An Efficient Synthesis of Substituted (Z)-Allylamines and 7-Membered Nitrogen Heterocycles from (Z)-3-(Tributylstannyl)allylamine

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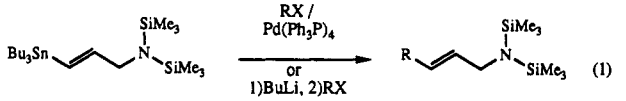
The reaction of *N*-(trimethylsilyl)allylamine with 2 mol of *n*-butyllithium, followed by treatment with chlorotributyltin and subsequent hydrolysis, gave (*Z*)-3-(tributylstannyl)allylamines in high yields. The N,N-disilylated derivatives, upon transmetalation of the C–Sn bond, led to unstable vinyllithium species. The latter readily underwent a [1,4] nitrogen to carbon silyl migration to give a lithium amide. The unprotected (*Z*)-3-(tributylstannyl)allylamine underwent a palladium-catalyzed cross-coupling reaction with aromatic bromides affording a stereospecific preparation of substituted allylic amines with *Z* configuration of the carbon–carbon double bond. The reactions of ortho-functionalized aryl bromides offer a one-step preparation of 7-membered nitrogen heterocycles in high yields.

Introduction

Organotin reagents have proved to be useful tools for the formation of C–C bonds.[1,2] One of the main interests of these reagents is that they allow reactions with usually very high chemo- and stereoselectivity. Vinyltin compounds are of particular interest since the vinylic moiety can be transferred in two ways with retention of configuration of the carbon–carbon bond. A chemo- and stereospecific cross-coupling reaction with organic halides occurs in the presence of palladium catalysts.[1,3] The transmetalation to a vinyllithium reagent was also shown to proceed with retention of the configuration of the C=C bond in various condensation reactions.[1,4] Therefore, vinyltin compounds appear to be versatile reagents for organic synthesis. In this respect, functionalized vinyltin reagents which allow the transfer of a functionalized carbon unit to an organic molecule are interesting synthons, providing for example, a propionaldehyde-d_3 equivalent.[5]

In connection with our current study of the use in organic synthesis of organometallic reagents containing Si–N bonds,[6-8] we decided to investigate the use of γ-[bis(trimethylsilyl)amino]vinyltin reagents. In a previous report,[9] we described the synthesis of the (*E*)-γ-[bis(trimethylsilyl)amino]vinyltin reagent and its application for the preparation of 3-substituted *E* primary allylic amines (eq 1).



(1)

A γ-amino vinyltin reagent with a *Z* configuration of the carbon–carbon double bond would be an even more interesting synthon since it should provide in an analogous way a facile route to (*Z*)-allylamines. Whereas several routes to (*E*)-allylamines have been reported,[10,11] stereospecific access to *Z* derivatives is more difficult and only few examples are known.[12] Moreover, owing to the cis orientation of the amino group, the condensation of (*Z*)-γ-functionalized vinyltin reagent with appropriate organic electrophiles should offer a short route to nitrogen heterocyclic compounds. We report here the selective synthesis and the reactivity of (*Z*)-3-(tributylstannyl)-allylamine and show that it provides facile and selective preparation of substituted *Z* allylic amines and 7-membered nitrogen heterocycles.

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(11) For recent synthesis, see: (a) Kresze, Gr.; Mansterer, M. *J. Org. Chem.* **1983**, *48*, 3561. (b) Laurent, A.; Mison, P.; Nafti, A.; Cheikh, R. B.; Chaabouni, R. *J. Chem. Res. (S)* **1984**, *354*. (c) Shea, R. G.; Fitzner, J. N.; Fankhauser, J. E.; Hopkins, P. B. *J. Org. Chem.* **1984**, *49*, 3647. (d) Shea, R. G.; Fankhauser, J. E.; Spaltenstein, A.; Carpino, P. A.; Peevey, R. M.; Pratt, D. V.; Tenge, B. J.; Hopkins, P. B. *J. Org. Chem.* **1986**, *51*, 5243. (e) Bargar, T. M.; Mc Cowan, J. R.; Mc Carthy, J. R.; Wagner, E. R. *J. Org. Chem.* **1987**, *52*, 678. (f) Connell, R. D.; Rein, T.; Akermark, B.; Helquist, P. *J. Org. Chem.* **1988**, *53*, 3845. (g) Deleris, G.; Dunogues, J.; Gadras, A. *Tetrahedron* **1988**, *44*, 4243. (h) Barluenga, J.; Aguilar, E.; Joglar, J.; Olano, B.; Fustero, S. *J. Chem. Soc., Chem. Commun.* **1989**, *1132*. (i) Capella, L.; Degl'Innocenti, A.; Reginato, G.; Ricci, A.; Taddei, M.; Seconi, G. *J. Org. Chem.* **1989**, *54*, 1473. (j) Capella, L.; Degl'Innocenti, A.; Mordini, A., Reginato, G.; Ricci, A.; Seconi, G. *Synthesis* **1991**, *1201*.

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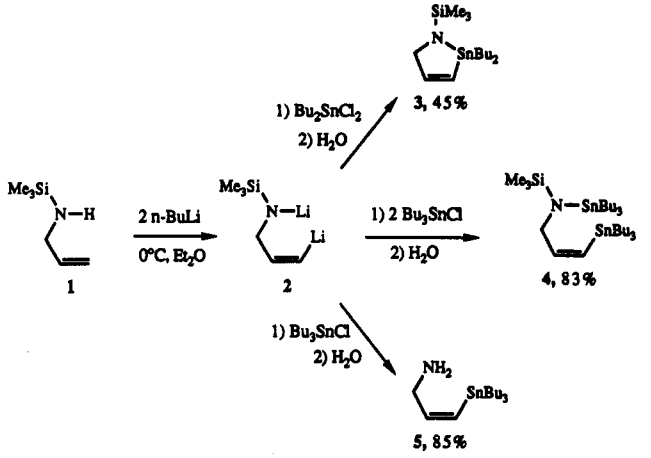
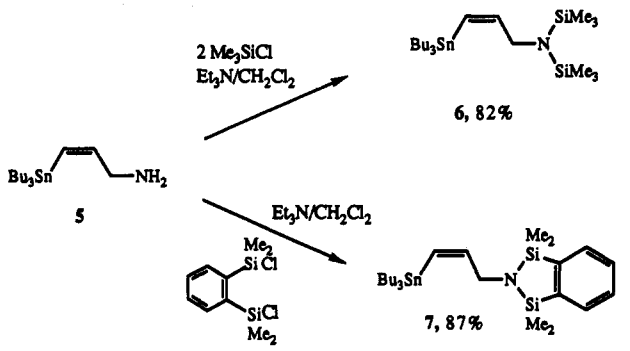
Scheme I. Lithiation and Stannylation of *N*-(Trimethylsilyl)allylamine (1)



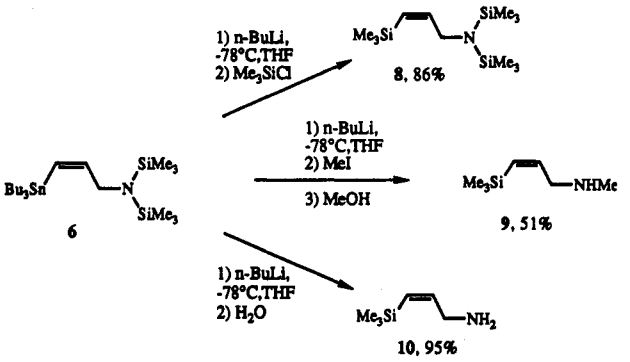
Results and Discussion

1. Synthesis of (*Z*)-3-(Tributylstannyl)allylamine (5). We first attempted preparation of tributylstannyl-substituted allylic amines from the readily available propargylic amine.[7] Whereas (*E*)-γ-aminovinyltin derivatives were easily obtained via hydrostannation,[9] the selective preparation of *Z* derivatives proved to be difficult. We thought that a vinyltin compound with *Z* stereochemistry of the C=C bond would be derived more easily from the reaction of *N*-(trimethylsilyl)-3,*N*-dilithioallylamine **2**.[13] We showed previously that (*Z*)-γ-amino vinylsilanes as well as cyclic compounds were directly obtained by use of this 1,4-dilithium reagent.[14] We thus treated **2** with organtin electrophiles (Scheme I). The dilithium reagent was prepared as described[14] upon treatment of monosilylated allylamine **1** with 2 mol of *n*-BuLi. The reaction of **2** with Bu_2SnCl_2 gave the tin heterocyclic compound **3**. Similarly 2 mol of Bu_3SnCl reacted with **2** to afford a *N*,*C*-bis(tributylstannyl) compound **4** in 83% yield. If only 1 mol of Bu_3SnCl was used, 3-(tributylstannyl)allylamine **5** was obtained in high yield after hydrolysis. The *Z* configuration of the double bond in **4** and **5** was assigned on the basis of ^1H NMR. ^{119}Sn NMR chemical shifts and coupling constants ($J_{^1H^1H(vinylic)}$ = 12.4, 12.5 Hz; δ ^{119}Sn −61.7, −61.8 ppm) in agreement with reported values for related compounds.[5,15] In order to prepare the *N*,*N*-bis(silyl)-protected derivative of **5**, we attempted a one-pot reaction of the dilithium reagent **2**, first with 1 mol of Bu_3SnCl, followed by 1 mol of Me_3SiCl. However, only a mixture of compounds, from which C-silylated derivatives were identified, was formed. The reaction of cyclic vinyltin compounds **3** with 1 mol of *n*-BuLi, followed by quenching with Me_3SiCl, also failed to give this *N*,*N*-bis(trimethylsilyl) derivative **6**. However, it was obtained in good yield by silylation of the primary amine **5** (Scheme II). The reaction of 2 mol of Me_3SiCl in the presence of Et_3N gave 82% yield of bis(trimethylsilyl) derivative **6**.

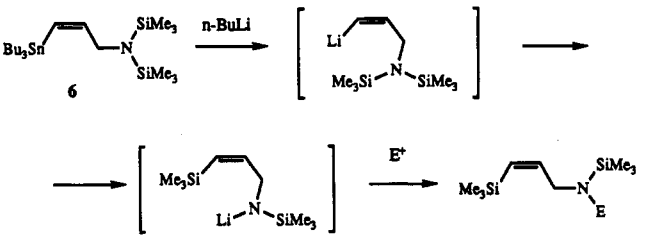
Scheme II. Silylation of γ-Amino Vinyltin 5



Scheme III. Reaction of 6 with *n*-BuLi



Scheme IV. Rearrangement of (*Z*)-γ-Amino Vinyllithium Reagent



Similarly the benzostabase[16] protected allylamine **7** was prepared in 87% yield (Scheme II).

2. Transmetalation Reactions of (*Z*)-γ-Amino Vinyltin Compounds 6–7. We examined the formation of (*Z*)-vinyllithium reagent via transmetalation[4] of C–Sn to C–Li bonds in compound **6**. The treatment of **6**, with 1 mol of *n*-BuLi at −78 °C, gave a red solution. Upon quenching with Me_3SiCl, the expected *Z* trisilylated allylamine **8** was isolated in a 86% yield (Scheme III). However, the reaction of the initially formed lithiated allylamine did not lead to the expected products upon reaction with MeI or water. C-Silylated products **9**, **10** were obtained, respectively. It seems that the intermediate vinyllithium reagent formed initially, upon transmetalation of the tin derivative **6**, is not stable and rearranges to a lithium amide. An intramolecular migration of the Me_3Si group from the nitrogen atom to the vinylic carbon accounts for the observed results (Scheme IV). Owing to the *Z* configuration of the C=C bond, an intramolecular nucleophilic attack at the silicon atom can lead to *Z* C-silylated derivatives **9**, **10**. A [1,4] nitrogen to carbon migration of a trimethylsilyl group in a related trisilylated

(13) (a) Hangessen, D.; Odenhausen, E. *Chem. Ber.* **1979**, *112*, 2389. (b) Schulze, J.; Boose, R.; Schmid, G. *Chem. Ber.* **1981**, *114*, 1297.
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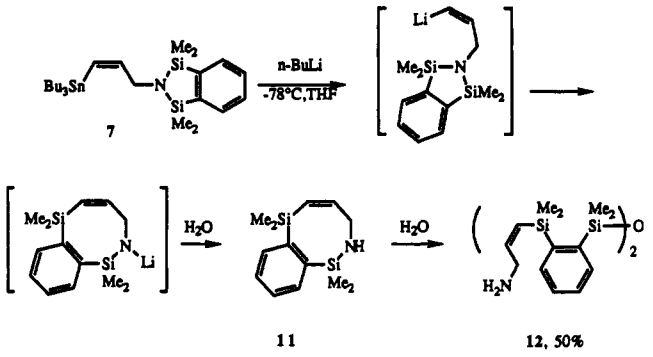
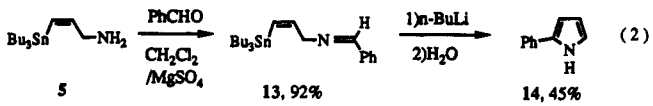
Scheme V. Transmetalation of Silyl-Protected γ-Amino Vinyltin 7

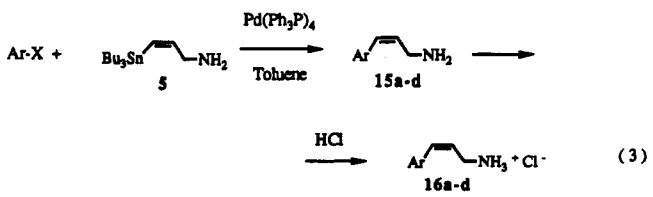


(aminoallyl)lithium has also been recently reported.[17] It is worth noting here that the transmetalation of a γ-amino vinyltin with an *E* configuration of the C=C bond gave the C-lithiated derivative quantitatively.[9] The resulting (*E*)-vinyllithium[9] was stable up to 0 °C, whereas with a *Z* configuration the γ-amino vinyllithium rearranges instantaneously even at −100 °C. A similar migration was obtained with a rigid cyclic protecting group. The transmetalation of the benzostabase derivative **7** with *n*-BuLi at −78 °C followed by hydrolysis gave the siloxane derivative **12**. The formation of **12** clearly arises from the ring opening of the intermediate cyclic amine **11** upon aqueous work up (Scheme V). It seems that even with this more stable cyclic protecting group, the N to C silyl migration resulting from the nucleophilic cleavage of Si–N bond occurred. Despite its usually high stability, we have previously observed that a bis(trimethylsilyl)amino group can easily react with a cis-oriented functional group.[8] No stable (*Z*)-vinyllithium species could be characterized. A similar high reactivity was also observed in the transmetalation of an imine-protected γ-amino vinyltin **13** (eq 2). The reaction of *n*-BuLi with **13** afforded 2-phenylpyrrole after aqueous workup of the reaction mixture. The isolation of Bu_4Sn from the reaction mixture is consistent with the initial formation of a vinyllithium species, the latter afforded the aromatic pyrrole derivative in a moderate yield.



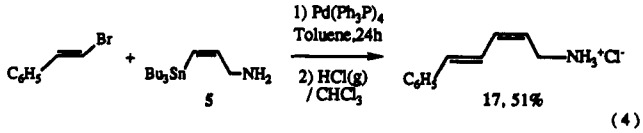
(2)

3. Palladium-Catalyzed Cross-Coupling Reactions of 5 with Organic Halides. We then examined the palladium-catalyzed reaction of γ-amino vinyltin **5**. The cross-coupling reactions of **5** with aryl bromides were performed in the presence of 2 mol % of $Pd(Ph_3P)_4$ in toluene (eq 3). The results are given in Table I. Good yields of (*Z*)-cinnamylamines were obtained. In most cases, pure samples were isolated upon crystallization of the HCl salts. The coupling reaction was carried out with aryl bromides bearing an electron-withdrawing substituent (entry c) or an electron-donating substituent (entry d) as well as with an heteroaromatic bromide (entry b). The free γ-amino vinylstannane **5** exhibited a reactivity similar to that of the *N,N*-bis(silyl)-protected *E* isomer.[9] In all cases, the ^1H NMR analysis showed a selective formation of *Z*-allylic amines.



(3)

The palladium-catalyzed cross-coupling was also achieved with a vinylic bromide. (*E*)-β-bromostyrene reacted with **5** to give a dienic amine in good yield (eq 4).

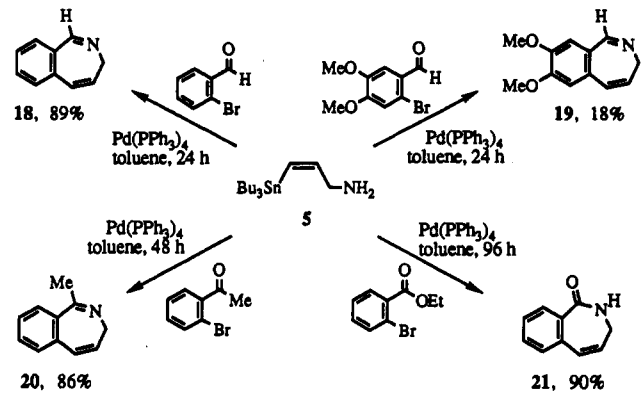


(4)

Retention of the configuration of the two C=C bonds was observed. ^1H NMR revealed coupling constants of 10.4 and 15.5 Hz for the vinylic protons in agreement with an *Z,E* stereochemistry of the dienic unit. Thus, the readily available vinyltin **5** allows the stereoselective transfer of γ-amino three-carbon unit to aryl and vinyl bromides. No protecting group at nitrogen was necessary in these coupling reactions.

Besides the interesting point that it offers a facile route to the (*Z*)-3-substituted allylic amines, it is possible to use the cis-oriented amino group to carry out further reactions. In this respect, we thought that the amino group in vinyl reagent **5** could lead to heterocyclization reaction. We therefore studied some reactions of functionalized aryl bromides. The palladium-catalyzed coupling reaction of functional aryl bromides are presented in Scheme VI.

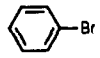
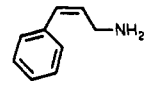
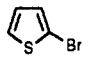
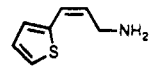
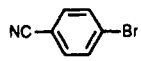
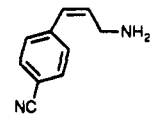
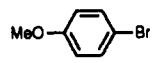
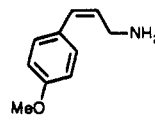
Scheme VI. Palladium-Catalyzed Coupling Reaction of Ortho-Functionalized Aryl Bromides



Heterocyclizations were obtained in one-pot reactions. The reaction of *o*-bromobenzaldehyde afforded in one step 3*H*-2-benzazepine (**18**) in 89% yield. Similarly, the coupling and subsequent cyclization of 3,4-dimethoxy-2-bromobenzaldehyde lead to the corresponding substituted benzazepine heterocycle **19**. It was isolated in a moderate yield owing to a low reactivity of the starting aryl bromide with two strong electron-donating substituents. By using *o*-bromoacetophenone, the 1-methyl-3*H*-2-benzazepine (**20**) was also isolated in a high yield. The formation of a seven-membered nitrogen heterocycle was also obtained upon reaction of *o*-(bromoethyl)benzoate, which yielded 3*H*-2-benzazepin-1-one, **21**. Seven-membered nitrogen heterocycles constitute an important class of compounds and benzazepine derivatives are of particular interest owing

(17) Degl'Innocenti, A.; Mordini, A.; Pinzani, D.; Reginato, G.; Ricci, A. *Synlett* **1991**, *713*.

Table I. Palladium-Catalyzed Coupling Reaction of 5 with Aryl Bromides[a]

entry	ArX	reaction time (h)	reaction temp (°C)	coupling products 15a–d	yield (%)	yield of recryst HCl salt 16
a		96	110		95[b]	47[c]
b		24	110		70[c]	
c		72	110		95[b]	65[c]
d		120	110		95[b]	40[d]

[a] The reactions were carried out under nitrogen using 1 mol of 5 and 1 mol of aryl bromide in toluene, in the presence of 2 mol % of $Pd(Ph_3P)_4$. [b] NMR yield. [c] Isolated yield. [d] In this case, treatment with saturated $CHCl_3$ solution of HCl(g) gave the *E* isomer.[9]

to their physiological properties and applications.[18-22] The γ-amino vinyltin reagent **5** offers a straightforward route to these heterocyclic compounds from functionalized aryl bromides.

Experimental Section

General. All the reactions were performed under an atmosphere of nitrogen and using standard vacuum line and Schlenk tube techniques. Solvents were dried and distilled before use. Unless otherwise stated, the indicated yields refer to isolated compounds with purity over 95% (as evaluated from their ^1H NMR spectrum). Melting points are uncorrected. Chemical shifts are relative to Me_4Si and to Me_4Sn as internal standards. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. *N*-(Trimethylsilyl)allylamine (1) was prepared by silylation of allylamine by standard procedure.[23] 1,2-Bis(chlorodimethylsilyl)benzene was prepared by silylation of 1,2-dihalobenzene.[24]

Lithiation and Stannylation Reaction of *N*-(Trimethylsilyl)allylamine (1): *N*-(Trimethylsilyl)-3,*N*-dilithioallylamine (2). To a stirred solution of *N*-(trimethylsilyl)allylamine (1) (10.0 g, 77.7 mmol) in anhydrous ether (200 mL) at 0 °C under N_2 was added 62.0 mL (155 mmol) of a 2.5 M *n*-butyllithium solution in hexane. After 15 min of stirring, the mixture was allowed to warm to rt and then stirred for 24 h to give a yellow green solution of the dilithium reagent 2.

***N*-(Trimethylsilyl)-2,2-dibutyl-2-stanna-Δ³-pyrroline (3).** To the stirred solution of dichlorobutyltin (11.0 g, 36 mmol) in anhydrous ether (200 mL) at −50 °C was added the above dilithium reagent (36 mmol). After 1 h at −50 °C, the mixture was allowed to warm to rt and stirred for 72 h, and then the mixture was refluxed for 24 h. After cooling to rt and filtration, the filtrate was concentrated. The residue was distilled, giving 5.7 g (44%): bp 110–115 °C (1 mmHg); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H, $(CH_3)_3Si$), 0.8–1.6 (m, 18 H, $(C_4H_9)_2Sn$), 3.91 (t, 2 H, *J* = 2.5 Hz, CH_2N), 6.40 (dt, 1 H, *J* = 10.4, 2.6 Hz), 7.07 (dt, 1 H, *J* = 10.4, 2.5 Hz); ^{13}C NMR ($CDCl_3$) 1.23 ($(CH_3)_3Si$), 14.2, 17.2, 26.7, 28.6 (C_4H_9), 55.5 (CH_2N), 125.5, 152.0 (CH=CH); ^{119}Sn NMR ($CDCl_3$) δ −11.5 ppm; IR (CCl_4) 1570 cm^{-1} (CH=CH); mass spectrum (EI) *m/z* (%) 362 (M^+). Anal. Calcd for $C_{14}H_{31}NSiSn$: C, 46.68; H, 8.67; Si, 7.80; Sn, 32.95. Found: C, 46.95; H, 854; Si, 7.87; Sn, 33.65.

(*Z*)-*N*-(Trimethylsilyl)-3,*N*-bis(tributylstannyl)allylamine (4). The experiment was carried out by addition of a solution of Bu_3SnCl (50.4 g, 155 mmol) in ether (150 mL) to a stirred solution of dilithium reagent 2 (77.5 mmol) at 0 °C. The mixture was then stirred for 24 h at rt and then hydrolyzed with saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times with ether, and the ethereal extracts were combined and dried over $MgSO_4$. After evaporation of the solvent, distillation of the residue then gave 45.4 g (83%) of compound 4. ^1H NMR ($CDCl_3$) δ −0.05 (s, 9 H, $(CH_3)_3Si$), 0.7–1.7 (m, 54 H, 2 $(C_4H_9)_3Sn$), 3.22 (d, 2 H, *J* = 6.4 Hz, CH_2 N), 5.88 (d, 1 H, *J* = 12.5 Hz, $J(^{119}Sn-H)$ = 68.0 Hz, HC=CHCH₂N), 6.56 (dt, 1 H, *J* = 12.5, 6.4 Hz, $J(^{119}Sn-H)$ = 135.6 Hz, CH=CHCH₂N); ^{119}Sn NMR ($CDCl_3$) δ −61.7 (Bu_3SnC=), 80.8 (Bu_3SnN); IR (CCl_4) 1600 cm^{-1} (C=C); mass spectrum (EI) *m/z* (%) 707 (M^+, 2), 649 (6), 360 (85), 128 (96), 73 (100), 57 (63). Anal. Calcd for $C_{30}H_{67}NSiSn_2$: C, 50.94; H, 9.55. Found: C, 50.55; H, 9.71.

(*Z*)-3-(Tributylstannyl)allylamine (5). As above for compound 4, a solution of Bu_3SnCl (25.9 g, 77.1 mmol) in ether (100 mL) was added to a stirred solution of dilithium reagent 2 (77.5 mmol) at 0 °C. The mixture was stirred for 24 h at rt. After aqueous workup, distillation gave 23.0 g (85%) of (*Z*)-3-(tributylstannyl)allylamine (5): bp 115–125 °C (0.15 mmHg); ^1H NMR ($CDCl_3$) δ 0.6–1.6 (m, 27 H, $(C_4H_9)_3Sn$), 2.10 (bs, 2 H, NH_2), 3.23 (dd, 2 H, *J* = 6.2, 0.9 Hz, CH_2N), 5.88 (dt, 1 H, *J* = 12.4, 0.9 Hz, $J(^{119}Sn-H)$ = 67.8 Hz, SnHC=CH), 6.57 (dt, 1 H, *J* = 12.4, 6.2 Hz, $J(^{119}Sn-H)$ = 138.7 Hz, CH=CHCH₂N); ^{13}C NMR ($CDCl_3$) δ 10.9, 14.1, 25.6, 27.7 (C_4H_9), 47.8 (CH_2N), 130.1, 149.1 (CH=CH); ^{119}Sn NMR ($CDCl_3$) δ −61.8; IR ($CDCl_3$) 3393, 3325, 1599 cm^{-1}; mass spectrum (FAB) *m/z* (%) 290 (M + H^+, 57, 59), 177 (100), 235 (20), 121 (32). Anal. Calcd for $C_{15}H_{33}NSn$: C, 52.05; H, 9.61; N, 4.05. Found: C, 51.75; H, 9.54; N, 3.95.

Silylation Reactions of 5. (*Z*)-3-(Tributylstannyl)allylamine (5) was mixed with triethylamine in CH_2Cl_2 as solvent. The chlorosilane solution in CH_2Cl_2 was added at rt under N_2. The reaction was stirred for several days. The mixture was then filtered, and the filtrate was concentrated. Upon distillation, high yield of the bis-silylated products were obtained.

(*Z*)-*N*,*N*-Bis(trimethylsilyl)-3-(tributylstannyl)allylamine (6). (*Z*)-3-(Tributylstannyl)allylamine (5) (43.5 g, 125 mmol) reacted with 32 g (296 mmol) of trimethylchlorosilane at rt for 4 d in the presence of 38 mL of triethylamine to give 50.5 g (82%) of 6: bp 125–130 °C (0.10 mmHg); ^1H NMR ($CDCl_3$) δ 0.08 (s, 18 H, 2 $(CH_3)_3Si$), 0.8–1.6 (m, 27 H, $(C_4H_9)_3Sn$), 3.46 (dd, 2 H, *J* = 5.0, 2.1 Hz, CH_2N), 5.76 (dt, 1 H, *J* = 12.9, 2.1 Hz, $J(^{119}Sn-H)$ = 64.7 Hz, SnCH=CH), 6.37 (dt, 1 H, *J* = 12.9, 5.0 Hz, $J(^{119}Sn-H)$ = 138.7 Hz, SnCH=CH); ^{13}C NMR ($CDCl_3$) δ 2.5

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(CH_3)$_3$Si), 10.4, 14.1, 27.6, 29.6 (C_4H_9)$_3$Sn), 49.6 (CH_2N), 125.6, 155.0 (*CH*=*CH*); ^{119}Sn NMR ($CDCl_3$) δ -61.5; IR (CCl_4) 2957, 1586, 1457, 1248, 1214, 1068, 1034 cm^{-1}; mass spectrum (EI) *m/z* (%) 434 (M^+ - 57, 6), 320 (2), 73 (100). Anal. Calcd for $C_{21}H_{49}NSi_2Sn$: C, 51.42; H, 10.07; N, 2.86. Found: C, 51.13; H, 10.12; N, 2.82.

(*Z*)-*N*-[3-(Tributylstannyl)allyl]-1,1,3,3-tetramethyl-1,3-disilaisoindoline (7). (*Z*)-3-(Tributylstannyl)allylamine (5) (23.3 g, 67.1 mmol) reacted with 17.1 g (67.1 mmol) of *o*-bis(chlorodimethylsilyl)benzene at rt for 2 d in the presence of 20 mL of triethylamine to give 31.3 g of 7 (87%): bp 160–165 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 12 H, 2 (CH_3)$_2$Si), 0.7–1.6 (m, 27 H, (C_4H_9)$_3$Sn), 3.63 (dd, 2 H, *J* = 6.0, 1.6 Hz, CH_2N), 5.84 (dt, 1 H, *J* = 12.6 Hz, *J* = 1.6 Hz, *J*(^{119}Sn–H) = 64.7 Hz, Sn*H*C=CH), 6.58 (dt, 1 H, *J* = 12.6, 6.0 Hz, *J*(^{119}SnH) = 140.0 Hz, SnCH=C*H*), 7.45 (dq, 4 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 1.1 (CH_3)$_3$Si), 10.7, 14.2, 27.6, 29.9 (C_4H_9)$_3$Sn), 47.7 (CH_2N), 127.4, 129.0, 131.6, 147.7, 152.2 (*HC*=*CH* and aromatic); ^{119}Sn NMR ($CDCl_3$) -61.7; IR (Cl_4C) 3102, 3050, 2959, 1593, 1464, 1248, 1125, 1028 cm^{-1}; mass spectrum (FAB) *m/z* (%) 480 (M^+ - 57, 16), 423 (4), 366 (12), 245 (100), 73 (23). Anal. Calcd for $C_{25}H_{47}NSi_2Sn$: C, 55.97; H, 8.83; Sn, 22.13. Found: C, 55.64; H, 8.85; Sn, 22.04.

Transmetalation Reactions of 6: (*Z*)-3,*N*,*N*-Tris(trimethylsilyl)allylamine (8). To a solution of (*Z*)-3-(tributylstannyl)-*N*,*N*-bis(trimethylsilyl)allylamine (6) (2.5 g, 5.1 mmol) in THF (10 mL) was added a solution of *n*-BuLi (5.1 mmol) in hexane at -78 °C. The solution turned red instantaneously. The resulting red reaction mixture was stirred for 2 h at -78 °C. Then 5.5 g (5.1 mmol) of Me_3SiCl in 10 mL of THF was added. The reaction was stirred for 4 h and allowed to warm to rt, and then the mixture was hydrolyzed with saturated aqueous NH_4Cl. The aqueous layer was extracted three times with ether, and the ethereal extracts were combined and dried over $MgSO_4$. Distillation gave 1.2 g (86%) of the known[14] (*Z*)-3-(trimethylsilyl)-*N*,*N*-bis(trimethylsilyl)allylamine (8): bp 115–125 °C (20 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 18 H, [(CH_3)$_3$Si]$_2$N), 0.10 (s, 9 H, (CH_3)$_3$SiCH=CH), 3.52 (dd, 2 H, *J* = 5.2, 2.2 Hz, CH_2N), 5.36 (dt, 1 H, *J* = 14.7, 2.2 Hz, (CH_3)$_3$Si*CH*=CH), 6.13 (dt, 1 H, *J* = 14.7, 5.2 Hz, [(CH_3)$_3$Si]CH=*CH*); IR (CCl_4) 2956, 1595, 1456, 1250, 1070, 1036 cm^{-1}; mass spectrum (EI) *m/z* (%) 273 (M^+, 6), 258 (14), 200 (25), 174 (57), 73 (100).

(*Z*)-*N*-Methyl-3-(trimethylsilyl)allylamine (9). The reaction was carried out as above, and the mixture was quenched with MeI. After hydrolysis, the reaction mixture was refluxed in methanol for 1 h. The above workup followed by distillation afforded compound 9 (51%): bp 70 °C (40 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H, (CH_3)$_3$Si), 2.11 (s, 3 H, CH_3), 3.26 (dd, 2 H, *J* = 6.8, 1.3 Hz, CH_2N), 5.66 (dt, 1 H, *J* = 14.2, 1.3 Hz, (CH_3)$_3$Si*CH*=CHCH_2N), 6.34 (dt, 1 H, *J* = 14.2, 6.8 Hz, (CH_3)$_3$SiCH=*CH*CH_2N); IR (CCl_4) 1608 cm^{-1}; mass spectrum (EI) *m/z* (%) 128 (M^+ - 15, 38).

(*Z*)-3-(Trimethylsilyl)allylamine (10). As above, but upon quenching the reaction mixture with water, the known[14] allylamine (10) (95%) was isolated: bp 50 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H, (CH_3)$_3$Si), 1.80 (s, 2 H, N*H*$_2$), 3.40 (d, 2 H, *J* = 6.8 Hz, CH_2N), 5.45 (d, 1 H, *J* = 14.1 Hz, (CH_3)$_3$Si*CH*=CH), 6.25 (dt, 1 H, *J* = 14.1, 6.8 Hz, CH=*CH*CH_2N); IR (CCl_4) 1606.8 cm^{-1}; mass spectrum (FAB) *m/z* (%) 130 (M + H$^+$, 16), 73 (100).

Reaction of 7 with *n*-Butyllithium. The transmetalation of 7 was performed as for compound 6 in THF at -78 °C. The reaction mixture was quenched with water, and the 2*H*,3*H*-1,1,6,6-tetramethyl-1,6-disila-2-benzazocine (11) was isolated as a crude reaction product (90%): ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 6 H, (CH_3)$_2$Si), 0.62 (s, 6 H, (CH_3)$_2$Si), 2.50 (bs, 1 H, N*H*), 3.69 (m, 2 H, CH_2N), 5.81 (dt, 1 H, *J* = 13.4, 2.3 Hz, (CH_3)$_3$Si*CH*=CH), 6.66 (dt, 1 H, *J* = 13.4, 2.9 Hz, CH=*CH*CH_2N), 7.4–7.8 (m, 4 H, aromatic); IR (CCl_4) 3436 (NH), 1615 (C=C) cm^{-1}; mass spectrum (EI) *m/z* (%) 247 (M^+, 18). The cyclic amine (11) was then hydrolyzed to 12. After extraction and crystallization from hexane, compound 12 (50%) was isolated as a colorless solid: mp 125.5–126.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 12 H, 2 (CH_3)$_2$Si), 0.52 (s, 12 H, 2 (CH_3)$_2$Si), 2.7 (bs, 4 H, 2 N*H*$_2$), 3.20 (d, 4 H, *J* = 7.5 Hz, CH_2N × 2), 5.89 (d, 2 H, *J* = 13.9 Hz, 2 (CH_3)$_2$Si*CH*=CHCH_2), 6.38 (dt, 2 H, *J* = 13.9, 7.5 Hz, 2 (CH_{32}SiCH=*CH*CH_2N), 7.3–7.8 (m, 8 H, aromatic); IR (KBr) 3335, 3270, 1613, 1594, 1453, 1404, 1382 cm^{-1}; mass spectrum (FAB) *m/z* (%) 513 (M + H$^+$, 3). Anal. Calcd for $C_{26}H_{44}N_2OSi_4$: C, 60.87; H, 8.65; N, 5.46. Found: C, 60.52; H, 8.60; N, 5.61.

Formation of Phenylpyrrole. *N*-[3-(Tributylstannyl)-allyl]benzaldimine (13). The condensation of 2.0 g (5.76 mmol) of (*Z*)-3-(tributylstannyl)allylamine (5) with 0.61 g (5.76 mmol) of benzaldehyde in 15 mL of CH_2Cl_2 at rt in the presence of $MgSO_4$ for 20 h gave after distillation 2.2 g of 13 (92%): bp 60–65 °C (0.01 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.7–1.8 (m, 27 H, (C_4H_9)$_3$Sn), 4.27 (d, 2 H, *J* = 6.5 Hz, CH_2N), 6.11 (d, 1 H, *J* = 12.7 Hz, *J*(^{119}Sn–H) = 66.0 Hz, (C_4H_9)$_3$Sn*CH*=CH), 6.78 (dt, 1 H, *J* = 12.7, 6.5 Hz, *J*(^{119}Sn–H) = 133.6 Hz, CH=*CH*CH_2N), 7.6 (m, 5 H, aromatic), 8.32 (s, 1 H, C*H*=N); ^{13}C NMR ($CDCl_3$) δ 10.7, 14.1, 27.8, 29.6 (C_4H_9), 66.8 (CH_2N), 128.5, 128.9, 131.0, 131.5, 136.7, 145.9 (*CH*=*CH* and aromatic), 161.6 (*CH*=N); ^{119}Sn NMR ($CDCl_3$) δ -62.0; IR (CCl_4) 3028, 2959, 2872, 1645, 1597, 1582, 1464 cm^{-1}; mass spectrum (EI) *m/z* (%) 379 (M^+ - 57, 100), 262 (29), 144 (18), 91 (20).

2-Phenylpyrrole (14). To a solution of 13 (2.02 g, 4.64 mmol) in THF at -100 °C was added 1.86 mL of a 2.5 M solution of *n*-BuLi in hexane (4.64 mmol). The resulting red solution was stirred for 30 min and was then allowed to warm to rt. The reaction mixture turned black. After hydrolysis with saturated aqueous NH_4Cl and extraction, the combined ethereal extracts were dried over $MgSO_4$ and the solvents were removed. The residue was purified by TLC. Elution with a mixture of ether and hexane (1/9) gave first Bu_4Sn (1.3 g, 80%) and then 2-phenylpyrrole (0.3 g, 45%) with identical characteristics to those reported.[14]

Palladium Cross-Coupling Reactions of Compound 5. The palladium-catalyzed cross-coupling reactions of the vinyltin compound 5 were performed according to the following general procedure. A solution containing 1 equiv of 5 and 1 equiv of aryl bromide in toluene was refluxed in the presence of 2 mol % of $Pd(Ph_3P)_4$. After refluxing for 1–5 d, the mixture was cooled to rt and filtered. The solvent was removed under reduced pressure. The identity and stereochemistry of the produced allylamine was established by ^{1}H NMR analysis of the crude reaction product. Pure samples were obtained upon distillation of the residue or upon crystallization of the hydrochloride salt from CH_2Cl_2/hexane solutions.

(*Z*)-3-Phenylallylamine (15a). Upon refluxing for 4 d, 5.5 g (8.2 mmol) of 5 and 1.3 g (8.2 mmol) of bromobenzene, in toluene, the known[25] 15a was isolated: ^{1}H NMR (yield, 95%) δ 3.50 (dd, 2 H, *J* = 6.4, 1.6 Hz, CH_2N), 5.69 (dt, 1 H, *J* = 11.8, 6.4 Hz, CH=*CH*CH_2N), 6.45 (dt, 1 H, *J* = 11.8, 1.6 Hz, C*H*=CHCH_2N), 7.0–7.4 (m, 5 H, phenyl); IR (CCl_4) 3382, 1636 cm^{-1}. **16a**: after crystallization 0.65 g (47%) were collected; mp 171–173 °C; ^{1}H NMR (D_2O) δ 4.06 (dd, 2 H, *J* = 6.7, 1.8 Hz, CH_2N), 5.92 (dt, 1 H, *J* = 11.7, 6.7 Hz, CH=*CH*CH_2N), 6.99 (dt, 1 H, *J* = 11.7, 1.8 Hz, C*H*=CHCH_2N), 7.6 (m, 5 H, phenyl); ^{13}C NMR (D_2O) δ 40.5 (CH_2N), 125.1, 131.1, 131.7, 137.6, 138.4 (*CH*=*CH* and phenyl); IR (KBr) 1580, 1475, 790, 755, 685 cm^{-1}; mass spectrum (FAB) *m/z* (%) 134 (M + H$^+$, 47), 117 (M^+ - 17, 100), 91 (15), 77 (5). Anal. Calcd for $C_9H_{12}NCl$: C, 63.71; H, 7.13. Found: C, 63.55; H, 7.27.

(*Z*)-3-(2-Thienyl)allylamine (15b). The crude reaction mixture was treated with a 2 N aqueous HCl solution and washed three times with ether. The aqueous solution was neutralized with aqueous NaOH solution and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried over $MgSO_4$ and concentrated to give the known[26] **15b** (70%): ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 2 H, N*H*$_2$), 3.70 (d, 2 H, *J* = 6.4 Hz, CH_2N), 5.60 (dt, 1 H, *J* = 12.0, 6.4, Hz, CH=*CH*CH_2N), 6.52 (d, 1 H, *J* = 12.0 Hz, C*H*=CHCH_2N), 6.8–7.8 (m, 3 H, aromatic); IR (CCl_4) 3385, 3309, 1662, 1628, 1581 cm^{-1}; mass spectrum (FAB) *m/z* (%) 140 (M + H$^+$, 20), 123 (M + H$^+$ - 17, 100). Anal. Calcd for C_7H_9NS: C, 60.39; H, 6.52; N, 10.06. Found: C, 60.07; H, 6.61; N, 9.92.

(*Z*)-3-(4-Cyanophenyl)allylamine (15c): ^{1}H NMR ($CDCl_3$) (yield, 95%) δ 3.50 (d, 2 H, *J* = 6.3 Hz, CH_2N), 5.75 (dt, 1 H, *J* = 12.0, 6.3 Hz, CH=*CH*CH_2N), 6.50 (d, 1 H, *J* = 12.0 Hz, C*H*=CHCH_2N), 7.0–7.5 (m, 4 H, phenyl); IR (CCl_4) 2231, 1666, 1606, 1590 cm^{-1}. **16c** (65%): mp 197–199 °C; ^{1}H NMR (D_2O) δ

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3.90 (d, 2 H, J = 6.7 Hz, CH_2N), 5.89 (dt, 1 H, J = 11.8, 6.7 Hz, CH=CHCH$_2$N), 6.82 (d, 1 H, J = 11.8 Hz, CH=CHCH$_2$N), 7.3–7.7 (m, 4 H, phenyl); ^{13}C NMR (D_2O) δ 40.2 (CH$_2$N), 112.9 (C=N), 127.6, 130.5, 132.1, 135.4, 136.1, 143.2 (CH=CH and aromatic); IR (KBr) 2221, 1650, 1600, 1475 cm^{-1}; mass spectrum (FAB) m/z (%) 159 (M + H$^+$, 65), 142 (M + H$^+$ – 17, 40). Anal. Calcd for $C_{10}H_{11}N_2Cl$: C, 61.70; H, 5.69. Found: C, 61.31; H, 5.59.

(*Z*)-3-(4-Methoxyphenyl)allylamine (15d): ^{1}H NMR ($CDCl_3$) (yield, 95%) δ 1.32 (s, 2 H, NH_2), 3.31 (d, 2 H, J = 6.5 Hz, CH_2N), 3.68 (s, 3 H, OCH_3), 6.07 (dt, 1 H, J = 11.5, 6.5 Hz, HC=CHCH$_2$N), 6.40 (d, 1 H, J = 11.5 Hz, CH=CHCH$_2$N), 7.2 (m, 4 H, aromatic). **16d** (40%) (*E* isomer):[9] mp 231–232 °C; ^{1}H NMR (D_2O) δ 3.70 (m, 5 H, CH_2N, CH_3O), 6.18 (dt, 1 H, J = 16.0, 6.8 Hz, CH=CHCH$_2$N), 6.75 (d, 1 H, J = 16.0 Hz, CH=CHCH$_2$N), 6.8–7.4 (m, 4 H, aromatic); ^{13}C NMR (D_2O) δ 44.3 (CH$_2$N), 58.3 (OCH$_3$), 117.2, 120.7, 131.1, 131.8, 138.6, 162.0 (CH=CH and aromatic); IR (KBr) 1590, 1495 cm^{-1}; mass spectrum (FAB) m/z (%) 164 (M + H$^+$, 15), 147 (M + H$^+$ – 17, 28). Anal. Calcd for $C_{10}H_{14}NOCl$: C, 60.15; H, 7.07. Found: C, 59.84; H, 7.15.

(*Z,E*)-5-Phenyl-2,4-pentadienylamine (17). According to the above coupling procedure, 3.5 g (10.1 mmol) of 5 reacted with 1.83 g (10.1 mmol) of (*E*)-β-bromostyrene to give 1.0 g of 17 (51%): mp 214–216 °C; ^{1}H NMR (D_2O) δ 3.89 (d, 2 H, J = 7.56 Hz, CH_2N), 5.55 (dt, 1 H, J = 7.67, 10.41 Hz, CH=CHCH$_2$N), 6.54 (dd, 1 H, J = 10.87, 11.23 Hz, CH=CHCH$_2$N), 6.80 (d, 1 H, J = 15.54 Hz, C_6H_5CH=CH), 7.15 (dd, 1 H, J = 15.15, 11.32 Hz, C_6H_5CH=CH), 7.3–7.6 (m, 5 H, phenyl); ^{13}C NMR ($CDCl_3$) δ 39.5 (CH$_2$N), 123.7, 125.5, 129.7, 131.5, 132.0, 137.6, 139.1, 139.6 (CH=CH and aromatic); IR (KBr) 1630, 1590 cm^{-1}; mass spectrum (FAB) m/z (%) 160 (M + H$^+$, 13), 143 (M + H$^+$ – 17, 100), 91 (11), 77 (9).

Synthesis of Benzazepine Derivatives: 3*H*-2-Benzazepine (18). To a solution of 5 (4.41 g, 12.7 mmol) and Pd(Ph$_3$P)$_4$ (0.156 g, 0.135 mmol) in toluene (20 mL) was added 2-bromobenzaldehyde (2.34 g, 12.7 mmol). The resulting solution was refluxed with stirring until the solution became brown (ca. 24 h). The mixture was then allowed to cool to rt and concentrated. The residue was chromatographed over silica gel. Elution with a mixture of ether and dichloromethane (3/10) gave 1.65 g (90%) of 3*H*-2-benzazepine (18): ^{1}H NMR ($CDCl_3$) δ 3.74 (d, 2 H, J = 6.5 Hz, CH_2N), 6.02 (dt, 1 H, J = 9.9, 6.5 Hz, CH=CHCH$_2$N), 6.74 (d, 1 H, J = 9.9 Hz, CH=CHCH$_2$N), 7.2–7.6 (m, 4 H, aromatic), 8.35 (s, 1 H, CH=N); ^{13}C NMR ($CDCl_3$) δ 48.9 (CH$_2$N) 135.5, 138.0, 126.8, 128.8, 129.3 (HC=CH and aromatic), 162.8 (CH=N); IR (CCl_4) 3036, 2977, 2845, 1631, 1560, 1485, 1458, 1441 cm^{-1}; mass spectrum (FAB) m/z (%) 144 (M + H$^+$, 77).

7,8-Dimethoxy-3*H*-2-benzazepine (19) (18%): ^{1}H NMR ($CDCl_3$) δ 3.72 (d, 2 H, J = 6.30 Hz, CH_2N), 3.83 (s, 6 H, OCH_3), 5.89 (dt, 1 H, J = 9.8, 6.30 Hz, CH=CHCH$_2$N), 6.62 (d, 1 H, J = 9.8 Hz, CH=CHCH$_2$N), 6.74 (s, 1 H, aromatic), 6.93 (s, 1 H, aromatic), 8.25 (s, 1 H, CH=N); IR (CCl_4) 2959, 1625, 1606, 1554, 1518, 1464, 1263, 1123 cm^{-1}; mass spectrum (EI) m/z (%) 203 (M$^+$, 100), 188 (80), 160 (72).

1-Methyl-3*H*-2-benzazepine (20) (86%): ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3 H, CH_3), 3.52 (d, 2 H, J = 6.5, CH_2N), 6.22 (dt, 1 H, J = 9.8, 6.5 Hz, CH=CHCH$_2$N), 6.70 (d, 1 H, J = 9.8 Hz, CH=CHCH$_2$N), 7.2–7.7 (m, 4 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.7 (CH$_3$), 48.6 (CH$_2$N), 126.4, 128.7, 129.2, 129.5, 132.2, 132.5, 137.4, 138.9 (CH=CH and aromatic); IR (CCl_4) 2951, 2924, 2854, 1635, 1626, 1464 cm^{-1}; mass spectrum (FAB) m/z (%) 158 (M + H$^+$, 100).

3*H*-2-Benzazepin-1-one (21) (89%): mp 104–106 °C; ^{1}H NMR ($CDCl_3$) δ 3.55 (t, 2 H, J = 6.3 Hz, CH_2N), 6.25 (dt, 1 H, J = 10.2, 6.6 Hz, CH=CHCH$_2$N), 6.75 (d, 1 H, J = 10.2 Hz, CH=CHCH$_2$N), 7.25 (dd, 1 H, aromatic), 7.35–7.55 (12 peaks, 2 H, aromatic), 8.05 (dd, 1 H, aromatic), 8.10 (bs, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 38.1 (CH$_2$N) 128.0, 129.3, 131.3, 131.4, 131.5, 134.1, 134.4, 135.7 (CH=CH and aromatic), 167.4 (HC=N), 172.1 (C=O); IR (CCl_4) 3420, 1650, 1598, 1560, 1480, 1400 cm^{-1}; mass spectrum (FAB) m/z (%) 160 (M + H$^+$, 100).

Supplementary Material Available: ^{1}H NMR spectra of compounds 17–21 (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering formation.