Palladium-Catalyzed Reactions of *N*-Allylbenzotriazoles with Amines: Intramolecular Allylamination Routes to 2-Vinylpyrrolidines and 2-Vinylpiperidines

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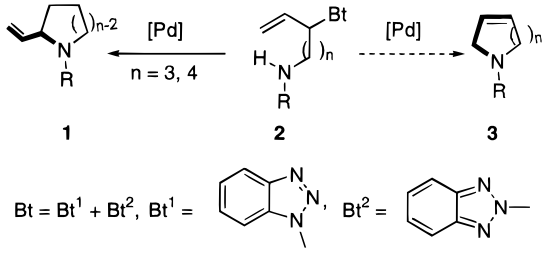
Reactions of allylbenzotriazole (**4a**−**d**) with 1-bromo-3-chloropropane, 1-bromo-2-methyl-3-chloropropane, epibromohydrin (**8**), and 1-bromo-4-chlorobutane afforded the corresponding α-substituted allylbenzotriazoles (**5a**−**d**, **9**, and **16a**,**b**), which with primary amines in one-pot sequences produce 2-vinylpyrrolidines (**7a**−**i**), 2-ethylpyrrole (**13**), and 2-vinylpiperidines (**18a**−**c**) in good yields under mild conditions.

Introduction

2-Vinylpyrrolidines and 2-vinylpiperidines are useful intermediates in organic synthesis,[1] and their structures are present in biologically active alkaloids.[2] Common routes to 2-vinylpyrrolidines and 2-vinylpiperidines include (i) silver(I), organolanthanide, or palladium-catalyzed cyclization of allenic amines;[1e,f,3] (ii) palladium-catalyzed transformations of *N*-tosyl-2-(1,3-butadienyl)aziridine;[4] (iii) ceric ammonium nitrate oxidative intramolecular amination of allylsilanes;[1i] (iv) Wittig reaction of 2-carboxyaldehydes;[1j,k,5] (v) intramolecular Mitsunobu reaction of γ-aminoallyl alcohols;[1h] and (vi) transition metal-catalyzed intramolecular allylamination of allyl acetates or allyl halides.[1f,6] Transition metal-catalyzed allylaminative cyclizations have led to important alkaloid skeletons,[6b,7] but the convenience of such reactions depends on the availability of the starting materials.

Scheme 1



Benzotriazole is a useful synthetic auxiliary in organic synthesis.[8] Transition metal-catalyzed allylic substitutions using benzotriazole as a leaving group are potentially advantageous because of the ease of preparation of α-substituted allylbenzotriazoles. Lithiation of allylbenzotriazole followed by reaction with various electrophiles (alkyl bromides or iodides, aldehydes, ketones, epoxides, imines, acyl chlorides, and isocyanates) affords a diversity of allylic substrates.[9] We previously reported that benzotriazole can be used as a leaving group in intermolecular palladium-catalyzed allylic aminations used to prepare substituted allylamines.[10] Intramolecular

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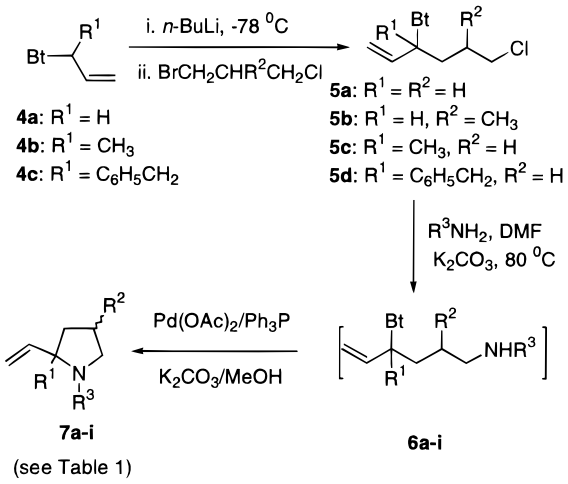
Table 1. Preparation of 2-Vinylpyrrolidines 7a−i

starting materials	substituents			cyclization conditions		products	overall yield (%)
	R^1	R^2	R^3	catalyst	temperature (°C)		
5a	H	H	$C_6H_5CH_2$	$Pd(OAc)_2/Ph_3P$	70	**7a**	85[a]
5a	H	H	$C_6H_5CH_2$	$(Ph_3P)_4Pd$	70	**7a**	80[b]
5a	H	H	$C_6H_5CH_2$	$(Ph_3P)_2PdCl_2$	70	**7a**	85[b]
5a	H	H	$C_6H_5CH_2$	$Pd(OAc)_2/Ph_3P$	25	**7a**	95[b]
5a	H	H	*n*-$C_{12}H_{25}$	$Pd(OAc)_2/Ph_3P$	25	**7b**	70[c]
5b	H	CH_3	*c*-C_6H_{11}	$(Ph_3P)_2PdCl_2$	25	**7c**	85[c]
5a	H	H	$C_6H_5CH(CH_3)$	$Pd(OAc)_2/Ph_3P$	25	**7d**	65[c]
5a	H	H	(*R*)-$C_6H_5CH(CH_3)$	$Pd(OAc)_2/Ph_3P$	25	**7e**	70[c]
5c	CH_3	H	$C_6H_5CH_2$	$Pd(OAc)_2/Ph_3P$	25	**7f**	70[c]
5a	H	H	$EtOCH_2CH_2$	$Pd(OAc)_2/Ph_3P$	50	**7g**	85[c]
5d	$C_6H_5CH_2$	H	$C_6H_5CH_2$	$Pd(OAc)_2/Ph_3P$	25	**7h**	75[c]
5a	H	H	$Et_2NCH_2CH_2$	$Pd(OAc)_2/Ph_3P$	50	**7i**	80[c]

[a] From **6**. [b] By GC from **6**. [c] Isolated yield from **5**.

Scheme 2



aminations of **2** could afford two types of heterocycles **1** or **3** (Scheme 1), depending on whether the amine attacks the α- or γ-position to benzotriazole. Structures of type **1** and **3** are both common structures in biologically active alkaloids.[2,11] We now document that intramolecular reactions of **2** ($n = 3$ or 4) indeed allow the syntheses of 2-vinylpyrrolidines (**1**, $n = 3$) and 2-vinylpiperidines (**1**, $n = 4$).

Results and Discussion

Syntheses of 2-Vinylpyrrolidines. Compounds **4a**−**c** were prepared as described in our previous papers.[9f,10] Lithiation of **4a**−**c** with *n*-BuLi at −78 °C followed by alkylation with 1-bromo-3-chloropropane or 1-bromo-3-chloro-2-methylpropane afforded the corresponding chlorides **5a**−**d** in good yields. Compound **5a** was reacted with benzylamine in DMF at 80 °C for 15 h to give compound **6a**. We used amine **6a** ($R^1 = R^2 = H$, $R^3 = C_6H_5CH_2$) as a model compound to optimize the intramolecular allylic amination conditions (Scheme 2, Table 1, entries i−iv). We found that **6a** cyclized under the previous[10] intermolecular reaction conditions (refluxing with K_2CO_3 and $Pd(OAc)_2/Ph_3P$ in methanol for 24 h) to provide 2-vinylpyrrolidine (**7a**) in 85% yield. However, the conversion **6a** → **7a** was also completed at 25 °C in 24 h, while its intermolecular counterpart did not proceed at room temperature.[10] Catalysts such as $(Ph_3P)_4Pd$ or $(Ph_3P)_2PdCl_2$ can be used instead of $Pd(OAc)_2/Ph_3P$ (Table 1). However, the use of other solvents (THF, DMF or toluene) without methanol inhibited the reaction; this is consistent with the previous conclusion[10] that methanol is the preferred solvent. The sequence **5a** → **6a** → **7a** can also proceed in one pot without purification of the intermediates **6a** simply by adding excess methanol (four volumes) and $Pd(OAc)_2/Ph_3P$ to the intermediate **6a** in DMF solution. Since the major solvent is methanol (methanol:DMF = 4:1, v/v) and the cyclization did not proceed in DMF, we concluded that the best cyclization conditions were to use methanol as solvent, $Pd(OAc)/Ph_3P$ as catalyst, K_2CO_3 as base to perform the reaction at room temperature and not to purify the intermediate amine **6**.

The reactions between chlorides **5a**−**d** and other amines were all carried out in DMF at 80 °C to give the expected **6** in situ, followed by the addition of methanol, $Pd(OAc)_2/Ph_3P$, and K_2CO_3, which resulted in the cyclization of **6** to **7**. The combined sequence of substitution and cyclization proceeded well at room temperature when the long chained molecules dodecylamine, cyclohexylamine, and α-methylbenzylamine were used to produce **7b**−**d** (65−85%). The sequence **5** → **6** → **7** was thus carried out successfully with a methyl group present in the γ-position (**5b**) or with a methyl (**5c**) or benzyl group (**5d**) on the α-carbon in the benzotriazole starting compounds; the products **7c**,**f**,**h** were each isolated in good yield. For 2-ethoxy-1-ethanamine and N^1,N^1-diethyl-1,2-ethanediamine, the cyclization step needed a higher temperature (50 °C) in order to form products **7g** and **7i** at a reasonable rate. Possibly the β-oxygen or β-nitrogen atom coordinates with the palladium, making complex **15** (Scheme 4) more stable and thus requiring a higher temperature for a reductive elimination to give **7g**,**i**. However, the cyclization of **10**, which has a free hydroxy group on the γ-carbon to benzotriazole, proceeded at room temperature (Scheme 3). The reason may be that the hydroxy group is conformationally unfavorable for coordination with the palladium in complex **15** (Scheme 4, $R^2 = OH$). No diasterioselectivity was observed in the cyclization step; product **7c** was formed as a mixture of *cis*- and *trans*-isomers (approximately 1:1 by GC analysis). We also tested the enantioselective induction of the cyclization step. Reaction of **5a** and optically active (*R*)-α-methylbenzylamine afforded the chiral precursor amine (**6e**), which cyclized in situ to give **7e** with low enantioselective induction (57:43 by GC analysis).[3b,12] Com-

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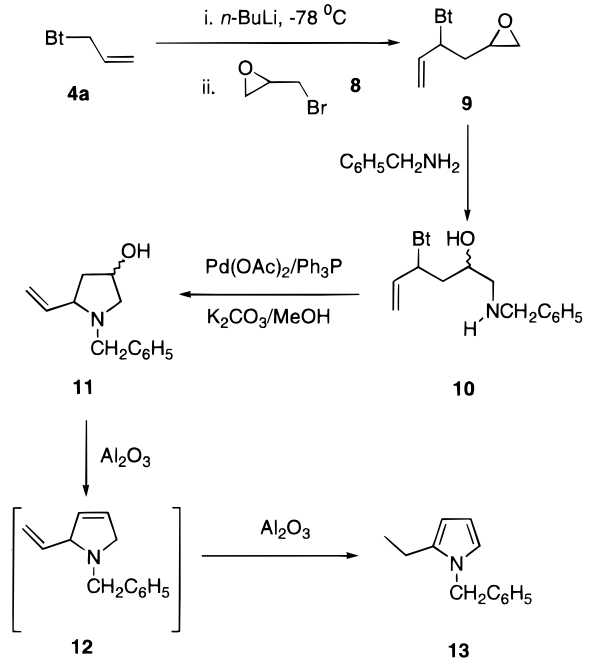
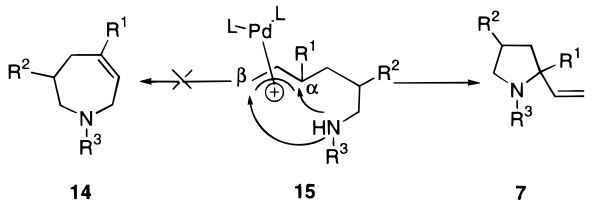
Scheme 3



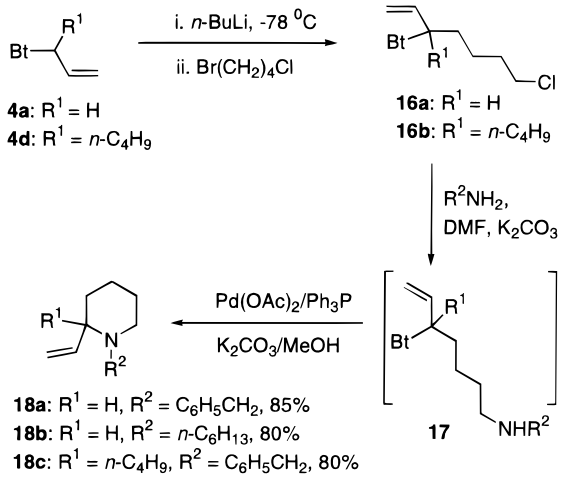
Scheme 4



pounds **7a**−**i** were characterized by ^{1}H and ^{13}C NMR spectra and by either CHN analysis or HRMS. Initially, compound **7f**, while showing a small peak at M − 1 together with large peaks at M − 15 and M − 31 on the mass spectrum, displayed nothing above M − 15 in the high-resolution mass spectrum. Possibly, under these conditions the loss of CH_3 from the initially formed radical cation proceeds easily to form the conjugated eniminium cation.

The presence of a hydroxy group on the γ-carbon to benzotriazole does not preclude the palladium-catalyzed cyclization. In fact, in the literature a hydroxy group was used to direct the regioselectivity of a transition metal-catalyzed allylic alkylation.[13] Compound **9** was prepared from **4a** and epibromohydrin (**8**) in 85% yield. Reaction of **9** and benzylamine in ethanol formed the β-hydroxyamine (**10**), which when subjected to the above cyclization conditions at room temperature for 48 h gave compound **11**, as detected by GC-MS. On column chromatography, compound **11** was converted into the 2-ethylpyrrole (**13**, Scheme 3), probably by elimination of water to give **12**, and subsequent isomerization to **13**.[14] 2-Vinyl-4-hydroxypyrrolidine (**11**) is potentially useful as an

Scheme 5



intermediate in the synthesis of indolizidinones and nine-membered ring lactams.[1d,g,15]

The reaction mechanism is evidently similar to that of previously reported allylic aminations.[6b,7h,16] Oxidative addition of allylbenzotriazole (**6**) to palladium(0) first forms complex **15** (Scheme 4), which can react with an intramolecular amine in two ways: (i) α-position attack to form a five-membered ring product **7** or (ii) γ-position attack to form a seven-membered ring compound **14**. In a recent paper, it was reported that a tertiary amine in the homoallylic position directed nucleophilic substitution to the terminus of the allylic moiety proximal to the tertiary amine.[17] This is consistent with our results. In the above reactions, the amino group regioselectively attacks the α-position to give five-membered ring products **7a**−**i**. The region selectivity of the intramolecular reaction is controlled by the favorably entropy of formation of a five- or six-membered ring, while in the intermolecular reaction the amine prefers to attack the less substituted carbon.[10]

Syntheses of 2-Vinylpiperidines. Similar intramolecular reactions were used for the synthesis of 2-vinylpiperidines (**18a**−**c**) (Scheme 5). Compounds **16a**,**b** were prepared from 1-bromo-4-chlorobutane and **4a**,**d**, respectively. The reactions of **16a**,**b** with benzylamine and *n*-hexylamine gave the corresponding intermediates **17**. Cyclizations of **17** under the standard conditions afforded the six-membered ring 2-vinylpiperidines (**18a**−**c**) in good yields. The reaction mechanism is similar to that for the formation of **7** (Scheme 4).

In conclusion, we have extended our benzotriazole methodology to palladium-catalyzed intramolecular allylamination reactions, which can readily be applied to the synthesis of five- and six-membered nitrogen heterocycles. The presence of a substitutent at the α- or γ-position to benzotriazole did not affect the cyclization, and both α- and β-substituted primary amines can be used.

Experimental Section

General Comments. Melting points were measured on a hot-stage microscope and are uncorrected. ^{1}H and ^{13}C NMR

(12) For the case of chiral amines and chiral amino acids in reductive eliminations of palladium complex with the formation of C−N bonds, see: (a) Wagaw, S.; Rennels, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 8451. (b) Ma, D.; Yao, J. *Tetrahedron*: *Asymmetry* **1996**, *7*, 3075. (c) Humphries, M. E.; Clark, B. P.; Williams, J. M. J. *Tetrahedron*: *Asymmetry* **1998**, *9*, 749.

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(16) Reductive eliminations of palladium complexes with the formation of C−N bonds have recently been reviewed by Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2047.

(17) Krafft, M. E.; Wilson, A. M.; Fu, Z.; Procter, M. J.; Dasse, O. A. *J. Org. Chem.* **1998**, *63*, 1748.

data were collected on a Gemini 300 MHz NMR spectrometer (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Compounds **4a**−**d** were prepared using literature methods.[10]

General Procedure for the Preparation of Compounds 5a−d, 9, and 16a,b. Under the protection of N_2, allylbenzotriazole (**4a**, 4.0 g, 25.2 mmol) was dissolved in anhydrous THF (150 mL) and cooled to −78 °C with a dry ice−acetone bath. This was followed by addition of *n*-BuLi (1.5 N in hexanes, 18 mL, 27 mmol) over 30 min; the resulting deep blue mixture was stirred at this temperature for another 2 h. Then 1-bromo-3-chloropropane (5.0 g, 34 mmol) was added and the reaction mixture was allowed to warm to room temperature overnight. The solvents were removed under vacuum, and the residue was dissolved in CH_2Cl_2 (80 mL) and then washed with a saturated NH_4Cl aqueous solution (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layer was dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel (eluent: hexanes:EtOAc 100:5) to afford **5a** (5.3 g, 89%).

1-[1-(3-Chloropropyl)-2-propenyl]-1*H*-1,2,3-benzotriazole (5a): colorless oil; ^{1}H NMR δ 1.81−1.84 (m, 2H), 2.49−2.53 (m, 2H), 3.50−3.57 (t, 2H, J = 5.2 Hz), 5.26 (dd, 1H, J = 3.6, 17.2 Hz), 5.33 (dd, 1H, J = 4.2, 10.6 Hz), 5.38−5.42 (m, 1H), 6.25−6.38 (m, 1H), 7.37−7.56 (m, 3H), 8.09 (d, 1H, J = 7.1 Hz); ^{13}C NMR δ 28.8, 30.7, 44.0, 61.6, 109.9, 118.2, 120.0, 123.9, 127.1, 135.3, 138.4, 146.2. Anal. Calcd for $C_{12}H_{14}N_3Cl$: C, 61.15; H, 5.99; N, 17.83. Found: C, 61.17; H, 6.09; N, 18.02.

1-[1-(3-Chloro-2-methylpropenyl)-1*H*-1,2,3-benzotriazole (5b): mixture of two isomers, colorless oil (81%); ^{1}H NMR δ 1.07 (d, 3H, J = 6.6 Hz) [minor isomer 0.99 (d, 3H, J = 6.5 Hz), 1.52−1.62 (m, 1H), 1.96−2.05 (m, 1H), 2.59−2.69 (m, 1H), 3.41 (d, 2H, J = 5.1 Hz), 5.18 (d, 1H, J = 17.1 Hz), 5.28 (d, 1H, J = 11.6 Hz), 5.42−5.53 (m, 1H), 6.17 (ddd, 1H, J = 6.1, 10.9, 17.8 Hz), 7.36 (t, 1H, J = 7.8 Hz), 7.46 (t, 1H, J = 7.8 Hz), 7.54 (d, 1H, J = 8.4 Hz), 8.07 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ 17.0 (minor isomer 18.0), 31.6, 37.4 (37.3), 50.8 (50.0), 59.8 (60.0), 109.9, 117.8, 120.1, 123.9, 127.2, 132.2, 135.6 (135.5), 146.1. Anal. Calcd for $C_{13}H_{16}N_3Cl$: C, 62.52; H, 6.46; N, 16.83. Found: C, 62.54; H, 6.92; N, 17.04.

1-[1-(3-Chloropropyl)-1-methyl-2-propenyl]-1*H*-1,2,3-benzotriazole (5c): colorless oil (80%); ^{1}H NMR δ 1.48−1.54 (m, 1H), 1.95−2.02 (m, 4H), 2.41−2.61 (m, 2H), 3.42−3.58 (m, 2H), 5.25 (dd, 1H, J = 2.5, 17.6 Hz), 5.41 (dd, 1H, J = 2.8, 10.1 Hz), 6.22 (dd, 1H, J = 10.7, 17.5 Hz), 7.34−7.41 (m, 2H), 7.64 (d, 1H, J = 8.3 Hz), 8.06 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ 24.9, 26.7, 36.6, 44.6, 65.5, 112.2, 115.6, 119.8, 123.4, 126.5, 131.9, 140.4, 146.5. Anal. Calcd for $C_{13}H_{16}N_3Cl$: C, 62.52; H, 6.46; N, 16.83. Found: C, 62.78; H, 6.77; N, 16.35.

1-[1-(3-Chloropropyl)-1-benzyl-2-propenyl]-1*H*-1,2,3-benzotriazole (5d): colorless oil (85%); ^{1}H NMR δ 1.52−1.62 (m, 1H), 1.75−1.85 (m, 1H), 2.32−2.45 (m, 1H), 2.52−2.61 (m, 1H), 3.52 (t, 2H, J = 6.9 Hz), 3.58 and 3.68 (ABq, 2H, J = 13.8 Hz), 5.26 (d, 1H, 17.6 Hz), 5.54 (d, 1H, 10.9 Hz), 6.21 (dd, 1H, J = 10.9, 17.6 Hz), 6.68 (d, 2H, J = 7.3 Hz), 7.21−7.30 (m, 3H), 7.35−7.48 (m, 2H), 7.60 (d, 1H, J = 7.9 Hz), 8.09 (d, 1H, J = 7.5 Hz); ^{13}C NMR δ 26.8, 34.2, 43.6, 44.8, 68.9, 112.6, 117.2, 120.2, 123.7, 126.7, 128.0, 130.3, 132.8, 134.6, 139.1, 146.5. Anal. Calcd for $C_{19}H_{20}N_3Cl$: C, 70.04; H, 6.19; N, 12.90. Found: C, 70.08, H, 6.17; N, 12.85.

1-[1-(2-Oxiranylmethyl)-2-propenyl]-1*H*-1,2,3-benzotriazole (9): mixture of two isomers, colorless oil (88%); ^{1}H NMR δ 2.42−3.05 (m, 5H), 5.29−5.40 (m, 2H), 5.52−5.54 (m, 1H), 6.21−6.42 (m, 1H), 7.36−7.51(m, 2H), 7.56 (d, 1H, J = 8.4 Hz), 8.08 (d, 1H, J = 8.3 Hz); ^{13}C NMR δ 36.6 (minor isomer 36.8), 47.0 (47.2), 48.9, 59.7 (59.5), 109.7, 117.0 (117.1), 118.9, 119.9, 123.9 (124.0), 127.2, 134.7 (135.3), 146.5. Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.61; H, 6.26; N, 19.81.

1-[1-(4-Chlorobutyl)-2-propenyl]-1*H*-1,2,3-benzotriazole (16a): colorless oil (80%); ^{1}H NMR δ 1.31−1.54 (m, 2H), 1.74−1.85 (m, 2H), 2.19−2.40 (m, 2H), 3.46 (t, 2H, J = 6.5 Hz), 5.20 (d, 1H, J = 17.3 Hz), 5.28 (d, 1H, J = 10.5 Hz), 5.30−5.35 (m, 1H), 6.17 (ddd, 1H, J = 6.6, 10.5, 17.1 Hz), 7.36 (t, 1H, J = 8.1 Hz), 7.46 (t, 1H, J = 8.3 Hz), 7.53 (d, 1H, J = 8.2 Hz), 8.06 (d, 1H, J = 8.3 Hz); ^{13}C NMR δ 23.4, 31.9, 32.8, 44.4, 62.2, 109.9, 118.0, 120.0, 123.9, 127.1, 135.6, 139.3, 145.9. Anal. Calcd for $C_{13}H_{16}N_3Cl$: C, 62.52; H, 6.46; N, 16.83. Found: C, 62.44; H, 6.69; N, 17.13.

1-[1-Butyl-1-(4-chlorobutyl)-2-propenyl]-1*H*-1,2,3-benzotriazole (16b): colorless oil (70%); ^{1}H NMR δ 0.83 (t, 3H, J = 7.1 Hz), 1.28−1.34 (m, 4H), 1.44−2.02 (m, 4H), 2.25−2.41 (m, 4H), 3.48 (t, 2H, J = 3.5 Hz), 5.27 (dd, 1H, J = 3.3, 17.8 Hz), 5.48 (dd, 1H, J = 3.3, 11.0 Hz), 6.22 (dd, 1H, J = 10.7, 17.5 Hz), 7.34−7.41 (m, 2H), 7.64 (d, 1H, J = 8.3 Hz), 8.08 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ 13.8, 20.7, 22.7, 25.2, 32.5, 35.8, 36.2, 44.5, 68.9, 112.5, 116.3, 120.0, 123.5, 126.4, 132.4, 140.0, 146.8. Anal. Calcd for $C_{17}H_{24}N_3Cl$: C, 66.76; H, 7.91; N, 13.74. Found: C, 66.54; H, 7.99; N, 13.94.

General Procedure for the Preparation of 2-Vinylpyrrolidines 7a−i 13 and 2-Vinylpiperidines 18a−c. Under N_2, **5a**−**d**, **9** (the reaction of **9** and benzylamine was conducted in ethanol instead of DMF**)** or **16a**,**b** (2.1 mmol), the amine (2.8 mmol), and K_2CO_3 in DMF (5 mL) were heated to 80 °C for 12 h, after cooling to room temperature, $Pd(OAc)_2$ (20 mg, 0.09 mmol), Ph_3P (100 mg, 0.4 mmol), K_2CO_3 (0.8 g), and methanol (20 mL) were added under argon, and the resulting mixture was stirred at room temperature for 24 h. Water (20 mL) was added to the reaction mixture followed by extraction with CH_2Cl_2 (3 × 40 mL). The solvent was removed, and the residual oil was purified by chromatography (neutral alumina) to give the desired product.

1-Benzyl-2-vinylpyrrolidine (7a):[1j] colorless oil; ^{1}H NMR δ 1.62−1.72 (m, 3H), 1.82−2.02 (m, 1H), 2.10 (q, 1H, J = 8.8 Hz), 2.78 (q, 1H, J = 7.9 Hz), 2.91 (t, 1H, J = 7.1 Hz), 3.06 and 4.02 (AB q, 2H, J = 12.9 Hz), 5.13 (dd, 1H, J = 1.4, 10.2 Hz), 5.17 (d, 1H, J = 17.0 Hz), 5.79 (ddd, 1H, J = 1.5, 9.5, 17.6 Hz), 7.21−7.30 (m, 5H); ^{13}C NMR δ 22.0, 31.5, 53.2, 58.1, 68.4, 116.5, 126.7, 128.1, 129.0, 139.8, 141.0.

1-Dodecanyl-2-vinylpyrrolidine (7b): colorless oil; ^{1}H NMR δ 0.88 (t, 3H, J = 6.7 Hz), 2.60 (t, 1H, J = 8.3 Hz), 2.66−2.79 (m, 1H), 3.18 (t, 1H, J = 7.8 Hz), 1.22−2.25 (m, 26H), 5.07 (d, 1H, J = 10.5 Hz), 5.12 (d, 1H, J = 19.5 Hz), 5.63−5.78 (m, 1H); ^{13}C NMR δ 14.1, 22.1, 22.7, 27.8, 28.8, 29.3, 29.6 (br), 29.7, 31.5, 31.9, 53.6, 54.5, 69.3, 118.2, 141.1; HRMS (EI) calcd for $C_{18}H_{35}N$ 265.2769, found 265.2740.

1-Cyclohexyl-4-methyl-2-vinylpyrrolidine (7c): mixture of *cis*- and *trans*-isomers (about 1:1 by GC analysis), colorless oil; ^{1}H NMR δ 0.99 (d, 3H, J = 6.5 Hz) [minor isomer 1.01 (d, 3H, J = 6.3 Hz), 1.08−1.42 (m, 6H), 1.45−1.85 (m, 5H), 2.05−2.25 (m, 2H), 2.45−2.55 (m, 2H), 3.07 (t, 1H, J = 7.2 Hz) [2.89 (t, 1H, J = 8.4 Hz)], 3.28−3.42 (m, 1H), 4.99 (dd, 1H, J = 9.6, 8.5 Hz), 5.07 (d, 1H, J = 17.2 Hz), 5.71−5.80 (m, 1H); ^{13}C NMR δ 19.4 (minor isomer 20.4), 25.5 (25.6), 26.0 (26.21), 26.4 (27.1), 30.5 (31.2), 32.8 (32.9), 40.6 (41.6), 56.6 (54.5), 58.9 (57.6), 63.2 (64.3), 114.1 (114.8), 142.6 (141.2); HRMS (EI) calcd for $C_{13}H_{23}N$ 193.1830, found: 193.1590.

***N*-α-Methylbenzyl-2-vinylpyrrolidine (7d)**:[3b] mixture of two isomers, colorless oil; ^{1}H NMR δ 1.36 (dd, 3H, J = 6.5, 6.5 Hz) [1.46 (dd, 3H, J = 6.6, 6.9 Hz, minor isomer)], 1.58−1.68 (m, 4H), 2.45−3.25 (m, 3H), 3.75−3.95 (m, 1H), 4.96 (dd, 1H, J = 2.1, 11.5 Hz), 5.12 (dd, 1H, J = 1.5, 18.5 Hz), 5.65−5.85 (m, 1H), 7.25−7.45 (m, 5H); ^{13}C NMR δ 16.2, 22.4 (minor isomer 22.1), 31.9 (31.7), 48.2 (48.1), 58.6, 64.4 (63.9), 114.5 (115.4), 126.5 (126.7), 127.8 (127.9), 128.3, 141.1 (141.9), 142.3.

(*R*)-*N*-α-Methylbenzyl-2-vinylpyrrolidine (7e):[3b] mixture of two isomers, colorless oil; ^{1}H NMR δ (1.46 (d, 3H, J = 7.1 Hz) [minor isomer 1.35 (d, 3H, J = 6.8 Hz)], 1.55−1.95 (m, 4H), 2.32−2.52 (m, 1H), 2.88−2.98 (m, 1H), 3.25−3.35 (m, 1H) [2.68−2.78 (m, 1H)], 3.88 (q, 1H, J = 6.9 Hz) [3.83 (q, 1H, J = 6.8 Hz), 5.05 (m, 2H), 5.84 (ddd, 1H, J = 8.4, 9.2, 17.6 Hz) [5.72 (dd, 1H, J = 10.1, 17.9 Hz)], 7.15−7.35 (m, 5H); ^{13}C NMR δ 16.2 (minor isomer 21.6), 22.1 (22.4), 31.7 (31.9), 47.7 (48.2), 58.6 (58.7), 63.9 (64.4), 114.5 (115.4), 126.5 (126.7), 127.7 (127.8), 127.9 (128.3), 141.1 (141.9), 150.2 (142.5).

1-Benzyl-2-methyl-2-vinylpyrrolidine (7f): colorless oil; ^{1}H NMR δ 1.16 (s, 3H), 1.65−1.92 (m, 2H), 2.8−2.85 (m, 1H), 2.99−3.04 (m, 1H), 3.58 and 3.83 (AB q, 2H, J = 12.8 Hz), 5.09−5.18 (m, 2H), 5.88−5.98 (m, 1H), 7.30 (m, 5H); ^{13}C NMR δ 17.5, 21.1, 39.0, 50.4, 53.4, 62.2, 113.0, 126.5, 128.1, 128.4,

140.5, 144.6; GCMS(EI) 200 (M − 1), 186, 170, 91; HRMS (EI) calcd for $C_{14}H_{19}N$ 186.1282 (M^+ − 15), found 186.1286.

1-(2-Ethyloxyethyl)-2-vinylpyrrolidine (7g): colorless oil; ^{1}H NMR δ 1.21 (t, 3H, J = 6.9 Hz), 1.55−1.95 (m, 4H), 2.15−2.35 (m, 2H), 2.71 (q, 1H, J = 7.7 Hz), 2.96−3.04 (m, 1H), 3.21−3.27 (m, 1H), 3.47−3.58 (m, 4H), 5.09 (d, 1H, J = 10.1 Hz), 5.16 (d, 1H, J = 17.1 Hz), 5.72 (ddd, 1H, J = 7.6, 9.8, 16.9 Hz); ^{13}C NMR δ 15.1, 22.3, 31.2, 53.5, 54.3, 66.3, 69.4, 69.6, 116.4, 140.8; HRMS (EI) calcd for $C_{10}H_{19}NO$ 168.1388 (M^+ − 1), found 168.1416.

1,2-Dibenzyl-2-vinylpyrrolidine (7h): colorless oil; ^{1}H NMR δ 1.59−1.68 (m, 3H), 1.7−1.95 (m, 1H), 2.42−2.45 (m, 1H), 2.80−2.83 (m, 1H), 2.89 and 3.01 (AB q, 2H, J = 13.2 Hz), 3.49 and 4.01 (AB q, 2H, J = 13.5 Hz), 5.08 (d, 1H, J = 17.6 Hz), 5.23 (d, 1H, J = 11.0 Hz), 5.98 (dd, 1H, J = 10.8, 17.4 Hz), 7.26−7.41 (m, 10 H); ^{13}C NMR δ 20.8, 33.7, 41.9, 50.7, 53.0, 67.6, 114.2, 125.9, 126.6, 127.6, 128.2, 128.4, 130.7, 139.5, 139.8, 140.2; HRMS (EI) calcd for $C_{20}H_{23}N$ 277.1830, found 277.1805.

***N,N*-Diethylaminoethyl-2-(2-vinyl-1-pyrrolidine)-1-ethanamine (7i)**: colorless oil; ^{1}H NMR δ 1.04 (t, 6H, J = 7.2 Hz), 1.5−1.95 (m, 4H), 2.12−2.22 (m, 2H), 2.56 (q, 4H, J = 6.8 Hz), 2.58−2.72 (m, 3H), 2.86−2.95 (m, 1H), 3.18−3.25 (m, 1H), 5.10 (d, 1H, J = 10.2 Hz), 5.16 (d, 1H, J = 19.0 Hz), 5.72 (ddd, 1H, J = 9.9, 10.2, 19.0 Hz); ^{13}C NMR δ 11.6, 22.2, 31.2, 47.4, 51.7, 52.2, 53.9, 69.4, 116.4, 140.7; HRMS (EI) calcd for $C_{12}H_{24}N_2$ 196.1936, found 196.1999.

1-Benzyl-2-ethylpyrrole (13): colorless oil (52%); ^{1}H NMR δ 1.20 (t, 3H, J = 7.3 Hz), 2.47 (q, 2H, J = 7.4 Hz), 5.03 (s, 2H), 5.98 (br, 1H), 6.15 (br, 1H), 6.63 (br, 1H), 6.98 (d, 2H, J = 6.9 Hz), 7.26−7.30 (m, 3H); ^{13}C NMR δ 12.9, 19.4, 50.2, 105.1, 107.1, 120.9, 126.3, 127.3, 128.7, 134.8, 138.2. Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.36; H, 8.71; N, 7.62.

1-Benzyl-2-vinylpiperidine (18a):[1k] colorless oil; ^{1}H NMR δ 1.25−1.95 (m, 7H), 2.64−2.71 (m, 1H), 2.78−2.83 (m, 1H), 3.05 and 4.06 (AB q, 2H, J = 13.5 Hz), 5.10 (dd, 1H, J = 1.7, 10.2 Hz), 5.19 (d, 1H, J = 17.3 Hz), 5.90 (ddd, 1H, J = 1.6, 10.1, 17.6 Hz), 7.31 (m, 5H); ^{13}C NMR δ 24.0, 25.8, 33.7, 52.1, 59.8, 66.7, 115.5, 126.6, 128.0, 129.0, 139.6, 142.6.

1-Hexyl-2-vinylpiperidine (18b): colorless oil; ^{1}H NMR δ 0.88 (t, 3H, J = 6.5 Hz), 1.27−1.73 (m, 14H), 1.99−2.25 (m, 2H), 2.54−2.74 (m, 2H), 2.95−2.99 (m, 1H), 5.03 (d, 1H, J = 10.2 Hz), 5.12 (d, 1H, J = 14.2 Hz), 5.72−5.84 (m, 1H); ^{13}C NMR δ 14.1, 22.6, 23.9, 25.8, 26.0, 27.4, 31.8, 33.6, 52.1, 55.7, 66.6, 115.0, 142.2; HRMS (EI) calcd for $C_{13}H_{25}N$ 195.1987, found 195.1990.

1-Benzyl-2-butyl-2-vinylpyrrolidine (18c): colorless oil; ^{1}H NMR δ 0.93 (t, 3H, J = 6.8 Hz), 1.35−1.85 (m, 12H), 2.38−2.45 (m, 2H), 3.48 and 3.65 (AB q, 2H, J = 14.3 Hz), 5.13 (d,. 1H, J = 17.9 Hz), 5.20 (d, 1H, J = 11.1 Hz), 6.01 (dd, 1H, J = 11.1, 17.9 Hz), 7.21−7.38 (m, 5H); ^{13}C NMR δ 14.2, 20.8, 23.6, 25.9, 26.0, 33.9, 46.6, 53.5, 60.2, 114.1, 126.3, 128.1, 128.2, 141.4, 142.3. Anal. Calcd for $C_{18}H_{27}N$: C, 83.99; H, 10.57; N, 5.44. Found: C, 83.87; H, 11.04; N, 5.46.

Supporting Information Available: ^{1}H NMR and HRMS spectra for compounds **7b**,**c**,**f**−**i** and **18b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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