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Cyclization Reactions of 3,4-Diazaheptatrienyl Metal Compounds. Pyridines from an Anionic Analogue of the Fischer Indole Synthesis: Experiment and Theory

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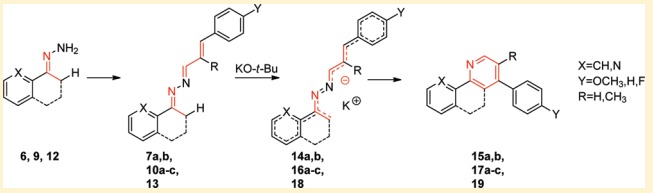
Supporting Information

ABSTRACT: Unsymmetrical *N,N′*-bisalkylidene hydrazines **7a,b**, **10a−c** and **13**, which are accessible in good to excellent yields from hydrazones **6**, **9**, and **12** and commercially available α,β-unsaturated carbonyl compounds, are converted into 3,4-diazaheptatrienyl anions **14a,b**, **16a−c**, and **18** by treatment with KO-*t*-Bu as base. These anionic species form pyridines **15a, b**, 5,6-dihydrobenzo[*h*]quinolones **17a−c**, and bipyridine **19** in moderate yields. We interpret thermodynamics and kinetics of these reactions by quantum chemical calculations and discuss this multistep anionic rearrangement, based on an electrocyclic ring formation with a Möbius aromatic transition structure **22**, the N−N bond fission (**25**), and the *6-exo-trig* cyclization (**27**) as key steps, considering the results of NICS and NBO-charge calculations. This novel anionic reaction sequence bears an interesting analogy to the mechanism of the (cationic) Fischer indole synthesis. Precursor **10c** and product **16c** could be characterized by X-ray diffraction.

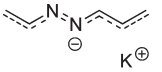


INTRODUCTION

Pyridines are among the most important and versatile organic substances that are known to organic chemistry. They are widely used as pharmaceuticals and agrochemicals, as ligands, and in organocatalysis.[1,2] Thus, the development of new synthetic routes for pyridines has always been in the focus of organic chemists.[1−3] Hydrazones, on the other hand, are reactive starting compounds for organic synthesis with the Fischer indole rearrangement as the best known example.[4] In our group, we have learned that cationic and anionic intermediates derived from unsaturated hydrazones are interesting precursors for unprecedented ring-closure reactions preceding under mild conditions.[5,6] N−N bond fission, sometimes observed in such compounds, is an additional synthetically useful property.[7] Recently, we reported on ring-forming reactions of hydrazone-derived 1,2-diaza-4,5-benzoheptatrienyl anions, specifically their alkali metal compounds, for the synthesis of 3*H*-benzodiazepines and 1,2-dihydrophthalzines.[6] Now, we present 3,4-diazaheptatrienyl anions **1**, specifically potassium compounds (Scheme 1), employed as substrates in a new versatile pyridine synthesis formed by a complex multistep reaction cascade, not requiring external oxidants or transition metals.

The species **1** may be understood as 2-fold vinylogues of 1,2-diazaallyl anions,[8] interesting heteroallyl anions like enolates and azaenolates.[9] Electrocyclization reactions are among the most useful tools for the preparation of carbocycles.[10,11] However, in the field of heterocompounds, apart from the conservation of the orbital symmetry, kinetics and thermodynamics of such reactions highly depend on the electronegativity and position of the heteroatoms within the unsaturated chain. Due to their respective

Scheme 1. 3,4-Diazaheptatrienyl Potassium Compound 1



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electronegativity such heteroatoms greatly disturb the electronic structure of polyenyl anions.[12] Thus, if an electronegative heteroatom such as nitrogen is located in an odd position of the unsaturated chain, ring-forming reactions are unlikely; otherwise, with the electronegative heteroatom in an even position, ring-forming reactions are frequently observed.[13] These observations were sufficiently explained by coincided positions of the heteroatoms in the unsaturated chain with positions with a large coefficient of the HOMO (stabilizing effect), otherwise, with nodal positions of the HOMO (destabilizing influence).[13] The ambiguous character of N3 in odd and N4 in even positions turns anion **1** into an interesting model compound. Initially, we expected possible ring-forming reactions of **1** leading to interesting heterocycles such as pyrazoles, pyridazines or diazepines (Scheme 2). The scope of such ring-closure reactions is well-known and often applied in synthetic chemistry.[11,14]

However, as this study will show below, this particular work combines the ring-forming aptitude of azapolyenyl anions **1** with a novel, unexpected organometallic rearrangement reminiscent of the mechanism of the Fischer indole synthesis.[4] It outlines a

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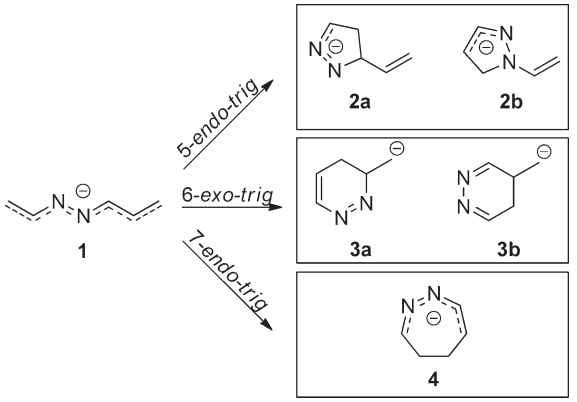
Scheme 2. Expected Possible Cyclization Reactions of Anion 1



procedure that allows the synthesis of pyridines or more complex analogues from commercially or easy available substrates.

RESULTS AND DISCUSSION

Hydrazones **6**,[15] **9**,[16] and **12**[17] are prepared by condensation of ketones **5**, **8**, and **11** with an excess of hydrazine hydrate in high dilution to suppress the formation symmetrical bishydrazones (azines) as a result of double condensation. In a second step, hydrazones **6**, **9**, and **12** are reacted under solvent free conditions with α,β-unsaturated carbonyl compounds to give unsymmetrical *N*,*N*′-bisalkylidene hydrazines **7a**−**c**, **10a**−**c**, and **13** (Scheme 3) without formation of byproducts. We were able to grow single crystals of **10c** and to characterize them by X-ray diffraction (Figure 1).

Treatment of *N*,*N*′-bisalkylidene hydrazines **7a-c, 10a-c** and **13** with KO-*t*-Bu in THF at room temperature generates the reactive anions, specifically potassium salts **14a,b**, **16a**−**c**, and **18**, by abstraction of a proton in α-position to the hydrazone subunit. Via a complex sequence of rearrangement reactions pyridines **15a, b**,[18] 5,6-dihydrobenzo[*h*]quinolones **17a**−**c**, and bipyridine **19**[19] (Scheme 4) were isolated after aqueous workup. We were able to grow single crystals of **17c** and to characterize them by X-ray diffraction (Figure 2).

For the investigation of scope and limitation of this novel multistep reaction we used a variety of precursors with differing substitution patterns. Modifications at C6 of the 3,4-diazaheptatrienyl chain are tolerated and allow access to *meta*-substituted pyridine **15b**, while methylation at C5 inhibits the formation of any specific product. Furthermore C1 may be part of a cyclic structure to give access to *meta*-substituted examples **10a**−**c** → **17a**−**c**. These α-tetralone-derived hydrazones (**10a**−**c**) widen the application of the concept to polycyclic, ring-fused, and more rigid analogues. Examples **10a**−**c** were also studied for investigations on the influence of *p*-substituents at C7 with electron-withdrawing or -donating properties, as the electron density of the delocalized anions is expected to be a sensitive precondition for their reactivity. Thus, the phenyl moiety at C7 with its minor yet stabilizing effect (**17b**) may be changed to electron-poor (**17a**) and electron-rich (**17c**) aromatics with little influence on

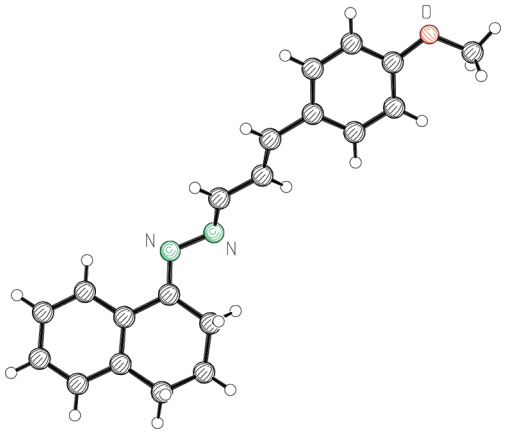
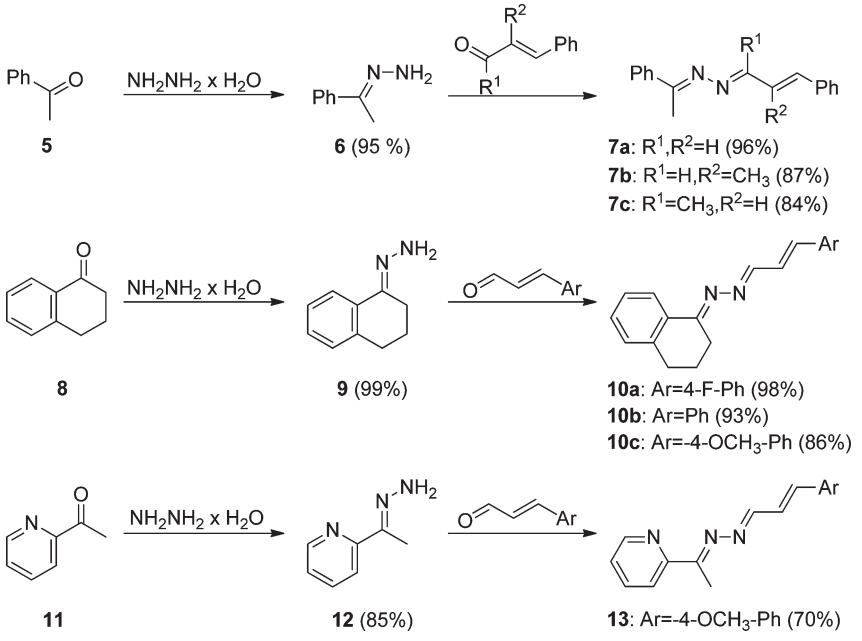


Figure 1. Molecular structure of **10c** as obtained by X-ray diffraction (Schakal plot).

Scheme 3. Synthesis of Hydrazones 6, 9, and 12 and *N*,*N*′-Bisalkylidene Hydrazines 7a−c, 10a−c, and 13



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the yield. In means of scope the most interesting variation is the 2-acetylpyridine-derived hydrazone **13** from which bipyridine **19** is obtained.

The scope of this procedure is quite general. While the yields are merely moderate, this deficiency is more than offset by the facility with which a high degree of complexity can straightforwardly be obtained from easily accessible and in many examples commercially available starting materials. In particular, the method provides access to a pyridine core unit with up to four different substituents with full regiochemical control in one operation. Careful analysis of the crude reaction mixture (HPLC-MS(ESI)) proved the formation of a number of unspecific byproducts. This may be a result of the complex multistep rearrangement reaction (see below).

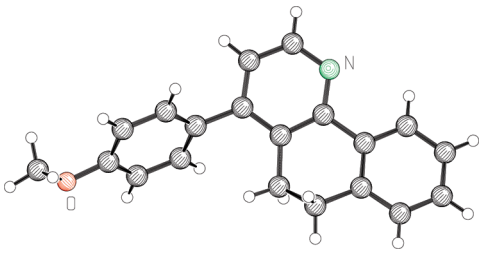
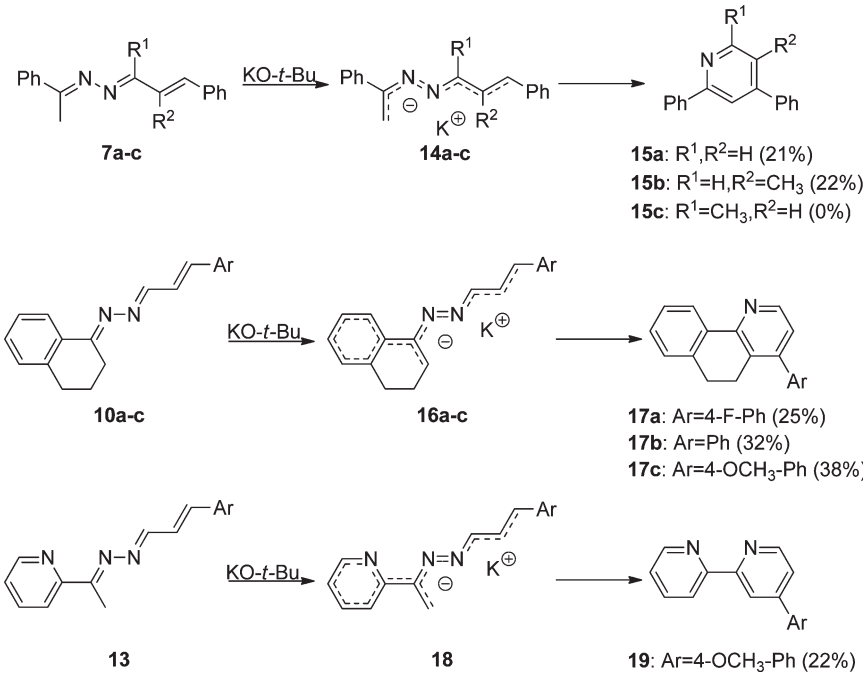


Figure 2. Molecular structure of **17c** as obtained by X-ray diffraction (Schakal plot).

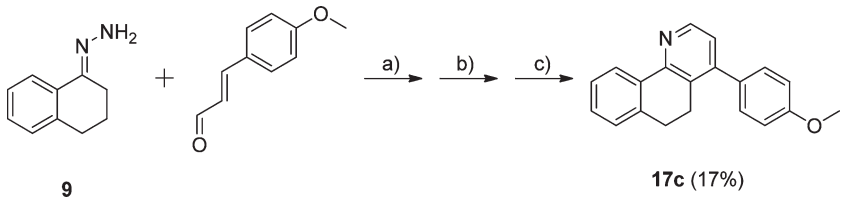
In one example we performed the whole reaction sequence as a one-pot procedure, indicating the preparative simplicity of this new method. Starting from the hydrazone **10c** the condensation and the subsequent deprotonation step, inducing the rearrangement, the *N*-heterocycle **17c** was formed within 1 h at ambient temperature in 17% yield. In this case a repeated acidic/basic pendulum extraction workup process without further purification proved to be advantageous (Scheme 5).

For this unprecedented formation of *N*-heterocyles of type **15**, **17**, and **19**, we suggest an anionic mechanism that is somewhat related to the rearrangement of the Fischer indole synthesis.[4] We discuss it on the basis of quantum chemical calculations starting with hydrazone **10c** via model anion **20** to give pyridine **17c** (without counterion or solvent effects) carried out at the B2PLYPD/6-311+G(d,p)//B3LYP/6-31+G(d,p)[20] level of theory (corrected for zero point energies).[21] The use of the double-hybrid functional B2PLYPD for the energy determinations including dispersion interaction is known to give improved total and relative energies (Scheme 6). All stationary points were fully optimized and subjected to frequency analyses.

Scheme 4. Synthesis of Pyridines 15a−c, 5,6-Dihydrobenzo[*h*]quinolones 17a−c, and Bipyridine 19



Scheme 5. One-Pot Formation of 17c[a]



[a] Overall yield is in parentheses. Reagents and conditions: (a) 50 °C, 30 min, no solvent; (b) addition of 1.1 equiv of KO*t*Bu in THF (20 mL/mmol), 1 h; (c) HCl (2 M), NaOH (2 M) repeated extraction process

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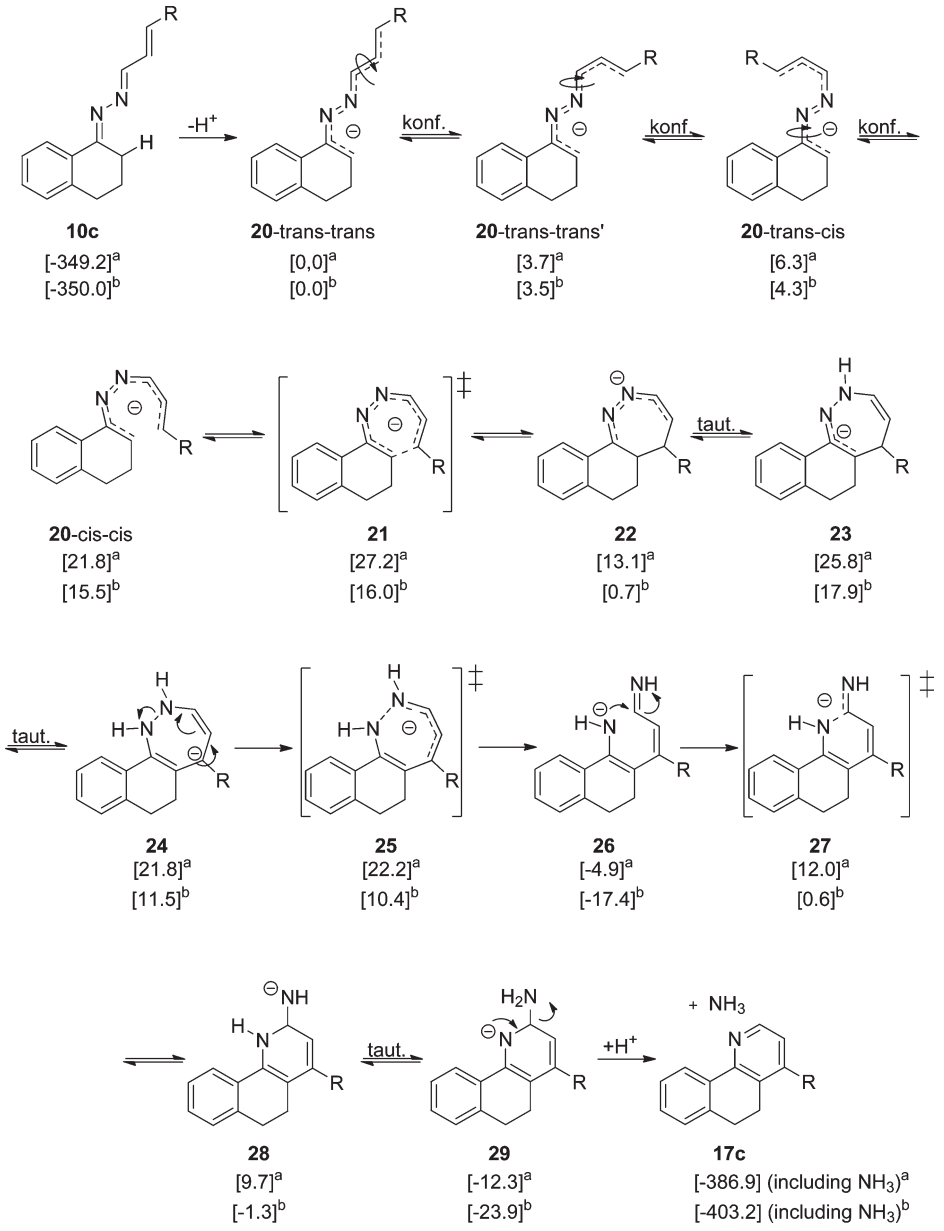
Scheme 6. Suggested Mechanism for the Formation of 5,6-Dihydrobenzo[*h*]quinolone 17c (R = 4-OMe-Ph)[a]



[a] Calculated energies relative to **20**-*cis-cis* at two levels of theory: (a) B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) and (b) (B2PLYPD/6-311+G(d,p)//B3LYP/6-31+G(d,p) (both corrected for zero-point energies) [kcal/mol]; see Supporting Information for optimized structures.

Once the open chain anion **20** adopts a suitable helical conformation (**20**-*trans-trans* → **20**-*cis-cis*) with a maximal effort of 15.5 kcal/mol (B2PLYPD; 21.8 kcal/mol at B3LYP), a new C−C bond is formed among the terminal carbon atoms (C1, C7) to give diazepinyl anion **22** in a 7-*endo-trig* cyclization reaction via transition state **21**. The barriers of internal rotations of the conformers of anion **20** were not considered in the calculations due to the involvement of counterion and solvent effects. We assume that these barriers are surmounted easily under the reaction conditions employed.[22] Then, we assume that cyclic anion **22** tautomerizes to give **24**, which then allows the cleavage of the N−N bond via transition state **25**. The resulting 1,7-diazaheptatrienyl anion **26** will finally form pyridine **17c** in a 6-*exo-trig* ring-forming reaction (transition state **27**) by attack of the amine at the iminic carbon, tautomerism (**28**, **29**), and after protonation, elimination of ammonia. Additional calculations show that the alternative formation of a tertiary amine anion in the bridgehead position requires more energy. The key steps (ring-formation **20**-*cis-cis* → **22**; N−N bond cleavage **24** → **26**; aromatization **29** → **17c**) are exothermic and shift the equilibrium to the product side. All ring-forming and -breaking transition states are surprisingly low in energy and are well in accordance with the reaction conditions applied (room temperature reaction). Comparison of the neutral structures **10c** and **17c** indicate a distinct exothermic reaction (B2PLYPD,: −53.2 kcal/mol; B3LYP, −37.7 kcal/mol) due to aromatization and cleavage of the high-energy N−N bond. Many details of this suggested mechanism (the pericyclic mode, the N−N fission, the necessary

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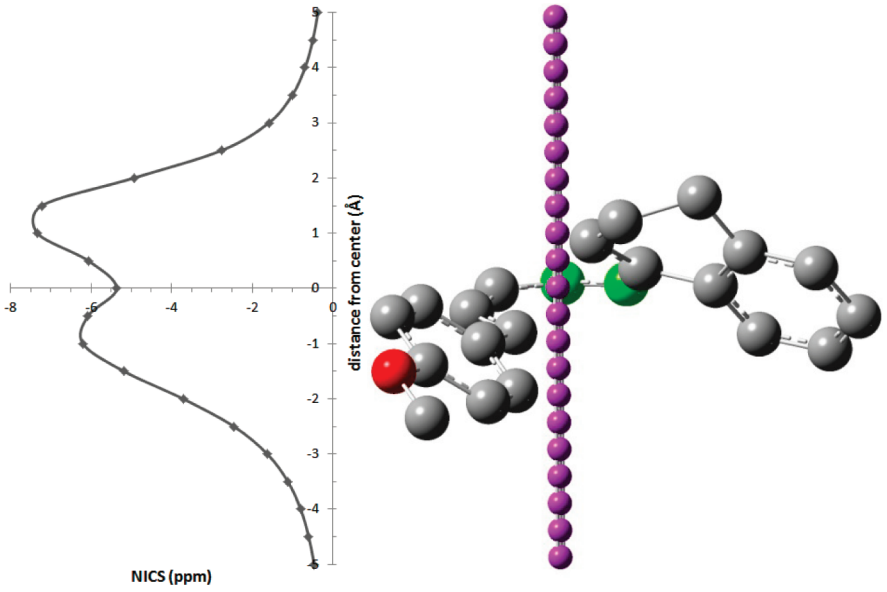

Figure 3. Calculated NICS values for transition structure **21**. Measuring points along an axis perpendicular to the center of the cyclic moiety of the transition structure are shown in purple (B3LYP/6-311+G(d,p)) (hydrogen atoms omitted for clarity).

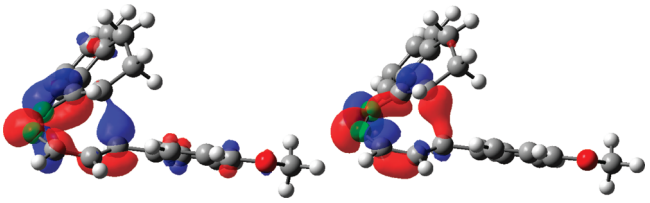

Figure 4. Molecular orbitals HOMO-1 (left) and HOMO-2 (right) of **22** (side view, isocontour value 0.05/0.05; B3LYP/6-311+G(d,p)).

tautomerisms, the NH_3 cleavage) bear close mechanistic resemblance to the acid-promoted Fischer indole synthesis,[4,23] although in our case an anionic (organometallic) route to form a six-membered heterocycle is realized. Alternative mechanistic pathways involving three-membered cyclic intermediates (derived from **22** or **23**) require much higher activation barriers according to calculations.

On the basis of geometries, charges (determined by NBO[24]), and by NICS[25,26] values (B3LYP/6-311+G(d,p)) we studied the transition structures for the 7-*endo-trig* cyclization reaction (transition structure **21**), the N−N bond fission (**25**), and the 6-*exo-trig* cyclization (**27**).

For the helical, conrotatory, 8π electron transition structure **21** the calculated NICS values of −7.3 ppm (Figure 3) along an axis perpendicular to the center of the ring being formed and the small charge separation of only 0.03 e (C1, −0.23 e; C7, −0.26e) are indicators of a bond-forming step with a predominantly electrocyclic character. The distinct negative enthalpy of the cyclization is reflected in the comparatively long distance between the bond forming atoms C1 and C7 of 2.21 Å. The helically shaped geometry (deviation from plane C1−C2−N3−N4 7.0°, C2−N3−C4−C5 23.2°, N3−N4−C5−C6 13.6°, N4−C5−C6−C7 2.5°, Σ 46.3°) of **21** indicates Möbius aromaticity.[26,27]

The Möbius aromatic character of the transition structure is also represented by strong binding interactions in the HOMO-1 and HOMO-2 (Figure 4).

The next transition state **25**, which is related to the rather exothermic N−N bond fission, appears to have some minor electrocyclic character, which is indicated by a calculated NICS value of −5.7 ppm (Figure 5) and a small charge separation of 0.02 e (N3, −0.57 e; N4, −0.55 e). The helical shape of this transition structure **25** (deviation from plane N3−C2−C1−C7 −6.6°, C2−C1−C7−C6 −17.5°, C1−C7−C6−C5 −6.9°, C7−C6−C5−N4 0.9°, Σ 31.9°) with a N−N distance of 1.67 Å (N−N distance of structure **24** = 1.47 Å) reflects the structural closeness to intermediate **24** (early transition state).

Finally, by inspection of transition structure **27** of the endothermic 6-*exo-trig* reaction **26** → **28** we found strong evidence for a charge-controlled electrophile−nucleophile mechanism with huge charge separation of 0.86e (N, −0.73 e; C, +0.13 e) and no markedly magnetic phenomena (NICS, −2.4 ppm). The C−N-distance (1.94 Å) classifies this transition state to be a late one.

CONCLUSION

In summary, we have presented a new, widely applicable preparation of substituted pyridines **15a,b**, 5,6-dihydrobenzo[*h*]quinolines **17a−c**, and bipyridine **19** from 3,4-diazaheptatrienyl metal compounds **1** as easily accessible starting materials. This novel transition metal free pyridine synthesis does not require external oxidants and allows the introduction of at least four different substituents into the pyridine core unit in one step under full regiochemical control. For the formation of products **15a,b**, **17a−c**, and **19** we suggest an anionic multistep reaction mechanism resembling the acid-promoted Fischer indole rearrangement and discuss it on the basis of comprehensive quantum chemical calculations referring to model reaction **10c** → **17c**. The transition structure **21** of the 7-*endo-trig* ring-forming reaction was found to have the characteristics of a Möbius aromatic electrocyclization reaction involving 8π electrons. Then follow an electrocyclic N−N bond fission step (transition structure **25**) and a final charge-controlled 6-*exo-trig* cyclization that involves an amine nucleophile attacking an iminic bond (transition structure **27**) leading to the pyridine derivatives. This work demonstrates the

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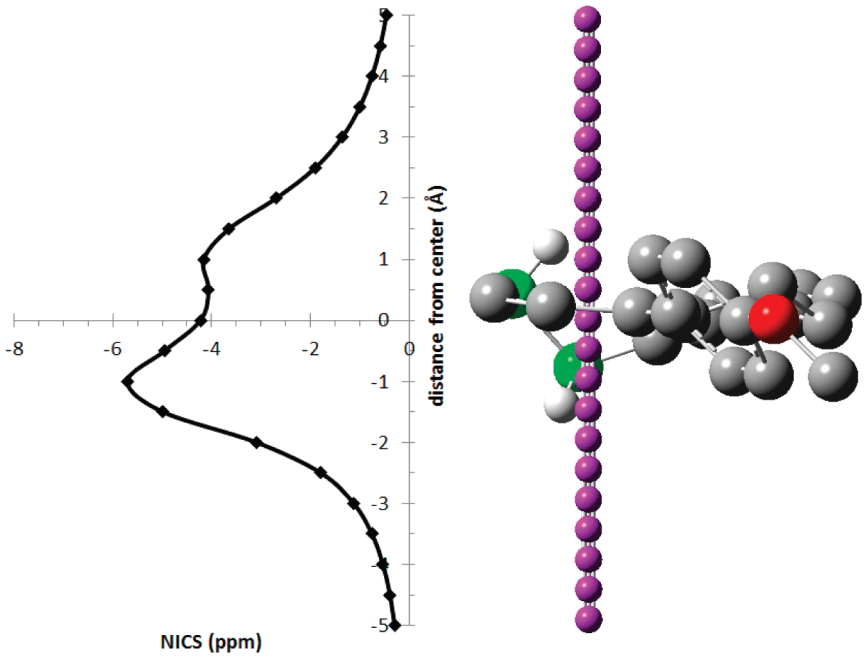

Figure 5. Calculated NICS values for transition structure **21**. Measuring points along an axis perpendicular to the center of the cyclic moiety of the transition structure are shown in purple (B3LYP/6-311+G(d,p)) (hydrogen atoms omitted for clarity).

versatility of anionic polyunsaturated hydrazone derivatives for the development of novel synthetic pathways.

EXPERIMENTAL SECTION

Melting points are uncorrected. ^{1}H, ^{13}C NMR spectroscopy: TMS (^{1}H) (0.00 ppm), $CDCl_3$ (^{1}H) (7.26 ppm), C_6D_6 (^{1}H) (7.16 ppm), $CDCl_3$ (^{13}C) (77.0 ppm), and C_6D_6 (^{13}C) (128.1 ppm) were used as internal reference. All signals in the ^{1}H NMR and ^{13}C spectra were assigned on the basis of relative intensities, coupling constants, and GCOSY, GHSQC, and GHMBC experiments. When necessary, the experiments were carried out with complete exclusion of moisture.

Acetophenone Hydrazone 6. A three-necked flask with a Dean−Stark head was charged with 60 mL (1.2 mol) of hydrazine hydrate and heated to 120 °C. A solution of acetophenone (4.81 g, 40.0 mmol) in 30 mL of $CHCl_3$ was added over a period of 4 h. After cooling to room temperature the aqueous layer was washed with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Compound **6** was obtained as a light yellow solid in 5.23 g (39.0 mmol, 95%) yield. Mp 67 °C (lit. 24−25 °C[15]); ^{1}H NMR (300 MHz, C_6D_6) δ 1.52 (s, 3H, CH_3), 4.69 (br, 2H, NH_2), 7.06−7.10 (m, 1H, *p*-CH_{ar}), 7.12−7.17 (m, 2H, *m*-CH_{ar}), 7.70−7.75 (m, 2H, *o*-CH_{ar}); ^{13}C NMR (75 MHz, C_6D_6) δ 10.6 (CH_3), 125.7 (*m*-CH_{ar}), 127.9 (*o*-CH_{ar}), 128.4 (*p*-CH_{ar}), 140.1 (*i*-C_{ar}), 145.1 (*C*N); HRMS (ESI) calcd for $C_8H_{11}N_2^+$ 135.0917, found 135.0935.

α-Tetralone Hydrazone 9. A three necked flask with a Dean−Stark head was charged with 60 mL (1.2 mol) of hydrazine hydrate and heated to 120 °C. A solution of α-tetralone (11.7 g, 80.0 mmol) in 40 mL of $CHCl_3$ was added over a period of 5 h. After cooling to room temperature, the aqueous layer was washed with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Compound **9** was obtained as a light yellow solid in 12.67 g (78.8 mmol, 99%) yield. Mp 41 °C (lit. 38−40 °C[16]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79−1.90 (m, 2H, γ-CH_2), 2.34−2.44 (m, 2H, δ-CH_2), 2.58−2.69 (m, 2H, β-CH_2), 5.21 (s, 2H, NH_2), 6.96−7.05 (m, 1H, CH_{ar}), 7.05−7.15 (m, 2H, CH_{ar}), 7.81−7.89 (m, 1H, CH_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5 (γ-CH_2), 23.9 (δ-CH_2), 29.7 (β-CH_2), 123.9 (CH_{ar}), 126.4 (CH_{ar}), 127.9 (CH_{ar}), 128.2 (CH_{ar}), 133.4 (*i*-CCH_2), 138.5 (*i*-*C*CN), 147.4(*C*N); HRMS (ESI) calcd for $C_{10}H_{13}N_2^+$ 161.1073, found 161.1072.

2-Acetylpyridine Hydrazone 12. A three necked flask with a Dean−Stark head was charged with 60 mL (1.2 mol) of hydrazine hydrate and heated to 120 °C. A solution of 2-acetylpyridine (5.13 g, 42.4 mmol) in 30 mL of $CHCl_3$ was added over a period of 5 h. After cooling to room temperature, the aqueous layer was washed with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Compound **12** was obtained as light yellow solid in 4.87 g (36.0 mmol, 85%) yield. Mp 61 °C (lit. 77 °C[17]); ^{1}H NMR (300 MHz, C_6D_6) δ 2.09 (s, 3H, CH_3), 4.96 (br, 2H, NH_2), 6.62 (ddd, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 4.9 Hz, $^{5}J_{HH}$ = 0.8 Hz, 1H, 5-CH_{py}), 7.11 (m, 1H, 4-CH_{py}), 8.21 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, 3-CH_{py}), 8.45 (d, $^{3}J_{HH}$ = 4.7 Hz, 1H, 6-CH_{py}); ^{13}C NMR (75 MHz, C_6D_6) δ 8.92 (CH_3), 119.60 (5-CH_{py}), 122.15 (3-CH_{py}), 135.57 (4-CH_{py}), 146.44 (*C*N), 148.51 (6-CH_{py}), 157.29 (2-C_{py}); HRMS (ESI) calcd for $C_7H_{10}N_3^+$ 136.0869, found 136.0859.

General Procedure A for the Formation of *N,N′*-Bisalkylidene Hydrazine Derivatives. Hydrazone **6**, **9**, or **12** (1 equiv) and 1 equiv of the corresponding cinnamaldehyde derivative were each dissolved in 2 mL of TBME and mixed in a round-bottom flask. The mixture was heated to 50 °C, and the solvent was removed under reduced pressure. The mixture was stirred at 50 °C, 5 mbar for 2 h. The products were obtained without noteworthy byproducts.

N-Cinnamylideneacetophenone Hydrazone ***7a***. According to general procedure A **7a** was obtained from hydrazone **6** (1.32 g, 10.0 mmol) and *trans*-3-phenyl-2-propenal (1.32 g, 10.0 mmol) after purification by column chromatography (cyclohexane 98%, TBME 2%) as a yellow solid in 2.38 g (9.59 mmol, 96%) yield. Mp = 92 °C; IR (neat) $\tilde{\nu}$ = 3053 (w), 3038 (w), 3021 (w), 1626 (m), 1597 (m), 1578 (m), 1487 (w), 1447 (m), 1364 (m), 1285 (m), 1159 (w), 1074 (w), 976 (s), 947 (m), 760 (m), 746 (s), 687 (s), 662 (m), 625 (w), 567 (s), 517 (s), 513 (s), 501 (s); ^{1}H NMR (300 MHz, C_6D_6) δ 2.50(s, 3H, CH_3), 6.75 (d, $^{3}J_{HH}$ = 16.1 Hz, 1H, *i*-CCH_{olef}), 7.09−7.18 (m, 3H, CH_{ar}) 7.20−7.30 (m, 5H,

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CH_{ar}), 7.34 (dd, $^3J_{HH}$ = 16.1, 9.6 Hz, 1H, N=CHCH_{olef}), 8.04−8.15 (m, 2H, CH_{ar}), 8.49 (dd, $^3J_{HH}$ = 9.6 Hz, 1H, N=C*H*); ^{13}C NMR (75 MHz, C_6D_6) δ 14.5 (CH_3), 126.5 (*i*-CCH$_{olef}$), 127.1 (CH_{ar}), 127.3 (CH_{ar}), 128.2 (CH_{ar}), 128.6 (CH_{ar}), 128.9 (*p*-CH_{ar}), 129.9 (N=CHCH_{olef}), 136.2 (*i-C*), 138.7 (*i-C*),141.4 (*p*-CH_{ar}), 160.5 (N=*C*H), 163.9 (*i*-CC=N); HRMS (ESI) calcd for $C_{17}H_{17}N_2^+$ 249.1386, found 249.1383. Anal. Calcd for $C_{17}H_{16}N_2$ (248.32): C 82.22, H 6.49, N 11.28. Found: C 82.20, H 6.38, N 11.25.

N-(α-Methylcinnamylidene)acetophenone Hydrazone ***7b***. According to general procedure A **7b** was obtained from hydrazone **6** (670 mg, 5.0 mmol) and α-methyl-*trans*-3-phenyl-2-propenal (730 mg, 5.0 mmol) after purification by column chromatography (cyclohexane 87%, TBME 13%) as a yellow solid in 1.14 g (4.3 mmol, 87%) yield. Mp = 90 °C; IR (neat) $\tilde{\nu}$ = 3057 (w), 3030 (w), 2959 (w), 1599 (m), 1576 (m), 1491 (w), 1445 (m), 1362 (m), 1287 (m), 1200 (w), 1180 (w), 1078 (w), 1024 (m), 962 (m), 922 (m), 876 (w), 756 (s), 689 (s), 654 (s);^{1}H NMR (500 MHz, C_6D_6) δ 1.40 (s, 3H, $C_{olef}CH_3$), 2.34 (d, $^3J_{HH}$ = 1.2 Hz, 3H, CH_3C=N), 6.66 (s, 1H, *i*-CCH_{olef}), 7.01−7.23 (m, 10H, CH_{ar}, CH_{olef}), 8.52 (s, 1H, CH_{ar}); ^{13}C NMR (125 MHz, C_6D_6) δ 13.2 ($C_{olef}CH_3$), 26.9 (CH_3C=N), 126.7 (CH_{ar}), 127.6 (CH_{ar}), 127.6 (CH_{ar}), 128.0 (CH_{ar}), 128.1 (*i*-C_{ar}), 128.2 (CH_{ar}), 129.3 (*i*-C_{ar}), 129.5 (CH_{ar}), 135.5 ($C_{olef}CH_3$), 136.7 (CH_3C=N), 139.9 (*i*-$C_{ar}CH_{olef}$), 166.2 (CHN); HRMS (ESI) calcd for $C_{18}H_{19}N_2^+$ 263.1543, found 263.1540. Anal. Calcd for $C_{18}H_{18}N_2$ (262.35): C 82.41, H 6.92, N 10.68. Found: C 82.16, H 6.93, N 10.60.

N-(4-Phenyl-3-buten-2-ylidene)acetophenone Hydrazone ***7c***. According to general procedure A **7c** was obtained from hydrazone **6** (0.67 g, 5.0 mmol) and *trans*-4-phenyl-3-buten-2-one (0.73 g, 5.0 mmol) after purification by column chromatography (cyclohexane 98%, TBME 2%) as a yellow solid in 1.1 g (4.2 mmol, 84%) yield. Mp = 87 °C; IR (neat) $\tilde{\nu}$ = 3383 (br), 3217 (br), 3063 (w), 1605 (m), 1568 (w), 1493 (w), 1445 (m), 1362 (m), 1310 (w), 1285 (m), 1179 (w), 1076 (w), 1024 (m), 758 (s), 689 (s), 652 (m), 563 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 2.08 (s, 3H, $CH_{olef}CCH_3$), 2.25 (s, 3H, *i*-$C_{ar}CCH_3$), 6.88 (d, $^3J_{HH}$ = 16.6 Hz, 1H, *i*-CCH_{olef}), 7.00−7.14 (m, 3H, CH_{ar}), 7.17−7.24 (m, 3H, CH_{ar}), 7.24−7.31 (m, 2H, CH_{ar}), 7.35 (d, $^3J_{HH}$ = 16.6 Hz, 1H, CH_{olef}C=N), 7.90−8.00 (m, 2H, CH_{ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2 ($CH_{olef}CCH_3$), 14.6 (*i*-$C_{ar}CCH_3$), 127.2 (CH_{ar}), 127.4 (CH_{ar}), 128.5 (CH_{ar}),128.6 (*i*-$C_{ar}CH_{olef}$), 129.0 (CH_{ar}), 129.8 (*p*-CH_{ar}), 130.8 (CH_{olef}C=N), 134.8 (*p*-CH_{ar}), 137.0 (*i*-C_{ar}), 139.2 (*i*-C_{ar}), 158.4 (*C*=N), 160.6 (*C*=N); HRMS (ESI) calcd for $C_{18}H_{19}N_2^+$ 263.1543, found 263.1536.

N-(4′-Fluoro)cinnamylidene-α-tetralone Hydrazone ***10a***. According to general procedure A **10a** was obtained from hydrazone **9** (802 mg, 5.0 mmol) and *trans*-3-(4-fluorophenyl)-2-propenal (750 mg, 5.0 mmol) after purification by column chromatography (cyclohexane 87%, TBME 13%) as a yellow solid in 1.49 g (4.9 mmol, 98%) yield. Mp = 92 °C; IR (neat) $\tilde{\nu}$ = 3034 (vw), 2930 (w), 2866 (vw), 1624 (m), 1593 (m), 1584 (m), 1506 (s), 1290 (w), 1223 (s), 1159 (s), 980 (s), 949 (m), 858 (m), 814 (vs), 756 (s), 729 (vs), 658 (m), 640 (m); ^{1}H NMR (400 MHz, C_6D_6) δ 1.42−1.71 (m, 2H, γ-CH_2), 2.36−2.47 (m, 2H, δ-CH_2), 2.99−3.08 (m, 2H, β-CH_2), 6.53 (d, $^3J_{HH}$ = 16.1 Hz, 1H, *i*-$C_{ar}CH_{olef}$), 6.66 (dd, $^3J_{HH,HF}$ = 8.6, 8.8 Hz, 2H, *m*-$CH_{4\text{-}F\text{-}ph}$), 6.95−6.84 (m, 3H, *o*-$CH_{4\text{-}F\text{-}ph}$, CH_{ar}), 7.09 (dd, $^3J_{HH}$ = 16.2, 9.5 Hz, 1H, N=CHCH_{olef}), 7.10−7.15 (m, 1H, CH_{ar}), 7.22−7.16 (m, 1H, CH_{ar}), 8.41 (d, $^3J_{HH}$ = 9.6 Hz, 1H, N=C*H*), 8.83 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CH_{ar}); ^{13}C NMR (101 MHz, C_6D_6) δ 22.4 (γ-CH_2), 27.7 (δ-CH_2), 30.2 (β-CH_2), 115.9 (d, $^2J_{CF}$ = 21.8 Hz, *m*-$CH_{4\text{-}F\text{-}ph}$), 126.4 ($CH_{ar}$), 126.6 ($CH_{ar}$), 126.7 (d, $^5J_{CF}$ = 2.5 Hz, *i*-CC*H_{olef}*), 129.0 (CH_{ar}), 129.2 (CH_{ar}), 130.3 (N=CHCH_{olef}), 132.7 (d, $^3J_{CF}$ = 3.4 Hz, *o*-$CH_{4\text{-}F\text{-}ph}$), 133.4 (*i*-$C_{ar}$), 139.9 (d, $^4J_{CF}$ = 1.2 Hz, *i*-$C_{4\text{-}F\text{-}ph}$), 141.6 (*i*-C_{ar}), 160.1 (NCH), 163.3 (d, $^1J_{CF}$ = 249.1 Hz, *p*-$C_{4\text{-}F\text{-}ph}$), 164.3 (α-*C*N); HRMS (ESI) calcd for $C_{19}H_{18}FN_2^+$ 293.1449, found 293.1448. Anal. Calcd for $C_{19}H_{17}FN_2$ (292.35): C 78.06, H 5.86, N 9.59. Found: C 77.72, H 5.97, N 9.33.

N-Cinnamylidene-α-tetralone Hydrazone ***10b***. According to general procedure A **10b** was obtained from hydrazone **9** (3.20 g, 20.0 mmol) and *trans*-3-phenyl-2-propenal (2.64 g, 20.0 mmol) after purification by column chromatography (cyclohexane 80%, TBME 15%, TEA 5%) as a yellow solid in 5.12 g (18.7 mmol, 93%) yield. Mp = 74 °C; IR (neat) $\tilde{\nu}$ = 3034 (w), 2932 (w), 2866 (w), 2835 (w), 1624 (m), 1589 (m), 1449 (m), 1321 (m), 1292 (m), 1161 (w), 1123 (w), 976 (m), 768 (m), 752 (s), 733 (s), 691 (s); ^{1}H NMR (300 MHz, C_6D_6) δ 1.47−1.65 (m, 2H, γ-CH_2), 2.32−2.51 (m, 2H, δ-CH_2), 2.92−3.14 (m, 2H, β-CH_2), 6.69 (d, $^3J_{HH}$ = 16.0 Hz, 1H, *i*-CCH_{olef}), 6.89−6.96 (m, 1H, CH_{ar}), 6.99−7.08 (m, 3H, CH_{ar}), 7.09−7.21 (m, 4H, CH_{ar}), 7.28 (dd, $^3J_{HH}$ = 16.0, 9.6 Hz, 1H, N=CHCH_{olef}), 8.43 (d, $^3J_{HH}$ = 9.6 Hz, 1H, NC*H*), 8.83 (d, $^3J_{HH}$ = 7.7 Hz, 1H, CH_{ar}); ^{13}C NMR (75 MHz, C_6D_6) δ 22.4 (γ-CH_2), 27.7 (δ-CH_2), 30.2 (β-CH_2), 126.4, 126.6, 127.0, 127.5, 128.9, 128.9, 129.1, 130.2, 133.4, 136.5, 141.4, 141.5 (CH_{ar}), 160.3 (NCH), 164.2 (α-*C*N); HRMS (ESI) calcd for $C_{19}H_{19}N_2^+$ 275.1543, found 275.1537. Anal. Calcd for $C_{19}H_{18}N_2$ (274.36): C 83.18, H 6.61, N 10.21. Found: C 82.89, H 6.80, N 10.11.

N-(4′-Methoxy)cinnamylidene-α-tetralone Hydrazone ***10c***. According to general procedure A **10c** was obtained from hydrazone **9** (320 mg, 2.0 mmol) and *trans*-3-(4-methoxyphenyl)-2-propenal (324 mg, 2.0 mmol) after purification by column chromatography (cyclohexane 80%, TBME 15%, TEA 5%) as a yellow solid in 520 mg (1.7 mmol, 86%) yield. Mp = 91 °C; IR (neat) $\tilde{\nu}$ = 3055 (w), 2938 (m), 2837 (w), 1599 (m), 1589 (m), 1508 (m), 1452 (m), 1296 (m), 1252 (s), 1173 (m), 1152 (m), 1026 (s), 989 (s), 820 (vs), 770 (vs), 733 (s), 652 (w), 530 (m), 505 (m), 494 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 1.53−1.61 (m, 2H, γ-CH_2), 2.40−2.49 (m, 2H, δ-CH_2), 3.02−3.13 (m, 2H, β-CH_2), 3.24 (s, 3H, OCH_3), 6.67−6.62 (m, 2H, *m*-$CH_{4\text{-}OMe\text{-}ph}$), 6.73 (d, $^3J_{HH}$ = 16.0 Hz, 1H, *i*-CCH_{olef}), 6.94 (dd, $^3J_{HH}$ = 7.8, 7.2 Hz, 1H, CH_{ar}), 7.15−7.09 (m, 1H, CH_{ar}, 2H, *o*-$CH_{4\text{-}OMe\text{-}ph}$), 7.20−7.16 (m, 1H, CH_{ar}), 7.23 (dd, $^3J_{HH}$ = 16.0, 9.6 Hz, 1H, N=CHCH_{olef}), 8.52 (d, $^3J_{HH}$ = 9.6 Hz, 1H, NC*H*), 8.85 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH_{ar}); ^{13}C NMR (126 MHz, C_6D_6) δ 22.4 (γ-CH_2), 27.7 (δ-CH_2), 30.2 (β-CH_2), 54.8 (OCH_3), 114.5 (*m*-$CH_{4\text{-}OMe\text{-}ph}$), 124.8 (N=CHC$H_{olef}$), 126.3, 126.5, 128.8, 128.9, 129.0 (CH_{ar}), 129.3 (*i*-CCH_{olef}), 129.6 (*p*-$C_{4\text{-}OMe\text{-}ph}$), 130.1 (*i-C*), 133.5 (*i-C*), 141.2 (*i*-CCH_{olef}), 160.8 (NCH), 163.9 (*i*-CN); HRMS (ESI) calcd for $C_{20}H_{21}N_2O^+$ 305.1648, found 305.1653. Anal. Calcd for $C_{20}H_{20}N_2O$ (304.39): C 78.92, H 6.62, N 9.20. Found: C 78.81, H 6.63, N 9.19. X-ray crystal structure analysis of **10c** can be found in the Supporting Information.

N-(4′-Methoxy)cinnamylidene-2-acetylpyridine Hydrazone ***13***. According to general procedure A **13** was obtained from hydrazone **12** (1.35 g, 10 mmol) and *trans*-3-(4-methoxyphenyl)-2-propenal (1.65 g, 10 mmol) after purification by recrystallization from cyclohexane as a yellow solid in 1.94 g (7.0 mmol, 70%) yield. Mp = 82 °C; IR (neat) $\tilde{\nu}$ = 3013 (w), 2965 (w), 2932 (w), 2839 (w), 1630 (m), 1601 (s), 1585 (m), 1564 (m), 1510 (s), 1468 (m), 1437 (m), 1362 (w), 1306 (m), 1298 (m), 1258 (s), 1248 (s), 1173 (s), 1155 (s), 1109 (m), 1030 (s), 991 (s), 976 (m), 959 (w), 833 (s), 814 (s), 785 (s), 762 (m), 741 (m), 671 (m); ^{1}H NMR (400 MHz, C_6D_6) δ 2.92 (s, 3H, CCH_3), 3.23 (s, 3H, OCH_3), 6.48−6.74 (m, 2H, *m*-$CH_{4\text{-}OMe\text{-}ph}$, 1H, CH_{olef}, 1H, CH_{py}), 7.02−7.25 (m, 2H, *o*-$CH_{4\text{-}OMe\text{-}ph}$, 1H, CH_{olef}, 1H, CH_{py}), 8.38 (d, $^3J_{HH}$ = 9.6 Hz, 1H, CH_{py}), 8.46−8.51 (m, 1H, CH_{olef}, 1H, CH_{py}); ^{13}C NMR (101 MHz, C_6D_6) δ 14.0 (CCH_3), 54.8 (OCH_3), 114.5 (*m*-$CH_{4\text{-}OMe\text{-}ph}$), 121.3 (5-$CH_{py}$), 124.1 (*i*-$CCH_{olef}$), 124.6 (3-$CH_{py}$), 129.1 (*o*-$CH_{4\text{-}OMe\text{-}ph}$), 129.2 (*i*-$C_{4\text{-}OMe\text{-}ph}$), 135.7 (4-$CH_{py}$), 141.9 (N=CHC$H_{olef}$), 149.0 (NC$H_{olef}$), 156.7 (2-$C_{py}$), 161.0 (2-$C_{py}$CN), 161.1 (6-$CH_{py}$), 165.6 (*p*-$C_{4\text{-}OMe\text{-}ph}$); HRMS (ESI) calcd for $C_{17}H_{18}N_3O^+$ 280.1444, found 280.1449.

General Procedure B for the Synthesis of 2,4-Diarylpyridine Derivatives. *N,N′*-Bisalkylidene hydrazines **7a,b**, **10a−c**, and **12** were dissolved in 20 mL of dry THF and treated with 1.5 equiv of KO*t*Bu solution (1 M, THF) at room temperature. After the reaction

was completed according to TLC reaction control (0.5−2 h), the mixture was washed with brine, dried over $MgSO_4$, filtered, and concentrated.

2,4-Diphenylpyridine ***15a***. According to general procedure B **15a** was obtained from *N,N′*-bisalkylidene hydrazine **7a** (400 mg, 1.6 mmol) after purification by column chromatography (cyclohexane 70%, TBME 30%) as colorless solid in 78 mg (0.34 mmol, 21%) yield. Mp = 80 °C. For spectroscopic data see ref 18.

2,4-Diphenyl-5-methylpyridine ***15b***. According to general procedure B **15b** was obtained from *N,N′*-bisalkylidene hydrazine **7b** (524 mg, 2 mmol) after purification by column chromatography (cyclohexane 85%, TBME 15%) as colorless solid in 110 mg (0.44 mmol, 22%) yield. Mp = 101 °C. For spectroscopic data see ref 18.

4-(4-Fluorophenyl)-5,6-dihydrobenzo[h]quinoline ***17a***. According to general procedure B **17a** was obtained from *N,N′*-bisalkylidene hydrazine **10a** (585 mg, 2.0 mmol) after purification by column chromatography (cyclohexane 85%, TBME 15%) as colorless solid in 131 mg (0.51 mmol, 25%) yield. Mp = 103 °C; IR (neat) $\tilde{\nu}$ = 3044 (vw), 2924 (w), 2853 (w), 1603 (m), 1545 (w), 1508 (s), 1450 (m), 1439 (m), 1387 (m), 1225 (s), 1157 (m), 1097 (w), 843 (w), 831 (vs), 818 (s), 795 (m), 746 (vs), 733 (s), 650 (w), 621 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 2.41−2.55 (m, 4H, 5-CH_2, 6-CH_2), 6.68 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 3-CH_{quin}), 6.76−6.83 (m, 3H, *m*-C$H_{4\text{-F-ph}}$, CH_{quin}), 7.00 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH_{quin}), 7.12−7.20 (m, 2H, *o*-C$H_{4\text{-F-ph}}$), 7.30 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 1.2 Hz, 1H, CH_{quin}), 8.56 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 2-CH_{quin}), 8.95 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.2 Hz, 1H, 10-CH_{quin}); ^{13}C NMR (75 MHz, C_6D_6) δ 25.5 (6-CH_2), 28.1 (5-CH_2), 115.4 (d, $^2J_{CF}$ = 21.4 Hz, *m*-$CH_{4\text{-F-ph}}$), 123.3 (3-CH_{quin}), 126.4, 127.5, 127.7 (CH_{quin}), 129.2 (4-C_{quin}), 129.4 (CH_{quin}), 130.8 (d, $^3J_{CF}$ = 8.0 Hz, *o*-$CH_{4\text{-F-ph}}$), 135.3 (d, $^4J_{CF}$ = 3.4 Hz, *i*-$C_{4\text{-F-ph}}$), 135.7 (4a-C_{quin}), 138.1 (6a-C_{quin}), 147.2 (10a-C_{quin}), 147.8 (2-CH_{quin}), 153.7 (10b-C_{quin}), 162.8 (d, $^1J_{CF}$ = 247.0 Hz, *p*-$C_{4\text{-F-ph}}$); HRMS (ESI) calcd for $C_{19}H_{15}FN^+$ 276.1183, found 276.1171. Anal. Calcd for $C_{19}H_{14}FN$ (275.32): C 82.89, H 5.13, N 5.09. Found: C 82.64, H 5.53, N 4.78.

4-Phenyl-5,6-dihydrobenzo[h]quinoline ***17b***. According to general procedure B **17b** was obtained from *N,N′*-bisalkylidene hydrazine **10b** (548 mg, 2.0 mmol) after purification by column chromatography (cyclohexane 88%, TBME 12%) as colorless solid in 165 mg (0.64 mmol, 32%) yield. Mp = 77 °C; IR (neat) $\tilde{\nu}$ = 3042 (w), 2947 (w), 2882 (w), 1605 (w), 1589 (w), 1568 (m), 1545 (m), 1497 (w), 1450 (w), 1439 (w), 1391 (m), 1275 (w), 1209 (w), 1074 (w), 1030 (w), 895 (w), 845 (m), 793 (m), 773 (m), 764 (m), 746 (s), 733 (m), 704 (s), 642 (m), 625 (s); ^{1}H NMR (500 MHz, C_6D_6) δ 2.44 (dd, $^3J_{HH}$ = 8.5, 6.1 Hz, 2H, 6-CH_2), 2.61 (dd, $^3J_{HH}$ = 8.5, 6.1 Hz, 2H, 5-CH_2), 6.81 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 3-CH_{quin}), 6.98 (d, $^3J_{HH}$ = 7.5 Hz, 1H, CH_{quin}), 7.10−7.05 (m, 2H, CH_{ph}), 7.12−7.18 (m, 4H, CH_{quin}, CH_{ph}), 7.30 (m, 1H, CH_{quin}), 8.58 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 2-CH_{quin}), 8.96 (d, $^3J_{HH}$ = 6.9 Hz, 1H, 10-CH_{quin}); ^{13}C NMR (126 MHz, C_6D_6) δ 25.6 (6-CH_2), 28.2 (5-CH_2), 123.3 (3-CH_{quin}), 126.4 (CH_{ar}), 127.4 (CH_{ar}), 127.6 (CH_{ar}), 127.9 (CH_{ar}), 128.5 (CH_{ar}), 129.0 (CH_{ar}), 129.2 (4-C_{quin}), 129.3 (4a-C_{quin}), 135.8 (*o*-CH_{ph}), 138.2 (10-CH_{quin}), 139.5 (6a-C_{quin}), 147.7 (2-C_{quin}), 148.3 (10a-C_{quin}), 153.6 (10b-C_{quin}); HRMS (ESI) calcd for $C_{19}H_{16}N^+$ 258.1277, found 258.1268. Anal. Calcd for $C_{19}H_{15}N$ (257.33): C 88.68, H 5.88, N 5.44. Found: C 88.35, H 5.97, N 5.30.

4-(4-Methoxyphenyl)-5,6-dihydrobenzo[h]quinoline ***17c***. According to general procedure B **17c** was obtained from *N,N′*-bisalkylidene hydrazine **10c** (330 mg, 1.1 mmol) after purification by column chromatography (cyclohexane 70%, TBME 30%) as orange solid in 120 mg (0.42 mmol, 38%) yield. Mp = 112 °C; IR (neat) $\tilde{\nu}$ = 3036 (vw), 2951 (w), 2930 (w), 2835 (w), 1607 (m), 1574 (w), 1512 (s), 1450 (m), 1439 (m), 1387 (m), 1292 (m), 1246 (vs), 1179 (s), 1113 (m), 1034 (s), 829 (vs), 814 (s), 795 (m), 750 (vs), 737 (m), 650 (m), 621 (s); ^{1}H NMR (300 MHz, C_6D_6) δ 2.49 (dd, $^3J_{HH}$ = 8.6, 5.9 Hz, 2H, CH_2), 2.69 (dd, $^3J_{HH}$ = 8.6, 5.9 Hz, 2H, CH_2), 3.33 (s, 2H, OCH_3), 6.76−6.82 (m, 2H, *m*-$CH_{4\text{-OMe-ph}}$), 6.87 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 3-CH_{quin}), 6.89−7.07 (m, 2H, *o*-$CH_{4\text{-OMe-ph}}$, CH_{quin}), 7.13−7.20 (m, 1H, CH_{quin}), 7.31 (m, 1H, CH_{quin}), 8.61 (d, $^3J_{HH}$ = 4.9 Hz, 1H, 2-CH_{quin}), 8.98 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, 10-CH_{quin}); ^{13}C NMR (75 MHz, C_6D_6) δ 25.7 (CH_2), 28.3 (CH_2), 54.8 (CH_3), 114.1 (*m*-$CH_{4\text{-OMe-ph}}$), 123.5 (3-CH_{quin}), 126.4, 127.5, 127.6 (CH_{quin}), 129.2 (4-C_{quin}), 129.4 (4a-C_{quin}), 130.3 (*o*-$CH_{4\text{-OMe-ph}}$), 131.7 (*i*-$C_{4\text{-OMe-ph}}$), 136 (10-CH_{quin}), 138.2 (6a-C_{quin}), 147.8 (2-C_{quin}), 148.1 (10a-C_{quin}), 153.6 (10b-C_{quin}), 159.9 (*p*-$C_{4\text{-OMe-ph}}$); HRMS (ESI) calcd for $C_{20}H_{18}NO^+$ 288.1383, found 288.1372. X-ray crystal structure analysis of **17c** can be found in the Supporting Information.

4-(4-Methoxyphenyl)-2,2′-bipyridine ***19***. According to general procedure B **19** was obtained from *N,N′*-bisalkylidene hydrazine **13** (425 mg, 1.5 mmol) after purification by column chromatography (cyclohexane 40%, TBME 40%, TEA 20%) as orange solid in 101 mg (0.33 mmol, 22%) yield. Mp = 133 °C (lit 131−132.5 °C[19]); IR (neat) $\tilde{\nu}$ = 3059 (w), 2934 (w), 2839 (w), 1672 (w), 1599 (s), 1580 (m), 1512 (s), 1456 (s), 1443 (m), 1391 (w), 1290 (m), 1250 (s), 1182 (s), 1040 (m), 1024 (s), 989 (m), 824 (s), 793 (s), 748 (s), 739 (m), 662 (m), 617 (m); ^{1}H NMR (300 MHz, C_6D_6) δ 3.28 (s, 3H, CH_3), 6.72 (ddd, $^3J_{HH}$ = 7.5, 4.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, 5′-CH_{bipy}), 6.79−6.73 (m, 2H, *m*-$CH_{4\text{-OMe-ph}}$), 7.12 (dd, $^3J_{HH}$ = 5.1, $^4J_{HH}$ = 1.9 Hz, 1H, 5-CH_{bipy}), 7.26 (ddd, $^3J_{HH}$ = 8.0, 7.5, $^4J_{HH}$ = 1.8 Hz, 1H, 4′-CH_{bipy}), 7.49−7.39 (m, 2H, *o*-$CH_{4\text{-OMe-ph}}$), 8.58 (ddd, $^3J_{HH}$ = 4.7, $^4J_{HH}$ = 1.8, $^5J_{HH}$ = 0.9 Hz, 1H, 6′-CH_{bipy}), 8.65 (dd, $^3J_{HH}$ = 5.1, $^5J_{HH}$ = 0.8 Hz, 1H, 6-CH_{bipy}), 8.84−8.88 (m, 1H, 3′-CH_{bipy}), 9.20 (dd, $^3J_{HH}$ =1.9, $^4J_{HH}$ = 0.8 Hz, 1H, 3-CH_{bipy}); ^{13}C NMR (75 MHz, C_6D_6) δ 54.8 (OCH_3), 114.7 (*m*-$CH_{4\text{-OMe-ph}}$), 118.7 (3-CH_{bipy}), 121.2 (5-CH_{bipy}), 121.4 (3′-CH_{bipy}), 123.7 5′-CH_{bipy}), 128.5 (*o*-$CH_{4\text{-OMe-ph}}$), 131.1 (*i*-$C_{4\text{-OMe-ph}}$), 136.6 (4′-CH_{bipy}), 148.8 (4-C_{bipy}), 149.3 (6-CH_{bipy}), 150.0 (6′-CH_{bipy}), 156.9 (2-C_{bipy}), 157.2 (2′-C_{bipy}), 160.9 (*p*-$C_{4\text{-OMe-ph}}$); HRMS (ESI) calcd for $C_{17}H_{15}N_2O^+$ 263.1179, found 263.1172.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H and ^{13}C spectra for the new compounds; optimized Cartesian coordinates (B3LYP/6-31+G(d,p) and B2PLYPD/6-311+G(d,p)//B3LYP/6-31+G-(d,p)+ZPE energies for the calculated structures; graphics of crystal structures with thermal ellipsoids with 50% probability. This material is available free of charge via the Internet at http://pubs.acs.org.

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