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Synthesis of stable tail-to-tail-conjugated primary enamines containing hetarene substituents

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Abstract

A method is described that allows the preparation of stable conjugated primary enamines containing furyl or pyridyl substituents. In a template reaction (butadiene)zirconocene is 1,4-selectively coupled to two 2-cyanopyridine equivalents to give the nine-membered metallacycle **8b**. Subsequent treatment with methanol removes the bent metallocene template and leads to the formation of 1,6-diamino-1,6-bis(2-pyridyl)-1,3,5-hexatriene (**9b**). The 1,6-diamino-1,6-bis(2-furyl)-1,3,5-hexatriene system (**9a**) was prepared analogously (69% isolated). Subsequent addition of benzonitrile to (butadiene)$ZrCp_2$, followed by 2-cyanopyridine or 2-cyanofurane gave the respective unsymmetrically substituted 1,6-diaminohexatrienes in good yield.

Key words: Zirconium complexes; Zirconocene complexes; Ketimido complexes; Enamines

We have recently described a novel type of stable, isolable primary enamines [1]. These compounds (e.g. **6**) contain two alkenamine moieties, substituted at their α-positions, which are tail-to-tail connected by means of a conjugated $-CH=CH-$ unit. There is evidence that the 1,6-diaminohexatrienes are thermodynamically favored over any of their ketimine tautomers. We have prepared and characterized examples (some with X-ray crystal structure analyses) of this novel class of compounds bearing simple aryl, substituted aryl or alkyl substituents at each terminus of the conjugated hexatriene chain. We considered it interesting to have analogues of these compounds available that contain α-hetarene end groups. Provided that in such cases the enamine is still the predominating tautomer, such compounds would have the alkene-bonded $-NH_2$ group and the heteroatom of the hetarene substituent in an ideal chelate position to bind incoming metals. We here describe some first examples showing that such enamine/hetarene systems can readily by synthesized by variations of our previously developed general route to stable 1,6-diaminohexatrienes [2–6].

Our synthesis makes use of the strictly 1,4-selective sequential addition of organonitrile electrophiles to butadiene coordinated to bis(cyclopentadienyl)zirconium [7,8]. We have shown that one molar equivalent of benzonitrile adds to the readily available (butadiene)zirconocene reagent (s-*cis*-/s-*trans*-**1**) to yield the metallacyclic (enamido)zirconium complex **3**. Addition of a second equivalent of benzonitrile then furnishes the nine-membered metallacyclic system **4** which eventually rearranges to the thermodynamically favored C_2-symmetric metallacycle **5**. The controlled hydrolysis of **5** (H_2O/THF or CH_3OH) finally leads to the stable primary enamine system **6** (isolated in 91% yield and characterized by X-ray diffraction) [1].

We have now treated the (s-*cis*-/s-*trans*-η^4-butadiene)zirconocene equilibrium mixture with two molar equivalents of 2-cyanofurane in toluene solution. The reaction was complete after *c.* 18 h at ambient temperature. Workup gave a 9:91 mixture of the nine-membered metallacycles **7a** and **8a**. The mixture of metallacyclic N-metallated imine/enamine tautomers is isolated in almost 90% yield as an orange–brown solid. The major bis(metallaimine) component **8a** appears to be C_2-symmetric in solution as expected and thus exhibits only a single $^1H/^{13}C$ NMR Cp resonance at δ 5.79/108.9 and three resonances of the symmetry-equivalent pairs of carbon atoms of the central nine-membered metallacyclic core. In the IR spectrum there is a C=N band at $\tilde{\nu}=1650$ cm^{-1}. The minor component **7a** shows an N–H stretching bands at $\tilde{\nu}=3107$ cm^{-1}. The mixture of the metallacyclic tautomers **7a**/**8a** was then dissolved in tetrahydrofuran and the metal template removed by

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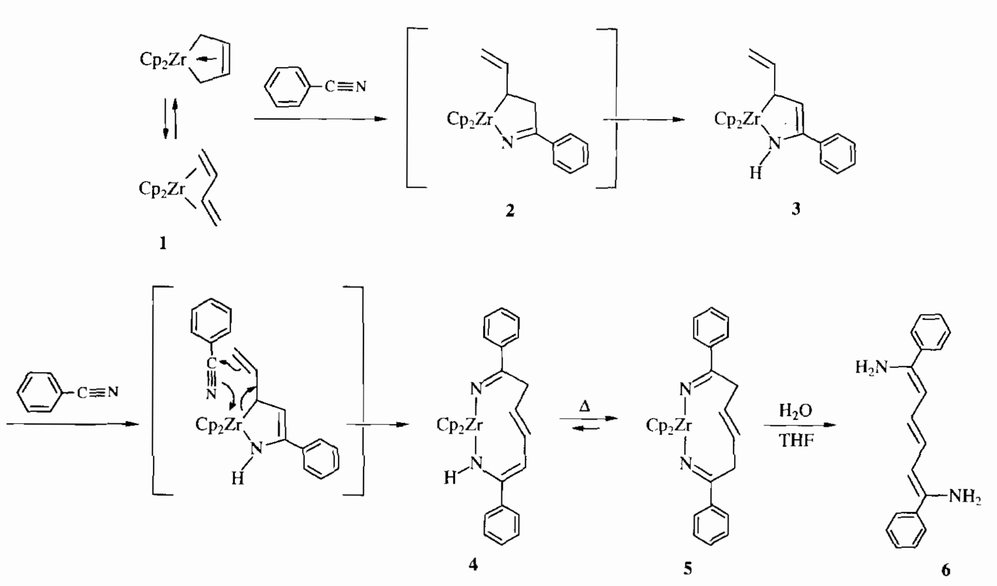
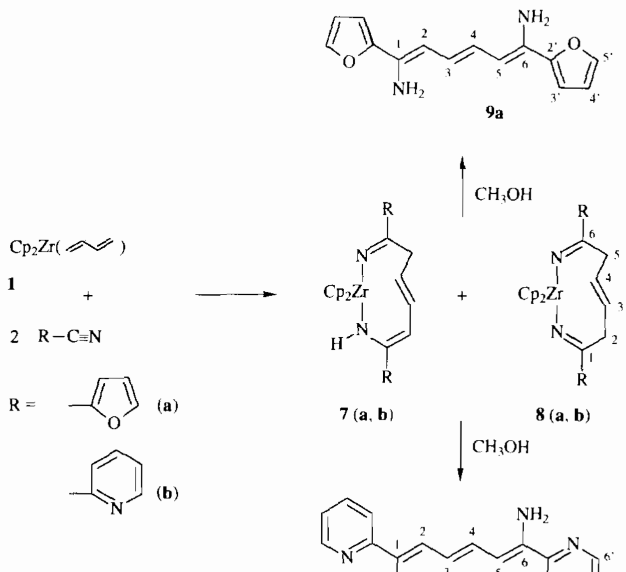


the reaction with methanol (c. 11-fold excess) at room temperature. Conventional workup gave a single product (c. 70% isolated, m.p. = 131 °C, after recrystallization from dichloromethane). The tail-to-tail-conjugated primary enamine **9a** shows two NH stretching bands in the IR at $\tilde{\nu}$ = 3427 and 3366 cm^{-1}. The ^{1}H NMR $-NH_2$ resonance is at δ = 3.12 (br s, 4H). The ^{13}C NMR signals of the central C_i-symmetric 1,6-diamino-1,3,5-hexatriene section of the molecule appear at δ 131.0 (C$^\alpha$), ~104 (C$^\beta$) and 122.7 (C$^\gamma$) [$(H_2N)-C^\alpha R=C^\beta H-C^\gamma H=$].

A similar reaction took place when the (butadiene)zirconocene reagent (**1**) was treated with two molar equivalents of 2-cyanopyridine. We have isolated the nine-membered metallacyclic coupling product (**7b**/**8b**; <2:98 mixture of the enamido/imido and bisimido tautomers) in 86% yield. Complex **8b** shows ^{1}H NMR signals of butadiene-derived portions of the molecule at δ 4.57/3.39 (CH_2) and 5.09 ($-CH=$). The corresponding ^{13}C NMR signals are at δ 39.1 and 123.4. There is an IR band at $\tilde{\nu}$ = 3072 cm^{-1} that may be attributed to the N-metallated imino functionality. In one respect, complex **8b** represents a somewhat exceptional case among the four differently substituted diazazirconacyclononatrienes prepared and described in this study. Whereas the systems **5**, **7a**/**8a**, **10a**/**11a** and **10b**/**11b** (see below) are all orange colored solids, complex **8b** was recovered from the toluene solution as an intensely blue–violet colored microcrystalline material which appears almost black in the reflecting light.

Cleavage of the Zr–N bonds in **7b**/**8b** is achieved analogously to that described above by treatment with methanol in tetrahydrofuran. The organic product was extracted from the reaction mixture with ether. The primary enamine system **9b** was obtained pure after recrystallization from methylene chloride as a red–brown solid (m.p. 130 °C).



The formal ternary coupling reaction of two nitriles with butadiene at the zirconocene template as used here is mechanistically proceeding stepwise [1,9,10]*. The differentiation in rate between the first and second coupling step is often so large that the corresponding intermediate can even be isolated or at least kept for a while in the reaction mixture. This has allowed us to achieve selective cross-coupling of butadiene with

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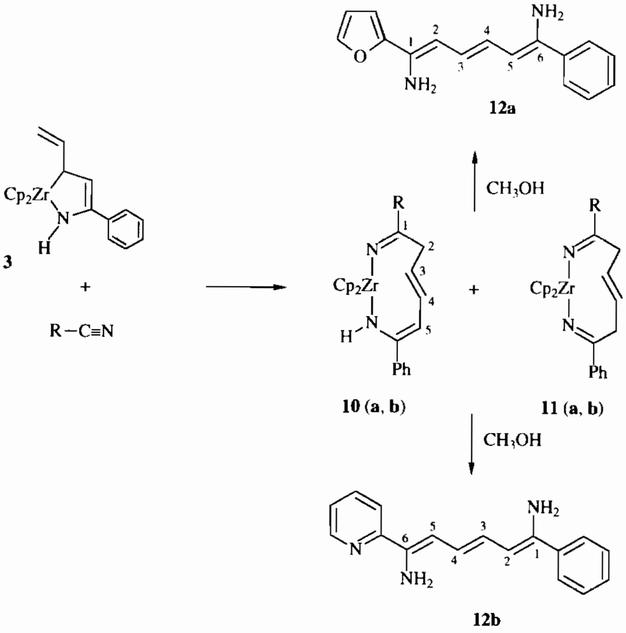
*In contrast to the (butadiene)zirconocene reagent, other butadiene dianion equivalents react predominantly by means of electrophilic 1,2-addition [11].

two different nitriles very easily and thereby attach two different aromatic groups to the ends of the diaminohexatriene chain. For this purpose we have first treated (butadiene)zirconocene with one molar equivalent of benzonitrile and isolated the stable metallacyclic (enamido)zirconocene complex **3**. This was then treated with one molar equivalent of 2-cyanofurane in toluene solution at room temperature. The reaction was complete after 18 h. Workup gave the nine-membered metallacycle **10a/11a**, bearing a phenyl and a furyl substituent at the respective ring positions, in *c*. 81% yield as an orange colored solid. From the reaction mechanism of the sequential cross-coupling reaction [1] it is clear that the enamido function in **10a** has to be located at the site of the first introduced aryl nitrile building block. Subsequent treatment of the **10a/11a** mixture with methanol in tetrahydrofuran produced the 1-furyl,6-phenyl-substituted tail-to-tail-conjugated primary enamine **12a** in *c*. 90% yield. 1,6-Diamino-1-furyl-6-phenyl-1,3,5-hexatriene (**12a**) can be recrystallized from dichloromethane or toluene (orange crystals).



The analogous reaction between **3** and 2-cyanopyridine in a 1:1 ratio in toluene at room temperature proceeds equally well. We have isolated and characterized the phenyl/pyridyl-substituted metallacycle **10b/11b** (see 'Experimental' for details) and converted it to the stable primary enamine **12b** by subsequent methanolysis. 1,6-Diamino-1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene (**12b**) was isolated as a red solid in 73% yield.

These examples show that template coupling [12] of the conjugated diene with two nitrile molecules at the bis(η-cyclopentadienyl)zirconium unit is a useful and easily performed reaction to give ring systems that serve as organometallic precursors for the synthesis of stable primary alkenamine systems that contain tail-to-tail-connected conjugated primary enamines. Diene conjugation [13] makes these systems presumably thermodynamically slightly more favorable than any of their ketimine tautomers [14]. We have now shown that 2-furyl and 2-pyridyl substituents are easily introduced into these systems by employing 2-cyanofurane or 2-cyanopyridine as educts in the template reaction. The resulting hetarene substituted 1,6-diaminohexatrienes have some of their heteroatom pairs in ideal positions for binding as chelates to suitable metal centers. We will explore the potential of such ligand systems for preparing interesting novel mono- and polynuclear coordination compounds. Using the organic π-system [15], which is so easily formed in these systems, for electronically coupling pairs of metal centers is especially tempting in applying these stable tail-to-tail-conjugated primary enamine systems containing a hetarene end group.

Experimental

Reactions and handling of organometallic reagents and the primary enamines were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. NMR spectra were measured with a Bruker AC 200 P (200 MHz ^{1}H; 50 MHz ^{13}C) or WM 300 (300 MHz ^{1}H; 75.5 MHz ^{13}C) NMR spectrometer. IR spectra were recorded on a Nicolet 5 DXC FT IR spectrometer. Melting points: Büchi SMP 20 (melting points are uncorrected) or DuPont DSC 910 (STA Instruments). Elemental analyses were carried out with a Foss-Heraeus CHNO-RAPID. (s-*Cis*-/s-*trans*-butadiene)zirconocene [16] and its benzonitrile addition product **3** [1] were prepared as described in the literature.

Reaction of (butadiene)ZrCp$_2$ with 2-cyanofurane to give 7a/8a

(Butadiene)zirconocene (4.31 g, 15.6 mmol) (**1**) was dissolved in 80 ml of toluene. To this 2-cyanofurane (2.91 g, 2.74 ml, 31.3 mmol) dissolved in 20 ml of toluene was added dropwise at room temperature and the mixture was stirred for 18 h. The solvent was removed *in vacuo* to yield 6.42 g (89%) of the **7a/8a** mixture as an orange–brown powder, (**7a**:**8a** = 9:91), m.p. 68 °C (DSC, decomp.). *Anal.* Calc. for $C_{24}H_{22}N_2O_2Zr$ (471.67): C, 62.44; H, 4.80; N, 6.07. Found: C, 62.56; H, 4.97; N, 6.21%. ^{1}H NMR (C_6D_6): major component **8a**: δ = 7.11 (dd, 2H, furyl-5′-H), 6.45 (dd, 2H, furyl-3′-H), 6.18 (dd, 2H, furyl-4′-H), 5.79 (s, 10H, Cp), 4.87 (m, 2H, 3-H, 4-H), 3.58 (br m, 2H) and 2.96 (br m, 2H, 2-H, 5-H). ^{13}C NMR (C_6D_6): **8a**:

$\delta = 157.6$, 155.2 (C1, C6 and furyl-C$_{ipso}$), 143.2 (furyl-C5′), 130.2 (C3, C4), 111.6 (furyl-C3′), 108.9 (Cp), 108.5 (furyl-C4′), 39.9 (C2, C5). IR (KBr): $\tilde{\nu} = 3107$, 3022, 2924, 2889, 1650, 1476, 1006, 979, 793 cm^{-1}.

Reaction of (butadiene)ZrCp$_2$ with 2-cyanopyridine to give 8b

Complex **8b** was prepared analogously to that described for **7a/8a** by reacting 2.90 g (10.5 mmol) of **1** with 2.19 g (2.03 ml, 21.0 mmol) of cyanopyridine to yield 4.38 g of the dark violet colored product (86%), m.p. 185 °C (DSC, decomp.). *Anal.* Calc. for $C_{26}H_{24}N_4Zr$ (483.72): C, 64.56; H, 5.00; N, 11.58. Found: C, 64.68; H, 5.02; N, 12.17%. Only **8b** (not its isomer **7b**) was detected by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6): $\delta = 8.59$–8.56 (m, 2H, pyridyl-6′-H), 7.81–7.76 (m, 2H, pyridyl-4′-H), 7.39–7.31 (m, 2H, pyridyl-5′-H), 6.83–6.76 (m, 2H, pyridyl-3′-H), 5.72 (s, 10H, Cp), 5.09 (m, 2H, 3-H, 4-H), 4.57 (br m, 2H), and 3.39 (br m, 2H, 2-H, 5-H). ^{13}C NMR (C_6D_6): $\delta = 168.8$, 155.8 (C1, C6 and pyridyl-C$_{ipso}$), 149.0 (pyridyl-C6′), 135.6, 132.0 and 121.1 (pyridyl-*C*H), 123.4 (C3, C4), 109.0 (Cp), 39.1 (C2, C5). IR (KBr): $\tilde{\nu} = 3072$, 3037, 2996, 2882, 1661, 1460, 992, 972, 793 cm^{-1}.

Reaction of the (enamido)zirconocene complex 3 with 2-cyanofurane to give 10a/11a

The (enamido)zirconium complex **3** (1.72 g, 4.54 mmol) was dissolved in 100 ml of toluene. 2-Cyanofurane (0.42 g, 0.40 ml, 4.54 mmol) was added dropwise at 0 °C and the mixture was stirred for 18 h at room temperature. The obtained dark orange–brown colored solution was filtered and the solvent was removed *in vacuo*. The oily residue was washed with 40 ml of pentane and the residue dried *in vacuo* to give 1.73 g (81%) of an orange powder **10a/11a** (containing > 95% **10a** by ^{1}H NMR), m.p. 56 °C (DSC, decomp.). *Anal.* Calc. for $C_{26}H_{24}N_2OZr$ (471.71): C, 66.20; H, 5.13; N, 5.94. Found: C, 65.07; H, 5.34; N, 5.88%. ^{1}H NMR (C_6D_6): **10a**: $\delta = 7.56$ (m, 2H, phenyl), 7.30–7.15 (m, 3H, phenyl), 7.05 (dd, 1H, furyl), 6.29 (dd, 1H, furyl), 6.19 (m, 1H) and 5.77 (m, 1H, 3-H, 4-H), 6.12 (dd, 1H, furyl), 5.82 (s, 10H, Cp), 5.45 (m, 1H, 5-H), 4.21 (br s, 1H, N-H), 3.39 (m, 2H, 2-H). ^{13}C NMR (C_6D_6): **10a**: $\delta = 159.8$, 156.8, 153.7, 145.6 (each C$_{quart.}$, C1, C6, furyl- and Ph–C$_{ipso}$), 133.4, 132.7, 129.0, 128.8, 126.5, 126.0, 124.7, 111.8, 111.6 (C3, C4, Ph, furyl), 110.1 (Cp), 103.6 (C5), 40.0 (C2). During recording of the ^{13}C NMR spectrum part of the product **10a** had rearranged to the thermodynamically favored isomer **11a**. IR (KBr): $\tilde{\nu} = 3356$, 3093, 3017, 2992, 2906, 2878, 1652, 1595, 1487, 1444, 1012, 802, 796 cm^{-1}.

Reaction of 3 with 2-cyanopyridine to give 10b/11b

The reaction was carried out analogously to that described above for the **10a/11a** preparation. Reaction of 3.87 g (10.2 mmol) of **3** with 1.06 g (0.98 ml, 10.2 mmol) of 2-cyanopyridine gave 3.55 g (71%) of the **10b/11b** (97:3) product mixture as a brown powder, m.p. 136 °C (DSC, decomp.). *Anal.* Calc. for $C_{27}H_{25}N_3Zr$ (482.74): C, 67.18; H, 5.22; N, 8.70. Found: C, 66.29; H, 5.37; N, 8.67%. ^{1}H NMR (C_6D_6): **10b**: $\delta = 8.52$ (m, 1H, pyridyl), 7.58–7.48 (m, 3H, pyridyl, Ph), 7.32–7.17 (m, 4H, pyridyl, Ph), 6.80–6.72 (m, 1H, pyridyl), 6.59–6.39 (m, 1H) and 6.10–6.00 (dd, 1H, 3-H, 4-H), 5.79 (s, 10H, Cp), 5.42 (dd, 1H, 5-H), 4.39 (br s, 1H, N-H), 4.03 (br d, 2H, 2-H). ^{13}C NMR (CD_2Cl_2): **10b**: $\delta = 157.4$, 156.3, 152.6, 148.7 (each C$_{quart.}$, C1, C6, pyridyl- and Ph-C$_{ipso}$), 136.5, 133.5, 128.9, 127.8, 126.5, 126.1, 125.7, 121.1, 120.8, 118.7 (C3, C4, Ph, pyridyl), 112.1 (Cp), 104.7 (C5), 42.0 (C2). During recording the product **10b** was constantly changing to **11b**. IR (KBr): $\tilde{\nu} = 3335$, 3076, 3043, 3023, 2908, 2885, 1657, 1582, 1562, 1459, 1442, 1014, 993, 799 cm^{-1}.

(1Z,3E,5Z)-1,6-Diamino-1,6-bis(2-furyl)-1,3,5-hexatriene (9a)

The **7a/8a** mixture (1.18 g, 2.56 mmol) was dissolved in 100 ml of tetrahydrofuran and 1.2 ml of methanol was added dropwise. After stirring for 3 h at room temperature the solvent was removed *in vacuo*. The residue was extracted with ether (4 × 80 ml). The combined ethereal extracts were dried over magnesium sulfate. The ether was removed *in vacuo*, and the residue dissolved in 20 ml of methylene chloride. At −30 °C the enamine product 0.43 g (69%) crystallized as a yellow solid, m.p. 131 °C (DSC, decomp.). $C_{14}H_{14}N_2O_2$ (242.28): HRMS found 242.1052 (calc. 242.1055). ^{1}H NMR (C_6D_6): $\delta = 7.01$ (dd, 2H, furyl), 6.27–6.03 (several m, 4H furyl, 4H olefin), 3.12 (br s, 4H, NH$_2$). ^{13}C NMR ($CDCl_3$): $\delta = 152.3$ (furyl-C$_{ipso}$), 141.7 (furyl-C5′), 131.0 (C1, C6), 122.7 (C3, C4), 111.7 (furyl-C3′), 104.8, 103.0 (furyl-C2′, C2, C5). IR (KBr): $\tilde{\nu} = 3427$ (NH), 3366 (NH), 1636, 1615, 1015, 961 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max} = 410$ nm, ($\epsilon = 15\,900$), 275 (13 200).

(1Z,3E,5Z)-1,6-Diamino-1,6-bis(2-pyridyl)-1,3,5-hexatriene (9b)

The enamine **9b** was prepared analogously to that described above. The reaction of 2.63 g (5.44 mmol) of **8b** with 1.4 ml of methanol gave 0.25 g (18%) of **9b** as a red–brown powder, m.p. 130 °C (DSC, decomp.). $C_{16}H_{16}N_4$ (264.33): HRMS found 264.1384 (calc. 264.1375). ^{1}H NMR ($CDCl_3$): **9b**: $\delta = 8.53$–8.50 (m, 2H, pyridyl-6′-H), 7.71–7.56 (m, 4H, pyridyl), 7.15–7.09 (m, 2H, pyridyl), 6.59–6.54 (m, 2H, =CH), 6.10–6.04 (m, 2H, =CH). ^{13}C NMR ($CDCl_3$): $\delta = 153.6$ (pyridyl-C$_{ipso}$), 148.3 (pyridyl-C6′), 139.1 (C1, C6), 135.9 (pyridyl-C4′), 124.5 (C3, C4), 121.8, 119.0 (pyridyl-C3′/C5′), 104.1 (C2, C5). IR (KBr): $\tilde{\nu}=3460$ (NH), 3354 (NH), 1617, 966 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}=447$ nm ($\epsilon=11\,700$).

(1Z,3E,5Z)-1,6-Diamino-1-(2-furyl)-6-phenyl-1,3,5-hexatriene (12a)

Analogously to that described above 2.14 g (4.54 mmol) of **10a**/**11a** were treated with 1.2 ml of methanol to yield 1.03 g of the enamine **12a** (90%), obtained after crystallization from methylene chloride as an orange solid, m.p. 107 °C (DSC, decomp.). $C_{16}H_{16}N_2O$ (252.32): HRMS found 252.1255 (calc. 252.1263). ^1H NMR ($CDCl_3$): $\delta=7.45$–7.40 (m, 2H, phenyl), 7.28–7.14 (m, 4H, 3×phenyl, furyl-5′-H), 6.31–6.29 (m, 2H, furyl-3′-H and 4′-H), 6.29–6.24 (m, 2H, =CH), 5.78–5.73, 5.56–5.50 (each m, 1H, =CH), 3.65 and 3.57 (br s, each 2H, $2\times NH_2$). ^{13}C NMR ($CDCl_3$): $\delta=152.3$ (furyl-C_{ipso}), 141.6 (furyl-C5′), 140.6, 139.2 (C6, phenyl-C_{ipso}), 130.7 (C1), 128.5, 127.9, 125.3 (phenyl), 123.7, 122.3 (C3, C4), 111.6 (furyl-C3′), 104.7, 104.2, 103.1 (C2, C5, furyl-C4′). IR (KBr): $\tilde{\nu}=3460$, 3362, 1612 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}=405$ nm ($\epsilon=15\,300$).

(1Z,3E,5Z)-1,6-Diamino-1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene (12b)

Analogously to that described for **9a** the reaction of 2.51 g (5.20 mmol) of **10b**/**11b** with 1.5 ml of methanol yielded 1.06 g of the enamine **12b** (73%), crystallized from pentane as a red solid, m.p. 138 °C (DSC). $C_{17}H_{17}N_3$ (263.34): HRMS found 263.1416 (calc. 263.1422). ^1H NMR (C_6D_6): $\delta=8.39$–8.36 (m, 1H, pyridyl-6′-H), 7.52–7.44 (m, 3H, 2×phenyl, 1×pyridyl), 7.15–6.97 (m, overlapping with C_6D_5H solvent signal, phenyl, pyridyl), 6.59–6.56 (m, 1H, =CH), 6.45–6.39 (m, 1H, =CH), 6.13–6.08 (m, 1H, =CH), 5.81–5.75 (m, 1H, =CH), 4.65/3.21 (br s, each 2H, $2\times NH_2$). ^{13}C NMR ($CDCl_3$): $\delta=153.8$ (pyridyl-C_{ipso}), 148.3 (pyridyl-C6′), 141.0, 139.1, 138.5 (phenyl-C_{ipso}, C1, C6), 135.8 (pyridyl-C4′), 128.5, 128.0, 125.3, 124.4, 123.4, 121.6, 118.7 (pyridyl-C5′, pyridyl-C3′, phenyl-CH, C3, C4), 104.2 (C2, C5). IR (KBr): $\tilde{\nu}=3367$–3349 (broad, NH), 3053, 2975, 2929, 2867, 1623, 1617, 958, 797, 741, 697 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max}=428$ nm ($\epsilon=16\,700$).

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