# Convenient Syntheses of Unsymmetrical Imidazolidines

Alan R. Katritzky,* Kazuyuki Suzuki, and Hai-Ying He

*Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200*

*katritzky@chem.ufl.edu*

*Received August 24, 2001*

Unsymmetrical imidazolidines **10**−**14**, optically active imidazolidines **20**−**22**, and 2,3-dihydro-1*H*-benzimidazoles **28** and **29** were synthesized in good to excellent yields by Mannich reactions of 1,2-ethanediamines **8a**−**c**, **18a**−**c**, or *N*-methyl-1,2-benzenediamine (**26a**) with benzotriazole and formaldehyde, followed by the nucleophilic substitution of the benzotriazolyl group with C-nucleophiles (Grignard reagents, sodium cyanide), an S-nucleophile (benzenethiol), and a P-nucleophile (triethyl phosphite).

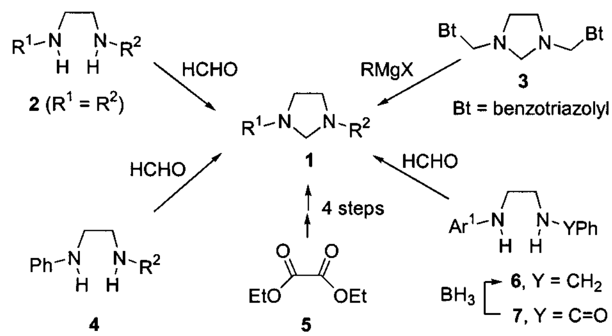
## Introduction

Imidazolidines **1** are important building blocks in biologically active compounds,[1] and carriers of pharmacologically active carbonyl compounds.[2] Symmetrical imidazolidines **1** ($R^1 = R^2 = Ar$) were prepared early, by Bischoff[3a] in 1898 and by Scholtz[3b] in 1901, by condensations of *N*,*N*′-diaryl-1,2-ethanediamines **2** with formaldehyde (Scheme 1). The same methodology was applied to synthesize other symmetrical 1,3-diarylimidazolidines **1** ($R^1 = R^2 = Ar$)[4] and 1,3-dialkylimidazolidines **1** ($R^1 = R^2 =$ alkyl or allyl) from *N*,*N*′-dialkyl-1,2-ethanediamines **2**.[5] Another route to symmetrical imidazolidines **1** involves the reduction of symmetrical cyclic ureas with $LiAlH_4$.[6] Reactions of 1,3,6,8-tetraazatricyclo[4.4.1.1$^{3,8}$]-dodecane with *para*-substituted phenols afford symmetrical **1** in about 21−28% yields.[7] Mannich reactions of 1,2-ethanediamine, benzotriazole, and formaldehyde led to 1,3-bis(benzotriazolylmethyl)imidazolidine (**3**), which easily undergoes nucleophilic substitutions with Grignard reagents to afford symmetrical **1** (Scheme 1).[8]

As pointed out by Lambert,[9] relatively few papers have been published on the preparation of unsymmetrical *N*,*N*′-disubstituted imidazolidines. In 1977, Kliegel obtained three 1-phenyl-3-alkylimidazolidines **1** ($R^1$ = Ph, $R^2$ = alkyl) by the reaction of formaldehyde with *N*-alkyl-*N*′-phenyl-1,2-ethanediamines **4** (Scheme 1), obtained by the condensation of *β*-aminosulfonic acids (need to be prepared) and primary amines.[10] Lambert synthesized three unsymmetrical imidazolidines **1** (in ca. 25% overall yields) from diethyl oxalate (**5**) via selective amidations of **5** with primary amines, $LiAlH_4$ reduction of the corresponding oxamides to unsymmetrical *N*,*N*′-disubstituted 1,2-ethanediamines, and final reactions with formaldehyde (Scheme 1).[9] Perillo[11] recently prepared two 1-benzyl-3-arylimidazolidines from formaldehyde and *N*-benzyl-*N*′-aryl-1,2-ethanediamines **6**, produced by the $BH_3$ reduction of the corresponding *N*-benzoyl-*N*′-aryl-1,2-ethanediamines **7** (Scheme 1).[12]

These and other reported methods generally introduce $R^1$ and $R^2$ (alkyl or aryl) groups into the imidazolidine ring directly from *N*,*N*′-disubstituted 1,2-ethanediamines. It is difficult to convert such *N*-alkyl or *N*-aryl substituents into other functionalities. We have shown that the weak C−N bond of *N*-substituted benzotriazoles allows easy replacement of the benzotriazolyl group via nucleophilic substitution, elimination, reduction, cyclization, etc.[13] We now report a simple and efficient way to prepare novel unsymmetrical imidazolidines **10**−**14** and optically active imidazolidines **20**−**22** in good to excellent yields

**Scheme 1**




* To whom correspondence should be addressed.

(1) (a) Sharma, V.; Crankshaw, C. L.; Piwnica-Worms, D. *J. Med. Chem.* **1996**, *39*, 3483. (b) Sage, C. R.; Michelitsch, M. D.; Stout, T. J.; Biermann, D.; Nissen, R.; Finer-Moore, J.; Stroud, R. M. *Biochemistry* **1998**, *37*, 13893. (c) Olmos, G.; Ribera, J.; Garcia-Sevilla, J. A. *Eur. J. Pharm.* **1996**, *310*, 273. (d) Chang-Fong, J.; Benamour, K.; Szymonski, B.; Thomasson, F.; Morand, J.-M.; Cussac, M. *Chem. Pharm. Bull.* **2000**, *48*, 729. (e) Rogers, J. A.; Choi, Y. W. *Pharm. Res.* **1993**, *10*, 913. (f) Sakuta, H.; Okamoto, K. *Eur. J. Pharm.* **1994**, *259*, 223.

(2) (a) Crank, G.; Harding, D. R. K.; Szinai, S. S. *J. Med. Chem.* **1970**, *13*, 1212. (b) Crank, G.; Harding, D. R. K.; Szinai, S. S. *J. Med. Chem.* **1970**, *13*, 1215.

(3) (a) Bischoff, C. A. *Chem. Ber.* **1898**, *31*, 3248. (b) Scholtz, M.; Jaross, K. *Chem. Ber.* **1901**, *34*, 1504.

(4) Jaenicke, L.; Brode, E. *Liebigs Ann. Chem.* **1959**, *624*, 120.

(5) (a) Donia, R. A.; Shotton, J. A.; Bentz, L. O.; Smith, G. E. P., Jr. *J. Org. Chem.* **1949**, *14*, 952. (b) Heaney, H.; Papageorgiou, G.; Wilkins, R. F. *Tetrahedron* **1997**, *53*, 14381.

(6) Bates, H. A.; Condulis, N.; Stein, N. L. *J. Org. Chem.* **1986**, *51*, 2228.

(7) Rivera, A.; Gallo, G. I.; Gayon, M. E.; Joseph-Nathan, P. *Synth. Commun.* **1993**, *23*, 2921.

(8) Katritzky, A. R.; Pilarski, B.; Urogdi, L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 541.

(9) Lambert, J. B.; Huseland, D. E.; Wang, G.-T. *Synthesis* **1986**, 657.

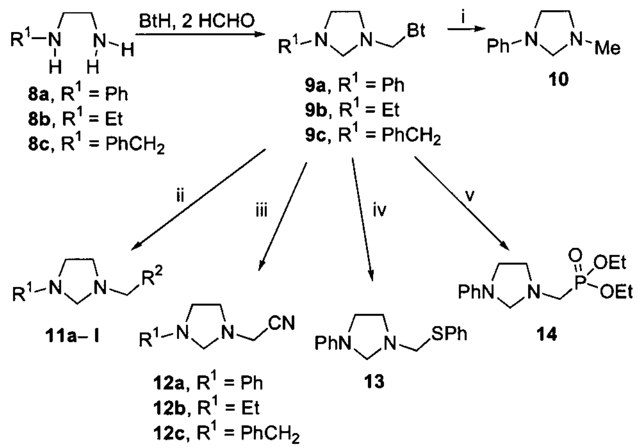
(10) Kliegel, W.; Franckenstein, G.-H. *Liebigs Ann. Chem.* **1977**, 956.

(11) Salerno, A.; Hedrera, M. E.; D'Accorso, N. B.; Alho, M. M.; Perillo, I. A. *J. Heterocycl. Chem.* **2000**, *37*, 57.

(12) Orelli, L. R.; Salerno, A.; Hedrera, M. E.; Perillo, I. A. *Synth. Commun.* **1998**, *28*, 1625.

10.1021/jo010868n CCC: $22.00 
Published on Web 04/06/2002

**Scheme 2**[a,b]




[a] Reagents and conditions: (i) $NaBH_4$ ($R^1$ = Ph); (ii) $R_2MgX$; (iii) NaCN; (iv) PhSH/NaH ($R^1$ = Ph); (v) $P(OEt)_3/ZnBr_2$ ($R^1$ = Ph). [b] Bt = benzotriazol-1-yl and -2-yl.

and extend this methodology for the preparation of 2,3-dihydro-1*H*-benzimidazoles **28** and **29** using benzotriazole as a synthetic auxiliary.

## Results and Discussion

**Preparation of 1-Substituted 3-(benzotriazolylmethyl)imidazolidines 9a–c.** Mannich condensations of *N*-substituted 1,2-ethanediamines **8a–c** with 1 equiv of benzotriazole and 2 equiv of formaldehyde (37% aqueous solution) in MeOH/$H_2O$ at room temperature gave 1-substituted 3-(benzotriazolylmethyl)imidazolidines **9a–c** in 96%, 85%, and 92% yields, respectively (Scheme 2). Compound **9a** was initially obtained as a sole $Bt^1$ isomer; in $CDCl_3$, it gradually changes to a mixture of $Bt^1$ and $Bt^2$ isomers in a ca. 5.6:1 ratio after 3 days. Compounds **9b,c** were obtained as mixtures of $Bt^1$ and $Bt^2$ isomers, each in a ca. 5:1 ratio. On the bais of our previous results showing a small difference in the reactivity of the $Bt^1$ and $Bt^2$ isomers,[14] **9b,c** were used directly as mixtures for the subsequent reactions. In the $^{13}C$ NMR spectrum of **9a**, the 145.8 ppm peak is believed to contain two carbons, since it changes to two signals (145.0 and 146.0 ppm, respectively) in DMSO-$d_6$. Benzotriazolyl intermediates **9a–c** were used as crude products for the subsequent reactions.

**Nucleophilic Substitutions of 9a–c with $NaBH_4$, Grignard Reagents, Sodium Cyanide, Benzenethiol, and Triethyl Phosphite.** (Cf. Scheme 2.) Treatment of **9a** with 2 equiv of sodium borohydride in refluxing THF replaced the Bt group with hydrogen to give 1-phenyl-3-methylimidazolidine (**10**) in 96% yield. The methylene protons between the two nitrogen atoms in **10** appear at 3.97 ppm as a singlet.

We previously reported that the benzotriazolyl group attached to the α-position to a nitrogen is easily replaced by nucleophilic reagents.[15] Nucleophilic substitutions of **9a–c** with alkyl-, vinyl-, aryl-, and (phenylethynyl)-magnesium bromide and, for the preparation of **11c,g,i**, benzylmagnesium chloride in dry THF or toluene furnished novel unsymmetrical 1,3-disubstituted imidazolidines **11a–l** in 63–96% yields. The isolated yields and the reaction conditions for **11** are summarized in Table 1. Compounds **11g–l** easily decompose on silica gel, so they were isolated by neutral aluminum oxide column chromatography. The structures of **11a–l** were clearly supported by their $^1H$ and $^{13}C$ NMR spectra and microanalyses or HRMS results. The methylene protons between the two nitrogens in **11a–f** appear at around 4.0 ppm as singlets.

**Table 1. Preparation of 1,3-Disubstituted Imidazolidines 11a–l**

| 11 | $R^1$ | $R^2$ [a] | yield (%) | method[b] |
|---|---|---|---|---|
| **a** | Ph | *n*-Bu | 80 | A, 1.4 equiv of GR[c] |
| **b** | Ph | $CH_2CH_2Ph$ | 96 | A, 1.2 equiv of GR |
| **c** | Ph | $CH_2Ph$ | 96 | A, 2.0 equiv of GR |
| **d** | Ph | $C_6H_4OMe$-*p* | 81 | A, 1.2 equiv of GR |
| **e** | Ph | C≡CPh | 80 | A, 1.2 equiv of GR |
| **f** | Ph | CH=$CH_2$ | 75 | A, 1.2 equiv of GR |
| **g** | Et | $CH_2Ph$ | 75 | B, 2.0 equiv of GR |
| **h** | Et | $C_6H_4Me$-*p* | 71 | B, 2.0 equiv of GR |
| **i** | $PhCH_2$ | $CH_2Ph$ | 79 | B, 2.0 equiv of GR |
| **j** | $PhCH_2$ | CH=$CH_2$ | 63 | B, 2.0 equiv of GR |
| **k** | $PhCH_2$ | C≡CPh | 65 | B, 1.2 equiv of GR |
| **l** | $PhCH_2$ | *n*-$C_5H_{11}$ | 80 | B, 1.6 equiv of GR |

[a] $R^2MgBr$ was used except in the case of **11c,g,i** when $PhCH_2MgCl$ was used. [b] Method A: in THF (10 mL), rt 0.5 h and then reflux 1 h. Method B: in toluene (10 mL), rt 0.5 h and then 1 h at 50 °C. [c] GR = Grignard reagent.

The benzotriazolyl group in **9a–c** can be substituted by a cyano anion to furnish 2-(3-substituted 1-imidazolidinyl)acetonitriles **12a–c** in 77–97% yields. Reaction of **9a** with benzenethiol in the presence of sodium hydride produced 1-phenyl-3-(phenylthiomethyl)imidazolidine (**13**) in 66% yield. The benzotriazolyl group in **9a** was replaced in the presence of $ZnBr_2$ by a P-nucleophile (triethyl phosphite) to afford diethyl (3-phenyl-1-imidazolidinyl)-methylphosphonate (**14**) in 70% yield. The Lewis acid $ZnBr_2$ facilitates loss of the benzotriazolyl anion to form an iminium cation, which is then attacked by the P-nucleophile.[15c] Thus, various useful functionalities were introduced to the imidazolidine ring system via the nucleophilic substitutions of the benzotriazolyl group as a synthetic auxiliary.

**Syntheses of Optically Active Imidazolidines.** (Cf. Scheme 3.) We further investigated the preparation of optically active imidazolidines starting from commercially available *N*-Boc-α-amino acids **15a–c**. On the basis of our recent paper,[16] α-amino amides **17a–c** were easily obtained in two steps from the optically active *N*-Boc-α-amino acids **15a–c** ($R^3$ = Me, *i*-Bu, or $PhCH_2$) and 4-methylphenylamine. Crombie and Hooper reduced 2-amino-*N*-phenylpropanamide with $LiAlH_4$ to 2-aminopropylaniline without reporting a detailed procedure.[17] We found that refluxing of **17b** ($R^3$ = *i*-Bu) with 3 equiv of $LiAlH_4$ in dry THF for 1 day gave a 1:1 mixture of **17b** and **18b**. When 6 equiv of $LiAlH_4$ in dry THF for 2 days was used, reduction of **17a–c** afforded chiral diamines

(13) For a review of using benzotriazole as an auxiliary for organic syntheses, see: Katritzky, A. R.; Lan, X.; Yang J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409.

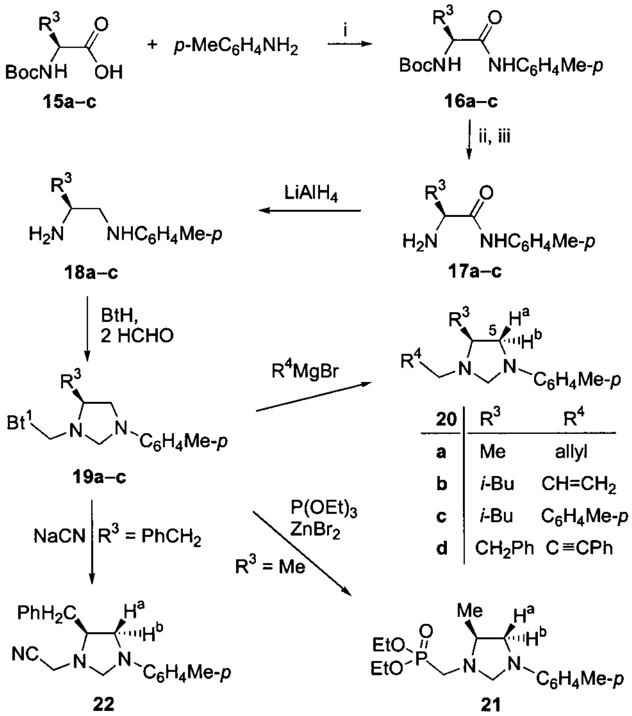
(14) (a) Katritzky, A. R.; Rachwal, S.; Hitchings, G. J. *Tetrahedron* **1991**, *47*, 2683. (b) Katritzky, A. R.; Mehta, S.; He, H.-Y. *J. Org. Chem.* **2001**, *66*, 148.

(15) (a) Katritzky, A. R.; Yannakopoulou, K.; Lue, P.; Rasala, D.; Urogdi, L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 225. (b) Katritzky, A. R.; Mehta, S.; He, H.-Y.; Cui, X. *J. Org. Chem.* **2000**, *65*, 4364. (c) Katritzky, A. R.; Qiu, G.; He, H.-Y.; Yang, B. *J. Org. Chem.* **2000**, *65*, 3683.

(16) Katritzky, A. R.; Xu, Y.-J.; He, H.-Y.; Steel, P. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1767.

(17) Crombie, L.; Hooper, K. C. *J. Chem. Soc.* **1955**, 3010.

**Scheme 3**[a]




[a] Reagents and conditions: (i) ClCOOBu-*i*, *N*-methylmorpholine; (ii) HCl/$Et_2O$ (2 M); (iii) aq NaOH.

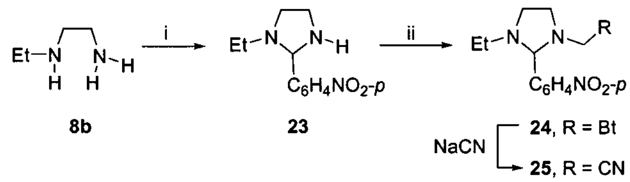
**18a–c** in more than 90% yields. Intermediates **16a–c**, **17a–c**, and **18a–c** were all used as crude products without further purification for subsequent reactions.

Reaction of diamines **18a–c** with benzotriazole and formaldehyde generated benzotriazol-1-yl intermediates **19a–c** in 85%, 93%, and 93% yields, respectively. Nucleophilic substitutions of **19a–c** by Grignard reagents, triethyl phosphite, or sodium cyanide gave optically active imidazolidines **20a–d**, **21**, or **22** in 66–99% yields. The structures of **20–22** are supported by their $^1$H and $^{13}$C NMR spectra and microanalyses. The two diastereotopic methylene hydrogens at the 5-position appear at different chemical shifts due to the 4-postion chirality. For **20a** and **21**, irradiation of the annular $CH_3$ caused a distinct positive NOE effect for one of the methylene hydrogens at the 5-position; thus, this hydrogen at a higher field is assigned to be the *anti*-hydrogen $H^a$. We did not attempt to assign $H^a$ and $H^b$ for **20b–d** and **22** because of their overlapping with other protons; however, we believe that their *anti*-$H^a$ would be upfield by analogy to what was observed for **20a** and **21**.

**Modification of the 2-Position of the Imidazolidine Ring.** Following a previously reported procedure,[18] a 4-nitrophenyl group was introduced onto the imidazolidine ring at the 2-position by the reaction of *N*-ethyl-1,2-ethanediamine with 4-nitrobenzaldehyde using azeotropic distillation. To avoid the formation of chain tautomers due to possible ring–chain tautomerism,[18] we did not attempt using *N*-phenyl-1,2-ethanediamine (**8a**) as the starting material. Compound **23** exists only in its cyclic form since no spectral evidence for the open tautomer was observed.

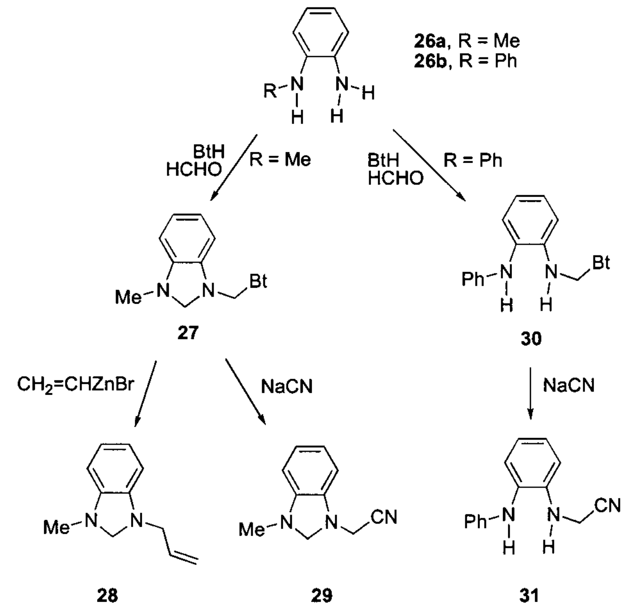
Reaction of **23** with 1 equiv of benzotriazole and formaldehyde gave Bt intermediate **24**, which was further treated with sodium cyanide to afford 2-[3-ethyl-2-(4-nitrophenyl)-1-imidazolidinyl]acetonitrile (**25**) in 92% yield (Scheme 4).

**Scheme 4**[a]




[a] Reagents and conditions: (i) p-$O_2NC_6H_4CHO$; (ii) BtH, HCHO.

**Scheme 5**




**Preparation of 3-Substituted 1-Methyl-2,3-dihydro-1*H*-benzimidazoles 28 and 29.** 2,3-Dihydro-1*H*-benzimidazoles are usually prepared by the condensations of the corresponding *N*,*N'*-disubstituted 1,2-benzenediamines with formaldehyde.[19] We previously reported the formation of 1,3-bis(benzotriazolylmethyl)-2,3-dihydro-1*H*-benzimidazole on the treatment of 1,2-benzenediamines with benzotriazole and formaldehyde.[20] We now find that condensation of *N*-methyl-1,2-benzenediamine (**26a**) with benzotriazole and 2 equiv of formaldehyde produces Bt intermediate **27** in 85% yield (Scheme 5). Compound **27** was obtained as a mixture of $Bt^1$ and $Bt^2$ isomers in a ca. 5.9:1 ratio, which was used directly for the subsequent reactions.

Reaction of **27** with vinylmagnesium bromide was found to give unidentifiable products probably opening the five-membered ring. The weaker nucleophile vinylzinc bromide (prepared from vinylmagnesium bromide and zinc chloride) gave 1-allyl-3-methyl-2,3-dihydro-1*H*-benzimidazole (**28**) in 83% yield. Compound **28** is extremely sensitive to silica gel or neutral $Al_2O_3$; it was finally purified by flash column chromatography on basic $Al_2O_3$. It also easily decomposes in $CDCl_3$ with disappearance of the $NCH_2N$ methylene group, so its NMR

(18) Parrinello, G.; Mülhaupt, R. *J. Org. Chem.* **1990**, *55*, 1772.

(19) (a) Morgan, G. T.; Challenor, W. A. P. *J. Chem. Soc.* **1921**, 1537. (b) Harvey, I. W.; McFarlane, M. D.; Moody, D. J.; Smith, D. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1939.

(20) Katritzky, A. R.; Rachwal, S.; Wu. J. *Can. J. Chem.* **1990**, *68*, 446.

spectra were recorded in DMSO-$d_6$. Treatment of **27** with 2 equiv of NaCN produced a 94% yield of 2-(3-methyl-2,3-dihydro-1*H*-benzimidazol-1-yl)acetonitrile (**29**), which was also purified by flash basic $Al_2O_3$ column chromatography. Compounds **28** and **29** are both labile to air, so they may be used in situ for other transformations, since their crude NMR spectra and GC analyses show more than 90% purity. In the absence of mechanistic studies, a possible reason for instability is that compounds **28** and **29** are readily oxidized.

Condensation of **26b** (R = Ph) with benzotriazole and formaldehyde (1 or 2 equiv) only generated the acyclic intermediate **30** possibly due to the increased steric hindrance caused by the PhNHAr fragment. The Bt group in **30** was further substituted by cyano anion to furnish 2-(2-anilinoanilino)acetonitrile (**31**) in 77% yield.

In summary, a short and efficient method has been developed for the preparation of unsymmetrical imidazolidines and 2,3-dihydro-1*H*-benzimidazoles via Mannich reactions of diamines with benzotriazole and formaldehyde, followed by the nucleophilic substitutions of the benzotriazolyl group with other functionalities. Compared to the previous methods (multiple steps and low yields) for the preparation of unsymmetrical imidazolidines,[9-11] our method needs only two steps, utilizes easily available starting materials, and generally affords the desired products in good to excellent yields.

## Experimental Section

THF or toluene was distilled from sodium−benzophenone prior to use. Melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded (300 and 75 MHz, respectively) in $CDCl_3$ (with TMS for $^1$H and chloroform-*d* for $^{13}$C as the internal reference), unless otherwise stated. Elemental analyses were performed on a Carlo Erba-1106 instrument. Optical rotation values were measured with the use of the sodium D line. Column chromatography was performed on silica gel (200−425 mesh), neutral alumina (60−325 mesh), or basic alumina (60−325 mesh). All of the reactions were carried out under $N_2$.

**General Procedure for the Preparation of 1-Substituted 3-(Benzotriazolylmethyl)imidazolidines 9a−c.** A mixture of an *N*-substituted 1,2-ethanediamine, **8a−c** (3.0 mmol), BtH (0.36 g, 3.0 mmol), and formaldehyde (37% aqueous solution, 0.49 g, 6 mmol) in $CH_3OH/H_2O$ (10 mL/5 mL) was stirred for 4 h at 20 °C. For **9a**, the precipitate formed was filtered and washed with cool $Et_2O$. For **9b,c**, the mixture was extracted with EtOAc, and the organic fraction was washed with 1 M NaOH and brine and dried over anhyd $Na_2SO_4$. Removal of the solvents in vacuo gave **9b,c** as an oil. Bt intermediates **9a−c** were used as crude products for the subsequent reactions.

**Data for 1-(1*H*-1,2,3-Benzotriazolylmethyl)-3-phenylimidazolidine (9a)**: white microcrystals (from $CHCl_3$/hexanes); yield 96%; mp 123−124 °C; $^1$H NMR $\delta$ 3.20 (t, $J$ = 6.1 Hz, 2H), 3.35 (t, $J$ = 6.1 Hz, 2H), 4.24 (s, 2H), 5.62 (s, 2H, $Bt^1$-$CH_2$), 6.43 (d, $J$ = 7.9 Hz, 2H), 6.70 (t, $J$ = 7.2 Hz, 1H), 7.19 (t, $J$ = 7.7 Hz, 2H), 7.37 (t, $J$ = 7.5 Hz, 1H), 7.51 (t, $J$ = 7.5 Hz, 1H), 7.65 (d, $J$ = 8.2 Hz, 1H), 8.06 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 45.9, 49.6, 64.4, 67.0 ($Bt^1CH_2$), 109.6, 111.6, 116.8, 119.9, 124.1, 127.7, 129.1, 133.4, 145.8, 145.8. Anal. Calcd for $C_{16}H_{17}N_5$: C, 68.79; H, 6.13; N, 25.07. Found: C, 68.96; H, 6.18; N, 25.13.

**Procedure for the Reduction of 9a with $NaBH_4$.** A mixture of **9a** (0.28 g, 1.0 mmol) and $NaBH_4$ (0.076 g, 2.0 mmol) was refluxed in dry THF (10 mL) overnight. After removal of the solvent in vacuo, the residue was diluted with EtOAc. The organic extracts were washed with 1 M NaOH and brine and dried over anhyd $MgSO_4$. Evaporation of the solvent in vacuo gave 1-methyl-3-phenylimidazolidine (**10**): colorless flakes (from $Et_2O$); yield 96%; mp 33−34 °C (lit.[10] mp 32−34 °C); $^1$H NMR $\delta$ 2.48 (s, 3H), 2.96 (t, $J$ = 6.3 Hz, 2H), 3.42 (t, $J$ = 6.3 Hz, 2H), 3.97 (s, 2H), 6.53 (d, $J$ = 7.8 Hz, 2H), 6.69 (t, $J$ = 7.3 Hz, 1H), 7.23 (t, $J$ = 7.3 Hz, 2H); $^{13}$C NMR $\delta$ 40.8, 46.3, 54.8, 71.8, 111.4, 116.1, 129.2, 146.4.

**General Procedure for the Nucleophilic Substitutions of 9a−c with Grignard Reagents.** To a solution of 1-substituted 3-(benzotriazolylmethyl)imidazolidine **9a−c** (1.0 mmol) in dry THF or toluene (10 mL) at 0 °C was added dropwise an appropriate Grignard reagent. The amount of the Grignard reagent and the subsequent reaction conditions are collected in Table 1. After being cooled, the mixture was quenched with water and extracted with $Et_2O$. The combined extracts were washed with 1 M NaOH and brine and dried over anhyd $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by column chromatography (silica gel) with hexanes/EtOAc as an eluent to give 1,3-disubstituted imidazolidine **11a−f**. Compounds **11g−l** were purified by neutral $Al_2O_3$ column chromatography.

**Data for 1-Pentyl-3-phenylimidazolidine (11a)**: colorless oil; yield 80%; $^1$H NMR $\delta$ 0.91 (t, $J$ = 6.3 Hz, 3H), 1.34−1.40 (m, 4H), 1.53−1.58 (m, 2H), 2.55 (t, $J$ = 7.5 Hz, 2H), 2.95 (t, $J$ = 6.3 Hz, 2H), 3.40 (t, $J$ = 6.3 Hz, 2H), 3.98 (s, 2H), 6.48 (d, $J$ = 8.2 Hz, 2H), 6.68 (t, $J$ = 7.3 Hz, 1H), 7.22 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 14.0, 22.6, 28.5, 29.6, 46.1, 52.9, 54.7, 70.3, 111.3, 116.0, 129.1, 146.4. Anal. Calcd for $C_{14}H_{22}N_2$: C, 77.01; H, 10.16; N, 12.83. Found: C, 77.30; H, 10.49; N, 13.14.

**Data for 1-Ethyl-3-phenethylimidazolidine (11g)**: colorless oil; yield 75%; $^1$H NMR $\delta$ 1.10 (t, $J$ = 7.5 Hz, 3H), 2.56 (q, $J$ = 7.4 Hz, 2H), 2.78−2.86 (m, 8H), 3.46 (s, 2H), 7.19−7.31 (m, 5H); $^{13}$C NMR $\delta$ 14.1, 35.8, 49.3, 52.2, 52.5, 57.4, 76.4, 126.0, 128.3, 128.6, 140.1. Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87. Found: C, 76.53; H, 9.77.

**Data for 1-Benzyl-3-phenethylimidazolidine (11i)**: colorless oil; yield 79%; $^1$H NMR $\delta$ 2.76 (br s, 4H), 2.84 (br s, 4H), 3.44 (s, 2H), 3.70 (s, 2H), 7.19−7.33 (m, 10H); $^{13}$C NMR $\delta$ 35.8, 52.3, 52.5, 57.1, 59.5, 76.5, 126.0, 126.9, 128.2, 128.3, 128.4, 128.5, 139.2, 140.1. Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.21; H, 8.63; N, 10.31.

**General Procedure for the Reaction of 9a−c with NaCN.** A mixture of **9a−c** (1.0 mmol) and NaCN (0.050 g, 1.0 mmol) in DMSO (5 mL) was stirred at 25 °C for 20 h. The mixture was poured into 20 mL of water. For **12a**, the precipitate formed was filtered to give a white powder, which was recrystallized from EtOH. For **12b,c**, the mixture was extracted with $CH_2Cl_2$, and the organic extracts were washed with 1 M NaOH, water, and brine and dried over anhyd $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography to give **12b,c**.

**Data for 2-(3-Phenyl-1-imidazolidinyl)acetonitrile (12a)**: white microcrystals (from EtOH); yield 77%; mp 65−66 °C; $^1$H NMR $\delta$ 3.15 (t, $J$ = 6.2 Hz, 2H), 3.49 (t, $J$ = 6.2 Hz, 2H), 3.74 (s, 2H), 4.15 (s, 2H), 6.51 (d, $J$ = 8.1 Hz, 2H), 6.75 (t, $J$ = 7.3 Hz, 1H), 7.25 (t, $J$ = 7.9 Hz, 2H); $^{13}$C NMR $\delta$ 40.6, 46.2, 51.3, 68.6, 111.7, 114.9, 117.0, 129.3, 145.9. Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.31; H, 7.14; N, 22.45.

**Procedure for the Nucleophilic Substitution of 9a with Benzenethiol.** To a solution of benzenethiol (0.13 g, 1.2 mmol) in dry THF (10 mL) was added NaH (60% in mineral oil, 0.05 g, 1.3 mmol), and the mixture was stirred at 20 °C for 10 min. One drop of methanol was added to quench excess NaH, and then **9a** (0.28 g, 1.0 mmol) was added. The mixture was refluxed for 38 h. After removal of THF in vacuo, the residue was extracted with $Et_2O$. The organic extracts were washed with 2 M NaOH and brine and dried over anhyd $MgSO_4$. The desired compound was purified by column chromatography with hexanes/EtOAc (4:1) as an eluent.

**Data for 1-Phenyl-3-(phenylthiomethyl)imidazolidine (13)**: white flakes (from $CH_3OH$); yield 66%; mp 64−65 °C; $^1$H NMR $\delta$ 3.12 (t, $J$ = 6.2 Hz, 2H), 3.99 (t, $J$ = 6.3 Hz, 2H), 4.14 (s, 2H), 4.55 (s, 2H), 6.43−6.46 (m, 2H), 6.70 (t, $J$ = 7.3 Hz, 1H), 7.18−7.30 (m, 5H), 7.45−7.48 (m, 2H); $^{13}$C NMR $\delta$ 46.3, 49.6, 60.2, 67.1, 111.6, 116.4, 126.6, 129.0, 129.2, 130.9, 137.1, 146.2. Anal. Calcd for $C_{16}H_{18}N_2S$: C, 71.07; H, 6.71; N, 10.36. Found: C, 71.09; H, 6.88; N, 10.30.

**Procedure for the Nucleophilic Substitution of 9a with Triethyl Phosphite.** To a solution of **9a** (0.28 g, 1.0 mmol) in dry $CH_2Cl_2$ (20 mL) at 0 °C were sequentially added $ZnBr_2$ (0.22 g, 1.0 mmol) and triethyl phosphite (0.34 mL, 2.0 mmol). The reaction mixture was stirred at 0 °C for 2 h and at room temperature overnight. After extraction with $CH_2Cl_2$, the combined organic layers were washed with 1 M NaOH and brine and dried over anhyd $MgSO_4$. After removal of the solvent in vacuo, the desired product was purified by column chromatography with hexanes/EtOAc (4:1) as an eluent.

**Data for Diethyl (3-Phenyl-1-imidazolidinyl)methylphosphonate (14)**: yellow oil; yield 70%; $^1$H NMR $\delta$ 1.36 (t, $J$ = 7.0 Hz, 6H), 3.02 (d, $J$ = 12.5 Hz, 2H), 3.17 (t, $J$ = 6.3 Hz, 2H), 3.41 (t, $J$ = 6.1 Hz, 2H), 4.05−4.23 (m, 6H), 6.50 (d, $J$ = 8.2 Hz, 2H), 6.71 (t, $J$ = 7.3 Hz, 1H), 7.23 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 16.5 (d, $J$ = 5.3 Hz), 45.8, 50.2 (d, $J$ = 167.3 Hz), 54.7 (d, $J$ = 10.6 Hz), 62.3 (d, $J$ = 6.4 Hz), 71.5 (d, $J$ = 12.7 Hz), 111.5, 116.4, 129.2, 146.2. Anal. Calcd for $C_{14}H_{23}N_2O_3P$: C, 56.37; H, 7.77; N, 9.39. Found: C, 56.39; H, 7.89; N, 9.59.

**General Procedure for the Preparation of Chiral Diamines 18a−c from *N*-Boc-α-amino Acids 15a−c.** α-Amino amides **17a−c** were obtained according to our recent paper.[16]

A mixture of **17a−c** (3 mmol) and $LiAlH_4$ (powder, 0.68 g, 18 mmol) in dry THF (30 mL) was refluxed for 2 days. The mixture was slowly quenched with water under an ice bath. The precipitate formed was filtered off and washed with $CH_2Cl_2$. The combined filtrate was washed with 1 M NaOH and brine and dried over anhyd $K_2CO_3$. Removal of the solvents afforded diamine **18a−c**, which was directly used for the subsequent reaction. GC analyses show that the purity of **18a−c** is more than 90%.

**Data for (2*S*)-*N*$^1$-(4-Methylphenyl)-1,2-propanediamine (18a)**: yellow oil; yield 96%; $^1$H NMR $\delta$ 1.20 (d, $J$ = 7.1 Hz, 3H), 1.20−1.80 (br s, 2H), 2.31 (s, 3H), 2.90 (dd, $J$ = 12.1, 8.0 Hz, 1H), 3.14−3.22 (m, 2H), 3.80−4.25 (br s, 1H), 6.62 (d, $J$ = 8.4 Hz, 2H), 7.05 (d, $J$ = 8.1 Hz, 2H); $^{13}$C NMR $\delta$ 20.1, 21.8, 45.9, 52.3, 112.8, 126.1, 129.5, 146.0.

**General Procedure for the Preparation of Optically Active Imidazolidines 20a−d, 21, and 22.** A mixture of a diamine, **18a−c** (3.0 mmol), BtH (0.36 g, 3.0 mmol), and formaldehyde (37% aq solution; 0.49 g, 6.0 mmol) in $CH_3OH/H_2O$ (10 mL/5 mL) was stirred for 4 h at 20 °C. The precipitate formed was filtered and washed with cool $Et_2O$ to give **19a−c**.

To a solution of **19a−c** (1.0 mmol) in dry THF (15 mL) was added dropwise an appropriate Grignard reagent (1.2 mmol) in THF. The reaction mixture was stirred at room temperature for 30 min and then refluxed for 1 h. The same workup as used for the preparation of **11** gave **20a−d**, which was purified by flash column chromatography (silica gel).

The same procedure as used for the preparation of **14** and **12b** afforded **21** and **22**, respectively.

**Data for 1-{[(5*S*)-5-Methyl-3-(4-methylphenyl)tetrahydro-1*H*-imidazol-1-yl]methyl}-1*H*-1,2,3-benzotriazole (19a)**: colorless microcrystals (from EtOH); yield 85%; mp 129−130 °C; $[\alpha]^{25}_D$ = −16.2 ($c$ 1.71, $CHCl_3$); $^1$H NMR $\delta$ 1.41 (d, $J$ = 6.1 Hz, 3H), 2.21 (s, 3H), 3.02 (t, $J$ = 8.1 Hz, 1H), 3.25−3.31 (m, 1H), 3.45 (t, $J$ = 7.3 Hz, 1H), 4.13, 4.38 (AB, $J$ = 4.1 Hz, 2H), 5.64 (d, $J$ = 3.5 Hz, 2H), 6.34 (d, $J$ = 8.5 Hz, 2H), 7.00 (d, $J$ = 8.2 Hz, 2H), 7.38 (t, $J$ = 7.2 Hz, 1H), 7.52 (t, $J$ = 7.5 Hz, 1H), 7.65 (d, $J$ = 8.4 Hz, 1H), 8.07 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR $\delta$ 16.9, 20.2, 54.1, 54.6, 61.8, 68.1, 109.5, 111.7, 120.0, 124.0, 126.0, 127.7, 129.7, 133.6, 143.9, 145.9. Anal. Calcd for $C_{18}H_{21}N_5$: C, 70.33; H, 6.89; N, 22.78. Found: C, 70.24; H, 7.11; N, 22.95.

**Data for (4*S*)-3-(3-Butenyl)-4-methyl-1-(4-methylphenyl)tetrahydro-1*H*-imidazole (20a)**: yellow oil; yield 94%; $[\alpha]^{25}_D$ = +111 ($c$ 2.17, $CHCl_3$); $^1$H NMR $\delta$ 1.20 (d, $J$ = 6.0 Hz, 3H), 2.24 (s, 3H), 2.30−2.37 (m, 3H), 2.82−2.94 (m, 2H), 3.02 (t, $J$ = 8.2 Hz, 1H, H$^a$), 3.44 (t, $J$ = 7.4 Hz, 1H, H$^b$), 3.68, 4.43 (AB, $J$ = 4.1 Hz, 2H), 5.04 (d, $J$ = 10.2 Hz, 1H), 5.11 (d, $J$ = 17.0 Hz, 1H), 5.79−5.92 (m, 1H), 6.40 (d, $J$ = 8.4 Hz, 2H), 7.02 (d, $J$ = 8.2 Hz, 2H); $^{13}$C NMR $\delta$ 16.8, 20.2, 33.2, 51.8, 53.9, 58.7, 70.8, 111.3, 115.8, 125.1, 129.6, 136.3, 144.3. Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.05; H, 9.63; N, 11.99.

**Data for Diethyl [(5*S*)-5-Methyl-3-(4-methylphenyl)tetrahydro-1*H*-imidazol-1-yl]methylphosphonate (21)**: yellow oil; yield 90%; $[\alpha]^{25}_D$ = +50.6 ($c$ 1.58, $CHCl_3$); $^1$H NMR $\delta$ 1.22 (d, $J$ = 5.4 Hz, 3H), 1.35 (t, $J$ = 7.0 Hz, 6H), 2.24 (s, 3H), 2.77 (dd, $J$ = 15.1, 6.6 Hz, 1H, H$^a$), 2.98−3.02 (m, 2H), 3.20 (dd, $J$ = 17.7, 15.1 Hz, 1H, H$^b$), 3.46−3.47 (m, 1H), 3.87, 4.65 (AB, $J$ = 4.7 Hz, 2H), 4.12−4.22 (m, 4H), 6.42 (d, $J$ = 8.4 Hz, 2H), 7.03 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR $\delta$ 16.4 (d, $J$ = 5.7 Hz), 16.5 (d, $J$ = 5.7 Hz), 16.7, 20.2, 47.8 (d, $J$ = 167.2 Hz), 53.4, 60.1 (d, $J$ = 17.8 Hz), 61.9 (d, $J$ = 6.3 Hz), 62.5 (d, $J$ = 6.3 Hz), 71.9 (d, $J$ = 2.3 Hz), 111.5, 125.4, 129.6, 144.2. Anal. Calcd for $C_{16}H_{27}N_2O_3P$: C, 58.88; H, 8.34; N, 8.58. Found: C, 58.58; H, 8.33; N, 8.60.

**Data for 2-[(5*S*)-5-Benzyl-3-(4-methylphenyl)tetrahydro-1*H*-imidazol-1-yl]acetonitrile (22)**: yellow flakes (from EtOH); yield 99%; mp 76−77 °C; $[\alpha]^{25}_D$ = +40.4 ($c$ 1.98, $CHCl_3$); $^1$H NMR $\delta$ 2.23 (s, 3H), 2.71 (dd, $J$ = 13.0, 7.1 Hz, 1H), 2.98 (dd, $J$ = 13.3, 5.1 Hz, 1H), 3.14 (br s, 1H), 3.36−3.41 (m, 2H), 3.63 (s, 2H), 4.05, 4.37 (AB, $J$ = 4.0 Hz, 2H), 6.38 (d, $J$ = 8.4 Hz, 2H), 7.02 (d, $J$ = 8.2 Hz, 2H), 7.21−7.35 (m, 5H); $^{13}$C NMR $\delta$ 20.2, 38.6, 38.9, 52.3, 62.1, 69.9, 111.9, 114.8, 126.2, 126.7, 128.6, 128.8, 129.6, 137.5, 143.7. Anal. Calcd for $C_{19}H_{21}N_3$: C, 78.31; H, 7.26; N, 14.42. Found: C, 78.45; H, 7.45; N, 14.11.

**Procedure for the Preparation of the Bt Intermediate 24 and Its Substitution with NaCN.** A mixture of 1-ethyl-2-(4-nitrophenyl)imidazolidine (**23**; 0.66 g, 3.0 mmol), BtH (0.36 g, 3.0 mmol), formaldehyde (37% aq solution; 0.25 g, 3.0 mmol) in $CH_3OH/H_2O$ (10/4 mL) was stirred at room temperature for 24 h. The precipitate formed was filtered and recrystallized from EtOH to give **24**.

A mixture of **24** (0.35 g, 1.0 mmol) and NaCN (0.10 g, 2.0 mmol) was stirred in DMSO (3 mL) at 25 °C for 24 h. The mixture was diluted with $CH_2Cl_2$, washed with water, and dried over anhyd $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash basic $Al_2O_3$ column chromatography with hexanes/EtOAc (6:4) as an eluent to afford **25**.

**Data for 1-{[3-Ethyl-2-(4-nitrophenyl)-1-imidazolidinyl]methyl}-1*H*-1,2,3-benzotriazole (24)**: pale yellow microcrystals (from EtOH); yield 85%; mp 121−122 °C; $^1$H NMR $\delta$ 0.92 (t, $J$ = 7.2 Hz, 3H), 2.06−2.13 (m, 1H), 2.29−2.42 (m, 2H), 3.10−3.17 (m, 1H), 3.33−3.40 (m, 1H), 3.51 (q, $J$ = 7.4 Hz, 1H), 4.11 (s, 1H), 5.29, 5.45 (AB, $J$ = 14.0 Hz, 2H), 7.34−7.39 (m, 2H), 7.48 (t, $J$ = 7.1 Hz, 1H), 7.75 (d, $J$ = 8.5 Hz, 2H), 8.04 (d, $J$ = 7.4 Hz, 1H), 8.21 (d, $J$ = 8.7 Hz, 2H); $^{13}$C NMR $\delta$ 13.4, 46.4, 48.1, 50.6, 62.2, 83.4, 109.4, 119.9, 123.4, 124.0, 127.6, 130.2, 133.6, 145.6, 147.4, 148.3. Anal. Calcd for $C_{18}H_{20}N_6O_2$: C, 61.35; H, 5.72; N, 23.85. Found: C, 61.29; H, 5.83; N, 23.90.

**Data for 2-[3-Ethyl-2-(4-nitrophenyl)-1-imidazolidinyl]acetonitrile (25)**: brown oil; yield 92%; $^1$H NMR $\delta$ 1.00 (t, $J$ = 7.2 Hz, 3H), 2.22−2.34 (m, 1H), 2.42−2.54 (m, 1H), 2.62−2.71 (m, 1H), 2.99−3.06 (m, 1H), 3.24 (d, $J$ = 17.6 Hz, 1H), 3.39−3.54 (m, 2H), 3.57 (d, $J$ = 17.7 Hz, 1H), 3.92 (s, 1H), 7.67 (d, $J$ = 8.6 Hz, 2H), 8.23 (d, $J$ = 8.6 Hz, 2H); $^{13}$C NMR $\delta$ 13.4, 39.0, 46.5, 49.5, 50.2, 85.4, 115.0, 123.7, 129.9, 146.4, 148.6. Anal. Calcd for $C_{13}H_{16}N_4O_2$: C, 59.99; H, 6.20; N, 21.52. Found: C, 59.93; H, 6.17; N, 21.80.

**Procedure for the Preparation of 1-Substituted 3-Methyl-2,3-dihydro-1H-benzimidazoles 28 and 29.** A mixture of *N*-(2-aminophenyl)-*N*-methylamine (**26a**; 0.37 g, 3.0 mmol), BtH (0.36 g, 3.0 mmol), and formaldehyde (37% aq solution; 0.49 g, 6.0 mmol) in $CH_3OH/H_2O$ (10 mL/4 mL) was stirred at room temperature overnight. Then an additional 10 mL of water was added, and the mixture was stirred for 1 h. The precipitate formed was filtered and washed with cool ethanol to give **27**.

To a solution of vinylmagnesium bromide (2.0 M in THF; 0.7 mL, 1.4 mmol) at 0 °C was added dropwise $ZnCl_2$ (0.5 M in $Et_2O$; 3.0 mL, 1.5 mmol). After the mixture was stirred for 15 min, a solution of **27** (0.26 g, 1.0 mmol) in dry THF (10 mL) was added dropwise. The reaction mixture was stirred for 20 min at room temperature and then refluxed for 2 h. After being cooled, the mixture was quenched with water and extracted with $CH_2Cl_2$. The organic extracts were washed with 1 M NaOH, water, and brine and dried over anhyd $K_2CO_3$. Evaporation of the solvent in vacuo gave the crude product **28**, which was purified by flash basic $Al_2O_3$ column chromatography with hexanes/EtOAc (8:2) as an eluent.

The same procedure as used for the preparation of **25** afforded **29**.

**Data for 1-(Benzotriazolylmethyl)-3-methyl-2,3-dihydro-1*H*-benzimidazole (27)**: obtained as a mixture of $Bt^1$ and $Bt^2$ isomers in a ca. 6:1 ratio ($^1$H and $^{13}$C NMR data for the $Bt^1$ isomer only are presented); white microcrystals (from $CH_3OH$); yield 85%; mp 122−124 °C; $^1$H NMR $\delta$ ($Bt^1$) 2.66 (s, 3H), 4.61 (s, 2H), 5.96 (s, 2H), 6.38−6.41 (m, 1H), 6.67−6.77 (m, 2H), 6.81−6.83 (m, 1H), 7.34−7.39 (m, 1H), 7.46 (t, $J$ = 7.2 Hz, 1H), 7.58 (d, $J$ = 8.0 Hz, 1H), 8.06 (d, $J$ = 8.3 Hz, 1H); $^{13}$C NMR $\delta$ ($Bt^1$) 34.0, 60.2, 76.0, 106.6, 106.7, 109.7, 118.8, 119.9, 120.8, 124.1, 127.8, 132.7, 138.6, 142.9, 146.1. Anal. Calcd for $C_{15}H_{15}N_5$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.72; H, 5.46; N, 26.40.

**Data for 1-Allyl-3-methyl-2,3-dihydro-1*H*-benzimidazole (28)**: $R_f$ = 0.70 [eluent hexanes/$CH_2Cl_2$, 7:3; $Al_2O_3$ TLC plate (Aldrich, Catalog No. Z23421-4)]; extremely labile to air; yellow oil; yield 83%; $^1$H NMR (DMSO-$d_6$) $\delta$ 2.64 (s, 3H), 2.79 (d, $J$ = 6.1 Hz, 2H), 4.29 (s, 2H), 5.19 (d, $J$ = 12.1, 2.1 Hz, 1H), 5.30 (dd, $J$ = 17.2, 2.0 Hz, 1H), 5.84−5.94 (m, 1H), 6.38−6.45 (m, 2H), 6.50−6.55 (m, 2H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 34.0, 50.4, 77.5, 105.8, 106.2, 117.5, 118.5, 118.7, 134.1, 141.9, 143.2; GC−MS (EI) $m/z$ 174 ($M^+$).

**Data for 2-(3-Methyl-2,3-dihydro-1*H*-benzimidazol-1-yl)acetonitrile (29)**: $R_f$ = 0.70 [eluent hexanes/$CH_2Cl_2$, 7:3; $Al_2O_3$ TLC plate (Aldrich, Catalog No. Z23421-4)]; separated by flash basic $Al_2O_3$ column chromatography with $CH_2Cl_2$ as an eluent; extremely labile to air; brown oil; yield 94%; $^1$H NMR (DMSO-$d_6$) $\delta$ 2.72 (s, 3H), 4.38 (s, 2H), 4.46 (s, 2H), 6.55 (d, $J$ = 7.2 Hz, 1H), 6.65−6.78 (m, 3H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 34.0, 35.4, 76.7, 106.7, 115.9, 118.7, 120.8, 139.4, 143.3; GC−MS (EI) $m/z$ 173 ($M^+$). Anal. Calcd for $C_{10}H_{11}N_3$: H, 6.40; N, 24.26. Found: H, 6.54; N, 24.16.

**Procedure for the Preparation of 2-(2-Anilinoanilino)-acetonitrile (31).** The same procedure as used for the preparation of **24** and **25** gave compounds **30** and **31**, respectively.

**Data for *N*-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-*N*′-phenyl-1,2-benzenediamine (30)**: white microcrystals; yield 92%; mp 146−147 °C; $^1$H NMR $\delta$ 5.18 (s, 1H), 5.51 (t, $J$ = 6.8 Hz, 1H), 6.07 (d, $J$ = 7.0 Hz, 2H), 6.85 (d, $J$ = 7.9 Hz, 2H), 6.78−6.85 (m, 2H), 7.05−7.16 (m, 5H), 7.31−7.42 (m, 2H), 7.49 (d, $J$ = 7.9 Hz, 1H), 8.03 (d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR $\delta$ 57.9, 109.9, 112.8, 115.2, 119.6, 120.0, 120.1, 124.0, 126.1, 126.8, 127.4, 128.8, 129.3, 132.3, 141.2, 145.6, 146.4. Anal. Calcd for $C_{19}H_{17}N_5$: C, 72.36; H, 5.43; N, 22.21. Found: C, 72.47; H, 5.79; N, 22.27.

**Data for 31:** separated by basic $Al_2O_3$ flash column chromatography; yellow plates (from ethanol/hexanes); yield 77%; mp 102−103 °C; $^1$H NMR $\delta$ 4.08 (d, $J$ = 7.0 Hz, 2H), 4.55 (t, $J$ = 6.7 Hz, 1H), 5.13 (s, 1H), 6.68 (d, $J$ = 7.8 Hz, 2H), 6.81−6.90 (m, 3H), 7.15−7.25 (m, 4H); $^{13}$C NMR $\delta$ 32.4, 111.9, 115.2, 116.8, 119.8, 120.2, 125.7, 126.5, 129.3, 129.4, 141.2, 145.3. Anal. Calcd for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87; N, 18.82. Found: C, 75.60; H, 5.65; N, 18.89.

**Supporting Information Available:** Characterization data for compounds **9b,c**, **11b−f,h,j−l**, **12b,c**, **18b,c**, **19b,c**, **20b−d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010868N