II)-Catalyzed Coupling−Cyclization of α- or β-Amino Allenes with Allylic Halides

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The palladium-catalyzed coupling−cyclization of α- or β-amino allenes with allylic halides leading to 3-allylic 2,5-dihydropyrroles and 1,2,3,6-tetrahydropyridines, respectively, was studied. The starting materials are easily available. The skeletons of both two classes of products were established by the X-ray diffraction studies of **7i** and **9b**. Through the study of the reaction of **2b** with 3-chloro-1-butene, 1-chloro-2-butene, and π-allyl palladium species and the stereochemical outcome of the coupling cyclization of (*S*)-**2m** and (*R*)-**2n**, it is believed that the current transformation most likely proceeded via a Pd(II)-catalyzed pathway, although a Pd(0) pathway cannot be completely excluded.

Introduction

Transition metal-catalyzed cyclization reactions have been receiving much attention as efficient methods for the preparation of carbocycles as well as oxygen and nitrogen-containing heterocycles.[1] Allenes tethered by one to four carbon atoms with an oxygen-[2−5] or nitrogen-containing[6−8] nucleophilic functionality have been attractive substrates for constructing three- to six-membered heterocycles.[1a,9] Although transition metals such as Pd(0)- or Pd(II)-, Ag(I)-, Hg(II)-, and Ru(III)-mediated cyclizations of functionalized allenes have been well documented,[2−9] the coupling-cyclization of functionalized allenes with allylic halides, which may provide an efficient pathway to the allyl-substituted cyclic compounds, have not been studied.

During the course of our studies on the chemistry of functionalized allenes,[10] we have developed some new methodologies for the efficient synthesis of butenolides starting from 2,3-allenoic acids.[11] The Pd(0)-catalyzed coupling−cyclization of 2,3-allenols with organic halides afforded vinylic epoxides highly diastereoselectively.[12] However, recently we observed that a catalytic amount

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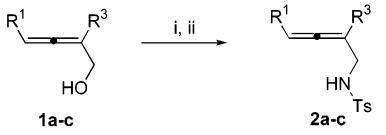
SCHEME 1[a]

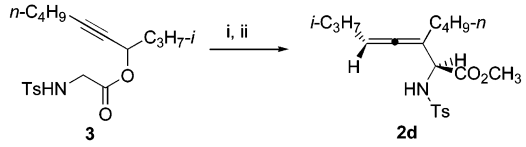


1a-c 2a-c

a: R^1 = H, R^3 = CH_2Ph
b: R^1 = C_6H_{13}-*n*, R^3 = CH_3
c: R^1 = C_6H_{13}-*n*, R^3 = H

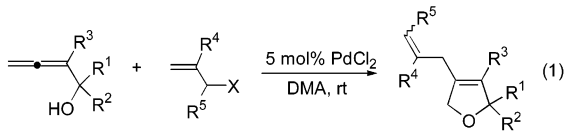
[a] Key: (i) PBr_3, pyridine, Et_2O, −30 °C to reflux; (ii) K_2CO_3, $TsNH_2$, acetone, reflux.

SCHEME 2[a]

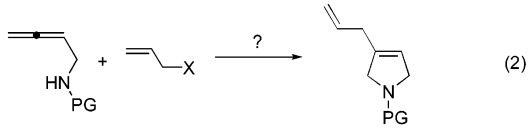


[a] Key: (i) LDA, $ZnCl_2$, THF, −78 °C to rt; (ii) CH_2N_2, Et_2O, −50 °C.

of palladium(II) can catalyze the coupling−cyclization of allenic alcohols with allylic halides in DMA at room temperature in the absence of a base to regioselectively provide five-membered 4-(2′-alkenyl)-2,5-dihydrofurans (eq 1).[13] Based on these results, we reasoned that a similar reaction with amino allenes may provide an efficient route to 2,5-dihydro-1*H*-pyrrole (eq 2). In this paper, we wish to present a full account of our observation on the coupling−cyclization of α- or *β*-amino allenes with allylic halides.



(1)



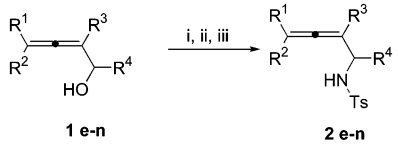
(2)

Results and Discussion

Preparation of the Starting Materials. α-Amino allenes **2a**−**c** were prepared by the amination reaction of the corresponding α-allenic bromides, which, in turn, were prepared from the bromination of α-allenols (Scheme 1).[14] α-Amino allene **2d** was prepared via chelation-controlled ester enolate Claisen rearrangement (Scheme 2).[15] α-Amino allenes **2e**−**n** and *β*-amino allenes **6a**−**l** were prepared from the protection of the corresponding amines, which were prepared via the Mitsunobu amination of the related allenols (Scheme 3).[7b,16]

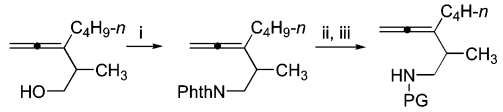
Palladium(II)-Catalyzed Coupling−Cyclization of Amino Allenes with Allylic Halides. Our initial work

SCHEME 3[a]



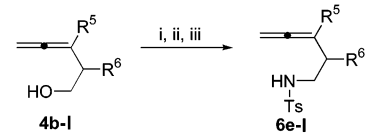
1 e-n 2 e-n

e: R^1 = R^2 = H, R^3 = *n*-C_4H_9, R^4 = CH_3
f: R^1 = R^2 = H, R^3 = allyl, R^4 = Ph
g: R^1 = R^2 = H, R^3 = CH_3, R^4 = *n*-C_4H_9
h: R^1 = R^2 = H, R^3 = CH_3, R^4 = *n*-C_5H_{11}
i: R^1 = R^2 = H, R^3 = CH_3, R^4 = Ph
j: R^1 = R^2 = H, R^3 = CH_3, R^4 = Bn
k: R^1, R^2 = $(CH_2)_5$, R^3 = H, R^4 = H
l: R^1 = R^2 = H, R^3 = H, R^4 = *n*-C_4H_9
m: R^1 = CH_3, R^2 = H, R^3 = *n*-C_4H_9, R^4 = H
n: R^1 = *n*-C_4H_9, R^2 = H, R^3 = CH_3, R^4 = H



4a 5a 6a-d

6a: PG = Ts **6c:** PG = Ac
6b: PG = Ns **6d:** Bz



4b-l 6e-l

4b, 6e: R^5 = C_4H_9-*n*, R^6 = H
4c, 6f: R^5 = C_4H_9-*t*, R^6 = CH_3
4d, 6g: R^5 = C_4H_9-*t*, R^6 = H
4e, 6h: R^5 = H, R^6 = CH_3
4f, 6i: R^5 = CH_3, R = CH_3
4g, 6j: R^5 = allyl, R^6 = CH_3
4h, 6k: R^5 = H, R^6 = H
4i, 6l: R^5 = C_4H_9-*n*, R^6 = C_3H_7-*n*

[a] Key: (i) phthalimide, DEAD, PPh_3, THF, 0 °C to rt; (ii) N_2H_4·H_2O, EtOH, reflux; (iii) NEt_3, CH_2Cl_2, PGCl, 0 °C to rt.

began with *N*-(2-benzylbuta-2,3-dienyl) *p*-toluenesulfonamide **2a** (eq 3 and Table 1). Under the catalysis of 5 mol % $PdCl_2$, the reaction afforded the desired product **7a** in 61% yield as a single product in DMA at room temperature (entry 1, Table 1). Interestingly, in the presence of K_2CO_3, the desired product **7a** was formed together with a significant amount of N-allylation product **8a** (compare entry 1 with entry 2, Table 1). Here, the base promoted the direct N-allylation reaction. When $PdCl_2(PhCN)_2$/CH_3CN was used instead of $PdCl_2$/DMA, the reaction provided the desired product **7a** exclusively in a moderate yield even in the presence of K_2CO_3 (entries 3 and 4, Table 1). The yield of **7a** was further improved to 83% when the reaction was catalyzed by $PdCl_2(PhCN)_2$ or $Pd(OAc)_2$ in DMA (entries 5 and 6, Table 1).

The scope of amino allenes was screened, and the results are summarized in Table 2. The five-membered structure of **7** was established by the single-crystal X-ray diffraction study of **7i** (Figure 1 in the Supporting Information).[21] We found that under the standard conditions all the reactions of 2-alkyl-substituted α-amino

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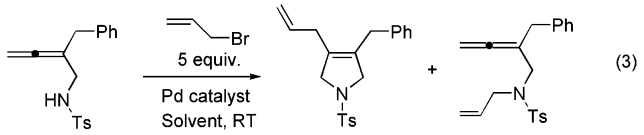
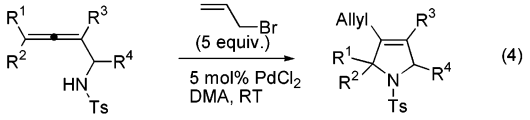
TABLE 1. Pd-Catalyzed Coupling−Cyclization Reaction of α-Amino Allene 2a with Allyl Bromide[a]



entry	palladium catalyst	base (1.5 equiv)	solvent	reaction time (h)	product yield[b] (%)
1	$PdCl_2$		DMA	4	61 (**7a**) 0 (**8a**)
2	$PdCl_2$	K_2CO_3	DMA	23	44 (**7a**) 17 (**8a**)
3	$PdCl_2(PhCN)_2$		CH_3CN	4	44 (**7a**) 0 (**8a**)
4[c]	$PdCl_2(PhCN)_2$	K_2CO_3	CH_3CN	16	45 (**7a**) 0 (**8a**)
5	$Pd(OAc)_2$		DMA	4	83 (**7a**) 0 (**8a**)
6	$PdCl_2(PhCN)_2$		DMA	4	83 (**7a**) 0 (**8a**)

[a] The reaction was carried out at rt using **2a**, allylic bromide (5 equiv), and Pd (5 mol %) in solvent. [b] Isolated yield based on **2a**. [c] 10 mol % of catalyst was applied.

TABLE 2. Pd-Catalyzed Coupling−Cyclization Reaction of α-Amino Allenes 2 with Allyl Bromide[a]

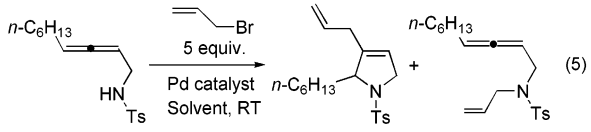


entry	substrate **2** R[1]	R[2]	R[3]	R[4]		reaction time (h)	yield of product[b] (%)
1[c]	C_6H_{13}-*n*	H	CH_3	H	(**2b**)	15	91 (**7b**)
2	C_6H_{13}-*n*	H	CH_3	H	(**2b**)	15	95 (**7b**)
3	C_3H_7-*i*	H	C_4H_9-*n*	CO_2CH_3	(**2d**)	44	85 (**7d**)[d]
4	H	H	C_4H_9-*n*	CH_3	(**2e**)	12	83 (**7e**)
5	H	H	allyl	Ph	(**2f**)	5	96 (**7f**)
6	H	H	CH_3	C_4H_9-*n*	(**2g**)	3	85 (**7g**)
7	H	H	CH_3	C_5H_{11}-*n*	(**2h**)	3	75 (**7h**)
8	H	H	CH_3	Ph	(**2i**)	3	81 (**7i**)
9	H	H	CH_3	Bn	(**2j**)	2	98 (**7j**)
10	$(CH_2)_5$		H	H	(**2k**)	131[e]	18 (**7k**)[f]
11	H	H	H	C_4H_9-*n*	(**2l**)	120[g]	12 (**7l**)
12	CH_3	H	C_4H_9-*n*	H	(**2m**)	2	92 (**7m**)
13	C_4H_9-*n*	H	CH_3	H	(**2n**)	3	88 (**7n**)

[a] The reaction was carried out at rt using **2**, allyl bromide (5 equiv), and $PdCl_2$ (5 mol %) in DMA. [b] Isolated yield based on **2**. [c] 5 mol % $PdCl_2(PhCN)_2$ was applied as catalyst. [d] Trans/cis = 96/4. The stereochemistry was assigned based on the oxypalladation mechanism.[26] [e] rt, 60 h; 50 °C, 35 h; 70 °C, 36 h. [f] 48% of **2k** was recovered. [g] rt, 48 h; 50 °C, 36 h.

allenes **2b**−**j**,**m**,**n** proceeded smoothly to afford the expected 2,5-dihydro-1*H*-pyrrole products **7b**−**j**,**m**,**n** in good to excellent yields (entries 1−9, 12, and 13, Table 2). However, to our disappointment, under identical conditions, 2-nonsubstituted amino allenes **2k**,**l** did not undergo the coupling−cyclization reaction smoothly with the starting materials recovered (entries 10 and 11, Table 2; entries 1 and 2, Table 3). Tamaru[6b,c] has reported that base was essential to promote the reaction. However, in the current reaction, only N-allylation product **8c** was detected when 1.5 equiv of K_2CO_3 was added (entry 3, Table 3). When $PdCl_2(PhCN)_2$ was used instead of $PdCl_2$, the expected cyclic product **7c** was isolated in 5% yield together with 59% of the N-allylation product **8c** (entry 4, Table 3). The N-allylation product **8c** was afforded exclusively again when the reaction was carried out in DMF in the presence of K_2CO_3 (entry 5, Table 3). We envisioned that the favored formation of N-allylation product **8c** may be due to the high concentration of the sulfonamide anion.[6b,c] To keep the concentration of the sulfonamide anion low, we switched the solvent from DMA to THF, acetone, and acetonitrile. In this way, the desired product **7c** was formed in moderate yield together with 4−22% yield of the *N*-allylation product **8c** (entries 6−8, Table 3). The results are base-dependent (entries 8−15, Table 3). The corresponding reaction in THF using $Ca(OH)_2$, HCOONa, LiOAc, NaOAc, KOAc, Na_2HPO_4, DMAP, NEt_3, and DABCO as the base did not yield either **7c** or **8c**.

TABLE 3. Pd-Catalyzed Coupling−Cyclization Reaction of α-Amino Allene 2c with Allyl Bromide[a]



entry	palladium catalyst	base (1.5 equiv)	solvent	reaction time (h)	product yield[b] (%) **7c**	**8c**
1	$PdCl_2$		DMA	40	NR[c]	
2	$PdCl_2(PhCN)_2$		DMA	40	NR[d]	
3	$PdCl_2$	K_2CO_3[e]	DMA	6.5	0	67
4	$PdCl_2(PhCN)_2$	K_2CO_3	DMA	12	5	59
5	$PdCl_2(PhCN)_2$	K_2CO_3	DMF	13.5	0	55
6	$PdCl_2(PhCN)_2$	K_2CO_3	Acetone	24	32	11
7	$PdCl_2(PhCN)_2$	K_2CO_3	CH_3CN	12	39	4
8	$PdCl_2(PhCN)_2$	K_2CO_3	THF	12	39	22
9	$PdCl_2(PhCN)_2$	LiOH	THF	72	12	28
10	$PdCl_2(PhCN)_2$	NaOH	THF	60	11	49
11	$PdCl_2(PhCN)_2$	KOH	THF	50	8	25
12	$PdCl_2(PhCN)_2$	$Ba(OH)_2$	THF	72	6[f]	0
13	$PdCl_2(PhCN)_2$	$NaHCO_3$	THF	72	18	25
14	$PdCl_2(PhCN)_2$	Cs_2CO_3	THF	72	19	27
15	$PdCl_2(PhCN)_2$	K_3PO_4	THF	72	33	12

[a] The reaction was carried out at rt using **2c**, allylic bromide (5 equiv), and Pd catalyst (for entries 1−3, 5 mol %; for entries 4−15, 10 mol %). [b] Isolated yield based on **2c**. [c] 76% of **2c** was recovered. [d] 78% of **2c** was recovered. [e] 2 equiv of K_2CO_3 was added. [f] 41% of **2c** was recovered.

The reaction of α-amino allene **2b** with various substituted allylic halides was also examined (Scheme 4). With 3-chloro-1-butene, the reaction afforded product **7o** as an *E* and *Z* mixture (*E*/*Z* = 1) in 83% combined yield

(17) (a) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1989**, *28*, 342. (b) Sakakibara, M.; Takahashi, Y.; Sakai, S.; Ishii, Y. *Chem. Comunm.* **1969**, 396.

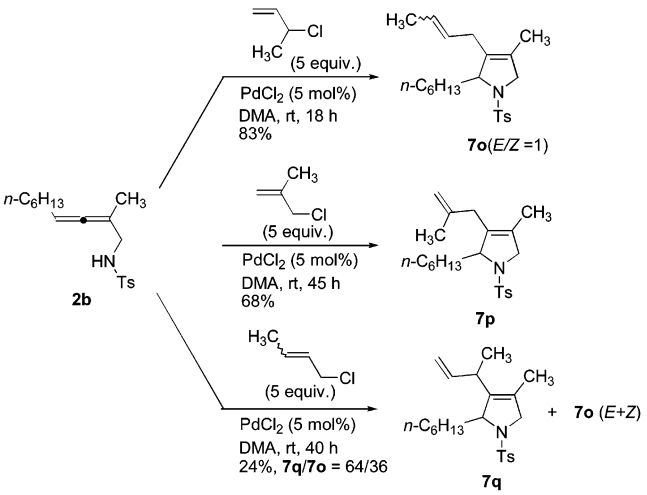
(18) Recently, Hiemstra et al. reported their results on the coupling-cyclization of allenes containing lactam and oxazolidinone moiety. The author proposed a Pd(0)-catalyzed pathway because of the experimental fact that a stoichiometric amount of π-allyl palladium chloride dimer could successfully promote the reaction to afford the products in moderate yield; see ref 6d.

(19) Treatment of allenic sulfonamide **2b** with 20 mol % of $AgNO_3$ afforded **15** in 96% yield.

(20) Redemann, C. D.; Rice, F. O.; Roberts, R.; Ward, H. P. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 244.

(21) Crystal data for **7i**: $C_{21}H_{23}NO_2S$, MW = 353.46, monoclinic, space group *P*2(1)/*n*, Mo Kα, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0484, wR2 = 0.1188, *a* = 11.4023(10) Å, *b* = 11.8131(10) Å, *c* = 14.3594(12) Å, α = 90°, β = 91.307(2)°, γ = 90°, *V* = 1933.7 (11) Å^3, *T* = 293 K, *Z* = 4, reflections collected/unique: 11463/4462 (R_{int} = 0.0477), no observation [$I > 2\sigma(I)$] 2996, parameters 297.

SCHEME 4

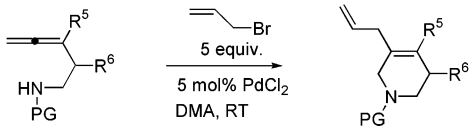


while the reaction of 1-chloro-2-butene underwent very slowly to afford **7q** together the formation of **7o**, indicating that the steric hindrance of the C−C double bond has an obvious effect on the reaction (Scheme 4). The formation of **7o** from the corresponding reaction of **2b** with 1-chloro-2-butene may be due to the in situ formation of 3-chloro-1-butene via isomerization. The reaction of **2b** with 3-chloro-2-methyl-1-propene provided desired product **7p** in a good yield.

Two examples of optically active 2,3-allenylamines (*S*)-**2m** and (R)-**2n** were prepared sucessfully on the basis of the synthetic route presented in Scheme 5.[23−25] Under the same reaction conditions, they were transformed to (*S*)-**7m**[26] and (*R*)-**7n**[26] in 88% and 92% yields, respectively, indicating that the axial chirality was transformed into the final products efficiently.

Subsequently, we wished to expand the current transformation from α-amino allenes to *β*-amino allenes. Thus, under the standard conditions successfully applied for the α-amino allenes, the reaction of *β*-amino allenes with allyl bromide was studied, and the results are summarized in Table 4. The protecting group of the nitrogen atom has much effect on the outcome of the reaction. We found that Ts (toluenesulfonyl) provides the best results among the protecting groups we tested, while Bz-protected *β*-amino allene **6d** afforded unidentified mixture (entries 1−5, Table 4). Similar to the results for α-amino allenes, the corresponding 3-alkyl-substituted *β*-amino allenes underwent the coupling−cyclization reaction smoothly to afford 1,2,3,6-tetrahydropyridine products **9** in good yields. The structure of the product was confirmed by the single-crystal X-ray diffraction study of **9b** (Figure 2 in the Supporting Information).[22]

TABLE 4. Pd-Catalyzed Coupling−Cyclization Reaction of *β*-Amino Allenes 6 with Allyl Bromide[a]



entry	substrate R^5	R^6	PG		reaction time (h)	yield of product[b] (%)
1	C_4H_9-*n*	CH_3	Ts	(**6a**)	12	91 (**9a**)
2	C_4H_9-*n*	CH_3	Ns	(**6b**)	24	77 (**9b**)
3	C_4H_9-*n*	CH_3	Ac	(**6c**)	20	45 (**9c**)
4[c]	C_4H_9-*n*	CH_3	Ac	(**6c**)	24	47 (**9c**)
5	C_4H_9-*n*	CH_3	Bz	(**6d**)	96	*d*
6	C_4H_9-*n*	H	Ts	(**6e**)	5	76 (**9e**)
7	C_4H_9-*t*	CH_3	Ts	(**6f**)	96	46 (**9f**)[e]
8[f]	C_4H_9-*t*	CH_3	Ts	(**6f**)	48	79 (**9f**)
9	C_4H_9-*t*	H	Ts	(**6g**)	30	79 (**9g**)
10	H	CH_3	Ts	(**6h**)	171[g]	14 (**9h**)[g,h]
11	CH_3	CH_3	Ts	(**6i**)	4	80 (**9i**)
12	allyl	CH_3	Ts	(**6j**)	17	97 (**9j**)
13	H	H	Ts	(**6k**)	25	32 (**9k**)
14	C_4H_9-*n*	C_3H_7-*n*	Ts	(**6l**)	4	67 (**9l**)

[a] The reaction was carried out at rt using **6** (0.50 mmol), allyl bromide (5 equiv), and $PdCl_2$ (5 mol %) in DMA (3 mL). [b] Isolated yield based on **6**. [c] 5 mol % of $PdCl_2(PhCN)_2$ was used as the catalyst. [d] A complex mixture of products was formed. [e] 34% of **6f** was recovered. [f] The reaction was performed at 50−55°C. [g] rt, 48 h; 50°C, 72 h; 70°C, 51 h. [h] 31% of **6h** was recovered.

Mechanistic Considerations. Scheme 6 illustrates the mechanism which involves Pd(II) species.[6a] It is assumed that the transformation occurs by an initial intramolecular aza-palladation reaction to form vinyl palladium intermediate **10**, followed by insertion of the carbon−carbon bond of allylic halide to give a *σ*-carbon−palladium intermediate **11**, which undergoes *β*-elimination affording dihydropyrrole product **7**. A Pd(0) mechanism[6b,c] which involves a *π*-allyl palladium intermediate **12** is illustrated in Scheme 7. There are two alternative pathways: in pathway a, the reaction starts with the coordination of *π*-allyl palladium complex **12** with **2** and subsequent cyclic aza-palladation of **2** affords vinyl *π*-allyl palladium intermediate **13**, which undergoes reductive elimination to provide product **7** and regenerate Pd(0); in pathway b, the carbopalladation of *π*-allyl palladium complex **12** with one of the two double bonds in allene provides a new *π*-allyl palladium intermediate **14**, which upon the subsequent nucleophilic substitution furnishes **7** and regenerates Pd(0) species.

To clarify the mechanism of the reaction, the reactions employing a stoichiometric amount of *π*-allyl palladium chloride dimer[17] as the allylating agent were performed (Scheme 8).[18] The reaction of bis(η^3-allyl)di-μ-chlorodipalladium[17] with **2b** proceeded slowly to provide **7b** in a relatively low yield together with the cycloisomerization product **15.**[19] A similar phenomenon was observed when bis(1-methyl-η^3-allyl)di-μ-chlorodipalladium[17] was applied. However, the combined yield of **7b**, **7o**, and **15** was increased to 75% when 20 equiv of 3-chloro-1-butene was added. Thus, a useful corollary could be obtained: vinyl palladium complex **10** would rather undergo insertion reaction with the double bond of allylic halides than reductive elimination or reduction indicating that the Pd(0)-catalyzed mechanism is probably less competitive

(22) Crystal data for **9b**: $C_{19}H_{26}N_2O_4S$, MW = 378.48, monoclinic, space group *P*2(1)/*c*, Mo Kα, final *R* indices [$I > 2\sigma(I)$], R1 = 0.0608, wR2 = 0.1249, a = 19.0973(16) Å, b = 7.8121(6) Å, c = 13.1877(11) Å, α = 90°, β = 91.457(2)°, γ = 90°, V = 1966.8 (3) Å^3, T = 293 K, Z = 4, reflections collected/unique: 11646/4577 (R_{int} = 0.0948), no observation [$I > 2\sigma(I)$] 2121, parameters 305.

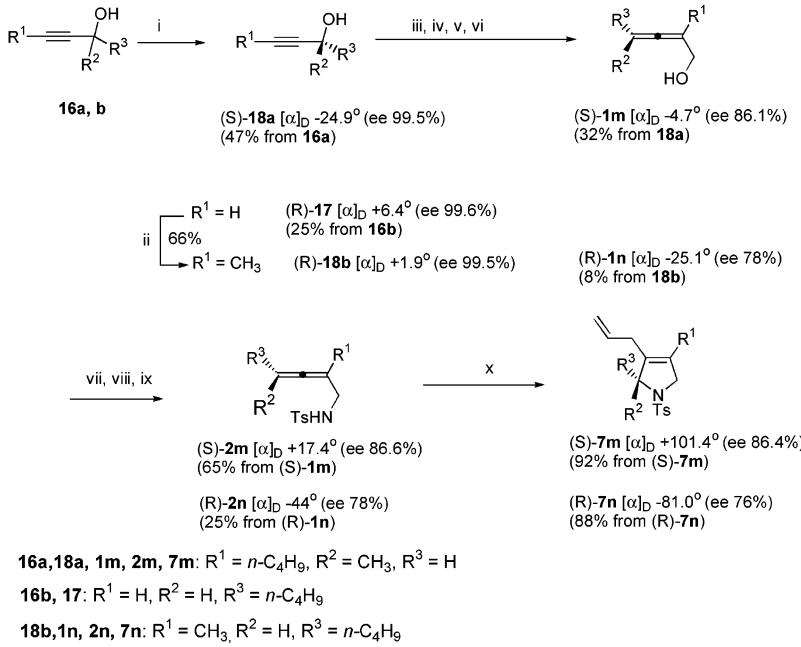
(23) Xu, D. W.; Li, Z, Y.; Ma. S. M. *Tetrahedron Lett.*, in press.

(24) (a) Marshall. J. A.; Robinson. E. D.; Zapata. A. *J. Org. Chem.* **1989**, *54*, 4, 5854. (b) Marshall. J. A.; Wang. X. *J. Org. Chem.* **1991**, *56*, 4913.

(25) (a) Burgess. K.; Jennings. L. D. *J. Am. Chem. Soc.* **1990**, *112*, 7434; (b) Witulski. B.; Zimmermann. A. *Synlett* **2002**, *11*, 1855.

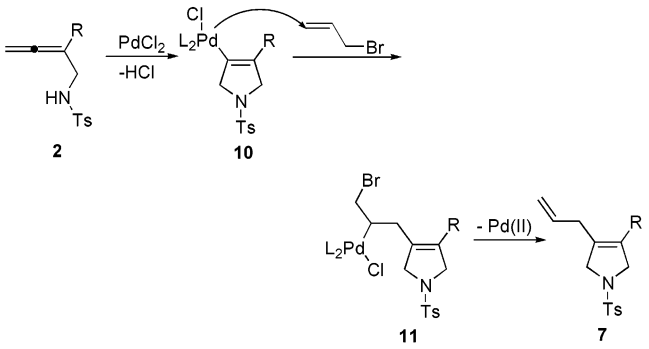
(26) The absolute configurations of (*S*)-**7m** and (*R*)-**7n** were tentatively assigned based on the stereochemical outcome of oxymetalation of optically active 2,3-allenoic acids, see refs 11e−f.

SCHEME 5[a]

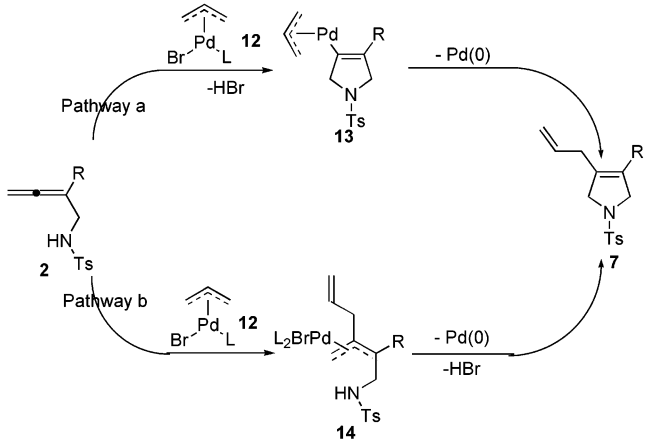


[a] Key: (i) Novozym 435, vinyl acetate, 70 °C; (ii) TBDMSCl, imid, DMF; *n*-BuLi, CH_3I; then 5% HF, CH_3CN; (iii) NaH, $ClCH_2COOH$; (iv) LDA, THF, −78 °C; (v) $NaIO_4$, MeOH; (vi) $LiAlH_4$, THF, 0 °C; (vii) phthalimide, DEAD, PPh_3, THF, 0 °C to rt; (viii) $N_2H_4 \cdot H_2O$, EtOH, reflux; (ix) NEt_3, CH_2Cl_2, TsCl, 0 °C to rt; (x) allyl bromide, 5 mol % $PdCl_2$, DMA, rt.

SCHEME 6. Pd(II)-Catalyzed Pathway



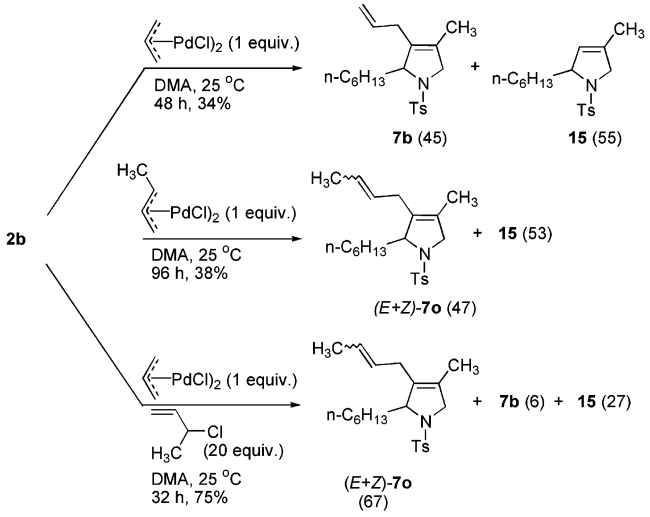
SCHEME 7. Pd(0)-Catalyzed Pathway



and the current reaction proceeds favorable via a Pd(II)-catalyzed pathway.

The Pd(II)-catalyzed pathway seemed to be further supported by the experimental facts outlined in Schemes

SCHEME 8



4 and 5. If the current transformation proceeded via the Pd(0)-catalyzed pathway illustrated in Scheme 7, the reaction of **2b** with 3-chloro-1-butene or 1-chloro-2-butene should provide identical products. Furthermore, the Pd(0)-involved π-allyl palladium pathway would result in low efficiency in chirality transformation of (*S*)-**2m** and (*R*)-**2n**.[11f] However, the experimental facts were in sharp contrast with these predictions. Thus, the Pd(0)-catalyzed pathway is less competitive, and this transformation proceeds more likely via a Pd(II)-catalyzed pathway.

Conclusion

We have developed an efficient synthesis of 2,5-dihydro-1*H*-pyrroles or 1,2,3,6-tetrahydropyridines in good yields via the palladium-catalyzed coupling−cy-

clization of α- or β-amino allenes with allylic halides. Further investigation indicated that the transformation may proceed via a palladium(II)-catalyzed pathway.

Experimental Section

Starting Materials. Synthesis of α-Amino Allenes. Compounds **2a**−**c** were prepared from the amination reaction of sulfonamide with 2,3-dienyl bromides, which were prepared from the corresponding reaction of 2,3-dien-1-ols with PBr_3 as reported.[14]

***N*-(2-Benzylbuta-2,3-dienyl)-*p*-toluenesulfonamide (2a).** The reaction of 2-benzylbuta-2,3-dien-1-ol (**1a**) (3.205 g, 20.0 mmol), pyridine (0.20 mL), and phosphorus tribromide (0.75 mL, 7.97 mmol) afforded 3.364 g (75%) of allenyl bromide:[14b] liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.10 (m, 5 H), 5.00−4.65 (m, 2 H), 3.88 (d, J = 1.5 Hz, 2 H), 3.45 (t, J = 2.5 Hz, 2 H); MS (*m*/*z*) 224 ($M^+(Br^{81})$, 5.69), 222 ($M^+(Br^{79})$, 5.66), 143 (100); IR (neat) 1953, 1601 cm^{-1}.

A mixture of the above-prepared allenyl bromide (1.682 g, 7.54 mmol), potassium carbonate (1.264 g, 9.16 mmol), *p*-toluenesulfonamide (5.665 g, 33.1 mmol), and 40 mL of acetone was heated to reflux for 5 h. After being cooled to room temperature, ether was added. The mixture was washed with brine (three times) and dried over anhydrous sodium sulfate. Evaporation and flash chromatography on silica gel (petroleum ether/ether = 3/1) produced 1.053 g (45%) of **2a**: solid; mp 71−73°C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2 H), 7.33−7.15 (m, 5 H), 7.10−7.00 (m, 2 H), 4.82−4.64 (m, 2 H), 4.49 (bs, 1 H), 3.54−3.38 (m, 2 H), 3.25−3.20 (m, 2 H), 2.41 (s, 3 H); MS (*m*/*z*) 313 (M^+, 0.52), 91 (100); IR (neat) 3262, 1961, 1597 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_2S$: C, 68.98; H, 6.11; N, 4.47. Found: C, 68.92; H, 6.00; N, 4.38.

Synthesis of 2-(Benzenesulfonylamino)-3-butyl-6-methylhepta-3,4-dienoic Acid Methyl Ester (2d).[15] Typical procedure: To a solution of diisopropylamine (0.262 g, 2.59 mmol) in 3 mL of THF was added dropwise *n*-BuLi (1.30 mL, 2.0 M in cyclohexane, 2.60 mmol) with cooling (ice bath). After being stirred for 30 min at 0 °C, the mixture was cooled to −78 °C with a dry ice−acetone bath. To this freshly prepared LDA solution was added a solution of propargylic ester (**3**) (0.320 g, 0.88 mmol) in 5 mL of THF. After vigorous stirring for 10 min, a solution of anhydrous zinc chloride (0.154 g, 1.13 mmol) in 2 mL of THF was added, and the reaction was allowed to warm to room temperature overnight. The reaction was then diluted with ether (15 mL) and hydrolyzed with 1 N HCl (15 mL). The aqueous phase was extracted with ether, and the combined organic phase was dried over anhydrous sodium sulfate. After removal of the solvent in vacuo, the crude product was dissolved in ether and the solution was cooled to −50 °C. Then a freshly prepared diazomethane solution in ether[20] was added. After stirring for further 10 min, the solvent was evaporated and the crude product was purified by flash chromatography on silica gel (petroleum ether/ether = 2/1) to afford 0.201 g (60%) of **2d**: solid; mp 69−71°C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2 H), 7.16 (d, J = 8.2 Hz, 2 H), 5.18−5.10 (m, 1 H), 5.04 (d, J = 9.8 Hz, 1 H), 4.22 (d, J = 9.8 Hz, 1 H), 3.36 (s, 3 H), 2.29 (s, 3 H), 2.15−2.05 (m, 1 H), 1.95−1.78 (m, 2 H), 1.25−1.05 (m, 4 H), 0.81 (d, J = 6.6 Hz, 6 H), 0.74 (t, J = 7.0 Hz, 3 H); MS (*m*/*z*) 380 (M^++1, 3.24), 379 (M^+, 0.25), 209 (100); IR (neat) 3435, 1967, 1746 cm^{-1}. Anal. Calcd for $C_{20}H_{29}NO_4S$: C, 63.30; H, 7.70; N, 3.69. Found: C, 63.16; H, 7.76; N, 3.52.

α-Amino allenes **2e**−**n** and β-amino allenes **6a**−**l** were prepared from the corresponding amines, which were prepared via the Mitsunobu amination of the related allenols.[7b,16]

***N*-(2-Methyl-3-butyl-3,4-pentadienyl)-*p*-toluenesulfonamide (6a).** Typical procedure: To a solution of 2-methyl-3-butylpenta-3,4-dien-1-ol (**4a**) (1.542 g, 10.0 mmol), triphenylphosphine (3.932 g, 15.0 mmol), and phthalimide (1.471 g, 10.0 mmol) in 40 mL of anhydrous THF was added dropwise diethyl azodicarboxylate (6.565 g, 40% in toluene, 15.0 mmol) with cooling (ice bath). The resulting yellow solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo followed by the addition of ether. The resulting solid was filtered off. After evaporation, the filtrate was purified by flash chromatography on silica gel to afford 2.573 g (91%) of **5a**: solid; mp 52−53 °C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80−7.72 (m, 2 H), 7.68−7.60 (m, 2 H), 4.68−4.50 (m, 2 H), 3.66 (dd, J = 13.4 and 6.4 Hz, 1 H), 3.50 (dd, J = 13.4 and 8.6 Hz, 1 H), 2.50−2.38 (m, 1 H), 2.00−1.76 (m, 2 H), 1.40−1.08 (m, 4 H), 0.96 (d, J = 6.7 Hz, 3 H), 0.80 (t, J = 7.2 Hz, 3 H); MS (*m*/*z*) 283 (M^+, 9.67), 160 (100); IR (neat) 1953, 1769, 1714, 1396, 1041 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.37 H, 7.49; N, 4.87.

A solution of phthalimide (**5a**) (1.270 g, 4.49 mmol) and hydrazine hydrate (0.55 mL, 85% purity, 9.49 mmol) in 20 mL of absolute EtOH was heated to reflux for 1.5 h resulting in the formation of a white precipitate. Then 2 mL of concentrated HCl was added with cooling (ice bath), and the precipitate was removed by filtration. The filtrate was brought to pH >10 by the addition of 1 N NaOH and extracted with ether (50 mL × 3). The combined extracts were dried over anhydrous magnesium sulfate. After concentration in vacuo, the crude product was used without further purification. To a solution of the above crude product and triethylamine (0.70 mL, 5.06 mmol) in 20 mL of dichloromethane was added tosyl chloride (0.855 g, 4.48 mmol) in one portion with cooling (ice bath). The mixture was allowed to warm to room temperature overnight. After removal of the solvent, the mixture was submitted to flash chromatography on silica gel to produce 1.018 g (74%) of **6a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 4.72−4.60 (m, 3 H), 3.00−2.80 (m, 2 H), 2.41 (s, 3 H), 2.16−2.04 (m, 1 H), 1.82−1.70 (m, 2 H), 1.35−1.20 (m, 4 H), 0.96 (d, J = 6.3 Hz, 3 H), 0.85 (t, J = 7.1 Hz, 3 H); MS (*m*/*z*) 307 (M^+, 4.14), 152 (100); IR (neat) 3291, 1951 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20; N, 4.56. Found: C, 65.98; H, 8.00; N, 4.47.

(*S*)-*N*-(2-Butylpent-2,3-dienyl)-*p*-toluenesulfonamide ((*S*)-2m). The reaction of (*S*)-2-butylpenta-2,3-dien-1-ol ((*S*)-**1m**) (1.203 g, 8.6 mmol, 86% ee),[23,24] triphenylphosphine (3.467 g, 13.2 mmol), phthalimide (1.328 g, 8.9 mmol), and diethyl azodicarboxylate (5.6 mL, 40% in toluene, 12.9 mmol) afforded 2.269 g of the corresponding phthalimide. The resulting phthalimide was treated with hydrazine hydrate (0.96 mL, 85% purity, 16.6 mmol) in MeOH followed by tosylation and then recrystallized three times to produce 1.628 g (overall yield: 65%) of (*S*)-**2m**: solid; mp 47−49 °C (*n*-hexane); 87% ee (detemined by HPLC analysis, Chiralcel AD, 5% *i*-PrOH in hexane, 230 nm), t_R 20.71 (*S*-isomer), 22.58 (R-isomer); $[\alpha]^{20}_D$ +17.4 (c = 0.98, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2 H), 7.30 (d, J = 7.8 Hz, 2 H), 5.21−5.12 (m, 1 H), 4.47 (t, J = 5.4 Hz, 1 H), 3.53−3.34 (m, 2 H), 2.42 (s, 3 H), 1.90−1.78 (m, 2 H), 1.59 (d, J = 3.6 Hz, 3 H), 1.35−1.15 (m, 4 H), 0.84 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 200.20, 143.20, 136.79, 129.49, 127.05, 100.44, 90.22, 44.37, 29.78, 29.35, 22.03, 21.40, 14.50, 13.77; MS (*m*/*z*) 293 (M^+, 1.61), 91 (100); IR (neat) 3266, 1925, 1597 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.36; H, 7.78; N, 4.78.

(*R*)-*N*-(2-Methylocta-2,3-dienyl)-*p*-toluenesulfonamide ((*R*)-2n). The reaction of (*R*)-2-methylocta-2,3-dien-1-ol ((*R*)-**1n**) (0.03 g, 0.21 mmol, 78% ee), triphenylphosphine (0.090 g, 0.34 mmol), phthalimide (0.037 g, 0.25 mmol), and diethyl azodicarboxylate (0.14 mL, 40% in toluene, 0.32 mmol) afforded 0.044 g of the corresponding phthalimide. The resulting phthalimide was treated with hydrazine hydrate (0.02 mL, 85% purity, 0.35 mmol) in MeOH followed by tosylation to produce 0.023 g (overall yield: 25%) of (*R*)-**2n**: liquid; 78% ee (detemined by HPLC analysis, Chiralcel AS, 5% *i*-PrOH in hexane, 230 nm), t_R 44.62 (*S*-isomer), 49.84 (*R*-isomer); $[\alpha]^{20}_D$ −44 (c = 0.24, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2 H), 7.20 (d, J = 8.7 Hz, 2 H), 5.05−4.98 (m,

1 H), 4.66 (brs, 1 H), 3.41−3.27 (m, 2 H), 2.33 (s, 3 H), 1.84−1.72 (m, 2 H), 1.52 (d, J = 2.7 Hz, 3 H), 1.26−1.15 (m, 4 H), 0.78 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 199.38, 143.20, 136.86, 129.50, 127.01, 95.92, 94.21, 45.53, 31.02, 28.45, 21.99, 21.39, 16.74, 13.75; MS (*m*/*z*) 293 (M^+, 1.25), 155 (100); IR (neat) 3283, 1969, 1599 cm^{-1}. Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.90; H, 7.73; N, 4.62.

Palladium(II)-Catalyzed Coupling−Cyclization of α-Amino Allenes 2a−n with Allylic Halides. Synthesis of 2,5-Dihydropyrrole Products 7. 3-Allyl-4-benzyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (7a). Typical procedure: A mixture of α-amino allene **2a** (0.048 g, 0.15 mmol), allyl bromide (0.112 g, 0.93 mmol), and $PdCl_2$ (5 mol %) was stirred at 25 °C in 1 mL of DMA for 4 h. When the reaction was complete, ether was added. The reaction mixture was washed with brine (three times) and dried over Na_2SO_4. After evaporation, the residue was subjected to column chromatography on silica gel (petroleum ether/ ether = 5/1) to produce 0.033 g (61%) of **7a**: solid; mp 71−73 °C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2 H), 7.40−7.10 (m, 5 H), 7.08−6.95 (m, 2 H), 5.79−5.59 (m, 1 H), 5.15−4.90 (m, 2 H), 4.10 (s, 2 H), 3.98 (s, 2 H), 3.35 (s, 2 H), 2.88 (d, J = 6.2 Hz, 2 H), 2.45 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.56, 138.11, 134.24, 134.18, 130.77, 129.95, 129.92, 128.84, 128.51, 127.63, 126.72, 117.03, 57.58, 57.48, 32.63, 30.86, 21.80; MS (*m*/*z*) 353 (M^+, 3.87), 91 (100); IR (KBr) 1640 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_2S$: C, 71.35; H, 6.56; N, 3.96. Found: C, 71.26; H, 6.45; N, 3.77.

***N*-Allyl-*N*-(2-benzylbuta-2,3-dienyl)-*p*-toluenesulfonamide 8a.** When K_2CO_3 was added as the base, the reaction of amino allene **2a** (0.046 g, 0.15 mmol), allyl bromide (0.111 g, 0.92 mmol), K_2CO_3 (0.033 g, 0.24 mmol), and $PdCl_2$ (5 mol %) at 25 °C in 2.5 mL of THF for 23 h produced 0.023 g (44%) of **7a** and 0.009 g (17%) of N-allylation product **8a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.56 (m, 2 H), 7.30−7.10 (m, 7 H), 5.55−5.40 (m, 1 H), 5.05−4.96 (m, 2 H), 4.62−4.55 (m, 2 H), 3.75 (d, J = 6.7 Hz, 2 H), 3.68 (s, 2 H), 3.23 (s, 2 H), 2.36 (s, 3 H); MS (*m*/*z*) 353 (M^+, 8.43), 224 (100); IR (neat) 1637 cm^{-1}; HRMS calcd for $C_{21}H_{23}NO_2S$ 353.1450, found 353.1446.

Compounds **7b**−**n** were prepared similarly.

(*S*)-3-Allyl-2-methyl-4-butyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole ((*S*)-7m). The reaction of (*S*)-**2m** (0.093 g, 0.32 mmol, 87% ee), allyl bromide (0.14 mL, 1.58 mmol), and $PdCl_2$ (5 mol %) at 25 °C in 2 mL of DMA for 2 h produced 0.097 g (92%) of (*S*)-**7m**: liquid; 86% ee (detemined by HPLC analysis, Chiralcel AS, 5% *i*-PrOH in hexane, 230 nm), t_R 16.73 (*S*-isomer), 20.67 (*R*-isomer); $[\alpha]^{20}_D$ +101.4 (c = 1.04, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.7 Hz, 2 H), 5.53−5.37 (m, 1 H), 4.90 (dd, J = 1.5, 10.2 Hz, 1 H), 4.78 (dd, J = 1.5, 17.1 Hz, 1 H), 4.37 (t, J = 5.1 Hz, 1 H), 4.08−3.90 (m, 2 H), 2.80 (dd, J = 4.8, 15.3 Hz, 1 H), 2.53 (dd, J = 7.2, 15.6 Hz, 1 H), 2.39 (s, 3 H), 1.93 (t, J = 6.6 Hz, 2 H), 1.33 (d, J = 6.6 Hz, 3 H). 1.28−0.98 (m, 4 H), 0.79 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ = 143.15, 134.58, 134.29, 132.85, 131.08, 129.45, 127.29, 116.03, 64.80, 56.50, 29.78, 29.36, 25.62, 22.10, 21.41, 21.22, 13.79; MS (*m*/*z*) 333 (M^+, 0.79), 318 (100); IR (neat) 1638, 1598 cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_2S$: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.80; H, 8.29; N, 4.67.

(*R*)-3-Allyl-2-butyl-4-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole ((*R*)-7n). The reaction of (*R*)-**2n** (0.020 g, 0.07 mmol, 78% ee), allyl bromide (0.03 mL, 0.34 mmol), and $PdCl_2$ (5 mol %) at 25 °C in 1.5 mL of DMA for 3 h produced 0.02 g (88%) of (*R*)-**7n**: liquid; 76% ee (detemined by HPLC analysis, Chiralcel OC, 3% *i*-PrOH in hexane, 230 nm), t_R 17.53 (*R*-isomer), 20.41 (*S*-isomer); $[\alpha]^{20}_D$ −81.0 (c = 0.55, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 2 H), 5.41−5.31 (m, 1 H), 4.82 (dd, J = 1.2, 10.2 Hz, 1 H), 4.69 (dd, J = 1.8, 16.8 Hz, 1 H), 4.35 (s, 1 H), 3.90 (s, 2 H), 2.74 (dd, J = 4.8, 15.3 Hz, 1 H), 2.38 (dd, J = 7.5, 16.5 Hz, 1 H), 2.32 (s, 3 H), 1.85−1.72 (m, 1 H), 1.53−1.20 (m, 1 H), 1.45 (s, 3 H). 1.33−0.94 (m, 4 H), 0.78 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ = 143.03, 134.82, 133.99, 130.85, 129.39, 127.64, 127.18, 115.86, 68.47, 59.04, 32.56, 29.45, 25.07, 22.64, 21.37, 14.04, 11.09; MS (*m*/*z*) 333 (M^+, 0.26), 276 (100); IR (neat) 1637, 1608 cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_2S$: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.03; H, 8.27; N, 4.40.

Palladium(II)-Catalyzed Coupling−Cyclization of β-Amino Allenes 6a−l with Allylic Halides. Synthesis of 1,2,3,6-Tetrahydropyridine Products 9. 5-Allyl-4-butyl-3-methyl-1-(*p*-toluenesulfonyl)-1,2,3,6-tetrahydropyridine (9a). The reaction of **6a** (0.083 g, 0.27 mmol), allyl bromide (0.167 g, 1.38 mmol), and $PdCl_2$ (5 mol %) in 1.6 mL of DMA at 25 °C for 12 h produced 0.085 g (91%) of **9a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H), 5.70−5.50 (m, 1 H), 5.02−4.89 (m, 2 H), 3.56 (d, J = 15.5 Hz, 1 H), 3.15 (dd, J = 11.1 and 3.6 Hz, 1 H), 3.06 (d, J = 15.5 Hz, 1 H), 2.80−2.65 (m, 2 H), 2.53 (dd, J = 15.3 and 6.3 Hz, 1 H), 2.36 (s, 3 H), 2.32−2.18 (m, 1 H), 2.17−2.00 (m, 1 H), 1.90−1.65 (m, 1 H), 1.40−1.05 (m, 4 H), 1.04 (d, J = 6.8 Hz, 3 H), 0.80 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.35, 136.03, 135.32, 133.16, 129.57, 127.71, 123.40, 115.79, 49.76, 47.63, 34.78, 32.45, 30.84, 29.68, 22.86, 21.51, 17.84, 13.98; MS (*m*/*z*) 347 (M^+, 3.46), 306 (100); IR (neat) 1633 cm^{-1}; HRMS calcd for $C_{20}H_{29}NO_2S$ 347.1919, found 347.1924.

Compounds **9b**−**l** were prepared similarly.

Mechanistic Study. (1) The reaction of amino allene **2b** (0.052 g, 0.16 mmol) and bis(η^3-allyl)-di-μ-chlorodipalladium (0.055 g, 0.15 mmol) in DMA (1.0 mL) at room temperature for 48 h afforded 0.019 g (34%) of **7b** and **15** (**7b**/**15** = 45:55) as a mixture.

(2) The reaction of amino allene **2b** (0.108 g, 0.34 mmol) and bis(1-methyl-η^3-allyl)di-μ-chlorodipalladium (0.146 g, 0.37 mmol) in DMA (2.0 mL) at room temperature for 96 h afforded 0.044 g (38%) of **7o** and **15** (**7o**/**15** = 47:53) as a mixture.

(3) The reaction of amino allene **2b** (0.089 g, 0.28 mmol), 3-chlorobut-1-ene (0.506 g, 5.59 mmol), and bis(η^3-allyl)di-μ-chlorodipalladium (0.100 g, 0.27 mmol) in DMA (2.0 mL) at room temperature for 32 h afforded 0.075 g (75%) of **7b**, **7o** and **15** (**7b**/**7o**/**15** = 6:67:27) as a mixture.

Synthesis of Authentic 15.[8,19] The reaction of **2b** (0.072 g, 0.22 mmol) and $AgNO_3$ (20 mol %) at 25 °C in 2.5 mL of acetone for 5 h produced 0.069 g (96%) of **15**.

2-Hexyl-4-methyl-1-(*p*-toluenesulfonyl)-2,5-dihydro-1*H*-pyrrole (15): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2 H), 7.29 (d, J = 8.2 Hz, 2 H), 5.22−5.16 (m, 1 H), 4.45−4.34 (m, 1 H), 4.05−3.92 (m, 2 H), 2.41 (s, 3 H), 1.85−1.60 (m, 2 H), 1.73 (s, 3 H), 1.42−1.19 (m, 8 H), 0.87 (t, J = 6.7 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.42, 135.08, 134.30, 129.84, 127.58, 123.87, 67.94, 58.75, 36.60, 32.08, 29.55, 24.79, 22.86, 21.75, 14.35, 14.18; MS (*m*/*z*) 321 (M^+, 11.96), 236 (100); IR (neat) 1598 cm^{-1}; HRMS calcd for $C_{18}H_{27}NO_2S$ 321.1763, found 321.1807.

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Supporting Information Available: Analytical data and ^{1}H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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