Synthesis of Substituted Piperidines from *N*,*N*-Bis[(benzotriazol-1-yl)methyl]amines

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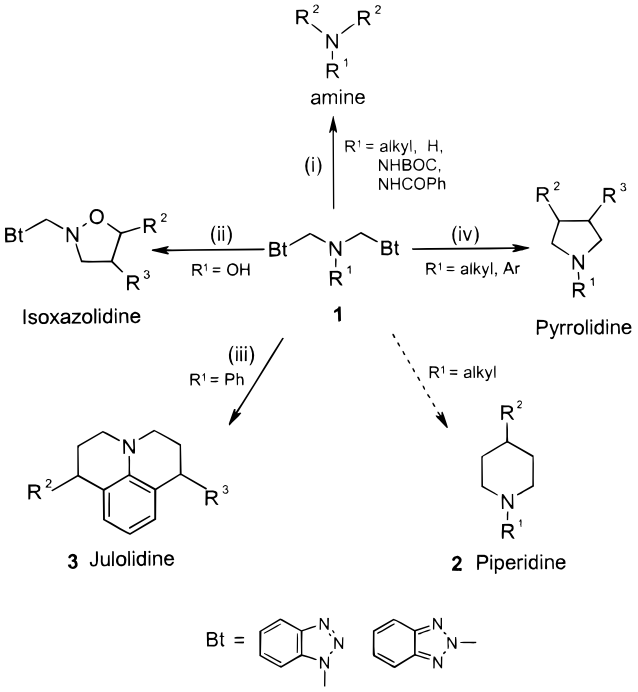
N,*N*-Bis[(benzotriazol-1-yl)methyl]benzylamines and *N*,*N*-bis[(benzotriazol-1-yl)methyl](*p*-*N*′,*N*′-dimethylphenyl)amine on reaction with allyltrimethylsilanes yielded substituted piperidines. Other *N*,*N*-bis[(benzotriazol-1-yl)methyl]anilines (unsubstituted and *p*-CH_3, OCH_3, Cl) gave julolidines (2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*] quinoline).

Introduction

Syntheses of piperidines are well documented,[1a−d] due to their physical and biological properties and their presence in numerous natural products.[2a−d] *N*,*N*-Bis-[(benzotriazol-1-yl)methyl]amines **1**, readily prepared from 1-(hydroxymethyl)benzotriazole and amines or from benzotriazole, aqueous formaldehyde, and amines,[3a,b] are useful (Scheme 1) in the preparation of the following: (i) Secondary and tertiary amines (R^1 = alkyl, H),[4a,b] *N*,*N*-disubstituted hydroxylamines (R^1 = OH),[5] and 1,1-disubstituted hydrazines and their 2-acyl derivatives (R^1 = NHCOR)[6] via displacement by Grignard reagents or $NaBH_4$ reduction of benzotriazole; (ii) isoxazolidines (R^1 = OH)[7] by conversion of bis[(benzotriazol-1-yl)methyl]-hydroxylamine to the nitrone and 1,3-dipolar additions; (iii) julolidines (R^1 = Ph),[8] through elimination of benzotriazole, formation of methylene immonium cation, and subsequent reaction with two molecules of vinyl ether or vinyl amide; and (iv) pyrrolidines (R^1 = Ar, alkyl)[9] by reductive cleavage of the Bt−C bond by SmI_2 to generate dianion and reaction with alkenes. We now report the application of **1** for the synthesis of piperidines.

Scheme 1



[3 + 3] cycloaddition reactions are of considerable importance and utility in the syntheses of six-membered heterocyclic systems.[10a−d] Most such reactions involve the condensation of a 1,3-dinucleophile (e.g. amidine, guanidine, urea, thiourea, or sulfamide) with a 1,3-dielectrophile (e.g., 1,3-dicarbonyl compound, related species such as cyanoacetic esters and malononitriles, or α,β-unsaturated aldehydes, ketones, esters, and nitriles). These [3 + 3] cycloaddition reactions are mainly used for the synthesis of aromatic heterocycles. However, Grieco et al.[11a−c] elegantly prepared 4-hydroxypiperidines by a

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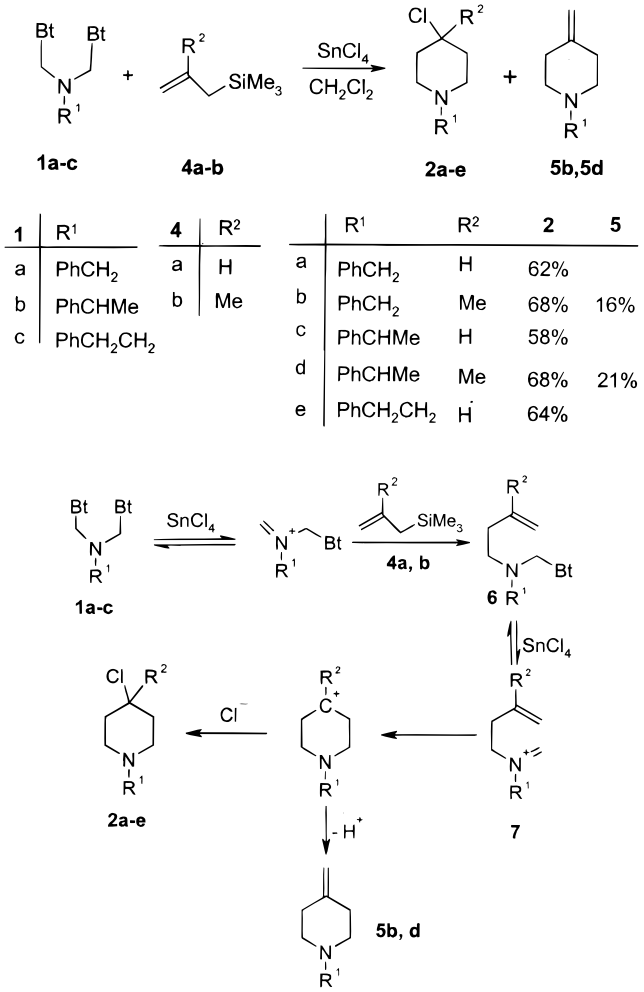
Scheme 2



1	R^1
a	$PhCH_2$
b	PhCHMe
c	$PhCH_2CH_2$

4	R^2
a	H
b	Me

	R^1	R^2	2	5
a	$PhCH_2$	H	62%	
b	$PhCH_2$	Me	68%	16%
c	PhCHMe	H	58%	
d	PhCHMe	Me	68%	21%
e	$PhCH_2CH_2$	H	64%	

related [3 + 1 + 1 + 1] reaction of allyltrimethylsilanes with *N*-benzylammonium trifluoroacetate and aqueous formaldehyde in water.

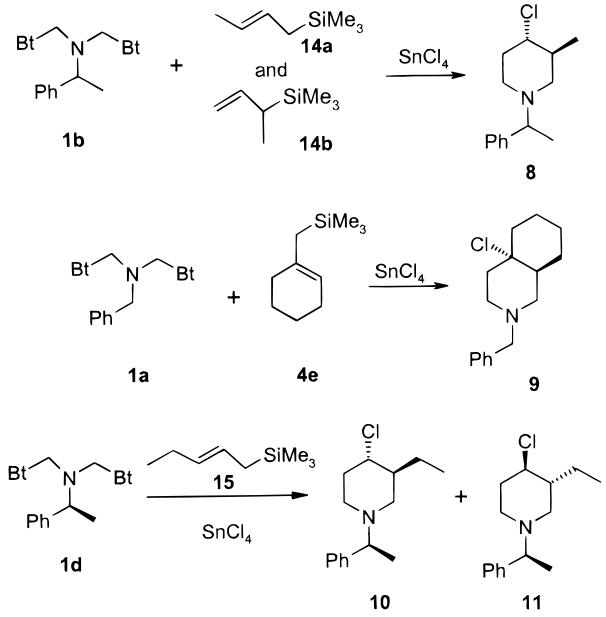
In an extension of Grieco's work, we now show that 4-functionalized piperidines can be prepared by the reaction of **1** with allyltrimethylsilane: allyltrimethylsilane serves as a three-carbon dipole equivalent[12] and **1** as a nitrogen atom centered 1,3-dication synthon. Depending on the substitution pattern of **1**, allyltrimethylsilane can serve alternatively as an alkene to give julolidines by intramolecular electrophilic cyclization (Scheme 1).

Results and Discussion

Reaction of *N,N*-Bis[(benzotriazol-1-yl)methyl]-alkylamines 1 with Allyltrimethylsilanes To Prepare Substituted Piperidines 2. Compounds **1a**−**c** were reacted with allyltrimethylsilanes **4a**,**b** in the presence of $SnCl_4$ to give 1,4-di-, and 1,4,4-trisubstituted piperidines **2a**−**e** in 58−68% yields (Scheme 2). Compound **2a** was previously prepared by Grieco[11a] in 48% yield by reacting benzylamine hydrochloride with aqueous formaldehyde and allyltrimethylsilane in the presence of lithium chloride.

Reactions of **1a**,**b** with 2-methylallyltrimethylsilane **4b** gave both the products **2b**,**d** of chloride ion trapping and

Scheme 3



the elimination products **5b**,**d**. Compounds **2b**,**d** can be converted into compounds **5b**,**d** with either base or acid catalysts. Quenching the reaction with dry methanol instead of water reduced the percentage of product **5b** from 16% to 5%.[13] The mechanism of this reaction could be as shown in Scheme 2. Since only traces of the byproduct homoallylamine **6** were isolated, it is probable that the departure of the second benzotriazole and the subsequent cyclization are faster than the initial homoallyl formation. Grieco[11a] suggested that the final step from intermediate **7** (Scheme 2) was a concerted olefin−iminium cyclization.

Additional substituted allyltrimethylsilanes can be used in this reaction (Scheme 3). The mixture of crotyltrimethylsilane **4c** and 1-methylallyltrimethylsilane **4d** (prepared according to the literature[14]) reacted with **1b** under the same conditions to give the 1,3,4-trisubstituted piperidine **8**. Cyclic allylsilane **4e** afforded the bicyclic amine **9**. By analogy with the literature reports,[11a,c] we locate the chloride trans to the alkyl substituent in compounds **8** and **9**.

Chiral piperidines can be prepared from chiral starting amines. Chiral (L) **1d** (analogous to racemic compound **1b**) reacted with trimethyl[(*E*)-2-pentenyl]silane to give **10** and **11** in 58% yield; however, the mixture could not be separated by a silica gel column. On the basis of their NMR spectra, the ratio of **10**:**11** was about 60:40 as measured from the $-CH_3$ group integrals.

Thus, starting from readily available **1**, 4-chloropiperidines **2a**−**e** were prepared via a [3 + 3] cycloaddition under mild reaction conditions while avoiding the use of trifluoroacetic acid. 4-Chloropiperidines **2a**−**e** are useful building blocks for many biologically active compounds, e.g., antihistaminic N-heterocyclic 4-piperidinamines[2a] and fentanyl analogues.[2b,c]

Reaction of *N,N*-Bis[(benzotriazol-1-yl)methyl]-anilines 1 with Allyltrimethylsilanes To Give Trimethylsilyl Julolidines 3. Substituted julolidines were prepared by our group via the reaction of *N*,*N*-bis-

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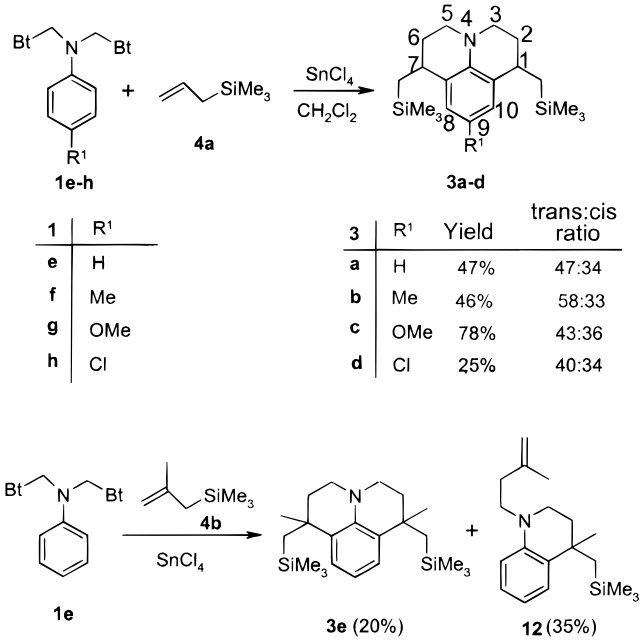
Scheme 4



[(benzotriazol-1-yl)methyl]aniline (**1**) (R = Ph) with electron-rich alkenes, e.g., *N*-vinyl-2-pyrrolidinone, ethyl vinyl ether, and enolizable aldehydes.[8] In a previous paper, we reported that allyltrimethylsilanes reacted with the iminium ions derived from *N*-(benzotriazol-1-yl)methylanilines to give tetrahydroquinolin-4-ylsilanes.[15] Under similar conditions, reactions of *N*,*N*-bis[(benzotriazol-1-yl)methyl]anilines **1** with allyltrimethylsilanes **4** now yield 1,7,9-trisubstituted trimethylsilyl julolidines **3a**−**d** for which the isolated yields and trans/cis ratios (from GC/MS) are indicated in Scheme 4.

The ^{13}C NMR spectra of the crude products **3** indicated a mixture of cis and trans isomers, though ^{1}H NMR spectra were identical. The predominant isomer was isolated by silica gel chromatography and assigned as trans geometry by comparison of the ^{13}C NMR spectra to the literature.[8] Reaction of **1e** with 2-methylallyltrimethylsilane (**4b**) gave an inseparable cis, trans mixture of julolidine **3e** (yield 20%), along with the desilylation product **12** (35% yield).

As shown in Scheme 4, para electron-releasing substituents (CH_3, OCH_3) on the aniline favored the formation of the julolidine product **3**, whereas electron-withdrawing substituents (Cl) led to **3** in low yield. This can be explained by the ease of electrophilic attack on the electron-rich ortho position of the aromatic ring that bears a para electron-releasing group. There were no significant effects from the para substituents on the ratios of trans/cis products, which were 1:1 to 1.5:1 in all the entries.

A somewhat surprising result occurred when R^1 was the strongest electron-releasing group $-N(Me)_2$; 4-chloropiperidine **13** was obtained instead of the julolidine (Scheme 5). Possibly because of the cationic π resonance system, **1i** acted as a 1,3-dication synthon and was trapped by allyltrimethylsilane (a 1,3-dianion equivalent) to form the piperidine ring through a [3 + 3] cycloaddition reaction.

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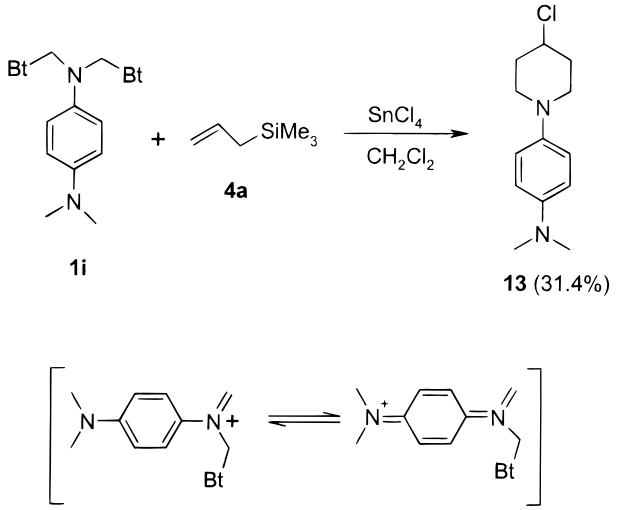
Scheme 5



Conclusion

In summary, piperidine derivatives **2** and trimethylsilyl julolidines **3** were prepared from the same synthons, *N*,*N*-bis[(benzotriazol-1-yl)methyl]amino derivatives **1**. Reactions of *N*,*N*-bis[(benzotriazol-1-yl)methyl]benzylamines and *N*,*N*-bis[(benzotriazol-1-yl)methyl](*p*-*N*′,*N*′-dimethylphenyl)amine with allyltrimethylsilanes yielded substituted piperidines **2**. Other *N*,*N*-bis[(benzotriazol-1-yl)methyl]anilines (unsubstituted and *p*-CH_3, OCH_3, Cl) gave access to julolidine analogues.

Experimental Section

General Comments. The NMR spectra were recorded with tetramethylsilane as the internal reference for ^{1}H (300 MHz) or solvent as the internal reference for ^{13}C (75 MHz).

See the literature for the preparation and characterization of *N*,*N*-bis[(benzotriazol-1-yl)methyl]amines: for **1a** and **1c**,[3a] for **1b** and **1d**,[9] for **1e**−**i**.[3b]

General Procedure for the Reaction of 1 Reacted with Allyltrimethylsilanes. Allyltrimethylsilane (3 mmol) was added to a solution of **1** (1 mmol) in dry CH_2Cl_2 (20 mL) being cooled by an ice−water bath. $SnCl_4$ (1 mmol) was then added to the stirred mixture. The resulting mixture was kept at this temperature for 2 h and then allowed to warm to room-temperature overnight. A NaOH solution (2 N, 20 mL) was added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude products, which were further purified by silica gel column chromatography to give the pure products.

1-Benzyl-4-chloropiperidine (2a).[11a] **1a** reacted with **4a**: yield 62%; ^{1}H NMR δ 1.95−2.09 (m, 2H), 2.11−2.26 (m, 2H), 2.26−2.42 (m, 2H), 2.78−2.90 (m, 2H), 3.62 (s, 2H), 4.20−4.09 (m, 1H), 7.35−7.44 (m, 5H); ^{13}C NMR δ 35.6, 51.3, 57.5, 62.9, 127.1, 128.2, 129.0, 138.3; MS *m*/*z* 209 (M^+, 10), 174 (M − Cl, 50), 91 (100).

1-Benzyl-4-chloro-4-methylpiperidine (2b). 1a reacted with **4b** to give **2b** and **5b**. **2b**: yield 68%; ^{1}H NMR δ 1.62 (s, 3H), 1.77−2.48 (m, 4H), 2.45 (t, J = 11.0 Hz, 2H), 2.60−2.72 (m, 2H), 3.54 (s, 2H), 7.20−7.32 (m, 5H); ^{13}C NMR δ 39.2, 40.8, 49.6, 63.0, 69.8, 127.0, 128.2, 129.1, 138.5. Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.78; H, 8.13; N, 6.26. Found: C, 69.58; H, 8.32; N, 6.47.

1-Benzyl-4-methylenepiperidine (5b): yield 16%, if quenched with dry methanol instead of 2 N NaOH solution, the yield of **5b** was 5%; ^{1}H NMR δ 2.38−2.49 (m, 4H), 2.57−2.70 (m, 4H), 3.70 (s, 2H), 4.83 (s, 2H), 7.36−7.52 (m, 5H); ^{13}C

NMR δ 34.6, 55.0, 62.9, 107.6, 126.9, 128.1, 129.1, 138.6, 146.7; HRMS calcd for $C_{13}H_{17}N$ 188.1439 (M + 1), found 188.1437 (M + 1).

1-(1-Phenylethyl)-4-chloropiperidine (2c). 1b reacted with **4a** to give **2c**: yield 58%; ^{1}H NMR δ 1.38 (d, *J* = 6.7 Hz, 3H), 1.82−1.99 (m, 2H), 1.99−2.15 (m, 2H), 2.15−2.28 (m, 2H), 2.69−2.79 (m, 1H), 2.80−2.91 (m, 1H), 3.45 (q, *J* = 6.7 Hz, 1H), 3.92−4.15 (m, 1H), 7.24−7.33 (m, 5H); ^{13}C NMR δ 19.4, 35.9, 48.6, 57.8, 64.4, 126.9, 127.5, 128.2, 143.9. Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.78; H, 8.13; N, 6.26. Found: C, 69.75; H, 8.35; N, 6.56.

1-(1-Phenylethyl)-4-chloro-4-methylpiperidine (2d). 1b reacted with **4b** to give **2d** and **5d**. **2d**: yield 68%; ^{1}H NMR δ 1.60 (d, *J* = 6.8 Hz, 3H), 1.83 (s, 3H), 1.94−2.20 (m, 4H), 2.58−2.70 (m, 2H), 2.72−2.85 (m, 1H), 3.00−3.11 (m, 1H), 3.68 (q, *J* = 6.8 Hz, 1H), 7.43−7.55 (m, 5H); ^{13}C NMR δ 19.5, 33.1, 41.1, 47.3 [46.3], 64.6, 70.0, 126.8, 127.5, 128.2, 144.3. Anal. Calcd for $C_{14}H_{20}ClN$: C, 70.71; H, 8.50; N, 5.89. Found: C, 70.73; H, 8.72; N, 6.23.

1-(1-Phenylethyl)-4-methylenepiperidine (5d): yield 21%; ^{1}H NMR δ 1.55 (d, *J* = 6.8 Hz, 3H), 2.30−2.42 (m, 4H), 2.52−2.68 (m, 4H), 3.65 (q, *J* = 6.7 Hz, 1H), 4.77 (s, 2H), 7.32−7.50 (m, 5H); ^{13}C NMR δ 19.3, 34.8, 52.0, 64.2, 107.1, 126.7, 127.6, 128.1, 143.8, 147.0. Anal. Calcd for $C_{14}H_{19}N$: N, 6.96. Found: N, 7.15.

1-Phenethyl-4-chloropiperidine (2e). 1c reacted with **4a** to give **2e**: yield 64%; ^{1}H NMR δ 2.04−2.20 (m, 2H), 2.20−2.39 (m, 2H), 2.39−2.58 (m, 2H), 2.70−2.82 (m, 2H), 2.88−3.09 (m, 4H), 4.16−4.32 (m, 1H), 7.30−7.50 (m, 5H); ^{13}C NMR δ 33.8, 35.5, 51.2, 57.3, 60.3, 126.0, 128.4, 128.6, 140.2. Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.78; H, 8.13; N, 6.26. Found: C, 69.62; H, 8.37; N, 6.36.

1-(1-Phenylethyl)-3-methyl-4-chloropiperidine (8). 1b reacted with the mixture of **14a** and **14b**[14] to give **8**: yield 42%; ^{1}H NMR δ 0.98 (d, *J* = 6.3 Hz, 3H) [1.06 (d, *J* = 6.3 Hz, 3H)], 1.37 (d, *J* = 3.6 Hz, 3H) [1.39 (d, *J* = 3.5 Hz, 3H)], 1.60−2.20 (m, 5H), 2.78−2.88 (m, 1H), 2.96−3.08 (m, 1H), 3.38−3.50 (m, 2H), 7.20−7.39 (m, 5H); ^{13}C NMR δ 17.2 [17.3], 19.4, 36.7 [36.6], 40.1, 50.1 [50.4], 57.3 [57.6], 64.0 [63.9], 65.5 [65.4], 126.9, 127.5, 128.2, 143.6. Anal. Calcd for $C_{14}H_{20}ClN$: N, 5.89. Found: N, 6.07.

2-Benzyl-4a-chlorodecahydroisoquinoline (9). 1a reacted with **15** to give **9**: yield 36%; ^{1}H NMR δ 1.18−1.26 (m, 2H), 1.26−1.72 (m, 5H), 1.72−1.98 (m, 4H), 2.09 (t, *J* = 11.0 Hz, 1H), 2.43 (dd, *J* = 2.7, 11.0 Hz, 1H), 2.55 (td, *J* = 4.2, 11.0 Hz, 1H), 2.71 (d, *J* = 11.0 Hz, 1H), 3.48 (s, 2H), 7.15−7.27 (m, 5H); ^{13}C NMR δ 21.7, 25.4, 25.7, 40.9, 41.1, 45.2, 49.4, 54.9, 63.0, 76.6, 127.0, 128.2, 129.1, 138.5; HRMS calcd for $C_{16}H_{22}ClN$ 264.1519 (M + 1), found 264.1504 (M + 1).

1-[(1*S*)-1-Phenylethyl)-3-ethyl-4-chloropiperidine (10). 1d reacted with **16** to give **10** and **11** (in brackets): yield 58%; ^{1}H NMR δ 0.90 (t, *J* = 7.5 Hz, 3H) [0.81 (t, *J* = 7.5 Hz, 3H)], 1.36 (d, *J* = 5.4 Hz, 3H) [1.38 (d, *J* = 6.6 Hz, 3H)], 1.60−1.80 (m, 3H), 1.85−2.20 (m, 4H), 2.72−3.14 (m, 2H), 3.40−3.50 (m, 1H), 3.50−3.63 (m, 1H), 7.20−7.38 (m, 5H); ^{13}C NMR δ 10.9 [10.8], 19.7 [18.9], 24.0 [23.8], 36.3 [36.2], 45.9, 49.7 [49.8], 54.3 [54.2], 63.9 [63.7], 64.3, 126.8 [126.9], 127.4 [127.5], 128.2, 143.5. Anal. Calcd for $C_{15}H_{22}ClN$: C, 71.54; H, 8.82; N, 5.56. Found: C, 71.26; H, 9.20; N, 5.74.

1,7-Bis[(trimethylsilyl)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (3a). 1e reacted with **4a** to give **3a**: yield 47%; ^{1}H NMR δ 0.20 (s, 18H), 1.01 (dd, *J* = 10.2, 14.8 Hz, 2H), 1.14 (dd, *J* = 4.2, 14.9 Hz, 2H), 1.85−1.91 (m, 2H), 2.05−2.20 (m, 2H), 3.04−3.09 (m, 2H), 3.20−3.27 (m, 2H), 3.34−3.41 (m, 2H), 6.65−6.68 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR δ −0.6, 25.3, 28.9, 32.7, 46.5, 115.2, 125.9, 128.4, 140.6; MS *m*/*z* 345 (M^+, 50), 258 (100). Anal. Calcd for $C_{20}H_{35}NSi_2$: N, 4.05. Found: N, 4.20.

9-Methyl-1,7-bis[(trimethylsilyl)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (3b). 1f reacted with **4a** to give **3b**: yield 46%; ^{1}H NMR δ 0.20 (s, 18H), 1.00 (dd, *J* = 10.5, 14.8 Hz, 2H), 1.15 (dd, *J* = 4.0, 11.0 Hz, 2H), 1.83−1.87 (m, 2H), 2.08−2.23 (m, 2H), 2.33 (s, 3H), 2.97−3.09 (m, 2H), 3.09−3.22 (m, 2H), 3.24−3.33 (m, 2H), 6.80 (s, 2H); ^{13}C NMR δ −0.6, 20.5, 25.7, 29.3, 32.7, 46.9, 126.5, 126.6, 128.8, 138.2; MS *m*/*z* 359 (M^+, 80), 272 (100). Anal. Calcd for $C_{21}H_{37}NSi_2$: C, 70.11; H, 10.39; N, 3.89. Found: C, 69.96; H, 10.26; N, 4.26.

9-Methoxy-1,7-bis[(trimethylsilyl)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (3c). 1g reacted with **4a** to give **3c**: yield 78%; ^{1}H NMR δ 0.20 (s, 18H), 1.02 (dd, *J* = 10.5, 14.9 Hz, 2H), 1.17 (dd, *J* = 3.8, 14.9 Hz, 2H), 1.78−1.90 (m, 2H), 2.10−2.22 (m, 2H), 2.98−3.07 (m, 2H), 3.07−3.17 (m, 2H), 3.20−3.29 (m, 2H), 3.88 (s, 3H), 6.62 (s, 2H); ^{13}C NMR δ −0.6, 25.8, 29.6, 33.0, 47.3, 55.8, 112.0, 130.3, 135.8, 150.7; MS *m*/*z* 375 (M^+, 100), 360 (40), 288 (90). Anal. Calcd for $C_{21}H_{37}NOSi_2$: N, 3.73. Found: N, 3.91.

9-Chloro-1,7-bis[(trimethylsilyl)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (3d). 1h reacted with **4a** to give **3d**: yield 25%; ^{1}H NMR δ 0.20 (s, 18H), 0.97 (dd, *J* = 10.4, 14.8 Hz, 2H), 1.10 (dd, *J* = 4.1, 15.0 Hz, 2H), 1.75−1.87 (m, 2H), 2.08−2.16 (m, 2H), 2.96−3.01 (m, 2H), 3.16−3.22 (m, 2H), 3.31−3.39 (m, 2H), 6.91 (s, 2H); ^{13}C NMR δ −0.6, 25.1, 28.6, 32.9, 46.4, 119.6, 125.4, 130.0, 139.1; MS *m*/*z* 379 (M^+, 90), 292 (100). Anal. Calcd for $C_{20}H_{34}NClSi_2$: C, 63.19; H, 9.03; N, 3.69. Found: C, 63.47; H, 9.10; N, 3.71.

1,7-Dimethyl-1,7-bis[(trimethylsilyl)methyl]-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline (3e). 1e reacted with **4b** to give **3e** (20%) and **12** (35%): ^{1}H NMR δ 0.17 (s, 9H), 0.20 (s, 9H), 1.37 (dd, *J* = 5.5, 14.8 Hz, 2H), 1.48 (dd, *J* = 11.8, 16.6 Hz, 2H), 1.62 (s, 3H), 1.63 (s, 3H), 1.95−2.10 (m, 2H), 2.23−2.31 (m, 2H), 3.32−3.46 (m, 4H), 6.82−6.90 (m, 1H), 7.22−7.31 (m, 2H); ^{13}C NMR δ 33.2 [32.1], 33.9 [33.3], 35.2 [35.1], 36.8 [36.7], 47.1 [46.9], 115.3 [115.4], 123.8, 124.3, 131.8; MS *m*/*z* 373 (M^+, 60), 358 (40), 286 (100). Anal. Calcd for $C_{22}H_{39}NSi_2$: C, 70.70; H, 11.54; N, 3.75. Found: C, 71.02; H, 11.13; N, 4.01.

1-(3-Methyl-3-butenyl)-4-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroquinoline (12): ^{1}H NMR δ 0.22 (s, 9H), 1.35, 1.42 (AB, *J* = 14.8 Hz, 2H), 1.62 (s, 3H), 2.09 (s, 3H), 1.95−2.20 (m, 2H), 2.50−2.62 (m, 2H), 3.58 (t, *J* = 6.0 Hz, 2H), 3.69 (t, *J* = 7.7 Hz, 2H), 5.04 (s, 1H), 5.08 (s, 1H), 6.82−6.90 (m, 2H), 7.26−7.34 (m, 1H), 7.46 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR δ 0.8, 22.8, 32.0, 32.4, 33.7, 34.8, 36.8, 45.6, 50.1, 110.5, 111.4, 115.3, 126.1, 126.7, 132.6, 143.4, 143.9. Anal. Calcd for $C_{19}H_{31}NSi$: N, 4.65. Found: N, 4.69.

***N*-[4-(4-Chloropiperidino)phenyl]-*N*,*N*-dimethylamine (13). 1i** reacted with **4a** to give **13**: yield 31%; mp 70.0−72.0 °C; ^{1}H NMR δ 2.12−2.26 (m, 2H), 2.30−2.44 (m, 2H), 3.03 (s, 6H), 3.03−3.10 (m, 2H), 3.45−3.58 (m, 2H), 4.25−4.36 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 35.5, 41.5, 49.4, 57.3, 114.4, 119.0, 142.9, 145.9; HRMS calcd for $C_{13}H_{19}ClN_2$ 238.1236, found 238.1139.

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