Rearrangement and Substitution of Pentadienyl Groups in Homopentadienylamines on Treatment with Organolithium Reagents

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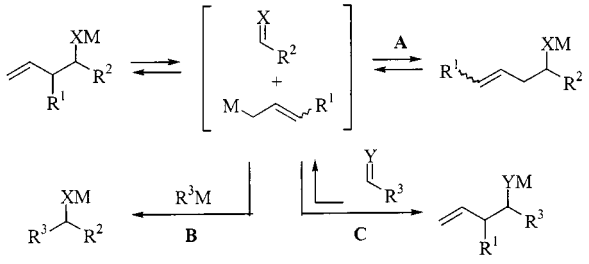
(4*R*,5*R*)-*N*,*N*′-Bis[(1*S*)-1-phenylethyl]-3,6-divinyl-1,7-octadiene-4,5-diamine underwent rearrangement and/or substitution of one/two pentadienyl groups on treatment with 2–4 equiv. of an organolithium reagent (*n*BuLi, PhLi) in THF. By careful choice of experimental conditions, C_1- or C_2-symmetric 1,2-disubstituted 1,2-diamines could generally be obtained with good stereocontrol. It is proposed that the reaction proceeds through competitive pathways involving a 1,3-shift of the branched homopentadienyllithium amide moiety with retention of configuration and retro-pentadienyllithiation to form an intermediate imine. In contrast, only rearrangement was observed on treatment of (1*R*,*S*)-*N*-[(1*S*)-1-phenylethyl]-1-(2-pyridyl)-2-vinyl-3-butenylamine with 2 equiv. of *n*BuLi at –78 °C.

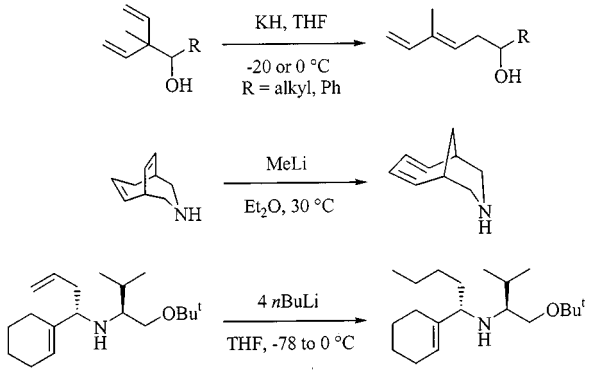
Introduction

It has been known for a long time that allylmetallations of carbonyl compounds[1–8] and imines[9–12] are reversible reactions. In other words, homoallylic alkoxides and amides are in equilibrium with the parent carbonyl compounds or imines and the allylmetal reagents. This has been demonstrated, for example, by the isomerization of the branched homoallylic compounds to the linear ones (route **A** in Scheme 1) on increasing the reaction time before quenching the organometallic reactions.



Scheme 1

The rate of the retro-allylmetallation is affected by steric hindrance in the homoallylic alkoxides or amides and by the nature of the metal, decreasing in the order: ZnX > Li > MgX for alkoxides,[5,7,8] and Li > ZnX > MgX for amides.[9,10] Moreover, electron-withdrawing substituents on the allyl group facilitate the retro-allylmetallation: pentadienyl- and cinnamyllithium and -zinc bromide are known to add reversibly to carbonyl compounds, differing in this respect from 2-pentenyl- and 3,3-dimethylallyllithium.[1–3] Some more recent examples of base-promoted rearrangements of branched homopentadienyl alcohols[13–15] and an amine[16] to their linear isomers are depicted in Scheme 2.



Scheme 2

In a few cases, the carbonyl compounds formed in situ from the homoallylic alkoxides have been trapped by diverse organometallic reagents to give novel alcohols (route **B** in Scheme 1), but mixtures of products have generally been obtained.[1,5–7] In an analogous process, allyl/*n*Bu substitution occurred when *n*BuLi was added to the enantiopure homoallylic amine shown in Scheme 2, but the yield and diastereomeric ratio of the amine obtained were not given; the same treatment of a few other homoallylic amines, moreover, resulted in a different reaction course or in no reaction occurring.[17] Actually, the usefulness of the routes **B** and **C** is limited because the same products are available by means of straightforward addition of organometallic reagents to carbonyl compounds and imines. However, a clever synthetic application of route **C** has recently been reported, in which allylic groups were efficiently transferred from tertiary zinc alkoxides to a range of electrophiles, with high regioselectivities and diastereoselectivities in the case of substituted allylic groups.[8]

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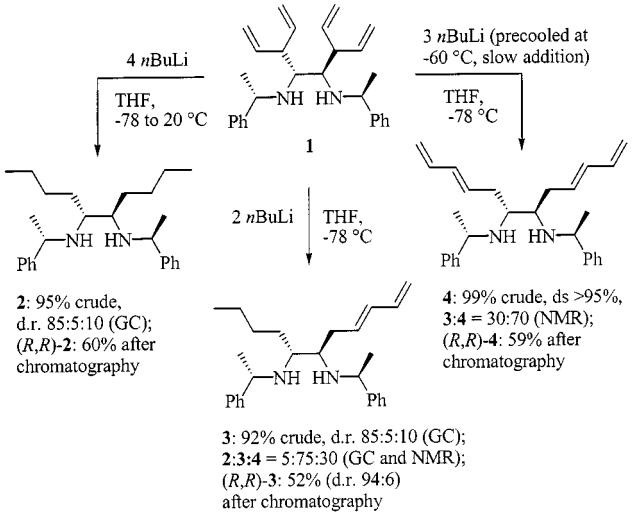
Results and Discussion

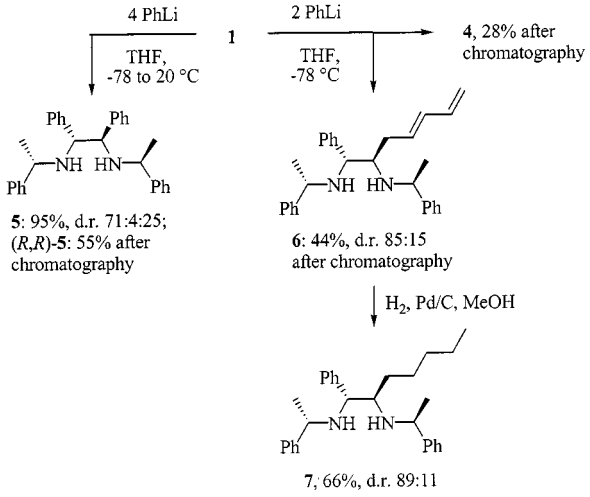
On the basis of the previous reports, we were surprised to discover that treatment of the branched diamine **1**[18] with 4 equiv. of *n*BuLi in THF at −78 to 20 °C resulted in its complete conversion into the 1,2-diamine **2** as a mixture of diastereomers, from which (*R*,*R*)-**2** could be isolated pure in 60% yield by column chromatography (Scheme 3). Monitoring the reaction by GC-MS analysis, we observed that an intermediate product was already formed at the start at −78 °C − at low levels of conversion of **1**, in other words − and was completely converted into the product **2** on raising the temperature. When the reaction was repeated with only 2 equiv. of *n*BuLi, the intermediate was isolated in high yield by quenching after 2 h at −78 °C, and was identified as the asymmetrical 1,2-diamine **3**, with *n*-butyl and linear pentadienyl substituents. The crude reaction product contained mainly **3**, as a mixture of diastereomers (*dr* = 85:5:10 in order of increasing GC-MS analysis elution time), and minor amounts of another compound, which decomposed during the GC analysis. This latter compound was later identified as the linearly disubstituted 1,2-diamine **4**[19] by ^{1}H NMR analysis (this compound decomposed during GC-MS analysis, precluding quantitative determination). After column chromatography (SiO_2) of the crude product, the compound (*R*,*R*)-**3** was obtained in 52% yield and in good diastereomeric purity (*dr* = 94:6), since the last eluted (GC-MS) diastereomer had been eliminated. It should be underlined that the C_2-symmetric 1,2-diamine **2** was formed only in trace amounts at the low temperature, even when 4 equiv. of *n*BuLi were used.



Scheme 3

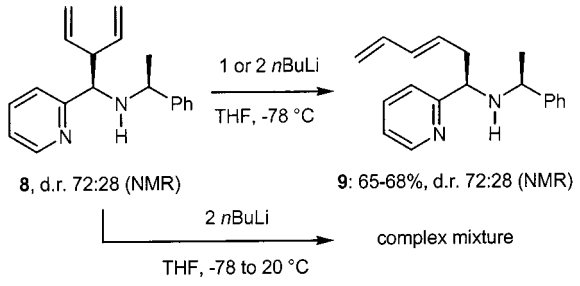
Further experiments were carried out to assess possibilities for better control over the course of the reaction. Very slow addition of *n*BuLi (3 equiv., pre-cooled at −60 °C) to the branched 1,2-diamine **1** at −78 °C mainly gave the isomeric 1,2-diamine **4** as a single (*R*,*R*) diastereomer, in 59% yield after chromatographic separation of minor amounts of the substitution product **3**. We also investigated the reaction between the linear bis(homopentadienyl)-1,2-diamine **4** and 4 equiv. of *n*BuLi; following the progress of this reaction by GC and TLC analysis we ascertained that no reaction took place at −78 °C, while, after slow raising of the temperature, the double substitution product **2** was then formed as a diastereomeric mixture at 0−20 °C.

It is noteworthy that the compounds **2** and **3** were produced with high diastereoselectivities, as the configurations at the stereocentres involved in the isomerization and/or substitution processes were retained to a large extent; in particular, the diastereomeric ratio (*dr*) of the known diamine **2** was higher than that obtained by the straightforward addition of *n*BuLi to the corresponding glyoxal bis(imine).[19] The good stereocontrol obtained prompted us to explore further the behaviour of **1** towards other organolithium reagents, in view of the fact that that organometallic additions to glyoxal diimine are still narrow in scope,[18−24] especially for the preparation of asymmetrical 1,2-diamines.[24] Thus, we performed the addition of 4 equiv. of PhLi to the 1,2-diamine **1** in THF at −78 to 20 °C and observed the formation of the double substitution product **5**[22] (Scheme 4) in 55% isolated yield, but with slightly lower diastereoselectivity than found on treatment with *n*BuLi. On the other hand, addition of 2 equiv. of PhLi at −78 °C gave a mixture of the 1,2-diamines **6** and **4**, which were separated by column chromatography and obtained in 44% and 28% yields, respectively. Once again, the isomerization processes producing the 1,2-diamine **4** had occurred with complete retention of configuration, and the diamine **6** was isolated as a mixture of diastereomers; subsequent hydrogenation gave the corresponding saturated 1,2-diamine **7** with a similar diastereomeric purity (*dr* = 89:11) after chromatography, indicating that the isomeric diamine with (*Z*) internal double bond geometry should not be present in the crude mixture of the precursor **6**. Similar results were obtained on performing the reactions with PhLi (2 equiv. at −60 °C and 4 equiv. at −60 to −20 °C, respectively) in DME. Unfortunately, the reactions between **1** and MeLi and *t*BuLi (4 equiv., THF, −78 to −20 °C) gave complex mixtures of products with low diastereoselectivities.



Scheme 4

We wondered whether it might be possible to observe not only branched-to-linear isomerization of the pentadienyl substituent on treatment of the substrate **1** at very low temperatures, but also displacements of the branched pentadienyl by butyl or phenyl groups, as seen in the previously reported isomerizations described in Scheme 2. Thus, hoping to verify whether another branched homopentadienyl amine would display the same behaviour, we prepared the pyridyl-substituted amine **8** (63% yield, *dr* = 72:28) by the addition of pentadienylzinc chloride/TMEDA complex to the appropriate 2-pyridylimine. Without separation of the diastereomers, the amine **8** was then treated in separate experiments with 1 and 2 equiv. of *n*BuLi at −78 °C, and in both cases the isomeric product **9** was obtained with *dr* = 72:28, and thus with complete retention of configuration of the stereocentre involved in the isomerization process (Scheme 5). Moreover, the substitution product was not detected at −78 °C, but when the reaction mixture was allowed to come to room temperature a complex reaction mixture was obtained, owing to the reactivity of the pyridine ring towards excess *n*BuLi present.



Scheme 5

Reaction Pathways and Mechanisms

The formation of rearrangement and substitution products from homopentadienyl amines on treatment with organolithium compounds and the stereochemical outcomes of these transformations warrant some discussion, albeit speculative, of the reaction pathways and mechanisms. The following features of the reactions should be pointed out.

(1) The branched-to-linear isomerization of homopentadienyl amines takes place through the lithium amides even at −78 °C, with retention of configuration at the stereogenic centre involved, e.g. compounds **4** and **9**.

(2) Only one branched pentadienyl group of the 1,2-diamine **1** undergoes substitution by the *n*Bu or Ph group of RLi at −78 °C, whereas substitution of the linear homopentadienyl groups of **3**, **4** and **6** requires higher temperature (0−20 °C).

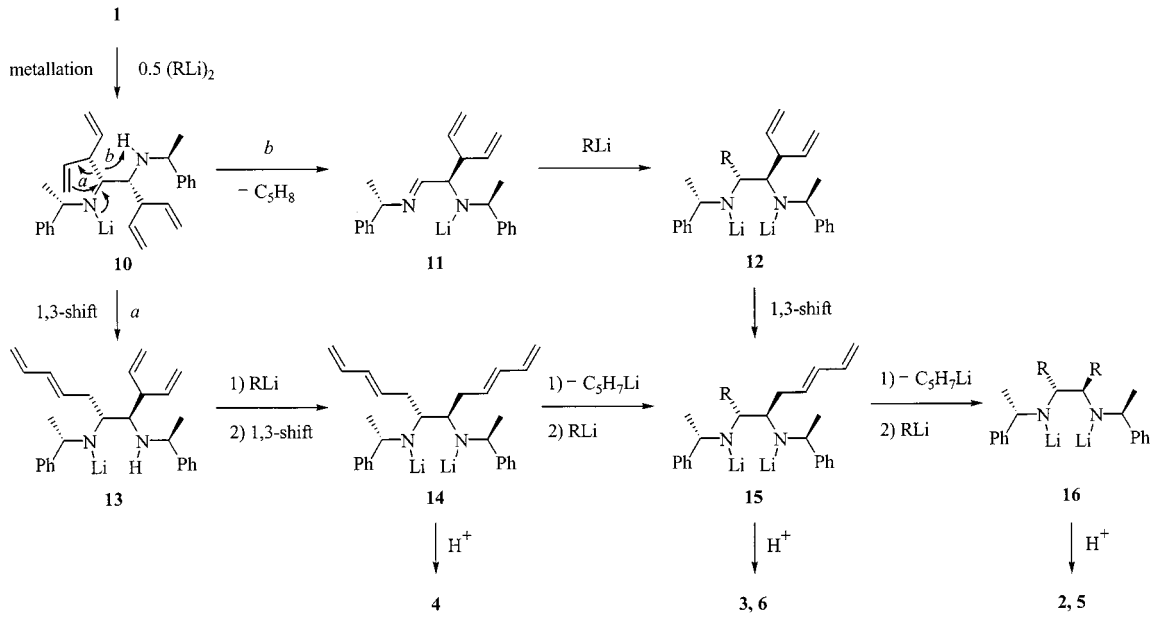
(3) The products derived from **1** by rearrangement/substitution and double rearrangement − that is, **3** and **4**, respectively − are formed concomitantly by competitive processes, which are only partially affected by variation of the experimental conditions. In fact, the formation of **3** was reduced when cold *n*BuLi was added very slowly to the diamine **1**, but could not be improved at the expense of the isomerization product **4** by use of an excess of *n*BuLi or by use of the inverse addition procedure.

On the basis of these facts and of reasonable suppositions, a plausible description of the reaction course is depicted in Scheme 6. We first make the assumption that only one NH function of the diamine **1** undergoes metallation by dimeric RLi in the first step, to give the lithium amide **10**. At this point, two competitive processes can take place. In the first pathway, described by the arrow *a*, a charge-promoted 1,3-shift produces the partially isomerized amide **13**; repetition of the metallation/rearrangement sequence then gives the fully isomerized 1,2-diamide **14**. The complete stereocontrol found in the formation of the linearly disubstituted 1,2-diamine **4** is in agreement with the occurrence of a charge-accelerated rearrangement.[25,26] In this regard, it should be observed that the isomerization of the bridged bicyclic homopentadienylamine described in Scheme 2, promoted by MeLi (Et_2O, 30 °C, 1 min; no reaction below 20 °C), is explained by this mechanism. This hypothesis was strengthened by two findings: (i) the retention of stereochemistry at the migrating carbon atom in deuterium labelling studies, and (2) the failure of attempts to trap the imine, which might have been formed by ring opening of the anion, by MeLi or PhLi.[12]

The retro-pentadienyllithiation of the amide **10** is a competitive pathway, favoured by the stability of the pentadienyl anion. The latter anion might add to the C=N bond at the terminal carbon atom, thus giving the same isomeric amide **13** as produced by the 1,3-shift, although a partial loss of diastereoselectivity would be expected in this case. Alternatively, as described by the arrow *b*, the leaving pentadienyl anion can act as a base towards the second N−H bond, affording the amide-imine **11**. Addition of a second RLi equiv. to **11** to give the dilithium 1,2-diamide **12** and subsequent 1,3-shift at the low temperature would then produce the isomeric diamide **15**.

We suppose that both the 1,3-shift and the retro-pentadienyllithiation processes from **1** occur at −78 °C, a much lower temperature than given in known reports, because of the release of steric strain. Conversely, only the 1,3-shift, and not the retro-pentadienyllithiation process, occurs in **12** at −78 °C: In fact, when the temperature of the reaction medium was carefully controlled during the organometallic addition, the double substitution products **2** and **5** were not formed even in the presence of an excess of RLi. Upon raising the temperature and in the presence of more RLi reagent, the diamide **14** is converted into **15** and onward to the disubstituted diamide **16** through sequential retro-pentadienyllithiation/RLi addition steps.

Finally, the stereochemical purity of the diamine **4** and the good diastereomeric ratios of the 1,2-diamines **3/6**, and **2/5** are an indication that the glyoxal bis(imine) is not an intermediate in our reaction medium, since we have reported that the additions of pentadienyllithium and RLi reagents gave the corresponding double addition products **4** and **2/5** with low diastereoselectivities (1,3-asymmetric induction). Instead, the compounds **3/6** and **2/5** are obtained



Scheme 6

here by the addition of RLi to α-amido-substituted C=N bonds, in which 1,2-asymmetric induction is operating.

Conclusions

This work demonstrates that the branched diamine **1** works as a "masked chiral glyoxal diimine" in the organometallic reactions, allowing both asymmetrically and symmetrically 1,2-disubstituted 1,2-diamines to be prepared, depending on the experimental conditions, with satisfactory to good yields and stereoselectivities. In order to improve the synthetic usefulness of this methodology, it is necessary to widen the range of organolithium reagents that can be used, and to improve the stereoselectivity. We are therefore examining other bis(homoallylic) 1,2-diamines, in which the migrating and leaving group ability of the substituted allyl groups can be controlled and the overall stereoselectivity enforced by the electronic and/or steric effects of the allylic substituents. As a further implementation of the methodology, we plan to investigate sequential additions of organolithium reagents, R^1Li and R^2Li, at different temperatures, in order to prepare 1,2-diamines with R^1 and R^2 substituents at C-1 and C-2.

Experimental Section

General Conditions: Melting points are uncorrected. − THF was distilled prior to use under N_2 and from sodium benzophenone ketyl and then from $LiAlH_4$. − Optical rotations were measured with a digital polarimeter in a 1-dm cell and $[\alpha]_D$ values are given in 10^{-1} deg cm^3 g^{-1}. − ^{1}H NMR spectra were recorded with a Varian Gemini instrument at 300 or 200 MHz for samples in $CDCl_3$, which was stored over Mg. ^{1}H NMR chemical shifts are reported in ppm relative to $CHCl_3$ (δ_H = 7.27) and *J* values are given in Hz. − MS spectra were taken at an ionizing voltage of 70 eV with a Hewlett−Packard 5970 or 5890 spectrometer with GLC injection. − Chromatographic purifications were carried out on columns of silica gel (Merck, 230−400 mesh) at medium pressure. − *n*BuLi (1.6 M in hexanes) and PhLi (1.8 M in cyclohexane/ether, 70:30) were purchased from Aldrich. − All organometallic reactions were performed in flame-dried apparatus under a static pressure of dry N_2. − The diamine **1** was prepared as previously described.[18]

Treatment of the 1,2-Diamine 1 with Organolithium Reagents

General Procedures. − Preparation of Unsymmetrical Diamines: The 1,2-diamine **1** (2.00 g, 5 mmol) was dissolved in anhydrous THF (20 mL) and the solution was cooled to −78 °C. After 10 min, the organolithium reagent (10 mmol) was added over 15 min while stirring. The mixture was stirred further for 2 h, then quenched at the low temperature with de-aerated H_2O (10 mL).[19] The organic phase was extracted with Et_2O (3 × 20 mL), and the collected ethereal layers were dried with Na_2SO_4 and concentrated to leave an oily residue. Chromatography on an SiO_2 column, eluting with cyclohexane/EtOAc mixtures, enabled the 1,2-diamines to be separated.

Preparation of Symmetrical 1,2-Diamines: The same general procedure as described above was followed, but 4 equiv. of RLi was added at −78 °C. The mixture was stirred for 1 h, the temperature was then allowed to come to 20 °C over 2 h, and the reaction was quenched after 30 min. Usual workup and purification gave the desired 1,2-diamines. The diamines **2**,[19] **4**,[19] and **5**[19,22] were isolated and identified by comparison of their physical and spectroscopic properties with those reported for the authentic materials.

(3*E*,5*R*,6*R*)-*N*,*N*′-Bis[(1*S*)-1-phenylethyl]undeca-1,3-diene-5,6-diamine (3): 1.01 g, 52%; *dr* = 94:6 (GC/MS). − $[\alpha]\cong_D^{20}$ = −148.6 (*c* = 0.6, $CHCl_3$). − ^{1}H NMR (200 MHz): δ = 7.40−7.13 (m, 10 H, Ph), 6.11 (dt, *J* = 3.6 and 9.8 Hz, 1 H, CH_2CH=CH), 5.54 (m, 1 H, CH=C*H*−CH=CH_2), 5.20 (m, 1 H, C*H*=CH_2) 5.05−4.82 (m, 2 H, CH=CH_2), 3.76 (2 q, *J* = 6.2 Hz, 2 H, C*H*CH_3), 2.20−1.94 (m, 4 H, NC*H*C*H*CH_2CH=CH), 1.48 (br, 2 H, NH), 1.40−1.10 (m, 6 H, CH_2CH_2CH_2CH_3), 1.30 and 1.27 (2 d, *J* = 6.7 Hz, CHCH_3), 0.72 (t, *J* = 6.8 Hz, 3 H, CH_2CH_3). − MS (70

EV, EI): *m*/*z* (%) = 105 (100), 190 (60), 86 (32), 200 (31), 96 (16), 79 (13), 323 (9). − $C_{26}H_{38}N_2$ (378.58): calcd. C 82.48, H 10.12, N 7.40; found C 82.53, H 10.14, N 7.33.

(1*R*,2*R*,4*E*)-1-Phenyl-*N*,*N*′-bis[(1*S*)-1-phenylethyl]-4,6-heptadiene-1,2-diamine (6): 0.90 g (44%); *dr* = 85:15 (GC-MS). − $[\alpha]_D^{20}$ = −154.0 (*c* = 0.3, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40−7.0 (m, 15 H, Ph), 6.18 (dt, *J* = 3.6 and 9.8 Hz 1 H, CH_2CH=CH), 5.76 (m, 1 H, CH=C*H*−CH=CH_2), 5.38 (m, 1 H, C*H*=CH_2), 5.04−4.86 (m, 2 H, CH=CH_2), 3.81 and 3.40 (2 q, *J* = 6.6 Hz, 2 H, C*H*CH_3), 3.14 (d, *J* = 6.7 Hz, 1 H, NC*H*Ph), 2.43 (m, 1 H, NC*H*CH_2), 2.17 (m, 2 H, NCHCH_2), 1.85 (br, 2 H, NH), 1.30 and 1.22 (2 d, *J* = 6.6 Hz, 6 H, CHCH_3). − MS (70 eV, EI): *m*/*z* (%) = 105 (100), 200 (37), 96 (22), 79 (17), 77 (16), 135 (8), 201 (6), 343 (4). − $C_{29}H_{34}N_2$ (410.58): calcd. C 84.83, H 8.35, N 6.82; found C 84.87, H 8.36, N 6.77.

(1*R*,2*R*)-1-Phenyl-*N*,*N*′-bis[(1*S*)-1-phenylethyl]heptane-1,2-diamine (7): A mixture of compound **6** (0.36 g, 0.8 mmol), 10% Pd/C (0.03 g) and MeOH (7 mL) was submitted to 1 atm H_2 (balloon) while stirring with a magnetic bar at room temperature for 2 h. The solution was then filtered and concentrated to leave crude **7** as an oil: 0.32 g (0.76 mmol, 95%); *dr* = 85:15 (GC/MS). Column chromatography gave pure **7**: 0.22 g (66%); *dr* = 89:11 (GC-MS). − $[\alpha]_D^{20}$ = −131.6 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40−7.0 (m, 15 H, Ph), 3.75 and 3.41 (2 q, *J* = 6.6 Hz, 1 H, C*H*Me), 3.16 (d, *J* = 7.0 Hz, 1 H, NCHPh), 2.32 (m, 1 H, NC*H*CH_2), 1.77 (broad, 1 H, NH), 1.32 and 1.24 (2 d, *J* = 6.6 Hz, 3 H, CH*Me*), 1.40−0.80 (m, 8 H, CH_2), 0.78 (t, *J* = 6.4, 3 H, CH_2*Me*). − MS (70 eV, EI): *m*/*z* (%) = 204 (100), 105 (85), 100 (41), 205 (18), 106 (17), 79 (11), 77 (6). − $C_{29}H_{38}N_2$ (414.61): calcd. C 84.00, H 9.24, N 6.76; found C 84.03, H 9.25, N 6.72.

(1*R*,*S*)-*N*-[(1*S*)-1-Phenylethyl]-1-(2-pyridyl)-2-vinylbut-3-en-1-amine (8): (1*S*)-1-Phenyl-*N*-(2-pyridylmethylidene)ethylamine[27,28] (0.63 g, 3 mmol), dissolved in THF (4 mL), was slowly added at −78 °C with stirring to a solution of pentadienylzinc chloride/TMEDA complex (6 mmol) in *n*-hexane/THF (1:1, 10 mL), prepared as previously described.[18] After 2 h, the mixture was quenched by addition of aq. NH_4Cl (10 mL) and the organic phase was extracted with Et_2O (3 × 10 mL). The collected ethereal layers were dried with Na_2SO_4 and concentrated to leave a crude mixture of isomeric amines **8** and **9** in 4:1 ratio (^{1}H NMR) as an oil. Column chromatography (SiO_2), eluting with a cyclohexane/EtOAc mixture (9:1), gave the pure amine **8**: 0.524 g, 63%; *dr* = 72:28 (^{1}H NMR and GC/MS). The main diastereomer (*R*,*S*)-**8** gave the following absorptions in the ^{1}H NMR spectrum (300 MHz, $CDCl_3$): δ = 8.53 (m, 1 H, Py), 7.50 (t, *J* = 5.7 Hz, 1 H, Py), 7.28−7.05 (m, 7 H, Ph and Py), 5.88−5.68 (m, 2 H, C*H*=CH_2), 5.14−4.92 (m, 4 H, CH=CH_2), 3.86 (d, *J* = 7.2 Hz, 1 H, NC*H*Py), 3.70 (q, *J* = 6.6 Hz, 1 H, C*H*Me), 3.23 (q, *J* = 7.5 Hz, NCHC*H*), 1.9 (broad, 1 H, NH), 1.35 (d, *J* = 6.6 Hz, CH*Me*). The spectrum of the minor diastereomer (*S*,*S*)-**8** differed in the following absorptions: δ = 8.62 (2 m, 2 H, Py), 7.60 (t, *J* = 5.7 Hz, 5.64−5.46 (m, 2 H, C*H*=CH_2), 4.94−4.78 (m, 4 H, CH=CH_2), 3.44 (d, *J* = 7.2 Hz, 1 H, NC*H*Py), 3.38 (q, *J* = 6.6 Hz), C*H*Me), 3.13 (q, *J* = 7.5 Hz, NCHC*H*), 1.27 (d, *J* = 6.6 Hz, 3 H, CH*Me*). − MS (70 eV, EI): *m*/*z* (%) = 107 (100), 105 (87), 79 (27), 211 (26), 77 (22), 78 (12), 51 (11). − $C_{19}H_{22}N_2$ (278.38): calcd. C 81.97, H 7.97, N 10.06; found C 81.94, H 7.98, N 10.08.

(1*R*,3*E*)-*N*-[(1*S*)-1-Phenylethyl]-1-(2-pyridyl)hexa-3,5-dien-1-amine (9): *n*BuLi (1.6 M in hexanes, 0.65 mL, 1 mmol) was slowly added at −78 °C to a solution of the amine **8** (0.278 g, 1 mmol) in THF (5 mL), while stirring with a magnetic bar. After 1 h, the reaction mixture was quenched at −78 °C with H_2O (5 mL). The organic phase was extracted with Et_2O (3 × 5 mL) and the collected ethereal layers were dried with Na_2SO_4 and concentrated to leave an oily residue. Column chromatography (SiO_2, cyclohexane/EtOAc, 85:15) gave pure **9**: 0.18 g (65%); *dr* = 72:28 (GC/MS). The main diastereomer (*R*,*S*)-**9** gave the following absorptions in the ^{1}H NMR spectrum (200 MHz, $CDCl_3$): δ = 8.58 (d, *J* = 4.2 Hz, 1 H, Py), 7.57 (m, 1 H, Py), 7.40−7.08 (m, 7 H, Ph and Py), 6.39−5.92 (m, 2 H, vinylic), 5.16−4.88 (m, 2 H, vinylic), 3.87 (t, *J* = 6.6 Hz, NC*H*Py), 3.78 (q, *J* = 6.6 Hz, 1 H, C*H*Me), 2.59 (t, *J* = 6.4 Hz, CHCH_2), 2.0 (br, 1 H, NH), 1.39 (d, *J* = 6.6 Hz, 3 H, CH*Me*). The spectrum of the minor diastereomer (*S*,*S*)-**9** differed in the absorptions at δ = 8.62 (d, *J* = 4.2 Hz, 1 H, Py), 7.61 (m, 1 H, Py), 3.53 (t, *J* = 6.6 Hz, NC*H*Py), 3.47 (q, *J* = 6.6 Hz, 1 H, C*H*Me), 2.48 (t, *J* = 6.4 Hz, m, 2 H, CHCH_2), 1.31 (d, *J* = 6.6 Hz, 3 H, CH*Me*). − MS (70 eV, EI): *m*/*z* (%) = 107 (100), 105 (63), 211 (58), 79 (16), 77 (12), 106 (9). − $C_{19}H_{22}N_2$ (278.38): calcd. C 81.97, H 7.97, N 10.06; found C 81.99, H 7.98, N 10.03.

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