

# Synthesis of 1-Amino-3-(trimethylsilyl)allenes by Organocuprate Addition to 3-(Trimethylsilyl)propyne Iminium Salts <sup>1)</sup>

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**Abstract.** 1-Dialkylamino-3-(trimethylsilyl)allenes **2a–q** were obtained by conjugate addition of alkyl, vinyl, aryl, hetaryl, and silyl groups, *via* the respective organocuprates, to 3-(trimethylsilyl)propyne iminium triflates **1a–d**. Similarly,

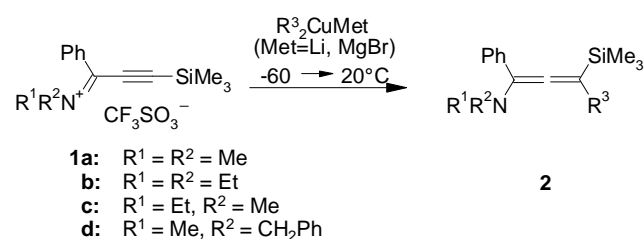
2-vinylidene-2,3-dihydro-1,3-benzothiazoles **4a,b** were synthesized from semicyclic propyne iminium triflates **3a,b** and a di-*tert*-butyl cuprate.

Highly substituted and functionalized 1-aminoallenes have been found to undergo a number of synthetically useful transformations. They allow addition and cycloaddition reactions across the electron-rich enamino double bond [1, 2] and readily rearrange by a prototropic shift to form 1- and 2-amino-1,3-dienes when they bear a CHR<sub>2</sub> substituent [3–6]. Particularly remarkable is the thermal cycloisomerization of 1-dialkylamino-3-vinyl (aryl, hetaryl)-allenes which gives rise to a broad range of monocyclic and condensed dihydroazepine derivatives [7, 8]. Especially in connection with mechanistic investigations on these latter isomerization reactions, but also with respect to the synthetic usefulness of the vinylsilane functionality, we were interested in a versatile synthesis of 1-dialkylamino-3-(trimethylsilyl)allenes. Three novel approaches to trimethylsilylallenes were reported recently. One of them converts acylsilanes in four steps into 1-[bis(trimethylsilyl)amino]-3-(trimethylsilyl)allenes [9]. The second one constructs the allenes from 1,1-bis(trimethylsilyl)-2-propynes and iminium salts [10]. In our own approach [3], a 1,3-diphenylpropyne iminium salt gave 1-amino-3-silylallenes by conjugate addition of silyl cuprates; this method allowed silyl to be SiPh<sub>2</sub>tBu and SiPh<sub>3</sub> but not SiMe<sub>3</sub>. Recently, we have found a convenient synthesis of 3-(trimethylsilyl)propyne iminium salts [11], and it was hoped that they would react with a broad range of organocuprates to yield 1-amino-3-(trimethylsilyl)allenes. We report here that this is the case indeed.

## Results and Discussion

3-(Trimethylsilyl)propyne iminium triflates **1a–d** were prepared as published [11] by N-alkylation of the corresponding propyne imines with alkyl triflates. When they were allowed to react with organocuprates of the Gilman or Lipshutz type [12], conjugate addition of one

organic residue took place, and 1-dialkylamino-3-(trimethylsilyl)allenes **2** with a tetrasubstituted cumulene system were obtained (Table 1). When an appropriate organocuprate formulation [12], generated from an organolithium or Grignard compound and a copper(I) salt (CuCN or CuBr·SMe<sub>2</sub>) in a 2:1 ratio, was chosen, this procedure allowed to introduce *tert*-butyl, vinyl, aryl, hetaryl, and silyl groups usually in good to high yields.



See Table 1 for specification of substituents R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>

## Scheme 1 Synthesis of 1-Amino-3-(trimethylsilyl)allenes **2**

It appears that the new allenes **2a–q** are more resistant to hydrolytic transformation of the enamine function than related aminoallenes having a morpholino group instead of dialkylamino and *tert*-butyl instead of SiMe<sub>3</sub> [3]. Thus, they remained unchanged when exposed to air for some time, and the 3-*t*-Bu,3-TMS substituted aminoallenes **2g,k** survived column chromatography on silica gel without hydrolysis. In general, however, purification by chromatography on a reversed-phase column was preferred. Furthermore, allenes **2g,k,q** displayed a remarkable thermal stability and remained unaltered when heated in toluene solution at 190 °C for several hours in a thick-walled Schlenk tube. The thermally induced cycloisomerization reactions of some of the other allenes, occurring at 100 °C and higher, will be reported in a subsequent paper. Unfortunately, all

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**Table 1** 1-Dialkylamino-3-(trimethylsilyl)allenes **2a–q** prepared <sup>a)</sup>

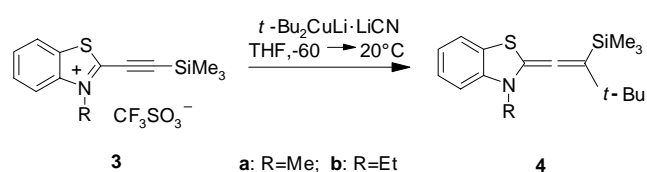
Comp.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Precursors	Yield (%)	Formula (g/mol)	Elemental Analysis		
							Calcd./Found	C	H
<b>2a</b>	CH <sub>3</sub>	CH <sub>3</sub>	H <sub>2</sub> C=CH	<b>1a</b> + (H <sub>2</sub> C=CH) <sub>2</sub> CuMgBr	85	C <sub>16</sub> H <sub>23</sub> NSi (257.45)	74.65 74.32	9.00 8.76	5.44 5.74
<b>2b</b>	CH <sub>3</sub>	CH <sub>3</sub>	Ph	<b>1a</b> + Ph <sub>2</sub> CuLi · LiCN	98	C <sub>20</sub> H <sub>25</sub> NSi (307.51)	78.12 77.89	8.19 7.84	4.55 4.35
<b>2c</b>	CH <sub>3</sub>	CH <sub>3</sub>	4-chlorophenyl	<b>1a</b> + (4-Cl-C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CuLi · LiBr	95	C <sub>20</sub> H <sub>24</sub> ClNSi (341.96)	70.25 70.04	7.07 7.28	4.10 4.30
<b>2d</b>	CH <sub>3</sub>	CH <sub>3</sub>	4-methoxyphenyl	<b>1a</b> + (4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CuLi · LiBr	93	C <sub>21</sub> H <sub>27</sub> NOSi (337.54)	74.73 75.01	8.06 8.34	4.15 3.95
<b>2e</b>	CH <sub>3</sub>	CH <sub>3</sub>	2-furyl	<b>1a</b> + (2-furyl) <sub>2</sub> CuLi · LiCN	74	C <sub>18</sub> H <sub>23</sub> NOSi (297.47)	72.67 72.89	7.79 7.53	4.70 4.93
<b>2f</b>	CH <sub>3</sub>	CH <sub>3</sub>	2-thienyl	<b>1a</b> + (2-thienyl) <sub>2</sub> CuLi · LiCN	75	C <sub>18</sub> H <sub>23</sub> NSSi (313.53)	68.96 68.61	7.39 7.68	4.47 4.25
<b>2g</b>	CH <sub>3</sub>	CH <sub>3</sub>	<i>t</i> -Bu	<b>1a</b> + <i>t</i> -Bu <sub>2</sub> CuLi · LiCN	70	C <sub>18</sub> H <sub>29</sub> NSi (287.52)	75.19 74.87	10.16 9.83	4.87 5.03
<b>2h</b>	CH <sub>3</sub>	CH <sub>3</sub>	<i>t</i> -BuPh <sub>2</sub> Si	<b>1a</b> + ( <i>t</i> -BuPh <sub>2</sub> Si) <sub>2</sub> CuLi · LiCN	95	C <sub>30</sub> H <sub>39</sub> NSi <sub>2</sub> (469.81)	76.69 77.01	8.36 8.12	2.98 3.21
<b>2i</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H <sub>2</sub> C=CH	<b>1b</b> + (H <sub>2</sub> C=CH) <sub>2</sub> CuMgBr	92	C <sub>18</sub> H <sub>27</sub> NSi (285.50)	75.72 76.02	9.53 9.27	4.91 5.14
<b>2j</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	2-furyl	<b>1b</b> + (2-furyl) <sub>2</sub> CuLi · LiCN	83	C <sub>20</sub> H <sub>27</sub> NOSi (325.52)	73.79 73.54	8.35 8.61	4.30 4.06
<b>2k</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	<i>t</i> -Bu	<b>1b</b> + <i>t</i> -Bu <sub>2</sub> CuLi · LiCN	98	C <sub>20</sub> H <sub>33</sub> NSi (315.57)	76.12 75.86	10.53 10.87	4.43 4.24
<b>2l</b>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	<i>t</i> -Bu	<b>1c</b> + <i>t</i> -Bu <sub>2</sub> CuLi · LiCN	76	C <sub>19</sub> H <sub>31</sub> NSi (301.54)	75.68 75.29	10.36 9.98	4.64 4.63
<b>2m</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	H <sub>2</sub> C=CH	<b>1d</b> + (H <sub>2</sub> C=CH) <sub>2</sub> CuMgBr	32	C <sub>22</sub> H <sub>27</sub> NSi (333.55)	79.22 78.89	8.16 8.02	4.20 4.46
<b>2n</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	Ph	<b>1d</b> + Ph <sub>2</sub> CuLi · LiCN	58	C <sub>26</sub> H <sub>29</sub> NSi (383.61)	81.41 81.76	7.62 7.94	3.65 3.33
<b>2o</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	2-furyl	<b>1d</b> + (2-furyl) <sub>2</sub> CuLi · LiCN	76	C <sub>24</sub> H <sub>27</sub> NOSi (373.56)	77.16 76.89	7.28 7.50	3.74 4.11
<b>2p</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	2-thienyl	<b>1d</b> + (2-thienyl) <sub>2</sub> CuLi · LiCN	81	C <sub>24</sub> H <sub>27</sub> NSSi (389.63)	73.98 74.34	6.98 7.05	3.59 3.25
<b>2q</b>	CH <sub>3</sub>	CH <sub>2</sub> Ph	<i>t</i> -Bu	<b>1d</b> + <i>t</i> -Bu <sub>2</sub> CuLi · LiCN	84	C <sub>24</sub> H <sub>33</sub> NSi (363.31)	79.27 78.95	9.14 8.97	3.85 4.06

<sup>a)</sup> All allenes were obtained as oils.

efforts to remove the SiMe<sub>3</sub> group in order to arrive at trisubstituted 1-aminoallenes met with failure. Some of the allenes resisted all desilylation procedures (KF/18-crown-6, KHF<sub>2</sub>, CsF, benzyltrimethylammonium fluoride, pyridine/HF), others underwent unspecific decomposition under the reaction conditions.

In a similar manner as the acyclic propyne iminium triflates **1**, semicyclic propyne iminium salts **3a,b** reacted with (*t*-Bu)<sub>2</sub>CuLi · LiCN to give 1,1-S,N-substituted allenes **4a,b** in good yield. Reactions with other organocuprates of this type did not allow to isolate the expected allene, but gave either an undefined product mixture (R<sub>2</sub>CuLi · LiCN, R = vinyl, 2-thienyl, phenyl) or a 2:2 adduct (R=2-furyl) the formation of which probably includes a Diels–Alder reaction between initially formed allene and residual propyne iminium salt [13].

Allenes **2a–q** and **4a,b** display a low- or medium-intensity IR absorption at 1880–1920 cm<sup>-1</sup> which is caused by the stretching vibration of the cumulene system. In the <sup>13</sup>C NMR spectra, the chemical shift of the



**Scheme 2** Synthesis of 2-Vinylidene-2,3-dihydro-1,3-benzothiazoles **4**

central allenic carbon atom is characteristic. The  $\delta$  values for the 1-dialkylamino-1-phenyl-3-*tert*-butyl-3-(trimethylsilyl)allenes **2g,k,l,q** ( $\delta = 202.7 \pm 1.0$  ppm) are a little bit lower, and all others, where the 3-*t*-Bu group is replaced by vinyl, (het)aryl and SiPh<sub>2</sub>*t*-Bu, are somewhat larger ( $\delta = 206–215$  ppm) than for 1-(dimethylamino)allene itself ( $\delta = 204.2$  ppm [14]). For the 2-vinylidene-2,3-dihydro-1,3-benzothiazoles **4a,b**, however, a shielding of the central allenic carbon atom is found ( $\delta \approx 194$  ppm), certainly as a consequence of the 1,1-bis(donor) substitution of these allenes.

**Table 2** IR and NMR data of 1-dialkylamino-3-(trimethylsilyl)allenes **2a–q**

Comp.	IR (film) $\nu/\text{cm}^{-1}$ (C=C=C)	$^1\text{H}$ NMR ( $\text{CDCl}_3$ , TMS, 200.13 MHz) $\delta/\text{ppm}$	$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 50.32 MHz) $\delta/\text{ppm}$
<b>2a</b>	1887	0.27 (s, 9H, $\text{SiMe}_3$ ), 2.53 (s, 6H, $\text{NMe}_2$ ), 5.16 (dd, $J = 10.3, 1.4$ Hz, 1H, $\text{CH}=\text{}$ ), 5.38 (dd, $J = 17.6, 1.4$ Hz, $\text{CH}=\text{}$ ), 6.39 (dd, $J = 17.6, 10.3$ Hz, $\text{CH}=\text{}$ ), 7.21–7.35 (m, 5H, Ph)	–0.65 ( $\text{SiMe}_3$ ), 43.57 (NMe), 115.85 ( $=\text{CH}_2$ ), 110.05/123.17 ( $\text{C}=\text{C}=\text{C}$ ), 126.54, 126.82, 128.20, 135.47, 136.07, 208.70 ( $\text{C}=\text{C}=\text{C}$ )
<b>2b</b>	1894	0.42 (s, 9H, $\text{SiMe}_3$ ), 2.68 (s, 6H, $\text{NMe}_2$ ), 7.31–7.55 (m, 10H, $2\times\text{Ph}$ )	–0.12 ( $\text{SiMe}_3$ ), 43.57 (NMe), 111.45/124.21 ( $\text{C}=\text{C}=\text{C}$ ), 126.46, 126.89, 127.13, 127.52, 128.26, 128.42, 136.06, 138.33, 207.15 ( $\text{C}=\text{C}=\text{C}$ )
<b>2c</b>	1894	0.19 (s, 9H, $\text{SiMe}_3$ ), 2.45 (s, 6H, $\text{NMe}_2$ ), 7.14–7.43 (m, 9H, $\text{CH}_{\text{arom}}$ )	–1.53 ( $\text{SiMe}_3$ ), 44.73 (NMe), 124.78, 125.40, 126.67, 128.10, 128.74, 129.95, 130.25, 132.14, 135.78, 137.00, 207.60 ( $\text{C}=\text{C}=\text{C}$ )
<b>2d</b>	1891	0.21 (s, 9H, $\text{SiMe}_3$ ), 2.46 (s, 6H, $\text{NMe}_2$ ), 3.72 (s, 3H, OMe), 7.13–7.45 (m, 9H, $\text{CH}_{\text{arom}}$ )	–1.34 ( $\text{SiMe}_3$ ), 44.88 (NMe), 56.68 (OMe), 112.36, 115.51, 124.86, 125.10, 126.62, 126.95, 128.03, 129.63, 130.15, 158.00, 206.21 ( $\text{C}=\text{C}=\text{C}$ )
<b>2e</b>	1895	0.29 (s, 9H, $\text{SiMe}_3$ ), 2.55 (s, 6H, $\text{NMe}_2$ ), 6.31–6.40 (m, 2H, 3-,4- $\text{H}_{\text{Fu}}$ ), 7.18–7.53 (m, 6H, Ph + 5- $\text{H}_{\text{Fu}}$ )	–0.64 ( $\text{SiMe}_3$ ), 43.47 (NMe), 102.37/124.92 ( $\text{C}=\text{C}=\text{C}$ ), 106.68, 111.16, 126.74, 127.06, 128.23, 135.91, 141.55, 151.79, 206.38 ( $\text{C}=\text{C}=\text{C}$ )
<b>2f</b>	1889	0.27 (s, 9H, $\text{SiMe}_3$ ), 2.53 (s, 6H, $\text{NMe}_2$ ), 6.93–6.95 (m, 2H, $\text{CH}_{\text{arom}}$ ), 7.11–7.30 (m, 4H, $\text{CH}_{\text{arom}}$ ), 7.44–7.50 (m, 2H, $\text{CH}_{\text{arom}}$ )	–0.41 ( $\text{SiMe}_3$ ), 43.30 (NMe), 105.84/124.82 ( $\text{C}=\text{C}=\text{C}$ ), 124.15, 126.84, 127.19, 127.33, 128.25, 135.97, 143.76 ( $\text{C}=\text{C}=\text{C}$ ), 206.57 ( $\text{C}=\text{C}=\text{C}$ )
<b>2g</b>	1917	0.30 (s, 9H, $\text{SiMe}_3$ ), 1.30 (s, 9H, $\text{CMe}_3$ ), 2.59 (s, 6H, $\text{NMe}_2$ ), 7.31–7.59 (m, 5H, Ph)	1.45 ( $\text{SiMe}_3$ ), 31.31 ( $\text{CMe}_3$ ), 36.45 ( $\text{CMe}_3$ ), 43.84 (NMe), 119.32/122.79 ( $\text{C}=\text{C}=\text{C}$ ), 125.98, 126.18, 128.10, 137.01, 201.68 ( $\text{C}=\text{C}=\text{C}$ )
<b>2h</b>	1882	0.09 (s, 9H, $\text{SiMe}_3$ ), 1.24 (s, 9H, $\text{CMe}_3$ ), 2.76 (s, 6H, $\text{NMe}_2$ ), 7.56–7.96 (m, 15H, $3\times\text{Ph}$ )	0.68 ( $\text{SiMe}_3$ ), 19.65 ( $\text{SiCMe}_3$ ), 28.02 ( $\text{CMe}_3$ ), 43.61 (NMe), 99.27/116.66 ( $\text{C}=\text{C}=\text{C}$ ), 125.88, 127.40, 127.52, 127.79, 128.22, 129.22, 134.65, 134.88, 135.65, 135.82, 136.42, 136.76, 215.44 ( $\text{C}=\text{C}=\text{C}$ )
<b>2i</b>	1884	0.21 (s, 9H, $\text{SiMe}_3$ ), 1.02 (t, $J = 7.0$ Hz, 6H, $2\times\text{Me}$ ), 2.68–2.86 (m, 4H, $2\times\text{NCH}_2$ ), 5.05 (d, $J = 10.3$ Hz, 1H, $\text{CH}=\text{}$ ), 5.25 (d, $J = 17.6$ Hz, 1H; $\text{CH}=\text{}$ ), 6.28 (dd, $J = 17.6, 10.3$ Hz, 1H, $\text{CH}=\text{}$ ), 7.11–7.46 (m, 5H, Ph)	–0.48 ( $\text{SiMe}_3$ ), 12.01 (Me), 45.03 ( $\text{NCH}_2$ ), 109.07/119.59 ( $\text{C}=\text{C}=\text{C}$ ), 115.72 ( $=\text{CH}_2$ ), 126.70, 128.29, 135.08, 137.10, 210.73 ( $\text{C}=\text{C}=\text{C}$ )
<b>2j</b>	1905	0.18 (s, 9H, $\text{SiMe}_3$ ), 0.95 (t, $J = 7.1$ Hz, 6H, $2\times\text{Me}$ ), 2.74 (q, $J = 7.1$ Hz, 2H, $\text{NCH}_2$ ), 2.75 (q, $J = 7.1$ Hz, 2H, $\text{NCH}_2$ ), 6.14–6.16 and 6.24–6.27 (m, 2H, 3-,4- $\text{H}_{\text{Fu}}$ ), 7.10–7.43 (m, 6H, Ph + 5- $\text{H}_{\text{Fu}}$ )	–0.4 ( $\text{SiMe}_3$ ), 11.8 (Me), 44.4 ( $\text{NCH}_2$ ), 101.4/121.7 ( $\text{C}=\text{C}=\text{C}$ ), 106.5, 111.1 (2C), 126.8, 126.9, 128.1, 136.7, 141.4, 151.8, 208.5 ( $\text{C}=\text{C}=\text{C}$ )
<b>2k</b>	1912	0.06 (s, 9H, $\text{SiMe}_3$ ), 0.94 (t, $J = 7.1$ Hz, 6H, $2\times\text{Me}$ ), 1.09 (s, 9H, $\text{CMe}_3$ ), 2.71 (q, $J = 7.1$ Hz, 4H, $2\times\text{NCH}_2$ ), 7.05–7.40 (m, 5H, Ph)	1.6 ( $\text{SiMe}_3$ ), 12.1 (Me), 31.3 ( $\text{CMe}_3$ ), 36.8 ( $\text{CMe}_3$ ), 44.2 ( $\text{NCH}_2$ ), 118.2/120.6 ( $\text{C}=\text{C}=\text{C}$ ), 126.1, 126.2, 127.9, 138.3, 203.6 ( $\text{C}=\text{C}=\text{C}$ )
<b>2l</b>	1914	0.06 ( $\text{SiMe}_3$ ), 0.96 (t, $J = 7.2$ Hz, 3H, $\text{CH}_2\text{Me}$ ), 1.08 (s, 9H, $\text{CMe}_3$ ), 2.36 (s, 3H, NMe), 2.64 (q, $J = 7.2$ Hz, 2H, $\text{NCH}_2$ ), 7.05–7.37 (m, 5H, Ph)	1.4 ( $\text{SiMe}_3$ ), 12.0 ( $\text{CH}_2\text{Me}$ ), 31.3 ( $\text{CMe}_3$ ), 36.5 ( $\text{CMe}_3$ ), 39.3 (NMe), 48.9 ( $\text{NCH}_2$ ), 118.8/122.0 ( $\text{C}=\text{C}=\text{C}$ ), 126.0, 126.1, 128.0, 137.5, 202.7 ( $\text{C}=\text{C}=\text{C}$ )
<b>2m</b>	1890	0.33 (s, 9H, $\text{SiMe}_3$ ), 2.39 (s, 3H, NMe), 3.82 (s, 2H, $\text{NCH}_2$ ), 5.05 (d, $J = 10.3$ Hz, $\text{CH}=\text{}$ ), 5.26 (d, $J = 16.2$ Hz, $\text{CH}=\text{}$ ), 6.19 (dd, $J = 16.2, 10.3$ Hz, 1H, $\text{CH}=\text{}$ ), 7.25–7.57 (m, 10H, $2\times\text{Ph}$ )	–0.62 ( $\text{SiMe}_3$ ), 40.14 (NMe), 59.00 ( $\text{NCH}_2$ ), 109.91/122.01 ( $\text{C}=\text{C}=\text{C}$ ), 115.91 ( $=\text{CH}_2$ ), 126.55, 126.67, 126.88, 128.16, 128.33, 128.49, 136.21, 138.63, 209.34 ( $\text{C}=\text{C}=\text{C}$ )
<b>2n</b>	1896	0.41 (s, 9H, $\text{SiMe}_3$ ), 2.59 (s, 3H, NMe), 4.03 (s, 2H, $\text{NCH}_2$ ), 7.26–7.81 (m, 15H, $3\times\text{Ph}$ )	–0.08 ( $\text{SiMe}_3$ ), 39.98 (NMe), 58.84 ( $\text{NCH}_2$ ), 111.40/123.10 ( $\text{C}=\text{C}=\text{C}$ ), 126.44, 126.91, 127.06, 127.50, 127.78, 128.15, 128.36, 128.40, 128.54, 136.21, 138.13, 138.28, 207.98 ( $\text{C}=\text{C}=\text{C}$ )
<b>2o</b>	1897	0.16 (s, 9H, $\text{SiMe}_3$ ), 2.32 (s, 3H, NMe), 3.77 (s, 2H, $\text{NCH}_2$ ), 6.09–6.11 (m, 1H, $\text{CH}_{\text{Fu}}$ ), 6.23–6.26 (m, 1H, $\text{CH}_{\text{Fu}}$ ), 7.12–7.28 (m, 9H, $\text{CH}_{\text{Ph}}$ + 1 $\text{CH}_{\text{Fu}}$ ), 7.47–7.52 (m, 2H, $\text{CH}_{\text{Ph}}$ )	–0.61 ( $\text{SiMe}_3$ ), 39.81 (NMe), 58.75 ( $\text{NCH}_2$ ), 102.34/123.95 ( $\text{C}=\text{C}=\text{C}$ ), 106.78/111.14 (C-3,- $\text{Fu}$ ), 126.81, 126.91, 127.20, 128.21, 128.37, 128.53, 136.09, 138.65, 141.54 (C-5 $\text{Fu}$ ), 151.74 (C-2 $\text{Fu}$ ), 207.00 ( $\text{C}=\text{C}=\text{C}$ )
<b>2p</b>	1891	0.29 (s, 9H, $\text{SiMe}_3$ ), 2.47 (s, 3H, NMe), 3.93 (s, 2H, $\text{NCH}_2$ ), 6.96–7.66 (m, 13H, $\text{CH}_{\text{Ph}}$ + $\text{CH}_{\text{Th}}$ )	–0.38 ( $\text{SiMe}_3$ ), 39.58 (NMe), 58.60 ( $\text{NCH}_2$ ), 105.77, 124.01 ( $\text{C}=\text{C}=\text{C}$ ), 124.23, 126.92, 127.31, 128.26, 128.40, 128.52, 136.18, 138.52, 143.75 (C-2 $\text{Th}$ ), 207.26 ( $\text{C}=\text{C}=\text{C}$ )
<b>2q</b>	1883	0.30 (s, 9H, $\text{SiMe}_3$ ), 1.29 (s, 9H, $\text{CMe}_3$ ), 2.49 (s, 3H, NMe), 3.93 (s, 2H, $\text{NCH}_2$ ), 7.31–7.72 (m, 10H, $2\times\text{Ph}$ )	1.46 ( $\text{SiMe}_3$ ), 31.31 ( $\text{CMe}_3$ ), 36.52 ( $\text{CMe}_3$ ), 39.93 (NMe), 59.35 ( $\text{NCH}_2$ ), 119.30, 122.16, 126.08, 126.35, 126.88, 127.63, 128.21, 128.59, 137.30, 138.97, 202.38 ( $\text{C}=\text{C}=\text{C}$ )

In summary, we have demonstrated that 3-(trimethylsilyl)propyne iminium salts undergo conjugate addition with organocuprates to form 1-amino-3-(trimethylsilyl)allenes having a tetrasubstituted cumulene unit. These allenes are more resistant to hydrolysis and have higher thermal stability than other tetrasubstituted aminoallenes, *e.g.* with a *tert*-butyl instead of the SiMe<sub>3</sub> substituent and a morpholino instead of an acyclic dialkylamino group.

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## Experimental

All reactions were carried out in oven-dried glassware and under argon. Solvents were dried by standard procedures. Column chromatography was performed under MPLC conditions on a Merck-Hitachi system (gradient pump L 6200, UV monitor 655A, integrator D 7000) on prepacked columns [Merck LiChroprep Si 60 (40–63 μm) and RP-8 (40–63 μm)]. – NMR spectra were taken on a Bruker AC 200 instrument. As the internal reference, Me<sub>4</sub>Si was used for the proton spectra, and the solvent signal for the <sup>13</sup>C NMR spectra [ $\delta$ (CDCl<sub>3</sub>) = 77.0 ppm]. Signal assignments were based on C,H correlation and HMBC spectra, if necessary. IR spectra were recorded on a Perkin Elmer IR 883 spectrometer. Microanalyses were carried out in the Division of Analytical Chemistry, University of Ulm, with an elemental analyzer Perkin-Elmer EA 240.

## Synthesis of 1-Dialkylamino-3-(trimethylsilyl)allenes 2a–q

Allenes **2** were synthesized from propyne iminium triflates **1a–d** [11] and an organocuprate (Table 1) at low temperature (–60 °C). The organocuprates were prepared as follows: (H<sub>2</sub>C=CH)<sub>2</sub>CuMgBr from vinyl magnesium bromide and CuBr·SMe<sub>2</sub> (see below), Ph<sub>2</sub>CuLi·LiCN from phenyllithium and CuCN [3b], (4-Cl–C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CuLi·LiBr and (4-CH<sub>3</sub>O–C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CuLi·LiBr from 4-chlorophenyl lithium (4-methoxyphenyl lithium) and CuBr·SMe<sub>2</sub> (see below), (2-furyl)<sub>2</sub>CuLi·LiCN and (2-thienyl)<sub>2</sub>CuLi·LiCN from 2-furyl lithium (2-thienyl lithium) and CuCN (see below), *t*-Bu<sub>2</sub>CuLi·LiCN from *tert*-butyl lithium and CuCN [3b], (*t*-BuPh<sub>2</sub>Si)<sub>2</sub>CuLi·LiCN from (*tert*-butyldiphenyl)silyl lithium and CuCN [3a, 15].

The following procedures are typical. For yields and elemental analyses, see Table 1; for NMR and IR data, see Table 2.

### 1-Dimethylamino-1-phenyl-3-(trimethylsilyl)penta-1,2,4-triene (2a)

Preparation of (H<sub>2</sub>C=CH)<sub>2</sub>CuMgBr: Diethyl ether (20 ml) was cooled at 0 °C and solid CuBr·SMe<sub>2</sub> (0.42 g, 2 mmol) was added, followed by dropwise addition of a solution of vinyl magnesium bromide in THF (1M, 4 ml, 4 mmol). The suspension was stirred for another 20 min at 0 °C, then cooled at –60 °C for further use.

A solution of **1a** [11] (0.76 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added, the mixture was stirred for 1 h at –60 °C, and then brought to room temperature. The solvent was evaporated (0.01 mbar), and the residue was extracted with pentane (70 ml). After removal of the solvent from the extract, an oil was left which was chromatographed on a reversed-phase column (RP-8) to give **2a** as a yellow oil; yield: 0.44 g (85%).

### 3-(4-Chlorophenyl)-1-dimethylamino-1-phenyl-3-(trimethylsilyl)allene (2c)

A solution of 1-bromo-4-chlorobenzene (0.5 ml, 4 mmol) in THF (10 ml) was cooled at –78 °C, and *tert*-butyl lithium in pentane (1.6M, 5 ml, 8 mmol) was added gradually. The mixture was stirred for 2 h at –78 °C, solid CuBr·SMe<sub>2</sub> (0.42 g, 2 mmol) was added at once, and stirring was continued until a homogeneous solution had formed. A solution of **1a** [11] (0.76 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added, the mixture was stirred for 1 h at –60 °C, and then brought to room temperature. After workup as described above, allene **2c** (0.70 g, 95%) was obtained as a brown oil which for analytical purposes was chromatographed on a reversed-phase column (RP-8) using acetonitrile as the eluent.

### 1-(*N*-Benzyl-*N*-methylamino)-3-(2-furyl)-1-phenyl-3-(trimethylsilyl)allene (2o)

Preparation of (2-furyl)<sub>2</sub>CuLi·LiCN: THF (10 ml) was cooled at 0 °C and furan (0.5 ml, excess) and then *tert*-butyl lithium (1.6M in pentane, 2.5 ml, 4 mmol) were added. After stirring for 30 min, solid CuCN (0.18 g, 2 mmol) was added at once. The mixture was allowed to come to room temp. and stirred until a homogeneous yellow solution had formed which was then cooled at –60 °C for further use.

Reaction with **1d** [11] (0.90 g, 2 mmol) and work-up were carried out in the same manner as described above for **2a** and gave **2o** as a yellow oil; yield: 0.56 g (76%).

## Synthesis of S,N-substituted Allenes 4a,b

### [1-(*tert*-Butyl)-2-(3-methyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)vinyl](trimethyl)silane (4a)

To a suspension of CuCN (0.18 g, 2 mmol) in THF (10 ml), cooled at 0 °C, was added *tert*-butyl lithium (1.6M in pentane, 2.5 ml, 4 mmol). The suspension was stirred until a homogeneous yellow solution had formed which was then cooled at –60 °C. A solution of **3a** [11] (0.78 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added, and after 1 h, the mixture was allowed to assume room temperature. The solvent was removed at 0.01 mbar, and the residue was extracted with pentane (70 ml). The extract was concentrated and set aside at –18 °C to give **4a** as a yellow powder (0.54 g, 88%), *m.p.* 62–64 °C. – IR (KBr):  $\nu$ /cm<sup>–1</sup> = 2958, 2896, 1917 (C=C=C), 1578, 1475, 1371, 1338, 1245. – <sup>1</sup>H NMR (200 MHz):  $\delta$ /ppm = 0.10 (s, 9H, SiMe<sub>3</sub>), 1.04 (s, 9H, CMe<sub>3</sub>), 2.76 (s, 3H, NMe), 6.29–6.32 (m, 1H, CH<sub>arom</sub>), 6.50–6.58 (m, 1H, CH<sub>arom</sub>), 6.86–6.94 (m, 2H, CH<sub>arom</sub>). – <sup>13</sup>C NMR (50 MHz):  $\delta$ /ppm = 1.35 (SiMe<sub>3</sub>), 30.68 (CMe<sub>3</sub>), 31.05 (NMe), 37.93 (CMe<sub>3</sub>), 106.15, 118.11, 120.53, 125.48 (CH<sub>arom</sub>), 125.81, 134.86, 144.18 (C<sub>q</sub>), 194.54 (C=C=C).

C <sub>17</sub> H <sub>25</sub> NSSi	Calcd.:	C 67.27	H 8.30	N 4.61
(303.54)	Found:	C 66.96	H 8.42	N 4.58.

*[1-(tert-Butyl)-2-(3-ethyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)vinyl](trimethyl)silane (4b)*

Prepared as described for **4a** from **3b** [11] (0.68 g, 2 mmol); yield 0.46 g (75%); *m.p.* 68–70 °C. – IR (KBr):  $\nu/\text{cm}^{-1}$  = 2959, 2897, 1923 (C=C=C), 1576, 1474, 1393, 1329, 1245. –  $^1\text{H}$  NMR (200 MHz):  $\delta/\text{ppm}$  = 0.19 (s, 9H, SiMe<sub>3</sub>), 1.12 (s, 9H, CMe<sub>3</sub>), 1.15 (t, *J* = 7.2 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 3.33 (q, *J* = 7.2 Hz, NCH<sub>2</sub>), 6.38 (d, *J* = 7.5 Hz, 1H, CH<sub>arom</sub>), 6.61 (t, *J* = 6.6 Hz, 1H, CH<sub>arom</sub>), 6.92–7.02 (m, 2H, CH<sub>arom</sub>). –  $^{13}\text{C}$  NMR (50 MHz):  $\delta/\text{ppm}$  = 1.47 (SiMe<sub>3</sub>), 11.61 (CH<sub>2</sub>CH<sub>3</sub>), 30.79 (CMe<sub>3</sub>), 38.34 (CMe<sub>3</sub>), 39.48 (NCH<sub>2</sub>), 106.00, 117.88, 120.60, 125.44 (CH<sub>arom</sub>), 119.42 and 126.03 (C=C=C), 134.71, 143.30 (C<sub>q</sub>), 194.29 (C=C=C).

C<sub>18</sub>H<sub>27</sub>NSSi Calcd.: C 68.08 H 8.57 N 4.41  
(317.57) Found: C 67.83 H 8.76 N 4.29.

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