Asymmetric Alkylation of Chiral 2-Azapentadienyl Metal Compounds: Diastereoselective Synthesis of Alkyl-Substituted *N*-Allylimines (2-Aza-1,4-pentadienes)

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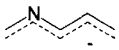
N-Allylimines (2-aza-1,4-pentadienes) **3** bearing a chiral auxiliary group at C-1 were prepared by a three-step sequence involving condensation of pivaloyl chloride with allylamine, chlorination and reaction with a chiral amine (SMP or SMEMP) as an auxiliary group. Deprotonation of **3** by treatment with butyllithium in *tert*-butyl methyl ether as solvent at −20 °C afforded the chiral 2-azapentadienyllithium compounds **4**. Transmetalation of **4a** with $MgBr_2 \cdot Et_2O$ gave the corresponding magnesium bromide **5**. Alkylation with primary alkyl halides is predominantly kinetically controlled and leads to the 3-substituted *N*-allylimines **6**. Secondary and tertiary alkyl halides, however, preferentially give 5-substituted 2-aza-1,3-pentadienes **7**. The diastereoselectivity of the alkylation reaction may be increased by transmetalation from the lithium compound to the corresponding magnesium bromide or by exchange of the SMP group for the stronger chelating SMEMP group. The halide ion of the alkylating agent strongly influences the configuration of the newly formed stereogenic center. Thus, the chlorides lead to the opposite stereochemistry compared to the bromides. The effect of different solvents on the regio- and diastereoselectivity of the alkylation reactions was studied. Semiempirical calculations (PM3, MNDO) were used to design a stereochemical model for the metalated intermediates in order to rationalize the stereochemistry observed in the experiments.

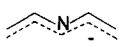
Like pentadienyl anions the isoelectronic azapentadienyl anions are stabilized reactive intermediates with a conjugated π-electron system. The positions of the nitrogen atom within the system has a pronounced influence on the relative energy and the reactivity of the system[2]. Whereas 1- and 3-azapentadienyl anions have similar, favorable total energies, 2-azapentadienyl anions are significantly destabilized by ca. 18 kcal/mol. This surprising result was explained by the electronic perturbation effect exercized by the nitrogen atom on the π orbitals of the pentadienyl system[2].

Pentadienyl anion

1-Azapentadienyl anion



2-Azapentadienyl anion



3-Azapentadienyl anion

From the synthetic point of view azapentadienyl anions or their metal derivatives are interesting intermediates for carbon−carbon bond formations. Within this series of compounds, 1-azapentadienyl anions may be used as a four-carbon moiety (d4 synthon), 2-azapentadienyl anions as a three-carbon building block (d3 synthon), and 3-azapentadienyl anions as two-carbon unit (d2 synthon). In all these applications, the nitrogen atom serves as a predetermined breaking point at which the corresponding carbon chain is split off after the reaction, for instance by hydrolysis.

The relative destabilization and the resulting enhanced reactivity on the one hand and their possible use as a d3 reagent on the other hand make 2-azapentadienyl metal compounds particularly interesting. They may also be considered to be imino-substituted allyl anions[3], leading to primary allylic amines after hydrolytic cleavage of the C=N bond. 2-Azapentadienyl metal compounds have only rarely been investigated in organic chemistry[4]. To our knowledge they were only very recently applied in asymmetric synthesis by Barrett et al. to the preparation of amino alcohols using a chiral borane auxiliary group[5] attached to the 5-position. As homoenolate equivalents[6], their behavior resembles that of 1-aminoallyl anions (deprotonated tertiary allylamines), which were studied in great detail by Ahlbrecht et al.[7] (see also ref.[8]). We were able to show that 2-azapentadienyllithium compounds may be used in regioselective C−C bond forming reactions with carbonyl compounds[2]. In this paper we report on applications of these systems in diastereoselective alkylation reactions.

Since a chiral auxiliary group may be readily introduced into the appropriate 1-position of 2-azapentadienyl com-

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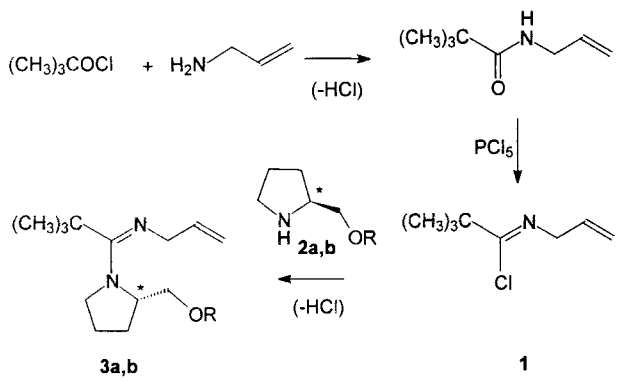
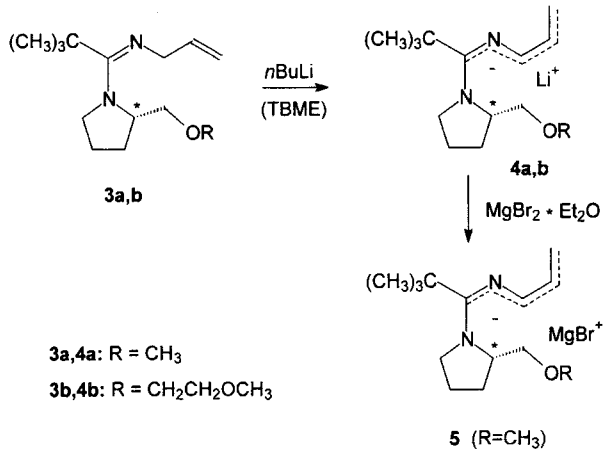
pounds, we decided to investigate first the applicability of these reactive intermediates in asymmetric synthesis using the auxiliary-controlled approach. When we start from *N*-allylimines the introduction of a new stereogenic carbon atom into the 3-position of the chain represents the most challenging problem. A solution of this question requires a regio- and diastereo-controlled addition of the electrophile to the 3-position of the chain. The conditions of kinetic attack should help to reach this goal, avoiding the formation of thermodynamically controlled products resulting from attack in the 5-position. The resulting chiral *N*-allylimines and their derived chiral allylamines are very valuable building blocks for the synthesis of complex organic molecules[9].

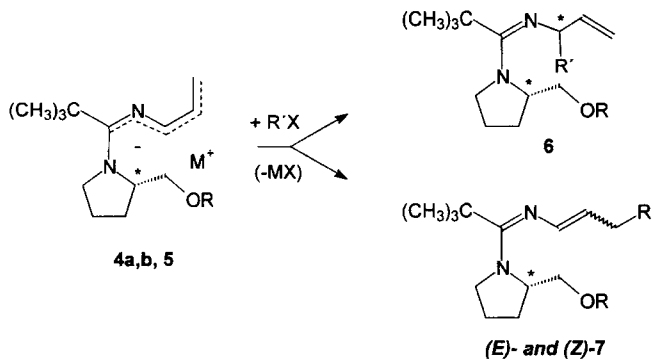
Our synthetic protocol starts with a simple, high-yield three-step procedure for the preparation of chiral *N*-allylimines (2-aza-1,4-pentadiene)[10,11]. The amide formed from allylamine and pivaloyl chloride is converted into the imidoyl chloride **1**, which in turn is treated with (*S*)-2-(methoxymethyl)pyrrolidine (**2a**) (SMP[12]) or (*S*)-2-[(2-methoxyethoxy)methyl]pyrrolidine (**2b**) (SMEMP[13]) to yield the *N*-allylimines (*N*-allyl amidines, 2-aza-1,4-pentadienes) **3a**, **b**. The bulky *tert*-butyl group, introduced as pivaloyl chloride, proved particularly useful as it provides steric shielding giving rise to high regio- and diastereoselectivity (in comparison with the phenyl analog[2,10]). This approach permits the introduction of various chiral auxiliaries by nucleophilic substitution. In our hands, however, best results with regard to stereoinduction were obtained by using SMP (**2a**) and SMEMP (**2b**). Other systems studied (fenchol, chiral alcohols, glycerinaldehyde) were less successful[1,10].



Due to their substitution pattern, our amino-substituted *N*-allylimines **3a**, **b** are not particularly acidic. Hence, their deprotonation requires *n*-butyllithium as a base at a temperature of −20 °C in *tert*-butyl methyl ether (TBME) as solvent for almost complete deprotonation. Lithium diisopropylamide is not applicable, since it is obviously not basic enough for this reaction; THF starts decomposing under the reaction conditions employed (see below). A special procedure for the optimal deprotonation and quenching reaction was developed (see Experimental). Besides the lithium compounds **4a**, **b** also the magnesium compound **5** was investigated in this study. It was prepared by transmetalation at −20 °C by adding a freshly prepared solution of the magnesium dibromide ether complex (from magnesium turnings and 1,2-dibromoethane[14]) to the lithium compounds **4a**, **b**.



The subsequent reactions with the various electrophiles were conducted at −78 °C. After aqueous workup and evaporation of the solvent the crude reaction mixture of the products **6** and **7** was invesigated by NMR spectroscopy. Pure material was obtained after preparative HPLC. This study mainly deals with the development of a new methodological approach. Therefore, 1- to 2-mmol batches were used. In several cases, however, synthetically interesting increased amounts of material were allowed to react (up to 10 mmol).



Results

Protonation and Silylation

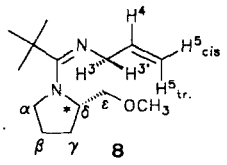
As Table 1 indicates, protonation, deuteration, and silylation of the metalated intermediates **4a**, **b**, **5** lead predominantly to 2-aza-1,3-pentadienes **7** carrying the added electrophile in the 5-position. We cannot completely rule out the possibility that the observed minor compound **6** (R′ = H) generated by protonation and deuteration is essentially the unreacted starting material **3**.

Table 1. Protonation, deuteration and silylation of the organometallic compounds **4**, **5**

Nr.	R′	X	From	Crude Yield (%)	**6** : **7**	***(E)*-7** : ***(Z)*-7**
6aa,7aa	H[1]	OMe	**4a**	93	11 : 89	22 : 78
6aa,7aa	H[1]	OMe	**5**	86	18 : 82	82 : 18
6ba,7ba	H[2]	OMe	**4b**	90	4 : 96	96 : 4
6ab,7ab	D	OMe	**4a**	90	14[3] : 86	26 : 74
6bb,7bb	D	OMe	**4b**	94	<5 : >95	91 : 9
6bc,7bc	$SiMe_3$	Cl	**4b**	85	<5 : >95	89 : 11

[1] **6aa** = **3a**. – [2] **6ba** = **3b**. – [3] Contains also compound **3** (starting material).

We interpret this reactivity as a result of a mainly thermodynamically controlled, possibly reversible production of the more stable isomer, either by direct attack of the electrophile or as the final material after an initially kinetically controlled attack at C-3 and subsequent rearrangement to the observed product. Protons and trimethylsilyl groups are well-known to undergo such rearrangements under the reaction conditions employed. It is interesting to look at the (*E*)/(*Z*) ratios of the protonated and deuterated products **7**. Whereas the lithium compound **4a** is predominantly converted into the (*Z*) isomers, **4b** and **5** are preferentially transformed into the (*E*) isomers. It may well be that this result reflects the stereochemistry of the respective metalated intermediates (see below). Of course, such reactions are of little value in stereoselective synthesis, since no new stereogenic center is produced; they are however of considerable mechanistic interest. The silyl-substituted products may find application for further chain elongation by deprotonation and subsequent Peterson-type olefination.



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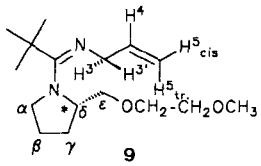

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Alkylation Reactions

Primary alkyl halides react as electrophiles with the SMP-substituted lithium compound **4a** to give mixtures of regioisomers **6** and **7** (attack at C-3 and C-5) and of the diastereomers of **6** (with regard to the stereochemistry at C-3) (see Table 2). The yields of crude products (after aqueous workup and evaporation of the solvents) are mainly in the range of 80–95% as determined by ^{1}H-NMR spectroscopy or HPLC analysis. Besides small amounts of starting materials no indications of other byproducts were found. Purification of the crude material was achieved by preparative HPLC.

Table 2. Alkylation reactions of lithium compound **4a**

Nr.	R′	X	Crude Yield (%)	**6** : **7**	**6**[1] Diast.I : Diast.II
6ad,7ad	C_2H_5	Br	90	88 : 12	21 : 79
6ad,7ad	C_2H_5	I	95[2]	56 : 44	27 : 73
6ae,7ae	C_3H_7	Cl	85	94 : 6	83 : 17
6ae,7ae	C_3H_7	Br	82	77 : 23	30 : 70
6af,7af	C_4H_9	Cl	94	92 : 8	85 : 15
6af,7af	C_4H_9	Br	74	87 : 13	13 : 87
6af,7af	C_4H_9	I	91[3]	42 : 58	37 : 63
6ag,7ag	$CH_2CH(CH_3)_2$	Cl	53	84 : 16	92 : 8
6ag,7ag	$CH_2CH(CH_3)_2$	Br	91	75 : 25	44 : 56
6ah,7ah	$(CH_2)_2CH(CH_3)_2$	Br	92	64 : 36	35 : 65
6ai,7ai	CH_2-CH=CH_2	Cl	92	82 : 18	45 : 55
6ai,7ai	CH_2-CH=CH_2	Br	74	84 : 16	40 : 60
6aj,7aj	$CH(CH_3)_2$	Cl	93[4]	69 : 31[5]	56 : 44
6aj,7aj	$CH(CH_3)_2$	Br	94	32 : 68[6]	38 : 62
6ak,7ak	$C(CH_3)_3$	Cl	83	<5 : >95[7]	/
6ak,7ak	$C(CH_3)_3$	Br	91	<5 : >95[8]	/

[1] Diastereomer I: low-field shift of proton at C-4; diastereomer II: high-field shift of proton at C-4 (see text). – [2] Contains 5% of **3a**. – [3] Contains 3% of **3a**. – [4] *n*-Hexane as solvent. – [5] (*E*):(*Z*) = 10:90. – [6] (*E*):(*Z*) = 52:48. – [7] (*E*):(*Z*) = 49:51. – [8] (*E*):(*Z*) = 61:39.

Most electrophiles (except for iodides) attack the 2-azapentadienyl system preferentially at C-3, i.e. these reactions are governed by kinetic control. Usually, one finds an excess of 40–80% (see Table 2) in favor of the *N*-allylimine (2-aza-1,4-pentadiene) **6**, using the standard conditions (see Experimental). Among **6**, one of the two possible diastereomers is usually formed in significant excess, depending on the size and steric demand of the alkyl group (*de*: 12–84%). Unfortunately, we have not yet been able to determine reliably the absolute configurations of the oily reaction products, since attempts to establish a correlation with compounds of known stereochemistry have failed so far. We therefore denote the unknown absolute configuration at C-3 by the ^{1}H-NMR shift of the proton at C-4 of the respective diastereomer (diastereomer I: Proton at C-4 at low field; diastereomer II: Proton at C-4 at high yield). Very interestingly, the configuration of the newly formed asymmetric center C-3 depends strongly on the nature of the halide. Thus, the chlorides lead preferential to diastereomer I (with the signal of the proton at C-4 at low field). However, bromides (and iodides) give an excess of the diastereomer II (with the NMR signal of the proton at C-4 at high field). These observations suggest the intriguing possibility of preparing both possible diastereomers just by changing the nature of the leaving halide ion. Similar observations were recently published by Beak et al.[15] and by Kobayashi and Ishitani[16]. The selectivity of the iodides is generally much lower than those of the chlorides and bromides. Secondary alkyl halides like isopropyl halides still give appreciable amounts of **6** in clean and reproducible reactions, but the diastereomeric excess drops considerably. *tert*-Butyl halides regioselectively attack the 2-azapentadienyl system at C-5 to afford **7**, certainly due to steric reasons. Although allyl halides attack the 3-position, the observed diastereose-

lectivity is not satisfactory. Under the reaction conditions employed, no sigmatropic rearrangement was observed.

Table 3. Comparison of the products **6**, **7** of alkylation reactions of lithium and magnesium compounds **4a** and **5**

Nr.	R'X	Crude Yield (%)		6 : 7		6 Diast. I : Diast. II	
		Counterion		Counterion		Counterion	
		Li	MgBr	Li	MgBr	Li	MgBr
6ad,7ad	BrC_2H_5	90	90	88 : 12	88 : 12	21 : 79	<3 : >97
6ae,7ae	1-BrC_3H_7	82	78	77 : 23	91 : 9	30 : 70	9 : 91
6af,7af	1-BrC_4H_9	74	78	87 : 13	89 : 11	13 : 87	<3 : >97
6ah,7ah	Br-$(CH_2)_2CH(CH_3)_2$	92	75	64 : 36	76 : 24	35 : 65	<3 : >97

The diastereoselectivity of the reaction may be influenced in two ways. Firstly, the exchange of the lithium counterion (compound **4a**) for the magnesium bromide ion[14] (compound **5**) does not markedly alter the crude yields of the reactions nor the regiochemistry (Table 3). However, a drastic improvement of the *de* was found when this counterion was used. Preferrably diastereromer II (with the ^{1}H-NMR high-field shift of the signal of the proton at C-4) was observed. In several cases, we were not able to detect the NMR signals of the second diastereomer I. We conclude from these findings that transmetalation from the lithium ion to the magnesium bromide ion improves considerably the diastereoselectivity, but leaves the regioselectivity almost unchanged.

As a second way to influence the diastereoselectivity of the reaction besides use of the SMP-derived organometallics compounds **4a**, **5**, we also investigated the SMEMP-substituted lithium system **4b** (Table 4). Compared to SMP, the SMEMP moiety offers one more coordination position. One may speculate[13] that a tighter binding of the cation to the anionic part of the molecule may result, which in turn may lead to improved stereoselectivity.

Table 4. Alkylation reactions of lithium compound **4b** with alkyl bromides

Nr.	R'	Crude Yield (%)	6 : 7	*(E)*-7 : *(Z)*-7	6 Diast.I : Diast.II
6bd,7bd	C_2H_5	71	94 : 6	>95 : <5	<2 : >98
6be,7be	C_3H_7	89	97 : 3	>95 : <5	<2 : >98
6bf,7bf	C_4H_9	87	94 : 6	>95 : <5	<2 : >98
6bg,7bg	$CH_2CH(CH_3)_2$	81	93 : 7	>95 : <5	<2 : >98
6bh,7bh	$(CH_2)_2CH(CH_3)_2$	90	93 : 7	>95 : <5	<2 : >98
6bi,7bi	CH_2-CH=CH_2	69	92 : 8	>95 : <5	<2 : >98
6bj,7bj	$CH(CH_3)_2$	85	39 : 61	>95 : <5	29 : 71
6bk,7bk	$C(CH_3)_3$	79	<5 : >95	>95 : <5	/
6bl,7bl	$(CH_2)_3$-CH=CH_2	56 (isol.)	92 : 8	>95 : <5	1 : 99
6bm,7bm	CH_2-C_6H_5	47 (isol.)	69 : 31	>95 : <5	<2 : >98

Indeed, the data in Table 4 demonstrate that both regiochemistry and diastereoselectivity of a number of quenching reactions using alkyl bromides as electrophiles are significantly improved, compared to the results obtained with SMP-lithium. Only minor amounts of the thermodynamically more stable 5-alkyl product **7** were found; in a number of cases only diastereomer II (with the high-field ^{1}H-NMR signal of the proton at C-4) was detected. Besides the organomagnesium compounds **5** described above, the 2-azapentadienyl lithium system **4b** with the SMEMP moiety as chiral auxiliary group offers an alternative synthetic route to configurationally pure 3-alkyl-substituted *N*-allylimines **6**. At present, we are investigating various reaction pathways to synthesize the chiral *N*-allylamines from the *N*-allylimines **6**.

Table 5. Solvent effects on the reaction of 1-*tert*-butyl-1-{(*S*)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-2-azapentadienyllithium (**4b**) with 1-bromobutane at −78 °C

Solvent	Crude yield (%)	6 : 7	6 Diast.I : Diast.II
TBME	87	94 : 6	<3: >97
THF	78	97 : 3	7 : 93
Et_2O	91	85 : 15	14 : 86
$MeOCH_2$-CH_2OMe	99	41 : 59[1]	27 : 73
Toluene[2]	83	> 95 : < 5	31 : 69
n-Hexane[2]	90	75 : 25	63 : 37

[1] Together with 33% of (*E*)-**7aa**. − [2] Together with unidentified by-products.

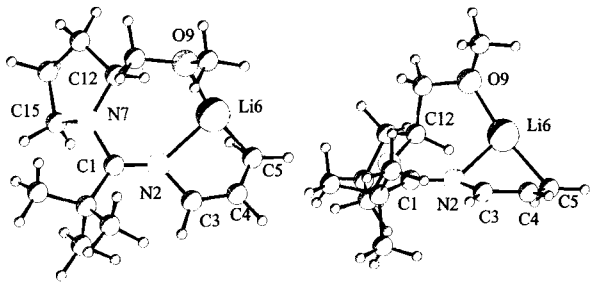
In order to investigate the influence of solvent effects on the stereochemical outcome of our reactions we performed the reaction of lithium compound **4b** with bromoethane in various solvents. As Table 5 indicates, the regiochemistry is mostly in favor of the products **6** (except in 1,2-dimethoxyethane). Generally, the diastereomeric excess achieved is highest when TMBE is used as solvent, all other solvents give less satisfactory results. Thus, TBME, which is easy to dry and to handle, seems to be the solvent of choice for this alkylation reaction[17].

Discussion

According to cryoscopic measurements the lithiated phenyl analog of the *tert*-butyl compound **4a** is monomeric in THF solution at low temperature[18]. Assuming a similar monomeric structure for the lithiated 2-azapentadiene **4a**, we performed extensive semiempirical MNDO[19] and PM3[20] calculations for this key intermediate using the MOPAC 6.0 package of programs[21] in order to derive a reasonable structural model for the lithiated intermediate in the alkylation reactions[22]. A thorough investigation of the potential energy surface resulted in the localization of several local minima. Due to a better description of the bonds from lithium to carbon, nitrogen and oxygen, we prefer PM3 over MNDO for the calculation of chelated systems like **4a**, **b**[20b,23]. We therefore concentrate our discussion on the PM3 results. Lower in energy compared to all other minima by at least 1.3 kcal/mol is the global energy minimum, whose structure is depicted in Figure 1.

As it can be clearly seen, the reactive 2-azapentadienyl moiety adopts a sickle-shaped structure, offering optimal contact to the lithium counterion. This sickle-type structure seems to be predominant in 1-alkyl-substitued 2-azapentadienyllithium compounds[22]. In **4a**, the nitrogen lone pair, the π system at C-5 (to a lesser extent also at C-3), and the methoxy function of the chiral auxiliary group all contrib-

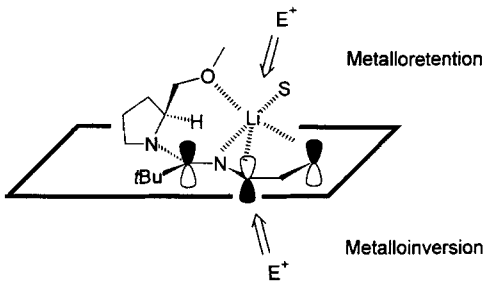
Figure 1. PM3-optimized structure of the lithiated 2-azapentadiene **4a**; view from top on the *Re* face (C-3) (left) and sideview (right) (computational numbering)[a]



[a] Selected PM3 data: Heat of formation: −26.72 kcal/mol; bond lengths [Å]: N7–C1 1.4690, C1–N2 1.3174, N2–C3 1.4006, C3–C4 1.4016, C4–C5 1.3954, N2–Li6 2.0951, C5–Li6 2.1306, O9–Li6 1.9969; bond angles [°]: N7–C1–N2 115.70, C1–N2–C3 127.62, N2–C3–C4 119.39, C3–C4–C5 126.44, Li6–N2–C3 88.80, Li6–C5–C4 83.07; dihedral angles [°]: C15–N7–C1–N2 107.14, C12–N7–C1–N2 339.61, C7–C1–N2–C3 176.85, C1–N2–C3–C4 175.71, N2–C3–C4–C5 349.92, Li6–N2–C3–C4 326.95, Li6–C5–C4–C3 44.49.

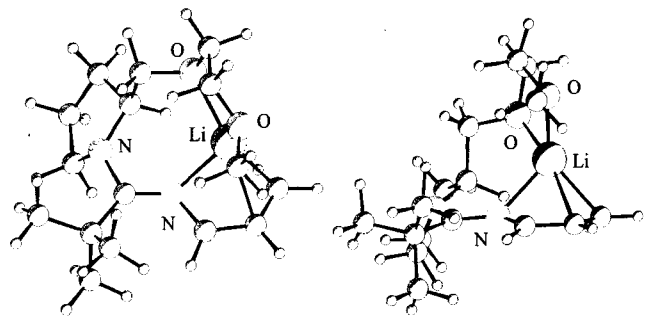
ute to an overall chelation of the lithium ion, which is located above the slightly nonplanar 2-azapentadienyl system. For sterical, but also for electronic reasons (to avoid a +M interaction of the amino group with the pentadienyl 6π-electron system), the auxiliary group is twisted by ca. 64° with respect to the 2-azapentadienyl part of the molecule. The bulky *tert*-butyl group provides a steric shielding against front-side attack. The location of the lithium ion above the plane (on the *Re* face with regard to C-3) divides the environment around the molecule into two quite different diastereotopic half-spheres. This stereochemical model fits also nicely to spectroscopic results. ^{1}H- and ^{13}C-NMR spectra of **4a** show only one set of signals at low temperature (233 K). The NOE data and the coupling constants are in full accord with the sickle-type structure[10].

Figure 2. Structural model of a lithiated 2-azapentadiene **4**



An approach of the attacking electrophile at C-3 (the α position of the allyl system) may proceed either with retention of configuration regarding the metal ion (from the top in Figure 2) or with inversion of configuration (from the bottom in Figure 2), similarly as discussed by Ahlbrecht et al. for the attack of electrophiles at aminoallyllithium compounds in γ-position[7,7c,7d]. Unfortunately, the lacking data regarding the absolute configuration of the preferred products obtained by quenching of the reactions still preclude the decision which mode of electrophilic attack is realized. However, the surprising dependence of the relative stereochemistry on the nature of the leaving group (chloride versus bromide, vide supra) clearly strongly indicate that both ways (metaloretention and metaloinversion) may be used selectively by the respective electrophiles. A complete change in mechanism (e.g. S_N2 versus SET) may be assumed as explanation. Further studies are under way to clarify this point. According to PM3, a diastereomer with the lithium ion located on the *Si* face is higher in energy by 1.33 kcal/mol. MNDO, however, favors the *Si* diastereomer by only 0.5 kcal/mol, indicating only little stereodifferentiation.

Figure 3. PM3-optimized structure of the lithiated 2-azapentadiene **4b**; view from top on the *Re* face (C-3) (left) and sideview (right)



Similar structural features are found in the PM3 minimum structure of the SMEMP derivate **4b** (Figure 3). The additional chelation of the lithium ion by the methoxyethoxy group provides increased steric shielding against attack from the top, whereas the environment on the lower side of the complex is quite similar to that of compound **4a**. Here the calculations predict the "*Re*" diastereomer to be lower in energy by 1.14 kcal/mol compared to the "*Si*" form.

In summary, we have shown that chiral-2-azapentadienyl metal compounds offer a preparatively easy and stereoselective route to both possible diastereomers of *N*-allylimines with a new stereogenic center in the 3-position. Thus, they promise new synthetic applications in the chemstry of α-chiral allyl compounds.

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Experimental

IR: Perkin-Elmer PE 298. – ^{1}H NMR: Bruker WM-300 (300 MHz), internal reference tetramethylsilane. – ^{13}C NMR: Bruker WM-300 (75.47 MHz) and AM-360 (90.56 MHz), internal reference tetramethylsilane. – MS: Finnigan MAT C312. – GC/MS: Varian MAT CH7A with GC Varian 1400 and data system SS200; Finnigan MAT 8230 with Varian 3400 and data system SS300. Silica capillary column OV 225 (30 m). – CHN: Perkin Elmer CHN analysator 240. – Optical rotations: Perkin Elmer Polarimeter 241. – HPLC: LiChrosorb Si60 (5 or 7 μm, resp., length 250 mm, diameter 16 mm). – Flash chromatography: Kieselgel 60 (Merck),

0.040–0.063 mm. – Melting points are uncorrected. – All solvents are rigorously dried by standard methods. All experiments are carried out with complete exclusion of moisture (argon; septum-syringe technique[24]) in glass ware, which is thoroughly dried by repeated heating under argon and subsequent evacuation.

Synthesis of the Chiral 2-Aza-1,4-pentadienes **3a, b**: To a solution of 0.02 mol of *N*-allyltrimethylacetimidoyl chloride[25] (**1**) in toluene (20 ml) a solution of 0.04 mol of triethylamine is added at 0°C. Then a solution of 0.02 mol of (*S*)-2-(methoxymethyl)pyrrolidine (**2a**, SMP)[12] or (*S*)-2-[(2-methoxyethoxy)methyl]pyrrolidine (**2b**, SMEMP)[13] in toluene (20 ml) is added slowly with stirring. To complete the reaction, stirring is continued at room temp. for 12 h. The precipitated triethylamine hydrochloride is separated by filtration and washed with toluene (10 ml). The combined filtrates are freed from the solvent by evaporation. Distillation yields the 2-aza-1,4-pentadienes **3a** and **3b** as colorless liquids.

1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**3a**): From 3.2 g (20.0 mmol) of *N*-allyltrimethylacetimidoyl chloride (**1**), 5.6 ml (40.2 mmol) of triethylamine, and 2.3 g (20.0 mmol) of (*S*)-2-(methoxymethyl)pyrrolidine (**2a**). Yield: 3.8 g (80%) of **3a**, b.p. 80°C/1 mbar. – IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2950 (vs)/2860 (vs)/2820 (sh, CH aliph.), 1640 (m, C=C), 1605 (vs, C=N), 1470 (sh), 1450 (m), 1390 (m), 1360 (m), 1300 (m, br), 1190 (m), 1115 (s). – ^{1}H NMR (300 MHz, $CDCl_3$, numbering according to **8**): δ = 1.22 [s, 9H, $C(CH_3)_3$], 1.69 (m, 2H, 1 β-CH_2, 1 γ-CH_2), 1.85 (m, 1H, β-CH_2), 2.09 (m, 1H, γ-CH_2), 2.95 (m, 1H, α-CH_2), 3.02 (dd, ^2J = 8.8, ^3J = 8.1 Hz, 1H, ε-CH_2), 3.19 (dd, ^2J = 9.0, ^3J = 4.1 Hz, 1H, ε-CH_2), 3.29 (s, 3H, OCH_3), 3.40 (m, 1H, α-CH_2), 3.81 (ddd, ^3J = 4.9, ^4J = 1.9, 1.9 Hz, 2H, $CH_2CH=CH_2$), 4.02 (m, 1H, δ-CH), 5.03 (ddt, ^2J = 1.9, ^3J = 10.3, ^4J = 1.9 Hz, 1H, $CH_2CH=HCH_{cis}$), 5.24 (ddt, ^2J = 2.0, ^3J = 17.1, ^4J = 2.0 Hz, 1H, $CH_2CH=HCH_{tr}$), 6.01 (ddt, ^3J = 5.1, 17.1, 10.2 Hz, 1H, $CH_2CH=CH_2$). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.50 (Cβ), 29.02 (Cγ), 29.65 [$C(CH_3)_3$], 39.83 [$C(CH_3)_3$], 51.52 (Cα), 53.06 ($CH_2CH=CH_2$), 57.96 (Cδ), 58.76 (OCH_3), 75.80 (Cε), 113.2 ($CH_2CH=CH_2$), 138.4 ($CH_2CH=CH_2$), 167.5 (C=N). – MS (70 eV), *m/z* (%): 238 (2) [M^+], 223 (5) [$M^+ - CH_3$], 207 (6) [$M^+ - CH_3O$], 193 (8), 181 (7) [$M^+ - C_4H_9$], 124 (54) [$C_8H_{14}N^+$], 114 (18) [$C_6H_{12}NO^+$], 97 (12), 82 (23) [$C_5H_8N^+$], 70 (21) [$C_4H_8N^+$], 68 (100) [$C_4H_6N^+$], 57 (49) [$C_4H_9^+$], 55 (26). – $[\alpha]_D^{22}$ = 215.0, (*c* = 1.0, $CHCl_3$). – $C_{14}H_{26}N_2O$ (238.4): calcd. C 70.54, H 10.99, N 11.75; found C 70.45, H 11.08, N 12.25.

1-tert-Butyl-1-{(S)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-2-aza-1,4-pentadiene (**3b**): 2.3 g (14.4 mmol) of *N*-allyltrimethylacetimidoyl chloride (**1**), 4.1 ml (29.4 mmol) of triethylamine, and 2.3 g (14.5 mmol) of (*S*)-2-[(2-methoxyethoxy)methyl]pyrrolidine (**2b**). Yield: 2.7 g (65%) of **3b**, b.p. 96–97°C/0.3 mbar. – IR (neat): $\tilde{\nu}$ = 3060 cm^{-1} (w, =C–H), 2960 (vs, br)/2850 (vs, CH aliph.), 1630 (sh, C=C), 1600 (vs, C=N), 1470 (s), 1450 (s), 1390 (s), 1350 (s), 1300 (s), 1240 (sh), 1210 (sh), 1190 (s), 1120 (s, br), 1020 (m). – ^{1}H NMR (300 MHz, $CDCl_3$, numbering according to **9**): δ = 1.20 [s, 9H, $C(CH_3)_3$], 1.70 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.05 (m, 1H, γ-CH_2), 2.90 (m, 1H, α-CH_2), 3.08 (dd, ^2J = 9.0, ^3J = 7.9 Hz, 1H, ε-CH_2), 3.24 (dd, ^2J = 9.0, ^3J = 4.1 Hz, 1H, ε-CH_2), 3.30 (s, 3H, OCH_3), 3.33 (m, 1H, α-CH_2), 3.46 (m, 4H, OCH_2CH_2O), 3.78 (m, 2H, $CH_2CH=CH_2$), 4.03 (m, 1H, δ-CH), 4.97 (ddt, ^2J = 2.3, ^3J = 10.4, ^4J = 1.9 Hz, 1H, $CH_2CH=HCH_{cis}$), 5.19 (ddt, ^2J = 2.3, ^3J = 17.1, ^4J = 1.9 Hz, 1H, $CH_2CH=HCH_{tr}$), 5.96 (ddt, ^3J = 5.1, 10.2, 17.3 Hz, 1H, $CH_2CH=CH_2$). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.47 (Cβ), 29.05 (Cγ), 29.78 [$C(CH_3)_3$], 39.97 [$C(CH_3)_3$], 51.70 (Cα), 53.04 ($CH_2CH=CH_2$), 58.14 (Cδ), 58.78 (OCH_3), 70.47 (CH_2O), 71.75 (CH_2O), 74.41 (Cε), 113.4 ($CH_2CH=CH_2$), 138.4 ($CH_2CH=CH_2$), 168.0 (C=N). – MS (70 eV), *m/z* (%): 283 (2) [$M^+ + 1$], 282 (4) [M^+], 267 (6) [$M^+ - CH_3$], 251 (6) [$M^+ - CH_3O$], 225 (6) [$M^+ - C_4H_9$], 223 (22) [$M^+ - C_3H_7O$], 207 (6) [$M^+ - C_3H_7O_2$], 193 (6), 158 (6) [$C_8H_{16}NO_2^+$], 124 (60) [$C_8H_{14}N^+$], 84 (12) [$C_5H_{10}N^+$], 82 (44) [$C_5H_8N^+$], 70 (46) [$C_4H_8N^+$], 68 (100), 57 (58) [$C_4H_9^+$], 55 (44). – $[\alpha]_D^{22}$ = 177.2 (*c* = 2.1, $CHCl_3$). – $C_{16}H_{30}N_2O_2$ (282.4): calcd. C 68.04, H 10.71, N 9.92; found C 67.87, H 10.47, N 10.13.

1-tert-Butyl-2-azapentadienyllithium Compounds **4a** *and* **4b**: 20 ml of freshly distilled *tert*-butyl methyl ether (TBME) are cooled to –20°C and treated with 3.4 ml (5.5 mmol) of *n*-butyllithium (1.6 M in hexane). A solution of 2.5 mmol of the respective 2-azapentadiene (**3a, b**) in TBME (10 ml) is added by use of a syringe in a period of 30 min at –20°C. The reaction mixture soon turns intensely yellow. After complete addition the mixture is kept at –20°C for 1 h, then cooled to –50°C. The mixture is subsequently allowed to warm to –20°C. This temp. is maintained for 30 min. Finally, the mixture is cooled again to –78°C, and the respective electrophile is added.

1-tert-Butyl-2-azapentadienylmagnesium Bromide **5**: A solution of the lithium compound **4a** is treated in situ at –20°C with 1.9 ml (5.0 mmol) of magnesium bromide–diethyl ether[14] by use of a syringe. The addition must proceed fast; otherwise the syringe will be plugged. The reaction mixture is kept for 15 min at –20°C. During this period, the suspension turns orange. Finally, the suspension of **5** is cooled to –78°C and treated with the respective electrophile.

Workup: After the addition of the electrophile to the organometallic intermediates (**4a, b, 5**) the reaction mixture is allowed to warm to room temp. for about 12 h. The organic layer is washed twice with a satd. sodium hydrogen carbonate solution (20 ml) and once with water (20 ml). The combined aqueous layers are extracted three times with diethyl ether (20 ml). The organic layers are combined and dried with magnesium sulfate. The solvent is removed in vacuo (0.1 mbar for 3 h). The crude yield is determined by weighting. The ratio of the isomers is determined by ^{1}H-NMR spectroscopy or HPLC by using the crude products. The indicated relative yields correspond to the amounts of 2-azapentadienes **3a, b** used in the metalations.

Reactions of Metalated 1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-azapentadienes with Electrophiles

Protonations

(E/Z)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,3-pentadiene [(*E/Z*)-**7aa**]: From 300 mg (1.3 mmol) of **3a**, 1.7 ml (2.8 mmol) of *n*-butyllithium, 0.2 ml (2.8 mmol) of methanol. Crude yield: 280 mg; yellow oil. A separation of (*E*)- and (*Z*)-**7aa** was not possible. The spectroscopic data are taken from the mixture of diastereomers. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1} (vs)/2920 (vs)/2860 (vs)/2820 (sh, CH aliph.), 1570 (vs, C=N), 1470 (m), 1390 (m), 1355 (m), 1315 (m, br), 1160 (m, br), 1110 (s). – MS (70 eV), *m/z* (%): 238 (6) [M^+], 223 (12) [$M^+ - CH_3$], 193 (20), 140 (38), 97 (45), 84 (64), 82 (37), 70 (82), 68 (66), 57 (95) [$C_4H_9^+$], 55 (100) [$C_4H_7^+$]. – $C_{14}H_{26}N_2O$ (238.4): calcd. C 70.54, H 10.99, N 11.75; found C 70.49, H 10.96, N 11.18.

(Z)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,3-pentadiene [(*Z*)-**7aa**]: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 [s, 9H, $C(CH_3)_3$], 1.64 (dd, ^3J = 6.7, ^4J = 1.6 Hz, 3H, CH=CH–CH_3), 1.78 (m, 3H, 2β-CH_2, 1γ-CH_2), 1.92 (m, 1H, γ-CH_2), 2.97 (dd, ^2J = 9.1, ^3J = 7.7 Hz, 1H, ε-CH_2), 3.06 (m, 1H, α-CH_2), 3.15 (dd, ^2J = 9.1, ^3J = 3.9 Hz, 1H, ε-CH_2), 3.23 (s, 3H, OCH_3), 3.45 (m, 1H, α-CH_2), 4.18 (m, 1H, δ-CH), 4.83 (dq, ^3J =

6.8, 7.9 Hz, 1H, CH=C*H*−CH$_3$), 6.37 (dq, ^3J = 8.0, ^4J = 1.7 Hz, 1H, NC*H*=CH). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 11.49 (CH−*C*H$_3$), 24.63 (Cβ), 28.17 (Cγ), 29.59 [C(*C*H$_3$)$_3$], 39.46 [*C*(CH$_3$)$_3$], 51.22 (Cα), 57.93 (Cδ), 58.84 (OCH$_3$), 74.34 (Cε), 111.3 (CH=*C*HCH$_3$), 136.6 (*C*H=CHCH$_3$), 165.7 (C=N).

(E)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,3-pentadiene [(*E*)-**7aa**]: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 [s, 9H, C(CH$_3$)$_3$], 1.69 (dd, ^3J = 6.8, ^4J = 1.6 Hz, 1H, CH=CHC*H*$_3$), 1.78 (m, 3H, 2β-CH$_2$, 1γ-CH$_2$), 2.01 (m, 1H, γ-CH$_2$), 3.05 (dd, ^2J = 9.1, ^3J = 7.6 Hz, 1H, ε-CH$_2$), 3.06 (m, 1H, α-CH$_2$), 3.20 (dd, ^2J = 9.2, ^3J = 4.2 Hz, 1H, ε-CH$_2$), 3.27 (s, 3H, OCH$_3$), 3.50 (m, 1H, α-CH$_2$), 4.17 (m, 1H, δ-CH), 5.36 (dq, ^3J = 6.8, 13.5 Hz, 1H, CH=C*H*−CH$_3$), 6.45 (dq, ^3J = 13,6, ^4J = 1.6 Hz, 1H, C*H*=CH). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 15.72 (CH−*C*H$_3$), 24.66 (Cβ), 28.23 (Cγ), 29.79 [C(*C*H$_3$)$_3$], 39.52 [*C*(CH$_3$)$_3$], 51.84 (Cα), 58.19 (Cδ), 58.95 (OCH$_3$), 74.85 (Cε), 115.5 (CH=*C*HCH$_3$), 138.5 (*C*H=CHCH$_3$), 166.8 (C=N).

Alkylations

1-tert-Butyl-3-ethyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6ad**, "low-field" diastereomer I): From 595 mg (2.5 mmol) of **3a**, 3.1 ml (5.0 mol) of *n*-butyllithium, 0.4 ml (5.0 mmol) of bromoethane. Crude yield: 590 mg (90%), yellow oil. Attempts to separate the diastereomers (ratio 21:79 as determined by ^{1}H-NMR analysis) failed. The spectroscopic data are taken from the mixture of diastereomers. − IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2950 (vs)/2920 (vs)/2860 (vs)/2820 (vs, CH aliph.), 1640 (sh, C=C), 1610 (vs, C=N), 1470 (sh), 1450 (m), 1360 (m), 1280 (m, br), 1190 (m), 1110 (s, br). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (dd, ^3J = 7.4, 7.4 Hz, 3H, CH$_2$C*H*$_3$), 1.22 [s, 9H, C(CH$_3$)$_3$], 1.50 (m, 2H, C*H*$_2$CH$_3$), 1.75 (m, 3H, 2β-CH$_2$, 1γ-CH$_2$), 2.06 (m, 1H, γ-CH$_2$), 2.90 (m, 1H, α-CH$_2$), 3.03 (dd, ^2J = 8.8, ^3J = 8.3 Hz, 1H, ε-CH$_2$), 3.14 (dd, ^2J = 9.0, ^3J = 4.2 Hz, 1H, ε-CH$_2$), 3.29 (s, 3H, OCH$_3$), 3.35 (m, 1H, α-CH$_2$), 3.87 (m, 1H, C*H*−CH=CH$_2$), 3.98 (m, 1H, δ-CH$_2$), 4.94 (ddd, ^2J = 1.9, ^3J = 10.4, ^4J = 1.9 Hz, 1H, CHCH=HC*H*$_{cis}$), 5.05 (ddd, ^2J = 1.9, ^3J = 17.2, ^4J = 1.9 Hz, CHCH=HC*H*$_{tr.}$), 5.96 (ddd, ^3J = 5.3, 10.5, 17.2 Hz, 1H, CHC*H*=CH$_2$). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 10.84 (CH$_2$*C*H$_3$), 24.55 (Cβ, *C*H$_2$CH$_3$), 29.53 (Cγ), 29.96 [C(*C*H$_3$)$_3$], 40.43 [*C*(CH$_3$)$_3$], 52.72 (Cα), 57.92 (Cδ), 58.59 (OCH$_3$), 62.65 (*C*HCH=CH$_2$), 76.47 (Cε), 112.1 (CHCH=*C*H$_2$), 141.8 (CH−*C*H=CH$_2$), 166.1 (C=N). − MS (70 eV), *m/z* (%): 266 (3) [M$^+$], 251 (10) [M$^+$ − CH$_3$], 223 (6), 124 (30) [C$_8$H$_{14}$N$^+$], 114 (14) [C$_6$H$_{12}$NO$^+$], 84 (38) [C$_5$H$_{10}$N$^+$], 69 (100), 68 (52), 57 (46) [C$_4$H$_9^+$].

1-tert-Butyl-3-ethyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6ad**, "high-field" diastereomer II): From 595 mg (2.5 mmol) of **3a**, 3.1 ml (5.0 mmol) of *n*-butyllithium, 1.9 ml (5.0 mmol) of MgBr$_2$−diethyl ether and 0.4 ml (5.0 mmol) of bromoethane according to the procedure used for the transmetalation. Crude yield: 600 mg (90%), yellow oil. Kugelrohr distillation of 300 mg of the crude product at 70°C/0.02 mbar gave 230 mg (70%) of **6ad**, (high-field diastereomer-II), pale yellow oil. − IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2950 (vs)/2920 (vs)/2860 (vs)/2820 (vs, CH aliph.), 1640 (sh, C=C), 1610 (vs, C=N), 1470 (sh), 1450 (m), 1390 (m), 1280 (m, br), 1190 (m), 1110 (s, br). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (dd, ^3J = 7.4, 7.5 Hz, 3H, CH$_2$C*H*$_3$), 1.19 [s, 9H, C(CH$_3$)$_3$], 1.54 (m, 2H, C*H*$_2$CH$_3$), 1.75 (m, 3H, 2β-CH$_2$, 1γ-CH$_2$), 2.06 (m, 1H, γ-CH$_2$), 2.95 (m, 2H, 1ε-CH$_2$, 1α-CH$_2$), 3.18 (dd, ^2J = 8.6, ^3J = 3.9 Hz, 1H, ε-CH$_2$), 3.28 (s, 3H, OCH$_3$), 3.30 (m, 1H, α-CH$_2$), 3.86 (m, 2H, δ-CH, C*H*CH=CH$_2$), 4.89 (ddd, ^2J = 2.0, ^3J = 10.2, ^4J = 2.0 Hz, 1H, CHCH=HC*H*$_{cis}$), 4.94 (ddd, ^2J = 2.0, ^3J = 17.2, ^4J = 2.0 Hz, 1H, CHCH=HC*H*$_{tr.}$), 5.73 (ddd, ^3J = 6.5, 10.4, 17.1 Hz, 1H, CHC*H*=CH$_2$). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 10.64 (CH$_2$*C*H$_3$), 24.43 (Cβ, *C*H$_2$CH$_3$), 29.50 (Cγ), 29.91 [C(*C*H$_3$)$_3$], 40.38 [*C*(CH$_3$)$_3$], 52.22 (Cα), 58.53 (Cδ), 58.80 (OCH$_3$), 62.31 (*C*HCH=CH$_2$), 76.41 (Cε), 112.3 (CHCH=*C*H$_2$), 141.9 (CH−*C*H=CH$_2$), 166.1 (C=N). − MS (70 eV), *m/z* (%): 266 (3) [M$^+$], 251 (10) [M$^+$ − CH$_3$], 165 (6), 141 (10), 124 (30) [C$_8$H$_{14}$N$^+$], 114 (14) [C$_6$H$_{12}$NO$^+$], 84 (38) [C$_5$H$_{10}$N$^+$], 69 (100), 68 (52), 57 (46) [C$_4$H$_9^+$]. − $[\alpha]_D^{22}$ = 73.9 (*c* = 0.9, $CHCl_3$). − C$_{16}$H$_{30}$N$_2$O (266.4): calcd. C 72.14, H 11.35, N 10.52; found C 71.81, H 11.62, N 11.12.

1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-3-propyl-2-aza-1,4-pentadiene (**6ae**, diastereomer I): From 400 mg (1.7 mmol) of **3a**, 2.4 ml (3.7 mmol) of *n*-butyllithium, 0.4 ml (4.0 mmol) of 1-chloropropane, using an electric pump for the addition of the electrophile over a period of 6 h at −78°C. Crude yield: 400 mg (85%), yellow oil. Preparative HPLC of 380 mg of the crude product (*n*-hexane/triethylamine/methanol, 500:4:1; flow rate: 5.0 ml/min; pressure: 19 bar; t_R = 12.8−16.2 min) yields 200 mg (45%) of **6ae** (light yellow oil). − IR (neat): $\tilde{\nu}$ = 3080 cm^{-1} (w, =C−H), 2980 (vs, br)/2880 (vs)/2820 (sh, CH aliph.), 1640 (sh, C=C), 1615 (vs, C=N), 1480 (s), 1460 (s), 1400 (s), 1365 (s), 1340 (m), 1310 (sh), 1295 (s), 1280 (sh), 1210 (sh), 1200 (s), 1160 (s), 1120 (vs), 1020 (sh), 1000 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.20 [s, 9H, C(CH$_3$)$_3$], 1.21 (m, 2H, C*H*$_2$CH$_3$), 1.41 (m, 2H, CH$_2$), 1.73 (m, 3H, 2β-CH$_2$, 1γ-CH$_2$), 2.04 (m, 1H, γ-CH$_2$), 2.89 (m, 1H, α-CH$_2$), 3.01 (dd, ^2J = 8.8, ^3J = 8.1 Hz, 1H, ε-CH$_2$), 3.19 (dd, ^2J = 8.9, ^3J = 4.2 Hz, 1H, ε-CH$_2$), 3.27 (s, 3H, OCH$_3$), 3.30 (m, 1H, α-CH$_2$), 3.97 (m, 2H, δ−CH, C*H*−CH=CH$_2$), 4.90 (ddd, ^2J = 2.2, ^3J = 10.4, ^4J = 1.6 Hz, 1H, CHCH=HC*H*$_{cis}$), 5.04 (ddd, ^2J = 2.2, ^3J = 17.4, ^4J = 1.7 Hz, 1H, CHCH=HC*H*$_{tr.}$), 5.94 (ddd, ^3J = 5.2, 10.3, 17.2 Hz, 1H, CHC*H*=CH$_2$). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.08 (CH$_2$*C*H$_3$), 22.57 (*C*H$_2$CH$_3$), 24.63 (Cβ), 29.18 (Cγ), 30.07 [C(*C*H$_3$)$_3$], 40.03 (*C*H$_2$CH$_2$), 40.27 [*C*(CH$_3$)$_3$], 52.77 (Cα), 58.29 (Cδ), 58.87 (OCH$_3$), 61.00 (*C*HCH=CH$_2$), 76.52 (Cε), 112.0 (CHCH=*C*H$_2$), 142.1 (CH−*C*H=CH$_2$), 166.8 (C=N). − MS (GC/MS), *m/z* (%): 281 (2) [M$^+$ + 1], 265 (13) [M$^+$ − CH$_3$], 249 (4) [M$^+$ − CH$_3$O], 235 (6), 223 (10), 209 (4), 166 (4), 154 (6), 141 (7), 124 (15) [C$_8$H$_{14}$N$^+$], 114 (8) [C$_6$H$_{12}$NO$^+$], 84 (30) [C$_5$H$_{10}$N$^+$], 83 (100) [C$_6$H$_{11}^+$], 68 (20), 57 (30) [C$_4$H$_9^+$], 55 (65), 41 (74) [C$_3$H$_5^+$]. − $[\alpha]_D^{22}$ = 189.0 (*c* = 1.1, $CHCl_3$). − C$_{17}$H$_{32}$N$_2$O (280.5): calcd. C 72.81, H 11.50, N 9.99; found C 72.61, H 11.40, N 10.23.

1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino)-3-propyl-2-aza-1,4-pentadiene (**6ae**, diastereomer II): From 710 mg (3.0 mmol) of **3a**, 3.2 ml (5.1 mmol) of *n*-butyllithium, 1.9 ml (5.0 mmol) of MgBr$_2$−diethyl ether and 0.5 ml (6.0 mmol) of 1-bromopropane according to the transmetalation procedure. Crude yield: 660 mg (78%), yellow oil. Preparative HPLC of 430 mg of the crude product (*n*-hexane/triethylamine/methanol, 150:3:1; flow rate: 7.5 ml/min; pressure: 15 bar; t_R = 8.8−10.4 min) gave 310 mg (57%) of **6ae** (colorless oil). − IR (neat): $\tilde{\nu}$ = 3080 cm^{-1} (w, =C−H), 2960 (vs)/2940 (vs)/2880 (vs)/2810 (sh, CH aliph.), 1640 (sh, C=C), 1620 (vs, C=N), 1490 (sh), 1470 (s), 1400 (s), 1370 (s), 1310 (s), 1300 (s), 1280 (sh), 1205 (s), 1160 (sh), 1125, (vs), 1000 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.2 Hz, 3H, CH$_2$C*H*$_3$), 1.20 [s, 9H, C(CH$_3$)$_3$], 1.41 (m, 2H, CH$_2$), 1.50 (m, 2H, CH$_2$), 1.70 (m, 3H, 2β-CH$_2$, 1γ-CH$_2$), 2.05 (m, 1H, γ-CH$_2$), 2.97 (m, 2H, α-CH$_2$, ε-CH$_2$), 3.19 (dd, ^2J = 9.1, ^3J = 3.8 Hz, 1H, ε-CH$_2$), 3.29 (s, 3H, OCH$_3$), 3.31 (m, 1H, α-CH$_2$), 3.86 (m, 1H, δ-CH), 3.97 (m, 1H, C*H*−CH=CH$_2$), 4.89 (ddd, ^2J = 1.9, ^3J = 10.4, ^4J = 1.1 Hz, 1H, CHCH=HC*H*$_{cis}$), 4.94 (ddd, ^2J = 2.1, ^3J = 17.3, ^4J = 1.3 Hz, CHCH=HC*H*$_{tr.}$), 5.74 (ddd, ^3J = 6.6, 10.4, 17.1 Hz, 1H, CHC*H*=CH$_2$). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.33 (CH$_2$*C*H$_3$), 19.60 (*C*H$_2$CH$_3$), 24.58 (Cβ), 29.68 (Cγ), 30.06

[C(CH_3)$_3$], 39.15 (CH_2CH_3), 40.52 [$C(CH_3)_3$], 52.33 (Cα), 58.64 (Cδ), 59.00 (OCH_3), 61.01 (CHCH=CH_2), 76.59 (Cε), 112.3 (CHCH=CH_2), 142.4 (CHCH=CH_2), 166.2 (C=N). – MS (70 eV), *m/z* (%): 281 (5) [M^+ + 1], 280 (9) [M^+], 265 (13) [M^+ – CH_3], 249 (10) [M^+ – CH_3O], 223 (14) [M^+ – C_4H_9], 165 (16) [M^+ – $C_6H_{12}NO^+$], 124 (32) [$C_8H_{14}N^+$], 114 (10) [$C_6H_{12}NO^+$], 84 (48) [$C_5H_{10}N^+$], 83 (100) [$C_6H_{11}^+$], 67 (64), 57 (68) [$C_4H_9^+$]. – $[\alpha]_D^{22}$ = 164.9 (*c* = 1.3, $CHCl_3$). – $C_{17}H_{32}N_2O$ (280.5): calcd. C 72.81, H 11.50, N 9.99; found C 72.42, H 11.19, N 10.02.

3-Butyl-1-tert-butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6af**, diastereomer I): From 740 mg (3.1 mmol) of **3a**, 4.3 ml (6.9 mmol) of *n*-butyllithium, 0.8 ml (7.6 mmol) of 1-chlorobutane. Crude yield: 860 mg (94%), yellow oil. Preparative HPLC of 640 mg of the crude product (*n*-hexane/triethylamine/methanol, 400:4:1; flow rate: 7.5 ml/min; pressure: 15 bar; t_R = 12.2–15.6 min) yields 430 mg (63%) of **6af** (colorless oil). – IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (w, =C–H), 2940 (vs)/2920 (vs)/2860 (vs)/2820 (sh, CH aliph.), 1640 (sh, C=C), 1610 (vs, C=N), 1470 (sh), 1450 (m), 1390 (m), 1360 (m), 1330 (w), 1300 (sh), 1290 (m), 1270 (sh), 1190 (m), 1150 (m), 1120 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 1.19 [s, 9H, $C(CH_3)_3$], 1.21 (m, 4H, $CH_2CH_2CH_3$), 1.40 (m, 2H, CH_2), 1.71 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.02 (m, 1H, γ-CH_2), 2.97 (m, 1H, α-CH_2), 3.00 (dd, ^2J = 8.8, ^3J = 8.4 Hz, 1H, ε-CH_2), 3.18 (dd, ^2J = 8.8, ^3J = 4.1 Hz, 1H, ε-CH_2), 3.24 (s, 3H, OCH_3), 3.25 (m, 1H, α-CH_2), 3.93 (m, 2H, δ-CH, C*H*–CH=CH_2), 4.88 (ddd, ^2J = 2.2, ^3J = 10.4, ^4J = 1.6 Hz, 1H, CHCH=HCH_{cis}), 5.02 (ddd, ^2J = 2.2, ^3J = 17.2, ^4J = 1.7 Hz, 1H, CHCH=HC$H_{tr.}$), 5.92 (ddd, ^3J = 5.3, 10.4, 17.3 Hz, 1H, CHC*H*=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.04 (CH_2CH_3), 22.58 (CH_2CH_3), 24.59 (Cβ), 28.71 (CH_2), 29.15 (Cγ), 29.96 [$C(CH_3)_3$], 37.37 (CH_2), 40.24 [$C(CH_3)_3$], 52.71 (Cα), 58.23 (Cδ), 58.77 (OCH_3), 61.13 (CHCH=CH_2), 76.54 (Cε), 111.9 (CHCH=CH_2), 142.0 (CH–CH=CH_2), 166.6 (C=N). – MS (GC/MS), *m/z* (%): 295 (6) [M^+ + 1], 279 (21) [M^+ – CH_3], 263 (7) [M^+ – CH_3O], 237 (13) [M^+ – C_4H_9], 223 (13), 124 (23) [$C_8H_{14}N^+$], 114 (9) [$C_6H_{12}NO^+$], 97 (100) [$C_7H_{13}^+$], 84 (28) [$C_5H_{10}N^+$], 57 (35) [$C_4H_9^+$], 55 (79), 41 (79) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 187.2 (*c* = 1.2, $CHCl_3$). – $C_{18}H_{34}N_2O$ (294.5): calcd. C 73.42, H 11.64, N 9.51; found C 73.50, H 11.44, N 9.78.

3-Butyl-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6af**, diastereomer II): From 600 mg (2.5 mmol) of **3a**, 3.2 ml (5.1 mmol) of *n*-butyllithium, 1.9 ml (5.0 mmol) of $MgBr_2$–diethyl ether, and 0.5 ml (5.0 mmol) of 1-bromobutane according to the transmetalation procedure. Crude yield: 580 mg (78%), orange oil. Preparative HPLC of 380 mg of the crude product (*n*-hexane/triethylamine/methanol, 150:3:1; flow rate: 7.5 ml/min; pressure: 15 bar; t_R = 9.4–10.7 min) gives 300 mg (63%) of **6af** (colorless oil). – IR (neat): $\tilde{\nu}$ = 3070 cm^{-1} (w, =C–H), 2940 (vs)/2900 (vs)/2860 (vs, CH aliph.), 1640 (sh, C=C), 1610 (vs, C=N), 1470 (sh), 1450 (s), 1390 (s), 1360 (s), 1330 (m), 1290 (s), 1270 (sh), 1195 (s), 1150 (sh), 1120 (vs, br). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, ^3J = 7.0 Hz, 3H, CH_2CH_3), 0.93 [s, 9H, $C(CH_3)_3$], 1.15 (m, 6H, $CH_2CH_2CH_2$), 1.50 (m, 3H, 2β-CH_2, 1γ-CH_2), 1.80 (m, 1H, γ-CH_2), 2.72 (m, 2H, α-CH_2, ε-CH_2), 2.93 (dd, ^2J = 9.0, ^3J = 4.0 Hz, 1H, ε-CH_2), 3.02 (s, 3H, OCH_3), 3.07 (m, 1H, α-CH_2), 3.60 (m, 1H, δ-CH), 3.70 (m, 1H, C*H*–CH=CH_2), 4.64 (ddd, ^2J = 2.1, ^3J = 10.2, ^4J = 0.9 Hz, 1H, CHCH=HCH_{cis}), 4.68 (ddd, ^2J = 1.9, ^3J = 16.8, ^4J = 2.1 Hz, 1H, CHCH=HC$H_{tr.}$), 5.49 (ddd, ^3J = 6.5, 10.5, 17.0 Hz, 1H, CHC*H*=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.09 (CH_2CH_3), 22.88 (CH_2CH_3), 24.55 (Cβ), 28.60 (CH_2), 29.61 (Cγ), 29.84 [$C(CH_3)_3$], 36.53 (CH_2), 40.48 [$C(CH_3)_3$], 52.31 (Cα), 58.94 (Cδ), 59.86 (OCH_3), 62.45 (CHCH=CH_2), 76.55 (Cε), 112.3 (CHCH=CH_2), 142.3 (CH–CH=CH_2), 166.2 (C=N). – MS (GC/MS), *m/z* (%): 295 (33) [M^+ + 1], 279 (66) [M^+ – CH_3], 263 (8) [M^+ – CH_3O], 249 (20), 237 (24) [M^+ – C_4H_9], 124 (28) [$C_8H_{14}N^+$], 114 (7) [$C_6H_{12}NO^+$], 109 (8), 97 (100) [$C_7H_{13}^+$], 84 (9) [$C_5H_{10}N^+$], 57 (30) [$C_4H_9^+$], 55 (92), 41 (76) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 154.1 (*c* = 1.0, $CHCl_3$). – $C_{18}H_{34}N_2O$ (294.5): calcd. C 73.42, H 11.64, N 9.51; found C 73.37, H 11.35, N 9.83.

1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-3-(2-methylpropyl)-2-aza-1,4-pentadiene (**6ag**, diastereomer I and II): From 530 mg (2.2 mmol) of **3a**, 3.0 ml (5.1 mmol) of *n*-butyllithium, 0.5 ml (5.1 mmol) of 1-bromo-2-methylpropane. Crude yield: 600 mg (91%), yellow oil. Preparative HPLC of 580 mg of the crude product (*n*-hexane/triethylamine/methanol, 700:4:1; flow rate: 5.0 ml/min; pressure: 28 bar; t_R = 15.0–17.2 min) yields as a first main fraction 205 mg (32%) of **6ag** (diastereomer I) (colorless oil). A second main fraction (t_R = 17.6–21.0 min) consists of 205 mg (32%) of **6ag** (diastereomer II) (colorless oil). – Diastereomer I: IR (neat): $\tilde{\nu}$ = 3080 cm^{-1} (w, =C–H), 2960 (vs)/2920 (vs)/2900 (sh)/2870 (s, CH aliph.), 1645 (m, C=C), 1610 (vs, C=N), 1460 (m), 1390 (m), 1380 (m), 1360 (m), 1340 (m), 1300 (sh), 1280 (sh), 1210 (sh), 1195 (m), 1120 (vs). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, ^3J = 6.7 Hz, 3H, CHCH_3), 0.87 (d, ^3J = 6.7 Hz, 3H, CHCH_3), 1.20 [s, 9H, $C(CH_3)_3$], 1.33 (m, 2H, NCHCH_2CH), 1.49 [m, 1H, C*H*(CH_3)$_2$], 1.73 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.04 (m, 1H, γ-CH_2), 2.94 (m, 1H, α-CH_2), 3.01 (dd, ^2J = 8.6, ^3J = 8.6 Hz, 1H, ε-CH_2), 3.19 (dd, ^2J = 8.8, ^3J = 4.1 Hz, 1H, ε-CH_2), 3.27 (s, 3H, OCH_3), 3.34 (m, 1H, α-CH_2), 4.01 (m, 2H, δ-CH, C*H*–CH=CH_2), 4.90 (ddd, ^2J = 2.2, ^4J = 1.4, ^3J = 10.4 Hz, 1H, CHCH=HCH_{cis}), 5.04 (ddd, ^2J = 2.2, ^4J = 1.4, ^3J = 17.5 Hz, 1H, CHCH=HC$H_{tr.}$), 5.94 (ddd, ^3J = 5.2, 10.4, 17.2 Hz, 1H, CHC*H*=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.14 (CH–CH_3), 23.48 (CH–CH_3), 24.67 [$CH(CH_3)_2$], 24.68 (Cβ), 29.18 (Cγ), 29.99 [$C(CH_3)_3$], 40.17 [$C(CH_3)_3$], 47.21 (CH_2), 52.73 (Cα), 58.37, (Cδ), 58.87 (OCH_3), 59.14 (CHCH=CH_2), 76.51 (Cε), 111.9 (CHCH=CH_2), 142.3 (CH–CH=CH_2), 166.3 (C=N). – MS (GC/MS), *m/z* (%): 295 (22) [M^+ + 1], 279 (16) [M^+ – 15], 263 (6) [M^+ – CH_3O], 249 (7), 237 (12), 223 (22), 179 (3), 166 (3) [$C_{11}H_{20}N^+$], 154 (3), 141 (7), 124 (23) [$C_8H_{14}N^+$], 114 (7) [$C_6H_{12}NO^+$], 97 (100) [$C_7H_{13}^+$], 84 (16), 69 (16), 57 (24) [$C_4H_9^+$], 55 (60), 41 (60) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 190.7 (*c* = 1.7, $CHCl_3$). – $C_{18}H_{34}N_2O$ (294.5): calcd. C 73.42, H 11.64, N 9.51; found C 73.35, H 11.60, N 9.69. – Diastereomer II: IR (CH_2Cl_2): $\tilde{\nu}$ = 2940 cm^{-1} (vs), 2920 (vs)/2900 (sh)/2880 (s, CH aliph.), 1635 (m, C=C), 1605 (vs, C=N), 1450 (s), 1390 (m), 1360 (m), 1270 (s), 1160 (sh), 1120 (vs). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 [d, ^3J = 6.4 Hz, 3H, CH(CH_3)$_2$], 0.90 [d, ^3J = 6.7 Hz, 3H, CH(CH_3)$_2$], 1.18 [s, 9H, $C(CH_3)_3$], 1.25 (m, 1H, 1-NCHCH_2CH), 1.49 (ddd, ^2J = 8.0, ^3J = 5.4, 13.4 Hz, 1H, 1-NCHCH_2CH), 1.74 [m, 4H, 2β-CH_2, γ-CH_2, C*H*(CH_3)$_3$], 2.05 (m, 1H, 1γ-CH_2), 2.97 (m, 2H, α-CH_2, ε-CH_2), 3.18 (dd, ^2J = 3.9, ^3J = 8.9 Hz, 1H, ε-CH_2), 3.28 (s, 3H, OCH_3), 3.33 (m, 1H, α-CH_2), 3.86 (m, 1H, δ-CH), 4.04 (m, 1H, C*H*–CH=CH_2), 4.88 (ddd, ^2J = 2.0, ^3J = 10.3, ^4J = 0.9 Hz, 1H, CHCH=HCH_{cis}), 4.94 (ddd, ^2J = 2.0, ^3J = 17.2, ^4J = 1.1 Hz, 1H, CHCH=HC$H_{tr.}$), 5.71 (ddd, ^3J = 6.9, 10.3, 17.2 Hz, 1H, CHC*H*=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.48 (CH–CH_3), 23.51 (CH–CH_3), 24.58 [$CH(CH_3)_2$], 24.83 (Cβ), 29.64 (Cγ), 30.01 [$C(CH_3)_3$], 40.43 [$C(CH_3)_3$], 45.95 (CH_2CH), 52.15 (Cα), 58.52 (Cδ), 58.96 (OCH_3), 59.47 (CHCH=CH_2), 76.52 (Cε), 112.2 (CHCH=CH_2), 142.4 (CH–CH=CH_2), 165.8 (C=N). – MS (GC/MS), *m/z* (%): 295 (4) [M^+ + 1], 279 (18) [M^+ – 15], 263 (2) [M^+ – CH_3O], 237 (14), 223 (14), 166 (3) [$C_{11}H_{20}N^+$], 141 (3), 124 (18) [$C_8H_{14}N^+$], 114 (4) [$C_6H_{12}NO^+$], 97 (100) [$C_7H_{13}^+$], 68 (12), 57 (24) [$C_4H_9^+$], 55 (53), 41 (42) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 168.6

(*c* = 1.5, $CHCl_3$). – $C_{18}H_{34}N_2O$ (294.5): calcd. C 73.42, H 11.64, N 9.51; found C 73.41, H 11.71, N 9.80.

1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-3-(3-methylbutyl)-2-aza-1,4-pentadiene (**6ah**, diastereomer II): From 600 mg (2.5 mmol) of **3a**, 3.5 ml (5.6 mmol) of *n*-butyllithium, 1.9 ml (5.0 mmol) of $MgBr_2$–diethyl ether, 0.6 ml (5.0 mmol) of 1-bromo-3-methylbutane according to the transmetalation procedure. Crude yield: 580 mg (75%), orange oil. Preparative HPLC of 350 mg of the crude product (*n*-hexane/triethylamine/methanol, 100:2:1; flow rate: 7.5 ml/min; pressure: 20 bar; t_R = 8.8–10.6 min) yields 170 mg (37%) of **6ah** (colorless oil). – IR (neat): $\tilde{\nu}$ = 3080 cm^{-1} (w, =C–H), 2960 (vs), 2940 (vs), 2880 (vs, C–H aliph.), 1640 (sh, C=C), 1615 (vs, C=N), 1480 (sh), 1465 (s), 1395 (m), 1385 (m), 1370 (s), 1200 (m), 1160 (m), 1120 (s). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 [d, ^3J = 6.8 Hz, 6H, $CH(CH_3)_2$], 1.18 [s, 9H, $C(CH_3)_3$], 1.23 [m, 3H, CH_2, $CH(CH_3)_2$], 1.60 (m, 5H, 2β-CH_2, 1γ-CH_2, CH_2), 2.05 (m, 1H, γ-CH_2), 2.97 (m, 2H, α-CH_2, ε-CH_2), 3.16 (dd, ^2J = 9.0, ^3J = 4.2 Hz, 1H, ε-CH_2), 3.26 (s, 3H, OCH_3), 3.30 (m, 1H, α-CH_2), 3.84 (m, 1H, δ-CH), 3.91 (m, 1H, CH–CH=CH_2), 4.88 (ddd, ^2J = 2.3, ^3J = 10.2, ^4J = 1.1 Hz, 1H, CHCH=HCH_{cis}), 4.93 (ddd, ^2J = 1.1, ^3J = 17.3, ^4J = 2.3 Hz, 1H, CHCH=HC$H_{tr.}$), 5.73 (ddd, ^3J = 6.6, 10.4, 17.1 Hz, 1H, CHCH=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 22.58 [$CH(CH_3)_2$], 22.71 [$CH(CH_3)_2$], 24.53 (Cβ), 28.19 [$CH(CH_3)_2$], 29.61 (Cγ), 30.02 [$C(CH_3)_3$], 34.58 (CH_2), 35.69 (CH_2), 40.47 [$C(CH_3)_3$], 52.26 (Cα), 58.63 (Cδ), 58.92 (OCH_3), 61.46 (CHCH=CH_2), 76.53 (Cε), 112.3 (CHCH=CH_2), 142.3 (CH–CH=CH_2), 166.1 (C=N). – MS (GC/MS), *m/z* (%): 309 (8) [M^+ + 1], 293 (22) [M^+ – CH_3], 277 (3) [M^+ – CH_3O], 251 (13) [M^+ – C_4H_9], 193 (2) [$C_{13}H_{24}N^+$], 124 (28) [$C_8H_{14}N^+$], 114 (8) [$C_6H_{12}NO^+$], 111 (56) [$C_8H_{15}^+$], 84 (19) [$C_5H_{10}N^+$], 69 (100) [$C_5H_9^+$], 57 (29) [$C_4H_9^+$], 41 (81) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 144.1 (*c* = 0.8, $CHCl_3$). – $C_{19}H_{36}N_2O$ (308.5): calcd. C 73.97, H 11.76, N 9.08; found C 73.62, H 11.58, N 9.38.

1-tert-Butyl-3-isopropyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6aj**, diastereomer I): From 310 mg (1.3 mmol) of **3a**, 1.8 ml (2.9 mmol) of *n*-butyllithium, 0.3 ml (3.2 mmol) of 2-chloropropane with *n*-hexane as solvent. The 2-chloropropane is added during 6 h at −78 °C by using an electric pump. Crude yield: 340 mg, yelllow oil. Preparative HPLC of 330 mg of the crude product (*n*-hexane/triethylamine/methanol, 600:4:1; flow rate: 5.0 ml/min; pressure: 11 bar; t_R = 12.6–14.4 min) yields 130 mg (37%) of **6aj** (colorless oil). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3060 cm^{-1} (w, =C–H), 2940 (vs)/2900 (vs)/2850 (vs)/2810 (sh, CH aliph.), 1630 (sh, C=C), 1600 (vs, C=N), 1470 (sh), 1450 (s), 1390 (m), 1370 (m), 1355 (s), 1260 (m, br), 1190 (s), 1150 (sh), 1100 (vs, br.). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 [d, ^3J = 6.7 Hz, 3H, $CH(CH_3)_2$], 0.85 [d, ^3J = 6.9 Hz, 3H, $CH(CH_3)_2$], 1.22 [s, 9H, $C(CH_3)_3$], 1.71 [m, 4H, $CH(CH_3)_2$, 2β-CH_2, 1γ-CH_2], 2.05 (m, 1H, γ-CH_2), 2.88 (m, 1H, α-CH_2), 3.02 (dd, ^2J = 8.8, ^3J = 8.3 Hz, 1H, ε-CH_2), 3.22 (dd, ^2J = 8.8, ^3J = 4.1 Hz, 1H, ε-CH_2), 3.29 (s, 3H, OCH_3), 3.34 (m, 1H, α-CH_2), 3.71 (tt, ^3J = 5.6, ^4J = 1.4 Hz, 1H, CH–CH=CH_2), 3.99 (m, 1H, δ-CH), 5.00 (ddd, ^2J = 2.4, ^3J = 10.5, ^4J = 1.4 Hz, 1H, CHCH=HCH_{cis}), 5.04 (ddd, ^2J = 2.4, ^3J = 17.3, ^4J = 1.5 Hz, 1H, CHCH=HC$H_{tr.}$), 5.96 (ddd, ^3J = 5.6, 10.5, 17.3 Hz, 1H, CHCH=CH_2). – ^{13}C NMR (75.47 (MHz, $CDCl_3$): δ = 18.43 [$CH(CH_3)$], 19.68 [$CH(CH_3)$], 24.70 (Cβ), 29.28 (Cγ), 30.03 [$C(CH_3)_3$], 34.41 [$CH(CH_3)_2$], 40.57 [$C(CH_3)_3$], 50.80 (Cα), 58.20 (Cδ), 58.94 (OCH_3), 67.03 (CHCH=CH_2), 76.62 (Cε), 113.2 (CHCH=CH_2), 140.7 (CH–CH=CH_2), 166.4 (C=N). – MS (GC/MS), *m/z* (%): 281 (4) [M^+ + 1], 265 (8) [M^+ – CH_3], 237 (12) [M^+ – C_3H_7], 223 (8), 166 (2) [M^+ – $C_6H_{12}NO$], 154 (3), 141 (7), 124 (40) [$C_8H_{14}N^+$], 114 (4) [$C_6H_{12}NO^+$], 83 (100) [$C_6H_{11}^+$], 68 (22), 57 (18) [$C_4H_9^+$], 55 (37), 41 (54) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 143.7 (*c* = 1.3, $CHCl_3$). – $C_{17}H_{32}N_2O$ (280.5): calcd. C 72.81, H 11.50, N 9.99; found C 72.81, H 11.55, N 9.02.

1-tert-Butyl-3-isopropyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-2-aza-1,4-pentadiene (**6aj**, diastereomer II): From 500 mg (2.1 mmol) of **3a**, 2.7 ml (4.2 mmol) of *n*-butyllithium, 0.4 ml (4.2 mmol) of 2-bromopropane. Crude yield: 550 mg (94%), yellow oil. Preparative HPLC of 430 mg of the crude product (*n*-hexane/triethylamine/methanol, 200:2:1; flow rate: 5.0 ml/min; pressure: 25 bar; t_R = 13.3–14.6 min) yields 90 mg (19%) of **6aj** (colorless oil). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3060 cm^{-1} (w, =C–H), 2940 (vs)/2900 (vs)/2850 (vs)/2810 (sh, CH aliph.), 1640 (sh, C=C), 1605 (vs, C=N), 1470 (m), 1450 (s), 1390 (m), 1370 (sh), 1355 (s), 1260 (m, br), 1190 (s), 1150 (s), 1100 (vs, br). – ^{1}H NMR (300 MHz, $CDCl_3$). δ = 0.89 [d, ^3J = 5.3 Hz, 3H, $CH(CH_3)_2$], 0.91 [d, ^3J = 5.0 Hz, 3H, $CH(CH_3)_2$], 1.20 [s, 9H, $C(CH_3)_3$], 1.62 [m, 4H, $CH(CH_3)_2$, 2β-CH_2, 1γ-CH_2], 2.05 (m, 1H, γ-CH_2), 2.95 (m, 2H, α-CH_2, ε-CH_2), 3.17 (dd, ^2J = 9.1, ^3J = 3.8 Hz, 1H, ε-CH_2), 3.27 (s, 3H, OCH_3), 3.34 (m, 1H, α-CH_2), 3.72 (ddt, ^3J = 5.7, 6.2 Hz, 1H, CH–CH=CH_2), 3.84 (m, 1H, δ-CH), 4.91 (m, 2H, CHCH=CH_2), 5.65 (m, 1H, CH–CH=CH_2). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 19.04 [$CH(CH_3)_2$], 24.56 (Cβ), 29.79 (Cγ), 30.09 [$C(CH_3)_3$], 34.07 [$CH(CH_3)_2$], 40.77 [$C(CH_3)_3$], 52.03 (Cα), 58.50 (Cδ), 59.00 (OCH_3), 65.98 (CHCH=CH_2), 76.49 (Cε), 113.0 (CHCH=CH_2), 140.4 (CH–CH=CH_2), 165.6 (C=N). – MS (GC/MS), *m/z* (%): 281 (6) [M^+ + 1], 265 (15) [M^+ – CH_3], 237 (16) [M^+ – C_3H_7], 223 (11), 166 (3) [M^+ – $C_6H_{12}NO$], 154 (3), 141 (6), 124 (62) [$C_8H_{14}N^+$], 114 (6) [$C_6H_{12}NO^+$], 83 (100) [$C_6H_{11}^+$], 68 (30), 57 (18) [$C_4H_9^+$], 55 (48), 41 (72) [$C_3H_5^+$]. – $[\alpha]_D^{22}$ = 107.5 (*c* = 1.1, $CHCl_3$). – $C_{17}H_{32}N_2O$ (280.5): calcd. C 72.81, H 11.50, N 9.99; found C 72.46, H 11.61, N 10.11.

(E/Z)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-6,6-dimethyl-2-aza-1,3-heptadiene [(*E*)/(*Z*)-**7ak**]: From 500 mg (2.1 mmol) of **3a**, 3.0 ml (4.7 mmol) of *n*-butyllithium, 0.4 ml (4.9 mmol) of 2-chloro-2-methylpropane. Crude yield: 510 mg (83%), yellow oil. An attempt to separate the (*E*/*Z*) isomers failed. The spectroscopic data are taken from the mixture of isomers. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1} (vs), 2900 (sh)/2860 (vs)/2820 (sh, CH aliph.), 1560 (vs, C=N), 1470 (s), 1450 (s), 1390 (m), 1360 (s), 1330 (s), 1190 (m), 1150 (m, br), 1110 (s). – MS (70 eV), *m/z* (%): 294 (22) [M^+], 279 (8) [M^+ – CH_3], 263 (4) [M^+ – CH_3O], 252 (18), 237 (40) [M^+ – C_4H_9], 223 (20), 165 (46), 149 (56), 124 (52) [$C_8H_{14}N^+$], 114 (40) [$C_6H_{12}NO^+$], 97 (42), 83 (56), 57 (100) [$C_4H_9^+$], 55 (70). – $C_{18}H_{34}N_2O$ (294.5): calcd. C 73.42, H 11.64, N 9.51; found C 73.21, H 11.61, N 9.50.

(Z)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-6,6-dimethyl-2-aza-1,3-heptadiene [(*Z*)-**7ak**]: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 [s, 9H, $C(CH_3)_3$], 1.24 [s, 9H, $C(CH_3)_3$], 1.72 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.00 (m, 1H, γ-CH_2), 2.13 (m, 2H, CH=CHCH_2), 3.03 (dd, ^2J = 9.1, ^3J = 7.9 Hz, 1H, ε-CH_2), 3.08 (m, 1H, α-CH_2), 3.21 (dd, ^2J = 9.1, ^3J = 4.1, 1H, ε-CH_2), 3.28 (s, 3H, OCH_3), 3.53 (m, 1H, α-CH_2), 4.26 (m, 1H, δ-CH), 4.91 (dt, ^3J = 7.2, 8.0 Hz, 1H, CH=C*H*–CH_2), 6.51 (dt, ^3J = 7.9, ^4J = 1.4 Hz, 1H, NC*H*=CH). – ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.63 (Cβ), 28.27 (Cγ), 29.49 [$C(CH_3)_3$], 31.61 [$C(CH_3)_3$], 39.67 [$C(CH_3)_3$], 40.10 [$C(CH_3)_3$], 45.90 [$CH_2C(CH_3)_3$], 51.34 (Cα), 58.13 (Cδ), 59.01 (OCH_3), 74.88 (Cε), 115.1 (CH=CHCH$_2$), 136.7 (CH=CHCH$_2$), 165.6 (C=N).

(E)-1-tert-Butyl-1-[(S)-2-(methoxymethyl)pyrrolidino]-6,6-dimethyl-2-aza-1,3-heptadiene [(*E*)-**7ak**]: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 [s, 9H, $C(CH_3)_3$], 1.22 [s, 9H, $C(CH_3)_3$], 1.71 (m, 3H, 2β-CH_2, 1γ-CH_2), 1.88 (m, 3H, γ-CH_2, CH=CHCH_2), 3.06

(dd, ^2J = 9.1, ^3J = 7.4 Hz, 1H, ε-CH_2), 3.10 (m, 1H, α-CH_2), 3.21 (dd, ^2J = 9.2, ^3J = 4.2 Hz, 1H, ε-CH_2), 3.27 (s, 3H, OCH_3), 3.50 (m, 1H, α-CH_2), 4.21 (m, 1H, δ-CH), 5.41 (ddd, ^3J = 6.7, 8.9, 13.5 Hz, 1H, CH=C*H*−CH_2), 6.42 (dt, ^3J = 13.5 Hz, 1H, NC*H*=CH). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.73 (Cβ), 28.17 (Cγ), 29.38 [C(CH_3)$_3$], 29.65 [C(CH_3)$_3$], 39.19 [*C*(CH_3)$_3$], 40.03 [*C*(CH_3)$_3$], 45.52 [CH_2C(CH_3)$_3$], 51.96 (Cα), 58.20 (Cδ), 58.94 (OCH_3), 74.88 (Cε), 118.0 (CH=*C*HCH_2), 139.3 (*C*H=CHCH_2), 167.1 (C=N).

Reactions of 1-tert-Butyl-1-{(S)-2-[(2-methoxyethoxy)methyl]-pyrrolidino}-2-azapentadiene (**4b**) *with Electrophiles*

Deuteration

(E)-1-tert-Butyl-5-deuterio-1-{(S)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-2-aza-1,3-pentadiene [(*E*)-**7bb**]: From 500 mg (1.8 mmol) of **3b**, 2.4 ml (3.9 mmol) of *n*-butyllithium, 0.3 ml (3.9 mmol) of CH_3OD. Crude yield: 470 mg (94%), yellow oil. Preparative HPLC of 150 mg of the crude product (*n*-hexane/triethylamine/methanol, 100:3:1; flow rate: 7.5 ml/min; pressure: 15 bar; t_R = 7.8−10.0 min) yields 130 mg (82%) of (*E*)-**7bb** (colorless oil). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2940 cm^{-1} (vs)/2920 (vs)/2880 (vs)/2810 (sh, CH aliph.), 1560 (vs, C=N), 1470 (s), 1460 (s), 1390 (m), 1360 (sh), 1340 (s), 1330 (sh), 1210 (s), 1190 (m), 1130 (sh), 1100 (vs, br), 1020 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 [s, 9H, C(CH_3)$_3$], 1.77 (m, 5H, 2β-CH_2, 1γ-CH_2, CH_2D), 2.05 (m, 1H, γ-CH_2), 3.09 (m, 1H, α-CH_2), 3.15 (dd, ^2J = 9.4, ^3J = 7.9 Hz, 1H, ε-CH_2), 3.32 (dd, ^2J = 9.4, ^3J = 4.5 Hz, 1H, ε-CH_2), 3.36 (s, 3H, OCH_3), 3.52 (m, 5H, 1α-CH_2, OCH_2CH_2O), 4.22 (m, 1H, δ-CH), 5.37 (dt, ^3J = 6.8, 13.6 Hz, 1H, NCH=C*H*), 6.47 (dt, ^3J = 13.6, ^4J = 1.6 Hz, 1H, NC*H*=CH). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 15.30 (CH−*C*H_2D), 24.40 (Cβ), 28.10 (Cγ), 29.52 [C(*C*H_3)$_3$], 39.02 [*C*(CH_3)$_3$], 51.76 (Cα), 58.03 (Cδ), 58.83 (OCH_3), 70.36 (CH_2O), 71.74 (CH_2O), 73.26 (Cε), 115.3 (NCH=*C*H), 138.4 (N*C*H=CH), 166.6 (C=N). − MS (GC/MS), *m/z* (%): 284 (2) [M^+], 268 (3) [M^+ − CH_3], 252 (7) [M^+ − CH_3O], 224 (261), 208 (25) [M^+ − $C_3H_8O_2$], 194 (15), 179 (10), 167 (3), 158 (5), 125 (76) [$C_8H_{14}N^+$], 111 (58), 84 (10) [$C_5H_{10}N^+$], 69 (100), 57 (25) [$C_4H_9^+$], 41 (58) [$C_3H_5^+$]. − $C_{16}H_{29}DN_2O_2$ (283.4): calcd. C 67.80, H 10.66, N 9.88; found C 67.74, H 10.66, N 9.37.

Silylation

(E)-1-tert-Butyl-1-{(S)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-5-(trimethylsilyl)-2-aza-1,3-pentadiene [(*E*)-**7bc**]: From 510 mg (1.8 mmol) of **3b**, 2.5 ml (4.0 mmol) of *n*-butyllithium, 0.5 ml (4.0 mmol) of trimethylsilyl chloride. Crude yield: 540 mg (85%), yellow oil. Preparative HPLC of 340 mg of the crude product (*n*-hexane/triethylamine/methanol, 100:2:1; flow rate: 7.5 ml/min; pressure: 17 bar; t_R = 7.0−8.6 min) yield 270 mg (67%) of (*E*)-**7bc** (light yellow oil). − IR (neat): $\tilde{\nu}$ = 2940 cm^{-1} (vs)/2860 (vs)/2820 (sh, CH aliph.), 1575 (vs, C=N), 1470 (s), 1450 (s), 1390 (s), 1360 (s), 1340 (s), 1320 (s), 1290 (s), 1240 (vs), 1190 (s), 1150 (sh), 1120 (vs, br), 1030 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 [s, 9H, Si(CH_3)$_3$], 1.22 [s, 9H, C(CH_3)$_3$], 1.48 [dd, ^3J = 8.5, ^4J = 1.1 Hz, 2H, C*H*$_2$Si(CH_3)$_3$], 1.75 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.02 (m, 1H, γ-CH_2), 3.05 (m, 1H, α-CH_2), 3.16 (dd, ^2J = 9.3, ^3J = 9.0 Hz, 1H, ε-CH_2), 3.33 (dd, ^2J = 9.2, ^3J = 4.3 Hz, 1H, ε-CH_2), 3.35 (s, 3H, OCH_3), 3.50 (m, 5H, 1α-CH_2, OCH_2CH_2O), 4.22 (m, 1H, δ-CH), 5.45 (dt, ^3J = 8.3, 13.2 Hz, 1H, NCH=C*H*−CH_2), 6.40 (dt, ^3J = 13.2 Hz, 1H, NC*H*=CH). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = −1.72 [Si(CH_3)$_3$], 20.74 [CH_2Si(CH_3)$_3$], 24.55 (Cβ), 28.27 (Cγ), 29.62 [C(*C*H_3)$_3$], 39.17 [*C*(CH_3)$_3$], 51.96 (Cα), 57.42 (Cδ), 58.01 (OCH_3), 70.47 (CH_2O), 71.86 (CH_2O), 73.74 (Cε), 118.4 (NCHCH=*C*HCH_2), 136.8 (NCH=*C*HCH_2), 165.9 (C=N). − MS (GC/MS), *m/z* (%): 355 (11) [M^+ + 1], 354 (19) [M^+], 339 (9) [M^+ − CH_3], 323 (10) [M^+ − CH_3O], 281 (70) [M^+ − Si(CH_3)$_3$], 212 (20), 196 (36), 140 (48), 124 (78) [$C_8H_{14}N^+$], 84 (36) [$C_5H_{10}N^+$], 73 (90) [Si(CH_3)$_3^+$], 59 (100), 57 (78) [$C_4H_9^+$]. − $[\alpha]_D^{22}$ = 97.3 (*c* = 1.6, $CHCl_3$). − $C_{19}H_{38}N_2O_2Si$ (354.3): calcd. C 64.36, H 10.81, N 7.91; found C 64.14, H 11.00, N 8.45.

Alkylation

1-tert-Butyl-1-{(S)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-3-(2-propenyl)-2-aza-1,4-pentadiene (**6bi**): From 470 mg (1.7 mmol) of **3b**, 2.3 ml (3.7 mmol) of *n*-butyllithium, 0.3 ml (4.0 mmol) of 3-bromo-1-propene. Crude yield: 370 mg (69%), yellow oil. Preparative HPLC of 240 mg of the crude product (*n*-hexane/triethylamine/methanol, 600:5:1; flow rate: 7.5 ml/min; pressure: 24 bar; t_R = 14.8−20.2 min) yields 130 mg (37%) of **6bi** (colorless oil). − IR (CH_2Cl_2): $\tilde{\nu}$ = 3060 cm^{-1} (w, =C−H), 2940 (vs)/2910 (vs)/2860 (vs)/2820 (sh, CH aliph.), 1630 (m, C=C), 1600 (vs, C=N), 1470 (m), 1460 (m), 1390 (m), 1360 (m), 1260 (s), 1200 (sh), 1190 (s), 1100 (vs, br), 1010 (sh). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 [s, 9H, C(CH_3)$_3$], 1.73 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.04 (m, 1H, γ-CH_2), 2.28 (m, 2H, C*H*$_2$CH=CH_2), 2.95 (m, 1H, α-CH_2), 3.06 (dd, ^2J = 9.1 Hz, ^3J = 8.3 Hz, 1H, ε-CH_2), 3.26 (dd, ^2J = 9.2, ^3J = 4.2 Hz, 1H, ε-CH_2), 3.33 (s, 3H, OCH_3), 3.30 (m, 1H, α-CH_2), 3.49 (m, 4H, OCH_2CH_2O), 3.90 (m, 1H, δ-CH), 4.03 (dtt, ^3J = 6.0, 6.0 Hz, ^4J = 1.1 Hz, 1H, C*H*−CH=CH_2), 4.90 (ddd, ^2J = 2.0, ^3J = 10.7, ^4J = 1.3, 1H, CHCH=HCH_{cis}), 4.94 (ddd, ^2J = 1.7, ^3J = 17.2, ^4J = 1.4 Hz, 1H, CHCH=HCH_{tr}), 4.96 (ddt, ^2J = 2.3, ^3J = 10.0, ^4J = 1.1 Hz, 1H, CH_2CH=HCH_{cis}), 5.01 (ddt, ^2J = 1.4, ^3J = 17.2, ^4J = 1.2 Hz, 1H, CH_2CH=HCH_{tr}), 5.74 (ddd, ^3J = 6.1, 10.3, 17.1 Hz, 1H, CHC*H*=CH_2), 5.82 (ddt, ^3J = 7.1, 10.0, 17.2 Hz, 1H, CH_2C*H*=CH_2). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.40 (Cβ), 29.52 (Cγ), 29.99 [C(*C*H_3)$_3$], 40.51 [*C*(CH_3)$_3$], 41.42 (*C*H_2CH=CH_2), 52.33 (Cα), 58.50 (Cδ), 58.90 (OCH_3), 60.69 (*C*HCH=CH_2), 70.43 (CH_2O), 71.78 (CH_2O), 74.99 (Cε), 112.6 (CHCH=*C*H_2), 115.7 (CH_2CH=*C*H_2), 136.5 (CH_2*C*H=CH_2), 141.5 (CH_2*C*H=CH_2), 166.7 (C=N). − MS (GC/MS), *m/z* (%): 323 (21) [M^+ + 1], 307 (2) [M^+ − CH_3], 291 (3) [M^+ − CH_3O], 281 (33), 263 (18), 247 (4), 233 (10), 164 (2), 124 (100) [$C_8H_{14}N^+$], 108 (5), 81 (80) [$C_6H_9^+$], 68 (20), 57 (18) [$C_4H_9^+$], 41 (40) [$C_3H_5^+$]. − $[\alpha]_D^{22}$ = 174.8 (*c* = 1.3, $CHCl_3$). − $C_{19}H_{34}N_2O_2$ (322.5): calcd. C 70.76, H 10.63, N 8.69; found C 70.66, H 10.63, N 9.19.

1-tert-Butyl-1-{(S)-2-[(2-methoxyethoxy)methyl]pyrrolidino}-3-(4-pentenyl)-2-aza-1,4-pentadiene (**6bl**): From 500 mg (1.8 mmol) of **3b**, 2.4 ml (3.9 mmol) of *n*-butyllithium, 0.3 ml (4.3 mmol) of 5-bromo-1-pentene. Crude yield: 1.1 g, yellow oil. Preparative HPLC of 1.0 g of crude product (*n*-hexane/triethylamine/methanol, 1000:7:1; flow rate: 10.0 ml/min; pressure: 28 bar; t_R = 13.0−17.2 min) yield 350 mg (62%) of **6bl** (colorless oil). − IR (CH_2Cl_2): $\tilde{\nu}$ = 3060 cm^{-1} (w, =C−H), 2920 (vs)/2890 (vs)/2860 (vs, CH aliph.), 1630 (s, C=C), 1605 (vs, C=N), 1470 (m), 1450 (s), 1390 (m), 1355 (s), 1330 (sh), 1260 (s, br), 1210 (vs), 1190 (sh), 1130 (sh), 1100 (vs, br). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 [s, 9H, C(CH_3)$_3$], 1.35 (m, 4H, CH_2CH_2), 1.70 (m, 3H, 2β-CH_2, 1γ-CH_2), 2.04 (m, 3H, γ-CH_2, C*H*$_2$CH=CH_2), 2.95 (m, 1H, α-CH_2), 3.04 (dd, $^2J \approx$ 8.8, ^3J = 8.6 Hz, 1H, ε-CH_2), 3.26 (dd, $^2J \approx$ 9.2, ^3J = 4.2 Hz, 1H, ε-CH_2), 3.33 (s, 3H, OCH_3), 3.29 (m, 1H, α-CH_2), 3.49 (m, 4H, OCH_2CH_2O), 3.88 (m, 1H, δ-CH), 3.94 (m, 1H, C*H*−CH=CH_2), 4.88 (m, 2H, CHCH=C*H*$_2$), 4.92 (ddt, ^2J = 1.9, ^3J = 10.3, ^4J = 1.4 Hz, 1H, CH_2CH=HCH_{cis}), 4.95 (ddt, ^2J = 2.2, ^3J = 17.2, ^4J = 1.4 Hz, 1H, CH_2CH=HCH_{tr}), 5.71 (ddd, ^3J = 6.7, 10.5, 17.3 Hz, 1H, CHC*H*=CH_2), 5.82 (ddt, ^3J = 6.7, 10.5, 17.2 Hz, 1H, CH_2C*H*=CH_2). − ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 24.43 (Cβ), 25.68 (CH_2), 29.59 (Cγ), 29.99 [C(*C*H_3)$_3$], 33.90 (CH_2), 36.33

($CH_2CH=CH_2$), 40.34 [$C(CH_3)_3$], 52.27 (Cα), 58.56 (Cδ), 58.90 (OCH_3), 60.93 ($CHCH=CH_2$), 70.43 (CH_2O), 71.81 (CH_2O), 75.00 (Cε), 112.4 ($CHCH=CH_2$), 114.0 ($CH_2CH=CH_2$), 139.0 ($CH_2CH=CH_2$), 142.2 ($CH_2CH=CH_2$), 166.2 (C=N). – MS (70 eV), *m/z* (%): 350 (9) [M^+], 335 (7) [$M^+ - CH_3$], 319 (6) [$M^+ - CH_3O$], 319 (6) [$M^+ - C_3H_5$], 296 (6), 291 (17), 281 (7), 267 (6), 261 (8), 247 (8), 235 (10), 221 (10), 209 (10), 192 (10), 185 (9), 178 (14), 158 (13), 149 (11), 127 (10), 124 (35) [$C_8H_{14}N^+$], 109 (69 [$C_8H_{13}^+$], 97 (16), 84 (50), 68 (42) [$C_5H_8^+$], 67 (100), 57 (50) [$C_4H_9^+$], 55 (55) [$C_4H_7^+$]. – $[\alpha]_D^{22} = 122.9$ ($c = 2.1$, $CHCl_3$). – $C_{21}H_{38}N_2O_2$ (350.5): calcd. C 71.95, H 10.93, N 7.99; found C 71.95, H 10.93, N 8.36.

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