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Synthesis of Semicyclic/Exocyclic Amino-1,3-dienes by Organocuprate Addition to Semicyclic Propyniminium Salts [1])

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Dedicated to Professor Dr. R. Gompper on the Occasion of his 70th Birthday

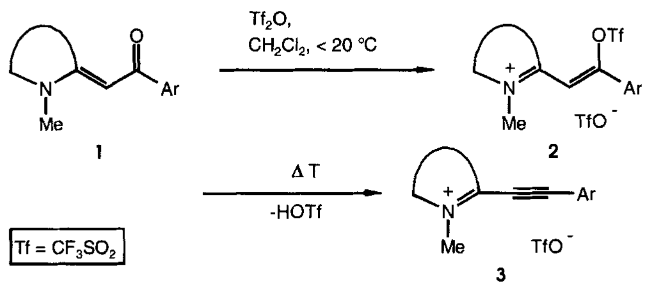
Abstract. Conjugate addition of organocuprates to the 2-ethynyl-substituted cyclic iminium triflates **3** generates aminoallenes which tautomerize immediately to semicyclic 2-amino-1,3-dienes (**6**, **8**) or exocyclic 1-amino-1,3-dienes (**9**, **10**) with the enamine function incorporated into or attached to a 5-, 6-, or 7-membered ring. In those cases where tautomeric equilibria between the two aminodiene species are possible, the five-membered ring exists virtually exclusively with an exocyclic enamine double bond, but the six-membered ring prefers the exocyclic form. The seven-membered ring can accomodate both forms quite well.

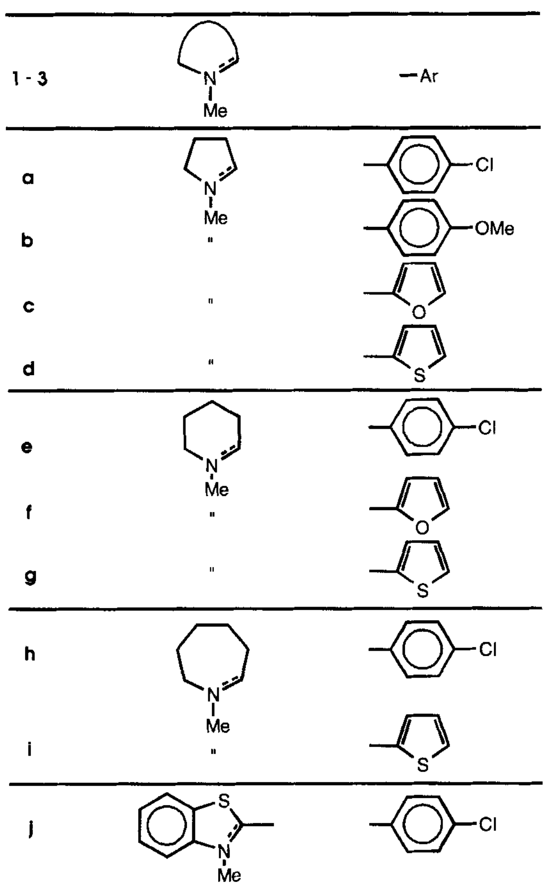
The combination of the enamine and 1,3-diene functionalities makes 1- and 2-amino-1,3-dienes („linear“ and „conjugated“ dienamines) to attractive building blocks in organic synthesis [1–4]. Among the various methods to prepare these aminodienes, the more or less rapid thermal [5–7] or base-induced [8] isomerization of aminoallenes bearing a CHR_2 substituent at either terminus of the allene unit has not found due attention in the past. Recently, we have reported that such aminoallenes can be prepared by conjugate addition of organocuprates to propyniminium salts; the rapid isomerization of the allenes, by a formal 1,3-hydrogen shift to the central allenic carbon atom, provides an access to a variety of functionalized, highly substituted amino-1,3-dienes [9, 10]. Whilst our previous work was focussed on dialkylamino-substituted, acyclic dienes, we report now on aminodienes where the enamine function is incorporated into or attached to a 5-, 6-, or 7-membered ring.

Synthesis of Semicyclic Propyniminium Triflates

The required propyniminium triflates **3** were prepared conveniently by O-sulfonylation of the enaminoketones **1** with triflic anhydride, followed by elimination of triflic acid (HOTf) from the resulting trifloxypropeniminium triflates **2**. The synthesis of salts **3a–d,i,j** by this method has already been described [11,12]. Enaminoketones **1e–g** were obtained by condensation of a (het)aryl methyl ketone with 2,2-diethoxy-1-methyl-piperidine. In line with our previous experience, the elimination step **2** → **3** occured more easily, when the aryl substituent in **2** was electron-rich. Thus, the elimination of triflic acid from (4-chlorophenyl)-substituted salts **2e**,**h** was achieved at 120–160 °C, whereas salts **2f**,**g** were not isolated because of rapid loss of HOTf under the conditions of their synthesis from **1** at or below 20 °C. Salts **3e**,**g**,**h** are crystalline compounds that could be isolated easily. In contrast, reaction of the furyl-enaminoketone **1f** with triflic anhydride yielded a black viscous mass that consisted mainly of salt **3f** and triflic acid in approximately equimolar ratio, together with a smaller amount of the C-protonated enaminoketone. The formation of the latter could not be suppressed by performing the reaction in the presence of diisopropylethylamine, nor could the triflic acid be removed by addition of a *tert*-amine base of by attempted vacuum distillation.

[1]) Presented in part at the 2nd Iminiumsalz-Tagung in Stimpfach-Rechenberg, Germany (September 20-22, 1995)

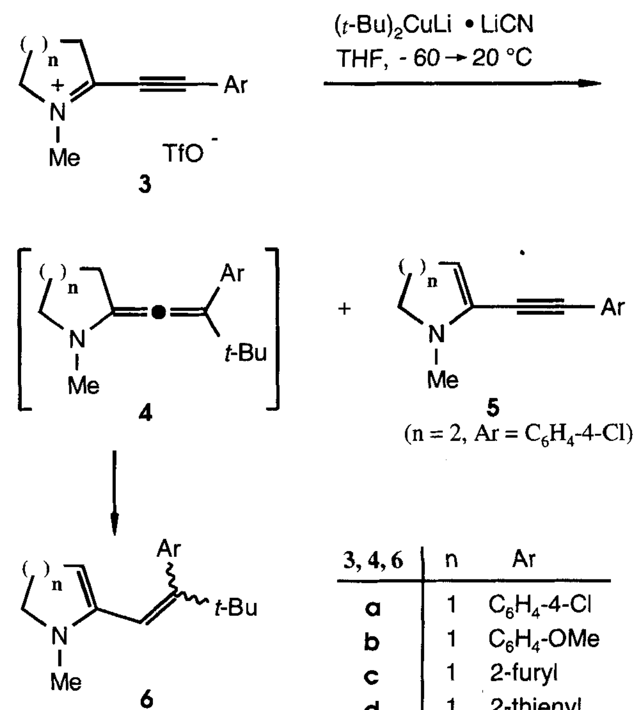




42–87% after non-aqueous workup. As described above, the furyl-substituted salt **3f** was available only in company with triflic acid. Therefore, an excess of the cuprate (3 equivalents) was applied in this case. Unfortunately, the resulting aminodiene **6f**, similar to **6c**, could not be separated from impurities. However, as shown for **6c** [14], further transformations with the crude aminodiene are possible.

In all cases except **6h**, only one diastereomer was detected. ^{1}H-NMR–NOE experiments with **6a–e,i** established the *Z*-configuration at the exocyclic double bond, since saturation of the *t*-Bu resonance resulted in considerable (15–40%) intensity enhancement of the =CH signal. This assignment is in agreement with a crystal structure determination on a product which resulted from a reaction at the enamine function of **6a** [14]. In the case of **6h**, a small amount of the *E*-isomer was also detected by ^{1}H-NMR.

When salt **3e** was combined with $(t\text{-Bu})_2Cu(CN)Li_2$, deprotonation of the cation, leading to alkynyl-enamine **5e**, occurred as a side reaction [15].



3, 4, 6	n	Ar
a	1	C_6H_4-4-Cl
b	1	C_6H_4-OMe
c	1	2-furyl
d	1	2-thienyl
e	2	C_6H_4-4-Cl
f	2	2-furyl
g	2	2-thienyl
h	3	C_6H_4-4-Cl
i	3	2-thienyl

Organocuprate Addition Reactions

Among the various organocopper reagents [13], the so-called higher-order cyanocuprates, prepared in-situ from an organolithium compound (R–Li) and copper(I) cyanide in a 2:1 molar ratio and represented either as $R_2Cu(CN)Li_2$ or as $R_2CuLi \cdot LiCN$, have recently found wide acceptance because of their favorable combination of thermal stability, reactivity and selectivity. By analogy with the reactions of acyclic propyniminium salts [9], the cuprate $(t\text{-Bu})_2CuLi \cdot LiCN$ underwent conjugate addition to the salts **3a–i**. However, the expected aminoallenes **4** tautomerized rapidly to the semicyclic 2-amino-1,3-dienes **6** which were isolated in yields of

The reaction of propyniminium triflates **3** with the cuprate $Me_2CuLi \cdot LiCN$ led to aminoallenes **7** that tautomerized instantaneously to provide semicyclic 2-amino-1,3-dienes **8** as well as exocyclic 1-amino-1,3-dienes **9**. It is likely that the tautomerization generally proceeds in the sequence **7** → **8** → **9**, which we could confirm indeed for **8i/9i** (see below). Interconversions of 1- and 2-amino-1,3-dienes are quite common, and it is clear that structural aspects influence the relative stability of the two species [1, 3]. For the equilibrium between the semicyclic, „cross-conjugated" dienamines **8** and the exocyclic, „linear" dienamines **9**, the results sampled in Table 1 as well as the thermal and photochemical isomerization studies reported below underline the importance of the ring size.

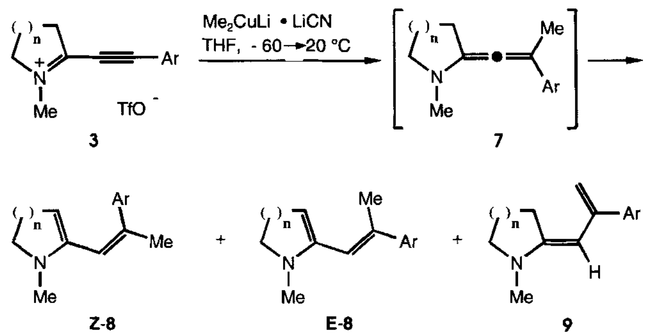


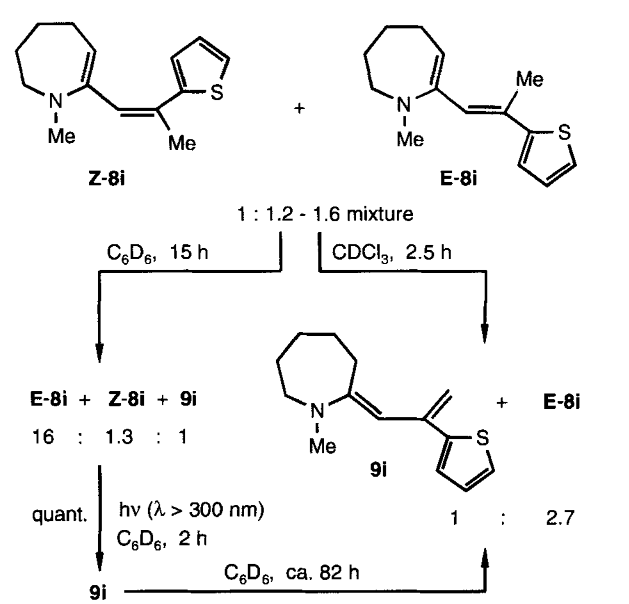
Table 1 Aminodienes **8** and **9**; yields and isomer ratios

7–9	n	Ar	yield (%) of (**8** + **9**)	ratio a) **8** / **9**
a	1	C_6H_4-4-Cl	77	< 1 / > 99
d	1	2-thienyl	78	< 1 / > 99
e	2	C_6H_4-4-Cl	82 b)	94 / 6
f	2	2-furyl	69	> 99 / < 1
g	2	2-thienyl	77	97 / 3
h	3	C_6H_4-4-Cl	65	76 / 24c)
i	3	2-thienyl	76	3 / 27

a) Measured in $CDCl_3$ solution. The ratios reported for **a-e** are those obtained after distillation at ≥ 150 °C, except for **8f** (crude product) and **8i** (equilibration in solution, see Scheme 1).
b) Compound **5** was also found (yield: 5%).
c) The ratio was 52:48 after 15 h in $CDCl_3$ solution.

For the five-membered rings, only the exocyclic forms **9a,d** were detected by ^{1}H-NMR spectroscopy. However, reactions with dimethyl acetylenedicarboxylate gave addition products derived from the endocyclic enamine form **8** exclusively [14]. In sharp contrast, the aminodienes **8f,g** dominate to a large extent for the six-membered ring systems. Finally, the seven-membered rings can accomodate both forms rather well (**8/9 h,i**). The preference of the five-membered ring for the exocyclic double bond (**9a,d**) is in complete agreement with the observation of a 9:1 equilibrium in the system 2-alkylidenepyrrolidine/5-alkyl-2,3-dihydro-1H-pyrrole, in contrast to the predominance of the analogous endocyclic six-membered enamine [16]. ^{13}C-NMR investigations on related 5- and 6-membered cyclic enolethers with an exo- or endocyclic double bond allow the conclusion that 2-methylene-tetrahydrofuran is strongly stabilized relative to 2-methylene-tetrahydropyran because of better n-π conjugation, whereas a much smaller stability difference exists between the corresponding endocyclic 5- or 6-ring enolethers [17]. Furthermore, thermodynamic investigations showed the lability of 2-methylene-tetrahydropyran towards the endocyclic tautomer [18].

As a representative example, the dienamine interconversion in the system **8i/9i** was studied by ^{1}H-NMR (T = 298 K). To this end, the diastereomeric mixture *E/Z*-**8i**, which was obtained by extraction with pentane from the reaction mixture, was used without further purification. The observations can be interpreted as follows:
a) In agreement with the analogous behavior of acyclic morpholinoallenes [9], the tautomerization **7** → **8** yields first the thermodynamically less favored diasteromer *Z*-**8i** which slowly isomerizes into *E*-**8i**.
b) Both the *Z* → *E* isomerization of **8i** and the tautomerization **8i** → **9i** appear to be acid-catalzyed since they occur faster in (unpurified) $CDCl_3$ than in C_6D_6 solution. While this conclusion appears trivial it should be noted that we have found earlier some 2-morpholino-1,3-dienes to isomerize at approximately the same rate in the two solvents [9].
c) In the absence of an acid, a valence equilibrium, maintained by a sigmatropic 1,5-H shift, connects *E*-**8i** and **9i**. Since the linear dienamine is the energetically less favored component, the isomerization *E*-**8i** → **9i**



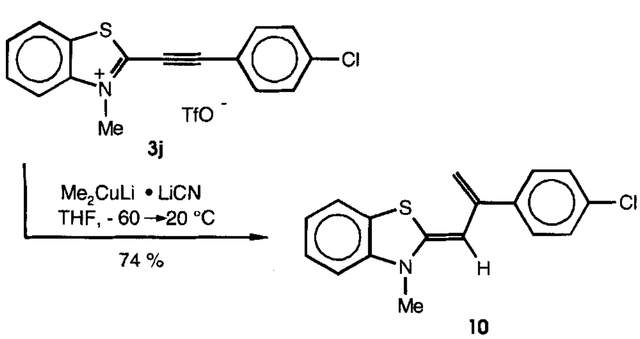
can be induced photochemically (1,5a-H shift), whereas **9i** is slowly transformed to the **8/9** equilibrium mixture by a thermal 1,5s-H migration.

The isomerization processes in the system **8g/9g** were similar to those just described. A pentane extract of the reaction mixture contained *Z*- and *E*-**8g** in a 86:14 ratio. A NMR spectrum recorded immediately after distillation showed a 45:52:3 mixture of Z-**8g**, *E*-**8g**, and **9g**. The fraction of **9g** could be raised by irradiation of the mixture in benzene for 4 h (*Z*-**8g** : *E*-**8g** : **9g** = 12.6 : 28.8 : 58.6), but after several hours, the composition of this solution had returned to the thermal equilibrium (91.5 : 5.3 : 3.2).

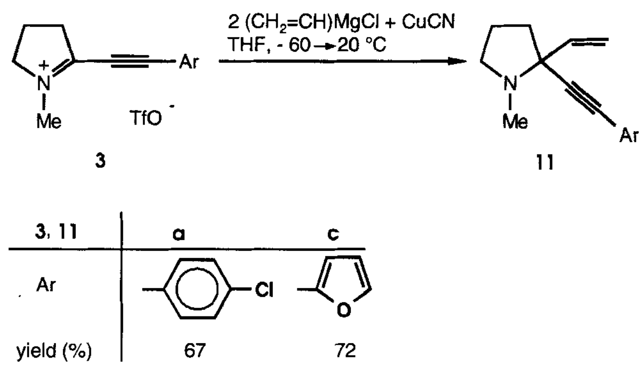
The mechanistic proposal of a pericyclic process interconnecting **8i** and **9i** requires the *E*-configuration at the exocyclic double bonds in both compounds. The observation of significant positive NOE effects on the exocyclic olefinic proton in the ^{1}H-NMR spectra (*Z*-**8i**: saturation of the =C-Me resonance; **9a** and **9i**: saturation of the N-Me resonance) supports the stereochemical assignments. In line with these arguments, the olefinic proton appears at δ = 6.56 in *E*-**8i** and at δ = 5.88 in *Z*-**8i** (Table 2). The low-field shift in the *E*-isomer is to be expected if the heteroaromatic ring and the olefinic moiety are coplanar. In fact, such an arrangement was found by crystal structure determination in a product derived from **8i** [14]. Based on this difference in δ(=CH), the diastereomer assignments were also made for compounds **8f,g** (Table 2).

In contrast, attempts to establish the *Z* or *E* configuration of the 4-chlorophenyl-substituted 2-aminodienes **8e,h** solely by ^{1}H chemical shift comparison with **8f,g,i** were not successful because of some discrepancies. For **8e**, NOE experiments support the assignment given in Table 2, but the evidence is not as strong as in the case of **8i**. Further efforts were not made, since facile *Z/E* isomerization and tautomerization was observed in these cases, too (see experimental part).

Conjugate methyl addition to the propiolthioamidium triflate **3j** could also be achieved. In this case, tautomerization of the initially formed allene was unequivocal and yielded the butadiene derivate **10** in good yield.



It should not be concealed that the „Normant-type reagent“ prepared in situ from 2 equivalents of vinylmagnesium chloride and one equivalent of CuCN delivered the vinyl group at the iminium function of salts **3a,c** rather than in a conjugate manner. The same result, but with lower yields, was obtained when CuCN was replaced by CuBr · Me_2S (2:1 stoichiometry as before, 1:1, or catalytic amounts of copper salt). The formation of **11a,c** contrasts with the successful formation of 1-morpholino-3-vinylallenes, when (2-propynylidene) morpholinium triflates were combined with the same reagent [9]. Although a straightforward explanation is not at hand, the lower reactivity and the lower solubility (in THF or ether) of magnesium cuprates as compared to lithium cuprates [19] may be the key factors for this divergent behavior. Furthermore, it should be recalled that reagents obtained from RMgX and CuHal are likely to exist in solution as a mixture of different species, among them mixed-metal clusters and organocopper compounds, all of which are less efficient in conjugate addition reactions than lithium cuprates [13a].



In summary, we have presented a convenient synthesis of novel exocyclic 1-amino-1,3-dienes and semicyclic 2-amino-1,3-dienes using organocuprate chemistry. Since a wide variety of organocopper reagents are available, other, differently substituted aminodienes will be easily accessible by this method. The chemistry of these elctron-rich dienes, such as thermal isomerization reactions, hydroboration, and cycloaddition reactions, will be the subject of forthcoming papers.

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Experimental

The NMR spectra were taken on Varian EM 390 (1H: 90 MHz), Bruker AC 200 (1H: 200 MHz) and Bruker AMX 400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz) instruments. If not stated otherwise, $CDCl_3$ was used as solvent; δ values (ppm) are

Table 2 ^{1}H-NMR data of 2-amino-1,3-dienes **6** and **8** [δ/ppm] [a])

Prod.	N-CH$_3$	N-CH$_2$	N-C=CH	N-C-CH=	other signals
6a	2.50	2.82	3.88	5.95	1.11 (s, t-Bu), 2.12 (m$_c$, 3-H$_2$), 6.96/7.27 (AA'BB', 4 H)
6b	2.51	2.82	3.85	5.93	1.10 (s, t-Bu), 2.12 (m$_c$, 3-H$_2$), 3.79 (OMe), 6.83/6.92 (AA'BB', 4 H)
6d	2.43	2.78	4.39	6.13	1.11 (s, t-Bu), 2.14 (m$_c$, 3-H$_2$), 6.66 (dd, 1 H), 6.79 (dd, 1 H), 6.96 dd, 1 H)
6e	2.54	2.75	4.09	6.00	1.09 (s, t-Bu), 1.54 (m$_c$, 3-H$_2$), 1.71 (m$_c$, 4-H$_2$), 6.95/7.21 (AA'BB', 4 H)
6f	2.52	2.83	4.30	6.08	1.12 (s, t-Bu), 1.65 (m$_c$, 3-H$_2$), 1.85 (m$_c$, 4-H$_2$), 6.04 (m$_c$, 1 H), 6.30 (m$_c$, 1 H), 7.35 (dd, 1 H)
6g	2.56	2.80	4.29	6.10	1.14 (s, t-Bu), 1.60 (m$_c$, 3-H$_2$), 1.77 (m$_c$, 4-H$_2$), 6.68 (dd, 1 H), 6.90 (dd, 1 H), 7.15 (dd, 1 H)
Z-6h	2.56	2.83	4.32	5.96	1.09 (s, t-Bu), 1.35 (m$_c$, 4-H$_2$), 1.61 (m$_c$, 3-H$_2$), 1.83 (m$_c$, 5-H$_2$), 6.95/7.22 (AA'BB', 4 H)
***E*-6h**	2.78	3.10	4.60	5.66	1.18 (s, t-Bu), 2.69 (m$_c$, 5-H$_2$); remaining signals covered by those of **Z-6h**
6i	2.61	2.94	4.47	6.05	1.14 (s, t-Bu), 1.34-1.48 (m, 2 H), 1.60-1.69 (m, 2 H), 1.84-1.92 (m, 2 H), 6.69 (dd, 1 H), 6.91 (dd, 1 H), 7.15 (dd, 1H)
***E*-8e** [b)]	2.55	2.94	4.61	6.17	2.18 (s, Me), 1.76-1.83 (m, 2 H, 3-H$_2$), 2.10-2.17 (m, 2 H, 4-H$_2$), 7.24/7.33 (AA'BB', 4 H)
***Z*-8e**	2.64	2.85	4.20	5.88	2.02 (s, Me); remaining signals covered by those of *Z*-**8e** and **9e**
***E*-8f**	2.53	2.93	4.62	6.43	1.77(m$_c$, 3-H$_2$), 2.08-2.10 (5 H, Me + 4-H$_2$), 6.20 (d, 1 H), 6.35 (dd, 1 H), 7.30 (d, 1 H)
***Z*-8g** [c)]	2.50	2.91	4.49	5.76	2.07 (s, Me), 1.71 (m$_c$, 2 H, 3-H$_2$), 2.01 (m$_c$, 2 H, 4-H$_2$), 6.80 (dd, 1 H), 6.90 (dd, 1 H), 7.00 (dd, 1 H)
***E*-8g**	2.45	2.86	4.55	6.23	2.13 (s, Me), 1.76 (m$_c$, 2 H, 3-H$_2$), 1.95 (m$_c$, 2 H, 4-H$_2$)
8hA [b)]	2.63'	3.15	4.74	6.13	2.14 (d, |^{4}J| = 1.2 Hz, Me), 2.22 (m$_c$, 2 H, 5-H$_2$)
8hB	2.44	2.90	4.44	5.83	1.94 (m$_c$, 2 H, 5-H$_2$), 2.04 (d, |^{4}J| = 1.5 Hz, Me). Common signals of **A** and **B:** 1.50-1.55 (m), 1.66 (m$_c$), 1.80 (m$_c$), 7.15-7.41 (H-aryl)
***Z*-8i** [d)]	2.59		4.96	5.88	2.00 (d, |^{4}J| = 1.4 Hz, =C-Me)
***E*-8i**	2.51		4.84	6.56	2.21 (d, |^{4}J| = 1.4 Hz, =C-Me). Common signals: 1.55-1.75 (m, 4 H), 2.14-2.16 (m, 2 H), 3.00-3.09 (m, 2 H), 6.72-6.80 (m, 2 H), 1 H), 7.00 (dd, ~ 0.5 H), 7.16 (broad s, ~ 0.5 H)

[a]) Solvent: C_6D_6 for **8i**, $CDCl_3$ for all others. Operating frequency: 200 MHz for **6a-d**, **8i**, and 400 MHz for all others.
[b]) The configurational assignment is supported by a NOE difference spectrum (irradiation at δ 6.17) and observation of the aromatic *ortho*-protons. [c]) The configurational assignment is supported by a NOE difference spectrum (irradiation at δ (N-C=CH)).
[d]) The configurational assignment is supported by NOE experiments on the two diastereomers; see text.

given. As the internal reference, Me_4Si was used for the proton spectra, and the solvent signal for the ^{13}C-NMR spectra [δ ($CDCl_3$) = 77.0, δ (CD_3CN) = 118.2 ppm]. IR spectra were recorded on a Perkin-Elmer IR 1310 spectrometer. Microanalyses were carried out with Perkin-Elmer EA 240 and EA 2400 instruments. Melting points were determined in a copper block and are not calibrated. Solvents were dried by established procedures. Triflic anhydride was distilled from phosphorus pentoxide prior to use.

Synthesis of Enaminoketones 1e–g

The following procedure, carried out in analogy to a published method [20], is typical.

2-[2-(4-Chlorophenyl-2-oxoethylidene]-1-methylpiperidine (**1e**)

A mixture of 2,2-diethoxy-1-methylpiperidine [21] (12.80 g, 69.3 mmol) and 4-chloroacetophenone (10.79 g, 69.3 mmol), protected from atmospheric moisture, was stirred for 90 h at 20 °C and was then kept at 90 °C for 3 h. The product crystallized when the solution was allowed to assume ambient temperature, and was purified by recrystallization from ethanol.

Pale-yellow crystals, m.p. 110 °C; yield: 14.05 g (86%). – IR (KBr): ν = 1599, 1546, 1470, 1398, 1470 cm^{-1}. – ^{1}H-NMR (90 MHz): δ = 1.55–2.00 (m, 4 H, 4-H, 5-H), 2.97 (s, 3 H, N–Me), 3.20–3.50 (m, 4 H, N–CH$_2$, 3-H), 5.53 (s, 1 H, =CH), 7.25 and 7.30 (AA'BB' system, 4 H).

$C_{14}H_{16}ClNO$	Calcd.	C 67.30	H 6.45	N 5.60
(235.7)	Found	C 67.10	H 6.50	N 5.70

2-[2-(2-Furyl-2-oxoethylidene]-1-methylpiperidine (**1f**)

The compound was prepared from 2,2-diethoxy-1-methylpiperidine (13.06 g, 70.5 mmol) and 2-acetylfuran (7.76 g, 70.9 mmol) as described for **1e**.

Brown crystals, m.p. 112 °C; yield: 12.01 g (83%). – IR (KBr): ν = 1602, 1584, 1562, 1531, 1482 cm^{-1}. – ^{1}H-NMR (400 MHz): δ = 1.62 and 1.80 (2 m$_c$, 4 H, 4-H, 5-H), 2.97 (s, 3 H, N–Me), 3.29 (m$_c$, 4 H, N–CH$_2$, 3-H), 5.65 (s, 1 H, =CH), 6.40 (m$_c$, 1 H), 6.86 (m$_c$, 1 H), 7.33 (m$_c$, 1 H). A difference NOE experiment (irradiation at δ = 5.65) established the *E,s-trans* configuration at the enaminone unit [11].

$C_{12}H_{15}NO_2$	Calcd.	C 70.22	H 7.37	N 6.82
(205.3)	Found	C 69.70	H 7.40	N 6.70

1-Methyl-2-[2-oxo-2-(2-thienyl)ethylidene]-piperidine (**1g**)

The compound was prepared from 2,2-diethoxy-1-methylpiperidine (14.00 g, 75.6 mmol) and 2-acetylthiophene (9.68 g, 75.6 mmol) as described for **1e**. During stirring of the mixture for 70 h at 20 °C, yellow crystals of **1g** separated; yield: 13.39 g (80%), m.p. 98–99 °C (from ethanol). – IR (KBr): ν = 1580, 1540–1500 cm^{-1} (s). – ^1H-NMR (200 MHz): δ = 1.62 and 1.75 (2 m_c, 4 H, 4-H, 5-H), 3.00 (s, 3 H, N–Me), 3.25 (m_c, 4 H, N–CH_2, 3-H), 5.55 (s, 1 H, =CH), 6.93 (dd, 1 H), 7.30 (d, 1 H), 7.45 (d, 1 H).

$C_{12}H_{15}NOS$	Calcd.	C 65.12	H 6.83	N 6.33
(221.3)	Found	C 65.10	H 6.90	N 6.40

Synthesis of Iminium Trifluoromethanesulfonates (Triflates) 2 and 3

6-[2-(4-Chlorophenyl)-2-(trifluoromethylsulfonyloxy) ethenyl]-2,3,4,5-tetrahydro-1-methylpyridinium Triflate (**2e**)

At –50 °C, a solution of **1e** (13.00 g, 55.1 mmol) in CH_2Cl_2 (20 ml) was added within 30 min to a solution of triflic anhydride (9.50 ml, 56.6 mmol) in CH_2Cl_2 (90 ml). After stirring for 1 h at –35 °C and for 1 h at 20 °C, the solution was concentrated to half of its volume. Ether was added until **2e** separated as an orange-colored solid. The supernatant solution was decanted off, and the solid residue was recrystallized from CH_2Cl_2/ ether; yield: 28.13 g (96%); m.p. 87 °C. – IR (KBr): ν = 1625–1580, 1400, 1260–1205, 1180, 1145, 1120, 1015, 970 cm^{-1}. – ^1H-NMR (CD_3CN, 400 MHz): δ = 1.84–1.90 (m, 2 H, 3-H), 1.90–2.02 (m, 2 H, 4-H), 3.06 (m_c, 2 H, 5-H), 3.65 (s, 3 H, N–Me), 3.91 (t, 2 H, N–CH_2), 7.05 (s, 1 H, =CH), 7.57 and 7.76 (AA'BB', 4 H). – ^{13}C-NMR (CD_3CN): δ = 17.0 (C-4), 20.9 (C-3), 33.1 (C-5), 47.0 (N–Me), 56.3 (N–CH_2), 114.9 (N=C–C̲H=), 118.9 (q, covalent CF_3SO_3), 121.8 (q, anionic CF_3SO_3), 129.5 (d), 129.7 (s), 130.3 (d), 139.2 (s), 151.1 (s), 180.7 (C-2).

$C_{16}H_{16}ClF_6NO_6S_2$	Calcd.	C 36.13	H 3.03	N 2.63
(531.9)	Found	C 36.3	H 3.10	N 2.60

7-[2-(4-Chlorophenyl)-2-(trifluoromethylsulfonyloxy)ethenyl]-2,3,4,5-tetrahydro-1-methyl-1H-azepinium Triflate (**2h**)

The salt was prepared from enaminoketone **1h** [20] and triflic anhydride as described above for **2e**.
Colorless crystals, m.p. 124 °C, yield 70%. – IR (KBr): ν = 1685, 1410, 1275–1180, 1150–1120, 1080, 1020, 965 cm^{-1}. – ^1H-NMR (400 MHz): δ = 1.83 (m_c, 4 H), 1.89–1.95 (m, 2 H), 3.20 (m_c, 2 H, 6-H), 3.70 (d, J = 0.7 Hz, 3 H, N–Me), 4.15 (m_c, 2 H, 2-H), 7.18 (d, J = 0.8 Hz, 1 H, N=C–CH=), 7.57 and 7.75 (AA'BB', 4 H). – ^{13}C-NMR (CD_3CN): δ = 22.3, 23.8, 29.3 (C-3,-4,-5), 36.9 (C-6), 48.9 (N–Me), 61.2 (C-2), 116.6 (N=C–C̲H=), 119.2 (q, covalent CF_3SO_3), 122.2 (q, anionic CF_3SO_3), 129.7 (d), 129.9 (s), 130.5 (d), 139.5 (s), 151.8 (=C–OTf), 185.7 (N=C).

$C_{17}H_{18}ClF_6NO_6S_2$	Calcd.	C 37.40	H 3.32	N 2.57
(545.9)	Found	C 37.47	H 3.40	N 2.58

The synthesis of salts **3a,c,d,i,j** [11] and **3b** [12] has been described.

6-[(4-Chlorophenyl)ethynyl]-2,3,4,5-tetrahydro-1-methylpyridinium Triflate (**3e**)

Solid **2e** (5.30 g, 9.97 mmol) was thermolyzed in a bulb-to-bulb distillation unit for 60 min at 165 °C/0.001 mbar. After cooling the crude product was dissolved in a minimum amount of acetonitrile and precipitated by addition of ether; yield: 3.10 g (82%). The product was obtained in the same yield, when a solution of **2e** was heated for 6 h at 120 °C in a Schlenk pressure tube.
Yellow crystals, m.p. 143–146 °C. IR (KBr): ν = 2180 (C≡C), 1625, 1575, 1390, 1225, 1080, 1025 cm^{-1}. – ^1H-NMR (CD_3CN, 400 MHz): δ = 1.81–1.86 and 1.96–2.03 (2 m, 4 H, 3-H, 4-H), 3.03 (m_c, 2 H, 5-H), 3.77 (s, 3 H, N–Me), 3.84 (t, 2 H, N–CH_2), 7.54 and 7.73 (AA'BB' system, 4 H). – ^{13}C-NMR (CD_3CN): δ = 17.0 (C-4), 21.0 (C-3), 34.3 (C-5), 47.5 (N–Me), 55.0 (N–CH_2), 83.0 (N=C–C̲≡), 112.6 (≡C̲–aryl), 117.8 (s), 121.9 (q, CF_3SO_3), 130.3 (d), 135.7 (d), 139.4 (s), 166.6 (N=C).

$C_{15}H_{15}ClF_3NO_3S$	Calcd.	C 47.19	H 3.96	N 3.67
(381.8)	Found	C 47.10	H 4.00	N 3.70

6-[(2-Furyl)ethynyl]-2,3,4,5-tetrahydro-1-methylpyridinium Triflate (Complex with Triflic Acid) (**3f**)

At –50 °C, a solution of enaminoketone **1f** (11.00 g, 53.6 mmol) in CH_2Cl_2 (20 ml) was added within 30 min to a solution of triflic anhydride (9.7 ml, 58.9 mmol) in CH_2Cl_2 (50 ml). After stirring of the mixture for 1 h at –30 °C and for 1 h at 20 °C, it was concentrated to half of its original volume. A dark oil was separated by addition of ether. The supernatant solution was decanted off, and the remaining oil was redissolved in acetonitrile (30 ml). A dark oil was separated again by addition of ether, isolated, and kept at 0.01 bar to remove the remaining volatiles. A black, viscous and hygroscopic mass was obtained, which consisted mainly of salt **3f** and triflic acid (CF_3SO_3H) in an approximately 1:1 composition (according to ^1H-NMR and microanalysis); yield: 15.16 g (58%). The triflic acid could not be removed by exposure to dimethylaminomethyl-polystyrene nor by treatment of the product at 150 °C/0.01 mbar. IR (KBr): ν = 3680–2660 (SO_3–H), 2180 (C≡C), 1280–1210, 1155, 1020 cm^{-1}. – ^1H-NMR (CD_3CN, 400 MHz): δ = 1.75–1.84 (m, 2 H, 4-H), 1.89–1.99 (m, 2 H, 3-H), 2.97 (m_c, 2 H, 5-H), 3.66 (s, 3 H, N–Me), 3.77 (2 H, N–CH_2), 6.69 (m_c, 1 H), 7.45 (m_c, 1 H), 7.84 (m_c, 1 H), 9.45 (s, br, HOTf). – ^{13}C-NMR (CD_3CN): δ = 14.1 (C-4), 21.2 (C-3), 33.9 (C-5), 47.5 (N–Me), 55.1 (N–CH_2), 88.9 (N=C–C̲≡), 104.3 (≡C̲–furyl), 114.2 (d), 121.3 (q, CF_3SO_3), 126.6 (d), 134.2 (s), 151.0 (d), 165.8 (N=C).
Depending on the batch, up to 20% of the material consisted of 6-[2-(2-furyl)-2-oxoethyl]-1,2,3,4-tetrahydro-1-methylpyridinium triflate. This material could be prepared independently from enaminoketone **1f** and triflic acid in dichloromethane as a red-brown solid in 62% yield, m. p. 103 °C. – ^1H-NMR (CD_3CN, 400 MHz): δ = 1.84 (m, 2 H, 4-H), 1.98–2.04 (m, 2 H, 3-H), 2.91 (m_c, 2 H, 5-H), 3.59 (s, 3 H, N–Me), 3.93 (2 H, N–CH_2), 4.56 (s, 2 H), 6.65 (dd, 1 H), 7.44 (d, 1 H), 7.71 (d, 1 H), 9.45 (s, br, HOTf). – ^{13}C-NMR (CD_3CN): δ = 16.3 (C-4), 20.3 (C-3), 34.5 (C-5), 44.7 (N–Me), 46.0 (C(O)–C̲H_2), 55.8 (N–CH_2), 113.1 (d), 120.5 (q, CF_3SO_3), 120.5 (d), 150.3 (s), 148.5 (d), 179.2 (C=N), 190.0 (C=O).

2,3,4,5-Tetrahydro-[(2-thienyl)ethynyl]-1-methylpyridinium Triflate (**3g**)

At 0 °C, a solution of enaminoketone **1g** (4.00 g, 18.0 mmol) in CH_2Cl_2 (100 ml) was added within 30 min to a solution of triflic anhydride (3.34 ml, 19.9 mmol) in CH_2Cl_2 (50 ml). After 30 min, during which time the color of the solution changed from yellow to dark-brown, half of the solvent volume was evaporated, and ether was added until a black oil separated. This mixture was stirred for 60 h, the upper layer was decanted off, and the remaining oil was dissolved in acetonitrile. Salt **3g** was precipitated by addition of ether, isolated and recrystallized from acetonitrile/ether; yield: 3.82 g (60%); Yellowish solid, m.p. 95 °C. – IR (KBr): ν = 2180 (C≡C), 1620, 1370, 1260–1220, 1140, 1010 cm^{-1}. – ^{1}H-NMR (CD_3CN, 400 MHz): δ =1.82 (m_c, 2 H, 4-H), 1.91–1.96 (m, 2 H, 3-H), 2.99 (m_c, 2 H, 5-H), 3.69 (s, 3 H, N–Me), 3.78 (t, 2 H, N–CH_2), 7.26 (dd, 1 H), 7.81 (dd, 1 H), 7.93 (dd, 1 H). – ^{13}C-NMR (CD_3CN): δ = 17.3 (C-4), 21.3 (C-3), 34.2 (C-5), 47.0 (N–Me), 54.6 (N–CH_2), 86.9 (N=C–C≡), 108.2 (≡C–thienyl), 121.9 (q, CF_3SO_3), 130.0 (d), 137.4 (d), 139.9 (d), 165.3 (N=C).

$C_{13}H_{14}F_3NO_3S_2$	Calcd.	C 44.19	H 3.99	N 3.96
(353.4)	Found	C 44.10	H 4.00	N 3.90

7-[(4-Chlorophenyl)ethynyl]-2,3,4,5-tetrahydro-1-methyl-1H-azepinium Triflate (**3h**)

Solid **2h** (1.55 g, 2.84 mmol) was placed in a bulb-to-bulb distillation unit and thermolyzed for 20 min at 160 °C/0.009 mbar. After cooling the crude product was dissolved in acetonitrile (15 ml) and precipitated by addition of ether; yield: 0.84 g (75%). Colorless powder, m.p. 76 °C. – IR (KBr): ν = 2160 (very weak, C≡C), 1415, 1255, 1220, 1195, 1130, 1085, 1020 cm^{-1}. – ^{1}H-NMR (400 MHz): δ = 1.81–1.90 (m, 4 H), 1.97 (m_c, 2 H), 3.29 (m_c, 2 H, 6-H), 4.00 (3 H, N–Me), 4.29 (m_c, 2-H), 7.43 and 7.63 (AA'BB' system, 4 H). – ^{13}C-NMR: δ = 21.7, 23.7, 28.7 (C-3,-4,-5), 37.6 (C-6), 48.8 (N–Me), 59.1 (C-2), 84.4 (N=C–C≡), 116.5 (≡C–aryl), 116.7 (s), 120.8 (q, CF_3SO_3), 129.4 (d), 134.8 (d), 139.6 (s), 170.4 (N=C).

$C_{16}H_{17}ClF_3NO_3S$	Calcd.	C 48.55	H 4.33	N 3.54
(395.8)	Found	C 48.50	H 4.55	N 3.54

Synthesis of Amino-1,3-dienes 6; General procedure

A solution of lithium di-*tert*-butyl(cyano)cuprate (3 mmol) in THF was prepared as described [9] and cooled to –60 °C. A suspension of a propyniminium triflate **3** (3 mmol) in THF (20 ml) was gradually added. The mixture was allowed to warm up to –35 °C, kept at this temperature for 1 h, and was then brought to room temparature within 2 h. The solvent was evaporated at 0.01 mbar, and the dark residue was extracted with three 50 ml portions of pentane. Removal of the solvent from the combined extracts left an oil which was purified further by bulb-to-bulb distillation as described below (oven temperatures are given). NMR data for the individual compounds are given in Tables 2 and 3.

5-[(1Z)-2-(4-Chlorophenyl)-3,3-dimethyl-1-butenyl]-2,3-dihydro-1-methyl-1H-pyrrole (**6a**)

Bulb-to-bulb distillation at 150 °C/0.005 mbar; yield 75%. – IR (film): ν = 1600, 1580, 1475, 1380, 1345, 1255, 1090, 1080, 1005 cm^{-1}.

$C_{17}H_{22}ClN$	Calcd.	C 74.03	H 8.04	N 5.08
(275.8)	Found	C 74.3	H 8.2	N 5.2

2,3-Dihydro-5-[(1Z)-2-(4-methoxyphenyl)-3,3-dimethyl-1-butenyl]-1-methyl-1H-pyrrole (**6b**)

Bulb-to-bulb distillation at 155 °C/0.005 mbar; yield 66%. – IR (film): ν = 1620, 1590 cm^{-1}.

$C_{18}H_{25}NO$	Calcd.	C 79.66	H 9.29	N 5.16
(271.4)	Found	C 78.8	H 9.4	N 4.7

5-[(1Z)-2-(2-Furyl)-3,3-dimethyl-1-butenyl]-2,3-dihydro-1-methyl-1H-pyrrole (**6c**)

The product could not be purified. Attempted bulb-to-bulb distillation at 150 °C/0.01 mbar resulted in extensive decomposition.

2,3-Dihydro-1-methyl-5-[(1Z)-2-(2-thienyl)-3,3-dimethyl-1-butenyl]-1H-pyrrole (**6d**)

Bulb-to-bulb distillation at 150 °C/0.01 mbar; yield 66%. – IR (film): ν = 1610 cm^{-1}.

$C_{15}H_{21}NS$	Calcd.	C 72.82	H 8.56	N 5.66
(247.4)	Found	C 73.2	H 9.0	N 5.3

6-[(1Z)-2-(4-Chlorophenyl)-3,3-dimethyl-1-butenyl]-1,2,3,4-tetrahydro-1-methylpyridine (**6e**)

The crude oil consisted of **6e** and *6-[2-(4-chlorophenyl)ethynyl]-1-methyl-1,2,3,4-tetrahydropyridine* (**5**) in a 3.5:1 ratio (yield of **6e**: 65%). This mixture could not be separated by bulb-to-bulb distillation at 150 °C/0.001 mbar.
NMR data for **5**: ^{1}H-NMR (400 MHz): δ = 1.71 (m_c, 2 H, 3-H), 2.11 (m_c, 2 H, 4-H), 2.79 (s, 3 H, N–Me), 2.95 (t, 2 H, N–CH_2), 5.15 (t, 1 H, 5-H), 7.22 and 7.26 (AA'BB' system, 4 H). – ^{13}C-NMR: δ = 21.6 (C-3), 22.8 (C-4), 40.7 (N–Me), 50.7 (N–CH_2), 88.0 (N–C–C≡), 110.0 (C-5), 121.6 (≡C–aryl), 128.5 (d), 130.9 (s), 132.5 (d), 133.8 (C–2), 139.0 (s).

6-[(1Z)-2-(2-Furyl)-3,3-dimethyl-1-butenyl]-1,2,3,4-tetrahydro-1-methylpyridine (**6f**)

A solution of the organocuprate was prepared [9] from CuCN (1.48g, 16.5 mmol) and *tert*-butyllithium (19.4 ml of a 1.7 M solution in hexane) in THF (20 ml). At –70 °C, a suspension of the (unpurified) complex **3f** · CF_3SO_3H (2.30 g, 5.50 mmol) in THF (30 ml) was added gradually. The mixture was allowed to react at –30 °C for 1 h, then at 0 °C for 90 min. After evaporation of the solvent, the residue was extracted with 5 × 20 ml of pentane. From the combined extracts, a viscous yellow oil (0.59 g) was obtained that contained **6f** in a ca. 65% purity (^{1}H-NMR). Attempted bulb-to-bulb distillation led to decomposition at 120 °C.

1,2,3,4-Tetrahydro-1-methyl-6-[(1Z)-2-(2-thienyl)-3,3-dimethyl-1-butenyl]pyridine (**6g**)

Bulb-to-bulb distillation at 185 °C/0.03 mbar furnished a yellow oil which turned dark rapidly; yield 87%. – IR (film): ν = 1615 cm^{-1}.

$C_{16}H_{23}NS$	Calcd.	C 73.51	H 8.87	N 5.36
(261.4)	Found	C 73.2	H 8.7	N 5.3

Table 3 ^{13}C-NMR data of 2-amino-1,3-dienes **6** and **8**; δ [ppm] [a])

Product	N-CH_3	N-CH_2	N-C=<u>C</u>H	N-C-<u>C</u>H=	other signals
6a	39.8	56.5	104.2	117.7	29.2 (C-3), 30.2 (C<u>Me</u>$_3$), 37.4 (<u>C</u>Me$_3$), 128.6 (d), 132.4 (d), 132.8 (s), 140.6 (s), 150.6 (s), 154.1 (s)
6b	39.6	55.6	104.0	115.4	29.0 (C-3), 29.5 (C<u>Me</u>$_3$), 36.9 (<u>C</u>Me$_3$), 54.9 (OMe), 112.9 (d), 115.4 (d),132.7 (s), 148.8 (s), 154.0 (s), 158.0 (s)
6d	39.6	56.0	103.6	120.6	29.6 (C<u>Me</u>$_3$), 29.8 (C-3), 36.9 (<u>C</u>Me$_3$), 124.8 (d), 126.4 (d), 126.9 (d), 140.8 (s), 146.6 (s), 149.4 (s)
6e	40.5	51.3	104.8	123.6	20.9 (C-3), 22.7 (C-4), 29.6 (C<u>Me</u>$_3$), 36.3 (<u>C</u>Me$_3$), 127.1 (d), 131.2 (d), 131.5 (s), 139.0 (s), 142.9 (s), 150.9 (s)
6f	40.6	51.4	104.0	127.5	21.1 (C-3), 22.8 (C-4), 29.5 (C<u>Me</u>$_3$), 36.6 (<u>C</u>Me$_3$), 108.5 (d), 109.9 (d), 140.3 (d), 141.0 (s), 142.1 (s), 152.4 (s)
6g	40.8	51.3	103.6	126.8	20.9 (C-3), 22.7 (C-4), 29.6 (C<u>Me</u>$_3$), 36.4 (<u>C</u>Me$_3$), 123.7 (d), 125.7 (d), 126.6 (d), 140.8 (s), 143.1 (s), 144.6 (s)
Z-6h	38.9	53.1	112.6	131.4	25.9/26.4/27.2 (3 x CH_2), 29.9 (C<u>Me</u>$_3$), 36.3 (<u>C</u>Me$_3$), 125.2 (d), 126.9 (d), 131.0 (d), 139.6 (s), 146.4 (s), 151.5 (s)
6i	39.2	53.0	111.6	128.3	25.7/26.4/27.2 (3 x CH_2), 29.7 (C<u>Me</u>$_3$), 36.5 (<u>C</u>Me$_3$), 123.5 (d), 125.6 (d), 126.3 (d), 141.2 (s), 145.4 (s), 146.4 (s)
***E*-8e**	40.6	51.5	103.6	126.4	17.4 (C-<u>Me</u>), 21.3 (C-3), 22.9 (C-4), 127.7 (d), 128.3 (d), 132.6 (s), 136.1 (s), 143.7 (s)
***E*-8f**	40.6	51.3	104.2	122.6	14.8 (C-<u>Me</u>), 20.9 (C-3), 22.9 (C-4), 105.6 (d), 111.0 (d), 126.2 (s), 141.3 (d), 143.1 (s), 156.0 (s)
***E*-8g**	40.7	51.4	104.3	124.4	17.4 (C-<u>Me</u>), 20.9 (C-3), 22.9 (C-4), 122.8 (d), 123.4 (d), 127.2 (d), 131.0 (s), 143.2 (s), 147.6 (s)
8hA	39.5	53.4	112.1	128.1	17.1 (C-<u>Me</u>), 26.3/26.6/27.5 (C-43, -4, -5), 127.0 (d), 128.2 (d), 132.6 (s), 136.7 (s), 142.0 (s), 147.1 (s)
***E*-8i**	39.5	53.2	112.6	126.3	17.1 (C-<u>Me</u>), 26.2/26.6/27.4 (C-3, -4, -5), 122.8 (d), 123.4 (d), 127.2 (d), 131.7 (s), 146.7 (s), 147.9 (s)

[a]) The following solvents were used: CD_3CN (**6a**), C_6D_6 (**6d**), $CDCl_3$ (all others).

7-[(1Z)-2-(4-Chlorophenyl)-3,3-dimethyl-1-butenyl]-2,3,4,5-tetrahydro-1-methyl-1H-azepine **(6h)**

Bulb-to-bulb distillation at 170 °C/0.006 mbar gave a yellow oil containing (*Z*)- and (*E*)-**6h** ((*Z*)/(*E*) = 14.3); yield: 42%. – IR (film): ν = 1628 cm^{-1}.

$C_{19}H_{26}ClN$	Calcd.	C 75.10	H 8.62	N 4.61
(303.9)	Found	C 74.74	H 8.74	N 4.50

2,3,4,5-Tetrahydro-1-methyl-7-[(1Z)-3,3-dimethyl-2-(2-thienyl)-1-butenyl]-1H-azepine **(6i)**

Bulb-to-bulb distillation at 145 °C/0.005 mbar gave an orange-red oil; yield 58 %. – IR (film): ν = 1610, 1590 cm^{-1}.

$C_{17}H_{25}NS$	Calcd.	C 74.11	H 9.15	N 5.08
(275.5)	Found	C 74.1	H 9.2	N 5.0

Synthesis of Aminodienes 8–10; General procedure

A solution of lithium dimethylcyanocuprate was prepared as follows: To a slurry of CuCN (0.269 g, 3.0 mmol) in THF (20 ml), cooled at –60 °C, a 1.6 M solution of methyllithium in ether (3.75 ml, 6 mmol) was added. The mixture was brought to 0 °C within 5 min, kept at this temperature for 15 min, and the solution so obtained was cooled to –60 °C. Addition of a propyniminium triflate **3** (3 mmol) and further processing was identical to the procedure described above for aminodienes **6**.

2(E)-[2-(4-Chlorophenyl)-2-propenylidene]-2,3-dihydro-1-methylpyrrolidine **(9a)**

Bulb-to-bulb distillation at 150 °C/0.005 mbar; yield 77 %. – IR (film): ν = 1650, 1600, 1560 cm^{-1}. – ^{1}H-NMR (200 MHz): δ = 1.79 (quin, 2 H), 2.42 (m_c, 2 H), 2.72 (s, 3 H, N–Me), 3.15 (t, 2 H), 4.72 (broadened s, 1 H, N–C=CH), 4.86/4.89 (2 s, 2 H, =CH_2), 7.23 and 7.34 (AA'BB', 4 H). – ^{13}C-NMR (CD_3CN): δ= 21.9 (C-4), 31.1 (C-3), 33.4 (N–Me), 53.4 (N–CH_2), 91.2 (N–C=CH), 107.5 (=CH_2), 128.3 (d), 129.2 (d), 132.9 (s), 144.0 (s), 147.0 (s), 152.1 (s).

$C_{14}H_{16}ClN$	Calcd.	C 71.94	H 6.90	N 5.99
(199.3)	Found	C 71.2	H 6.9	N 6.0

1-Methyl-2(E)-[2-(2-thienyl)-2-propenylidene]pyrrolidine **(9d)**

Bulb-to-bulb distillation at 155 °C/0.005 mbar; yield 78%. – IR (film): ν = 1600, 1555 cm^{-1}. – ^{1}H-NMR (400 MHz): δ= 1.86 (quin, 2H), 2.69 (t, 2H), 2.74 (s, 3H, N–Me), 3.19 (t, 2H), 4.75/4.76/5.21 (3 s, 3 H, N–C=CH–C=CH_2), 6.95 (m_c, 1H), 7.11 (m_c, 2 H). – ^{13}C-NMR: δ = 21.7 (C-4), 30.8 (C-3), 33.6 (N–Me), 53.7 (N–CH_2), 89.0 (d, N–C=CH), 105.2 (=CH_2), 123.3 (d), 123.6 (d, J = 185.4 Hz, 5–$C_{thienyl}$), 126.9 (d), 139.6 (s), 148.6 (s), 152.7 (s).

$C_{12}H_{15}NS$	Calcd.	C 70.20	H 7.36	N 6.82
(250.3)	Found	C 70.3	H 7.3	N 6.8

*6-[2-(4-Chlorophenyl)-1-propenyl]-1,2,3,4- tetrahydro-1-methylpyridine (**Z**- and **E**-**8e**)* and *2(E)-[2-(4-Chlorophenyl)-2-propenylidene]-1-methylpiperidine* **(9e)**

Bulb-to-bulb distillation at 170–176 °C/0.04 mbar yielded an orange-colored oil which consisted of **8e** (yield: 78%), **9e** (5.4 %), and **5** (4.9%). The original *E*/*Z* diastereomer ratio of

8e remained unchanged after storing at –30 °C for one week, but changed from 1.3 to 7.4 after 72 h in C_6D_6 solution; after one week, the *Z* isomer could no longer be detected.
NMR data of *Z*- and *E*-**8e**: Tables 2 and 3. Compound **9e** was detected in the product mixture by the following ^{1}H-NMR signals: δ = 4.93 and 5.30 (2 broadened s, $=CH_2$).
The microanalysis of the mixture gave the following values: C 72.6; H 7.2; N 5.7. $C_{15}H_{18}ClN$ requires: C 72.72; H 7.32; N 5. 65.

6-[2-(2-Furyl)-1-propenyl]-1,2,3,4-tetrahydro-1-methyl-pyridine (**8f**)

A THF solution of $Me_2CuLi \cdot LiCN$ (11.2 mmol) was combined with the (unpurified) complex **3f** · CF_3SO_3H (1.56 g, 3.2 mmol). Attempted purification of the crude product (yield: 69%) by bulb-to-bulb distillation failed because of decomposition above 120 °C. Only one diastereomer was detected in the ^{1}H-NMR spectrum, and the *E* configuration was tentatively assigned.
IR (film): ν = 1625–1575 cm^{-1}. – NMR data: Tables 2 and 3. The ^{1}H-NMR spectrum showed a multitude of small signals in the range δ = 1.5 – 3.1, probably resulting from oligomeric impurities.

1,2,3,4-Tetrahydro-1-methyl-6-[2-(2-thienyl)-1-propenyl]-pyridine (*Z*- and *E*-**8g**) and *1-Methyl-2(E)-[2-(2-thienyl)-2-propenylidene]piperidine* (**9g**)

Bulb-to-bulb distillation at 178 °C / 0.03 mbar furnished an orange-colored oil that rapidly turned dark and consisted of a 52 : 45 : 3 mixture of *E*- and *Z*-**8g** (yield: 75%) and **9g** (2%). Compound **9g** was detected in the product mixture by the following ^{1}H-NMR signals: δ = 4.70, 4.97, 5.38 (3 broadened s, $=C\underline{H}-C=C\underline{H}_2$).

$C_{13}H_{17}NS$)	Calcd.	C 71.19	H 7.81	N 6.39
(219.3)	Found	C 71.00	H 7.70	N 6.30

2,3,4,5-Tetrahydro-1-methyl-7-[2-(4-chlorophenyl)-1-propenyl]-1H-azepine (**8h**) and *Perhydro-1-methyl-2(E)-[2-(4-chlorophenyl)-2-propenylidene]azepine* (**9h**)

Bulb-to-bulb distillation at 190 °C/0.005 mbar furnished an oil that consisted of **8h** [mixture of diastereomers, **8hA** (major) and **8hB** (minor)] and **9h** in a 76 : 18 : 6 composition; yield: 65%. After 15 h in $CDCl_3$ solution, the ratio had changed to 52 : 5 : 43. After irradiation of a solution of this mixture in C_6D_6 for 2 h (λ ≥ 300 nm), about 95% consisted of **9h** which gave rise to the following NMR data: ^{1}H-NMR (C_6D_6): δ = 1.2–1.5 (m, 6 H), 2.48 (m_c, 6-H_2), 2.57 (s, N–Me), 2.88 (m_c, N–CH_2), 4.74 (s, 1 H, =CH), 5.11 and 5.34 (AB system, $|^2J|$ = 2.2 Hz, $=CH_2$). – ^{13}C-NMR (C_6D_6): δ = 27.8/28.7/28.9/29.2 (C-3,-4,-5,-6), 40.7 (N–Me), 54.2 (N–CH_2), 95.8 (N–C=$\underline{C}$H), 110.1 ($=CH_2$), 127.9 (d), 128.3 (d), 132.7 (s), 142.6 (s), 146.3 (s), 153.4 (s).
The microanalysis of the mixture gave the following values: C 72.50; H 7.70; N 5.27. $C_{16}H_{20}ClN$ (261.8) requires: C 73.41; H 7.70; N 5. 37.

*2,3,4,5-Tetrahydro-1-methyl-6-[2-(2-thienyl)-1-propenyl]-1H-azepine (Z- and E-***8i***)*

Work-up by extraction into pentane provided a dark-yellow oil, which was already sufficiently pure according to microanalysis and ^{1}H-NMR spectrum; yield: 76%, mixture of diastereomers, *Z*:*E* = 1: 1.2–1.6. See text for *Z/E* equilibrium. IR (film): ν = 1610–1570 cm^{-1}.

$C_{14}H_{19}NS$	Calcd.	C 72.05	H 8.21	N 6.00
(233.4)	Found	C 72.1	H 8.2	N 6.0

Perhydro-1-methyl-2(E)-[2-(2-thienyl)-2-propenylidene] azepine (**9i**)

A mixture of Z- and *E*-**8i** (0.20 g, 0.86 mmol) in benzene-[D_6] (0.5 ml) was placed in an NMR tube and allowed to equilibrate for 15 h, leading to a 16.3 : 1.3 : 1 mixture E-**8i**, Z-**8i**, and **9i**. Irradiation with a Philips HPK high-pressure mercury lamp (125 W, λ > 300 nm) for 2 h produced **9i** quantitatively, but after standing in the dark for ca. 82 h, an equilibrium mixture of *E*-**8i** and **9i** (2.7:1) had formed. – ^{1}H-NMR (C_6D_6, 200 MHz): δ = 1.23 – 1.62 (m, 6 H), 2.50 – 2.57 (m, 2 H), 2.67 (s, N–Me), 2.84 – 2.88 (m, N–CH_2), 4.85 (broadened s, 1 H), 4.96 (d, 1H, J = 1.4 Hz), 5.62 (broadened s, 1 H), 6.76 – 6.82 (m, 1 H), 6.85 – 6.88 (m, 1 H), 7.16–7.21 (m, 1 H).

2-[2-(4-Chlorophenyl)-2-propenylidene]-2,3-dihydro-3-methyl-benzothiazol (**10**)

The crude oil was dissolved in ether, and pentane was added. At –30 °C, yellow crystals separated, m.p. 118 °C; yield: 74%. – IR (KBr): ν = 1530, 1440 cm^{-1}. – ^{1}H-NMR (400 MHz): δ = 3.27 (s, 3 H, N–Me), 5.13 (s, 1 H), 5.24 (s, 1 H), 5.27 (s, 1 H), 6.73 (d), 6.86 (t), 7.14 (t), 7.23 (d), 7.30 and 7.37 (AA'BB', 4 H). – ^{13}C-NMR: δ = 31.3 (N–Me), 90.7 (N–C=$\underline{C}$H), 107.5 (d), 108.5 ($=CH_2$), 120.2 (d), 121.3 (d), 124.3 (s), 126.0 (d), 128.3 (d), 128.7 (d), 133.3 (s), 141.6 (s), 142.3 (s), 144.4 (s), 146.3 (s).

$C_{17}H_{14}ClNS$	Calcd.	C 68.10	H 4.71	N 4.67
(299.8)	Found	C 67.9	H 4.9	N 4.6

2-[(4-Chlorophenyl)ethynyl]-2-ethenyl-1-methylpyrrolidine (**11a**)

A suspension of CuCN (0.269 g, 3.0 mmol) in ether (20 ml) was cooled at –60 °C. A 15% solution of vinylmagnesium chloride in THF (3.74 ml, 6.0 mmol) was added slowly. The mixture was brought to 0 °C within 5 min, kept at this temperature for 3 min, and cooled again at –60 °C. To the brown suspension so obtained was added a suspension of salt **3a** (1.10 g, 3 mmol) in THF (15 ml). After 1 h at –35 °C and 2 h at 20 °C, the solvent was removed, and the residue was extracted with pentane (3 × 50 ml). Bulb-to-bulb distillation of the combined extracts at 160 °C/0.01 mbar gave a yellow oil; yield : 0.49 g (67%). – IR (film): ν = 2190 (w, C≡C), 1605 (s, C=C) cm^{-1}. – ^{1}H-NMR (CD_3CN, 400 MHz): δ = 1.87–2.03 (m, 3 H), 2.13–2.19 (m, 1 H), 2.27 (s, N–Me), 2.59 (q, 1 H), 3.06–3.11 (m, 1 H), 5.26 (dd, J = 9.6, 1.9 Hz, 1 H, $CH=C\underline{H}_2$), 5.62 (dd, J = 17.0, 1.9 Hz, 1 H, $CH=C\underline{H}_2$), 5.73 (dd, J = 17.1, 9.7 Hz, 1 H, $C\underline{H}=CH_2$), 7.27/7.37 (AA'BB', 4 H). – ^{13}C-NMR (CD_3CN): δ = 21.9 (C-3), 36.1 (N–Me), 41.2 (CH_2), 54.2 (CH_2), 67.7 (C-2), 88.0 and 88.8 ($\underline{C}≡\underline{C}$), 116.8 ($=CH_2$), 122.8 (s), 129.6 (d), 134.0 (d), 134.5 (C-Cl), 142.0 ($\underline{C}H=CH_2$).

$C_{15}H_{16}ClN$	Calcd.	C 73.31	H 6.56
(245.8)	Found	C 73.0	H 6.5

2-Ethenyl-2-[(2-furyl)ethynyl)]-1-methylpyrrolidine (**11b**)

Bulb-to-bulb distillation at 145 °C/0.02 mbar gave a yellow oil; yield : 0.43 g (72%).
IR (film): ν = 2200 (w, C≡C), 1595 (s, C=C) cm^{-1}. – ^{1}H-NMR (400 MHz): δ = 1.80 – 2.02 (m, 2 H), 2.14–2.20 (m, 2 H), 2.26 (s, N–Me), 2.58 (q, 1 H), 3.07 (m, 1 H), 5.25 (dd, J = 9.6, 1.9 Hz, 1 H, CH=C$\underline{H}_2$), 5.61 (dd, J = 17.1, 1.9 Hz, 1 H, CH=CH_2), 5.71 (dd, J = 17.1, 9.6 Hz, 1 H, C$\underline{H}$=CH_2), 6.36 (dd, J = 3.3, 1.9 Hz, 1 H), 6.54 (dd, J = 3.3, 0.8 Hz, 1 H), 7.35 (dd, J = 1.9, 0.8 Hz, 1 H). – ^{13}C-NMR: δ = 21.3 (C-3), 35.7 (N–Me), 40.4 (CH_2), 53.6 (CH_2), 67.1 (C-2), 78.6 and 91.0 ($\underline{C}$≡$\underline{C}$), 110.8 (d), 114.5 (d), 116.8 (=CH_2), 137.1 (s), 140.3 ($\underline{C}$H=CH_2), 143.0 (d, C-5_{furyl}).

$C_{13}H_{15}NO$	Calcd.	C 77.58	H 7.51
(201.3)	Found	C 77.7	H 7.8

References

[1] P. W. Hickmott, in: The chemistry of enamines, Part 2, Z. Rappoport (Ed.), Wiley, Chichester 1994, chapter 26
[2] A. G. Cook, Enamines: Synthesis, Structure and Reactions, M. Dekker, New York – Basel 1988
[3] P. W. Hickmott, Tetrahedron **40** (1984) 2989
[4] M. Petrzilka, J. J. Grayson, Synthesis **1981**, 753
[5] M. L. Farmer, W. E. Billups, R. B. Greenlee, A. N. Kurtz, J. Org. Chem. **31** (1966) 2885
[6] R. W. Jemison, T. Laird, W. D. Ollis, J. Chem. Soc., Chem. Commun. **1972**, 556
[7] L. E. Overman, L. A. Clizbe, J. Am. Chem. Soc. **98** (1976) 2352
[8] A. J. Hubert, H. G. Viehe, J. Chem. Soc. **1968**, 228
[9] G. Maas, T. Mayer, Synthesis **1991**, 1209
[10] M. Brunner, G. Maas, Synthesis **1995**, 957
[11] R. Reinhard, G. Maas, J. Bohrisch, J. Liebscher, Liebigs Ann. Chem. **1994**, 429
[12] M. Brunner, R. Reinhard, R. Rahm, G. Maas, Synlett **1994**, 627
[13] Recent reviews: (a) B. H. Lipshutz, S. Sengupta, Org. React. **41** (1992), 135. (b) B. H. Lipshutz, in: Organometallics in Synthesis, M. Schlosser (ed.), Wiley, Chichester 1994, chapter 4
[14] R. Reinhard, Dissertation, University of Kaiserslautern, 1994
[15] See ref. [12] for the analogous deprotonation of salts **3a–d**, **i** with sodium trimethylsilanolate.
[16] O. Cervinka, A. Fábryová, J. Josef, V. Sermek, S. Smrcková, Collect. Czech. Chem. Commun. **48** (1983) 3407
[17] E. Taskinen, Tetrahedron **34** (1978) 433
[18] E. Taskinen, Acta Chem. Scand. **B28** (1974) 1234
[19] B. H. Lipshutz, D. A. Parker, S. L. Nguyen, K. E. McCarthy, J. C. Barton, S. E. Withney, H. Kotsuki, Tetrahedron **42** (1986) 2873
[20] V. Virmani, M. B. Nigam, P. C. Jain, N. Anand, Indian J. Chem. **17B** (1979) 472
[21] V. G. Granik, A. B. Sukhoruchkin, N. S. Kuryatov, V. P. Pakhomov, R. G. Glushkov, Chem. Heterocycl. Compd. (USSR) (Engl. Transl.) **1974**, 880

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