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Lewis acid promoted Mannich type reactions of α,α-dichloro aldimines with potassium organotrifluoroborates

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Abstract—Potassium phenylethynyltrifluoroborate and potassium styryltrifluoroborates react with α,α-dichlorinated aldimines in the presence of $BF_3 \cdot OEt_2$ as a Lewis acid to give a new stable class of functionalized propargylamines and allylamines. The use of hexafluoroisopropanol as a co-solvent in this modified Petasis reaction allows high yield isolation of the target compounds.

1. Introduction

The boronic acid Mannich reaction (BAM reaction), also known as the Petasis reaction, is a one-step multicomponent process, involving an organoboronic acid, an amine, and a carbonyl derivative, which can produce novel multifunctional molecules, including geometrically pure allylamines,[1] α-amino acids,[2,3] anti-β-amino alcohols,[4,5] α-arylglycines,[6] amino phenol derivatives,[7] indolyl-*N*-substituted glycines,[8] 2-hydroxymorpholines,[9] α-hydrazinocarboxylic acids,[10] α-(4-*N*,*N*-dialkylamino-2-alkyloxyphenyl)carboxylic acids,[11,12] and heterocyclic systems.[13]

Only few papers report the use of potassium trifluoroborates in Petasis reactions. Kabalka et al. reported the three-component condensation of potassium alkynyltrifluoroborates with secondary amines and salicylaldehydes, in the presence of benzoic acid.[14] Heterocyclic aldehydes such as pyridine-2-carboxaldehyde also participate in a trifluoroborate Mannich process with chlorotrimethylsilane as Lewis acid, and gave rise to functionalized allylamines in 28–54% yield.[13] This variation of the boronic acid Mannich reaction also has been extended to other carbonyl components like formaldehyde and ethyl glyoxylate.[15] The reaction of potassium trifluoroborates with in situ generated iminium species with Lewis acid activation has been reported recently.[16]

In a previous attempt to extend the Petasis reaction to α,α-dichloroaldehydes **1**, no β,β-dichloroamines **5** were observed, instead, 1-aminoalkan-2-ones **3** were formed.[17] Therefore we turned our attention to the corresponding imines of the α,α-dichloroaldehydes **1**, which were evaluated as substrates in a reaction with potassium organotrifluoroborates **4** (Scheme 1).

In the classical Petasis reaction, secondary amines are predominantly used, giving rise to tertiary amine Mannich products, which often require an extra deprotection step. By applying the corresponding imines, this detour could be avoided. To the best of our knowledge, the combined use of potassium organotrifluoroborates and aldimines in the presence of a Lewis acid in the Petasis reaction has not been reported. Reactions of organometallic reagents with imines are well known,[18] and to a lesser extent with organoboron reagents.[19–22] The addition of organocuprate·BF_3 complexes or in situ prepared alkynyldifluoroboranes or alkynylborates to aldimines afforded secondary amines in good yields.[19–21] Propargylamines are very much in demand in medicinal chemistry, due to their pronounced physiological acivities.[23] The preparation of propargylic amines by direct additions of alkynes to imines has been recently reviewed by Bolm and Zani.[24] Next to the advantage of using imines as electrophiles, potassium organotrifluoroborates offer several advantages over their corresponding boronic acids and strongly basic organometallic reagents. Organoboronic acids are often subjected to dimerization and cyclic trimerization to generate, respectively, boronic acid anhydrides and boroxines. Trifluoroborates are monomeric, non-hygroscopic, crystalline solids that are indefinitely stable in the air at room temperature.[25] On the other hand, 2,2-dichloroaldehydes are valuable and very promising bifunctional substrates in synthetic organic chemistry.[26] The application of the corresponding α,α-dichloroimines in the preparation of β,β-dichloroamines **5**, more specific of allylic and propargylic amines would allow us to investigate the reactivity of these highly functionalized

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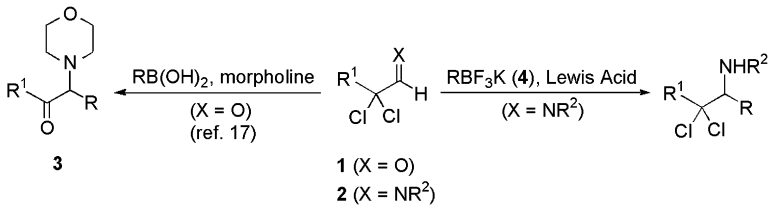
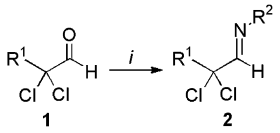


Scheme 1. Synthesis of β,β-dichloroamines.

compounds. Therefore, we examined the borono Mannich reaction between α,α-dichloroimines and potassium trifluoroborates in the presence of Lewis acids. Thus a new class of acyclic β,β-dichloroamines **5** would become available, which, to the best of our knowledge, has been prepared only once before.[27]

2. Results and discussion

The different α,α-dichloroimines **2** discussed in this article were prepared by reacting α,α-dichloroaldehydes **1**[28] with primary amines in CH_2Cl_2 in the presence of anhydrous $MgSO_4$ as desiccant. The more sterically hindered α,α-dichloroaldehyde **1ce** was transformed into the corresponding imine using titanium(IV) chloride (Scheme 2, Table 1).



Scheme 2. Synthesis of imines: Reagents and conditions: (i) Method a: R^2NH_2 (0.95–1.5 equiv), CH_2Cl_2, reflux or 0 °C or −10 °C, 2 h; Method b: R^2NH_2 (4 equiv), $TiCl_4$ (0.6 equiv), Et_2O, 0 °C→rt, 2 h.

First, as a control reaction, *N*-(2,2-dichloro-1-propylidene)-benzylamine (**2aa**) was reacted with 1 equiv of styrylboronic acid and $BF_3\cdot Et_2O$. In this case only starting material was isolated. This is not surprising, since it is known that to enhance the electrophilicity of the azomethine carbon, the C=N of the imine has to be activated by coordination of a Lewis acid with the nitrogen lone pair.[18]

Potassium organotrifluoroborates can be converted in situ into the very electrophilic tricoordinate difluoroboranes[29] using a Lewis acid activation. Common Lewis acids used for this conversion are $SiCl_4$,[30] gaseous BF_3,[31] Me_3SiCl,[32] and $BF_3\cdot OEt_2$.[16,33,34]

Table 1. Synthesis of 2,2-dichloroaldimines **2**

Imine **2**	R^1	R^2	Yield[a] (%)
2aa	Me	Bn	86
2ab	Me	*t*-Bu	88
2ac	Me	*i*-Pr	70
2ad	Me	*n*-Pr	66
2ae	Me	Allyl	84
2af	Me	Et	56[b]
2ag	Me	Me	74[c]
2be	Et	Allyl	47
2bf	Et	Et	96
2ce	*i*-Pr	Allyl	78[d]

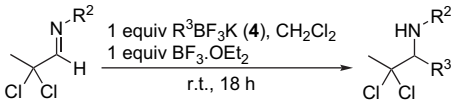
[a] Purity was sufficient for the next step (>92%, ^{1}H NMR).
[b] 0 °C.
[c] −10 °C.
[d] Method b.

In a preliminary attempt, *N*-(2,2-dichloro-1-propylidene)-benzylamine (**2aa**) was reacted with potassium styryltrifluoroborate (**4a**) and $BF_3\cdot OEt_2$. The presence of *N*-(4,4-dichloro-1-phenylpent-1-en-3-yl)benzylamine (**5aa**) in the crude reaction mixture was shown by ^{1}H NMR. With regard to the possible mechanism of this reaction some general considerations may be made. The RBF_2 species generated in situ acts as a Lewis acid and hence activates the imine for a nucleophilic attack.[5,13] After all, the majority of electrophiles in the Petasis reaction bear a hydroxyl group, suggesting that the formation of a boronate adduct with a pendant heteroatom on the electrophile is important for the reaction to proceed.[35]

Both $BF_3\cdot OEt_2$ and TMSCl were evaluated as Lewis acids in this conversion, using 1 equiv of each of the three components (imine, borate, and Lewis acid). A higher yield of **5aa** was obtained with $BF_3\cdot OEt_2$ as Lewis acid (24%, GC–MS) than with Me_3SiCl (8%, GC–MS).

Different amounts of the styryltrifluoroborate and $BF_3\cdot OEt_2$ were used in the BAM reaction on **2aa** in order to determine the optimal proportion of each compound. However, no clear conclusion could be drawn from these experiments and all attempts to purify the benzylamine **5aa** failed. Because of the problems encountered with the purification of **5aa**, we investigated another imine, namely *N*-(2,2-dichloro-1-propylidene)-*tert*-butylamine (**2ab**) as a substrate in this BAM reaction. As a consequence of extensive optimization reactions the optimal reaction condition for the boronic acid Mannich reaction between an α,α-dichloroimine, potassium trifluoroborate, and $BF_3\cdot OEt_2$, was an equimolar overnight reaction in dichloromethane at room temperature (Table 2, entry 3). These conditions were used to carry out the BAM reactions with the other α,α-dichloroimines **2** (Table 2). The yield of the reactions with potassium styryltrifluoroborate (**4a**) increases with a less sterically hindering nitrogen atom substituent of the imine. Electron donating substituents in the styryl group led to better yields of the Mannich product (entry 11) while electron withdrawing groups decreased this yield (entry 12). Potassium phenyltrifluoroborate and 1-phenylvinyltrifluoroborate were not reactive in the boronic acid Mannich reaction with α,α-dichloroimines **2**. Even the electron-rich 4-methoxyphenyltrifluoroborate and 2,5-dimethoxyphenyltrifluoroborate did not lead to any Mannich product. Instead, the deborylated products, anisole and 1,4-dimethoxybenzene were isolated in 34%. In case HFIP (vide infra) was added as a co-solvent, 1,4-dimethoxybenzene was isolated in 69% yield and anisole in 38% yield. When potassium phenylethynyltrifluoroborate (**4g**) was used, the yields

Table 2. Reaction between *N*-(2,2-dichloro-1-propylidene)amines **2a** and potassium trifluoroborates



2a **5**

Entry (product)	R^2 (**2a**)	R^3 (**4**)	Unreacted imine[a] (%)	Styrene[a] (%)	Product purity[a,b] (%)	Crude yield[a,b] (%)	Yield after purification[b] (%)
1 (**5aa**)	Bn (**2aa**)	PhCH=CH (**a**)	47 (GC)	19 (GC)	34 (GC)	24 (GC)	—
2 (**5ga**)	Bn (**2aa**)	Ph-C≡C (**g**)	0	—	92	81	—
3 (**5ab**)	*t*-Bu (**2ab**)	PhCH=CH (**a**)	36 (GC)	21 (GC)	43 (GC)	20 (GC)	9[c]
4 (**5ac**)	*i*-Pr (**2ac**)	PhCH=CH (**a**)	8–24	2–25	67–73	21–37	12[d]
5 (**5gc**)	*i*-Pr (**2ac**)	Ph–C≡C (**g**)	0	—	92	72	—
6 (**5ad**)	*n*-Pr (**2ad**)	PhCH=CH (**a**)	52	11	37	27	36[e]
7 (**5gd**)	*n*-Pr (**2ad**)	Ph–C≡C (**g**)	0	—	95	78	—
8 (**5ae**)	Allyl (**2ae**)	PhCH=CH (**a**)	0	0	100	44	44[e]
9 (**5ge**)	Allyl (**2ae**)	Ph–C≡C (**g**)	0	—	99	83	—
10 (**5af**)	Et (**2af**)	PhCH=CH (**a**)	13	7	66 (13)	32 (6)	26 (8)[e,f]
11 (**5bf**)	Et (**2af**)	4-MeC_6H_4CH=CH (**b**)	48	3	48	60	46[e]
12 (**5cf**)	Et (**2af**)	4-ClC_6H_4CH=CH (**c**)	12	23	59 (6)	23 (2)	16 (2)[e,f]
13 (**5ef**)	Et (**2af**)	(*Z*)-MeCH=CH (**e**)	20	—	80	30	17[g]
14 (**5gf**)	Et (**2af**)	Ph–C≡C (**g**)	0	—	100	80	80[e]
15 (**5ag**)	Me (**2ag**)	PhCH=CH (**a**)	28	18	24 (16)	20 (7)	—
16 (**5hd**)	*n*-Pr (**2ad**)	3-$MeOC_6H_4C$≡C (**h**)	0	0	99	88	88[e]
17 (**5id**)	*n*-Pr (**2ad**)	4-EtC_6H_4C≡C (**i**)	0	0	99	90	90[e]
18 (**5jd**)	*n*-Pr (**2ad**)	$MeOCH_2C$≡C (**j**)	0	0	99	44	44[e]

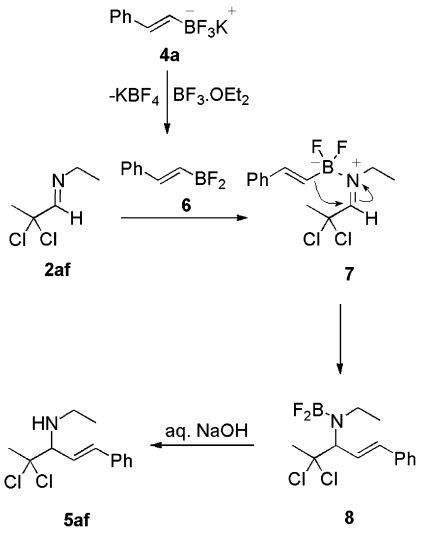
[a] Calculated from ^{1}H NMR of the crude reaction mixture.
[b] The number in brackets refers to the purity or yield of the double addition product.
[c] After high vacuum distillation.
[d] After acid–base extraction.
[e] Evaporation of unreacted imine and styrene.
[f] Yields calculated from the ^{1}H NMR.
[g] After flash chromatography (silica gel, Et_2O/pentane, 1:9).

dramatically increased, probably because of the electron richness of the alkynyl system (entries 2, 5, 7, 9, and 14). Since this reaction proceeded more readily the functionalized propargylamines were obtained in satisfactory purity (>92%) and hence needed no further purification. Electron-rich potassium phenylethynyltrifluoroborates **4h** and **i** even furnished the propargylic amines in higher yields and purities (entries 16 and 17). The reaction was also extended to aliphatic potassium (3-methoxypropynyl)trifluoroborate (**4j**) (entry 18).

In case potassium styryltrifluoroborate (**4a**) was used, also varying amounts of styrene were observed as a side product. In a model experiment, trifluoroborate **4a** was reacted with 1 equiv of $BF_3\cdot OEt_2$ in CH_2Cl_2 for 18 h. After evaporation of the solvent, ^{1}H NMR analysis showed the exclusive presence of styrene. On the other hand, simple basic treatment (0.5 M NaOH) of **4a** also induced hydrodeborylation. These tests prove that next to the known acid deborylation,[36] also thermal or aqueous basic deborylation of potassium alkenyltrifluoroborates may occur.

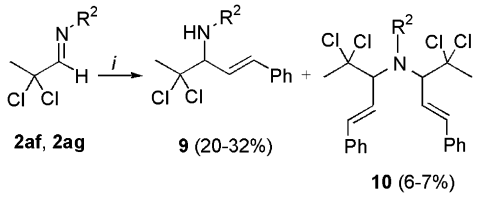
The purification of the crude reaction mixtures occurred in different ways, depending on the starting imine. The easiest way to purify the mixture is to evaporate the formed styrene and the unreacted imine, which was only possible for volatile imines of 2,2-dichloropropanal (entries 6, 8, 10, 11, 12, and 14) and the reaction products from alkynyltrifluoroborates **4g**. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)-*tert*-butylamine (**5ab**) was purified by high vacuum distillation because acid–base extraction gave a lower yield of 3%. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)isopropylamine (**5ac**) was purified by an acid–base extraction of the reaction mixture.

A number of experiments were conducted in order to deduce the mode of reactivity of **4a** in the presence of imines. Non-aqueous work up of a mixture, which was obtained by reaction of *N*-ethylimine **2af** with trifluoroborate **4a** and $BF_3\cdot Et_2O$, by simple filtration and evaporation of CH_2Cl_2 gave rise to an brown oil, which was analyzed by NMR. The ^{1}H NMR of this product was shifted downfield compared to **5af**, while in ^{19}F NMR a signal appeared at −131.87 ppm ($CDCl_3$) and in ^{11}B NMR at −0.7 ppm ($CDCl_3$). The solid, which was filtered off prior to evaporation was shown to be KBF_4 by comparison with an authentic sample. In accordance with the literature and with our observations the reaction mechanism of this Lewis acid-catalyzed Mannich reaction starts with the formation of the very electrophilic difluoroborane **6**,[16,29,33,34] which forms a complex with the imine **2**. The activated imino carbon atom of **7** will now undergo an alkyl transfer to give primarily an aminodifluoroborane **8**. Upon basic aqueous work up, the aminodifluoroborane **8** was converted to the desired β,β-dichloroamine **5af** (Scheme 3). Alternatively, $BF_3\cdot Et_2O$ may form a complex with the aldimine **2af**, which is then susceptible for nucleophilic attack by the alkenyltrifluoroborate **4a**.[37] This hypothesis was, however, rejected because of the immediate formation of difluoroboranes **6** and their much stronger Lewis acidity compared to $BF_3\cdot Et_2O$.[38]



Scheme 3. Proposed reaction mechanism.

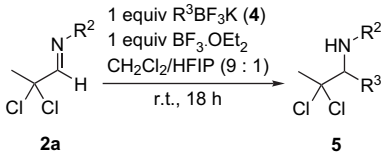
When the less sterically hindered *N*-ethyl- and *N*-methyl imines of 2,2-dichloropropanal were reacted with potassium styryltrifluoroborate (**4a**), the formation of a double addition product **10** was observed (Scheme 4). This product was formed due to the reaction of the intermediate aminodifluoroborane with the unreacted α,α-dichloroimine **2af** or **2ag** still present in the reaction medium. Subsequent expulsion of methylamine or ethylamine and addition of a styryl group to the intermediate iminium ion then lead to **10**. Despite several efforts, the double addition product **10** could not be separated from **9**.



Scheme 4. Reagents and conditions: (i) PhCH=CHBF$_3$K (**4a**, 1 equiv), $BF_3 \cdot Et_2O$ (1 equiv), CH_2Cl_2, rt, 18 h.

In a recent paper, Nanda and Trotter claim that the classic Petasis reaction can be accelerated using 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as co-solvent. It is supposed that the acidic HFIP accelerates the formation of the iminium species, which may then be attacked by organoboronic acids.[39] Because of this precedent, we repeated the reaction between an α,α-dichloroimine and a potassium trifluoroborate, with HFIP as co-solvent in dichloromethane (CH_2Cl_2/HFIP, 9:1) (Table 3). All the yields fluctuate around 60–70% for the BAM reactions with potassium styryltrifluoroborate (**4a**) when HFIP is used, which is much higher than the same reaction in pure CH_2Cl_2. In all cases, the β,β-dichloroamines **5** were of sufficient purity (>95%, GC) so that no extra purification was required. Attempted column chromatography of these products anyway resulted in big losses (10–20% yield). The steric hindrance of the nitrogen substituent does not play any role here and no double addition products are formed in the reactions with the ethylimine **2af** and methylimine **2ag**, probably because of the faster

Table 3. Reaction between *N*-(2,2-dichloro-1-propylidene)amines **2a** and potassium trifluoroborates in CH_2Cl_2/HFIP



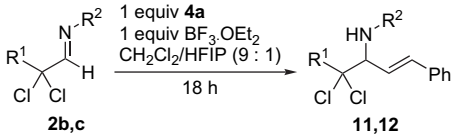
Entry (product)	R^2 (**2a**)	R^3 (**4**)	Yield[a] (%)
1 (**5aa**)	Bn	PhCH=CH	67
2 (**5aa**)	Bn	PhCH=CH	39[b]
3 (**5ab**)	*t*-Bu	PhCH=CH	64
4 (**5ac**)	*i*-Pr	PhCH=CH	62
5 (**5ad**)	*n*-Pr	PhCH=CH	74
6 (**5ae**)	Allyl	PhCH=CH	73
7 (**5af**)	Et	PhCH=CH	68
8 (**5ag**)	Me	PhCH=CH	69

[a] Isolated yields (purity >95% GC).
[b] $BF_3 \cdot OEt_2$—2 equiv.

reaction. By using the more reactive potassium phenylethynyltrifluoroborate (**4g**) the same results were obtained as when no HFIP was added. Potassium phenyltrifluoroborate, however, still did not react with the α,α-dichloroimines. In order to get some understanding of the function of the co-solvent, other additives were also tested. Phenol, which has a comparable pK_a (10) as HFIP, led to the same yields as without co-solvent. Addition of 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (pK_a 11) even decreased the yield. It was speculated that the use of HFIP as the sole solvent might further accelerate the reaction. Reaction of imine **2ad** with potassium styryltrifluoroborate (**4a**) in HFIP leads to a disappointing 24% yield of the β,β-dichloroamine **5ad**. If this reaction was repeated with potassium phenylethynyltrifluoroborate (**4g**) a comparable yield of 82% was obtained as in a 9:1 CH_2Cl_2/HFIP solvent system. In both cases the fluoroborate salts dissolved less readily in HFIP, giving rise to sluggish reaction upon addition of $BF_3 \cdot Et_2O$. The lower yields and inferior purity of the reaction products **5ad** and **5gd** in combination with the high cost of HFIP justify its use as a co-solvent with dichloromethane.

The reaction was expanded to α,α-dichloroimines **2b** and **2c**, derived from other 2,2-dichloroalkanals (Table 4). The

Table 4. Reaction of other 2,2-dichloroaldimines with potassium styryltrifluoroborate



Entry (product)	R^1	R^2	Reaction conditions	Purity[a] (%)	Yield[a,b] (%)
1 (**11af**)	Et	Et	Reflux	64	33 (9)
2 (**11af**)	Et	Et	Pressure tube	67	21 (5)
3 (**11ae**)	Et	Allyl	Reflux	58	50 (24)
4 (**11ae**)	Et	Allyl	Pressure tube	87	29 (14)
5 (**12ae**)	*i*-Pr	Allyl	Reflux	38	22 (10)
6 (**12ae**)	*i*-Pr	Allyl	Pressure tube	62	28 (12)

[a] Purity and crude yields were calculated from ^{1}H NMR.
[b] The number in brackets refers to the yield after acid–base extraction.

reaction with these imines was carried out under the above-defined optimal conditions (equimolar reaction in dichloromethane) with HFIP as co-solvent. However, these imines did not undergo any reaction at room temperature; therefore refluxing was required in order to induce some conversion. In an attempt to further increase the yield, the reaction was also carried out in a pressure tube at 80 °C. Under these circumstances no styrene was formed and less unreacted imine was left, but the yield of the reaction product remained very low. During these pressure reactions also the aldehydes **1b** and **1c** were formed, despite the dry conditions. Purification of the reaction mixtures could be executed by a simple acid–base extraction.

3. Conclusion

In summary, we have developed a convenient new synthesis of a stable new class of dichlorinated secondary propargylamines and allylamines, by reaction of potassium arylethynyltrifluoroborates and potassium styryltrifluoroborates with α,α-dichlorinated aldimines in the presence of $BF_3 \cdot OEt_2$ as a Lewis acid. The use of hexafluoroisopropanol as a co-solvent in this reaction allows high yield isolation of the pure target compounds.

4. Experimental

4.1. General

GC–MS analyses were performed using an Intersience GC 8000 series gas chromatograph with an 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. The mass spectrometer is a Fisons Instruments MD 800 using electron impact (70 eV) as ionization method. HRMS was measured with a VGQuattro II mass spectrometer (positive ion mode). Under our 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 **2** were dissolved in CH_3CN/MeOH (1:1). High resolution ^1H NMR (250 MHz), ^{13}C NMR (62.90 MHz), and ^{19}F NMR (235.3 MHz) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance DRX 250 spectrometer. ^{11}B NMR (160.5 MHz) spectra were recorded on a Bruker Avance II 500 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 FTIR apparatus (Thermo Nicolet). 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 $60F_{254}$. 2,2-Dichloroaldehydes **1** were prepared by halogenation of the corresponding aldehydes or alcohols with chlorine gas in the presence of tetraalkylammonium chlorides.[28] Potassium trifluoroborates **4a**,[40] **4b**,[16] **4d**,[41] **4f**,[29] **4g**,[42] and **4j**[43] and potassium 4-methoxyphenyltrifluoroborate[44] were prepared according to the literature procedures.

4.2. Synthesis of 2,2-dichloroaldimines; *N*-(2,2-dichloro-1-propylidene)benzylamine (2aa); typical procedure (method a)

To a stirred solution of 2,2-dichloropropanal (**1a**) (50 mmol, 6.35 g) in CH_2Cl_2 (50 mL) was added (150 mmol, 26.16 g) $MgSO_4 \cdot 3H_2O$ as desiccant, followed by (47.5 mmol, 5.09 g) benzylamine. The solution was stirred under reflux for 2 h. Afterward, the solution was filtered and concentrated under reduced pressure. Yield: 9.33 g (86%), light-yellow liquid. ^1H NMR (250 MHz, $CDCl_3$): δ=2.28 (s, 3H, CH_3), 4.63 (s, 2H, CH_2), 7.20–7.34 (m, 5H, Ph), 7.86 (t, J=1.4 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=32.5 (CH_3), 62.5 (CH_2), 84.6 (CCl_2), 127.6 ($CH_{arom.}$), 127.8 ($CH_{arom.}$), 128.4 ($CH_{arom.}$), 137.7 ($C_{arom.quat.}$), 161.0 (C=N). MS (EI, 70 eV): m/z (%)=219 (0.3) $[M+4]^+$, 217 (3) $[M+2]^+$, 215 (4) $[M^+]$, 182 (4), 180 (9), 144 (7), 118 (53), 104 (7), 92 (100), 89 (18), 77 (11), 75 (8), 65 (47), 63 (18), 62 (7), 61 (8), 51 (18), 50 (7). HRMS (ESI): m/z calcd for $C_{10}H_{12}NCl_2$+H: 216.0347; found: 216.0359. IR (NaCl): 1667 (C=N), 1496 (C=C aromate) cm^{-1}.

With volatile amines, 1.5 equiv was added instead of 0.95 equiv. The synthesis of imine **2ag** takes place at 0 °C and imine **2ah** at −10 °C. Unless otherwise stated, 2,2-dichloroaldimines were synthesized on a 50 mmol scale.

4.3. *N*-(2,2-Dichloro-3-methyl-1-butylidene)allylamine (2ce) (method b)

In a three-necked flask (100 mL), provided with a condenser and a $CaCl_2$ tube, was added a 20% solution of 2,2-dichloro-3-methylbutanal (**1c**) (30 mmol, 4.65 g) in dry Et_2O (23 mL). After cooling this solution to 0 °C, $TiCl_4$ (18 mmol, 2 mL) in dry pentane (5 mL) was added dropwise. Under vigorous stirring, allylamine (0.12 mol, 6.85 g) was added dropwise to this mixture at 0 °C. The reaction was stirred for another 2 h at room temperature before the workup. The mixture was poured into aqueous NaOH (0.5 M, 40 mL) and quickly extracted with Et_2O (3×30 mL). The organic fractions were combined, dried (K_2CO_3), and concentrated under reduced pressure. Yield: 4.50 g (78%, 30 mmol), light-yellow liquid. ^1H NMR (250 MHz, $CDCl_3$): δ=1.18 (d, J=6.6 Hz, 2×3H, $(CH_3)_2CH$), 2.64 (septet, J=6.7 Hz, 1H, $(CH_3)_2CH$), 4.17–4.21 (m, 2H, $CH_2CH{=}CH_2$), 5.13–5.24 (m, 2H, $CH_2CH{=}CH_2$), 5.90–6.06 (m, 1H, $CH_2CH{=}CH_2$), 7.72 (t, J=1.4 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=18.1 ($(CH_3)_2CH$), 40.3 ($(CH_3)_2CH$), 61.6 ($CH_2CH{=}CH_2$), 94.5 (CCl_2), 117.0 ($CH_2CH{=}CH_2$), 134.4 ($CH_2CH{=}CH_2$), 161.3 (C=N). MS (EI, 70 eV): m/z (%)=198 (0.32) $[M+5]^+$, 196 (2) $[M+3]^+$, 194 (3.5) $[M+H^+]$, 158 (29), 153 (16), 151 (26), 125 (15), 124 (13), 118 (20), 116 (44), 102 (20), 91 (20), 89 (42), 83 (75), 81 (14), 80 (39), 75 (22), 68 (100), 65 (22), 63 (27), 55 (22), 54 (14), 53 (51), 51 (38). HRMS (ESI): m/z calcd for $C_8H_{14}NCl_2$+H: 194.0503; found: 194.0446. IR (ATR): 1666 (C=N), 1461, 1445 (C=C) cm^{-1}.

4.3.1. *N*-(2,2-Dichloro-1-propylidene)-*tert*-butylamine (2ab). Yield: 7.98 g (88%), light-yellow liquid. Spectral data were in accordance with the literature.[45]

4.3.2. *N*-(2,2-Dichloro-1-propylidene)isopropylamine (2ac). Yield: 5.86 g (70%), colorless liquid; bp=27–31 °C/

17 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.19 (d, J=6.3 Hz, 6H, CH(CH_3)$_2$), 2.27 (s, 3H, CH_3CCl_2), 3.50 (septet, J=6.3 Hz, 1H, CH(CH_3)$_2$), 7.77 (s, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=23.5 (CH(CH_3)$_2$), 32.6 (CH_3CCl_2), 59.6 (CH(CH_3)$_2$), 84.9 (CCl_2), 157.6 (C=N). MS (EI, 70 eV): m/z (%)=171 (0.01) [M+4]$^+$, 169 (0.02) [M+2]$^+$, 167 (0.03) [M$^+$], 152 (1), 105 (8), 104 (100), 103 (48), 102 (9), 78 (50), 77 (24), 70 (32), 63 (10), 52 (8), 51 (24), 50 (11). HRMS (ESI): m/z calcd for $C_6H_{12}NCl_2$+H: 168.0347; found: 168.0340. IR (NaCl): 1664 (C=N) cm^{-1}.

4.3.3. *N*-(2,2-Dichloro-1-propylidene)propylamine (2ad). Yield: 5.55 g (66%), yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.91 (t, J=7.4 Hz, 3H, CH_2CH_3), 1.66 (sextet, J=7.2 Hz, 2H, $NCH_2CH_2CH_3$), 2.28 (s, 3H, CH_3CCl_2), 3.47 (td, J=6.8, 1.0 Hz, 2H, NCH_2), 7.77 (t, J=1.2 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.6 (CH_2CH_3), 23.4 ($NCH_2CH_2CH_3$), 32.6 (CH_3CCl_2), 61.1 (NCH_2), 84.6 (CCl_2), 160.1 (C=N). MS (EI, 70 eV): m/z (%)=172 (1) [M+5]$^+$, 170 (3) [M+3]$^+$, 168 (4) [M+H$^+$], 140 (12), 138 (19), 134 (21), 132 (47), 109 (12), 104 (18), 103 (10), 102 (41), 99 (12), 97 (22), 92 (20), 90 (49), 75 (33), 70 (100), 68 (37), 67 (15), 63 (26), 62 (13), 61 (33), 54 (36), 52 (16), 51 (20). HRMS (ESI): m/z calcd for $C_6H_{12}NCl_2$+H: 168.0347; found: 168.0345. IR (NaCl): 1669 (C=N) cm^{-1}.

4.3.4. *N*-(2,2-Dichloro-1-propylidene)allylamine (2ae). Yield: 6.95 g (84%), light-yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.29 (s, 3H, CH_3), 4.13–4.17 (m, 2H, NCH_2), 5.15–5.23 (m, 2H, CH_2CH=CH_2), 5.89–6.05 (m, 1H, CH_2CH=CH_2), 7.80 (t, J=1.3 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=32.5 (CH_3), 60.9 (CH_2CH=CH_2), 84.4 (CCl_2), 116.9 (CH_2CH=CH_2), 134.2 (CH_2CH=CH_2), 161.0 (C=N). MS (EI, 70 eV): m/z (%)=170 (1) [M+5]$^+$, 168 (8) [M+3]$^+$, 166 (12) [M+H$^+$], 132 (31), 130 (46), 104 (13), 102 (34), 101 (18), 99 (43), 97 (49), 94 (37), 77 (15), 76 (13), 75 (41), 68 (100), 66 (13), 65 (16), 64 (14), 63 (29), 62 (28), 61 (49), 54 (33), 53 (11), 52 (28), 51 (30). HRMS (ESI): m/z calcd for $C_6H_{10}NCl_2$+H: 166.0190; found: 166.0197. IR (ATR): 1668 (C=N), 1438, 1380 (C=C) cm^{-1}.

4.3.5. *N*-(2,2-Dichloro-1-propylidene)ethylamine (2af). Yield: 4.31 g (56%), colorless liquid; bp=36 °C/20 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.24 (t, J=7.3 Hz, 3H, NCH_2CH_3), 2.27 (s, 3H, CH_3CCl_2), 3.55 (q, J=7.3 Hz, 2H, NCH_2), 7.78 (t, J=1.3 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=15.5 (NCH_2CH_3), 32.6 (CH_3CCl_2), 53.7 (NCH_2), 84.7 (CCl_2), 159.6 (C=N). MS (EI, 70 eV): m/z (%)=158 (2) [M+5]$^+$, 156 (16) [M+3]$^+$, 154 (23) [M+H$^+$], 120 (42), 118 (50), 102 (36), 99 (31), 97 (40), 90 (48), 75 (33), 63 (36), 62 (31), 61 (36), 56 (100), 54 (38), 52 (31), 51 (35). HRMS (ESI): m/z calcd for $C_5H_{10}NCl_2$+H: 154.0190; found: 154.0201. IR (NaCl): 1668 (C=N) cm^{-1}.

4.3.6. *N*-(2,2-Dichloro-1-propylidene)methylamine (2ag). Yield: 5.15 g (74%), yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.26 (s, 3H, NCH_3), 3.40 (s, 3H, CH_3CCl_2), 7.78 (t, J=1.5 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=32.5 (NCH_3), 45.7 (CH_3CCl_2), 84.4 (CCl_2), 161.5 (C=N). MS (EI, 70 eV): m/z (%)=144 (1) [M+5]$^+$, 142 (7) [M+3]$^+$, 140 (14) [M+H$^+$], 124 (3), 106 (73), 104 (100), 102 (23), 97 (16), 75 (22), 68 (64), 66 (26), 64 (17), 63 (50), 62 (36), 61 (61), 60 (21), 54 (15), 52 (42), 51 (38). HRMS (ESI): m/z calcd for $C_4H_8NCl_2$+H: 140.0034; found: 140.0029. IR (NaCl): 1673 (C=N) cm^{-1}.

4.3.7. *N*-(2,2-Dichloro-1-butylidene)allylamine (2be). Yield: 420 mg (47%, 5 mmol), light-yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.23 (t, J=7.2 Hz, 3H, CH_3), 2.46 (q, J=7.2 Hz, 2H, $CH_3CH_2CCl_2$), 4.14–4.17 (m, 2H, CH_2–CH=CH_2), 5.11–5.22 (m, 2H, CH_2–CH=CH_2), 5.90–6.05 (m, 1H, CH_2–CH=CH_2), 7.78 (s, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=9.5 (CH_3), 37.0 (CH_2CCl_2), 61.3 (CH_2CH=CH_2), 90.0 (CCl_2), 116.9 (CH_2–CH=CH_2), 134.4 (CH_2CH=CH_2), 161.1 (C=N). MS (EI, 70 eV): m/z (%)=184 (0.21) [M+5]$^+$, 182 (1.5) [M+3]$^+$, 180 (2) [M+H$^+$], 146 (8), 144 (24), 116 (19), 113 (18), 111 (28), 108 (13), 102 (10), 83 (47), 77 (23), 75 (47), 68 (100), 54 (9), 53 (26), 52 (10), 51 (21). HRMS (ESI): m/z calcd for $C_7H_{12}NCl_2$+H: 180.0347; found: 180.0355. IR (ATR): 1665 (C=N), 1456, 1428 (C=C) cm^{-1}.

4.3.8. *N*-(2,2-Dichloro-1-butylidene)ethylamine (2bf). Yield: 807 mg (96%, 5 mmol), light-yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.22 (t, J=7.2 Hz, 3H, $CH_3CH_2CCl_2$), 1.24 (t, J=7.3 Hz, 3H, NCH_2CH_3), 2.44 (q, J=7.2 Hz, 2H, CH_2CCl_2), 3.55 (qd, J=7.3, 1.3 Hz, 2H, NCH_2CH_3), 7.76 (t, J=1.3 Hz, 1H, HC=N). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=9.5 ($CH_3CH_2CCl_2$), 15.6 (NCH_2CH_3), 37.1 (CH_2CCl_2), 54.0 (NCH_2), 87.7 (CCl_2), 159.6 (C=N). MS (EI, 70 eV): m/z (%)=170 (0.2) [M+5]$^+$, 168 (0.3) [M+3]$^+$, 166 (0.04) [M+H$^+$], 134 (6), 132 (17), 104 (7), 77 (6), 75 (19), 71 (17), 68 (7), 61 (7), 58 (10), 56 (100), 54 (6), 53 (12), 51 (15). HRMS (ESI): m/z calcd for $C_6H_{12}NCl_2$+H: 168.0347; found: 168.0340. IR (ATR): 1664 (C=N) cm^{-1}.

4.4. Synthesis of the potassium trifluoroborates

These compounds were prepared analogously to published methods.[13] Since no spectra have been reported for these compounds, they are given here.

4.4.1. Potassium 2,5-dimethoxyphenyltrifluoroborate. Yield: 2.68 g (89%, 11 mmol), white solid; mp >260 °C. ^{1}H NMR (250 MHz, DMSO): δ=3.55 and 3.61 (2×s, 2×3H, 2×Me), 6.50–6.60 (m, 2H, $CH_{meta+para}$), 6.85 (d, J=2.7 Hz, 1H, CH_{ortho}). ^{13}C NMR (62.90 MHz, DMSO): δ=55.3 and 56.1 (2×Me), 111.0 and 111.4 ($C_{arom.meta}$+$C_{arom.para}$), 119.4 (q, J=3.2 Hz, $CH_{arom.ortho}$), 153.0 ($C_{arom.quat.}$OMe$_{meta}$), 157.1 (q, J=0.7 Hz, $C_{arom.quat.}$OMe$_{ortho}$), $C_{arom.quat.}$B was not visible. IR (ATR): 1490, 1468, 1399 (C=C) cm^{-1}.

4.4.2. Potassium (*E*)-2-(4-chlorophenyl)vinyltrifluoroborate (4c). Yield: 440 mg (66%, 2.7 mmol), white solid; mp >260 °C. ^{1}H NMR (250 MHz, DMSO): δ=6.19 (dq, J=14.8, 3.3 Hz, 1H, CH=CHB), 6.44 (d, J=18.3 Hz, 1H, CH=CHB), 7.27 (d, J=8.6 Hz, 2H, (CH)$_2$$C_{arom.quat.}$CH=CH), 7.33 (d, J=8.6 Hz, 2H, Cl$C_{arom.quat.}$(CH)$_2$). ^{13}C NMR (62.90 MHz, DMSO): δ=126.9 ((CH)$_2$$C_{arom.quat.}$CH), 128.1 (Cl$C_{arom.quat.}$(C$H$)$_2$), 129.9 ($C_{arom.quat.}$CH), 131.6 (q, J=4.4 Hz, CH=CHB), 139.1 ($C_{arom.quat.}$Cl), CH=CHB was not visible. ^{11}B NMR (160.5 MHz, DMSO, B(OMe)$_3$

external standard): δ=2.4 (s). ^{19}F NMR (235.3 MHz, DMSO): δ=−138.4 (s). IR (ATR): 1624, 1589, 1564, 1488, 1402 (C=C) cm^{-1}.

4.4.3. Potassium (*Z*)-propenyltrifluoroborate (4e). Yield: 206 mg (24%, 5.8 mmol), white solid; mp >260 °C. ^{1}H NMR (250 MHz, DMSO): δ=1.60 (d, *J*=6.5 Hz, 3H, CH_3), 5.15 (dq, *J*=3.6, 1.7 Hz, 1H, CH_3CH), 5.21 (dq, *J*=3.7, 1.7 Hz, 1H, CHB). ^{13}C NMR (62.90 MHz, DMSO): δ=17.0 (CH_3), 129.0 (q, *J*=4.1 Hz, CH_3CH), CHB was not visible. ^{11}B NMR (160.5 MHz, DMSO, $B(OMe)_3$ external standard): δ=2.4 (q, *J*=175.5 Hz). ^{19}F (235.3 MHz, DMSO): δ=−132.6 (q, *J*=59.6 Hz). IR (ATR): 1633, 1404 (HC=CH) cm^{-1}.

4.4.4. Potassium (3-methoxyphenyl)ethynyltrifluoroborate (4h). Yield 32%, colorless crystals; mp >250 °C. ^{1}H NMR (250 MHz, DMSO-d_6): δ 3.72 (s, 3H, CH_3), 6.7–6.9 (m, 3H, Ar), 7.1–7.3 (m, 1H, Ar). ^{13}C NMR (62.90 MHz, DMSO): δ 60.2 (d, *J*=0.6 Hz, CH_3), 118.4 (C_{Ar}), 121.1 (d, *J*=0.9 Hz, C_{Ar}), 128.6 (d, *J*=0.8 Hz, C_{Ar}), 131.8 (d, *J*=0.7 Hz, C_{Ar}–C≡C), 134.6 (C_{Ar}), 164.2 (C_{Ar}–OCH_3). IR (ATR): 2184 (C≡C) cm^{-1}.

4.4.5. Potassium (4-ethylphenyl)ethynyltrifluoroborate (4i). Yield 60%, colorless crystals; mp >250 °C. ^{1}H NMR (250 MHz, DMSO): δ 1.09 (t, *J*=7.6 Hz, 3H, CH_3), 2.51 (q, *J*=7.6 Hz, 2H, CH_2), 7.05 (pseudo d, *J*=8.2 Hz, 2H, Ar), 7.14 (pseudo d, *J*=8.2 Hz, 2H, Ar). ^{13}C NMR (62.9 MHz, DMSO): δ 15.3 (CH_3), 27.9 (CH_2), 122.7 (C_{Ar}–C≡C), 127.6, 130.9, 142.3 (C_{Ar}–Et). IR (ATR): 2181 (C≡C) cm^{-1}.

4.5. Synthesis of the β,β-dichloroamines 5; general procedure

To a stirred solution of α,α-dichloroaldimine **2** (1 equiv) in CH_2Cl_2 (8 mL) was added the potassium trifluoroborate **4** (1 equiv) in one portion, followed by $BF_3\cdot Et_2O$ (1 equiv). The reaction mixture was stirred for 18 h at room temperature and poured into aqueous NaOH (0.5 M). After isolation of the organic layer, the aqueous phase was washed with CH_2Cl_2 (4×15 mL). The organic fractions were dried ($MgSO_4$) and concentrated under reduced pressure.

The reactions with trifluoroborate **4a** were carried out in CH_2Cl_2/HFIP (9:1). Unless otherwise stated, the yields described below for the α-alkenyl-β,β-dichloroamines are from the reactions with HFIP as co-solvent and the yields for the α-alkynyl-β,β-dichloroamines are from the reactions without HFIP.

Unless otherwise stated, all these reactions were performed on a 0.5 mmol scale.

4.5.1. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)benzylamine (5aa). Yield: 108 mg (67%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.18 (s, 3H, CH_3), 3.43 (d, *J*=8.6 Hz, 1H, C*H*NH), 3.75 and 4.02 (2×d, *J*=13.6 Hz, 2H, CH_2), 6.16 (dd, *J*=15.9, 8.6 Hz, 1H, C*H*=CHPh), 6.52 (d, *J*=15.9 Hz, 1H, CH=C*H*Ph), 7.23–7.45 (m, 10H, 2×Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$, assignment by HMQC and HMBC): δ=34.9 (CH_3), 50.8 (CH_2), 71.2 (CHNH), 92.9 (CCl_2), 126.7 (*C*H=CHPh), 127.1 (CH=CH$C_{arom.quat.}$), 127.6 ($HC_{arom.}$*para*(styryl)), 128.1 ($HC_{arom.}$*para* (benzyl)), 127.2 and 128.3 ($HC_{arom.}$*ortho+meta* (styryl)), 128.5 and 128.7 ($HC_{arom.}$*ortho+meta*(benzyl)), 129.1 ($CH_2C_{arom.quat.}$), 135.6 (CH=*C*HPh). MS (EI, 70 eV): *m/z* (%)=323 (trace) [M+4]$^+$, 321 (trace) [M+2]$^+$, 319 (0.02) [M$^+$], 249 (15), 247 (55), 223 (100), 158 (14), 156 (39), 130 (22), 128 (37), 115 (32), 91 (77), 77 (20), 65 (33). HRMS (ESI): *m/z* calcd for $C_{18}H_{20}NCl_2$+H: 320.0973; found: 320.0965. IR (ATR): 3335 (NH), 1494, 1449 (C=C), 1373 (HC=CH) cm^{-1}.

4.5.2. *N*-(4,4-Dichloro-1-phenylpent-1-yne-3-yl)benzylamine (5ga). Yield: 129 mg (81%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.95 (s, 1H, NH), 2.27 (s, 3H, CH_3), 3.88 (s, 1H, C*H*NH), 4.00 and 4.21 (2×d, *J*=13.3 Hz, 2H, CH_2), 7.55–7.24 (m, 10H, 2×Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$ internal standard, assignment by HMQC, HMBC and COSY): δ=34.8 (CH_3), 52.0 (NH*C*H$_2$), 63.4 (CHNH), 86.2 (*C*≡CPh), 86.7 (C≡*C*Ph), 91.5 (CCl_2), 122.9 (C≡C$C_{arom.quat.}$), 128.8 and 128.9 (2×$HC_{arom.}$*meta*), 127.7 and 129.0 (2×$HC_{arom.}$*para*), 128.7 and 132.3 (2×$HC_{arom.}$*ortho*), 139.5 ($CH_2C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=322 (0.03) [M+5]$^+$, 320 (0.08) [M+3]$^+$, 318 (0.10) [M+H$^+$], 220 (100), 204 (10), 193 (14), 178 (15), 142 (25), 141 (12), 139 (25), 129 (26), 128 (16), 115 (56), 113 (14), 102 (46), 99 (11), 97 (14), 91 (89), 89 (32), 78 (27), 77 (13), 76 (10), 74 (10), 65 (50), 63 (26), 61 (10), 51 (19). HRMS (ESI): *m/z* calcd for $C_{18}H_{18}NCl_2$+H: 318.0816; found: 318.0826. IR (ATR): 1489, 1455, 1443 (C=C) cm^{-1}.

4.5.3. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)-*tert*-butylamine (5ab). Yield: 92 mg (64%), yellow oil; bp 29 °C/1.9 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (s, 9H, $C(CH_3)_3$), 2.19 (s, 3H, CH_3CCl_2), 3.63 (d, *J*=8.1 Hz, 1H, C*H*NH), 6.21 (dd, *J*=16.0, 8.1 Hz, 1H, C*H*=CHPh), 6.55 (d, *J*=16.0 Hz, 1H, CH=C*H*Ph), 7.23–7.43 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=30.5 ($C(CH_3)_3$), 35.1 (CH_3CCl_2), 51.4 ($C(CH_3)_3$), 67.3 (CHNH), 94.6 (CCl_2), 127.8 ($HC_{arom.}$*para*), 126.5 and 128.6 ($HC_{arom.}$*ortho+meta*), 130.1 (*C*H=CHPh), 133.8 (CH=*C*HPh), 136.7 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=289 (trace) [M+4]$^+$, 287 [M+2]$^+$, 285 (0.01) [M$^+$], 274 (0.13), 272 (1), 270 (2), 188 (85), 177 (26), 158 (15), 143 (13), 142 (27), 141 (26), 133 (11), 132 (100), 130 (21), 128 (16), 115 (55), 91 (13), 77 (13), 57 (32). HRMS (ESI): *m/z* calcd for $C_{15}H_{21}NCl_2$+H: 286.1129; found: 286.1063. IR (ATR): 1494, 1448 (C=C), 1365 (HC=CH) cm^{-1}.

4.5.4. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)isopropylamine (5ac). Yield: 84 mg (62%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.06 and 1.09 (2×d, *J*=6.2 Hz, 6H, $CH(CH_3)_2$), 2.18 (s, 3H, CH_3CCl_2), 2.89 (septet, *J*=6.2 Hz, 1H, $CH(CH_3)_2$), 3.49 (d, *J*=8.4 Hz, 1H, C*H*NH), 6.14 (dd, *J*=15.9, 8.4 Hz, 1H, C*H*=CHPh), 6.55 (d, *J*=15.9 Hz, 1H, CH=C*H*Ph), 7.22–7.44 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=22.1 and 24.2 ($CH(CH_3)_2$), 35.0 (CH_3CCl_2), 45.8 ($CH(CH_3)_2$), 70.2 (CHNH), 93.4 (CCl_2), 126.8 (*C*H=CHPh), 127.9 ($HC_{arom.}$*para*), 126.6 and 128.6 ($HC_{arom.}$*ortho+meta*), 134.2 (CH=CH$C_{arom.quat.}$), 136.4 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=275 (trace) [M+4]$^+$, 273 (trace) [M+2]$^+$, 271

(0.01) [M$^+$], 238 (0.2), 236 (1), 177 (18), 175 (100), 158 (18), 143 (23), 142 (29), 141 (36), 132 (58), 130 (38), 128 (42), 117 (15), 116 (16), 115 (56), 91 (26), 77 (26). HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NCl_2$+H: 272.0973; found: 272.0974. IR (NaCl): 3324 (NH), 1495, 1448 (C=C), 1339 (HC=CH) cm^{-1}.

4.5.5. *N*-(4,4-Dichloro-1-phenylpent-1-yne-3-yl)isopropylamine (5gc). Yield: 97 mg (72%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.09 and 1.18 (2×d, *J*=6.2 Hz, 6H, CH(CH_3)$_2$), 2.28 (s, 3H, CH_3CCl_2), 3.20 (septet, *J*=6.2 Hz, 1H, C*H*(CH$_3$)$_2$), 3.94 (s, 1H, CCl_2CH), 7.24–7.35 (m, 3H, $CH_{arom.meta}$+$CH_{arom.para}$), 7.41–7.51 (m, 2H, $CH_{arom.ortho}$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=22.0 and 24.0 (CH(*C*H$_3$)$_2$), 34.3 (*C*H$_3$CCl$_2$), 47.2 (*C*H(CH$_3$)$_2$), 62.0 (CCl_2*C*H), 85.4 (*C*≡CPh), 86.8 (C≡*C*Ph), 91.4 (CCl_2), 122.6 ($C_{arom.quat.}$), 128.4 ($HC_{arom.para}$), 128.3 ($HC_{arom.meta}$), 131.8 ($HC_{arom.ortho}$). MS (EI, 70 eV): *m/z* (%)=274 (0.03) [M+5]$^+$, 272 (0.23) [M+3]$^+$, 270 (0.66) [M+H$^+$], 177 (23), 176 (30), 172 (100), 158 (12), 156 (33), 142 (32), 141 (14), 139 (36), 132 (13), 130 (70), 129 (31), 128 (21), 126 (13), 115 (59), 113 (20), 103 (80), 99 (16), 97 (20), 77 (49), 74 (13), 63 (27), 61 (13). HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NCl_2$+H: 270.0816; found: 270.0686. IR (ATR): 1489, 1442 (C=C) cm^{-1}.

4.5.6. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)propylamine (5ad). Yield: 101 mg (74%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.93 (t, *J*=7.4 Hz, 3H, CH_2CH_3), 1.52 (sextet, *J*=7.2 Hz, 2H, $CH_2CH_2CH_3$), 2.19 (s, 3H, CH_3CCl_2), 2.47–2.57 (m, 1H, (H)C*H*CH$_2$CH$_3$), 2.66–2.76 (m, 1H, (*H*)CHCH$_2$CH$_3$), 3.44 (d, *J*=8.5 Hz, 1H, C*H*NH), 6.12 (dd, *J*=15.9, 8.5 Hz, 1H, C*H*=CHPh), 6.58 (d, *J*=15.9 Hz, 1H, CH=C*H*Ph), 7.23–7.47 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.7 (CH_2CH_3), 23.1 (CH_2CH_3), 34.8 (CH_3CCl_2), 49.4 ($NHCH_2$), 72.8 (CHNH), 93.1 (CCl_2), 126.5 (*C*H=CHPh), 128.0 ($HC_{arom.para}$), 126.6 and 128.7 ($HC_{arom.ortho+meta}$), 134.9 (CH=*C*HPh), 136.3 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=276 (0.01) [M+5]$^+$, 274 (0.01) [M+3]$^+$, 272 (0.06) [M+H$^+$], 200 (12), 177 (15), 175 (100), 144 (14), 143 (22), 142 (30), 141 (34), 132 (33), 130 (26), 128 (34), 127 (12), 117 (20), 116 (13), 115 (53), 103 (13), 99 (10), 97 (12), 91 (37), 77 (24), 68 (11), 63 (10), 56 (11), 51 (11). HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NCl_2$+H: 272.0973; found: 272.0864. IR (ATR): 3309 (NH), 1494, 1448 (C=C), 1377 (HC=CH) cm^{-1}.

4.5.7. *N*-(4,4-Dichloro-1-phenylpent-1-yne-3-yl)propylamine (5gd). Yield: 105 mg (78%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.97 (t, *J*=7.3 Hz, 3H, CH_2CH_3), 1.52 (sextet, *J*=7.3 Hz, 2H, CH_2CH_3), 2.29 (3H, s, CH_3CCl_2), 2.67–2.77 (m, 1H, (H)C*H*CH$_2$CH$_3$), 2.93–3.07 (m, 1H, (*H*)CHCH$_2$CH$_3$), 3.91 (s, 1H, CHNH), 7.24–7.33 (m, 3H, $CH_{arom.meta+para}$), 7.42–7.51 (m, 2H, $CH_{arom.ortho}$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.7 (CH_2CH_3), 23.0 (CH_2CH_3), 34.2 (CH_3CCl_2), 50.1 ($NHCH_2$), 64.2 (CCl_2CH), 85.8 (*C*≡CPh), 86.3 (C≡*C*Ph), 91.3 (CCl_2), 122.5 ($C_{arom.quat.}$), 128.3 ($HC_{arom.meta}$), 128.5 ($HC_{arom.para}$), 131.8 ($HC_{arom.ortho}$). MS (EI, 70 eV): *m/z* (%)=274 (0.01) [M+5]$^+$, 272 (0.07) [M+3]$^+$, 270 (0.13) [M+H$^+$], 177 (11), 176 (10), 172 (100), 141 (26), 139 (19), 130 (57), 129 (16), 116 (31), 115 (18), 113 (11), 103 (23), 102 (22), 97 (11), 77 (14), 63 (15). HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NCl_2$+H: 270.0816; found: 270.0696. IR (ATR): 1489, 1458, 1443 (C=C) cm^{-1}.

4.5.8. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)allylamine (5ae). Yield: 99 mg (73%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.19 (s, 3H, CH_3), 3.20 (ddt, *J*=14.2, 6.8, 1.2 Hz, 1H, (H)C*H*CH=CH$_2$), 3.43 (ddt, *J*=14.2, 5.1, 1.6 Hz, 1H, (*H*)CHCH=CH$_2$), 3.50 (d, *J*=8.6 Hz, 1H, C*H*NH), 5.11–5.26 (m, 2H, CH_2CH=CH_2), 5.81–5.97 (m, 1H, CH_2CH=CH_2), 6.10 (dd, *J*=15.9, 8.6 Hz, 1H, C*H*=CHPh), 6.56 (d, *J*=15.9 Hz, 1H, CH=C*H*Ph), 7.24–7.50 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=34.9 (CH_3), 49.6 (CH_2CH=CH_2), 71.5 (CHNH), 93.0 (CCl_2), 116.6 (CH_2CH=*C*H$_2$), 125.9 (*C*H=CHPh), 128.1 ($HC_{arom.para}$), 126.6 and 128.7 ($HC_{arom.ortho+meta}$), 135.4 (CH=*C*HPh), 136.2 ($C_{arom.quat.}$), 136.5 (CH_2CH=CH_2). MS (EI, 70 eV): *m/z* (%)=273 (0.02) [M+4]$^+$, 271 (0.02) [M+2]$^+$, 269 (0.02) [M$^+$], 172 (100), 156 (13), 144 (16), 143 (15), 141 (29), 130 (67), 128 (52), 117 (13), 116 (12), 115 (79), 103 (18), 102 (17), 101 (11), 99 (36), 97 (57), 94 (13), 91 (36), 89 (15), 80 (12), 78 (10), 77 (43), 65 (11), 63 (31), 61 (34), 54 (26), 51 (24). HRMS (ESI): *m/z* calcd for $C_{14}H_{17}NCl_2$+H: 270.0816; found: 270.0706. IR (ATR): 3322 (NH), 1494, 1448 (C=C aromate), 1376 (HC=CH and CH=CH$_2$) cm^{-1}.

4.5.9. *N*-(4,4-Dichloro-1-phenylpent-1-yne-3-yl)allylamine (5ge). Yield: 111 mg (83%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.29 (s, 3H, CH_3CCl_2), 3.44 (ddt, *J*=14.0, 6.7, 1.2 Hz, 1H, (H)C*H*CH=CH$_2$), 3.65 (ddt, *J*=14.0, 5.3, 1.5 Hz, 1H, (*H*)CHCH=CH$_2$), 3.95 (s, 1H, C*H*NH), 5.14–5.35 (m, 2H, CH_2CH=CH_2), 5.85–5.99 (m, 1H, CH_2CH=CH_2), 7.25–7.31 (m, 3H, $CH_{arom.meta+para}$), 7.42–7.51 (m, 2H, $CH_{arom.ortho}$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=34.3 (CH_3CCl_2), 50.4 (CH_2CH=CH_2), 63.1 (CHNH), 85.9 (*C*≡CPh), 86.1 (C≡*C*Ph), 91.1 (CCl_2), 117.2 (CH_2CH=*C*H$_2$), 122.4 ($C_{arom.quat.}$), 128.3 ($HC_{arom.meta}$), 128.6 ($HC_{arom.para}$), 131.8 ($HC_{arom.ortho}$), 135.9 (CH_2CH=CH_2). MS (EI, 70 eV): *m/z* (%)=272 (0.01) [M+5]$^+$, 270 (0.03) [M+3]$^+$, 268 (0.04) [M+H$^+$], 172 (31), 170 (98), 141 (41), 139 (24), 130 (13), 128 (100), 116 (52), 115 (24), 113 (14), 104 (19), 103 (22), 99 (13), 97 (16), 91 (16), 78 (17), 77 (12), 65 (13), 63 (18), 61 (12), 51 (12). HRMS (ESI): *m/z* calcd for $C_{14}H_{15}NCl_2$+H: 268.0660; found: 268.0587. IR (ATR): 1489, 1443 (C=C), 1375, 1290 (CH=CH$_2$) cm^{-1}.

4.5.10. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)ethylamine (5af). Yield: 88 mg (68%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (t, *J*=7.1 Hz, 3H, CH_2CH_3), 2.19 (s, 3H, CH_3CCl_2), 2.60 and 2.80 (2×dq, *J*=11.5, 7.2 Hz, 2H, CH_2CH_3), 3.46 (d, *J*=8.9 Hz, 1H, C*H*NH), 6.12 (dd, *J*=15.9, 8.5 Hz, 1H, C*H*=CHPh), 6.58 (d, *J*=15.9 Hz, 1H, CH=C*H*Ph), 7.25–7.46 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$, assignment by HMQC and HMBC): δ=15.2 (CH_2CH_3), 34.8 (CH_3CCl_2), 41.8 (CH_2CH_3), 72.8 (CHNH), 93.0 (CCl_2), 126.5 (*C*H=CHPh), 126.6 ($HC_{arom.meta}$), 128.0 ($HC_{arom.para}$), 128.7 ($HC_{arom.ortho}$), 134.9 (CH=*C*HPh), 136.3 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=261 (0.03) [M$^+$+4], 259 (0.05) [M$^+$+2], 257 (0.03) [M$^+$], 224 (0.22), 222 (2), 187 (15), 162 (38), 161 (100), 144 (16), 141 (18), 130 (23), 117 (18), 115 (59), 105 (20), 91 (31), 82 (17), 77 (20). HRMS (ESI): *m/z*

calcd for $C_{13}H_{17}NCl_2$+H: 258.0816; found: 258.0766. IR (NaCl): 3323 (NH), 1494, 1448 (C=C) cm^{-1}.

4.5.11. *N*-(4,4-Dichloro-1-(3-methoxyphenyl)pent-1-yne-3-yl)propylamine (5hd). Yield: 132 mg (88%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.97 (t, J=7.4 Hz, 3H, $NHCH_2CH_2CH_3$), 1.49–1.67 (m, 2H, $NHCH_2CH_2CH_3$), 2.28 (s, 3H, CH_3CCl_2), 2.66–2.76 and 2.92–3.02 (2×m, 2H, $NHCH_2CH_2CH_3$), 3.79 (s, 3H, OMe), 3.90 (s, 1H, CCl_2CH), 6.87 (ddd, J=8.3, 2.6, 1.0 Hz, 1H, $CH_{arom.}$ $C_{arom.quat.}$OMe), 6.98 (dd, J=1.9, 1.9 Hz, 1H, $C_{arom.quat.}$ $CH_{arom.}C_{arom.quat.}$), 7.06 (ddd, J=7.6, 1.2, 1.2 Hz, 1H, $C{\equiv}CC_{arom.quat.}CH_{arom}$), 7.22 (dd, J=7.9, 7.9 Hz, 1H, $C_{arom.quat.}CH_{arom.}CH_{arom.}CH_{arom.}C_{arom.quat.}$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.7 ($NHCH_2CH_2CH_3$), 23.0 ($NHCH_2CH_2CH_3$), 34.2 (CH_3CCl_2), 50.2 ($NHCH_2$), 55.3 (OMe), 64.2 (CCl_2CH), 85.8 ($C{\equiv}CC_{arom.quat.}$), 86.2 ($C{\equiv}CC_{arom.quat.}$), 91.3 (CCl_2), 115.0 ($C_{arom.quat.}CH_{arom.}$ $C_{arom.quat.}$), 116.7 ($MeOC_{arom.quat.}CH_{arom.}$), 123.5 ($C{\equiv}$ $CC_{arom.quat.}$), 124.3 ($C{\equiv}CC_{arom.quat.}CH_{arom.}$), 129.4 (MeO-$C_{arom.quat.}CH_{arom.}CH_{arom.}$), 159.3 ($C_{arom.quat.}$OMe). MS (EI, 70 eV): m/z (%)=303 (0.2) $[M+4]^+$, 301 (0.5) $[M+2]^+$, 299 (0.3) $[M^+]$, 206 (27), 203 (100), 171 (22), 161 (20), 160 (43), 159 (21), 158 (22), 145 (30), 133 (22), 128 (32), 127 (27), 117 (25), 115 (32), 102 (29), 101 (29), 89 (22). HRMS (ESI): m/z calcd for $C_{15}H_{20}NOCl_2$+H: 300.0922; found: 300.0856. IR (ATR): 3294 (NH), 1597, 1574, 1488, 1480, 1463, 1426 (C=C) cm^{-1}.

4.5.12. *N*-(4,4-Dichloro-1-(4-ethylphenyl)pent-1-yne-3-yl)propylamine (5id). Yield: 134 mg (90%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.96 (t, J=7.4 Hz, 3H, $NHCH_2CH_2CH_3$), 1.21 (t, J=7.6 Hz, 3H, CH_2CH_3), 1.49–1.65 (m, 2H, $NHCH_2CH_2CH_3$), 2.28 (s, 3H, CH_3CCl_2), 2.63 (q, J=7.6 Hz, 2H, CH_2CH_3), 2.66–2.76 and 2.92–3.02 (2×m, 2H, $NHCH_2CH_2CH_3$), 3.90 (s, 1H, CCl_2CH), 7.13 (d, J=8.2 Hz, 2H, $CH_3CH_2C_{arom.quat.}(CH_{arom.})_2$), 7.38 (d, J=8.2 Hz, 2H, $C{\equiv}CC_{arom.quat.}(CH_{arom.})_2$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.7 ($NHCH_2CH_2CH_3$), 15.4 (CH_2CH_3), 23.0 ($NHCH_2CH_2CH_3$), 28.8 (CH_2CH_3), 34.2 (CH_3CCl_2), 50.2 ($NHCH_2$), 64.3 (CCl_2CH), 85.6 ($C{\equiv}$ $CC_{arom.quat.}$), 86.0 ($C{\equiv}CC_{arom.quat.}$), 91.4 (CCl_2), 119.7 ($C{\equiv}CC_{arom.quat.}$), 127.9 ($CH_3CH_2C_{arom.quat.}(C_{arom.})_2$), 131.8 ($C{\equiv}CC_{arom.quat.}(C_{arom.})_2$), 145.0 ($C_{arom.quat.}$Et). MS (EI, 70 eV): m/z (%)=301 (0.07) $[M+4]^+$, 299 (0.15) $[M+2]^+$, 297 (0.13) $[M^+]$, 239 (22), 201 (100), 189 (30), 159 (23), 158 (61), 156 (28), 154 (26), 153 (29), 152 (29), 143 (33), 142 (28), 141 (31), 139 (29), 131 (27), 129 (25), 128 (31), 127 (29), 116 (22), 115 (48), 103 (28), 97 (20), 93 (25), 91 (25), 77 (27), 63 (22). HRMS (ESI): m/z calcd for $C_{16}H_{22}NCl_2$+H: 298.1129; found: 298.1105. IR (ATR): 3317 (NH); 2360, 2335 (C≡C); 1509 and 1457 (C=C) cm^{-1}.

4.5.13. *N*-(5,5-Dichloro-1-methoxy-2-hexyne-4-yl)propylamine (5jd). Yield: 53 mg (44%), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=0.95 (t, J=7.4 Hz, 3H, $NHCH_2CH_2CH_3$), 1.46–1.62 (m, 2H, $NHCH_2CH_2CH_3$), 2.23 (s, 3H, CH_3CCl_2), 2.59–2.69 and 2.86–2.96 (2×m, 2H, $NHCH_2$), 3.40 (s, 3H, OMe), 3.74 (t, J=1.7 Hz, 1H, CCl_2CH), 4.18 (d, J=1.7 Hz, 2H, CH_2OMe). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=11.7 ($NHCH_2CH_2CH_3$), 23.0 ($NHCH_2CH_2CH_3$), 34.1 (CH_3CCl_2), 50.1 ($NHCH_2$), 57.6 (CCl_2CH), 59.9 (CH_2OMe), 63.8 (OMe), 81.6 and 83.5 (C≡C), 91.1 (CCl_2). MS (EI, 70 eV): m/z (%)=242 (0.4) $[M+5]^+$, 240 (2.7) $[M+3]^+$, 238 (4) $[M^+$+1], 210 (16), 208 (22), 202 (20), 140 (100), 111 (32), 110 (32), 109 (34), 108 (61), 97 (38), 96 (37), 94 (35), 93 (39), 82 (38), 81 (39), 80 (40), 79 (42), 77 (46), 71 (53), 68 (36), 65 (39), 55 (32), 53 (36), 51 (38). HRMS (ESI): m/z calcd for $C_{10}H_{18}NCl_2O$+H: 238.0765; found: 238.0758. IR (ATR): 3343 (NH) cm^{-1}.

4.5.14. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)-*N*-(difluoroboryl)ethylamine (8). Because of the impurities present in this labile reaction mixture only following signals could be distinguished in the spectra. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.31 (t, J=7.2 Hz, 3H, CH_2CH_3), 2.20 (s, 3H, CH_3CCl_2), 2.95 and 3.19 (2×dq, J=12.2, 7.2 Hz, 2H, CH_2CH_3), 3.87 (d, J=9.1 Hz, 1H, CHNH), 6.20 (dd, J=15.8, 9.1 Hz, 1H, CH=CHPh), 6.76 (d, J=15.8 Hz, 1H, CH=CHPh), 7.24–7.60 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$, assignment by HMQC): δ=13.2 (CH_2CH_3), 34.7 (CH_3CCl_2), 42.4 (CH_2CH_3), 72.6 (CHNH), 90.2 (CCl_2), 121.7 (CH=CHPh), 127.0 ($HC_{arom.meta}$), 128.6 ($HC_{arom.para}$), 128.8 ($HC_{arom.ortho}$), 138.6 (CH=CHPh). $C_{arom.quat.}$ could not be unambiguously assigned because of interfering signals. ^{11}B NMR (160.5 MHz, $CDCl_3$, $BF_3{\cdot}OEt_2$ external standard): δ=0.7 (s). ^{19}F NMR (235.3 MHz, $CDCl_3$): δ=−131.9 (s).

4.5.15. *N*-(4,4-Dichloro-1-(4-methylphenyl)pent-1-ene-3-yl)ethylamine (5bf). Yield: 63 mg (46%, without HFIP), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.13 (t, J=7.1 Hz, 3H, CH_2CH_3), 2.17 (s, 3H, CH_3CCl_2), 2.34 (s, 3H, $C_{arom.quat.}$–CH_3), 2.59 and 2.80 (2×dq, J=11.5, 7.2 Hz, 2H, CH_2CH_3), 3.44 (d, J=8.6 Hz, 1H, CHNH), 6.06 (dd, J=15.9, 8.6 Hz, 1H, $CH{=}CHC_6H_4$), 6.54 (d, J=15.9 Hz, 1H, $CH{=}CHC_6H_4$), 7.14 and 7.32 (2×d, J=8.1 Hz, 4H, C_6H_4). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=15.2 (CH_2CH_3), 21.2 ($C_{arom.quat.}CH_3$), 34.9 (CH_3CCl_2), 41.8 (CH_2CH_3), 72.9 (CHNH), 93.1 (CCl_2), 125.4 ($CH{=}CHC_6H_4$), 126.5 and 129.3 ($HC_{arom.ortho+meta}$), 133.5 ($C_{arom.quat.}CH_3$), 134.8 ($CH{=}CHC_6H_4$), 137.9 ($CH{=}CHC_{arom.quat.}$). MS (EI, 70 eV): m/z (%)=275 (0.02) $[M+4]^+$, 273 (0.03) $[M+2]^+$, 271 (0.05) $[M^+]$, 238 (0.2), 236 (1), 200 (16), 175 (100), 157 (11), 156 (11), 144 (17), 142 (16), 141 (18), 130 (12), 129 (24), 128 (20), 119 (37), 115 (28), 105 (13), 91 (18), 82 (26). HRMS (ESI): m/z calcd for $C_{14}H_{19}NCl_2$+H: 272.0973; found: 272.0980. IR (ATR): 3322 (NH), 1513, 1443 (C=C), 1377 (HC=CH) cm^{-1}.

4.5.16. *N*-(4,4-Dichloro-1-(4-chlorophenyl)pent-1-ene-3-yl)ethylamine (5cf). Yield: 24 mg (16%, without HFIP), yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.13 (t, J=7.1 Hz, 3H, CH_2CH_3), 2.18 (s, 3H, CH_3CCl_2), 2.59 and 2.79 (2×dq, J=11.6, 7.1 Hz, 2H, CH_2CH_3), 3.44 (d, J=8.5 Hz, 1H, CHNH), 6.10 (dd, J=15.9, 8.5 Hz, 1H, $CH{=}CHC_6H_4$), 6.53 (d, J=15.9 Hz, 1H, $CH{=}CHC_6H_4$), 7.26–7.37 (m, 4H, C_6H_4). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=15.2 (CH_2CH_3), 34.8 (CH_3CCl_2), 41.9 (CH_2CH_3), 72.7 (CHNH), 92.8 (CCl_2), 124.9 ($CH{=}CC_{arom.quat.}$), 127.2 ($CH{=}CHC_6H_4$), 127.8 and 128.9 ($HC_{arom.ortho+meta}$), 133.6 ($CH{=}CHC_6H_4$), 134.7 ($C_{arom.quat.}$–Cl). MS (EI, 70 eV): m/z (%)=297 (trace) $[M+6]^+$, 295 (0.01) $[M+4]^+$, 293 (0.01) $[M+2]^+$, 291 (0.01) $[M^+]$, 258 (0.46), 256 (1),

220 (10), 196 (64), 194 (100), 164 (10), 149 (15), 141 (21), 139 (21), 130 (11), 125 (11), 115 (20), 82 (13). HRMS: *m/z* calcd for $C_{13}H_{16}NCl_3$+H: 292.0427; found: 292.0320. IR (ATR): 3306 (NH), 1490, 1444 (C=C), 1378 (HC=CH) cm^{-1}.

4.5.17. (*Z*)-*N*-(5,5-Dichloro-2-hexene-4-yl)ethylamine (5ef). Yield: 23 mg (17%, without HFIP, 0.7 mmol), yellow oil. R_f=0.22 (Et_2O/pentane, 1:9). ^1H NMR (250 MHz, $CDCl_3$): δ=1.12 (t, J=7.1 Hz, 3H, CH_2CH_3), 1.73 (dd, J=6.8, 1.7 Hz, 3H, CH=CHCH_3), 2.15 (s, 3H, CH_3CCl_2), 2.56 and 2.75 (2×dq, J=11.4, 7.2 Hz, 2H, CH_2CH_3), 3.72 (dd, J=9.5, 0.7 Hz, 1H, C*H*NH), 5.35 (ddq, J=11.1, 9.5, 1.7 Hz, 1H, C*H*=CHCH$_3$), 5.85 (dq, J=11.1, 6.8 Hz, 1H, CH=C*H*CH$_3$). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ= 13.9 (CH_2CH_3), 15.3 (CH_2CH_3), 34.4 (CH=CHCH_3), 41.7 (CH_3CCl_2), 65.7 (CHNH), 93.7 (CCl_2), 128.1 (*C*H=CHCH$_3$), 129.7 (CH=*C*HCH$_3$). MS (EI, 70 eV): *m/z* (%)=200 (0.01) $[M+5]^+$, 198 (0.16) $[M+3]^+$, 196 (0.26) $[M+H^+]$, 162 (1), 160 (4), 125 (2), 124 (16), 99 (28), 98 (100), 96 (18), 82 (13), 81 (21), 79 (31), 77 (19), 70 (37), 69 (18), 68 (24), 61 (11), 56 (26), 55 (15), 53 (22). HRMS (ESI): (*m/z*) calcd for $C_8H_{15}N^{37}Cl^{35}Cl$: 198.0630; found: 198.0712. IR (ATR): 3335 (NH), 1445 (HC=CH) cm^{-1}.

4.5.18. *N*-(4,4-Dichloro-1-phenylpent-1-yne-3-yl)ethylamine (5gf). Yield: 102 mg (80%), yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ=1.19 (t, J=7.1 Hz, 3H, CH_2CH_3), 2.29 (s, 3H, CH_3CCl_2), 2.85 and 3.02 (2×dq, J=11.4, 7.1 Hz, 2H, CH_2CH_3), 3.93 (s, 1H, C*H*NH), 7.23–7.33 (m, 3H, $CH_{arom.meta+para}$), 7.45–7.48 (m, 2H, $CH_{arom.ortho}$). ^{13}C NMR (62.90 MHz, $CDCl_3$, assignment by HMQC, HMBC, and COSY): δ=15.5 (CH_2CH_3), 34.7 (CH_3CCl_2), 43.0 (CH_2CH_3), 64.5 (CHNH), 86.3 and 86.6 (C≡C), 91.6 (CCl_2), 122.9 ($C_{arom.quat.}$), 128.7 ($HC_{arom.meta}$), 128.9 ($HC_{arom.para}$), 132.2 ($HC_{arom.ortho}$). MS (EI, 70 eV): *m/z* (%)=260 (trace) $[M+5]^+$, 258 (0.06) $[M+3]^+$, 256 (0.21) $[M+H^+]$, 175 (10), 158 (100), 141 (29), 139 (25), 130 (43), 128 (54), 115 (59), 113 (17), 103 (69), 99 (13), 97 (15), 91 (12), 89 (10), 77 (40), 75 (11), 74 (13), 63 (26), 61 (13), 56 (13), 51 (19). HRMS (ESI): *m/z* calcd for $C_{13}H_{15}NCl_2$+H: 256.0660; found: 256.0538. IR (ATR): 1374, 1291 (C=C aromate) cm^{-1}.

4.5.19. *N*-(4,4-Dichloro-1-phenylpent-1-ene-3-yl)methylamine (5ag). Yield: 84 mg (69%), yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ=2.26 (s, 3H, NHCH_3), 2.47 (s, 3H, s, CH_3CCl_2), 3.34 (d, J=8.6 Hz, 1H, C*H*NH), 6.09 (dd, J=15.9, 8.6 Hz, 1H, C*H*=CHPh), 6.61 (d, J=15.9 Hz, 1H, CH=C*H*Ph), 7.22–7.47 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=34.4 ($NHCH_3$), 34.9 (CH_3CCl_2), 75.0 (CHNH), 92.7 (CCl_2), 125.6 (*C*H=CHPh), 128.1 ($HC_{arom.para}$), 126.6 and 128.7 ($HC_{arom.ortho+meta}$), 135.7 (CH=*C*HPh), 136.1 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=247 (0.02) $[M+4]^+$, 245 (0.03) $[M+2]^+$, 243 (0.02) $[M^+]$, 172 (16), 148 (32), 146 (100), 145 (14), 141 (12), 131 (11), 130 (12), 128 (19), 117 (12), 115 (58), 91 (57), 77 (16), 68 (15), 51 (12). IR (ATR): 1494, 1448 (aromate), 1376 (HC=CH) cm^{-1}.

4.5.20. *N*-(4,4-Dichloro-1-phenylhex-1-ene-3-yl)ethylamine (11af). Yield: 45 mg (33%, under reflux), yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ=1.13 (t, J=7.1 Hz, 3H, $CCl_2CH_2CH_3$), 1.21 (t, J=7.2 Hz, 3H, $NHCH_2CH_3$), 1.83 (s, 1H, NH), 2.34 (q, J=7.2 Hz, 2H, $NHCH_2$), 2.58 and 2.81 (2×qd, J=11.4, 7.1 Hz, 2H, CH_2CCl_2), 3.48 (d, J=8.6 Hz, 1H, C*H*NH), 6.15 (dd, J=15.9, 8.6 Hz, 1H, C*H*=CHPh), 6.55 (d, J=15.9 Hz, 1H, CH=C*H*Ph); 7.19–7.50 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=9.3 ($CH_3CH_2CCl_2$), 15.2 ($NHCH_2CH_3$), 38.5 ($CH_3CH_2CCl_2$), 41.6 ($NHCH_2CH_3$), 71.3 (CHNH), 99.0 (CCl_2), 126.4 (*C*H=CHPh), 128.0 ($HC_{arom.para}$), 126.6 and 128.7 ($HC_{arom.ortho+meta}$), 134.5 (CH=*C*HPh), 136.3 ($C_{arom.quat.}$). MS (EI, 70 eV): *m/z* (%)=275 (0.01) $[M+4]^+$, 273 (0.03) $[M+2]^+$, 271 (0.02) $[M^+]$, 200 (7), 162 (23), 160 (100), 141 (7), 130 (10), 129 (8), 128 (11), 127 (7), 117 (9), 115 (34), 105 (15), 91 (17), 82 (9), 77 (14), 75 (8). HRMS (ESI): *m/z* calcd for $C_{14}H_{19}NCl_2$+H: 272.0973; found: 272.1038. IR (ATR): 3321 (NH), 1494, 1449 (C=C), 1379 (HC=CH) cm^{-1}.

4.5.21. *N*-(4,4-Dichloro-1-phenylhex-1-ene-3-yl)allylamine (11ae). Yield: 71 mg (50%, under reflux), yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ=1.21 (t, J=7.2 Hz, 3H, CH_3), 1.66 (s, 1H, NH), 2.35 (q, J=7.2 Hz, 2H, CH_2CCl_2), 3.20 (dd, J=14.1, 6.9 Hz, 1H, (H)C*H*CH=CH_2), 3.43 (dd, J=14.1, 5.0 Hz, 1H, (*H*)CHCH=CH_2), 3.53 (d, J=8.7 Hz, 1H, C*H*NH), 5.11–5.25 (m, 2H, $CH_2CH=CH_2$), 5.81–5.97 (m, 1H, $CH_2CH=CH_2$), 6.14 (dd, J=15.9, 8.7 Hz, 1H, C*H*=CHPh), 6.54 (d, J=15.9 Hz, 1H, CH=C*H*Ph), 7.25–7.45 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=9.3 (CH_3), 38.5 (CH_3CH_2), 49.5 ($CH_2CH=CH_2$), 70.1 (CHNH), 99.0 (CCl_2), 116.6 ($CH_2CH=CH_2$), 125.9 (*C*H=CHPh), 128.0 ($HC_{arom.para}$), 126.6 and 128.7 ($HC_{arom.ortho+meta}$), 134.9 (CH=*C*HPh), 136.3 ($C_{arom.quat.}$), 136.6 ($CH_2CH=CH_2$). MS (EI, 70 eV): *m/z* (%)=287 (0.03) $[M+4]^+$, 285 (0.06) $[M+2]^+$, 283 (0.04) $[M^+]$, 212 (12), 172 (100), 170 (17), 157 (13), 156 (12), 144 (12), 141 (19), 131 (29), 130 (29), 129 (29), 127 (21), 118 (24), 117 (16), 115 (52), 105 (12), 103 (16), 102 (15), 94 (14), 91 (51), 77 (38), 75 (20), 65 (12), 54 (12), 51 (18). HRMS (ESI): (*m/z*) calcd for $C_{15}H_{19}N^{37}Cl^{35}Cl$: 286.0943; found: 286.0989. IR (ATR): 3332 (NH), 1494, 1448 (C=C), 1335, 1292 (HC=CH and CH=CH_2) cm^{-1}.

4.5.22. *N*-(4,4-Dichloro-1-phenyl-5-methylhex-1-ene-3-yl)allylamine (12ae). Yield: 41 mg (28%, pressure tube), yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ=1.16 and 1.37 (2×d, J=6.4 Hz, 2×3H, $CH(CH_3)_2$), 1.64 (s, 1H, NH), 2.66 (septet, J=6.4 Hz, 1H, C*H*$(CH_3)_2$), 3.18 (dd, J=13.9, 7.0 Hz, 1H, (H)C*H*CH=CH_2), 3.42 (dd, J=13.9, 5.1 Hz, 1H, (*H*)CHCH=CH_2), 3.59 (d, J=8.7 Hz, 1H, C*H*NH), 5.11–5.24 (m, 2H, $CH_2CH=CH_2$), 5.77–5.97 (m, 1H, $CH_2CH=CH_2$), 6.16 (dd, J=15.9, 8.7 Hz, 1H, C*H*=CHPh), 6.51 (d, J=15.9 Hz, 1H, CH=C*H*Ph), 7.24–7.45 (m, 5H, Ph). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ=18.1 ($CH(CH_3)_2$), 39.9 ($CH(CH_3)_2$), 49.3 ($CH_2CH=CH_2$), 68.1 (CHNH), 104.0 (CCl_2), 116.7 ($CH_2CH=CH_2$), 125.8 (*C*H=CHPh), 128.0 ($HC_{arom.para}$), 126.6 and 128.6 ($HC_{arom.ortho+meta}$), 134.5 (CH=*C*HPh), 136.3 ($C_{arom.quat.}$), 136.6 ($CH_2CH=CH_2$). MS (EI, 70 eV): *m/z* (%)=301 (trace) $[M+4]^+$, 299 (trace) $[M+2]^+$, 297 (trace) $[M^+]$, 172 (100), 144 (14), 131 (21), 130 (23), 129 (20), 127 (19), 118 (19), 117 (15), 115 (53), 106 (11), 104 (12), 91 (51), 89 (12), 77 (27), 52 (20). HRMS (ESI): *m/z* calcd for $C_{16}H_{21}NCl_2$+H: 298.1129; found: 298.0971. IR (ATR): 3318 (NH), 1495,

1448 (C=C aromate), 1386, 1367 (HC=CH and $CH=CH_2$) cm^{-1}.

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