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Synthesis and reactivity of alkenyl- and alkynyl-substituted β,β-dihalo-and β,β,β-trichloroamines

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ABSTRACT

β,β-Dihalo- and β,β,β-trichloroamines, obtained by Lewis acid-promoted Petasis-type reaction of α,α-dichlorinated and α,α,α-trichlorinated imines or reduction of α,α-dihaloaldimines, were subjected to a reactivity study and turned out to be remarkably stable compounds. In general, only the bases KO^{t}Bu and NaOMe cause a 1,2-dehydrochlorination with formation of unsaturated α-chloroimines or unsaturated α,α-dichloroimines. Hydrolysis of the α-chloroimines with aqueous oxalic acid resulted in the formation of the corresponding unsaturated α-chloroketones. The reaction of simple β,β-dihaloamines with NaOMe and KO^{t}Bu generated 2-haloprop-2-enylmines and 2,2-dimethoxypropylamines.

1. Introduction

Recently, a new Petasis reaction with α,α-dichlorinated aldimines or α-fluoroaldimines and potassium alkenyltrifluoroborates or potassium alkynyltrifluoroborates under Lewis acid promotion was described.[1–3] This reaction led to the formation of functionalized β,β-dichloroamines **6** and **7**.

There have been not many reports about the synthesis of acyclic β,β-dichloroamines. A free radical process for the addition of *N*-chlorodialkylamines across various olefins in order to obtain β,β-dichloroamines has been described.[4–7] Another, more convenient method reported the synthesis of β-chloroamines by reduction of α-chloro-, α,α-dichloro- and α,α,α-trichloroimines[8] and reduction of α-chloro-α-fluorocarboxylic amides[9] by borane–methyl sulfide complex. A convenient entry into β,β,γ-trichloroamines consisted of the reduction of α,α,β-trichloroimines by means of sodium cyanoborohydride in methanol in the presence of acetic acid.[10] Equally, syntheses of acyclic β,β,β-trichloroamines have not been extensively explored. The oldest reported method for the preparation of β,β,β-trichloroamines concerns the reaction of trichloroacetic acid with imines.[11,12] Other methods are based on the addition of aniline across ethyl 4,4,4-trichloro-2-cyano-2-butenoate.[13,14] A third entry to β,β,β-trichloroamines consists of the reaction of carbon tetrachloride or (trichloromethyl)benzene with phenyl(dialkylamino) acetonitriles under phase transfer catalysis.[15]

Because of the high specificity and the very limited choice of the existing syntheses for β,β,β-trichloroamines it was decided to extend the Lewis acid-promoted borono-Mannich reaction to α,α,α-trichloroaldimines. Moreover, because of the rather limited access to acyclic polychlorinated amines in general, almost no studies have appeared on their reactivity.[16] Therefore, the previously obtained dichlorinated secondary propargylamines and allylamines[1] and the envisaged β,β,β-trichloroamines were subjected to a wide variety of bases and nucleophiles in order to investigate their synthetic potential. It was expected that the β-chloro atom could participate in directed elimination and/or substitution reactions. Moreover, the presence of an unsaturated system (alkenyl- or alkynyl group) in α-position of the amino group could allow further rearrangements.

2. Results and discussion

Recently, we described the Lewis acid-promoted Mannich-type reaction as an extension of the classic Petasis reaction with potassium 2-phenylvinyl- and phenylethynyltrifluoroborates **2** as boron components and α,α-dichloroaldimines **1** as imine components (Scheme 1).[1] In a first step the electrophilic organodifluoroborane **3**, generated in situ by reaction between the corresponding organotrifluoroborate **2** and $BF_3 \cdot OEt_2$, formed a nitrogen–boron complex **4** with the α,α-dichloroimine. This complexation facilitates the transfer of the alkenyl or alkynyl group to the imino carbon atom. Therefore, it was expected that the same Lewis acid-promoted borono-Mannich reaction with α,α,α-trichloroaldimines would

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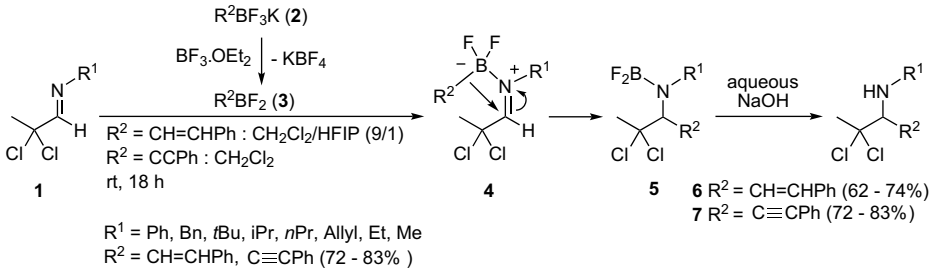


Scheme 1. Lewis acid-promoted Mannich-type reaction with α,α-dichloroaldimines.

proceed as well, if not better, because of the even higher electron-withdrawing properties of the trichloromethyl group.

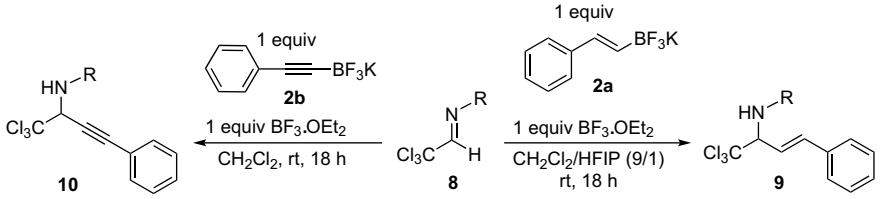
Indeed, this modified Petasis-type reaction of α,α,α-trichloroaldimines[17,18] **8** with styryl or phenylethynyltrifluoroborates in the presence of $BF_3{\cdot}OEt_2$ afforded the corresponding *N*-alkyl-(4,4,4-trichloro-1-phenylbut-1-en-3-yl)amines **9** and *N*-alkyl-(4,4,4-trichloro-1-phenylbut-1-yn-3-yl)amines **10** in good yields (Table 1). When the less reactive styryltrifluoroborate was used, 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) was added as cosolvent, to improve the yield.[1] In general, these trichloroamines could be simply purified by high vacuum evaporation to remove traces of styrene, phenylacetylene or starting imine, leaving the products in purities of over 95%.

Attempted purification of the obtained Mannich products (**9** and **10**) by flash chromatography on silica gel resulted in considerable loss of product (up to 60 mass % of the product degraded on the column). A comparable decrease in yield was noticed by purifying β,β-dichloroamines **6** or **7** on silica gel. Therefore, the influence of silica gel on β,β-dichloroamine **7a** was examined more closely. The Mannich product **7a** was dissolved in EtOAc/Hexane and stirred with an excess of silica gel (Table 2). After 1 day, a trace of side product was present, which could be identified by ^{1}H NMR as α-chloroimine **11a** by the characteristic appearance of a quadruplet at 4.69 ppm ($CDCl_3$). The reaction was continued with fresh silica and after 4 days only half of product **7a** remained. Silica was added one more time, and after a total contact time of 10 days between β,β-dichloroamine and silica gel, only 18 mol % of the starting substrate **7a** was present in the mixture. After a final filtration and evaporation of the solvents a yield of 70% could be calculated for α-chloroimine **11a**, taking into account the 82 mol % purity. Apparently, under the influence of silica gel, β,β-dichloroamines undergo a 1,2-elimination of HCl to generate the corresponding β-chloroenamines, which then tautomerize into α-chloroimines. The latter compounds are known to be hydrolytically unstable and can usually not be purified by flash chromatography on silica gel; this explains the abovementioned decrease in yield.

In order to perform the dehydrohalogenation of **6** and **7** in a more controlled manner, their reactivity towards different bases was investigated. When *N*-alkyl-(4,4-dichloro-1-phenylpent-1-en-3-yl) amines **6** and *N*-alkyl-(4,4-dichloro-1-phenylpent-1-yn-3-yl)amines **7** were reacted with 2–3 equiv of *n*-propylamine, Et_3N, NaH or MeMgCl either at 0 °C, room temperature or under reflux, no reaction took place. Treatment of β,β-dichloroamines **6** and **7** with stronger bases like LDA or *n*-BuLi (2 equiv) under an inert atmosphere at 0 °C always resulted in complete degradation of the starting material. Despite these negative results, there is one precedent in the literature in which *N*-(2,2-dichloro-1-phenylpropyl)aniline is converted in an α-chloroimine upon reaction with MeLi.[16,19]

The use of potassium *tert*-butoxide to synthesize vinyl chlorides or alkynes from geminally chlorinated alkyl ethers has been already reported by Tennyson and Romo.[20] When KO^{t}Bu in THF was added to *N*-alkyl-(4,4-dichloro-1-phenylpent-1-yn-3-yl)amines **7**, complete conversion into the corresponding α-chloroimines **11** occurred already with only 1.2 equiv of KO^{t}Bu. Yields fluctuated around 80–95% (purity >90%), depending on the amount of KO^{t}Bu added and the reaction time. Highest yields were obtained by adding 2 equiv of KO^{t}Bu in THF under reflux for 2 h. As evidenced by

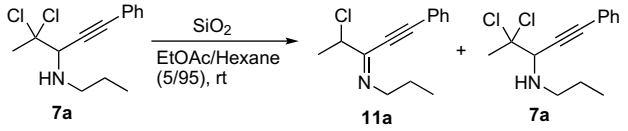
Table 1
Lewis acid-promoted Mannich-type reaction with α,α,α-trichloroaldimines



R (**8**)	Yield[a] of **9** (%)	Yield[a] of **10** (%)
^{t}Bu (**8a**)	79 (**9a**)	76 (**10a**)
^{i}Pr (**8b**)	61 (**9b**)	68 (**10b**)
^{n}Pr (**8c**)	55 (**9c**)	68 (**10c**)
Allyl (**8d**)	61 (**9d**)	65 (**10d**)

[a] Yields after high vacuum evaporation (purity >95%).

Table 2
Influence of SiO_2 on β,β-dichloroamines

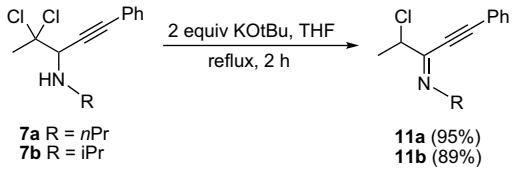


Number of days (reaction time)	Ratio of amine **7a**/imine **11a** (mol %)[a]
1	95/5
4	50/50
10	18/82

[a] Compound **7a** (0.5 mmol) is mixed every time with 2 g fresh SiO_2.

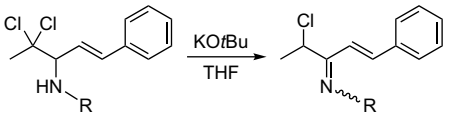
^{1}H NMR spectroscopy, α-chloroketimines **11** were obtained as one geometrical isomer, i.e., *E* with respect to the imino function (Scheme 2), which parallels similar results in the literature.[18]

For *N*-alkyl-(4,4-dichloro-1-phenylpent-1-en-3-yl)amines **6** the results strongly depended on the nitrogen substituent, the amount of KO^{t}Bu added and the reaction conditions (time and temperature), but conversion was almost never complete (Table 3). Yields of



Scheme 2.

Table 3
Dehydrochlorination of *N*-alkyl-(4,4-dichloro-1-phenylpent-1-en-3-yl)amines **6**



Entry	R	Reaction conditions[a]	Conversion: ratio **6**/**12** (%)	Ratio *E*/*Z* **12**	Yield of **12** (%)[c]
1	^{n}Pr (**6a**)	2 equiv KO^{t}Bu, THF, reflux, 2 h	62/38	20/80[b]	30 (**12a**)
2	^{n}Pr (**6a**)	3 equiv KO^{t}Bu, THF, reflux, 2 h	0/100	50/50[b]	85 (**12a**)
3	^{n}Pr (**6a**)	4 equiv KO^{t}Bu, THF, 0 °C, 30 min, rt 18 h	0/100	50/50[b]	75 (**12a**)
4	^{i}Pr (**6b**)	2 equiv KO^{t}Bu, THF, reflux, 2 h	65/35	0/100	32 (**12b**)
5	^{i}Pr (**6b**)	3 equiv KO^{t}Bu, THF, reflux, 2 h	56/44	0/100	36 (**12b**)
6	^{i}Pr (**6b**)	4 equiv KO^{t}Bu, THF, 0 °C, 30 min, rt 18 h	73/27	0/100	23 (**12b**)
7	^{i}Pr (**6b**)	4 equiv KO^{t}Bu, THF, reflux, 2 h	20/80	0/100	71 (**12b**)
8	^{i}Pr (**6b**)	5 equiv KO^{t}Bu, THF, reflux, 2 h	10/90	0/100	82 (**12b**)
9	^{i}Pr (**6b**)	10 equiv KO^{t}Bu, THF, reflux, 2 h	Complete degradation	—	—

[a] Reactions were carried out on 0.5 mmol scale.
[b] Determined by ^{1}H NMR spectroscopy in benzene-d_6.
[c] Determined by ^{1}H NMR spectroscopy.

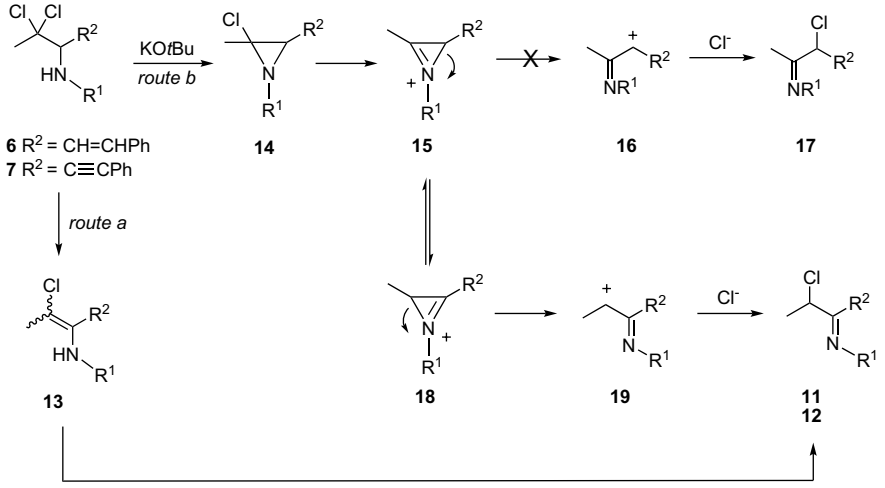
12 varied between 23% and 85%. With a *N*-*n*-propyl substituent, complete conversion to α-chloroimine **12a** was achieved when three or more equivalents of KO^{t}Bu were used (purity >90%) (entries 2, 3). In the case of an *N*-isopropyl substituent (entries 4–8), the more equivalents of base used, the higher the conversion rate, but a complete conversion to the α-chloroimine **12b** could not be accomplished. For sterical reasons ketimine **12b** existed exclusively as the *Z*-isomer.[18]

At first sight, the presence of a MeCHCl moiety in **11** and **12** would suggest an initial deprotonation of the CHN by *tert*-butoxide, probably favoured by the presence of an alkynyl or alkenyl substituent, followed by loss of a chloride anion, and final tautomerization of the β-chloroenamine **13** (route a). Since the reaction also went to completion with only 1.2 equiv of KO^{t}Bu, first the amine should be deprotonated. In accordance with the literature, intramolecular nucleophilic substitution occurs with formation of an intermediate 2-chloroaziridine **14**, which ionizes to give an azirinium chloride **15**.[16,19] Rearrangement of this azirinium chloride by a 1,2-hydride shift might then result in an isomeric azirinium ion **18** or its isomeric ring opened form, i.e., an α-imino carbenium ion **19** and consecutive attack of chloride at the carbenium ion finally affords the α-chloroketimine **11** or **12** (Scheme 3). No traces of the isomeric α-chloroketimine **17** have ever been observed.

A short-path high vacuum distillation (0.01 mmHg) was attempted to purify the obtained α-chlorinated imines **11** and **12**. Unfortunately, these imines were not stable under these conditions and afforded only black tars. Efforts made to purify the chlorinated imines by flash chromatography on neutral alumina (Al_2O_3) were unsuccessful.

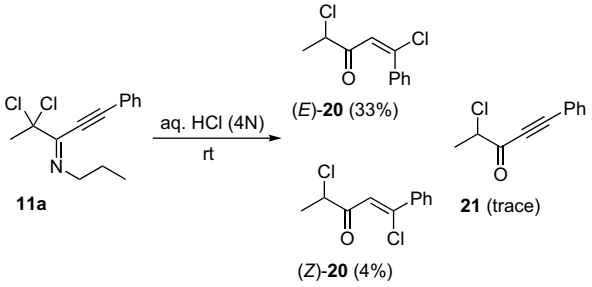
The use of NaOMe in methanol also resulted in the dehydrochlorination of *N*-alkyl-(4,4-dichloro-1-phenylpent-1-yn-3-yl)amines **7** (0.5 mmol). However, yields and purities of the corresponding α-chloroimines **11** were lower than with KO^{t}Bu as base. *N*-Alkyl-(4,4-dichloro-1-phenylpent-1-en-3-yl)amines **6** did not react with NaOMe in methanol. Probably, methoxide was not basic enough to deprotonate the nitrogen atom of amines **6**.

In general, the synthesized α-chloro-α′,β′-unsaturated ketimines **11** and **12** were unstable compounds and could only be stored for a few days under argon at −4 °C before degradation started. Analogous 1-aza-1,3-butadienes, i.e., *N*-unsubstituted α,α,α-trifluoromethyl-α′,β′-unsaturated imines, have also been reported as unstable compounds.[21] On the other hand, α-chlorinated imines are valuable substrates in synthetic organic chemistry.[22] Because syntheses of α-chloro-α′,β′-unsaturated ketones are rare [23–25] and publications about other α-halogeno-α′,β′-



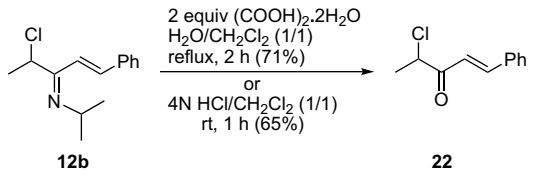
Scheme 3. Proposed mechanism for the formation of the α-chloroketimine.

unsaturated ketones (α-fluoroketones,[26–29] α-bromoketones[30–34]) are also scarce, efforts were made to hydrolyze the α-chloroimines **11** and **12** to the corresponding ketones. In general, hydrolysis of α-chlorinated ketimines into the corresponding α-chloroketones can be carried out via aqueous acid hydrolysis with hydrochloric acid or oxalic acid.[35] Hydrolysis of imine **11a** with 4 N hydrochloric acid afforded a mixture of 89 mol % (*E*)-, 9 mol % (*Z*)-1,4-dichloro-1-phenylpent-1-en-3-one (**20**) and 2 mol % 1-pentyn-3-one **21**. Both stereoisomers were separated by flash chromatography on silica gel. β-Chlorovinylketones **20** are formed by addition of hydrogen chloride to the alkyne moiety of the alkynyl ketone **21** (Scheme 4).[36]



Scheme 4.

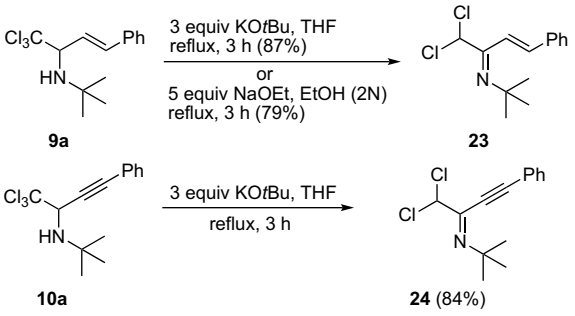
On the other hand, α-chloroketimine **12b** could be hydrolyzed to the corresponding ketone **22** either by reaction with aqueous hydrogen chloride[37] (65%) or with oxalic acid (71%) (Scheme 5). This method thus constitutes a valuable alternative for the synthesis of α-chloro-α′,β′-unsaturated ketones in good yields and only three steps starting from α,α-dichloroimines **1** (Petasis-type reaction, 1,2-dehydrochlorination with KO^{t}Bu and hydrolysis with oxalic acid).



Scheme 5. Hydrolysis of α-chloroimines into α-chloroketones.

The reaction of *N*-4-methoxyphenyl-(4,4,4-trifluoro-1-phenylbut-1-yn-3-yl)amine with sodium hydroxide in THF to give the corresponding difluoroimine, has been reported.[38,39] In view of this result, the same reaction was attempted using *N*-alkyl-(4,4,4-trichloro-1-phenylbut-1-en- and -yn-3-yl)amines **9a** and **10a**. Treatment of *N*-*tert*-butyl-(4,4,4-trichloro-1-phenylbut-1-yn-3-yl)amine (**10a**) with NaOH (4–5 equiv 0.5–3 N NaOH, acetone, rt to reflux, 2–18 h) afforded in all cases only starting material. By using stronger bases like KO^{t}Bu in THF or sodium ethoxide in ethanol, the expected α,α-dichloroimine **23** was formed in good yields but with a disappointing purity of 85% (NMR). Several efforts to purify imines **23** by high vacuum distillation were unsuccessful due to extensive degradation. Interestingly, no further reactions of **23** with sodium ethoxide to *N*-2-(1,1-diethoxyalkylidene)amine were observed.[37] The conversion of *N*-*tert*-butyl-(4,4,4-trichloro-1-phenylbut-1-en-3-yl)amine (**10a**) to the corresponding α,α-dichloroimine **24** could also be achieved using KO^{t}Bu in THF (Scheme 6). Dichloromethyl imine **24** was obtained with a purity of more than 95%.

In view of the rather unexpected results obtained in the reactions of β,β-dichloro- and β,β,β-trichloroamines with potassium *tert*-butoxide, less functionalized β,β-dihaloamines were evaluated



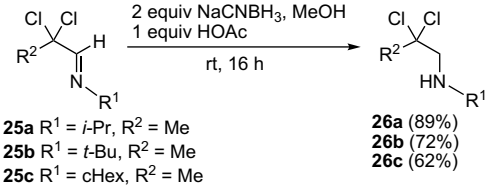
Scheme 6.

in this reaction. Since it has been shown that the reduction of *N*-alkyl-(2,2-dichloropropylidene)amines **25** with lithium aluminium hydride leads to 1,2-disubstituted aziridines,[40] α,α-dichloroimines **25** were treated with 2 equiv of sodium cyanoborohydride in the presence of 1 equiv of acetic acid in methanol, thus affording 2,2-dichloropropylamines **26a–c** in high purity after vacuum distillation (Scheme 7).

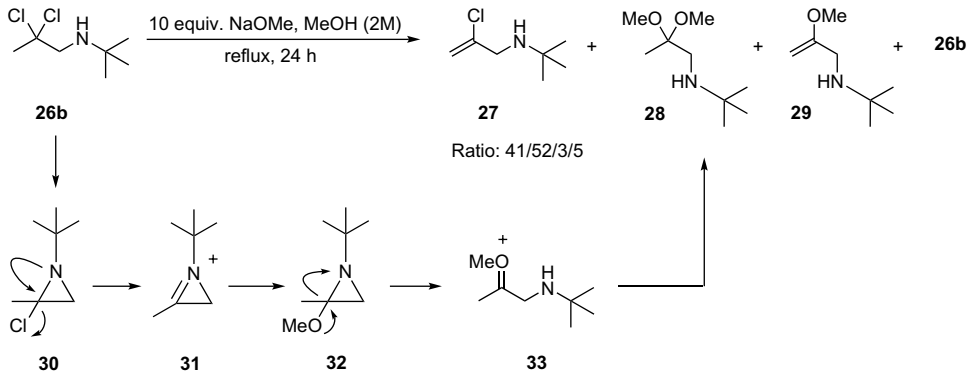
In order to investigate the dehydrochlorination of *N*-*tert*-butyl-(2,2-dichloropropyl)amine (**26b**) different concentrations of sodium methoxide in methanol were added and the reaction mixture was refluxed overnight. In all cases, varying amounts of starting material **26b**, *N*-*tert*-butyl-(2-chloroprop-2-enyl)amine (**27**), *N*-*tert*-butyl-(2,2-dimethoxypropyl)amine (**28**) and 2-methoxypropen-2-enylamine (**29**) were formed. The presence of the α-amino ketoacetal **28** can be interpreted as resulting from a 2-chloroaziridine **30**, which is converted into the azirinium intermediate **31**.[41] Methoxide addition across the iminium bond of **31** would then generate a 2-methoxyaziridine **32**, which after ring opening and a second methoxide addition finally leads to α-amino ketoacetal **28** (Scheme 8).

By using more dilute concentrations of sodium methoxide in methanol (0.5 M), more *N*-*tert*-butyl-(2,2-dimethoxypropyl)amine (**28**) was formed at the expense of *N*-*tert*-butyl-(2-chloroprop-2-enyl)amine (**27**). All attempts to separate compounds **28** and **27** by vacuum distillation failed. In an attempt to drive the reaction towards one single end product, 2,2-dichloropropylamine **26b** was reacted with an excess of concentrated sodium methoxide in methanol (10 equiv, 10 M). In this case, the formation of 2,2-dimethoxypropylamine (**28**) was accompanied by significant amounts of its elimination product 2-methoxypropen-2-enylamine (**29**) in a 65/35 ratio (GC).

Since the reaction of β,β-dichlorinated amines with potassium *tert*-butoxide furnished α-chloroimines, 2,2-dichloropropylamine **26b** was also subjected to a reaction with KO^{t}Bu. The overnight reaction of **26b** with 2 equiv of KO^{t}Bu in refluxing THF, however, did not lead to *N*-(2-chloropropylidene)-*tert*-butylamine but furnished a 1/3 mixture (GC) of starting material **26b** and *N*-(2-chloroprop-2-enyl)-*tert*-butylamine (**27**). The same reaction with 5 equiv of KO^{t}Bu in *tert*-butanol at room temperature gave rise to complete degradation.



Scheme 7.



Scheme 8.

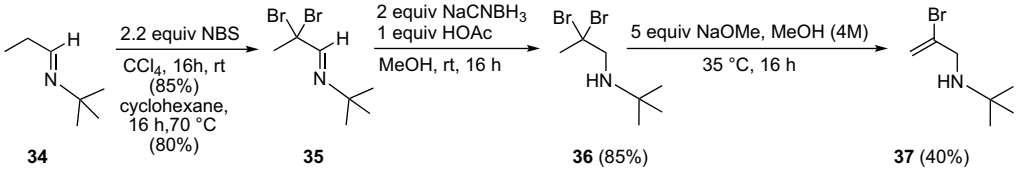
It was expected that the brominated analogue of **26b**, i.e., *N*-*tert*-butyl-(2,2-dibromopropyl)amine (**36**) would be a better substrate for the preparation of *N*-(2-bromoprop-2-enyl)-*tert*-butylamine. The dibromination of *N*-(propylidene)-*tert*-butylamine (**34**) could easily be effected by means of *N*-bromosuccinimide in CCl_4[43] or cyclohexane. It must be stressed that analogous brominations of *N*-(propylidene)propylamine only led to complex reaction mixtures even when the reaction was performed at room temperature. *N*-*tert*-Butyl-(2,2-dibromopropyl)amine (**36**) was obtained by reduction of α,α-dibromoaldimine **35** with sodium cyanoborohydride in methanol. In general, *N*-*tert*-butyl-(2,2-dibromopropyl)amine (**36**) showed higher reactivity towards NaOMe and KO^{t}Bu. With sodium methoxide in methanol complete conversions were effected and varying ratios of *N*-*tert*-butyl-(2,2-dimethoxypropyl)amine (**28**), *N*-(2-bromoprop-2-enyl)-*tert*-butylamine (**37**) and *N*-*tert*-butylpropargylamine were obtained. The extra elimination step of HBr from **37** could be avoided by using 5 equivalents of NaOMe in methanol at 35 °C. In this case, *N*-(2-bromoprop-2-enyl)-*tert*-butylamine (**37**) was obtained in 40% yield after vacuum distillation (Scheme 9). *N*-*tert*-Butyl-(2-haloprop-2-enyl)amines **27** and **37** have been prepared previously by reaction of 2,3-dihalopropene with *tert*-butylamine.[41]

KO^{t}Bu in tetrahydrofuran resulted in 2-haloprop-2-enylamines and 2,2-dimethoxypropylamines.

4. Experimental part

4.1. General

GC–MS analyses were performed using an Intersience GC 8000 series gas chromatograph with a EC™-5 column (length: 30 m, internal diameter: 0.32 mm, film thickness: 0.25 μm). Products are injected in a split injector (250 °C); the inert carrier gas is helium. Mass spectra were measured with a Fisons Instruments MD 800 using electron impact (70 eV) as ionization method. HRMS-data were obtained with a VGQuattro II mass spectrometer (positive ion mode). Under standard measurement conditions the sample was dissolved in CH_3CN/H_2O (1:1) containing 0.1% TFA. In order to avoid eventual hydrolysis, the imines **8** were dissolved in CH_3CN/MeOH (1:1). High resolution ^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance DRX 250 spectrometer. Chemical shifts are reported in parts per million downfield from TMS. ^{13}C NMR assignments were made using DEPT, HMQC and HMBC spectra. Infrared spectra were recorded with an Avatar 370 FT-IR apparatus (Thermo Nicolet).



Scheme 9.

3. Conclusion

In summary, we have successfully extended the Lewis acid-promoted Mannich-type reaction of aldimines with potassium organotrifluoroborates to the use of α,α,α-trichloro-acetaldimines. In addition to the obtained β,β,β-trichloroamines, the formerly prepared dichlorinated secondary propargylamines and allylamines were reacted with several bases. When KO^{t}Bu was used, 1,2-dehydrochlorinations took place, leading to α-chloroketimines **11** and **12**, which could be hydrolyzed into the corresponding α-chloroketones **20** and **22** in aqueous oxalic acid or hydrochloric acid/CH_2Cl_2 two-phase system, respectively. Treatment of β,β,β-trichloroamines **9** and **10** with NaOEt in ethanol or with KO^{t}Bu in tetrahydrofuran also resulted in the formation of the corresponding α,α-dichloroketimines **23** and **24**. On the other hand, the reaction of simple 2,2-dihalopropylamines with NaOMe in methanol and

Unless otherwise stated, the IR-spectra were recorded using the attenuated total reflection technology. Flash chromatography was performed using Merck silica (diameter 40–63 μm). TLC-analysis was performed on glass backed plates (Merck) coated with 0.2 mm silica with UV-indicator 60 F_{254}. Preparative HPLC was performed using a Gilson HPLC (332 PUMP) and a Gilson UV-detector (UV/VIS-156) with a reversed phase Discovery BIO wide pore C_{18} column (length: 25 cm, internal diameter: 21.2 mm, particle size: 10 μm) using a MeCN/H_2O gradient containing 0.1% TFA. β,β-Dichloroamines **6** and **7** were obtained as described before.[1]

4.2. Synthesis of *N*-alkyl-(2,2,2-trichloroethylidene)amines 8

The synthesis of *N*-alkyl-(2,2,2-trichloroethylidene)amines **8** was performed according to the literature procedures.[17,18] All

reactions have been performed starting from 0.15 mol of acetaldehyde.

*4.2.1. N-(2,2,2-Trichloroethyliden)-tert-butylamine[17] (**8a**)*

For the sake of completeness full spectral data are given here.

Yield: 17.3 g (57%), light-yellow liquid, bp=67 °C/22 mmHg. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (1H, s, HCN), 1.29 (9H, s, NC(CH_3)$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 152.0 (CN), 95.5 (CCl_3), 57.7 (N*C*(CH_3)$_3$), 29.2 (NC(CH_3)$_3$). IR (ATR, cm^{-1}): ν 1680, 1653 (C=N). MS (70 eV, *m*/*z* (%)): 208 ([M+7]$^+$, 2), 206 ([M+5]$^+$, 19), 204 ([M+3]$^+$, 37), 202 ([M+H$^+$], 34), 188 (54), 186 (43), 168 (48), 166 (42), 152 (66), 150 (71), 138 (51), 136 (45), 116 (48), 97 (41), 95 (51), 84 (50), 77 (46), 57 (100).

*4.2.2. N-(2,2,2-Trichloroethyliden)isopropylamine (**8b**)*

Yield: 13.5 g (48%), colourless liquid, bp=33 °C/17 mmHg. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.75 (1H, s, HCN), 3.68 (1H, septet, *J*=6.3 Hz, NC*H*(CH_3)$_2$), 1.26 (6H, d, *J*=6.3 Hz, NCH(C*H*$_3$)$_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 154.5 (CN), 94.2 (CCl_3), 59.2 (N*C*H(CH_3)$_2$), 23.3 (NCH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}): ν 1666 (C=N). MS (70 eV, *m*/*z* (%)): 194 ([M+7]$^+$, trace), 192 ([M+5]$^+$, 0.5), 190 ([M+3]$^+$, 3), 188 ([M+H$^+$], 4), 154 (13), 152 (19), 136 (13), 122 (14), 97 (11), 95 (16), 81 (12), 70 (100), 63 (17), 60 (16).

*4.2.3. N-(2,2,2-Trichloroethyliden)propylamine (**8c**)*

Yield: 7.6 g (27%), yellow liquid; bp=40 °C/18 mmHg. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.75 (1H, t, *J*=1.3 Hz, HCN), 3.60 (2H, td, *J*=7.2, 1.3 Hz, NC*H*$_2$CH$_2$CH$_3$), 1.74 (2H, sextet, *J*=7.2 Hz, NCH$_2$C*H*$_2$CH$_3$), 0.95 (3H, t, *J*=7.2 Hz, NCH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 156.7 (CN), 94.0 (CCl_3), 60.4 (N*C*H$_2$CH$_2$CH$_3$), 23.2 (NCH$_2$*C*H$_2$CH$_3$), 11.5 (NCH$_2$CH$_2$*C*H$_3$). IR (ATR, cm^{-1}): ν 1668 (C=N). MS (70 eV, *m*/*z* (%)): 194 ([M+7]$^+$, trace), 192 ([M+5]$^+$, 1), 190 ([M+3]$^+$, 3), 188 ([M+H$^+$], 4), 160 (13), 158 (13), 154 (12), 152 (18), 124 (11), 123 (13), 122 (22), 95 (20), 70 (100), 60 (21), 51 (17).

*4.2.4. N-(2,2,2-Trichloroethylidene)-2-propenylamine (**8d**)*

Yield: 2.77 g (10%), colourless liquid, bp=44 °C/20 mmHg. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.77 (1H, s, HC=N), 6.04–5.96 (1H, m, CH$_2$C*H*=CH$_2$), 5.27–5.25 (2H, m, CH$_2$CH=C*H*$_2$), 4.28 (2H, dd, *J*=5.6, 1.3 Hz, C*H*$_2$CH=CH$_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 157.5 (C=N), 133.4 (CH$_2$*C*H=CH$_2$), 117.9 (CH$_2$CH=*C*H$_2$), 94.0 (CCl_3), 60.3 (*C*H$_2$CH=CH$_2$). IR (ATR, cm^{-1}): ν 1665 (C=N), 1419, 1347, 1311 (CH=CH$_2$). MS (70 eV, *m*/*z* (%)): 192 ([M+7]$^+$, trace), 190 ([M+5]$^+$, 0.3), 188 ([M+3]$^+$, 1), 186 ([M+H$^+$], 2), 150 (12), 124 (11), 122 (31), 119 (10), 117 (14), 95 (18), 82 (13), 68 (100), 60 (20), 51 (19).

4.3. Synthesis of β,β,β-trichloroamines 9 and 10: general procedure

To a stirred solution of β,β,β-trichloroaldimine **8** (1 equiv, 4 mmol) in CH_2Cl_2 (8 mL) was added the potassium trifluoroborate **2a** or **2b** (1 equiv, 4 mmol, 840 mg **2a** or 832 mg **2b**) in one portion, followed by $BF_3\cdot Et_2O$ (1 equiv, 4 mmol, 568 mg). The reaction mixture was stirred for 18 h at room temperature and poured into aqueous NaOH (0.5 M, 8 mL). After isolation of the organic layer, the aqueous phase was washed with CH_2Cl_2 (8 mL, 8 mL, 4 mL, 4 mL). The organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure. In order to remove traces of starting material, styrene or phenylacetylene the crude reaction mixture was treated under high vacuum (50 °C, 0.01 mmHg) during 1–2 h. The reactions with trifluoroborate **2a** were carried out in CH_2Cl_2/HFIP (9/1) (8 mL). The yields described below for β,β,β-trichloroamines **9** and **10** are the yields after high vacuum evaporation and purities are >95%. Analytically pure samples were obtained by a preparative HPLC on a C18 column with MeCN/water gradient as eluent.

*4.3.1. N-tert-Butyl-(4,4,4-trichloro-1-phenylbut-1-en-3-yl)-amine (**9a**)*

Yield: 964 mg (79%), light brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.35–7.14 (5H, m, aromate), 6.57 (1H, d, *J*=15.9 Hz, CHC*H*C$_{arom.quat.}$), 6.11 (1H, dd, *J*=15.9, 8.0 Hz, C*H*CHC$_{arom.quat.}$), 3.89 (1H, dd, *J*=8.0, 0.3 Hz, CCl_3CH), 1.10 (9H, s, NC(CH_3)$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 135.3 (C$_{arom.quat.}$), 134.3 (CH*C*HC$_{arom.quat.}$), 127.6 (C$_{arom.ortho}$), 127.3 (C$_{arom.para}$), 126.8 (*C*HCHC$_{arom.quat.}$), 125.5 (C$_{arom.meta}$), 103.8 (CCl_3), 70.0 (CCl_3*C*H), 50.8 (*C*(CH_3)$_3$), 29.5 (C(*C*H$_3$)$_3$). IR (ATR, cm^{-1}): ν 1495, 1448 (C=C aromate), 1365, 1271 (CH=CH). MS (70 eV, *m*/*z* (%)): 312 ([M+7]$^+$, 0.1), 310 ([M+5]$^+$, 0.4), 308 ([M+3]$^+$, 1), 306 (M+H$^+$, 2), 235 (45), 233 (40), 197 (100), 188 (97), 177 (61), 162 (100), 143 (81), 127 (99), 119 (44), 115 (100), 102 (95), 91 (59), 89 (45), 86 (54), 73 (46), 65 (49), 63 (57), 57 (87), 51 (53). HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}Cl_3N$+H: 306.0583; found: 306.0521.

*4.3.2. N-(4,4,4-Trichloro-1-phenylbut-1-en-3-yl)isopropylamine (**9b**)*

Yield: 710 mg (61%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.38–7.17 (5H, m, aromate), 6.58 (1H, d, *J*=15.8 Hz, CHC*H*C$_{arom.quat.}$), 6.09 (1H, dd, *J*=15.8, 8.2 Hz, C*H*CHC$_{arom.quat.}$), 3.77 (1H, d, *J*=8.2 Hz, CCl_3*CH*NH), 2.92 (1H, septet, *J*=6.3 Hz, NHC*H*(CH_3)$_2$), 1.39 (1H, br s, NH), 1.06 and 1.04 (2×3H, 2×d, *J*=6.3 Hz, NHCH(C*H*$_3$)$_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 135.0 (C$_{arom.quat.}$), 134.4 (CH=*C*HC$_{arom.quat.}$), 127.7 (C$_{arom.ortho}$), 127.2 (C$_{arom.para}$), 125.7 (C$_{arom.meta}$), 124.1 (*C*H=CHC$_{arom.quat.}$), 103.5 (CCl_3), 73.1 (CCl_3CHNH), 45.7 (NH*C*H(CH_3)$_2$), 23.0, 21.3 (NHCH(*C*H$_3$)$_2$). IR (ATR, cm^{-1}): ν 1496, 1474, 1447 (C=C aromate), 1382, 1369 (HC=CH). MS (70 eV, *m*/*z* (%)): 298 ([M+7]$^+$, trace), 296 ([M+5]$^+$, trace), 294 ([M+3]$^+$, trace), 292 (M+H$^+$, 0.1), 174 (100), 162 (7), 161 (5), 143 (4), 132 (4), 131 (4), 130 (4), 129 (4), 128 (5), 127 (8), 126 (7), 117 (3), 116 (4), 115 (24), 91 (7), 77 (5). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}Cl_3N$+H: 292.0427; found: 292.0496.

*4.3.3. N-(4,4,4-Trichloro-1-phenylbut-1-en-3-yl)-n-propylamine (**9c**)*

Yield: 640 mg (55%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.44–7.12 (5H, m, aromate), 6.61 (1H, d, *J*=15.7 Hz, CHC*H*C$_{arom.quat.}$), 6.08 (1H, dd, *J*=15.7, 8.2 Hz, C*H*CHC$_{arom.quat.}$), 3.73 (1H, d, *J*=8.2 Hz, CCl_3*CH*NH), 2.76–2.55 (2H, m, NHC*H*$_2$CH$_2$), 1.56–1.43 (2H, m, NHCH$_2$C*H*$_2$), 0.87 (3H, t, *J*=7.3 Hz, NHCH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 135.0 (CH*C*HC$_{arom.quat.}$), 127.7 (C$_{arom.ortho}$), 127.3 (C$_{arom.para}$), 126.1 (C$_{arom.quat.}$), 125.7 (C$_{arom.meta}$), 123.7 (*C*HCHC$_{arom.quat.}$), 102.3 (CCl_3), 75.3 (CCl_3*C*HNH), 48.7 (NHCH$_2$CH$_2$), 22.1 (NHCH$_2$*C*H$_2$), 10.6 (NHCH$_2$CH$_2$*C*H$_3$). IR (ATR, cm^{-1}): ν 1495, 1448 (C=C aromate), 1380, 1300 (CH=CH). MS (70 eV, *m*/*z* (%)): 298 ([M+7]$^+$, trace), 296 ([M+5]$^+$, trace), 294 ([M+3]$^+$, trace), 292 (M+H$^+$, trace), 197 (5), 174 (100), 163 (5), 162 (11), 161 (8), 143 (6), 142 (5), 132 (34), 130 (7), 129 (5), 128 (6), 127 (12), 126 (7), 116 (7), 115 (41), 102 (4), 91 (6), 77 (7), 76 (5). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}Cl_3N$+H: 292.0427; found: 292.0465.

*4.3.4. N-(4,4,4-Trichloro-1-phenylbut-1-en-3-yl)-2-propenylamine (**9d**)*

Yield: 705 mg (61%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.44–7.12 (5H, m, aromate), 6.60 (1H, d, *J*=15.8 Hz, CHC*H*C$_{arom.quat.}$), 6.06 (1H, dd, *J*=15.8, 8.2 Hz, C*H*CHC$_{arom.quat.}$), 5.92–5.77 (1H, m, NHCH$_2$C*H*=CH$_2$), 5.22–5.07 (2H, m, NHCH$_2$CH=C*H*$_2$), 3.79 (1H, d, *J*=8.2 Hz, CCl_3*CH*), 3.44 (1H, ddt, *J*=14.1, 5.3, 6.7 Hz, NHC(*H*)HCH=CH$_2$), 3.26 (1H, ddt, *J*=14.1, 1.5, 1.2 Hz, NHCH(*H*)CH=CH$_2$), 1.67 (1H, br s, NH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 135.4 (NHCH$_2$*C*H=CH$_2$), 135.1 (CH*C*HC$_{arom.quat.}$), 134.9 (C$_{arom.quat.}$), 127.7 (C$_{arom.ortho}$), 127.3 (C$_{arom.para}$), 125.7 (C$_{arom.meta}$), 123.2 (*C*HCHC$_{arom.quat.}$), 116.1 (NHCH$_2$CH=*C*H$_2$), 102.1 (CCl_3), 74.0 (CCl_3*C*HNH), 49.0 (NH*C*H$_2$CH=CH$_2$). IR (ATR, cm^{-1}): ν 1461, 1495, 1448 (C=C aromate), 1258 (CH=CH). MS (70 eV, *m*/*z* (%)): 296 ([M+7]$^+$, trace), 294

([M+5]$^+$, trace), 292 ([M+3]$^+$, trace), 290 (M+H$^+$, trace), 172 (100), 162 (5), 130 (8), 129 (9), 128 (8), 127 (11), 126 (5), 117 (6), 116 (7), 115 (25), 102 (5), 91 (16), 77 (7), 76 (5), 51 (4). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}Cl_3N$+H: 290.0270; found 290.0228.

4.3.5. *N-tert-Butyl-(4,4,4-trichloro-1-phenylbut-1-yn-3-yl)-amine (**10a**)*

Yield: 921 mg (76%), light brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.39–7.33 (2H, m, $CH_{arom.ortho}$), 7.26–7.15 (3H, m, $CH_{arom.meta+para}$), 4.15 (1H, s, CCl_3CHNH), 1.18 (9H, s, $C(CH_3)_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 130.6 ($C_{arom.ortho}$), 127.6 ($C_{arom.para}$), 127.3 ($C_{arom.meta}$), 121.3 ($C_{arom.quat.}$), 101.8 (CCl_3), 86.7 (C≡CC$_{arom.quat.}$), 84.9 (C≡CC$_{arom.quat.}$), 61.7 (CCl_3CHNH), 50.8 ($C(CH_3)_3$), 28.8 ($C(CH_3)_3$). IR (ATR, cm^{-1}): ν 1490, 1443 (C=C aromate). IR (NaCl, cm^{-1}): ν 2226 (C≡C). MS (70 eV, *m*/*z* (%)): 310 ([M+7]$^+$, trace), 308 ([M+5]$^+$, trace), 306 ([M+3]$^+$, trace), 304 (M+H$^+$, 0.1), 198 (11), 196 (32), 186 (89), 170 (19), 130 (100), 102 (15), 57 (35). HRMS (ESI): *m*/*z* calcd for $C_{14}H_{16}Cl_3N$+H: 304.0427; found 304.0459.

4.3.6. *N-(4,4,4-Trichloro-1-phenylbut-1-yn-3-yl)-isoproylamine (**10b**)*

Yield: 786 mg (68%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.49–7.42 (2H, m, $CH_{arom.ortho}$), 7.38–7.25 (3H, m, $CH_{arom.meta+para}$), 4.24 (1H, s, CCl_3CHNH), 3.24 (1H, septet, *J*=6.2 Hz, NHC*H*$(CH_3)_2$), 1.68 (1H, br s, NH), 1.22 and 1.15 (2×3H, 2×d, *J*=6.2 Hz, NHCH$(CH_3)_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 131.8 ($C_{arom.ortho}$), 128.8 ($C_{arom.para}$), 128.3 ($C_{arom.meta}$), 122.2 ($C_{arom.quat.}$), 101.8 (CCl_3), 86.3 (C≡CC$_{arom.quat.}$), 85.5 (C≡CC$_{arom.quat.}$), 66.1 (CCl_3CHNH), 48.0 (NHCH$(CH_3)_2$), 23.9 and 22.3 (NHCH$(CH_3)_2$). IR (ATR, cm^{-1}): ν 2222 (C≡C), 1490, 1473, 1443 (C=C aromate). MS (70 eV, *m*/*z* (%)): 296 ([M+7]$^+$, trace), 294 ([M+5]$^+$, trace), 292 ([M+3]$^+$, trace), 290 (M+H$^+$, 0.1), 198 (6), 197 (6), 196 (19), 172 (100), 161 (4), 160 (6), 156 (6), 130 (76), 128 (5), 127 (5), 126 (9), 125 (7), 114 (7), 113 (8), 103 (10), 102 (17), 77 (7), 76 (6), 74 (6), 62 (5). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}Cl_3N$+H: 290.0270; found 290.0233.

4.3.7. *N-(4,4,4-Trichloro-1-phenylbut-1-yn-3-yl)propylamine (**10c**)*

Yield: 786 mg (68%), orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50–7.43 (2H, m, $CH_{arom.ortho}$), 7.38–7.26 (3H, m, $CH_{arom.meta+para}$), 4.24 (1H, s, CCl_3CHNH), 3.07–2.96 and 2.89–2.74 (2H, 2×m (AB), NHC*H*$_2CH_2$), 1.77 (1H, br s, NH), 1.68–1.51 (2H, m, NHCH$_2$C*H*$_2CH_3$), 0.99 (3H, t, *J*=7.4 Hz, NHCH$_2CH_2CH_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 131.9 ($C_{arom.ortho}$), 128.8 ($C_{arom.para}$), 128.3 ($C_{arom.meta}$), 122.1 ($C_{arom.quat.}$), 101.8 (CCl_3), 86.7 (C≡CC$_{arom.quat.}$), 84.9 (C≡CC$_{arom.quat.}$), 68.1 (CCl_3CHNH), 50.3 (NHCH$_2CH_2$), 23.1 (NHCH$_2$C*H*$_2$), 11.6 (NHCH$_2CH_2$C*H*$_3$). IR (ATR, cm^{-1}): ν 2227 (C≡C), 1490, 1459, 1443 (C=C aromate). MS (70 eV, *m*/*z* (%)): 296 ([M+7]$^+$, trace), 294 ([M+5]$^+$, trace), 292 ([M+3]$^+$, trace), 290 (M+H$^+$, 0.1), 198 (5), 197 (4), 196 (15), 172 (100), 161 (4), 160 (5), 149 (5), 130 (35), 127 (4), 126 (9), 115 (5), 114 (7), 113 (7), 103 (8), 102 (10), 77 (5), 76 (5), 74 (4). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}Cl_3N$+H: 290.0270; found 290.0265.

4.3.8. *N-(4,4,4-Trichloro-1-phenylbut-1-yn-3-yl)-2-propenylamine (**10d**)*

Yield: 746 mg (65%), orange oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50–7.42 (2H, m, $CH_{arom.ortho}$), 7.37–7.25 (3H, m, $CH_{arom.meta+para}$), 6.04–5.88 (1H, m, NHCH$_2$C*H*=CH$_2$), 5.38–5.12 (2H, m, NHCH$_2$CH=C*H*$_2$), 4.28 (1H, s, CCl_3CHNH), 3.69 (1H, ddt, *J*=14.1, 5.6, 6.6 Hz, NHC(*H*)HCH=CH$_2$), 3.53 (1H, ddt, *J*=14.1, 1.5, 1.2 Hz, NHCH(*H*)CH=CH$_2$), 1.93 (1H, br s, NH). ^{13}C NMR (62.90 MHz, $CDCl_3$): 135.6 (NHCH$_2$*C*H=CH$_2$), 131.9 ($C_{arom.ortho}$), 128.9 ($C_{arom.para}$), 128.4 ($C_{arom.meta}$), 122.0 ($C_{arom.quat.}$), 117.6 (NHCH$_2$CH=*C*H$_2$), 101.5 (CCl_3), 86.9 (*C*≡CC$_{arom.quat.}$), 84.5 (C≡*C*C$_{arom.quat.}$), 67.0 (CCl_3*C*HNH), 50.6 (NH*C*H$_2$CH=CH$_2$). IR (ATR, cm^{-1}): ν 2226 (C≡C), 1490, 1460, 1443 (C=C aromate), 1287 (CH=CH). MS (70 eV, *m*/*z* (%)): 294 ([M+7]$^+$, trace), 292 ([M+5]$^+$, trace), 290 ([M+3]$^+$, 0.1), 288 (M+H$^+$, 0.1), 198 (5), 197 (4), 196 (13), 170 (100), 161 (6), 160 (6), 152 (4), 151 (4), 149 (10), 141 (6), 140 (4), 129 (4), 128 (31), 127 (23), 126 (25), 115 (14), 114 (15), 113 (11), 103 (7), 102 (12), 91 (7), 84 (5), 77 (6), 76 (7), 75 (6), 74 (9), 63 (5), 62 (6), 51 (5), 50 (4). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{12}Cl_3N$+H: 288.0114; found 288.0145.

4.4. Synthesis of α-chloroimines 11 and 12 and α,α-dichloroimines 23 and 24: general procedure

To a solution of β,β-dichloroamine **6** or **7** or β,β,β-trichloroamine (**9** or **10**) (0.5 mmol) in dry THF (10 mL), KO^{t}Bu was added in one portion at room temperature. The mixture was heated under reflux for 2 h before it was quenched with 10 mL water. After extraction with CH_2Cl_2 (20 mL, 20 mL, 10 mL), the organic layers were combined and dried over $MgSO_4$. Filtration and concentration under reduced pressure resulted in the corresponding α-chloroimine **11** or **12** or α,α-dichloroimine **23** or **24**. The amount of KO^{t}Bu differs, depending on the product, which is synthesized. Reactions were performed on a 0.5 mmol scale, unless otherwise stated.

4.4.1. *(E)-N-(4-Chloro-1-phenylpent-1-yn-3-ylidene)-propylamine (**11a**)*

Amount of KO^{t}Bu used: 2 equiv. Yield: 111 mg (95%), dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.58–7.53 (2H, m, $CH_{arom.ortho}$), 7.41–7.32 (3H, m, $CH_{arom.meta+para}$), 4.69 (1H, q, *J*=6.8 Hz, CH_3CHCl), 3.68 (2H, t, *J*=6.8 Hz, NC*H*$_2CH_2CH_3$), 1.78 (3H, d, *J*=6.8 Hz, C*H*$_3$CHCl), 1.78–1.65 (2H, m, NCH$_2$C*H*$_2CH_3$), 0.97 (3H, t, *J*=7.4 Hz, NCH$_2CH_2CH_3$). Following signals for the *Z*-imine could be distinguished in the *E*/*Z* mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.64–7.24 (5H, m, aromate), 7.10 (1H, d, *J*=16.8 Hz, CH=C*H*C$_{arom.quat.}$), 6.87 (1H, d, *J*=16.8 Hz, C*H*=CHC$_{arom.quat.}$), 4.51 (1H, q, *J*=6.7 Hz, CH_3CHCl), 3.42 (2H, t, *J*=7.1 Hz, NC*H*$_2CH_2CH_3$), 1.71 (3H, d, *J*=6.7 Hz, C*H*$_3$CHCl), 1.68–1.59 (2H, m, NCH$_2$C*H*$_2CH_3$), 0.94 (3H, t, *J*=7.4 Hz, NCH$_2CH_2CH_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 153.5 (CN), 132.2 ($C_{arom.ortho}$), 129.8 ($C_{arom.para}$), 128.5 ($C_{arom.meta}$), 121.2 ($C_{arom.quat.}$), 98.5 (*C*≡CC$_{arom.quat.}$), 79.6 (C≡*C*C$_{arom.quat.}$), 60.0 (CHCl), 57.6 (NCH$_2CH_2CH_3$), 23.5 (NCH$_2$C*H*$_2CH_3$), 22.5 (*C*H$_3$CHCl), 12.0 (NCH$_2CH_2$C*H*$_3$). IR (ATR, cm^{-1}): ν 2205 (C≡C), 1655 (C=N), 1489, 1443 (C=C aromate). MS (70 eV, *m*/*z* (%)): 236 ([M+3]$^+$, 0.5), 235 ([M+2]$^+$, 1), 234 (M+H$^+$, 2), 233 (M$^+$, 2), 198 (33), 170 (69), 141 (30), 139 (31), 127 (100), 115 (50).

4.4.2. *(E)-N-(4-Chloro-1-phenylpent-1-yn-3-ylidene)-isopropylamine (**11b**)*

Amount of KO^{t}Bu used: 2 equiv. Yield: 104 mg (89%), dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.56–7.53 (2H, m, $CH_{arom.ortho}$), 7.40–7.37 (3H, m, $CH_{arom.meta+para}$), 4.65 (1H, q, *J*=6.8 Hz, CH_3CHCl), 4.09 (1H, septet, *J*=6.2 Hz, NC*H*$(CH_3)_2$), 1.76 (3H, d, *J*=6.8 Hz, C*H*$_3$CHCl), 1.22 and 1.20 (2×3H, 2×d, *J*=6.2 Hz, NCH$(CH_3)_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): 151.3 (CN), 132.3 ($C_{arom.ortho}$), 129.8 ($C_{arom.para}$), 128.5 ($C_{arom.meta}$), 121.3 ($C_{arom.quat.}$), 98.1 (*C*≡CC$_{arom.quat.}$), 79.3 (C≡*C*C$_{arom.quat.}$), 60.1 (CHCl), 55.7 (NCH$(CH_3)_2$), 23.2 and 23.1 (NCH$(CH_3)_2$), 22.5 (*C*H$_3$CHCl). IR (ATR, cm^{-1}): ν 2205 (C≡C), 1604 (C=N), 1489, 1443 (C=C aromate). MS (70 eV, *m*/*z* (%)): 236 ([M+3]$^+$, 2), 235 ([M+2]$^+$, 3), 234 (M+H$^+$, 10), 233 (M$^+$, 8), 198 (46), 182 (30), 170 (41), 142 (30), 141 (31), 139 (38), 128 (100), 115 (36), 77 (33), 63 (32).

4.4.3. *N-(4-Chloro-1-phenylpent-1-en-3-ylidene)-propylamine (**12a**)*

Amount of KO^{t}Bu used: 3 equiv. Yield: 100 mg (85%), dark yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.64–7.24 (5H, m, aromate), 7.10 (1H, d, *J*=16.8 Hz, CHC*H*C$_{arom.quat.}$), 6.87 (1H, d, *J*=16.8 Hz, C*H*CHC$_{arom.quat.}$), 4.95 (1H, q, *J*=6.7 Hz, CH_3CHCl), 3.55 (2H, t, *J*=7.1 Hz, NC*H*$_2CH_2CH_3$),

1.74 (3H, d, J=6.7 Hz, CH_3CHCl), 1.76–1.66 (2H, m, NCH$_2$CH_2CH$_3$), 0.97 (3H, t, J=7.4 Hz, NCH$_2$CH$_2$CH_3). ^{13}C NMR (62.90 MHz, $CDCl_3$): 164.2 (CN), 137.3 (CHCHC$_{arom.quat.}$), 128.8 (C$_{arom.ortho}$), 128.6 (C$_{arom.para}$), 127.2 (C$_{arom.meta}$), 123.2 (C$_{arom.quat.}$), 117.6 (CH=CHC$_{arom.quat.}$), 57.4 (CHCl), 53.4 (NCH$_2$CH$_2$CH$_3$), 24.2 (NCH$_2$CH$_2$CH$_3$), 22.2 (CH$_3$CHCl), 12.0 (NCH$_2$CH$_2$CH$_3$). IR (ATR, cm^{-1}): ν 1629 (C=N), 1494, 1449 (C=C aromate), 1376 (CH=CH).

4.4.4. (Z)-N-(4-Chloro-1-phenylpent-1-en-3-ylidene)-isopropylamine (**12b**)

Amount of KO^{t}Bu used: 5 equiv. Yield: 96 mg (82%), dark yellow oil. In the crude reaction mixture 10 mol% starting material was present. Following signals could be distinguished in the NMR spectra of this mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.51–7.27 (5H, m, aromate), 7.08 (1H, d, J=16.8 Hz, CHCHC$_{arom.quat.}$), 6.85 (1H, d, J=16.8 Hz, CHCHC$_{arom.quat.}$), 4.89 (1H, q, J=6.8 Hz, CH$_3$CHCl), 4.00 (1H, septet, J=6.2 Hz, NCH(CH$_3$)$_2$), 1.73 (3H, d, J=6.8 Hz, CH$_3$CHCl), 1.19 and 1.18 (2×3H, 2×d, J=6.2 Hz, NCH(CH$_3$)$_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): 162.1 (C=N), 137.0 (CHCHC$_{arom.quat.}$), 128.8 (C$_{arom.ortho}$), 128.6 (C$_{arom.para}$), 127.2 (C$_{arom.meta}$), 123.7 (C$_{arom.quat.}$), 117.6 (CHCHC$_{arom.quat.}$), 58.1 (CHCl), 50.6 (NCH(CH$_3$)$_2$), 23.7 and 23.6 (NCH(CH$_3$)$_2$), 22.3 (CH$_3$CHCl). IR (ATR, cm^{-1}): ν 1630 (C=N), 1494, 1448 (C=C aromate), 1376, 1362 (CH=CH). MS (70 eV, m/z (%)): 238 ([M+3]$^+$, 2), 237 ([M+2]$^+$, 14), 236 (M+H$^+$, 7), 235 (M$^+$, 30), 200 (60), 184 (30), 143 (32), 141 (30), 128 (100), 115 (35), 96 (49), 91 (34), 65 (30), 58 (34).

4.4.5. N-(4,4-Dichloro-1-phenylbut-1-en-3-ylidene)-tert-butyl amine (**23**)

Yield: 118 mg (87%), about 85% pure, brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50–7.15 (5H, m, aromate), 6.98 (1H, d, J=15.8 Hz, CHCHC$_{arom.quat.}$), 6.81 (1H, d, J=15.8 Hz, CHCHC$_{arom.quat.}$), 6.21 (1H, s, CHCl$_2$), 1.29 (9H, s, C(CH$_3$)$_3$). Sample was not pure enough for further analysis.

4.4.6. N-(4,4-Dichloro-1-phenylbut-1-yn-3-ylidene)-tert-butyl amine (**24**)

Yield: 113 mg (84%), brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.51–7.48 (2H, m, CH$_{arom.ortho}$), 7.36–7.22 (3H, m, CH$_{arom.meta+para}$), 6.08 (1H, s, CHCl$_2$), 1.36 (9H, s, NC(CH$_3$)$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 145.6 (CN), 131.0 (C$_{arom.ortho}$), 129.1 (C$_{arom.para}$), 127.6 (C$_{arom.meta}$), 120.0 (C$_{arom.quat.}$), 99.0 (C≡CC$_{arom.quat.}$), 78.8 (C≡C C$_{arom.quat.}$), 73.4 (CHCl$_2$), 56.3 (C(CH$_3$)$_3$), 28.0 (C(CH$_3$)$_3$). IR (ATR, cm^{-1}): ν 2199 (C≡C), 1607 (C=N), 1489, 1443 (C=C aromate). MS (70 eV, m/z (%)): 272 ([M+5]$^+$, 0.5), 271 ([M+4]$^+$, 1), 270 ([M+3]$^+$, 2), 269 ([M+2]$^+$, 2), 268 (M+H$^+$, 3), 267 (M$^+$, 3), 184 (72), 161 (32), 149 (69), 126 (100), 113 (42), 100 (30), 85 (31), 83 (33), 76 (58), 74 (37), 63 (32), 57 (87).

4.5. Synthesis of α-chloroketones 20 and 22: general procedure

A solution of 0.25 mmol of α-chloroimine **11** or **12** in CH_2Cl_2 (5 mL) was added to a solution of 0.25 mmol oxalic acid in water (5 mL). After 2 h of reflux, the organic layer was separated and the water layer was extracted with CH_2Cl_2 (5 mL, 5 mL, 3 mL). The CH_2Cl_2-extracts were dried over $MgSO_4$, filtered and the solvent evaporated in vacuo.

4.5.1. 4-Chloro-1-phenylpent-1-en-3-one (**22**)

Hydrolysis of *N*-(4-chloro-1-phenylpent-1-en-3-ylidene) isopropylamine (**12a**) (0.25 mmol, 59 mg) with oxalic acid furnished 4-chloro-1-phenylpent-1-en-3-one (**22**) in 71% yield (34 mg, yellow oil). Alternatively this product may be obtained by hydrolyzing *N*-(4-chloro-1-phenylpent-1-en-3-ylidene)isopropylamine (0.5 mmol, 118 mg) with 2 mL of 4 N HCl for 1 h at room temperature. The reaction was diluted in EtOAc (18 mL), washed with water (18 mL) and brine (18 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. Purification by flash chromatography (EtOAc/^{c}Hex (5/95), R_f=0.22) afforded **22** (65%, 32 mg) as a yellow oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.76 (1H, d, J=15.9 Hz, CHCHC$_{arom.quat.}$), 7.62–7.58 (2H, m, CH$_{arom.ortho}$), 7.46–7.40 (3H, CH$_{arom.meta+para}$), 7.09 (1H, d, J=15.9 Hz, CHCHC$_{arom.quat.}$), 4.59 (1H, q, J=6.8 Hz, CHCl), 1.70 (3H, d, J=6.8 Hz, CH$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 193.7 (C=O), 145.2 (CHCHC$_{arom.quat.}$), 134.2 (C$_{arom.quat.}$), 131.0 (C$_{arom.para}$), 129.0 (C$_{arom.ortho}$), 128.6 (C$_{arom.meta}$), 121.1 (CHCHC$_{arom.quat.}$), 57.8 (CHCl), 20.2 (CH$_3$). IR (NaCl, cm^{-1}): ν 1671, 1692 (CO), 1607, 1575 (C=C aromate), 1495, 1449 (HC=CH). MS (70 eV, m/z (%)): 196 ([M+2]$^+$, 0.7), 194 (M$^+$, 4), 133 (8), 131 (100), 115 (4), 103 (87), 91 (6), 77 (53), 76 (5), 74 (6), 66 (3), 63 (16), 51 (34). HRMS (ESI): m/z calcd for $C_{11}H_{11}ClO$+H: 195.0577; found 195.0523.

4.5.2. (E)- and (Z)-1,4-Dichloro-1-phenylpent-1-en-3-one (**20**)

(*E*)-*N*-(4-Chloro-1-phenylpent-1-yn-3-ylidene)propylamine (**11a**) (0.39 mmol, 92 mg) was cooled to 0 °C and treated with 1.4 mL 4 N HCl. After 1 h stirring at room temperature the reaction was diluted with EtOAc (14 mL), washed with water (14 mL) and brine (14 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. Purification by flash chromatography (EtOAC/^{n}Hex (1/9)) afforded (*E*)-**20** (R_f=0.28, 33%, 38 mg) and (*Z*)-**20** (R_f=0.32, 4%, 5 mg) as yellow oils (about 95% pure), which were contaminated with very small amounts of 4-chloro-1-phenyl-1-pentyn-3-one (**20**).

4.5.2.1. (E)-1,4-Dichloro-1-phenylpent-1-en-3-one ((E)-**20**).

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.77–7.70 (2H, m, CH$_{arom.ortho}$), 7.49–7.40 (3H, m, CH$_{arom.meta+para}$), 7.18 (1H, s, CHC$_{quat.}$), 4.53 (1H, q, J=6.8 Hz, CHCl), 1.69 (3H, d, J=6.8 Hz, CH$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 191.7 (CO), 147.4 (C$_{arom.quat.}$), 137.3 (C$_{quat.}$Cl), 131.2 (C$_{arom.para}$), 128.7 (C$_{arom.meta}$), 127.5 (C$_{arom.ortho}$), 118.9 (COCHCCl), 59.2 (CHCl), 20.1 (CH$_3$). IR (NaCl, cm^{-1}): ν 1697 (CO), 1587, 1574 (C=C aromate), 1490, 1445 (HC=CH). MS (70 eV, m/z (%)): 232 ([M+4]$^+$, trace), 230 ([M+2]$^+$, 0.3), 228 (M$^+$, 1), 168 (22), 167 (15), 165 (100), 137 (13), 130 (6), 129 (7), 103 (41), 102 (34), 77 (10), 76 (11), 75 (9), 64 (13), 63 (9), 51 (11), 50 (11). HRMS (ESI): m/z calcd for $C_{11}H_{10}Cl_2O$+H: 229.0187; found 229.0145.

4.5.2.2. (Z)-1,4-Dichloro-1-phenylpent-1-en-3-one ((Z)-**20**).

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.65–7.61 (2H, m, CH$_{arom.ortho}$), 7.48–7.38 (3H, m, CH$_{arom.meta+para}$), 6.89 (1H, s, CHC$_{quat.}$), 4.30 (1H, q, J=6.8 Hz, CHCl), 1.57 (3H, d, J=6.8 Hz, CH$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 191.7 (CO), 147.4 (C$_{arom.quat.}$), 137.3 (C$_{quat.}$Cl), 131.2 (C$_{arom.para}$), 128.7 (C$_{arom.meta}$), 127.5 (C$_{arom.ortho}$), 118.9 (COCHCCl), 59.2 (CHCl), 20.1 (CH$_3$). IR (NaCl, cm^{-1}): ν 1697 (CO), 1587, 1574 (C=C aromate), 1490, 1445 (HC=CH). MS (70 eV, m/z (%)): 232 ([M+4]$^+$, trace), 230 ([M+2]$^+$, 0.3), 228 (M$^+$, 1), 168 (22), 167 (16), 165 (100), 137 (15), 130 (4), 129 (5), 103 (36), 102 (34), 78 (4), 77 (9), 76 (11), 74 (10), 63 (20), 51 (10), 50 (10). HRMS (ESI): m/z calcd for $C_{11}H_{10}Cl_2O$+H: 229.0187; found 229.0122. Following signals of 4-chloro-1-phenylpent-1-yn-3-one (**21**) could be distinguished in the NMR spectrum of the crude reaction mixture. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50–7.30 (5H, m, aromate), 4.53 (1H, q, J=6.8 Hz, CHCl), 1.77 (3H, d, J=6.8 Hz, CH$_3$). MS (70 eV, m/z (%)): 194 ([M+2]$^+$, trace), 192 (M$^+$, 0.4), 158 (0.4), 157 (0.20), 131 (3), 129 (100), 103 (1), 101 (8), 99 (1), 78 (2), 77 (2), 76 (8), 74 (12), 64 (2), 63 (3), 62 (1), 51 (5), 50 (4).

4.6. Reduction of *N*-(2,2-dihalopropylidene)amines 25: synthesis of 2,2-dihalopropylamines 26: typical procedure

The following experiment is representative for the synthesis of compounds **26a–c** and **36**. To a solution of *N*-(2,2-dichloropropylidene)-

tert-butylamine (0.46 g, 2.5 mmol) in dry methanol (5 mL) was added acetic acid (0.15 g, 2.5 mmol). At 0 °C and sodium cyanoborohydride (0.33 g, 5 mmol) was added portionwise under vigorous stirring. After overnight reaction at room temperature the reaction mixture was poured into aqueous NaOH (01 M, 40 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic layers were combined and dried over $MgSO_4$. Filtration and concentration under reduced pressure, followed by vacuum distillation (bp 79–81 °C/25 mmHg, lit.[7] 73 °C/35 mmHg) furnished *N*-*tert*-butyl-(2,2-dichloropropyl)amine (**25b**) (72%, 0.33 g) as a colourless oil.

*4.6.1. N-tert-Butyl-(2,2-dichloropropyl)amine (**26b**)*

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.12 (2H, s, CH_2), 2.14 (3H, s, CH_3CCl_2), 1.45 (1H, br s, NH), 1.11 (9H, s, $C(CH_3)_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 90.9 (CCl_2), 58.1 (CH_2), 50.2 ($C(CH_3)_3$), 34.3 (CH_3CCl_2), 29.2 ($C(CH_3)_3$). IR (NaCl, cm^{-1}): ν 3340 (NH), 2965, 1479, 1455, 1364. MS (70 eV, *m*/*z* (%)): 187 ($[M+4]^+$, trace), 185 ($[M+2]^+$, 1), 185 (M^+, 2), 172 (8), 170 (40), 168 (66), 134 (50), 132 (72), 96 (13), 94 (15), 92 (44), 86 (87), 58 (39), 57 (100), 56 (40), 55 (15). HRMS (ESI): *m*/*z* calcd for $C_7H_{15}Cl_2N$+H: 184.0660; found 184.0643.

*4.6.2. N-(2,2-Dichloropropyl)isopropylamine (**26a**)*

Scale of the experiment: 45 mmol. Yield: 6.81 g (89%), colourless oil. Bp 54 °C/15 mmHg.

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.16 (2H, s, CH_2), 2.91 (1H, septet, *J*=6.3 Hz, $(CH_3)_2CH$), 2.15 (3H, s, CH_3CCl_2), 1.48 (1H, br s, NH), 1.09 (6H, d, *J*=6.3 Hz, $(CH_3)_2CH$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 90.3 (CCl_2), 62.1 (CH_2), 48.6 (CH), 34.5 (CH_3CCl_2), 23.0 ($CH(CH_3)_2$). IR (NaCl, cm^{-1}): ν 3328 (NH), 2965, 1468, 1446, 1381. MS (70 eV, *m*/*z* (%)): 171 ($[M+2]^+$, trace), 169 (M^+, 1), 158 (2), 156 (8), 154 (17), 134 (11), 120 (15), 118 (25), 94 (12), 92 (20), 84 (9), 72 (100), 56 (15). HRMS (ESI): *m*/*z* calcd for $C_6H_{13}Cl_2N$+H: 170.0503; found 170.0516.

*4.6.3. N-Cyclohexyl-(2,2-dichloropropyl)amine (**26c**)*

Scale of the experiment: 35 mmol. Yield: 4.56 g (62%), colourless oil. Bp 108–116 °C/15 mmHg.

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.19 (2H, s, CH_2N), 2.51 (1H, t×t, *J*=10.0, 3.6 Hz, NCH), 2.14 (3H, s, CH_3), 1.9–1.10 (10H, m, $(CH_2)_5$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 80.9 (CCl_2), 62.1 (CH_2N), 56.9 (CH), 34.8 (CH_3), 34.0 (2×CH_2), 26.3 ($(CH_2)_2CH_2(CH_2)_2$), 25.2 (2×CH_2). IR (NaCl, cm^{-1}): ν 2928, 2854, 1458, 1371, NH not visible. MS (70 eV, *m*/*z* (%)): 211 ($[M+2]^+$, trace), 209 (M^+, 1), 176 (2), 174 (4), 168 (16), 166 (22), 138 (14), 112 (100), 83 (24), 56 (11), 55 (19). HRMS (ESI): *m*/*z* calcd for $C_9H_{17}Cl_2N$+H: 210.0816; found 210.0838.

*4.6.4. N-tert-Butyl-(2,2-dibromopropyl)amine (**36**)*

Scale of the experiment: 20 mmol. Yield: 4.64 g (85%), yellow oil. Bp 82–85 °C/10 mmHg.

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.22 (2H, s, CH_2), 2.50 (3H, s, CH_3CBr_2), 1.13 (9H, s, $C(CH_3)_3$), NH was not visible. ^{13}C NMR (68 MHz, $CDCl_3$): δ 70.6 (CCl_2), 60.8 (CH_2), 50.6 ($C(CH_3)_3$), 38.1 (CH_3CCl_2), 29.7 ($C(CH_3)_3$). IR (NaCl, cm^{-1}): ν 3335 (NH), 2978, 2867, 1481, 1446, 1390, 1366. MS (70 eV, *m*/*z* (%)): 273 ($[M+2]^+$, trace), 256 (18), 258 (9), 260 (19), 176 (33), 178 (30), 138 (34), 136 (32), 98 (26), 97 (27), 86 (44), 82 (14), 58 (42), 57 (100), 56 (19). HRMS (ESI): *m*/*z* calcd for $C_7H_{15}Br_2N$+H: 271.9649; found 271.9670.

4.7. Reaction of *N-tert*-butyl-(2,2-dichloropropyl)amine 26b with sodium methoxide

A solution of sodium methoxide in methanol (2 M, 50 mL) was added to *N*-*tert*-butyl-(2,2-dichloropropyl)amine (1.84 g, 10 mmol). This reaction mixture was stirred overnight under reflux, poured out in water (150 mL) and extracted with dichloromethane (3×50 mL). After drying over $MgSO_4$, filtration and concentration under reduced pressure the residue was subjected to vacuum distillation. The fraction 56–64 °C/15 mmHg (0.61 g) consisted of a 7/3 mixture of *N*-(2-chloroprop-2-enyl)-*tert*-butylamine and *N*-*tert*-butyl-(2,2-dimethoxypropyl)amine (^{1}H NMR). Analytically pure samples of **27** and **28** were obtained by preparative gas chromatography.

*4.7.1. N-(2-Chloroprop-2-enyl)-tert-butylamine (**27**)*

^{1}H NMR (270 MHz, $CDCl_3$): δ 5.42 (1H, d, *J*=0.7 Hz, C*H*(H)), 5.26 (1H, d, *J*=0.7 Hz, CH(*H*)), 3.36 (2H, s, CH_2N), 1.4 (1H, br s, NH), 1.13 (9H, s, $C(CH_3)_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 141.6 (CCl), 110.9 (=CH_2), 49.7 (CH_2N), 48.6 ($C(CH_3)_3$), 28.3 ($C(CH_3)_3$). IR (NaCl, cm^{-1}): ν NH not visible, 1639 (C=C). MS (70 eV, *m*/*z* (%)): 149 ($[M+2]^+$, trace), 147 (M^+, 1), 134 (40), 132 (100), 96 (9), 77 (5), 75 (7), 58 (7), 57 (7), 56 (10).

*4.7.2. N-tert-Butyl-(2,2-dimethoxypropyl)amine (**28**)*

^{1}H NMR (270 MHz, $CDCl_3$): δ 3.21 (6H, s, $C(OCH_3)_2$), 2.65 (2H, s, CH_2), 1.36 (3H, s, $CH_3C(OCH_3)_2$), NH was not visible, 1.09 (9H, s, $C(CH_3)_3$). ^{13}C NMR (68 MHz, $CDCl_3$): δ 101.5 ($C(OCH_3)_2$), 49.9 ($C(CH_3)_3$), 48.1 (OCH_3), 46.7 (CH_2), 29.0 ($C(CH_3)_3$), 20.5 ($CH_3CC(OCH_3)_2$). IR (NaCl, cm^{-1}): ν NH not visible, 2965, 1232. MS (70 eV, *m*/*z* (%)): no M^+, 129 (17), 127 (15), 114 (23), 99 (12), 97 (11), 89 (12), 86 (18), 85 (29), 59 (29), 57 (100). In the ^{1}H NMR spectrum of compound **28** following signals of *tert*-butyl-(2-methoxypropen-2-enyl)amine (**29**) could be distinguished. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.08 (1H, d, *J*=1.8 Hz, C*H*(H)), 3.96 (1H, d, *J*=0.7 Hz, CH(*H*)), 3.57 (3H, s, OCH_3), 3.19 (2H, s, CH_2N), NH not visible, 1.12 (9H, s, $C(CH_3)_3$). MS (70 eV, *m*/*z* (%)): 143 (6), 128 (100), 96 (51), 86 (11), 72 (10), 59 (10), 58 (10), 57 (21).

4.8. Reaction of *N-tert*-butyl-(2,2-dibromopropyl)amine (36) with sodium methoxide and potassium *tert*-butoxide

This procedure is analogous to the procedure for the preparation of **27** and **28**. The crude reaction mixture was obtained by reaction of 6.5 mmol of **36** with sodium methoxide in methanol (8.13 mL, 4 M) at 35 °C during 18 h. Short path distillation gave *N*-(2-bromoprop-2-enyl)-*tert*-butylamine (**37**) as a light-yellow oil. Bp 82–88 °C/25 mmHg (lit.[42] 103–105 °C/90 mmHg). Yield: 0.56 g (40%).

^{1}H NMR (270 MHz, $CDCl_3$): δ 5.88 (1H, d, *J*=1.0 Hz, C*H*(H)), 5.50 (1H, d, *J*=1.0 Hz, CH(*H*)), 3.43 (2H, s, CH_2N), 1.13 (9H, s, $C(CH_3)_3$), NH was not visible. ^{13}C NMR (68 MHz, $CDCl_3$): δ 134.0 (CBr), 116.5 (=CH_2), 51.5 (CH_2N), 50.6 ($C(CH_3)_3$), 29.1 ($C(CH_3)_3$). IR (NaCl, cm^{-1}): ν 3315 (NH), 1635 (C=C). MS (70 eV, *m*/*z* (%)): 193 ($[M+2]^+$, 1), 191 (M^+), 178 (98), 176 (100), 121 (4), 119 (4), 97 (22), 96 (9), 82 (13), 58 (8), 57 (8), 56 (9). HRMS (ESI): *m*/*z* calcd for $C_7H_{14}BrN$+H: 192.0388; found 192.0363.

A solution of 2,2-dibromopropylamine (**36**) (0.27 g, 1 mmol) in dry THF (2 mL) was reacted with KO^{t}Bu (0.25 g, 2.2 mmol) during 3 h under reflux. After aqueous workup (20 mL) and extraction with CH_2Cl_2 (3×5 mL) the combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. This crude reaction mixture contained 67% of *N*-*tert*-butylpropargylamine as measured by capillary GC. Despite the fact that this crude product could not be further purified, following significant signals could be distinguished in the NMR spectra. These data differ slightly from those reported in literature, probably due to solvent related shifts.[44] ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.38 (2H, d, *J*=2.6 Hz, CH_2), 2.21 (1H, t, *J*=2.6 Hz, CH), 1.13 (9H, s, $C(CH_3)_3$), NH was not visible. ^{13}C NMR (68 MHz, $CDCl_3$): δ 83.2 (≡CCH_2), 70.4 (CH), 50.5 ($C(CH_3)_3$), 47.8 (CH_2), 28.5 ($C(CH_3)_3$). MS (70 eV, *m*/*z* (%)): 111 (5), 97 (14), 96 (100), 81 (7), 80 (7), 70 (9), 58 (9), 57 (7), 56 (7), 55 (7), 54 (9).

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References and notes

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