Synthesis of 2,3-Disubstituted Pyrroles and Pyridines from 3-Halo-1-azaallylic Anions

Wim Aelterman,[†] Norbert De Kimpe,*[,†] Vladimir Tyvorskii,[‡] and Oleg Kulinkovich[‡]

Department of Organic Chemistry, Faculty of Agricultural and Applied Biological Sciences, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium, and Department of Organic Chemistry, Belarussian State University, Fr. Scorina Avenue 4, 220050 Minsk, Belarus

norbert.dekimpe@rug.ac.be

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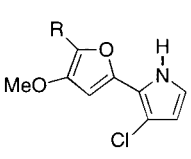
A new synthesis of 2,3-disubstituted pyrroles and pyridines is described. The reaction of 3-halo-1-azaallylic carbanions, regiospecifically generated from α-halogenated ketimines, with *ω*-iodoazides led to the regiospecific formation of *ω*-azido-α-haloketimines. Treatment of these functionalized imines with tin(II) chloride afforded halogenated five- and six-membered cyclic imines, which were transformed under mild conditions into 2,3-disubstituted pyrroles and pyridines. The stereoselective reduction of 2,3-dialkyl-3-chloro-1-pyrrolines to afford *cis*-2,3-dialkyl-3-chloropyrrolidines is also reported.

Introduction

Pyrroles and pyridines, and their di- and tetrahydro derivatives, are very important compounds as they occur in a large number of natural products and display a variety of physiological activities.[1,2]

In the present paper, a new entry into 2,3-disubstituted pyrroles (also containing a chloro atom at the 3-position) and pyridines is disclosed.

Several types of these N-heterocycles are used in agrochemistry and in the pharmaceutical field, which explains the interest in new and better strategies for the construction of these compounds. For example, roseophillin **1** is a 2-substituted-3-chloropyrrole containing antileukemic compound, isolated from *Streptomyces griseoviridis*,[3] while 3-chloro-2-(3-nitro-4-chlorophenyl) pyrrole **2** has bactericidal properties.[4]



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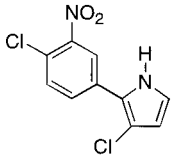

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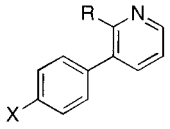
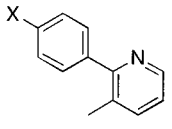


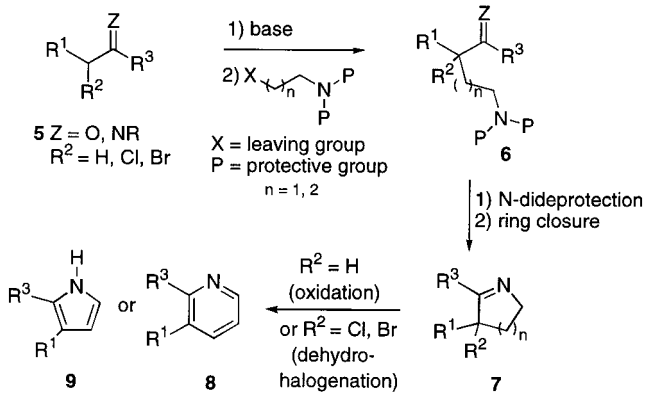
3 X = H, Cl; R = alkyl



4 X = H, Cl, F

On the other hand, 2-alkyl-3-arylpyridines **3** and 2-aryl-3-methylpyridines **4** are intermediates in the synthesis of physiologically active products, such as antitumor compounds.[5] Some simple 2- and 3-alkyl(aryl)-pyridines also have been identified as natural flavor compounds of cocoa,[6] tobacco,[6] and orange oil.[7]

Scheme 1



From a retrosynthetic point of view, 2,3-disubstituted pyrroles and pyridines **8** or **9** can be synthesized via a reaction sequence involving α-alkylation of carbonyl compounds **5** (Z = O) or imines **5** (Z = NR) with suitable N-protected *ω*-bromoamines, subsequent N-deprotection, ring closure, and final oxidation or dehydrohalogenation (Scheme 1). This seems to be a very attractive route because of the wide variety of substituents (R^1 and R^2) that can be used, originating from readily accessible starting materials. However, nonhalogenated 1-pyrrolines **7** ($n = 1$) and 2,3,4,5-tetrahydropyridines **7** ($n = 2$)

[†] Ghent University.
[‡] Belarussian State University.

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(R^2 = H), which are for example accessible via an intramolecular aza-Wittigreaction of *ω*-azidoketones,[8] can only be oxidized under harsh conditions such as palladium on alumina in refluxing nitrobenzene[9] or reflux in mesitylene in the presence of selenium.[10] Aromatization of cyclic imines can also be achieved by a halogenation−dehydrohalogenation sequence, but during the first step often mixtures of mono- and dihalogenated cyclic imines are obtained.[11] Cyclic imines can also be synthesized by α-alkylation of imines with ethylenetetramethyldisilyl-protected *ω*-bromoamines, followed by ring closure.[12] However, this method does not seem to be applicable to aliphatic α-halogenated imines.

In this paper, a straightforward and versatile synthetic route to 2,3-disubstituted pyrroles and pyridines via halogenated cyclic imines is disclosed. The latter are obtained in one step from *ω*-azidoketimines, synthesized by regiospecific α-alkylation of α-halogenated imines with *ω*-iodoazides.

Results and Discussion

α-Halo-*ω*-azidoketimines **13** were synthesized by regiospecific alkylation of α-haloketimines **10** with *ω*-iodoalkyl azides **12** via the intermediacy of 3-halo-1-azaallylic anions **11**,[13] generated with lithium diisopropylamide in tetrahydrofuran (Scheme 2, Table 1). The primary amino-protected electrophilic reagents **12** were easily prepared in good yields from 2-chloroethanol (n = 1) and 3-chloropropanol (n = 2) by successive reaction with sodium azide, tosylation, and substitution with sodium iodide.[14] The azides were purified by distillation and could be stored at −20 °C for several months without noticeable decomposition. To obtain good conversions of the 3-halo-1-azaallylic carbanions **11** into the α-alkylated imines **13**, after initial deprotonation with LDA at 0 °C, hexamethylphosphoramide (HMPA) was added at −78 °C and the *ω*-iodoazides **12** were added neat. The α,*γ*- and α,*δ*-difunctionalized ketimines **13** thus obtained were purified by vacuum distillation (except the derivatives with a too high boiling point) and have a reasonable shelf life when stored at −20 °C (Table 1).

The chemoselective reduction of the azides **13** with 1.5 equiv of tin(II) chloride[15] in methanol at room temperature led directly to the halogenated 1-pyrrolines **14** (n = 1) and 2,3,4,5-tetrahydropyridines **14** (n = 2). The transient primary amines could not be detected as the reaction resulted in an immediate transimination.

The cyclic imines **14** were obtained in pure form in good to excellent yields after flash chromatography (48−97%). For the reduction−cyclization of the aromatic *δ*-azidoketimine **13f**, a tandem Staudinger−intramolecular aza-Wittig reaction[8] with triphenylphosphine in the presence of water in THF gave better results (62% isolated yield) than reaction with tin(II) chloride in methanol. Somewhat surprisingly, reaction of the α-bromoketimine **13g** (R = i-Pr, R^1 = Me, R^2 = 4-MeC_6H_5, n = 2) with tin(II) chloride in methanol mainly led to the hydrodebromination product **18** which was isolated in 44% yield after flash chromatography. Alternatively, the 5-bromo-2,3,4,5-tetrahydropyridine **14g** could be synthesized by treatment of the α-bromo ketone **19,** obtained by acid hydrolysis of imine **13g**, with triphenylphosphine in pentane via an intramolecular aza-Wittig reaction (Scheme 3). The α-bromo imine unit is apparently more rapidly reduced by tin(II) chloride than the *δ*-azido function, necessitating a modification of the tin(II) chloride type reductive cyclization.

In a final step, treatment of 1-pyrrolines **14a,b** (n = 1) with sodium methoxide in methanol under reflux

Scheme 2

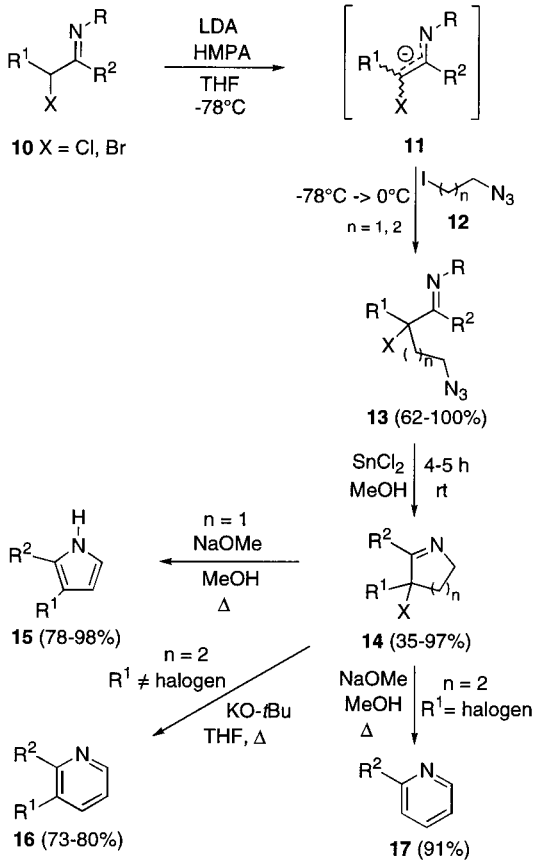

Table 1. Synthesis of α-Halo-*ω*-azidoketimines 13 by Deprotonation and Subsequent Alkylation of α-Haloketimines 10 with *ω*-Iodoazides 12[a]

entry	R	R^1	R^2	X	n[b]	product (yield, %)	bp (°C/mmHg)
1	*i*-Pr	Me	Me	Cl	1	**13a** (81)[c]	51−52/0.02−0.03
2	*t*-Bu	Et	Me	Cl	1	**13b** (77)[c]	55−59/0.05
3	*i*-Pr	Cl	C_6H_5	Cl	1	**13c** (96)[d]	
4	*i*-Pr	Me	Me	Cl	2	**13d** (62)[c]	47−51/0.01
5	*t*-Bu	Et	Me	Cl	2	**13e** (66)[c]	62−63/0.01
6	*i*-Pr	Cl	C_6H_5	Cl	2	**13f** (100)[d]	
7	*i*-Pr	Me	4-MeC_6H_4	Br	2	**13 g** (93)[d]	

[a] Deprotonation conditions: 1.2 equiv of LDA/THF, 25 min 0 °C; cooling to −78 °C, addition of 1 equiv of HMPA; 30 min at −78 °C. Alkylation conditions: 1 equiv of **10**; 5 h −78 → 0 °C. [b] Alkylation with 2-iodoethyl azide **12** (n = 1) or 3-iodopropyl azide **12** (n = 2). [c] Yield after distillation. [d] Crude yield.

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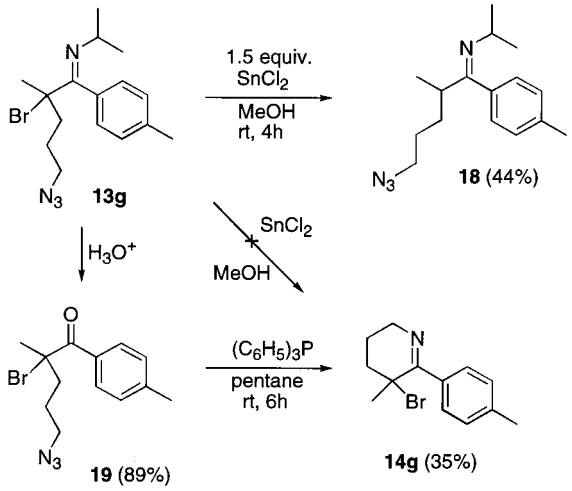
Table 2. Synthesis of Cyclic Imines 14 from ω-Azidoketimines 13 and Their Conversion into Pyrroles 15 and Pyridines 16 and 17

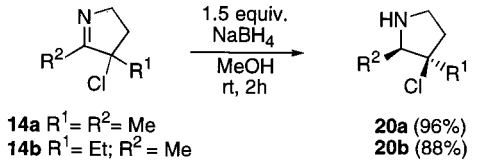
entry	R	R^1	R^2	X	*n*	reaction conditions	cyclic imine (yield, %)	reaction conditions	product (yield, %)
1	*i*-Pr	Me	Me	Cl	1	$SnCl_2$[a]	**14a** (97)[d]	NaOMe[f]	**15a** (98)[h]
2	*t*-Bu	Et	Me	Cl	1	$SnCl_2$[a]	**14b** (84)[d]	NaOMe[f]	**15b** (78)[d]
3	*i*-Pr	Cl	C_6H_5	Cl	1	$SnCl_2$[a]	**14c** (76)[d]	NaOMe[f]	**15c** (95)[h]
4	*i*-Pr	Me	Me	Cl	2	$SnCl_2$[a]	**14d** (48)[d]	KO*t*-Bu[g]	**16a** (80)[d]
5	*t*-Bu	Et	Me	Cl	2	$SnCl_2$[a]	**14e** (56)[d]	KO*t*-Bu[g]	**16b** (73)[d]
6	*i*-Pr	Cl	C_6H_5	Cl	2	$(C_6H_5)_3P$[b]	**14f** (62)[d]	NaOMe[f]	**17** (91)[d]
7	*i*-Pr	Me	4-MeC_6H_4	Br	2	$(C_6H_5)_3P$[c]	**14g** (35)[d,e]	KO*t*-Bu[g]	**16c** (80)[d]

[a] Imines **13** were reacted with 1.5 equiv of $SnCl_2$ in MeOH at room temperature for 5 h. [b] Imine **13f** was reacted with 1 equiv of both $(C_6H_5)_3P$ and H_2O in THF at room temperature for 20 h. [c] See, for example, Scheme 3. [d] Yields after flash chromatography. [e] Starting from ketone **19**. [f] Cyclic imines **14** were treated with 3 equiv of NaOMe in methanol (2 N) under reflux for 2 h. [g] Cyclic imines **14** were treated with 3 equiv of KO*t*-Bu in THF under reflux for 1 h and further stirred at room temperature for 20 h. [h] Crude yields.

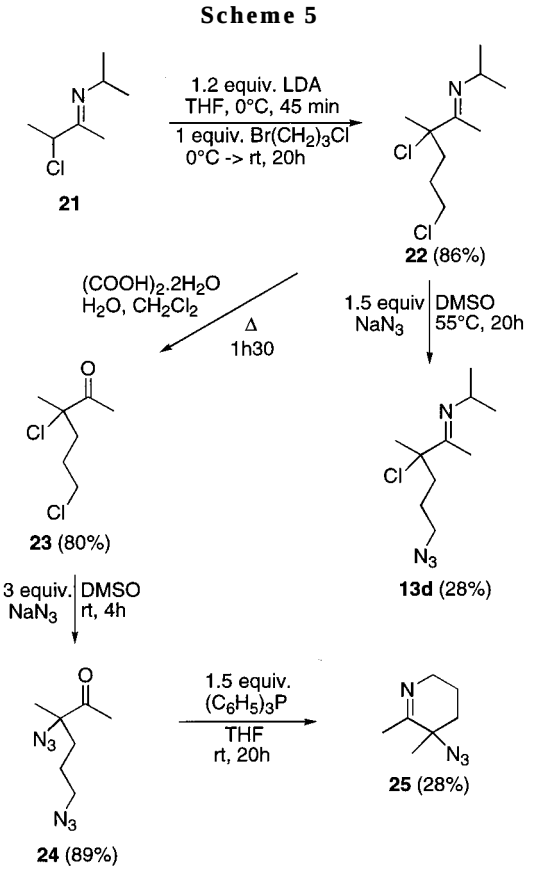
Scheme 3



Scheme 4



Scheme 5



furnished 2,3-disubstituted pyrroles **15**, which were obtained in pure form after flash chromatography (Table 2). When α,α-dichloro ketimines were used as starting compounds, 2-alkyl- or 2-aryl-3-chloropyrroles, such as **15c**, could be prepared via this synthetic strategy. These halogenated pyrroles are particularly interesting because of their potential biological activities.[3,4,11] 1,2-Dehydrohalogenation of the corresponding halogenated six-membered cyclic imines **14** ($n = 2$) with potassium *tert*-butoxide in THF led to the formation of pyridines **16**. During this reaction, spontaneous oxidation takes place as the intermediate dihydropyridines could not be detected. 5,5-Dichloro-2,3,4,5-tetrahydropyridine **14f** was converted to 2-phenylpyridine **17** ($R^2 = C_6H_5$) by reaction with sodium methoxide in methanol most probably by a successive 1,2- and 1,4-dehydrochlorination.

In addition, 2,3-dialkyl-3-chloro-1-pyrrolines **14** could be converted stereoselectively into the corresponding *cis*-pyrrolidines **20** by treatment with sodium borohydride in methanol at room temperature for 2 h. The *cis*-2-alkyl-3-chloropyrrolidines **20** were obtained as colorless oils in excellent isolated yields (Scheme 4). The relative stereochemistry of compounds **20** was established by NOE NMR experiments. Irradiation of the α-protons of the alkylsubstituent at C3 resulted in a NOE effect of the methine proton at C2. It is quite remarkable that no trace of the corresponding trans isomer was present in the reaction mixture, culminating in a stereospecific synthesis of chlorinated *cis*-pyrrolidines **20**.

Alternatively, the synthesis of ω-azido-α-haloketimines was tried via α,ω-dihalogenated imines in order to get an alternative access to pyrroles and pyridines. These dihalogenated imines, as demonstrated with imine **22**, are easily accessible by alkylation of α-chloroketimines, e.g., **21**, with 1-bromo-3-chloropropane. However due to the low chemoselectivity of the substitution reaction with sodium azide, the α-chloro-ω-azidoketimine **13d** was isolated in a low yield (28% after distillation). Also 3,6-dichloro-3-methyl-2-hexanone (**23**), obtained by hydrolysis of the corresponding imine **22b,** led to mixtures of mono- and diazidoketones, after treatment with 1.5 equiv of sodium azide in DMSO (Scheme 5).

Only α,δ-diazidoketone **24** could be obtained in pure form by treatment of the dihalide **23** with an excess of sodium azide in DMSO. Via a tandem Staudinger−aza-Wittig reaction with triphenylphosphine in THF the azido

ketone **24** was mainly converted into 5-azido-2,3,4,5-tetrahydropyridine (**25**) which was obtained in 28% yield after flash chromatography.

In conclusion, it was demonstrated that 3-halo-1-azaallylic anions, derived from α-halogenated ketimines, are versatile intermediates in the synthesis of nitrogen-containing heterocycles, e.g., pyrrolines, tetrahydropyridines, pyrroles, pyrrolidines, and pyridines. These 3-halo-1-azaallylic anions were regiospecifically α-alkylated with *ω*-iodoazides to give *ω*-iodoketimines which were transformed in two steps into 2,3-disubstituted pyrroles and pyridines.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz, respectively. The type of carbon and hydrogen atom was determined via DEPT and ^{13}C−^{1}H and ^{1}H−^{1}H COSY NMR techniques. Mass spectra were obtained at 70 eV (only major and diagnostic peaks are given). Thin-layer chromatography was carried out on plates coated with a 0.25 mm layer of silica gel. Column chromatography was performed using silica gel 60 of 40−63 μm particle size. THF was freshly distilled from sodium benzophenone ketyl.

Synthesis of α-Chloro-*ω*-azido Ketimines 13. A solution of LDA was prepared by addition of 2.5 M *n*-butyllithium (12 mL, 30 mmol) in hexane to an ice-cooled solution of diisopropylamine (3.28 g, 33 mmol) in dry THF (35 mL) under a nitrogen atmosphere. This solution was treated by syringe with a solution of α-haloketimine **10** (25 mmol) in THF (25 mL). After 25 min of stirring at 0 °C, the reaction mixture was cooled to −78 °C, hexamethylphosphoramide (CAUTION!) (4.48 g, 25 mmol) was added, and the mixture was stirred additionally for 30 min at −78 °C. Then, *ω*-iodoazide **12** (25 mmol) was added dropwise. The mixture was gradually warmed to 0 °C over 5 h then poured into an ice-cooled 0.5 M NaOH solution (100 mL), extracted with ether, and the combined organic extracts were dried with K_2CO_3. After filtration and removal of the solvents in vacuo, the crude α-chloro-*ω*-azido ketimines **13** were distilled in vacuo behind a safety shield (CAUTION) (Table 1) or were used as such in the next step (derivatives **13c**, **13f**, **13g**).

***N*-(5-Azido-3-chloro-3-methyl-2-pentylidene)isopropylamine (13a):** ^{1}H NMR ($CDCl_3$) δ 1.07 and 1.09 (2 × 3H, 2xd, J = 6.1 Hz, Me_2CH), 1.67 (3H, s, MeCCl), 1.97 (3H, s, *Me*C=N), 2.18 (1H, ABxdxd, J = 13.86, 9.8, 5.61 Hz, *H*CHCCl), 2.48 (1H, ABxdxd, J = 13.86, 9.57, 5.28 Hz, HC*H*CCl), 3.34 (1H, ABxdxd, J = 12.0, 9.57, 5.61 Hz, *H*CHN$_3$), 3.51 (1H, ABxdxd, J = 12.0, 9.8, 5.28 Hz, HC*H*N$_3$), 3.62 (1H, septet, J = 6.1 Hz, C*H*Me$_2$); ^{13}C NMR ($CDCl_3$) δ 13.0 (*Me*C=N), 23.1 (2x*Me*$_2$CH), 28.9 (*Me*CCl), 40.3 (*C*H$_2$CCl), 48.1 (*C*H$_2$N$_3$), 50.8 (*C*HMe$_2$), 74.4 (CCl), 164.0 (C=N); IR (NaCl, cm^{-1}) 2095 (N$_3$), 1658 (C=N); MS *m*/*z* (%) no M$^+$, 154(5), 127(14), 84(33), 55(3), 42(100). Anal. Calcd For $C_9H_{17}ClN_4$: C, 49.88; H, 7.91; N, 25.85. Found: C, 50.02; H, 7.85; N, 25.76.

***N*-(5-Azido-3-chloro-3-ethyl-2-pentylidene)-*tert*-butylamine (13b):** ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, J = 7.4 Hz, *Me*CH$_2$), 1.27 (9H, s, Me$_3$C), 2.04 (3H, s, *Me*C=N), 1.91−2.10 (3H, m, C*H*$_2$ Me and CH$_2$*H*CH), 2.55 (1H, ABxdxd, J = 16.08, 10.1, 5.28 Hz, NCH$_2$HC*H*), 3.32 and 3.51 (2H, ABxdxd, J = 11.88, 10.1, 5.28 Hz, N*H*CH). ^{13}C NMR ($CDCl_3$) δ 10.0 (*Me*CH$_2$), 17.9 (*Me*C=N), 31.0 (*Me*$_3$C), 35.9 (*C*H$_2$Me), 38.5 (*C*H$_2$-CH$_2$N$_3$), 49.1 (*C*H$_2$N$_3$), 56.2 (Me$_3$*C*), 80.9 (*C*Cl), 163.6 (*C*=N); IR (NaCl, cm^{-1}) 2096 (N$_3$), 1664 (C=N); MS *m*/*z* (%) no M$^+$, 181(4), 154(3), 98(18), 94(3), 57(100). Anal. Calcd For $C_{11}H_{21}$-ClN_4: C, 53.98; H, 8.65; N, 22.89. Found: C, 54.23; H, 8.56; N, 23.02.

***N*-(4-Azido-2,2-dichloro-1-phenyl-1-butylidene)isopropylamine (13c):** ^{1}H NMR ($CDCl_3$) δ 1.05 (6H, d, J = 6.1 Hz, Me_2), 3.00 (2H, ∼t, J = 7.59 Hz, CH_2CCl$_2$), 3.22 (1H, septet, J = 6.1 Hz, C*H*Me$_2$), 3.70 (2H, ∼t, J = 7.59 Hz, CH_2N$_3$), 7.22−7.29 (2H, m. and o. CH=’s), 7.38−7.46 (3H, m, m. and p. CH=’s); ^{13}C NMR ($CDCl_3$) δ 22.4 (Me$_2$), 43.0 (*C*H$_2$CC1$_2$), 47.5 (CH$_2$N$_3$), 52.4 (*C*HMe$_2$), 88.2 (*C*Cl$_2$), 127.1, 128.0 and 128.2 (CH=’s), 132.4 (=C$_{quat}$), 162.8 (C=N); IR (NaCl, cm^{-1}) 2100 (N$_3$), 1639 (C=N). MS *m*/*z* (%) no M$^+$, 235/7(5), 208(7), 146-(20), 104(100), 77(10). Anal. Calcd for $C_{13}H_{16}Cl_2N_4$: C, 52.18; H, 5.39; N, 18.72. Found: C, 52.03; H, 5.44; N, 18.76.

***N*-(6-Azido-3-chloro-3-methyl-2-hexylidene)isopropylamine (13d):** ^{1}H NMR ($CDCl_3$) δ 1.08 (6H, d, J = 6.27 Hz, *Me*$_2$CH), 1.66 (3H, s, MeCC1), 1.52−1.90 (2H, m, C*H*$_2$CH$_2$N$_3$), 1.90−2.26 (2H, m, CH$_2$CCl), 1.98 (3H, s, MeC=N), 3.28 and 3.30 (2H, ABxdxd, J = 12.12, 6.76, 2.64 Hz, CH$_2$N$_3$), 3.63 (1H, septet, J = 6.27 Hz, C*H*Me$_2$); ^{13}C NMR ($CDCl_3$) δ 13.0 (*Me*C=N), 23.1 and 23.2 (2x*Me*CH), 24.8 (*C*H$_2$CH$_2$Cl), 28.1 (*Me*CC1), 39.0 (*C*H$_2$CCl), 50.8 (NCH), 51.5 (*C*H$_2$N$_3$), 76.2 (CCl), 164.4 (C=N); IR (NaCl, cm^{-1}) 2098 (N$_3$), 1650 (C=N); MS *m*/*z* (%) no M$^+$, 195(M$^+$ − Cl, 4), 188/190(M$^+$ − N$_3$, 17), 147(11), 134-(7), 84(50), 42(100). Anal. Calcd for $C_{10}H_{19}ClN_4$: C, 52.05; H, 8.30; N, 24.28. Found: C, 52.27; H, 8.22; N, 24.20.

***N*-(6-Azido-3 chloro-3-ethyl-2-hexylidene)-*tert*-butylamine (13e):** ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J = 7.26 Hz, *Me*CH$_2$), 1.26 (9H, s, Me$_3$), 1.54−1.86 (2H, m, CH_2CH$_2$CC1), 1.80−2.25 (4H, m, MeCH_2CC1CH_2), 2.05 (3H, s, MeC=N), 3.27 (2H, t, J = 6.8 Hz, CH_2N$_3$); ^{13}C NMR ($CDCl_3$) δ 9.2 (*Me*CH$_2$), 17.5 (*Me*C=N), 24.6 (*C*H$_2$CH$_2$CC1), 30.2 (*Me*$_3$C), 34.0 and 36.3 (*C*H$_2$CC1*C*H$_2$), 51.7 (*C*H$_2$N$_3$), 55.1 (*C*Me$_3$), 82.2 (*C*C1), 163.1 (*C*=N); IR (NaCl, cm^{-1}) 2080−2100 (N$_3$), 1660 (C=N); MS *m*/*z* (%) no M$^+$, 216/8(4), 177(5), 162(9), 98(25), 57(100). Anal. Calcd for $C_{12}H_{23}ClN_4$: C, 55.70; H, 8.96; N, 21.65. Found: C, 55.86; H, 7.04; N, 21.55.

***N*-(5-Azido-2,2-dichloro-1-phenyl)isopropylamine (13f):** ^{1}H NMR ($CDCl_3$) δ 1.06 (2 × 3H, 2xd, J = 6.93 Hz, Me_2-CH), 2.00−2.13 (2H, m, CH_2CH$_2$N$_3$), 2.70−2.76 (2H, m, CH$_2$-CCl$_2$), 3.32 (1H, septet, J = 6.93 Hz, Me$_2$C*H*), 3.43 (2H, t, J = 6.27 Hz, CH$_2$N$_3$), 7.23−7.31 (2H, m, m-CH=), 7.39−7.47 (3H, m, o- and p-CH=); ^{13}C NMR ($CDCl_3$) δ 23.1 (*Me*$_2$CH), 25.5 (*C*H$_2$-CH$_2$N$_3$), 42.1 (*C*H$_2$CCl$_2$), 50.9 (*C*H$_2$N$_3$), 53.1 (Me$_2$*C*H), 91.7 (*C*Cl$_2$), 127.8 (o-CH=), 128.5 (p-CH=), 128.9 (m-CH=), 133.7 (=*C*−C=N), 164.0 (C=N); IR (NaCl, cm^{-1}) 2100 (N$_3$), 1643 (C=N). Anal. Calcd for $C_{14}H_{18}Cl_2N_4$: C, 53.68; H, 5.79; N, 17.89. Found: C, 53.76; H, 5.77; N, 17.80.

***N*-[5-Azido-2-bromo-2-methyl-2-(4-methylphenyl)-1-butylidene]isopropylamine (13g):** ^{1}H NMR ($CDCl_3$) δ 1.00 (6H, d, J = 6.26 Hz, Me_2CH), 1.69−1.94 (2H, m, CH$_2$CH_2-CH$_2$N$_3$), 1.82 (3H, s, *Me*CBr), 2.22−2.28 (2H, m, CH_2CBr), 2.38 (3H, s, *Me*C$_6$H$_4$), 3.16 (1H, septet, J = 6.26 Hz, C*H*Me$_2$), 3.31 (2H, m, CH_2N$_3$), 7.02−7.26 (4H, m, C$_6H_4$); ^{13}C NMR ($CDCl_3$) δ 21.6 (*Me*C$_6$H$_4$), 23.2 and 23.3 (*Me*$_2$CH), 26.0 (CH$_2$*C*H$_2$CH$_2$N$_3$), 29.3 (*Me*CBr), 40.0 (*C*H$_2$CBr), 51.4 (*C*H$_2$N$_3$), 52.8 (*C*HMe$_2$), 70.5 (*C*Br), 128.1 and 128.6 (*C*H=’s), 132.6 and 137.8 (C$_{quat.arom.}$), 167.7 (*C*=N); IR (NaCl, cm^{-1}) 2098 (N$_3$), 1632 (C=N); MS *m*/*z* (%) no M$^+$, 308/10 (M$^+$ − N$_3$), 160(16), 118(100), 91(8). Anal. Calcd for $C_{16}H_{23}BrN_4$: C, 54.71; H, 6.60; N, 15.95. Found: C, 54.59; H, 6.63; N, 15.91.

Synthesis of 1-Pyrrolines 14a−c and 2,3,4,5-Tetrahydropyridines 14d−g. The synthesis of 3-chloro-2,3-dimethyl-1-pyrroline (**14a**) is representative. To a solution of α-chloro-*ω*-azidoketimine **13a** (2.16 g, 10 mmol) in methanol (30 mL) was added $SnCl_2$ (2.84 g, 15 mmol). The mixture was stirred under nitrogen for 5 h at room temperature, poured into a 0.5 N NaOH solution, and extracted with ether. The combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo to yield 1.27 g (97%) of crude **14a** (purity > 95%, ^{1}H NMR) (light red oil) which was used as such in the next step.

3-Chloro-2,3-dimethyl-1-pyrroline (14a): ^{1}H NMR ($CDCl_3$) δ 1.75 (3H, s, *Me*CCl), 2.11 (3H, t, J = 1.98 Hz, *Me*C=N), 2.03−2.15 (1H, m, overlap, *H*CHCCl), 2.47 (1H, ABxt, J = 14.19, 4.95 Hz, HC*H*CCl), 3.81 (2H, txq, J = 4.95, 1.98 Hz, NCH_2); ^{13}C NMR ($CDCl_3$) δ 14.4 (*Me*C=N), 27.6 (*Me*CCl), 41.9 (*C*H$_2$-CCl), 57.0 (*C*H$_2$N), 76.1 (*C*Cl), 174.7 (*C*=N); IR (NaCl, cm^{-1}) 1638 (C=N); MS *m*/*z* (%) 131/3(M$^+$, 6), 96(M$^+$ − Cl, 10), 92-(14), 90(37), 55(100). Anal. Calcd for $C_6H_{10}ClN$: C, 54.76; H, 7.66; N, 10.64. Found: C, 54.60; H, 7.51; N, 10.48.

3-Chloro-3-ethyl-2-methyl-1-pyrroline (14b): purification by flash chromatography hexane/ether 9/1 (R_f = 0.26); ^{1}H NMR ($CDCl_3$) δ 1.05 (3H, t, J = 7.26 Hz, *Me*CH$_2$), 1.79 (1H, ABxq, J = 14.36, 7.26 Hz, *H*CHMe), 2.02−2.18 (2H, m,

HC*H*Me and *H*CHCH$_2$N), 2.09 (3H, t, J = 1.98 Hz, MeC=N), 2.33 (1H, ABxt, J = 14.19, 6.95 Hz, HC*H*CH$_2$N), 3.82 (2H, txq, J = 6.95, 1.98 Hz, NCH$_2$); ^{13}C NMR ($CDCl_3$) δ 9.4 (*Me*CH$_2$), 14.7 (*Me*C=N), 32.8 (*C*H$_2$Me), 38.1 (NCH$_2$*C*H$_2$), 57.3 (*C*H$_2$N), 81.3 (*C*Cl), 174.3 (*C*=N); IR (NaCl, cm^{-1}) 1640 (C=N); MS *m*/*z* (%) 145/7(M$^+$, 21), 104/6(78), 89(10), 69(78), 55(100). Anal. Calcd for $C_7H_{12}ClN$: C, 57.73; H, 8.31; N, 9.62. Found: C, 57.88; H, 8.30; N, 9.54.

5-Chloro-5,6-dimethyl-2,3,4,5-tetrahydropyridine (14d): purification by flash chromatography hexane/ether 4/1 (R_f = 0.20); ^{1}H NMR ($CDCl_3$) δ 1.56−1.74 and 1.82−2.00 (2 × 1H, 2xm, NCH$_2$C*H*$_2$), 1.71 (3H, s, *Me*CCl), 1.82−2.00 and 2.18−2.29 (2 × 1H, 2xm, C*H*$_2$CCl), 2.12 (3H, dxd, J = 2.18, 1.48 Hz, *Me*C=N), 3.43 and 3.79 (2H, ABxm, $J_{AB} \approx$ 18.1 Hz, NC*H*$_2$); ^{13}C NMR ($CDCl_3$) δ 19.2 (NCH$_2$*C*H$_2$), 21.9 (*Me*C=N), 29.9 (*Me*CCl), 38.3 (*C*H$_2$CCl), 49.6 (N*C*H$_2$), 63.7 (*C*Cl), 166.4 (*C*=N); IR (NaCl, cm^{-1}) 1650 (C=N); MS *m*/*z* (%) 145/7(M$^+$, 27), 110(M$^+$ − Cl, 44), 76/8(97), 69(69), 56(44), 42(100). Anal. Calcd for $C_7H_{12}ClN$: C, 57.73; H, 8.31; N, 9.62. Found: C, 57.92; H, 8.22; N, 9.56.

5-Chloro-5-ethyl-6-methyl-2,3,4,5-tetrahydropyridine (14e): purification by flash chromatography hexane/ether 92/8 (R_f = 0.25); ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, t, J = 7.26 Hz, *Me*CH$_2$), 1.56−2.00 (2H, m, NCH$_2$C*H*$_2$), 1.78−2.20 (4H, m, (C*H*$_2$)$_2$CCl), 2.08 (3H, dxd, J = 2.31, 1.32 Hz, MeC=N), 3.33 and 3.81 (2H, ABxm, $J_{AB} \approx$ 17.7 Hz, NC*H*$_2$); ^{13}C NMR ($CDCl_3$) δ 8.6 (*Me*CH$_2$), 18.7 (NCH$_2$*C*H$_2$), 21.9 (*Me*C=N), 34.0 and 34.2 (each *C*H$_2$CCl), 49.5 (N*C*H$_2$), 68.0 (*C*Cl), 166.4 (*C*=N); IR (NaCl, cm^{-1}) 1645 (C=N); MS *m*/*z* (%) 159/61(M$^+$, 19), 124-(82), 90/2(100), 69(19), 56(34), 55(89). Anal. Calcd for C_8H_{14}-ClN: C, 60.18; H, 8.84; N, 8.77. Found: C, 60.30; H, 8.74; N, 8.70.

Synthesis of Pyrroles 15 and Pyridine 17 by Reaction of Cyclic Imines 14 with Sodium Methoxide in Methanol. The synthesis of 2,3-dimethylpyrrole **15a** is representative (Table 2). To 1.04 g (8 mmol) of 1-pyrroline **14a** was added 12 mL (24 mmol) of a 2 M solution of sodium methoxide in methanol. The mixture was stirred for 2 h at reflux, poured into water, and extracted with ether. The combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo to give 0.74 g (98%) of pure (>97%; GC) pyrrole **15a** (light red oil).

2,3-Dimethylpyrrole 15a: ^{1}H NMR ($CDCl_3$) δ 2.02 and 2.16 (2 × 3H, 2xs, 2xMe), 5.98 (1H, t, J = 2.64 Hz, NCH=CH), 6.56 (1H, t, J = 2.64 Hz, NCH=), 7.60−7.85 (1H, broad s, NH); ^{13}C NMR ($CDCl_3$) δ 10.8 (2xMe, overlap), 109.8 (NCH=*C*H), 113.9 (NHC=*C*Me), 114.9 (NCH=), 123.6 (N*C*Me); IR (NaCl, cm^{-1}) 3370 (NH), 2915, 1466, 1102, 712; MS *m*/*z* (%) 95(M$^+$, 100), 93(14), 80(22), 67(12), 53(12). See ref 16. Anal. Calcd for C_6H_9N: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.88; H, 9.44; N, 14.68.

3-Ethyl-2-methylpyrrole (15b): purified by flash chromatography hexane/ethyl acetate 9/1 (R_f = 0.34); ^{1}H NMR ($CDCl_3$) δ 1.16 (3H, t, J = 7.59 Hz, *Me*CH$_2$), 2.18 (3H, s, MeC=C), 2.42 (2H, q, J = 7.59 Hz, CH$_2$), 6.04 (1H, t, J = 2.64 Hz, NCH=C*H*), 6.59 (1H, t, J = 2.64 Hz, NCH=), 7.56−7.95 (1H, broad s, NH); ^{13}C NMR ($CDCl_3$) δ 11.0 (*Me*C=C), 15.6 (*Me*CH$_2$), 19.0 (*C*H$_2$Me), 108.2 and 114.9 (2x =*C*H), 121.1 and 122.8 (C$_{quat}$); IR(NaCl, cm^{-1}) 3360−3390 (NH), 1451, 1105, 899; MS *m*/*z* (%) 109(M$^+$, 48), 94(100), 67(11), 53(9). See ref 17. Anal. Calcd for $C_7H_{11}N$: C, 77.01; H, 10.16; N, 12.83. Found: C, 77.18; H, 10.08; N, 12.76.

Synthesis of Pyridines 16 by Reaction of Cyclic Imines 14 with Potassium *tert*-Butoxide in THF. The synthesis of 2,3-dimethylpyridine **16a** is representative (Table 2). To a solution of 1.16 g (8 mmol) of 2,3,4,5-tetrahydropyridine **14d** in THF (20 mL) was added potassium *tert*-butoxide (2.69 g, 24 mmol). The reaction mixture was stirred for 1 h under reflux, cooled to room temperature, and further stirred for 20 h, poured into water, and extracted with ether. The combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo to give 0.86 g of crude pyridine **16a**, which was purified by flash chromatography (pentane/ether 1/1, R_f = 0.17) to afford 0.68 g (80%) of the pure substance as a colorless oil.

2,3-Dimethylpyridine (16a): ^{1}H NMR ($CDCl_3$) δ 2.28 and 2.50 (2 × 3H, 2xs, 2xMe), 7.03 (1H, dxd, J = 7.4 Hz, NCHC*H*), 7.39 (1H, broad d, J = 7.4 Hz, NCHCHC*H*), 8.32 (1H, dxd, J = 4.7, 0.99 Hz, NCH); ^{13}C NMR ($CDCl_3$) δ 19.2 and 22.6 (2xMe), 121.2 (NCH*C*H), 131.4 (CH*C*Me), 137.0 (NCHCH*C*H), 146.5 (NCH), 157.1 (N*C*Me); IR (NaCl, cm^{-1}) 1575, 1470, 1450, 1435; MS *m*/*z* (%) 107(M$^+$, 100), 106(69), 92(19), 79(24), 66-(27). See ref 18. Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.32; H, 8.40; N, 12.92.

3-Ethyl-2-methylpyridine (16b): Purified by flash chromatography pentane/ether 1/1 (R_f = 0.23); ^{1}H NMR ($CDCl_3$) δ 1.22 (3H, t, J = 7.59 Hz, *Me*CH$_2$), 2.54 (3H, s, *Me*CN), 2.63 (2H, q, J = 7.59 Hz, C*H*$_2$Me), 7.07 (1H, dxd, J = 7.7, 4.8 Hz, NCHC*H*), 7.43 (1H, dxd, J = 7.7, 1.4 Hz, NCHCHC*H*), 8.33 (1H, dxd, J = 4.8, 1.4 Hz, NCH); ^{13}C NMR ($CDCl_3$) δ 13.8 (*Me*CH$_2$), 22.0 (*Me*CN), 25.6 (CH$_2$), 121.4 (NCH*C*H), 135.4 (NCHCH*C*H), 137.1 (*C*CH$_2$Me), 146.3 (NCH), 156.5 (N*C*Me); IR (NaCl, cm^{-1}) 2960, 1600, 1490; MS *m*/*z* (%) 121(M$^+$, 87), 120(43), 106(100), 92(12), 79(34), 77(16). Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.20; H, 9.01; N, 11.46.

Synthesis of *N*-[5-Azido-2-methyl-2-(4-methylphenyl)-1-butylidene]isopropylamine (18). The same procedure as described for the preparation of **14** provided **18** as a light yellow oil in 44% yield after flash chromatography (hexane/ethyl acetate 9/1, R_f = 0.25). For **18**: ^{1}H NMR ($CDCl_3$) δ 1.03 and 1.04 (2 × 3H, 2xd, J = 5.94 Hz, *Me*$_2$CH), 1.06 (3H, d, J = 6.93 Hz, *Me*CH), 1.31−1.40 and 1.63−1.73 (4H, m, C*H*$_2$C*H*$_2$-CH$_2$N$_3$), 2.37 (3H, s, *Me*C$_6$H$_4$), 2.58 (1H, ∼sextet, $J \approx$ 6.7 Hz, CH$_2$C*H*Me), 3.27 (2H, t, J = 6.3 Hz, CH$_2$N$_3$), 3.31 (1H, septet, J = 5.94 Hz, C*H*Me$_2$), 6.90 and 7.19 (4H, AB, J_{AB} = 7.9 Hz, C$_6$H$_4$); ^{13}C NMR ($CDCl_3$) δ 18.4 (*Me*CHCH$_2$), 21.2 (*Me*C$_6$H$_4$), 23.7 and 23.9 (*Me*$_2$CH), 26.9 and 31.0 (*C*H$_2$*C*H$_2$CH$_2$N$_3$), 44.4 (*C*HC=N), 51.6 (CH$_2$N$_3$), 52.0 (CHMe$_2$), 126.4 and 128.9 (CH='s), 134.7 and 137.5 (C$_{quat}$), 172.6 (C=N); IR (NaCl, cm^{-1}) 2098 (N$_3$), 1641 (C=N); MS *m*/*z* (%) no M$^+$, 230(M$^+$ − N$_3$, 7), 229-(36), 188(11), 181(12), 118(100), 84(19), 44(24). Anal. Calcd for $C_{16}H_{24}N_4$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.70; H, 8.84; N, 20.50.

Synthesis of 6-Azido-3-bromo-3-methyl-1-(4-methylphenyl)-2-hexanone (19). A solution of 1.34 g (3.8 mmol) of ketimine **13g** in 15 mL of dichloromethane was stirred with 3.8 mL of a 1 M aqueous solution of HCl under reflux for 2 h. The organic layer was separated, and the water phase was extracted with CH_2Cl_2. The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo to yield 1.05 g (89%) of the crude ketone **19** (purity > 90%) which was used as such in the next step. For **19**: ^{1}H NMR ($CDCl_3$) δ 1.49−1.92 (2H, m, C*H*$_2$CH$_2$N$_3$), 2.01 (3H, s, MeCBr), 2.15−2.46 (2H, m, C*H*$_2$CBr), 2.41 (3H, s, *Me*C$_6$H$_4$), 3.29 (2H, t, J = 6.8 Hz, CH$_2$N$_3$), 7.24 and 8.04 (4H, AX, J_{AX} = 8.25 Hz, C$_6$H$_4$); ^{13}C NMR ($CDCl_3$) δ 21.6 (*Me*C$_6$H$_4$), 25.4 (CH$_2$CH$_2$N$_3$), 28.7 (*Me*CBr), 40.1 (CH$_2$CBr), 51.1 (CH$_2$N$_3$), 64.6 (CBr), 128.9 and 130.1 (CH='s), 132.3 and 143.4 (C$_{quat}$), 196.1 (C=O); IR (NaCl, cm^{-1}) 2100 (N$_3$), 1672 (C=O); MS *m*/*z* (%) no M$^+$, 160(2), 119(100), 91(21), 65-(8), 55(3), 43(7).

Synthesis of 5-Bromo-5-methyl-6-(4-methylphenyl)-2,3,4,5-tetrahydropyridine (14g). A solution of 0.93 g (3 mmol) of δ-azidoketone **19** in 10 mL of pentane was treated with 0.79 g (3 mmol) of triphenylphosphine. The reaction mixture was stirred for 6 h at room temperature, and the precipitate that formed was filtered off. The filtrate was evaporated, and 15 mL of pentane was added. The solution was stored overnight at −20 °C, and the precipitate that formed was again filtered off. The filtrate was purified by flash chromatography using hexane/ethyl acetate (70/30) as eluent (R_f = 0.31) yielding 0.28 g (35%) of pure 2,3,4,5-tetrahydropyridine **14g** as a semisolid colorless product: ^{1}H NMR ($CDCl_3$)

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δ 1.81 (3H, s, *Me*CBr), 1.72−1.99 and 2.17−2.46 (4H, m, CH_2CH_2CBr), 2.36 (3H, s, *Me*C$_6$H$_4$), 3.75 (1H, Abxdxd, J = 18.9, 11.7, 5.61 Hz, NC*H*CH), 4.18 (1H, Abxdxt, J = 18.9, 5.94, 1.32 Hz, NHC*H*), 7.15 and 7.63 (4H, AX, J_{AX} = 8.1 Hz, C$_6$*H*$_4$); ^{13}C NMR ($CDCl_3$) δ 19.7 (NCH_2*C*H_2), 21.2 (*Me*C$_6$H$_4$), 32.3 (*Me*CBr), 39.4 (*C*H_2CBr), 50.0 (NCH_2), 57.3 (CBr), 128.5 (CH═), 136.1 and 138.5 (C_{quat}), 167.8 (C═N); IR (NaCl, cm^{-1}) 1610, 1620 (C═N, C═C); MS *m*/*z* (%) no M$^+$, 182(46), 181(100), 166(27), 151(4), 90(7), 89(7), 83(9). Anal. Calcd for $C_{13}H_{16}BrN$: C, 58.66; H, 6.06; N, 5.26. Found: C, 58.76; H, 6.18; N, 5.13.

Synthesis of 3-Methyl-2-(4-methylphenyl)pyridine (16c). The same procedure as described for the preparation of **16a** and **16b** gave **16c** as a colorless oil in 80% yield after flash chromatography (hexane/ethyl acetate 4/1, R_f = 0.30): ^{1}H NMR ($CDCl_3$) δ 2.36 and 2.41 (2 × 3H, 2xs, 2xMe), 7.15 (1H, dxd, J = 7.8, 4.78 Hz, NCHC*H*), 7.26 and 7.42 (4H, AB, J_{AB} = 7.92 Hz, C$_6$H$_4$), 7.56 (1H, dxd, J = 7.8, 0.99 Hz, NCHCHC*H*), 8.51 (1H, dxd, J = 4.78, 0.99 Hz, NCH); ^{13}C NMR ($CDCl_3$) δ 20.2 and 21.3 (2xMe), 121.8 (NCH*C*HCH), 128.8 and 128.9 (CH's of C$_6$H$_4$), 138.4 (NCHCH*C*H), 146.9 (NCH), 130.8, 137.6, 137.7, and 159.7 (C_{quat}); IR (NaCl, cm^{-1}) 1447, 1425, 829, 790, 770; MS *m*/*z* (%) 183(M$^+$, 50), 182(100), 167(25), 83(8), 65(5). See ref 19. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.32; H, 7.03; N, 7.59.

Synthesis of 3-Chloropyrrolidines 20. To an ice-cooled solution of 1-pyrroline **14** (2 mmol) in methanol (10 mL) was added 3 mmol of sodium borohydride. After 2 h of stirring at room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The combined extracts were dried with $MgSO_4$, filtered, and concentrated in vacuo yielding pure 3-chloropyrrolidines **20** (purity > 98%; ^{1}H NMR).

***cis*-3-Chloro-2,3-dimethylpyrrolidine (20a):** ^{1}H NMR ($CDCl_3$) δ 1.18 (3H, d, J = 6.27 Hz, *Me*CH), 1.63 (3H, s, *Me*CCl), 1.9−2.1 (1H, broad s, NH), 2.00 (1H, ABxdxd, J = 14.0, 9.89, 8.5 Hz, *H*CHCCl), 2.34 (1H, Abxdxd, J = 14.0, 8.5, 2.97 Hz, *HCH*Cl), 2.75 (1H, q, J = 6.27 Hz, C*H*Me), 2.95 (1H, ABxdxd, J = 11.56, 9.89, 2.97 Hz, *H*CHN), 3.16 (1H, ABxt, J = 11.53, 8.5 Hz, HC*H*N); ^{13}C NMR ($CDCl_3$) δ 14.5 (*Me*CH), 26.2 (*Me*CCl), 43.2 (*C*H_2NH), 44.1 (*C*H_2CCl), 64.8 (*C*HMe), 80.4 (CCl); IR (NaCl, cm^{-1}) 3100−3320 (NH), 1443, 1378, 1112; MS *m*/*z* (%) 133/5(M$^+$, 13), 118/20(4), 98(11), 82(7), 69(4), 57(100). Anal. Calcd for $C_6H_{12}ClN$: C, 53.92; H, 9.05; N, 10.48. Found: C, 54.03; H, 8.98; N, 10.40.

***cis*-3-Chloro-3-ethyl-2-methylpyrrolidine (20b):** ^{1}H NMR ($CDCl_3$) δ 1.13 (3H, t, J = 7.26 Hz, *Me*CH_2), 1.18 (3H, d, J = 6.27 Hz, *Me*CH), 1.62 and 1.93 (2H, ABxq, J = 13.5, 7.26 Hz, C*H*$_2$Me), 1.88−2.11 (2H, m, NH en NCH_2*H*CH), 2.29 (1H, ABxdxd, J = 15.88, 8.41, 3.1 Hz, NCH_2HC*H*l), 2.72−2.84 (1H, m, C*H*Me), 2.86−3.04 and 3.08−3.24 (2H, m, NCH_2); ^{13}C NMR ($CDCl_3$) δ 10.3 (*Me*CH_2), 14.7 (*Me*CH), 32.4 (*C*H_2Me), 41.2 (NCH_2*C*H_2), 43.2 (*C*H_2NH), 64.3 (N*C*H), 85.8 (CCl); IR (NaCl, cm^{-1}) 3100−3580 (NH), 2968, 1460, 1379, 848; MS *m*/*z* (%) 147/9(M$^+$, 5), 112(7), 82(6), 69(3), 57(100). Anal. Calcd for $C_7H_{14}ClN$: C, 56.94; H, 9.56; N, 9.49. Found: C, 56.83; H, 9.46; N, 9.56.

Synthesis of 3,6-Dichloro-3-methyl-2-hexanone (23). A solution of imine **22** (9.55 g, 42.6 mmol) in 100 mL of CH_2Cl_2 was stirred with 43 mL of a 1 M aqueous solution of oxalic acid. The two-phase mixture was refluxed for 1.5 h, the organic layer was separated, and the water layer was extracted two times with CH_2Cl_2. After drying ($MgSO_4$), filtration, and evaporation of the solvent in vacuo, the crude ketone **23** was distilled to yield 6.23 g (80%) of pure compound **23**: bp 33−38 °C (0.04−0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.66 (3H, s, MeCCl), 1.80−2.22 (4H, m, CH_2CH_2CCl), 2.39 (3H, s, MeC═O), 3.51−3.62 (2H, m, CH_2Cl); ^{13}C NMR ($CDCl_3$) δ 25.1 (*Me*C═O), 26.6 (*Me*CCl), 27.9 (*C*H_2CH$_2$Cl), 38.1 (*C*HCCl), 44.5 (CH_2Cl), 74.2 (CCl), 204.7 (C═O); IR (NaCl, cm^{-1}) 1714 (C═O); MS *m*/*z* (%) no M$^+$, 148(M$^+$, 0.3), 146(1), 141(1), 108(2), 106(5), 103(3), 67(5), 43(100). Anal. Calcd for $C_7H_{12}Cl_2O$: C, 45.92; H, 6.61. Found: C, 45.80; H, 6.52.

Synthesis of 3,6-Diazido-3-methyl-2-hexanone (24). To a solution of ketone **23** (1.28 g, 7 mmol) in DMSO (20 mL) was added sodium azide (1.63 g, 21 mmol). The mixture was stirred for 24 h at room temperature, poured into water, and extracted with diethyl ether. The combined organic extracts were dried ($MgSO_4$) and evaporated to yield 1.22 g (89%) of crude diazido ketone **24** (purity > 95%, ^{1}H NMR): ^{1}H NMR ($CDCl_3$) δ 1.45 (3H, s, MeCN$_3$), 1.47−1.94 (4H, m, CH_2CH_2-CN$_3$), 2.25 (3H, s, MeC═O), 3.31 (2H, t, J = 6.4 Hz, CH_2N_3); ^{13}C NMR ($CDCl_3$) δ 20.9 (*Me*CN$_3$), 23.3 (*C*H$_2$CH$_2$N$_3$), 25.4 (*Me*C═O), 34.2 (*C*H_2CN$_3$), 50.9 (CH$_2$N$_3$), 70.7 (CN$_3$), 207.0 (C═O); IR (NaCl, cm^{-1}) 2090−2110 (N$_3$), 1718 (C═O); MS *m*/*z* (%) no M$^+$, 154(1), 125(2), 107(3), 84(2), 71(3), 69(9), 56(17).

Synthesis of 5-Azido-5,6-dimethyl-2,3,4,5-tetrahydropyridine (25). An analoguous procedure as described for the preparation of **14g** afforded **25** in 28% yield after flash chromatography (pentane/ether 40/60, R_f = 0.13): ^{1}H NMR ($CDCl_3$) δ 1.41 (3H, s, MeCN$_3$), 1.60−2.02 (4H, m, NCH$_2$-CH_2CH_2), 2.03 (3H, t, J = 1.98 Hz, MeC═N), 3.50−3.62 (2H, m, NCH$_2$); ^{13}C NMR ($CDCl_3$) δ 19.6 (NCH$_2$*C*H$_2$), 22.1 (*Me*C═N), 23.9 (*Me*CN$_3$), 33.4 (*C*H$_2$CN$_3$), 49.3 (NCH$_2$), 60.4 (CN$_3$), 166.7 (C═N); IR (NaCl, cm^{-1}) 2100 (N$_3$), 1656 (C═N); MS *m*/*z* (%) 152(M$^+$, 1), 124(3), 109(2), 96(2), 83(24), 69(18), 42(100). Anal. Calcd for $C_7H_{12}N_4$: C, 55.24; H, 7.95; N, 36.81. Found: C, 55.38; H, 7.75; N, 36.69.

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