Synthesis of Allylamines from Alkynes and Iminium Ions

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Dedicated to Professor Wolfgang Steglich on the occasion of his 70th birthday.

Abstract: The iminium salt $Bn_2N^+=CH_2$ $SnCl_5^-$ undergoes ene reactions with inverse electron demand with alkynes and with the triple bond of enynes to give benzylideneammonium ions in aprotic solvents. Their hydrolysis yields *N*-benzylallylamines in good yields. Mannich reaction products, which are the main products under more nucleophilic reaction conditions, have not been detected.

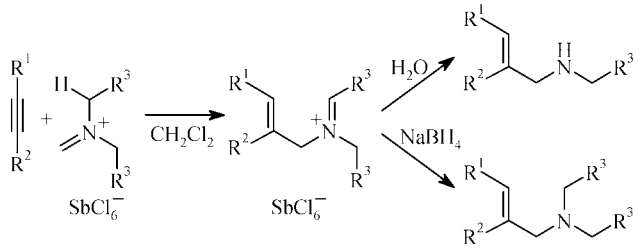
Key words: electrophilic additions, ene reactions, enynes, pericyclic reactions

Introduction

Allylamines are versatile building blocks for the synthesis of numerous organic compounds. Their synthesis via electrophilic aminations of non-functionalized alkenes having allylic C–H bonds is particularly attractive because the allylic functionality is readily introduced in one step.[2] Apart from metal-catalyzed electrophilic aminations with nitrenes and ArNHX compounds, the ene reactions of alkenes with aza enophiles[3] have been employed for the synthesis of allylamines.[4] However, highly reactive aza enophiles usually carry activating substituents which have to be removed from the initially formed ene products in additional reaction steps.[5]

Previously, only ene reactions with normal electron demand have been employed for the synthesis of allylamines.[2] However, interchanging the roles of ene and enophile is possible,[6] and recently a stereoselective synthesis of allylic amines by ene reactions of alkynes with preformed iminium salts has been reported that proceeds with inverse electron demand (Scheme 1).[7] Hydrolytic workup of the reaction mixture gave secondary allylamines, while reductive workup yielded tertiary allylamines.

Following the previously described protocol (Scheme 1), only activated alkynes could be converted into the corresponding ene products, mainly because of the poor solubility of the iminium hexachloroantimonates which resulted in low effective concentrations of the iminium ions in the biphasic reaction mixtures. Furthermore, the original method produced only allylamines carrying *N*-alkyl groups, which cannot easily be exchanged. Related syntheses of allylamines have also been described.[8–10]

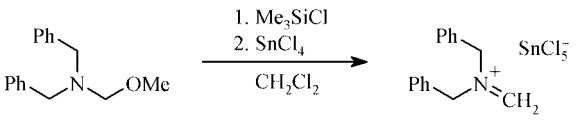


Scheme 1 Ene reaction of alkynes with iminium ions

We now report that the synthetic value of this method can greatly be enhanced by employing *N*,*N*-dibenzyliminium pentachlorostannates which give rise to a variety of *N*-benzyl protected allylamines.

Results

When solutions of the readily accessible *N*,*O*-acetal **1**[11,12] in dichloromethane or 1,2-dichloroethane were treated with 1 equivalent of chlorotrimethylsilane and 1 equivalent of tin(IV) chloride (Equation 1), a colorless precipitate formed which was separated by filtration. This precipitate dissolved in acetonitrile and was characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy.[13] The resonances for the $N^+=CH_2$ group[14] at $\delta_H = 7.95$ and $\delta_C = 169.7$ which showed couplings to ^{14}N ($I = 1$) were consistent with the structure of *N*,*N*-dibenzylmethyleneammonium pentachlorostannate **2**.[15]



1 **2**

Equation 1 Generation of iminium salt **2**

For the ene reactions (Scheme 2), usually 1–3 equivalents of the alkyne **3** were added to suspensions of **2** in dichloromethane or 1,2-dichloroethane freshly prepared from equimolar amounts of the *N*,*O*-acetal **1**, chlorotrimethylsilane and tin(IV) chloride. The suspension was stirred at 25–83 °C (see Table 1) until the complete dissolution of **2** was observed. Hydrolytic workup of the resulting *N*-benzyl-*N*-allylalkylidene ammonium salts **4** with 2 M NaOH

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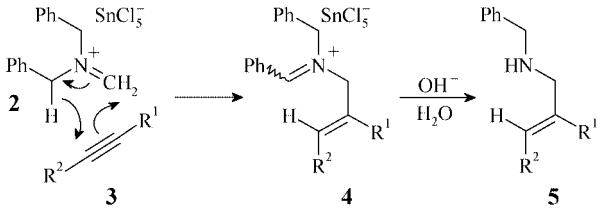


Scheme 2

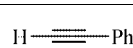
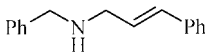
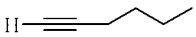
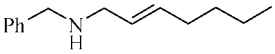
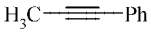
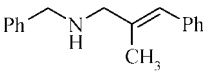
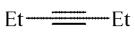
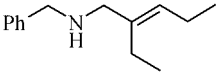
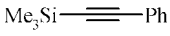
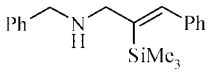
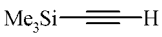
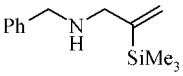
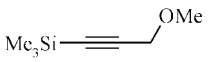
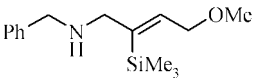
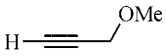
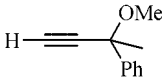
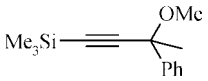
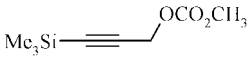
and distillation of the crude product gave the *N*-benzyl substituted allylamines **5**.

The higher solubility of the *N*,*N*-dibenzyliminium pentachlorostannate (**2**) compared with the previously used *N*,*N*-dialkyliminium hexachloroantimonates gave rise to higher effective concentrations of the ene component in the reaction mixtures. As a consequence, the reaction of phenyl(trimethylsilyl)acetylene (**3e**) with $Et_2N^+{=}CH_2$ $SbCl_6^-$ was reported[7] to proceed within 19 hours whereas the reaction of **3e** with $Bn_2N^+{=}CH_2$ $SnCl_5^-$ (**2**) was now found to be complete within 3 hours under analogous conditions (25 °C, CH_2Cl_2).

Terminal as well as internal alkynes **3a–f** gave secondary amines **5a–f** in 57–83% yield (Table 1).

The silylated propargyl ether **3g** gave product **5g** in 72% yield within 3 hours at 75 °C, whereas corresponding products of the propargyl ethers **3h–j** could not be obtained analogously.

Table 1 Products **5** of the Ene Reactions of Iminium Salt **2** with Alkynes **3a–k** in 1,2-Dichloroethane

Alkyne	$R^1C{\equiv}CR^2$	Temp (°C)	Time (h)	Product		Yield (%)
3a		25	24		**5a**	73[a]
3a		83	0.75		**5a**	75
3b		75	8		**5b**	71
3c		83	1.5		**5c**	83
3d		75	8		**5d**	57
3e		25	3		**5e**	76[a]
3f		75	5		**5f**	66
3g		75	3		**5g**	72
3h		75	24	–[b]	**5h**	–
3i		83	2	–[c]	**5i**	–
3j		83	2	–[c]	**5j**	–
3k		25	120	–[b]	**5k**	0[a]

[a] In CH_2Cl_2.
[b] No reaction, starting materials were recovered.
[c] Decomposition.

When propargyl methyl ether (**3h**) was heated with the iminium salt **2** in 1,2-dichloroethane in a pressure tube at 75 °C for 24 hours, compound **3h** and dibenzylamine were isolated after hydrolytic workup indicating the lower reactivity of **3h** compared to **3g**. Iminium salt **2** dissolved within 2 hours when heated with the tertiary propargyl ethers **3i** or **3j** in 1,2-dichloroethane at 83 °C and yielded red solutions that did not decolorize during hydrolysis. NMR analysis of the crude products showed the presence of complex mixtures of compounds which are probably formed via Lewis acid induced ionization of **3i** and **3j**.

Table 2 demonstrates that the conjugated enynes **3l**–**n** also underwent imino ene reactions at the CC triple bond and yielded the dienylamines **5l**–**n** under analogous conditions as discussed before. Attack at the CC double bond could not be detected in any of these cases.

The NMR resonances of the allylamines **5a**–**g** and the conjugated dienylamines **5l**–**m** are summarized in Tables 3 and 4, respectively. For further analytical data, see the Experimental section.

Discussion

As already described by Mannich in the 1930s,[16] the reaction of terminal alkynes with iminium ions generated in situ from formaldehyde and secondary amines usually yields propargyl amines (Equation 2).[17] These reaction conditions are comparable to those of the well known Mannich aminomethylations of other CH acidic compounds, e.g., enolizable carbonyl and dicarbonyl compounds, which are among the most important CC bond forming reactions.[18]

$$R–C{\equiv}C–H + H_2CO + HNR'_2 \rightarrow R–C{\equiv}C–CH_2–NR'_2$$

Equation 2

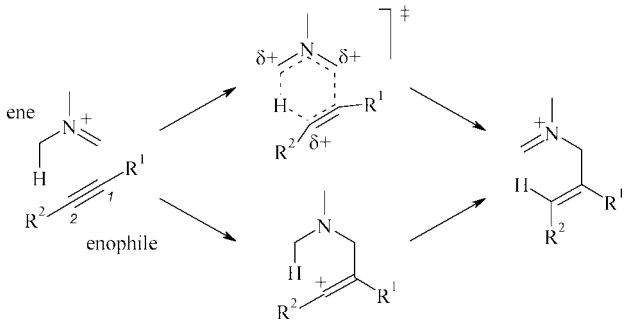
In contrast to the reactions under Mannich conditions and in analogy to previous experiments with *N*,*N*-diethyliminium hexachloroantimonates[7] we now find that also *N*,*N*-dibenzylmethyleneammonium pentachlorostannate (**2**) is capable of undergoing ene reactions with alkynes when a solvent of low nucleophilicity is used.

The formation of the allylamines **5b**, **5c**, **5d**, and **5f** from the alkynes **3b**–**d**,**f** and the iminium salt **2** exemplifies the enhanced synthetic potential of this procedure since reactions of hex-1-yne (**3b**), 1-phenylpropyne (**3c**), hex-3-yne (**3d**), and trimethylsilylacetylene (**3f**) with $Et_2N^+{=}CH_2$ $SbCl_6^-$ have previously not been reported.

Stereoselectivity

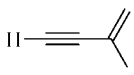
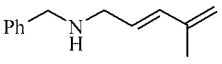
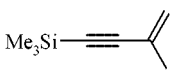
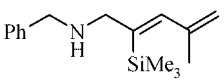
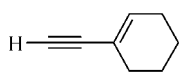
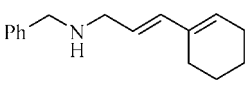
The NMR spectra of the isolated iminium salts **4**[19] and of the allylamines **5** reveal that R^1 and R^2 of the former substituents of the CC triple bond are exclusively *cis* positioned at the new CC double bond, in accord with previous results.[7]

Since concerted as well as stepwise ene reactions give rise to products with the substituents R^1 and R^2 in *cis* position (Scheme 3), the *syn*-stereoselectivity does not provide information on the reaction mechanism.



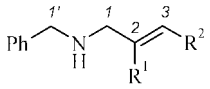
Scheme 3

Table 2 Products **5l**–**n** of the Ene Reactions of Iminium Salt **2** with Enynes **3l**–**n**

Enyne	$R^1C{\equiv}CR^2$	Temp (°C)	Time (h)	Product		Yield (%)
3l		83	2		**5l**	68[a]
3m		25	20		**5m**	86[b,c]
3n		25	0.5		**5n**	72[b]

[a] In 1,2-dichloroethane.
[b] In dichloromethane.
[c] Only 1.2 equiv of enophile **3m** was used.

Table 3 ^{1}H and ^{13}C NMR Chemical Shifts (δ), and Coupling Constants (*J* in Hz) of Allylamines **5a**–**g** in $CDCl_3$



Product	1′-H	NH	1-H	R^1	3-H	Other H	C-1′	C-1	R^1	C-3	Other C
5a	3.80	2.60	3.39 (dd, *J* = 6.4, 1.3)	6.28 (dt, *J* = 15.9, 6.3)	6.51 (d, *J* = 15.9)	7.16–7.39 (m, 10 H)	52.9 (t)	50.8 (t)	–	131.8 (d)	126.2, 127.0, 127.3, 127.6, 128.2, 128.36, 128.43 (7 d), 136.9, 139.4 (2 s)
5b	3.75	2.09	3.19 (d, *J* = 4.8)	5.47–5.63 (m, 2 H)		0.88 (t, *J* = 7.1, 3 H), 1.24–1.37 (m, 4 H), 1.98–2.05 (m, 2 H), 7.17–7.38 (m, 5 H)	52.9 (t)	50.8 (t)	–	–[a]	13.8 (q), 22.0 (t), 31.3 (t), 31.9 (t), 126.7, 127.7, 128.1, 128.2, 133.0 (5 d), 139.9 (s)
5c	3.79	2.89	3.31 (d, *J* = 1.0)	1.88 (d, 3 H, *J* = 1.4, CH_3)	6.45 (s)	7.02–7.40 (m, 10 H)	52.7 (t)	57.1 (t)	16.5 (q)	126.1 (d)	126.1, 126.9, 127.9, 128.1, 128.2, 128.7 (6 d), 136.4, 137.8, 139.8 (3 s)
5d	3.72	1.64	3.16 (d, *J* = 1.0)	–[b]	5.28 (t, *J* = 7.2)	0.96 (t, 3 H, *J* = 7.6), 0.97 (t, 3 H, *J* = 7.7), 2.07 (m_c, 4 H), 7.16–7.33 (m, 5 H)	53.0 (t)	54.3 (t)	–[a]	127.6 (d)	13.3, 14.5 (2 q), 20.6, 21.8 (2 t), 126.6, 128.0, 128.2 (3 d), 138.4, 140.5 (2 s)
5e	3.92	2.50	3.55 (d, *J* = 1.5)	0.08 [s, 9 H, $Si(CH_3)_3$]	–[b]	7.28–7.47 (m, 11 H)	53.0 (t)	56.8 (t)	0.3 (q)	142.1 (d)	126.8, 126.9, 127.7, 128.2, 128.3, 128.4 (6 d), 140.00, 140.03, 142.6 (3 s)
5f	3.88	1.60	3.50 (m)	0.25 [s, 9 H, $Si(CH_3)_3$]	5.54, 5.87 (2 m_c)	7.13–7.61 (m, 5 H)	53.3 (t)	54.5 (t)	–1.6 (q)	123.9 (t)	126.6, 127.9, 128.1 (3 d), 140.0, 140.4 (2 s)
5g	3.83	1.80	3.40 (s)	0.28 [s, 9 H, $Si(CH_3)_3$]	6.33 (t, *J* = 6.5)	3.42 (s, 3 H), 4.10 (d, 2 H, *J* = 6.5), 7.29–7.45 (m, 5 H)	53.2 (t)	56.6 (t)	0.0 (q)	139.1 (d)	58.0 (q), 71.4 (t), 126.7, 128.1, 128.2 (3 d), 140.4, 142.2 (2 s)

[a] For relevant signals, see the column 'other C'.
[b] For relevant signals, see the column 'other H'.

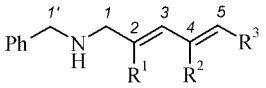
Structure Reactivity Relationships

The regioselectivities of the ene reactions in this work can be rationalized when one assumes that C-2 of the triple bond carries a partial positive charge in the transition state of the ene reaction (Scheme 3).

Electron-donating substituents R^2 (alkyl or phenyl) stabilize the transition state. Since phenyl stabilizes positive charge better than alkyl, the ene reaction of phenylacetylene (**3a**) proceeds faster than the analogous reaction with hex-1-yne (**3b**) (Table 1).

The β-silyl effect[20] offers another possibility to stabilize the transition state as demonstrated by the reaction of phenyl(trimethylsilyl)acetylene (**3e**) which yields amine **5e** in 76% yield within 3 hours at ambient temperature while the corresponding reaction with phenylacetylene (**3a**) requires 24 hours under the same conditions. However, the silyl substitution in the propargyl carbonate **3k** was not sufficient to compensate for the destabilizing effect of the electron-withdrawing carbonate group: No conversion was observed even after several days at ambient temperature.

Table 4 ^{1}H and ^{13}C NMR Chemical Shifts (δ) and Coupling Constants (*J* in Hz) of Dienylamines **5l–n** in $CDCl_3$



	1′-H	1-H	R^1	3-H	R^2	5-H	Other H	C-1′	C-1	C-3	R^2	C-5	Other C
5l	3.71 (s)	3.26 (dd, *J* = 6.4, 1.0)	5.71 (dt, 1 H, *J* = 16, 6.4)	6.23 (*J* =16)	1.81 (s, 3 H)	4.90 (br s, 2 H)	1.50 (s, 1 H, NH), 7.16–7.40 (m, 5 H)	53.0 (t)	50.7 (t)	133.9 (d)	18.3 (q)	115.4 (t)	126.5, 127.7, 127.8, 128.0 (4 d), 139.9, 141.2 (2 s)
5m	3.90 (s)	3.47 (d, *J* = 1.5)	0.34 (s, 9 H)	6.73 (m)	1.94 (m_c, 3 H)	5.00, 5.04 (2 m, 2 H)	7.37–7.50 (m, 5 H)	53.2 (t)	56.9 (t)	144.5 (d)	22.8 (q)	113.6 (t)	0.4 [q, $Si(CH_3)_3$], 126.6, 128.0, 128.1 (3 d), 139.3, 140.6, 144.7 (3 s)
5n	3.75 (s)	3.28 (dd, *J* = 6.5, 1.0)	5.62 (dtd, *J* = 16, 6, 0.6)	6.15 (*J* = 16)	–[a]	5.68 (m_c)	1.49 (s, 1 H, NH), 1.54–1.68 (m, 4 H), 2.07–2.14 (m, 4 H), 7.18–7.38 (m, 5 H)	53.1 (t)	51.2 (t)	135.1 (d)	-[b]	128.6 (d)	22.3, 22.4, 24.4, 25.6 (4 t), 123.9 (d, C-2), 127.9, 128.0, 128.2 (3 d), 135.2, 140.2 (2 s)

[a] For relevant signals, see the column 'other H'.
[b] For relevant signals, see the column 'other C'.

The similarity of the reaction conditions required for the conversion of hex-3-yne (**3d**) and trimethylsilylacetylene (**3f**) illustrates that the α-stabilizing effect of an alkyl and the β-stabilizing effect of a trimethylsilyl group are similar in the transition states of these ene reactions.

The activating effect of silyl substitution at the triple bond was also found in the reactions of the propargylic ethers **3g** and **3h**: whereas the propargyl methyl ether (**3h**) did not react, its trimethylsilylated analogue **3g** gave the ene product **5g** in 72% yield.

The good yields obtained from the reactions of **2** with enynes **5l–n** are surprising in view of the low nucleophilicities of enynes previously observed in their reactions with benzhydrylium ions.[21,22] The formation of products **5l–n** may, therefore be interpreted by the operation of a concerted mechanism. The conjugated dienylamines **5l–n** may be used as dienes in Diels–Alder reactions, which will be published separately.

Scope and Limitation

As discussed above, all types of alkyl and phenyl substituted triple bonds can be stereoselectively hydro-aminomethylated by the iminium salt **2**. The failure to observe a reaction with the propargyl ether **3h** indicates that even weakly electron accepting groups in the vicinity of the triple bond inhibit the reaction. From the fact that the retarding effect of the methoxy group can be compensated by a suitably located electron donor one can derive that oxygen functionalities in the enophile are in principle tolerable as long as they are not easily ionized under the reaction conditions.

All reactions were performed under dry N_2 at r.t. 1,2-Dichloroethane and CH_2Cl_2 were dried over P_4O_{10} and freshly distilled from CaH_2 prior to use. *N,O*-Acetal **1** was prepared from dibenzylamine, paraformaldehyde, and MeOH following the method described by Stewart and co-workers.[11,12] Enynes **3l** and **3n** were obtained by dehydration of the corresponding alcohols according to methods described in the literature.[23] Alkyne **3a** and enyne **3l** were silylated according to a standard Grignard procedure to give **3e** and **3m**, respectively.[24] 2-Methoxy-2-phenylbut-3-yne (**3i**) was prepared by methylation of 2-phenylbut-3-yn-2-ol using $NaNH_2$ and dimethyl sulfate as described in Ref.[25] Propargyl ethers **3h** and **3i** were treated with BuLi and chlorotrimethylsilane following a standard procedure[26] to give the silylated derivatives **3g** and **3j**, respectively. Methyl(3-(trimethylsilyl)prop-2-ynyl)carbonate (**3k**) was synthesized according to a literature method.[27] All other chemicals are commercially available.

^{1}H NMR spectra (300 or 400 MHz) refer to $CDCl_3$ (δ_H = 7.24) or CD_3CN (δ_H = 1.93). ^{13}C NMR spectra (75.5 or 100.6 MHz) were calibrated to $CDCl_3$ (δ_C = 77.00) or CD_3CN (δ_C = 1.30). DEPT experiments were used to obtain information about the multiplicity of the ^{13}C resonances. Further $^{1}H,^{13}C$-HETCOR, and NOESY experiments were performed for an unambiguous assignment of the NMR signals. ^{119}Sn NMR spectra (100.7 MHz) refer to Me_4Sn (δ_{Sn} = 0.0). Mass spectra were obtained on a Finnigan MAT 95 Q.

Allylamines 5 from the Iminium Salt 2 and Alkynes 3; General Procedure

A solution of *N,O*-acetal **1** in anhydrous CH_2Cl_2 or 1,2-dichloroethane (6–10 mL/mmol **1**) was stirred with equimolar amounts of chlorotrimethylsilane and $SnCl_4$, whereby **2** was formed as a colorless precipitate.[13] After ca. 30 min, the enophile **3** was added to the

suspension. The mixture was then stirred at the given temperature[28] until the iminium salt **2** was completely dissolved. For the hydrolysis, the mixture was cooled to 0 °C, aq 2 M NaOH (20 mL) was added, and the mixture was vigorously stirred for 30 min before the phases were separated. After extraction of the aqueous layer with CH_2Cl_2 (10 mL), the combined organic layers were washed with aq 2 M NaOH (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The secondary allylamines **5** were then obtained by bulb-to-bulb distillation, whereby excess enophile and benzaldehyde could be separated in a first fraction at 100 °C (bath temp). The NMR resonances of the allylamines **5** are listed in Tables 3 and 4.

Benzyl(3-phenylallyl)amine (5a)
The reaction of **2** (1.23 g **1**, 5.10 mmol) with **3a** (1.12 mL, 10.2 mmol) in 1,2-dichloroethane yielded 0.852 g (75%) of **5a** as a colorless liquid after 45 min at 83 °C; bp 250 °C/4 × 10^{-2} mbar (bath temp).

Anal. Calcd for $C_{16}H_{17}N$ (223.3): C, 86.06; H, 7.67; N, 6.27. Found: C, 85.60; H, 7.65; N, 6.24.

Benzylhept-2-enylamine (5b)
The reaction of **2** (0.640 g **1**, 2.65 mmol) with **3b** (0.605 mL, 5.30 mmol) in 1,2-dichloroethane yielded 0.385 g (71%) of **5b** as a colorless liquid after 8 h at 75 °C in a sealed tube; bp 225 °C/4 × 10^{-2} mbar (bath temp).

Anal. Calcd for $C_{14}H_{21}N$ (203.3): C, 82.70; H, 10.41; N, 6.89. Found: C, 83.27; H, 10.03; N, 6.55.

Benzyl(2-methyl-3-phenylallyl)amine (5c)
The reaction of **2** (0.991 g **1**, 4.10 mmol) with **3c** (0.952 g, 8.20 mmol) in 1,2-dichloroethane yielded 0.809 g (83%) of **5c** as a colorless liquid after 90 min at 83 °C; bp 250 °C/3.8 × 10^{-2} mbar (bath temp).

MS (EI, 70 eV): *m*/*z* (%) = 237 (M^+, 18), 222 (30), 146 (33), 106 (32), 92 (15), 91 (100).

Benzyl(2-ethylpent-2-enyl)amine (5d)
The reaction of **2** (0.550 g **1**, 2.28 mmol) with **3d** (0.780 mL, 6.84 mmol) in 1,2-dichloroethane yielded 0.261 g (57%) of **5d** as a colorless liquid after 8 h at 75 °C in a sealed tube; bp 225 °C/4 × 10^{-2} mbar (bath temp).

MS (EI, 70 eV): *m*/*z* (%) = 204 (14), 203 (M^+, 4), 174 (25), 120 (12), 108 (21), 106 (19), 96 (19), 91 (100).

Benzyl[3-phenyl-2-(trimethylsilyl)allyl]amine (5e)
The reaction of **2** (1.19 g **1**, 4.93 mmol) with **3e** (0.961 mL, 4.93 mmol) in dichloromethane yielded 1.11 g (76%) of **5e** as a colorless liquid after 3 h at 20 °C; bp 250 °C/3.9 × 10^{-2} mbar (bath temp).

Anal. Calcd for $C_{19}H_{25}NSi$ (295.5): C, 77.23; H, 8.53; N, 4.74. Found: C, 77.15; H, 8.20; N, 4.43.

Benzyl[2-(trimethylsilyl)allyl]amine (5f)
The reaction of **2** (0.650 g **1**, 2.69 mmol) with **3f** (1.14 mL, 8.08 mmol) in 1,2-dichloroethane yielded 0.391 g (66%) of **5f** as a colorless liquid after 5 h at 75 °C a sealed tube; bp 200 °C/4 × 10^{-2} mbar (bath temp).

MS (EI, 70 eV): *m*/*z* (%) = 220 (19), 219 (M^+, 5), 128 (19), 120 (68), 91 (100), 73 (11).

Benzyl[4-methoxy-2-(trimethylsilyl)but-2-enyl]amine (5g)
The reaction of **2** (0.590 g **1**, 2.44 mmol) with **3g** (0.696 g, 4.89 mmol) in 1,2-dichloroethane yielded 0.466 g (72%) of **5g** as a colorless liquid after 3 h at 75 °C in a sealed tube; bp 250 °C/3.5 × 10^{-2} mbar (bath temp).

MS (EI, 70 eV): *m*/*z* (%) = 156 (40), 141 (12), 120 (45), 91 (100), 89 (12), 73 (20).

Reaction of Iminium Salt 2 with Alkyne 3h
Heating a mixture of **2** (0.505 g **1**, 2.09 mmol) with **3h** (0.293 g, 4.19 mmol) for 24 h in 1,2-dichloroethane at 75 °C in a sealed tube and hydrolysis yielded a mixture of dibenzylamine and propargyl methyl ether **3h**.

Reaction of Iminium Salt 2 with Alkyne 3i
Heating a mixture of **2** (0.528 g **1**, 2.19 mmol) with **3i** (0.702 g, 4.38 mmol) for 2 h at 83 °C in 1,2-dichloroethane and hydrolysis yielded a complex mixture of unidentified compounds.

Reaction of Iminium salt 2 with Alkyne 3j
Heating a mixture of **2** (0.598 g **1**, 2.48 mmol) with **3j** (1.15 g, 4.96 mmol) for 2 h at 83 °C in 1,2-dichloroethane and hydrolysis yielded a complex mixture of unidentified compounds.

Reaction of Iminium Salt 2 and Alkyne 3k
Stirring a mixture of **2** (0.260 g **1**, 1.07 mmol) with **3k** (0.398 g, 2.14 mmol) in CH_2Cl_2 did not lead to the dissolution of the iminium salt after 5 d at 20 °C. The hydrolysis of the filtrate yielded a complex mixture of unidentified compounds.

Benzyl(4-methylpenta-2,4-dienyl)amine (5l)
The reaction of **2** (1.22 g **1**, 5.05 mmol) with **3l** (0.668 g, 10.1 mmol) in 1,2-dichloroethane yielded 0.641 g (68%) of **3l** as a colorless liquid after 2 h at 83 °C; bp 225 °C/4 × 10^{-2} mbar (bath temp).

Anal. Calcd for $C_{13}H_{17}N$ (187.3): C, 83.37; H, 9.15; N, 7.48. Found: C, 82.93; H, 9.04; N, 7.22.

Benzyl[4-methyl-2-(trimethylsilyl)penta-2,4-dienyl]amine (5m)
Reaction of **2** (4.21 g **1**, 17.4 mmol) with **3m** (3.55 g, 21.1 mmol) in CH_2Cl_2 yielded 3.88 g (14.9 mmol, 86%) of **5m** as a colorless liquid after 20 h at 20 °C; bp 175 °C/2.5 × 10^{-2} mbar (bath temp).

Anal. Calcd for $C_{16}H_{25}NSi$ (259.5): C, 74.07; H, 9.71; N, 5.40. Found: C, 73.89; H, 9.71; N, 5.35.

Benzyl(3-cyclohex-1-enylallyl)amine (5n)
Reaction of **2** (3.44 g **1**, 14.3 mmol) with **3n** (3.03 g, 28.5 mmol) in CH_2Cl_2 yielded 2.34 g (72%) of **5n** as a colorless liquid after 30 min at 20 °C; bp 200 °C/3.5 × 10^{-2} mbar (bath temp).

MS (EI, 70 eV): *m*/*z* (%) = 228 (12), 227 (M^+, 67), 226 (17), 136 (28), 132 (23), 106 (15), 92 (17), 91 (100), 79 (15), 77 (15), 65 (12).

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