# Novel Syntheses of Hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles and Octahydroimidazo[1,2-*a*]pyridines

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1-Phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (**18**) and 1-phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (**27**) were readily prepared from succindialdehyde or glutaraldehyde, benzotriazole, and *N*-phenylethylenediamine. Synthons **18** and **27** reacted with Grignard reagents, allylsilanes, silyl ethers, and triethyl phosphite to produce 1-phenyl-5-substituted-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **20a**−**f**, **22**, **24a**,**b**, and **25** and 1-phenyl-5-substituted-octahydroimidazo[1,2-*a*]pyridines **28a**−**e**, **32**, **33a**,**b**, and **34** in good to excellent yields. The configurations of **20**, **22**, **24**, and **25** were determined to be cis isomers by NOE experiment, while the configurations and conformations of **28a**−**e**, **32**, **33a**,**b**, and **34** were elucidated by $^1$H−$^1$H COSY and $^1$H−$^{13}$C COSY.

## Introduction

Hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **1** and octahydroimidazo[1,2-*a*]pyridines **2** are biologically active, demonstrating antiinflammatory,[1] antinociceptive, immunomodulating, and antioxidant activities.[2] They are also effective intermediates for the preparation of chiral pyrrolidines[3,4] and piperidines.[5] General routes reported for the preparation of hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **1** have included (Scheme 1) the following: (i) intermolecular condensation of ethylenediamine with γ-chloroalkyl ketones **3** to generate 7a-alkyl- or 7a-arylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **4**;[2a] (ii) An analogous condensation of ethylenediamine with 3-benzoylpropionic acid[6] or 3-acetylpropionic acid[7] gave the lactam **5**, which could be reduced with $LiAlH_4$ to form **4**. (iii) 1,3-Dipolar cycloaddition of 4,5-dihydroimidazolium ylides **6** with dipolarophiles afforded optically active hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **7**, but the dipolarophile must contain an electron-withdrawing group.[3,4,8]

Routes to octahydroimidazo[1,2-*a*]pyridines **2** include (Scheme 2): (i) Intermolecular condensation of ethylenediamine and 5-chloropentanal.[9] (ii) An analogous condensation of ethylenediamine with 4-benzoylbutyric acid

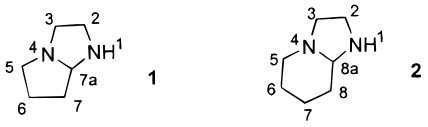
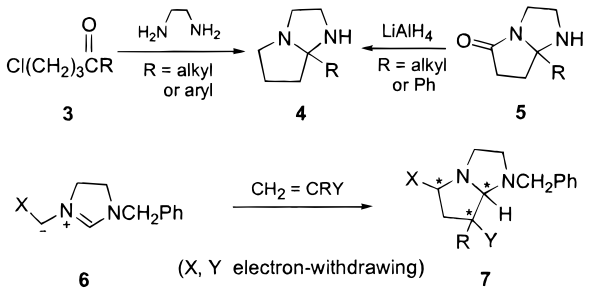


**Figure 1.**

**Scheme 1**



or γ-acetyl esters gave lactams **8**, which could also be reduced by $LiAlH_4$ to produce 1-phenyloctahydroimidazo[1,2-*a*]pyridine (**9a**)[6] or 6-alkyl-octahydroimidazo[1,2-*a*]pyridines **9b**.[10] (iii) The reaction of glutaraldehyde with *N*-substituted ethylenediamines, followed by catalytic hydrogenation over 10% $Pd(OH)_2$/C, produced **10**.[11] (iv) 1,3-Dipolar cycloaddition of nonstabilized azomethine ylide **11**, generated from the corresponding tertiary amine *N*-oxide, produced 1,2-diphenyloctahydroimidazo[1,2-*a*]pyridine (**12**).[12] (v) Intermolecular condensation of 2-aminopyridine (**13**) with styrene oxide, followed by hydrogenation, halogenation and intramolecular condensation, generated 2-phenyl-octahydroimidazo[1,2-*a*]pyridine (**14**).[1a] (vi) A multistep process, involving addition, hydrogenation and intramolecular condensation, led to octahydroimidazo[1,2-*a*]pyridines **16**.[5,13]

To our knowledge, no 1,5-disubstituted-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles have been reported; only one

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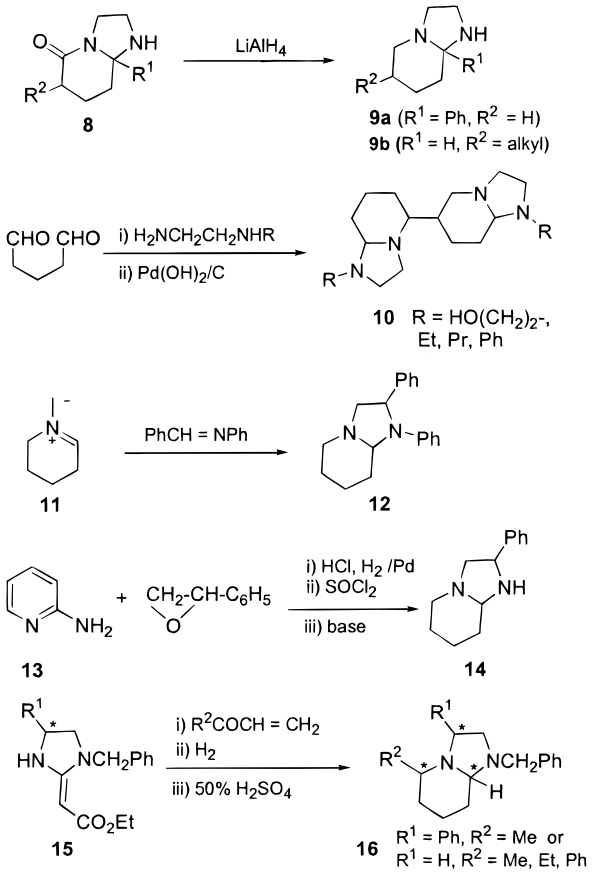
**Scheme 2**



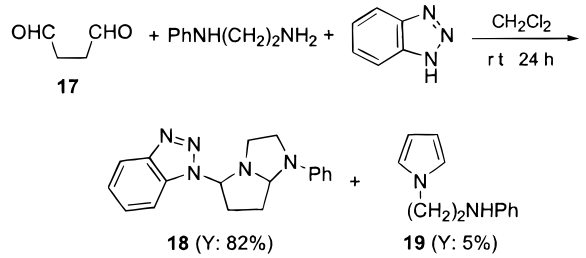

preparation was found for 1,5-disubstituted-octahydroimidazo[1,2-*a*]pyridines **16** ($R^1$ = H, $R^2$ = Me, Et, Ph).[13]

In previously reported synthesis of both of the ring systems **1** and **2**, it is difficult to vary the group at the 5-position by existing methods. Compounds of type **1** and **2** carrying a benzotriazole group at the 5-position should be advantageous, due to the potentially easy replacement of such a Bt group via nucleophilic substitution, elimination, reduction or cyclization.[14] We recently reported the syntheses of 2,5-disubstituted pyrrolidines[15] and 2,6-disubstituted piperidines[16] by the condensation of succindialdehyde or glutaraldehyde with (*S*)-2-phenylglycinol and benzotriazole, followed by the reactions of the benzotriazole-containing intermediates so produced with Grignard reagents and/or hydrogenation. The present paper describes the syntheses of 1-phenyl-5-(benzotriazol-1-yl)-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (**18**) and 1-phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (**27**) and the application of **18** and **27** as versatile synthons in novel reactions with Grignard reagents, allylsilanes, silyl ethers, and triethyl phosphite to furnish 1-phenyl-5-substituted-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **20**, **22**, **24**, and **25** and 1-phenyl-5-substituted-octahydroimidazo[1,2-*a*]pyridines **28** and **32**−**34**.

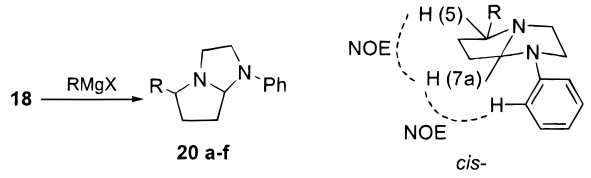
## Results and Discussion

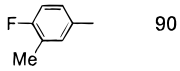
**Synthesis of 1-Phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (18).** Succindialdehyde **17**, generated in situ by the acid hydrolysis of 2,5-dimethoxy-3,4-dihydrofuran with 0.1 M HCl, reacted with *N*-phenylethylenediamine and benzotriazole in $CH_2Cl_2$ at room temperature for 24 h to produce 82% of 1-phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo-[1,2-*a*]imidazole (**18**), together with 5% of the elimination product *N*-[2-(1*H*-pyrrol-1-yl)ethyl]aniline (**19**) (Scheme 3). The $^1$H and $^{13}$C NMR spectra show that **18** was solely the Bt[1] isomer, which was further used for the nucleophilic substitution with Grignard reagents, allylsilane, silyl ethers, and triethyl phosphite.

**Scheme 3**




**Scheme 4**




| compd[a] | R | Y (%) | compd[a] | R | Y (%) |
|---|---|---|---|---|---|
| **20a** | $C_6H_5CH_2$ | 93 | **20e** | *p*-$CH_3C_6H_4$ | 88 |
| **20b** | *n*-$C_5H_{11}$ | 89 | **20f** |  | 90 |
| **20c** | $CH_3C{\equiv}C$ | 91 | | | |
| **20d** | $CH_2{=}CH$ | 86 | | | |

[a] RMgBr was used except for **20a** using $C_6H_5CH_2MgCl$.

**Substitution of the Benzotriazole Group from 18 Using Grignard Reagents.** Treatment of the intermediate **18** in dry THF with 1 equiv of Grignard reagents at −78 °C gave 1-phenyl-5-substituted-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **20a**−**f** in excellent yields (Scheme 4). The Grignard reagents used include examples of alkyl- (*n*-pentyl), aryl- (4-methylphenyl, 3-methyl-4-fluorophenyl), benzyl-, prop-1-ynyl-, and vinylmagnesium halides.

The H(5) and H(7a) in **20a**−**f** could be located cis or trans to each other. The $^{13}$C NMR spectra of **20a**−**f** show signals for one configurational isomer only. The configuration was then determined as cis by NOE experiments. Using 1-phenyl-5-(4-methylphenyl)hexahydro-1*H*-pyrrolo-[1,2-*a*]imidazole (**20e**) as an example, the $^1$H NMR peak of H(7a) with a chemical shift at 4.89 ppm is a double-doublet. When the peak at 4.89 ppm was irradiated, a strong NOE effect at the *o*-H of the phenyl ring provided clear evidence that the 4.89 ppm is to be attributed to H(7a). In addition, an NOE effect was demonstrated between H(7a) and the geminal hydrogens at the 7 position. Furthermore, a smaller but distinct NOE effect could also be observed between H(5) and H(7a). This is the direct evidence that these two hydrogens are located in the cis position. Thus, compound **20e** is determined to be the cis isomer. Similar results have been obtained

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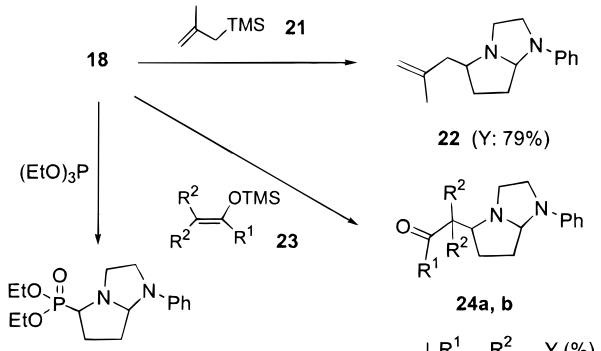
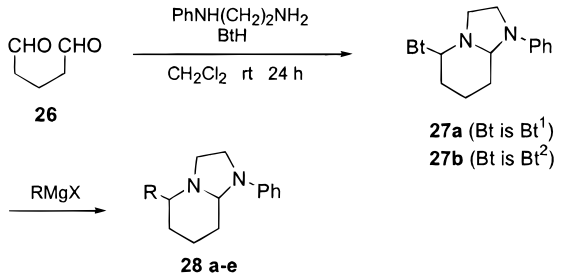
**Scheme 5**




| | $R^1$ | $R^2$ | Y (%) |
|---|---|---|---|
| **24a** | Ph | H | 87 |
| **24b** | OMe | Me | 79 |

**Scheme 6**




| compd[a] | R | Y (%) | compd[a] | R | Y (%) |
|---|---|---|---|---|---|
| **28a** | $C_6H_5CH_2$ | 91 | **28d** | *p*-$CH_3C_6H_4$ | 79 |
| **28b** | *n*-$C_3H_7$ | 89 | **28e** | *cyclo*-$C_5H_9$ | 83 |
| **28c** | $CH_3C{\equiv}C$ | 88 | | | |

[a] RMgBr was used except for **28a** using $C_6H_5CH_2MgCl$.

for the NOE experiments of compounds **20a**−**d**,**f** and prove their cis configurations. Compounds **20a**−**f** are aminals and would be expected to isomerize easily at the aminal CH center. For five-five fused cyclic ring systems, the cis isomers are usually more stable.[8b] Thus, the exclusive observation of the cis isomer of **20** is expected.

**Substitution of the Benzotriazole Group from 18 Using Allylsilane, Silyl Ethers, and Triethyl Phosphite.** The nucleophilic replacement of the Bt-group in **18** with 1 equiv of (2-methylpropenyl)trimethylsilane (**21**), 1-phenylvinyl trimethylsilyl ether (**23a**), and 1-methoxy-2-methyl-1-propenyl trimethylsilyl ether (**23b**) in the presence of $BF_3{\cdot}Et_2O$ produced **22**, **24a**, and **24b** in 79%, 87%, and 79% yield, respectively. The treatment of **18** with 2 equiv of triethyl phosphite in the presence of $ZnBr_2$ afforded diethyl 1-phenylhexahydro-1*H*-pyrrolo[1,2-*a*]-imidazol-5-ylphosphonate (**25**) in 74% yield (Scheme 5). The benzotriazole group of **18** easily eliminated in the presence of Lewis acid, such as $BF_3$ or $ZnBr_2$, to form the planar iminium cation, which could be attacked by the nucleophiles. When the H(7a) peaks of **22**, **24a**, **24b**, and **25** were irradiated, the distinct NOE effect between H(7a) and H(5) was observed and thus demonstrates their cis configurations.

**Synthesis of 1-Phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (27).** The reaction of glutaraldehyde (**26**) (50% aqueous solution), benzotriazole, and *N*-phenylethylenediamine in $CH_2Cl_2$ at room temperature for 24 h gave intermediate **27** in quantitative yield as a mixture of the $Bt^1$ and $Bt^2$ isomers with an approximately 7:3 ratio (Scheme 6). $Bt^1$ isomer **27a** and $Bt^2$ isomer **27b** could not be separated due to their easy decomposition on silica gel; however, our previous work[16,17] has shown that $Bt^1$ and $Bt^2$ groups are both good leaving groups and that elimination of either group leads to the same planar iminium cation. Thus, the crude intermediate **27** was used directly as a mixture of $Bt^1$ and $Bt^2$ isomers for the subsequent reactions.

**Substitution of the Benzotriazole Group from 27 Using Grignard Reagents.** The nucleophilic substitution of the intermediate **27** in dry THF with 1 equiv of Grignard reagent at −78 °C gave 1-phenyl-5-substituted-octahydroimidazo[1,2-*a*]pyridines **28a**−**e** in 79% to 91% yield (Scheme 6). Compounds **28** could be cis or trans isomers, depending on the relative orientation of H(5) and H(8a). This cis isomer can exist in two conformations **A** and **B** interconvertible by N-inversion, while the third conformation **C** is not sterically favored with two axial ring substituent interactions. The trans isomer can exist in three conformations **D**, **E,** and **F** interconvertible by N- or ring-inversion. A detailed study was carried out on **28d**. The $^1H-^1H$ COSY analysis (cf. Table 1) for **28d** demonstrates that the chemical shifts at 3.30 and 3.56 ppm should be assigned to H(5) and H(8a), respectively. Both these NMR peaks have double-doublet patterns with one typical large aa coupling [$J$ = 10.1, 2.8 Hz [for H(5)] and 8.8, 2.1 Hz [for H(8a)]]. This proves that both H(5) and H(8a) are located in an axial position. Thus, the configuration of **28d** is the cis isomer (cf. Figure 2 **A**).

**Table 1. $^1H$ and $^{13}C$ NMR Data of the Six-Membered Ring for 28d by Analysis of $^1H-^1H$ and $^1H-^{13}C$ COSY**

| H | $\delta_{ppm}$(a) [$\delta_{ppm}$(e)] | C | $\delta_{ppm}$ |
|---|---|---|---|
| H (5) | 3.30 | C (5) | 67.2 |
| H (6) | 1.43 [1.65] | C (6) | 29.5 |
| H (7) | 1.59 [1.95] | C (7) | 21.1 |
| H (8) | 1.80 [2.15] | C (8) | 23.3 |
| H (8a) | 3.56 | C (8a) | 79.5 |

By nitrogen inversion, *cis*-**28d** should have two possible conformations, illustrated as **A** (ring-trans-conformer) with the lone electron pair of the bridged nitrogen axial and **B** (ring cis-conformer) with the lone electron pair of the bridged nitrogen equatorial. However, **A** should be of a significantly lower energy because of the gauche butane interaction in **B**. In 1993, Jones et al.[5] proved that compound **29** possessed a cis configuration with a trans-ring conformation. The $^1H$ NMR spectrum of **30** showed the absorption of the H(5) at $\delta$ 3.94 ppm as a near triplet ($J$ = 3.6 Hz), indicating the axial CN group in ring-trans-conformation.[18] The similar 2-alkylperhydroimidazo-[1,5-*a*]pyridines **31** also have predominant ring-trans-conformations.[19] Therefore, we believe that in the equilibria of **28d** the ring-trans-conformer **A** dominates.

For compounds **28a**, **28b**, and **28e**, double-doublet patterns of H(8a) with coupling constants ∼9.0, 2.1 Hz also demonstrate that H(8a) is located axial in each compound. The $^1H$ NMR signal of H(5) becomes more complicated in **28a**, **28b**, and **28e** as a multiplet due to its spin−spin interaction with $H_a(6)$, $H_e(6)$ as well as

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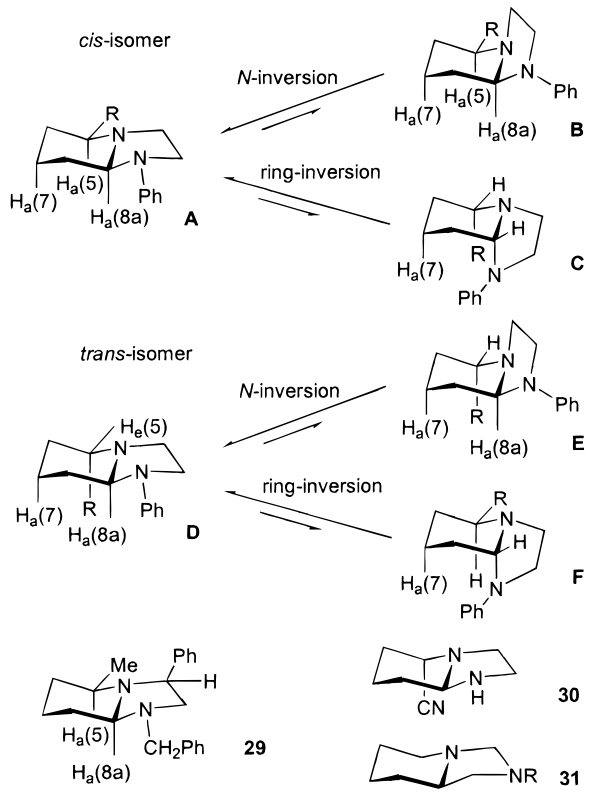



**Figure 2.**

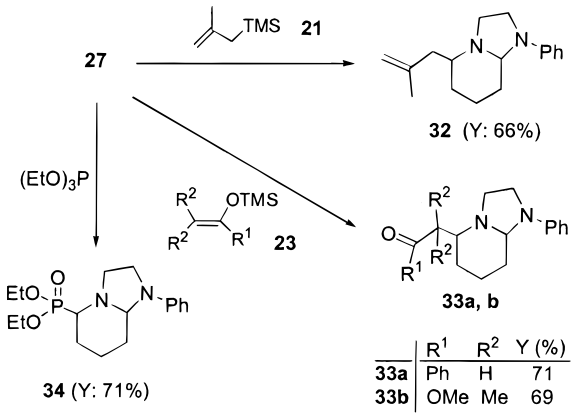
**Table 2. $^1$H NMR Data of H(5) and H(8a) and $^{13}$C NMR Data of C(5) and C(8a) for 28c**

| conformation | H | $\delta_{ppm}$ | C | $\delta_{ppm}$ |
|---|---|---|---|---|
| **A** and **B** | $H_a(5)$ | 3.19 | C (5) | 53.0 |
| | $H_a(8a)$ | 3.49 | C (8a) | 78.6 |
| **C** | $H_e(5)$ | 4.03 | C (5) | 49.9 |
| | $H_e(8a)$ | 3.94 | C (8a) | 75.6 |

the adjacent hydrogens of the substituent at the 5-position. However, the $^1$H−$^1$H COSY analyses have clearly shown that H(5) has the same long-distance interaction as $H_a(8a)$ with $H_a(7)$. So, each H(5) is proved to occupy an axial position. Therefore, the configurations of **28a**, **28b**, **28d**, and **28e** are all cis isomers with H(5) and H(8a) axial. These results are easily understandable as the substituents prefer to occupy the equatorial positions to make the molecules more thermodynamically stable. In addition, these compounds are also believed to have predominant ring-trans-conformations.

For reasons we do not understand, the $^1$H NMR spectrum of **28c** is much more complicated. The careful $^1$H−$^1$H COSY and $^1$H−$^3$C COSY analyses (cf. Table 2) suggest that there are two diastereoisomers with H(5) and H(8a) both located in the axial position or in the equatorial positions. For example, the chemical shifts 3.49 and 3.19 ppm are attributed to H(8a) and H(5) as axial as shown in **A** and **B**; while 3.94 and 4.03 ppm are attributed to H(8a) and H(5) as equatorial as shown in **C** (Figure 2). In conformation **C**, no nitrogen inversion could occur, so only one conformation is expected. Thus, the configuration of **28c** is cis. On the basis of the above-mentioned discussion, the ring-trans-conformation (**A**) should dominate in the equilibrium of **A** and **B** in **28c**. By the integration of $^1$H NMR spectrum, the ratio of **A** to **C** in **28c** is about 2:3, which indicates that the conformation with H(5) and H(8a) equatorial is more stable.

**Scheme 7**




**Substitution of the Benzotriazole Group from 27 Using Allylsilane, Silyl Ethers, and Triethyl Phosphite.** The crude intermediate **27** reacted with (2-methylpropenyl)trimethylsilane (**21**) and silyl ethers **23a** and **23b** in the presence of $BF_3{\cdot}Et_2O$ to afford **32**, **33a**, and **33b** in 66%, 71%, and 69% yield, respectively (Scheme 7). Intermediate **27** easily eliminates the benzotriazole anion in the presence of $BF_3{\cdot}Et_2O$ to form the planar iminium cation, which is further attacked by the nucleophiles allylsilane **21** or silyl ethers **23a** and **23b**, followed by hydrolysis, to furnish the final products **32**, **33a**, and **33b**. The treatment of **27** with 2 equiv of triethyl phosphite in the presence of $ZnBr_2$ afforded **34** in 71% yield.

The $^1$H−$^1$H COSY analyses show that the chemical shift of H(8a) in **32**, **33a**, and **33b** is 2.65, 3.06, and 3.60 ppm, respectively. The double-doublet patterns with the coupling constants ~9.0, 2.1 Hz indicate that H(8a) in each compound occupies an axial position. Because the H(5) has the same long-distance interaction as $H_a(8a)$ with $H_a(7)$, the configurations of **29**, **30a**, and **30b** are all cis isomers with H(5) and H(8a) axial. The $^1$H NMR and $^{13}$C NMR spectra of **34** is much more complicated. The $^1$H−$^1$H COSY and $^1$H−$^{13}$C COSY analyses show that H(5) and H(8a) are located not only in the axial position (**A**) but also in the equatorial positions (**C**). By the integration of $^1$H NMR spectrum, the ratio of **A** to **C** in **34** is about 3:2, which indicates that the molecule with H(5) and H(8a) axial is more stable.

## Conclusion

In this paper, we have developed an efficient and convenient route to 1-phenyl-5-substituted-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazoles **20**, **22**, **24**, and **25** and 1-phenyl-5-substituted-octahydroimidazo[1,2-*a*]pyridines **28** and **32**−**34** via the benzotriazole methodology. The intermolecular condensation of succindialdehyde/glutaraldehyde, benzotriazole and *N*-phenylethylenediamine gave the intermediates 1-phenyl-5-(benzotriazol-1-yl)-hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (**18**) and 1-phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (**27**) as versatile synthons, which reacted with various nucleophiles, e.g., Grignard reagents, allylsilanes, silyl ethers, and triethyl phosphite, to furnish the final products **20**, **22**, **24**, and **25** and **28** and **32**−**34** in good to excellent yields.

## Experimental Section

**General Procedure for the Preparation of 1-Phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (18).** A mixture of 2,5-dimethoxytetrahydrofuran (1.3 mL, 10 mmol) and 0.1 M HCl aqueous solution (40 mL) was refluxed under $N_2$ for 1 h and then cooled to room temperature. A solution of benzotriazole (1.19 g, 10 mmol) and *N*-phenylethylenediamine (1.36 g, 10 mmol) in $CH_2Cl_2$ (100 mL) was added and the mixture stirred overnight. The reaction mixture was washed with 2 M NaOH solution and $H_2O$. The organic layer was dried over anhyd $Na_2SO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel) with hexane/EtOAc (10:1) as eluent to give 1-phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo[1,2-*a*]-imidazole (**18**) and *N*-[2-(1*H*-pyrrol-1-yl)ethyl]aniline (**19**).

**1-Phenyl-5-(benzotriazol-1-yl)hexahydro-1*H*-pyrrolo-[1,2-*a*]imidazole (18):** colorless crystal; mp 98.0−99.0 °C; $^1$H NMR $\delta$ 2.10−2.22 (m, 1H), 2.42−2.70 (m, 3H), 3.12−3.40 (m, 3H), 3.68−3.81 (m, 1H), 4.97−5.03 (m, 1H), 5.98 (t, $J$ = 6.3 Hz, 1H), 6.63 (d, $J$ = 8.0 Hz, 2H), 6.78 (t, $J$ = 7.1 Hz, 1H), 7.27 (t, $J$ = 7.7 Hz, 2H), 7.36 (t, $J$ = 7.8 Hz, 1H), 7.47 (t, $J$ = 7.8 Hz, 1H), 7.86 (d, $J$ = 8.2 Hz, 1H), 8.07 (d, $J$ = 8.2 Hz, 1H); $^{13}$C NMR $\delta$ 29.7, 31.0, 46.8, 49.2, 79.6, 81.0, 111.5, 113.2, 117.2, 119.8, 123.9, 126.9, 129.1, 131.5, 145.8, 146.8. Anal. Calcd for $C_{18}H_{19}N_5$: C, 70.79; H, 6.27; N, 22.93. Found: C, 70.61; H, 6.40; N, 22.90.

***N*-[2-(1*H*-Pyrrol-1-yl)ethyl]aniline (19):** light yellow oil; $^1$H NMR $\delta$ 3.45 (t, $J$ = 5.9 Hz, 2H), 3.50−3.75 (brs, 1H), 4.04 (t, $J$ = 6.0 Hz, 2H), 6.14−6.20 (m, 2H), 6.57 (d, $J$ = 8.0 Hz, 2H), 6.60−6.68 (m, 2H), 6.73 (t, $J$ = 7.4 Hz, 1H), 7.17 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR $\delta$ 44.9, 48.4, 108.6, 113.1, 117.9, 120.7, 129.3, 147.1. Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.16; H, 7.89.

**General Procedure for the Nucleophilic Substitution of 18 with Grignard Reagents.** To a solution of **18** (0.3 g, 1 mmol) in dry THF (10 mL) under $N_2$ at −78 °C was added dropwise a solution of an appropriate Grignard reagent (1 mmol) in diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, the mixture was successively washed with 2 M NaOH and water. The combined aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhyd $Na_2SO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel) with hexane/EtOAc (10:1) as eluent to afford **20a**−**f**.

**1-Phenyl-5-benzylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (20a):** light yellow oil; $^1$H NMR $\delta$ 1.60−1.80 (m, 2H), 1.82−1.93 (m, 1H), 2.23−2.37 (m, 1H), 2.65 (dd, $J$ = 12.9, 8.0 Hz, 1H), 2.94−3.18 (m, 4H), 3.19−3.28 (m, 1H), 3.52−3.63 (m, 1H), 4.77 (dd, $J$ = 5.5, 2.6 Hz, 1H), 6.53 (d, $J$ = 8.0 Hz, 2H), 6.69 (t, $J$ = 7.2 Hz, 1H), 7.13−7.38 (m, 7H); $^{13}$C NMR $\delta$ 30.8, 31.6, 42.6, 46.2, 49.4, 65.6, 81.1, 112.9, 116.4, 126.1, 128.3, 129.0, 129.1, 139.5, 146.1. Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.82; H, 8.33; N, 10.28.

**1-Phenyl-5-pentylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (20b):** colorless oil; $^1$H NMR $\delta$ 0.90 (t, $J$ = 6.1 Hz, 3H), 1.24−1.41 (m, 7H), 1.45−1.58 (m, 1H), 1.62−1.72 (m, 1H), 1.74−1.84 (m, 1H), 1.97−2.10 (m, 1H), 2.25−2.36 (m, 1H), 2.71−2.83 (m, 1H), 3.13−3.22 (m, 2H), 3.22−3.30 (m, 1H), 3.55−3.64 (m, 1H), 4.74 (dd, $J$ = 5.5, 3.3 Hz, 1H), 6.55 (d, $J$ = 8.3 Hz, 2H), 6.70 (t, $J$ = 7.1 Hz, 1H), 7.22 (t, $J$ = 8.0 Hz, 2H); $^{13}$C NMR $\delta$ 14.0, 22.6, 26.5, 31.0, 31.6, 32.2, 36.1, 46.2, 49.3, 64.1, 81.0, 112.9, 116.3, 129.1, 146.2. Anal. Calcd for $C_{17}H_{26}N_2$: C, 79.00; H, 10.16; N, 10.84. Found: C, 78.60; H, 10.47; N, 11.09.

**1-Phenyl-5-(prop-1-ynyl)hexahydro-1*H*-pyrrolo[1,2-*a*]-imidazole (20c):** pale yellow needles; mp 53.0−54.0 °C; $^1$H NMR $\delta$ 1.75−1.88 (m, 1H), 1.86 (s, 3H), 1.91−2.09 (m, 1H), 2.09−2.21 (m, 1H), 2.32−2.44 (m, 1H), 3.18−3.32 (m, 2H), 3.33−3.42 (m, 1H), 3.53−3.67 (m, 2H), 4.76 (dd, $J$ = 5.3, 2.3 Hz, 1H), 6.51 (d, $J$ = 8.2 Hz, 2H), 6.71 (t, $J$ = 7.2 Hz, 1H), 7.22 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR $\delta$ 3.6, 31.0, 32.9, 45.8, 48.7, 54.3, 78.4, 79.3, 79.8, 112.9, 116.5, 129.1, 145.9. Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.95; H, 8.25; N, 12.77.

**1-Phenyl-5-vinylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (20d):** colorless oil; $^1$H NMR $\delta$ 1.70−1.88 (m, 2H), 1.94−2.06 (m, 1H), 2.30−2.43 (m, 1H), 3.04−3.32 (m, 4H), 3.57−3.68 (m, 1H), 4.78 (dd, $J$ = 5.8, 2.2 Hz, 1H), 5.13 (d, $J$ = 10.1 Hz, 1H), 5.23 (d, $J$ = 17.0 Hz, 1H), 5.72−5.87 (m, 1H), 6.53 (d, $J$ = 8.0 Hz, 2H), 6.70 (t, $J$ = 7.4 Hz, 1H), 7.22 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 31.1, 32.6, 45.7, 47.8, 66.7, 80.4, 112.8, 116.3, 116.5, 129.1, 140.5, 146.0. Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.25; H, 8.72; N, 13.06.

**1-Phenyl-5-(4-methylphenyl)hexahydro-1*H*-pyrrolo-[1,2-*a*]imidazole (20e):** pale yellow plate; mp 74.0−75.0 °C; $^1$H NMR $\delta$ 1.80−1.97 (m, 2H), 2.01−2.24 (m, 1H), 2.35 (s, 3H), 2.38−2.48 (m, 1H), 3.00−3.11 (m, 2H), 3.21−3.30 (m, 1H), 3.63−3.73 (m, 1H), 3.87 (dd, $J$ = 9.9, 4.2 Hz, 1H), 4.89 (dd, $J$ = 5.5, 3.5 Hz, 1H), 6.57 (d, $J$ = 8.2 Hz, 2H), 6.72 (t, $J$ = 7.2 Hz, 1H), 7.16 (d, $J$ = 7.8 Hz, 2H), 7.24 (t, $J$ = 8.0 Hz, 2H), 7.32 (d, $J$ = 7.9 Hz, 2H); $^{13}$C NMR $\delta$ 21.1, 31.5, 35.9, 45.9, 48.4, 67.3, 80.6, 112.9, 116.3, 127.2, 129.1, 129.2, 136.8, 139.9, 146.1. Anal. Calcd for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06. Found: C, 81.59; H, 8.29; N, 9.87.

**1-Phenyl-5-(4-fluoro-3-methylphenyl)hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (20f):** colorless oil; $^1$H NMR $\delta$ 1.80−1.94 (m, 2H), 2.10−2.20 (m, 1H), 2.28 (s, 3H), 2.37−2.48 (m, 1H), 2.96−3.14 (m, 2H), 3.21−3.30 (m, 1H), 3.60−3.72 (m, 1H), 3.82 (dd, $J$ = 8.8, 3.4 Hz, 1H), 4.87 (dd, $J$ = 5.8, 3.3 Hz, 1H), 6.55 (d, $J$ = 8.3 Hz, 2H), 6.71 (t, $J$ = 7.1 Hz, 1H), 6.95 (t, $J$ = 8.8 Hz, 1H), 7.14−7.30 (m, 4H); $^{13}$C NMR $\delta$ 14.6 (d, $J$ = 3.4 Hz), 31.5, 35.9, 45.8, 48.3, 66.9, 80.5, 112.9, 114.7 (d, $J$ = 22.4 Hz), 116.3, 124.6 (d, $J$ = 17.3 Hz), 126.0 (d, $J$ = 7.8 Hz), 129.1, 130.0 (d, $J$ = 5.1 Hz), 138.3 (d, $J$ = 3.3 Hz), 146.1, 160.5 (d, $J$ = 242.0 Hz). Anal. Calcd for $C_{19}H_{21}FN_2$: C, 77.00; H, 7.14; N, 9.45. Found: C, 76.55; H, 7.52; N, 9.36.

**General Procedure for the Reaction of 18 with Allylsilane and Silyl Ethers.** To a solution of **18** (0.30 g, 1 mmol) and (2-methylpropenyl)trimethylsilane (**21**) or silyl ether **23a**,**b** (1 mmol) in dry $CH_2Cl_2$ (10 mL) under $N_2$ was added $BF_3{\cdot}Et_2O$ (0.12 mL, 1 mmol) at 0 °C and the mixture stirred for 3 h. The mixture was warmed to room temperature and stirred for another 3 h. The mixture was washed with 5% $NaHCO_3$ and $H_2O$, and the combined aqueous phase was extracted with EtOAc. The combined organic layers were dried over anhyd $Na_2SO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel) with hexane/EtOAc (5:1) as eluent to afford **22** or **24a**,**b**.

**1-Phenyl-5-(2-methyl-2-propenyl)hexahydro-1*H*-pyrrolo[1,2-*a*]imidazole (22):** light yellow oil; $^1$H NMR $\delta$ 1.52−1.68 (m, 1H), 1.77 (s, 3H), 1.70−1.86 (m, 1H), 1.96−2.04 (m, 1H), 2.04−2.14 (m, 1H), 2.26−2.37 (m, 1H), 2.42 (dd, $J$ = 12.2, 2.4 Hz, 1H), 2.96−3.07 (m, 1H), 1.13−3.31 (m, 3H), 3.58−3.68 (m, 1H), 4.72−4.82 (m, 3H), 6.55 (d, $J$ = 8.3 Hz, 2H), 6.71 (t, $J$ = 7.1 Hz, 1H), 7.23 (t, $J$ = 8.2 Hz, 2H); $^{13}$C NMR $\delta$ 22.9, 30.7, 31.5, 44.5, 46.2, 49.2, 62.0, 80.9, 112.1, 112.9, 116.3, 129.0, 143.3, 146.1. Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.12; H, 9.59; N, 11.47.

**1-Phenyl-2-(1-phenylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazol-5-yl)-1-ethanone (24a):** colorless needles; mp 101.0−102.0 °C; $^1$H NMR $\delta$ 1.53−1.68 (m, 1H), 1.81−1.94 (m, 1H), 2.17−2.39 (m, 2H), 3.03−3.41 (m, 5H), 3.47−3.58 (m, 1H), 3.58−3.68 (m, 1H), 4.77 (dd, $J$ = 5.2, 3.3 Hz, 1H), 6.56 (d, $J$ = 8.2 Hz, 2H), 6.71 (t, $J$ = 7.1 Hz, 1H), 7.23 (t, $J$ = 8.0 Hz, 2H), 7.47 (t, $J$ = 7.4 Hz, 2H), 7.57 (t, $J$ = 7.1 Hz, 1H), 7.99 (d, $J$ = 7.6 Hz, 2H); $^{13}$C NMR $\delta$ 31.0, 31.9, 45.3, 46.5, 49.8, 60.3, 80.7, 112.9, 116.4, 128.1, 128.6, 129.1, 133.1, 137.1, 146.1, 199.2. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.36; H, 7.55; N, 9.14.

**Methyl 2-methyl-2-(1-phenylhexahydro-1*H*-pyrrolo-[1,2-*a*]imidazol-5-yl)propanoate (24b):** colorless oil; $^1$H NMR $\delta$ 1.15 (s, 3H), 1.22 (s, 3H), 1.63−1.74 (m, 1H), 1.84−2.00 (m, 2H), 2.01−2.12 (m, 1H), 3.02−3.11 (m, 1H), 3.12−3.31 (m, 3H), 3.44−3.58 (m, 1H), 3.69 (s, 3H), 4.64 (dd, $J$ = 5.3, 3.2 Hz, 1H), 6.58 (d, $J$ = 8.2 Hz, 2H), 6.70 (t, $J$ = 7.4 Hz, 1H), 7.22 (t, $J$ = 7.9 Hz, 2H); $^{13}$C NMR $\delta$ 21.2, 21.4, 26.6, 31.4,

47.3, 47.9, 51.6, 53.5, 71.7, 82.1, 112.8, 116.4, 129.0, 146.5, 177.9; HRMS calcd for $C_{17}H_{25}N_2O_2$ 289.1916 (M + 1), found 289.1942.

**Diethyl 1-Phenylhexahydro-1*H*-pyrrolo[1,2-*a*]imidazol-5-ylphosphonate (25).** To a solution of **18** (1 mmol) in dry $CH_2Cl_2$ (20 mL) at 0 °C were added sequentially triethyl phosphite (0.34 mL, 2 mmol) and $ZnBr_2$ (0.22 g, 1 mmol). The reaction mixture was stirred at 0 °C for 2 h and then was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with 2 M NaOH, and the aqueous suspension was extracted with $CH_2Cl_2$. The combined organic extracts were washed with brine and dried over anhyd $Na_2SO_4$. After removal of the solvent in vacuo, the residue was separated by column chromatography (silica gel) with hexane/EtOAc (4:1) as eluent to afford **25**: colorless oil; $^1$H NMR $\delta$ 1.35 (t, $J$ = 7.2 Hz, 6H), 1.86−1.96 (m, 1H), 2.08−2.22 (m, 2H), 2.28−2.30 (m, 1H), 3.16 (td, $J$ = 7.8, 2.4 Hz, 1H), 3.24−3.36 (m, 3H), 3.58−3.65 (m, 1H), 4.14−4.28 (m, 4H), 4.73−4.80 (m, 1H), 6.57 (d, $J$ = 8.1 Hz, 2H), 6.72 (t, $J$ = 7.2 Hz, 1H), 7.22 (t, $J$ = 7.8 Hz, 2H); $^{13}$C NMR $\delta$ 16.9 (d, $J$ = 5.7 Hz), 26.9, 31.4 (d, $J$ = 7.4 Hz), 47.3, 52.0 (d, $J$ = 4.5 Hz), 61.0 (d, $J$ = 178.1 Hz), 62.6 (d, $J$ = 6.8 Hz), 62.8 (d, $J$ = 6.8 Hz), 82.1 (d, $J$ = 15.9 Hz), 113.4, 117.2, 129.4, 146.5. Anal. Calcd for $C_{16}H_{25}N_2O_3P$: C, 59.25; H, 7.77; N, 8.64. Found: C, 59.08; H, 8.05; N, 8.66.

**General Procedure for the Preparation of 1-Phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (27) and Nucleophilic Substitution of 27 with Grignard Reagents.** A mixture of glutaraldehyde (**26**) (50% weight aqueous solution, 2 mL, 10 mmol), benzotriazole (1.65 g, 14 mmol), and *N*-phenyl-1,2-ethylenediamine (1.35 g, 10 mmol) in $CH_2Cl_2$ (20 mL) was stirred at room temperature for 24 h. The reaction mixture was washed with 1 M NaOH solution and extracted with $CH_2Cl_2$. The combined organic layers were dried over anhyd $Na_2SO_4$. Removal of the solvent in vacuo gave 1-phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (**27**), which could be directly used in the subsequent step.

To a solution of the crude intermediate **27** (2 mmol) in dry THF (10 mL) was added dropwise a solution of an appropriate Grignard reagent (2 mmol) in ether at −78 °C. The mixture was stirred at this temperature for 2 h, warmed to room temperature, and stirred for further 4 h. The same workup for the preparation of **20a**−**f** furnished **28a**−**e**.

**1-Phenyl-5-benzotriazolyloctahydroimidazo[1,2-*a*]pyridine (27).** Obtained as a mixture of $Bt^1$ and $Bt^2$ isomers in an approximately 7:3 ratio: yellow oil; yield ∼100%; $^1$H NMR $\delta$ 1.48−1.98 (m, 2H), 2.06−2.80 (m, 4H), 3.12−3.30 (m, 2H), 3.68−3.90 (m, 2H), 4.61−4.71 (m, 0.7H in $Bt^1$), 5.58 (dd, $J$ = 10.0, 2.8 Hz, 0.7H in $Bt^1$), 5.90−5.98 (m, 0.3H in $Bt^2$), 6.10−6.18 (m, 0.3H in $Bt^2$), 6.60−6.85 (m, 3H), 7.16−7.52 (m, 4H), 7.82−8.14 (m, 2H).

**1-Phenyl-5-benzyloctahydroimidazo[1,2-*a*]pyridine (28a):** colorless crystal; mp 118.0−119.0 °C; $^1$H NMR $\delta$ 1.18−1.44 (m, 3H), 1.45−1.54 (m, 1H), 1.76−1.86 (m, 1H), 2.28−2.38 (m, 1H), 2.50−2.74 (m, 3H), 3.13 (dd, $J$ = 12.4, 3.6 Hz, 1H), 3.31(t, $J$ = 7.8 Hz, 1H), 3.44 (t, $J$ = 7.3 Hz, 1H), 3.63 (dd, $J$ = 8.8 Hz, 2.1 Hz, 1H), 3.72−3.82 (m, 1H), 6.65 (d, $J$ = 8.2 Hz, 2H), 6.73 (t, $J$ = 7.1 Hz, 1H), 7.16−7.34 (m, 7H); $^{13}$C NMR $\delta$ 22.6, 29.0, 29.5, 41.3, 47.5, 49.9, 62.3, 78.7, 113.8, 116.9, 126.1, 128.2, 128.9, 129.3, 139.0, 148.0. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 81.82; H, 8.60; N, 9.58.

**1-Phenyl-5-propyloctahydroimidazo[1,2-*a*]pyridine (28b):** colorless oil; $^1$H NMR $\delta$ 0.94 (t, $J$ = 6.9 Hz, 3H), 1.20−1.52 (m, 6H), 1.58−1.74 (m, 2H), 1.82−1.94 (m, 1H), 2.26−2.36 (m, 1H), 2.37−2.52 (m, 2H), 3.25−3.36 (m, 2H), 3.62 (dd, $J$ = 9.6, 2.1 Hz, 1H), 3.65−3.78 (m, 1H), 6.63 (d, $J$ = 8.0 Hz, 2H), 6.71 (t, $J$ = 7.1 Hz, 1H), 7.21 (t, $J$ = 7.9 Hz, 2H); $^{13}$C NMR $\delta$ 14.4, 18.8, 22.8, 28.8, 29.4, 36.5, 46.7, 49.6, 60.5, 78.5, 113.6, 116.7 128.8, 148.0. Anal. Calcd for $C_{16}H_{24}N_2$: C, 78.64; H, 9.90; N, 11.46. Found: C, 78.72; H, 10.21; N, 11.80.

**1-Phenyl-5-(1-propynyl)octahydroimidazo[1,2-*a*]pyridine (28c).** Obtained as a mixture of conformation **A** and **C** in a ratio of 2:3 (minor conformer in parentheses): pale yellow needles; mp 78.0−79.0 °C; $^1$H NMR $\delta$ 1.19−1.39 (m, 1H) [1.40−1.58 (m, 1H)], 1.66−1.95 (m, 4H), 1.83 (s, 3H), 2.30−2.41 (m, 1H), 2.78−2.88 (m, 1H) [2.41−2.55 (m, 1H)], 2.90−3.00 (m, 1H) [3.50−3.58 (m, 1H)], 3.21−3.31 (m, 1H), 3.68−3.81 (m, 1H), 3.90−3.98 (m, 1H) [3.43−3.50 (m, 1H)], 3.98−4.05 (m, 1H) [3.12−3.21 (m, 1H)], 6.58−6.75 (m, 3H), 7.14 (m, 2H); $^{13}$C NMR $\delta$ 3.4, 19.4 (22.6), 29.0 (32.1), 30.1 (30.0), 48.1 (49.7), 49.8 (49.1), 53.0 (49.9), 72.4 (78.1), 78.6 (75.6), 81.5 (79.1), 113.7, 116.8 (116.9), 128.8, 148.3 (148.0). Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 80.01; H, 8.74; N, 11.74.

**1-Phenyl-5-*p*-tolyloctahydroimidazo[1,2-*a*]pyridine (28d):** colorless needles; mp 107.0−108.0 °C; $^1$H NMR $\delta$ 1.36−1.50 (m, 1H), 1.55−1.86 (m, 3H), 1.90−2.00 (m, 1H), 2.10−2.20 (m, 1H), 2.34 (s, 3H), 2.43−2.52 (m, 1H), 2.86 (t, $J$ = 7.7 Hz, 1H), 3.14 (t, $J$ = 8.0 Hz, 1H), 3.30 (dd, $J$ = 10.1, 2.8 Hz, 1H), 3.56 (dd, $J$ = 9.4, 1.7 Hz, 1H), 3.66−3.78 (m, 1H), 6.69 (d, $J$ = 8.3 Hz, 2H), 6.74 (t, $J$ = 7.4 Hz, 1H), 7.10−7.32 (m, 6H); $^{13}$C NMR $\delta$ 21.1, 23.3, 29.5, 34.7, 49.0, 50.6, 67.2, 79.5, 114.5, 117.3, 127.4, 128.8, 129.1, 136.9, 140.2, 148.6. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 81.84; H, 8.57; N, 9.43.

**1-Phenyl-5-cyclopentyloctahydroimidazo[1,2-*a*]pyridine (28e):** colorless oil; $^1$H NMR $\delta$ 1.20−1.91 (m, 13H), 1.96−2.06 (m, 1H), 2.06−2.17 (m, 1H), 2.47−2.57 (m, 1H), 2.70−2.78 (m, 1H), 3.20−3.38 (m, 2H), 3.51−3.61 (m, 1H), 3.97 (dd, $J$ = 9.9, 2.1 Hz, 1H), 6.57 (d, $J$ = 8.3 Hz, 2H), 6.67 (t, $J$ = 7.4 Hz, 1H), 7.19 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 23.1, 24.7, 25.4, 25.6, 27.2, 28.7, 30.1, 43.0, 44.8, 48.0, 63.8, 77.0, 112.7, 116.1, 128.9, 147.2. Anal. Calcd for $C_{18}H_{26}N_2$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.57; H, 9.74; N, 10.71.

**General Procedure for the Reaction of 27 with Allylsilane and Silyl Ethers.** To a solution of the crude intermediate **27** (1 mmol) and (2-methylpropenyl)trimethylsilane (**21**) or silyl ether **23a**,**b** (2 mmol) in dry $CH_2Cl_2$ (10 mL) was added $BF_3{\cdot}Et_2O$ (0.12 mL, 1 mmol) at 0 °C and the mixture stirred for 3 h. The same procedure for the preparation of **22** and **24** afforded **32** or **33a**,**b**.

**1-Phenyl-5-(2-methyl-2-propenyl)octahydroimidazo-[1,2-*a*]pyridine (32):** light yellow oil; $^1$H NMR $\delta$ 1.14−1.38 (m, 2H), 1.40−1.56 (m, 1H), 1.60−1.78 (m, 1H), 1.75 (s, 3H), 1.82−1.94 (m, 1H), 2.04−2.16 (m, 1H), 2.26−2.38 (m, 1H), 2.40−2.54 (m, 2H), 2.65 (dd, $J$ = 8.9, 2.2 Hz, 1H), 3.23−3.40 (m, 2H), 3.60−3.78 (m, 2H), 4.76 (s, 1H), 4.80 (s, 1H), 6.63 (d, $J$ = 8.0 Hz, 2H), 6.71 (t, $J$ = 7.1 Hz, 1H), 7.21 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 22.6, 22.8, 28.8, 29.4, 43.3, 46.8, 49.7, 58.6, 78.6, 112.8, 113.7, 116.8, 128.9, 142.6, 148.0. Anal. Calcd for $C_{17}H_{24}N_2$: C, 79.64; H, 9.44; N, 10.93. Found: C, 79.28; H, 9.75; N, 11.22.

**1-Phenyl-2-(1-phenyloctahydroimidazo[1,2-*a*]pyridin-5-yl)-1-ethanone (33a):** colorless needles; mp 104.0−105.0 °C; $^1$H NMR $\delta$ 1.20−1.70 (m, 3H), 1.73−1.92 (m, 2H), 2.32−2.44 (m, 1H), 2.48−2.60 (m, 1H), 3.06 (dd, $J$ = 9.0, 2.1 Hz, 1H), 3.12−3.42 (m, 4H), 3.64−3.80 (m, 2H), 6.65 (d, $J$ = 8.2 Hz, 2H), 6.73 (t, $J$ = 7.1 Hz, 1H), 7.22 (t, $J$ = 7.6 Hz, 2H), 7.48 (t, $J$ = 7.1 Hz, 2H), 7.58 (t, $J$ = 7.1 Hz, 1H), 7.98 (d, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 22.7, 29.0, 31.0, 43.8, 47.8, 49.9, 56.8, 78.5, 114.0, 117.1, 128.1, 128.6, 128.9, 133.2, 137.1, 148.0, 198.4. Anal. Calcd for $C_{21}H_{24}N_2O$: C, 78.71; H, 7.55; N, 8.74. Found: C, 78.43; H, 7.85; N, 8.53.

**Methyl 2-(1-phenyloctahydroimidazo[1,2-*a*]pyridin-5-yl)acetate (33b):** white crystal; mp 84.0−85.0 °C; $^1$H NMR $\delta$ 1.17 (s, 3H), 1.26 (s, 3H), 1.22−1.70 (m, 4H), 1.88−1.98 (m, 1H), 2.20−2.30 (m, 1H), 2.43−2.53 (m, 1H), 2.98−3.10 (m, 2H), 3.13−3.23 (m, 1H), 3.60 (dd, $J$ = 8.7, 2.2 Hz, 1H), 3.67 (s, 3H), 3.74−3.82 (m, 1H), 6.60 (d, $J$ = 8.3 Hz, 2H), 6.70 (t, $J$ = 7.4 Hz, 1H), 7.20 (t, $J$ = 7.7 Hz, 2H); $^{13}$C NMR $\delta$ 18.6, 23.0, 24.0, 25.7, 28.5, 45.6, 46.1, 49.7, 51.8, 65.0, 78.6, 113.5, 116.7, 128.9, 147.8, 179.0. Anal. Calcd for $C_{18}H_{26}N_2O_2$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.03; H, 8.97; N, 9.24.

**Diethyl 1-Phenyloctahydroimidazo[1,2-*a*]pyridin-5-ylphosphonate (34).** To a solution of crude **27** (1 mmol) in dry $CH_2Cl_2$ (20 mL) at 0 °C were added sequentially triethyl phosphite (0.34 mL, 2 mmol) and $ZnBr_2$ (0.22 g, 1 mmol). The same procedure for the preparation of **25** gave **34**. Obtained as a mixture of conformation **A** and **C** in the ratio 3:2 (minor part in the parentheses): colorless oil; $^1$H NMR $\delta$ 1.33 (t, $J$ = 7.1 Hz, 3H), 1.36 (t, $J$ = 7.1 Hz, 3H), 1.44−1.62 (m, 1H), 1.62−1.84 (m, 1H), 1.84−2.10 (m, 3H), 2.22−2.32 (m, 1H), 2.76−

2.88 (m, 1H) [3.44−3.50 (m, 1H)], 2.95−3.07 (m, 1H) [3.50−3.60 (m, 1H)], 3.22−3.40 (m, 2H), 3.62−3.78 (m, 2H), 4.08−4.24 (m, 4H), 6.53−6.63 (m, 2H), 6.71 (t, $J$ = 7.5 Hz, 1H), 7.21 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR $\delta$ 16.5 (d, $J$ = 5.7 Hz) [19.3 (d, $J$ = 4.0 Hz)], 23.1 (d, $J$ = 15.4 Hz), 24.3 (d, $J$ = 4.0 Hz), 26.9 (d, $J$ = 157.6 Hz), 46.1, 48.9 (d, $J$ = 66.2 Hz) [49.5 (d, $J$ = 12.5 Hz)], 57.9 (d, $J$ = 159.4 Hz) [54.9 (d, $J$ = 161.6 Hz)], 61.9 (d, $J$ = 6.8 Hz) [61.7 (d, $J$ = 6.8 Hz)], 62.1 (d, $J$ = 6.8 Hz) [62.5 (d, $J$ = 6.8 Hz)], 78.6 (d, $J$ = 18.2 Hz), 113.3 [111.8], 116.8 [116.0], 128.9 [129.1], 147.4 [146.5]. Anal. Calcd for $C_{17}H_{27}N_2O_3P$: C, 60.34; H, 8.04; N, 8.28. Found: C, 60.12; H, 8.40; N, 8.44.

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