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Extended π Systems

Novel π-Extended Quinazoline-Ferrocene Conjugates: Synthesis, Structure, and Redox Behavior

Burkhon Elmuradov,[a,b] Gerald Dräger,[a] and Holger Butenschön*[a]

Dedicated to the memory of Professor Kilian Muñiz

Abstract: Novel ferrocene conjugates of tricyclic quinazoline derivatives are prepared by condensation of active C-6 methylene groups of mackinazolinones with ferrocenecarbaldehyde. Following this route the conjugated parent alkaloid as well as derivatives with nitro, amino, and alkanoylamino groups at C-2 were attached at the ferrocene moiety, thereby significantly extending the delocalized π system. In addition, the parent compound was subjected to the reaction with ferrocene-1,1′-dicarbaldehyde, giving rise to the symmetrical and unsymmetrical double condensation products – 1,1′-disubstituted ferrocene derivatives, which bear two alkaloid substituents. Some of the compounds obtained were subjected to X-ray crystallographic analyses. The influence of the substituents at C-2 through the extended conjugated π system on the iron atom is reflected by results of cyclovoltammetric measurements.

Introduction

Modification of natural products and their synthetic analogues is a perspective direction for the creation of new derivatives with various biological activities.[1–3] Although in the literature syntheses as well as the stereochemistry of organometallic bioconjugates with natural products such as amino acids, peptides, proteins, nucleic acids or carbohydrates have broadly been reported,[4–14] there are only few publications regarding ferrocenyl-substituted alkaloids and related conjugates.[15–20] Recently, we reported the first examples of ferrocene 7*H*-deoxyvasicinone conjugates.[21]

The alkaloids deoxyvasicinone {2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one, **1**} and mackinazolinone (6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one, **4**) were isolated from different plants such as *Nitraria schoberi* or *Adhatoda vasica* (Figure 1).[22–26] These alkaloids and their structural analogues have pronounced anti-inflammatory, anti-microbial, antidepressant and anti-oxidant activities.[22,24,27–30] Therefore a number of effective methods for the synthesis of these alkaloids, their analogues and derivatives, e.g. **2**, **3**, **5**–**8**, have been developed.[31–39]

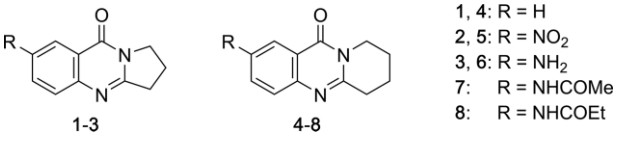

Figure 1. Deoxyvasicinone (**1–3**) and mackinazolinone (**4–8**) derivatives.

The use of ferrocene-based compounds for medicinal applications is an active research area.[40,41] Ferrocene containing compounds have recently been reported to have antitumor activity due to the metabolic formation of ferrocenium ions.[42] A number of reports have demonstrated that some ferrocenyl derivatives are highly active against several diseases, including cancer.[43–46] Some heterocycles attached to ferrocene[6,47–59] and ferrocenyl hybrids with antibiotic properties are known,[60] which are efficient redox sensors, β-lactamase inhibitors, and have antitubercular, antiplasmodial or antitumor activities.[4,61] Mono- and disubstituted formyl- and ethynylferrocenes widely used as electrophilic reagents in organic synthesis may serve as starting materials for the formation of ferrocene-alkaloid conjugates.[62–70]

Recently we reported on the first tricyclic quinazoline alkaloids connected to ferrocene with formation of a more extended π system.[21] The first ferrocenylmethylene-substituted 7*H*-deoxyvasiconine derivatives have been prepared in good yields; these include a 1,1′-disubstituted derivative as the second example of a 1,1′-disubstituted ferrocene derivative bearing two alkaloid subunits.[15] The extension of the π systems is confirmed by cyclic voltammetry measurements, with the highest halfwave potentials among the monosubstituted derivatives for the nitro-substituted compound indicating electron delocalization from the nitro group through the conjugated π system to the iron atom.[21] The electronic interaction between the

[a] *Leibniz Universität Hannover, Institut für Organische Chemie, Schneiderberg 1B, 30167 Hannover, Germany*
E-mail: holger.butenschoen@mbox.oci.uni-hannover.de
http://www.ak-butenschoen.uni-hannover.de
[b] *Institute of the Chemistry of Plant Substances, Academy of Sciences of Uzbekistan, 100170, Mirzo-Ulugbek str. 77, Tashkent, Uzbekistan*
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highly conjugated alkaloid substituent and the iron atom makes such sandwich ferrocene-quinazoline derivatives interesting with regard to their biological properties.

Here, we report the syntheses of the next higher homologues, which are ferrocenes bearing one or two mackinazolinone substituents, which will presumably adopt conformations different from those of the respective deoxyvasicinone-ferrocene conjugates.

Results and Discussion

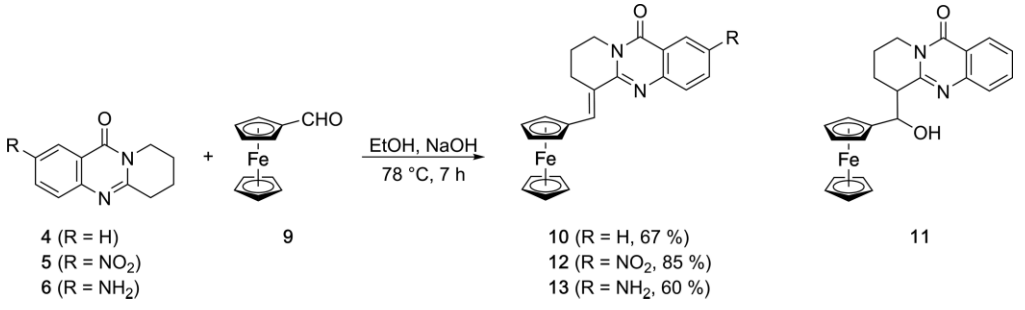
Mackinazolinone (**4**, Figure 1) is a tricyclic quinazoline alkaloid with a six-membered ring anellated at the quinazoline entity, which has been isolated from the plant *Mackinlaya subulata Philipson*.[22] Its biosynthesis as well as some chemical syntheses start from anthranilic acid.[37,71]

The methylene groups at C3 in **1**–**3** and at C6 in **4**–**8** are reactive and can undergo addition or condensation reactions with arylcarbonyl compounds yielding respective 3-hydroxy(aryl)methyl and 6-hydroxy(aryl)methyl or, after water elimination, 3-arylmethylene and 6-arylmethylene derivatives, respectively, which usually show the *E* configuration.[72] In contrast to phenyl substituents a ferrocenyl moiety is three dimensional and redox active, and may therefore be used for sensing the electronic effect of a substituent at C2 across the conjugated alkaloid spacer on C6, as long as the ferrocene moiety adopts a coplanar conformation with the mackinazolinone π system. To obtain the first tricyclic mackinazolinone alkaloids bearing a ferrocenyl substituent derivatives **4**–**8** were treated with ferrocenecarbaldehyde (**9**).

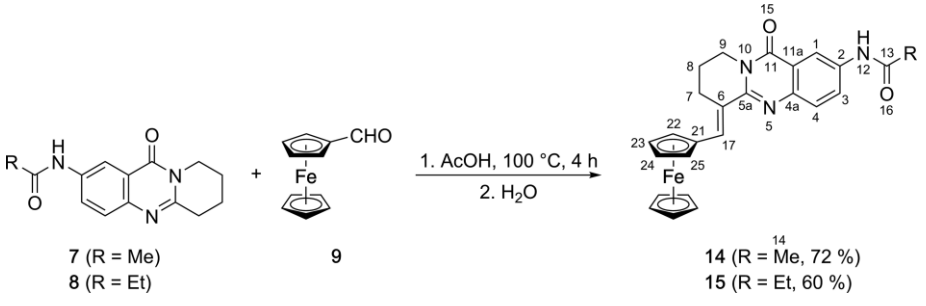
The parent compound mackinazolinone (**4**) was prepared according to Shakhidoyatov et al. in 80 % yield from anthranilic acid and δ-valerolactam.[71] Subsequent treatment of **4** with ferrocenecarbaldehyde (**9**) under basic reaction conditions afforded (*E*)-6-(ferrocenylmethylene)mackinazolinone (**10**) as the first representative of its class in 67 % yield as a red solid. The intermediate **11** was not observed (Scheme 1). Acidic reaction conditions afforded the same product, albeit in smaller yield (up to 45 %). The observed *E* configuration may be explained by unfavorable steric interactions in a Z isomer as well as by a hydrogen bridge between the hydroxy proton and the imine nitrogen atom in intermediate **11**.

In continuation of this investigation, we studied the reactions 2-nitro- (**5**), 2-amino- (**6**), 2-acetylamino- (**7**) and 2-(propanoylamino)mackinazolinones (**8**) with ferrocenecarbaldehyde (**9**). Under comparable reaction conditions, 2-nitromackinazolinone (**5**) and 2-aminomackinazolinone (**6**) were treated with ferrocenecarbaldehyde (**9**) to give condensation products **12** and **13** in 85 % and 60 % yield, respectively. Reactions were carried out in ethanol at reflux for 3–10 h in the presence of sodium hydroxide. Whereas nitro compound **12** was isolated as a dark purple solid in 85 % yield, the corresponding amino compound **13** was obtained as an orange-red solid in 60 % yield (Scheme 1).

Acetamido derivative **7** is easily obtained in 96 % yield by treatment of **6** with acetic anhydride.[73] Subsequent treatment with ferrocenecarbaldehyde (**9**) under the usual reaction conditions (Method A, glacial acetic acid, 100 °C, 4 h) afforded complex **14** in 72 % yield (Scheme 2). Alternatively, **14** was obtained in 65 % yield by using a one-pot procedure in which the amino derivative **6** reacted with ferrocenecarbaldehyde (**9**) in acetic acid by heating at reflux for 3–4 h (Method B). Crystallization from chloroform gave crystals suitable for an X-ray crystal structure analysis of **14**·$CHCl_3$ (Figure 2).



Scheme 1. Formation of (*E*)-6-(ferrocenylmethylene)mackinazolinone (**10**) and derivatives **12** and **13**. Possible intermediate **11** was not observed.



Scheme 2. Condensation products **14** and **15** and atom numbering scheme (arbitrary).

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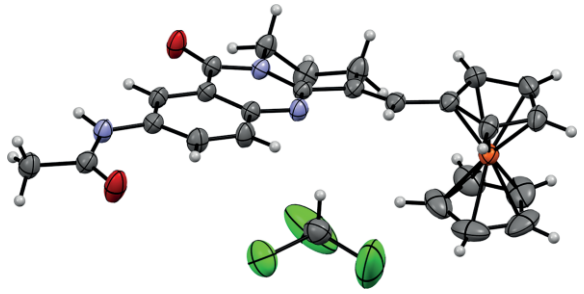
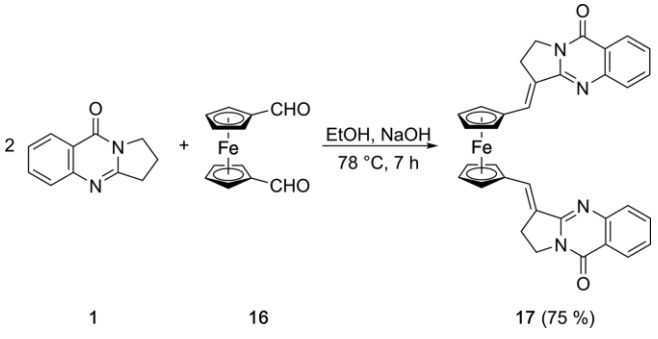


Figure 2. Structure of **14**·$CHCl_3$ in the crystal; elipsoids at 50 % probability level.[74] Red: O; orange: Fe; purple: N; green Cl (chloroform). Selected bond lengths [pm], interatom distances [pm] and bond angles [°] (for atom numbers see Scheme 4): C1–C2 136.1(5), C1–C11a 140.2(7), C2–C3 140.7(7), C2–N12 142.2(7), C3–C4 136.1(5), C4–C4a 139.5(5), C4a–C11a 140.1(7), C4a–N5 137.9(6), C5a–C6 148.6(7), C5a–N5 129.3(5), C5a–N10 139.3(7), C6–C7 151.2(6), C6–C16 133.8(7), C7–C8 151.6(9), C8–C9 148(10), C9–N10 147.4(5), N10–C11 139.2(6), C11–C11a 144.8(5), C11–O15 122.1(6), N12–C13 134.3(5), C13–C14 150.0(8), C13–O16 122.7(7), C17–C21 146.0(9); C5a–C6–C17 118.0(5), C6–C17–C21 129.1(5), C7–C6–C17 122.0(5).

The propanoylamino derivative **8** was obtained in 93 % yield by treatment of **6** with propionic anhydride. Subsequent treatment of **8** with ferrocenylcarbaldehyde (**9**) in propionic acid at reflux for 3 h gave condensation product **15** in 60 % yield, and by using the one-pot procedure amino compound **6** reacted with ferrocenecarbaldehyde (**9**) in propionic acid at 100 °C for 7 h and gave compound **15** in 58 % yield.

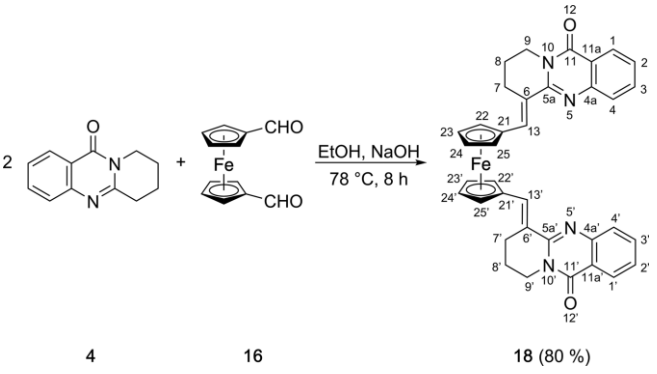
The structure of **14**·$CHCl_3$ shows that the mackinazolinone substituent adopts a more or less planar conformation, only the methylene groups of the six-membered ring slightly deviate from the molecular plane. The ferrocenylmethylene moiety shows *E* configuration with the cyclopentadienyl π system almost coplanar to the substituent π system thereby fulfilling the condition of electronic interaction between the substituent at C2 and the ferrocene moiety. The amido substituent at C2 also only slightly deviates from coplanarity with the basic π system.

We have shown that deoxyvasicinone (**1**) is able to undergo a double condensation process with ferrocene-1,1′-dicarbaldehyde (**16**) yielding the respective double condensation product (**17**) with *E* configurations at both of the new double bonds in 75 % yield (Scheme 3).[21]



Scheme 3. Double condensation of deoxyvasicinone (**1**) with ferrocene-1,1′-dicarbaldehyde (**16**).[21]

In an attempt to achieve the corresponding double condensation of mackinazolinone (**4**) the compound was treated with **16** under usual reaction conditions to give the double condensation product **18** in 80 % yield (Scheme 4).



Scheme 4. Double condensation of mackinazolinone (**4**) with ferrocene-1,1′-dicarbalehyde (**16**) and atom numbering scheme (arbitrary).

Double condensation product **18** has been identified spectroscopically reflecting the symmetry of **18**, as well as by an X-ray crystal structure analysis (Figure 3), which was obtained after crystallization from chloroform. As in the case of the lower homologue the ferrocene moiety adopts an eclipsed *syn* conformation, possibly because of packing effects combined with some π,π interaction of the highly delocalized π systems. The alkaloid substituents only slightly (ca. 12°) deviate from coplanarity with the respective cyclopentadienyl ligands. The distance between the alkaloid substituents is about 335 pm and thus in the range of other π,π interactions.[75]

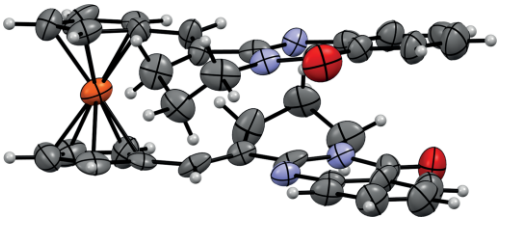


Figure 3. Structure of **18** in the crystal; elipsoids at 50 % probability level.[74] Red: O; orange: Fe; purple: N. Selected bond lengths [pm], interatom distances [pm] and bond angles [°] (for atom numbers see Scheme 4): C1–C2 141(2), C1–C11a 139(2), C2–C3 140(2), C3–C4 138(2), C4–C4a 147(2), C4a–C11a 139(2), C4a–N5 139(1), N5–C5a 132(1), C5a–N10 140(2), C5a–C6 150(1), C6–C7 151(1), C6–C13 132(2), C7–C8 152(2), C8–C9 148(2), C9–N10 150(1), N10–C11 137(1), C11–C11a 150(2), C11–O12 125(2), C13–C21 147(2); C7–C6–C13 118(1), C6–C13–C21 128(1), C5a–C6–C13 119(1). C8′–C9′ 151(2), C9′–N10′ 148(2), C7′–C8′ 153(1), C6′–C7′ 149(1), C5a′–C6′ 146(2), C6′–C13′ 138(1), N5′–C5a′ 129(2), C5a′–N10′ 144(1), C4a′–N5′ 140(1), C4′–C4a′ 138(2), C4a′–C11a′ 145(2), C3′–C4′ 139(2), C2′–C3′ 144(2), C1′–C2′ 136(2), C1′–C11a′ 141(2), C11′–C11a′ 144(2), N10′–C11′ 142(2), C11′–O12′ 125(2), C13′–C21′ 146(2); C7′–C6′–C13′ 121(1), C6′–C13′–C21′ 127(1), C5a′–C6′–C13′ 116(1).

In order to obtain the asymmetric double condensation product **19**, we conducted a "*step by step*" reaction by treating ferrocene-1,1′-dicarbaldehyde (**16**) first with 1.0 equivalent of **1** followed by 1.0 equivalent of **4**. This sequence afforded **19** in 74 % yield (Scheme 5).

To obtain an information about the different relative reactivities of the alkaloids **1** and **4** in the reaction with ferrocene-1,1′-dicarbaldehyde (**16**) the reaction was performed using a 1:1 mixture deoxyvasicinone (**1**) and mackinazolinone (**4**) giving

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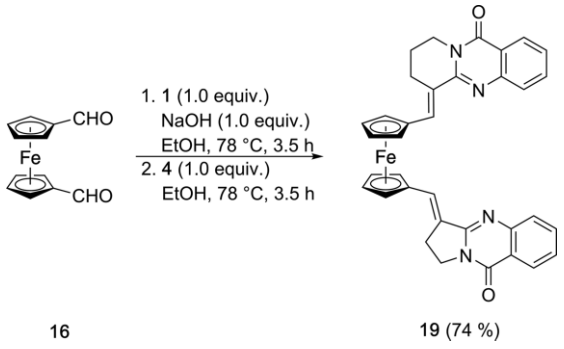
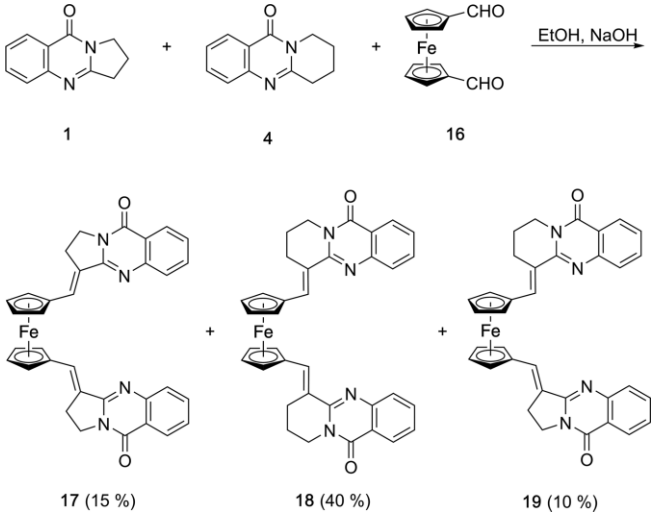


Scheme 5. Synthesis of unsymmetrical double-condensation product **19**.

the two symmetrical derivatives **17** and **18** in 15 % and 40 % yield, respectively, in addition to the unsymmetrical **19**, which was obtained in 10 % yield (Scheme 6). All three compounds were separated by column chromatography and identified spectroscopically. This indicates that mackinazolinone (**4**) reacts with ferrocene-1,1′-dicarbaldehyde more rapidly than its five-membered analogue (**1**).



Scheme 6. Comparable reactivities of deoxyvasicinone (**1**) and mackinazolinone (**4**).

Expanding the scope of this chemistry, nitro substituted derivatives 7-nitrodeoxyvasicinone (**2**) and 2-nitromackinazolinone (**5**) were treated with 0.5 equivalents of ferrocene-1,1′-dicarbaldehyde (**16**) under the usual reaction conditions. Interestingly, only the single condensation products **20** and **21** were obtained in 80 % and 87 % yield (Figure 4), respectively, possibly as a result of a somewhat decreased nucleophilicity of the deprotonated alkaloid. Obviously, the electron withdrawing effect of the nitro groups is transferred to the reacting methylene group all over the conjugated π system.

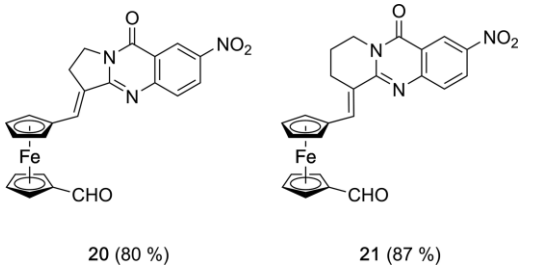


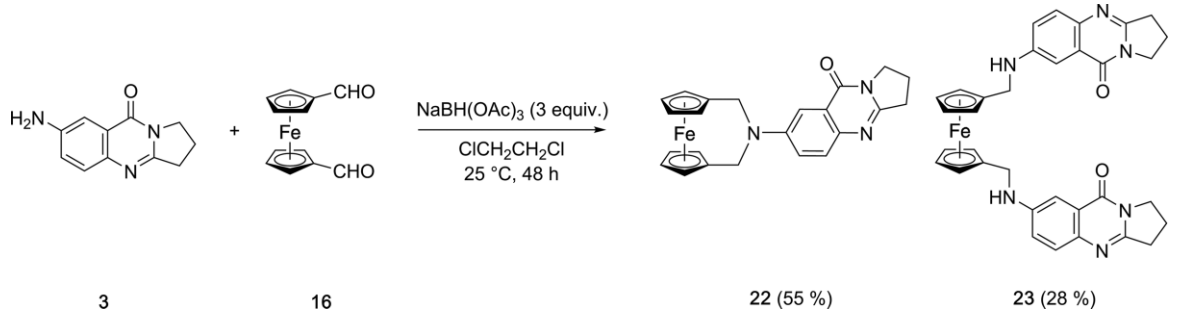
Figure 4. Condensation products **20** and **21**.

The double reductive amination of ferrocene-1,1′-dicarbaldehyde (**16**) allows the formation of either 2-aza-[3]-ferrocenophanes or 1,1′-di(aminomethyl) substituted derivatives. In order to synthesize deoxyvasicinone or mackinazolinone based 2-aza-[3]-ferrocenophanes or the respective disubstituted ferrocenes, **16** was treated with 7-aminodeoxyvasicinone (**3**) in the presence of $NaBH(OAc)_3$ as the reducing reagent to give amines **22** and **23** in 55 % and 28 % yield, respectively, as a mixture, which was separated chromatographically (Scheme 7).

The reaction of 2-aminomackinazolinone (**6**) and ferrocene-1,1′-dicarbaldehyde (**16**) under these conditions proceeds analogously to that of 7-aminodeoxyvasicinone (**3**) and leads to the corresponding mixture of reductive amination products, ferrocenophane **24** and the 1,1′-di(aminomethyl)ferrocene **25** in 64 % and 25 % yield, respectively (Figure 5).

1,1′-Di(aminomethyl)ferrocenes **23** and **25** can selectively be obtained in 80 % and 85 % yield, respectively, by using 2 equiv. of **3** or **6** and 1 equiv. of **16** in 1,2-dichloroethane at 25 °C within only 28 h. Crystals of ferrocenophane **24** suitable for a crystal structure analysis (Figure 6) were obtained after separation by column chromatography on silica gel (ethyl acetate/methanol, 25:1 to 15:1).

Due to its ferrocenophane nature, the structure shows an eclipsed ferrocene conformation, in which the interatom distance C21–C21′ (305.8 pm) is significantly shorter than that of the more remote carbon atoms (C23–C23′ 346.3 pm, C24–C24′ 342.6 pm) indicating a significant deviation of the cyclopentadi-



Scheme 7. Reductive amination of **16** with 2-aminodeoxyvasicinone (**3**).

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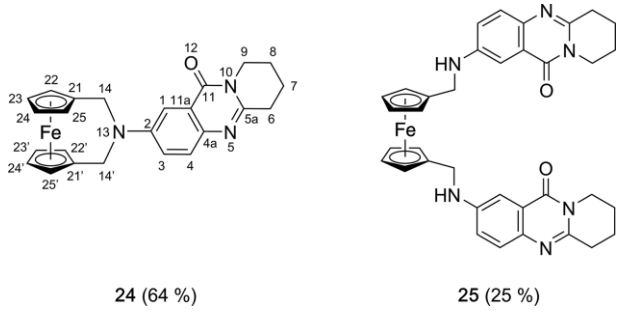

Figure 5. Products of the reductive amination of **16** with 2-aminomackinazolinone (**6**).

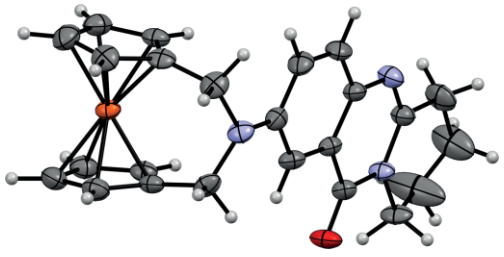

Figure 6. Structure of ferrocenophane **24** in the crystal; elipsoids at 50 % probability level.[74] Red: O; orange: Fe; purple: N. Selected bond lengths [pm], bond angles [°], and torsional angles [°] (for atom numbers see Figure 5): C1–C2 141(1), C1–C11a 139(1), C2–N13 139(1), C2–C3 142(1), C3–C4 136(1), C4a–N5 138.0(9), C4a–C11a 141(1), C4–C4a 141(1), C5a–C6 150(1), C5a–N5 129(1), C5a–N10 139(1), C6–C7 152(1), C7–C8 140(2), C8–C9 147(2), C9–N10 147.7(9), N10–C11 141.5(9), C11–C11a 146(1), C11–O12 122(1), N13–C14 147.4(9), N13–C14′ 148(1), C14–C21 153(1), C21–C22 145(1), C21–C25 143(1), C22–C23 141(1), C23–C24 142(1), C24–C25 142(1) Fe–C21 202.2(8), Fe–C22 204.0(8), Fe–C23 206.6(9), Fe–C24 205.5(9), Fe–C25 203.3(8), Fe–C21′ 201.9(8), Fe–C22′ 205.6(7), Fe–C23′ 206.2(9), Fe–C24′ 201(1), Fe–C25′ 202.3(8); N13–C14–C21 114.6(7), C14–N13–C14′ 113.1(6), N13–C14′–C21′ 115.2(7); C21–C14–N13–C2 –81.8(9), C21′–C14′–N13–C2 80.2(9).

enyl moieties from coplanarity. The mackinazolinone substituents adopt a conformation almost perpendicular to the ferrocene π system as indicated by the respective torsional angles.

To assess their redox properties some of the synthesized compounds were investigated by cyclic voltammetry, for which a representative example is given in Figure 7. All derivatives show a reversible wave attributed to the ferrocene/ferrocenium redox process. Results are summarized in Table 1.

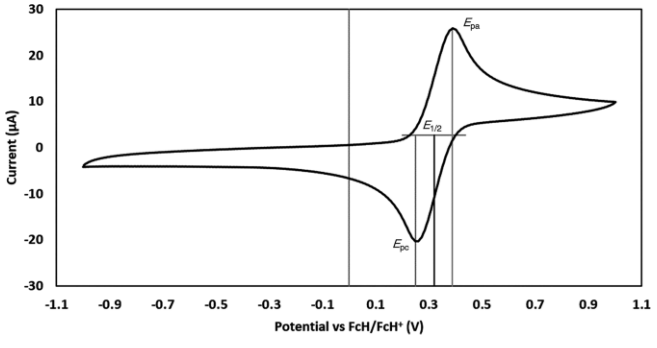

Figure 7. Representative cyclovoltammogram of **12**. For conditions see Table 1.

Table 1. Redox properties of ferrocene-deoxyvasicinone and -mackinazolinone conjugates. E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential; $\Delta E = E_{pa} - E_{pc}$; $E_{1/2}$ = half-wave potential. Potentials vs. FcH/FcH$^+$, solvent CH_2Cl_2 unless otherwise indicated, T = 20 °C, v = 100 mV/s, supporting electrolyte tetrabutylammonium phosphate. For details see experimental section.

Compound	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]	Color
10	0.419	0.173	0.246	0.296	Bordeaux red
12	0.395	0.245	0.150	0.320	dark purple
14	0.368	0.206	0.162	0.287	Bordeaux red
15	0.386	0.149	0.237	0.267	orange red
18	0.443	0.047	0.396	0.245	dark violet
19	0.389	0.038	0.351	0.213	dark violet
20	0.338	0.098	0.240	0.243	dark purple
21	0.401	0.086	0.315	0.243	dark purple
22	0.392	0.134	0.258	0.263	yellow
23	0.380	0.080	0.300	0.230	yellow
24	0.413	0.026	0.387	0.219	yellow
25	0.374	0.086	0.288	0.230	yellow

The cyclovoltammograms show similar shapes with rather high ΔE values indicating imperfect reversibility of the redox processes. The compounds investigated can be assigned to three categories, which correspond to the colors of the compounds: In compounds **10**, **14** and **15** the monosubstituted ferrocene moiety is conjugated to the extended π system of the electron rich alkaloid system. These compounds show Bordeaux red or orange red color and half-wave potentials of 0.267–0.296 V. Compounds **18**–**21** are 1,1′-disubstituted ferrocenes in conjugation with extended, in **20** and **21** electron poor, π systems. Presumably, as a consequence of the extended electron delocalization these compounds show dark violet or dark purple color and half-wave potentials of 0.213–0.245 V. Compounds **22**–**25** are non-conjugated 1,1′-di(aminomethyl) substituted ferrocenes, which are yellow and show half-wave potentials of 0.219–0.263 V.

Conclusions

In conclusion, we reported the syntheses and full characterization of the first ferrocene-mackinazolinone conjugates including compounds with the mackinazolinone at only one or at both of the cyclopentadienyl ligands. The crystal structure analyses indicate a coplanar conformation of the π systems of the ferrocene and the mackinazolinone moieties. Reductive amination afforded non-conjugated representatives including a 2-aza-[3]ferrocenophane with the mackinazolinone moiety adopting a perpendicular conformation with respect to the cyclopentadienyl ligands. Redox potentials obtained by cyclovoltammetric measurements reflect the electronic properties of the substituents present.

Experimental Section

General: Starting materials were either commercially acquired or were prepared according to published procedures. Ferrocene was obtained as a donation from Innospec Deutschland GmbH.

2,3-Dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**1**), 7-nitro-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**2**), 7-amino-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**3**), 6,7,8,9-tetrahydro-11*H*-pyr-

ido[2,1-*b*]quinazolin-11-one (**4**), 2-nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**5**), 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**), and *N*-(11-oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl)acetamide (**7**) were prepared according to the published procedure.[76] Ferrocenecarbaldehyde (**9**) and ferrocene-1,1′-dicarbaldehyde (**16**) were also prepared according to published procedures.[70,77,78]

^{1}H and ^{13}C NMR spectra were obtained with Bruker AVS 400 (^{1}H: 400 MHz, ^{13}C: 100.6 MHz) and AVS 500 (^{1}H: 500 MHz, ^{13}C: 125.7 MHz) instruments. Chemical shifts δ refer to δ_{TMS} = 0 ppm or to residual solvent signals. Primary, secondary, tertiary and quaternary carbon atom signals were identified as such by the APT or DEPT spectra. IR spectra were obtained using the Shimadzu IRAffinity-1S with quest ATR unit (32 scans). Signal characteristics are abbreviated as s (strong), m (medium), w (weak), and br (broad). HR-EI-MS: GCT (Micromass) with direct insertion probe; 70 eV electron energy and 250 °C source temperature. Mass spectra were obtained with a Micromass LCT premier instrument with lockspray source and direct injection and with a Q-TOF premier (Waters) LC-MS/MS instrument with an ESI source (3 kV, 250 °C). In all cases acetonitrile was used as the solvent. Crystal structure analyses were obtained with a Bruker SMART X2S instrument and were deposited with the CCDC.[74] Analytical TLC was performed with Merck 60F-254 silica gel thin layer plates. Column chromatography was performed with silica gel (60 µm) as the stationary phase using the flash chromatography method.[79] Cyclic voltammetry (CV) measurements were performed with a Gamry Instrument Reference 600 Potentiostat/Galvanostat/ZRA. 0.02 mmol of the sample compound were dissolved in freshly distilled dichloromethane (10 mL), and tetrabutylammonium phosphate (TBAP, 0.387 g, 98 %) was added corresponding to a concentration of 0.1 mol/L. The reference electrode was a Ag/Ag$^+$ ($AgNO_3$) electrode in acetonitrile with 0.01 mol/L $AgNO_3$ and 0.1 mol/L of TBAP. A 0.25 mm and a 0.1 mm thick platinum wire were used as the counter and working electrodes. Unless otherwise mentioned the scan rate was 100 mV/s. Freshly sublimed ferrocene (FcH) was used for calibration, potentials refer to the FcH/FcH$^+$ redox couple. Melting points were measured with an instrument Electrothermal IA9000.

***N*-(11-Oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl)propionamide (8):** Propionic anhydride (2 mL) was added to 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.215 g, 1.0 mmol), and the mixture was stirred at 25 °C for 21h. After addition of water (10 mL) and stirring at 25 °C for 2 h, aqueous NH_4OH (25 %) was added up to pH 8–9, and the formed precipitate was filtered off, washed with water (3 × 8 mL) and dried in the air. After recrystallization from ethanol, **8** (0.253 g, 0.93 mmol, 93 %) was obtained as a colorless solid; m.p. 212–214 °C; R_f = 0.55 (chloroform/methanol, 10:1). IR: $\tilde{\nu}$ = 3320 (m, NH), 2957 (m), 1652 (s, CO), 1621 (w, CO), 1580 (s), 1538 (s), 1492 (s), 1421 (m), 1393 (m), 1334 (m), 1290 (m), 1189 (s), 1076 (m), 915 (w), 845 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.5 Hz, 3H, CH_3), 1.77–2.06 (m, 4H, $NCH_2CH_2CH_2$), 2.47 (q, *J* = 7.6 Hz, 2H, CH_3CH_2), 3.00 (t, *J* = 6.7 Hz, 2H, $NCH_2CH_2CH_2CH_2$), 4.09 (t, *J* = 6.08 Hz, 2H, NCH_2CH_2), 7.6 (d, *J* = 8.8 Hz, 1H, HNCCHCH), 7.84 (s, 1H, NH), 8.08 (d, *J* = 2.5 Hz, 1H, HNCCHCCO), 8.32 (dd, *J* = 1.9 Hz, *J* = 8.8 Hz, 1H, HNCCHCH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.7 (CH_3), 19.3 ($NCH_2CH_2CH_2$), 22.1 (NCH_2CH_2), 30.7 ($NCH_2CH_2CH_2CH_2$), 31.8 (NCH_2), 42.5 (H_3CCH_2), 115.5 (HNCCH), 120.5 (HCCCO), 127.2 (HNCCHCH), 127.4 (HNCCHCCO), 136.5 (HNCCHCH), 143.9 (HNCCHCHCN), 153.7 (HCCCO), 161.9 (HNCO), 172.3 (NCN) ppm. MS (70 eV): *m/z* (%) = 271 (25) [M]$^+$, 215 (100) [M – $(CH_2)_2CO$]$^+$, 214 (16) [M – CH_3CH_2CO]$^+$, 200 (3.8) [M – $(CH_2)_2CONH$]$^+$, 69 (4.4). HR-EI-MS calcd. for $C_{15}H_{17}N_3O_2$: 271.1321, found 271.1298.

***(E)*-6-(Ferrocenylmethylene)-6,7,8,9-tetrahydro-11*H*-pyrido-[2,1-*b*]quinazolin-11-one (10):** 6,7,8,9-tetrahydro-11*H*-pyrido-[2,1-*b*]quinazolin-11-one (**4**; 0.2 g, 1.0 mmol) and ferrocenecarbaldehyde (**9**; 0.214 g, 1.0 mmol) were added to sodium hydroxide (0.04 g, 1.0 mmol) in ethanol (3 mL). After stirring at reflux for 7 h and standing for 14 h at 25 °C, water (15 mL) was added, and the mixture was stirred at 25 °C for 1 h. The reaction mixture was extracted with dichloromethane (3 × 25 mL), and the combined organic layers were dried with anhydrous $MgSO_4$. After solvent removal the obtained crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:3). After recrystallization from hexanes, **10** (0.26 g, 0.67 mmol, 67 %) was obtained as a Bordeaux red solid; m.p. 175–176 °C; R_f = 0.18 (ethyl acetate/petroleum ether, 1:3). IR: $\tilde{\nu}$ = 3078 (w), 2945 (m, CpH), 2958 (m, CpH), 1681 (s, CO), 1608 (m), 1529 (w), 1471 (s), 1390 (s), 1205 (m), 1166 (w), 1056 (s), 920 (m), 820 (s), 771 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07–2.1 (m, 2H, NCH_2CH_2), 2.83 (dt, 2H, *J* = 2.0 Hz, *J* = 8.4 Hz, $NCH_2CH_2CH_2$), 4.18 (dt, 2H, *J* = 4.0 Hz, NCH_2), 4.22 (s, 5H, CpH), 4.45 + 4.60 (AA′BB′, 2 × 2H, CpH), 7.42 (td, *J* = 8.0 Hz, 1H, OCCCHCHCH), 7.74 (dd, *J* = 1.2 Hz, *J* = 4.8 Hz, 2H, OCCCHCHCHCH), 8.02 (t, *J* = 2.0 Hz, 1H, $NCH_2CH_2CH_2CCH$), 8.28 (td, *J* = 8.0 Hz, 1H, OCCCHCH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.9 ($NCH_2CH_2CH_2$), 26.2 (NCH_2CH_2), 41.9 (NCH_2), 69.4 ($C_{Cp}H$), 69.6 ($C_{Cp}H$), 70.9 (5 $C_{Cp}H$), 80.0 ($C_{Cp}C$), 119.8 ($NCH_2CH_2CH_2CCH$), 125.4 ($NCH_2CH_2CH_2C$), 125.6 (OCCCHCH), 126.7 (OCCCH), 127.2 (OCCCHCHCHCH), 134.1 (OCCCHCHCH), 135.7 (OCCHCHCHCHCN), 147.9 (OCC), 151.9 (NCO), 162.3 (NCN) ppm. MS (70 eV): *m/z* (%) = 396 (48.1) [M]$^+$, 331 (100) [M – Cp]$^+$, 219 (25.6), 130 (13.7), 120 (6.9), 69 (25.5). EI-HRMS calcd. for $C_{23}H_{20}FeN_2O$: 396.0925, found 396.0928.

***(E)*-6-(Ferrocenylmethylene)-2-nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (12):** 2-Nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**5**; 0.245 g, 1.0 mmol) and ferrocenecarbaldehyde (**9**; 0.214 g, 1.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (5 mL). After stirring at reflux for 3 h and standing for 2 h at 25 °C, water (25 mL) was added, and the mixture was stirred at 25 °C for 0.5 h. The reaction mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layers were dried with anhydrous $MgSO_4$. After solvent removal the obtained crude product was purified by column chromatography (30 × 3 cm, SiO_2 ethyl acetate/petroleum ether, 1:6 to 3:2 with 3 % triethylamine). After recrystallization from dioxane, **12** (0.376 g, 0.9 mmol, 85 %) was obtained as dark-purple crystals; m.p. > 230 °C (dec.); R_f = 0.26 (ethyl acetate/petroleum ether, 1:3). IR: $\tilde{\nu}$ = 3101 (w), 2933 (w, CpH), 2881 (w, CpH), 1662 (s, CO), 1614 (s), 1523 (s, NO_2), 1471 (m), 1382 (m), 1274 (s), 1107 (s), 918 (m), 786 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (br. s, 2H, NCH_2CH_2), 2.84 (br. s, 2 H, $NCH_2CH_2CH_2$), 4.21 (t, *J* = 5.0 Hz, 2H, NCH_2), 4.24 (s, 5H, CpH), 4.53 (s, 2H, CpH), 4.64 (s, 2H, CpH), 7.79 (d, *J* = 7.2 Hz, 1H, $OCCHCNO_2CHCH$), 8.2 (s, 1H, $NCH_2CH_2CH_2CCH$), 8.5 (d, *J* = 6.4 Hz, 1H, $OCCHC(NO_2)CH$), 9.14 (s, 1H, OCCCH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.5 (NCH_2CH_2), 25.9 ($NCH_2CH_2CH_2$), 42.3 (NCH_2), 69.6 ($C_{Cp}H$), 71.2 ($C_{Cp}H$), 71.3 (5 $C_{Cp}H$), 79.3 ($C_{Cp}C$), 119.2 ($NCH_2CH_2CH_2CCH$), 123.8 ($NCH_2CH_2CH_2C$), 124.2 (O_2NC), 128.1 ($O_2NCCHCCO$), 128.4 ($O_2NCCHCH$), 139.5 ($O_2NCCHCCO$), 144.4 ($O_2NCCHCH$), 152.0 ($O_2NCCHCHC$), 155.0 (NCO), 161.4 (NCN) ppm. MS (ESI, ES$^+$): *m/z* = 442 [M + H$^+$], ESI-HRMS: *m/z* calcd. for $C_{23}H_{20}FeN_3O_3$ [M + H]$^+$ 442.0854, found 442.0855.

2-Amino-(*E*)-6-(ferrocenylmethylene)-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (13): 2-Amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.215 g, 1.0 mmol) and ferrocenecarbaldehyde (**9**; 0.428 g, 2.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (5 mL). After stirring at

reflux for 10 h and standing for overnight at 25 °C, water (10 mL) was added, and the mixture was stirred at 25 °C for 0.5 h. The reaction mixture was extracted with dichloromethane (3 × 30 mL), and the combined organic layers were dried with anhydrous $MgSO_4$. After solvent removal the obtained crude product was purified by column chromatography [30 × 3 cm, SiO_2 ethyl acetate/petroleum ether, 1:1 to ethyl acetate (100 %)]. After crystallization from ethanol, **13** (0.25 g, 0.6 mmol, 60 %) was obtained as red crystals; m.p. > 285 °C (dec.); R_f = 0.21 (ethyl acetate/petroleum ether, 1:1). IR: $\tilde{\nu}$ = 3375, 3255 (s, NH_2), 2926 (w, CpH), 2894 (w, CpH), 1670 (s, CO), 1525 (w), 1476 (s), 1387 (w), 1280 (s), 1110 (w), 923 (w), 780 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.05 (m, 2H, NCH_2CH_2), 2.82 (dt, 2H, J = 6.8 Hz, $NCH_2CH_2CH_2$), 3.94 (s, 2H, NH_2), 4.18 (dt, 2H, J = 6.4 Hz, NCH_2), 4.21 (s, 5H, CpH), 4.42 + 4.58 (AA′BB′, 2 × 2H, CpH), 7.13 (dd, J = 2.4, 7.6 Hz, 1H, $H_2NCCHCH$), 7.48 (d, J = 2.0 Hz, 1H, $H_2NCCHCCO$), 7.59 (d, J = 6.8 Hz, 1H, $H_2NCCHCH$), 7.87 (s, 1H, $NCH_2CH_2CH_2CCH$) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 22.0 (NCH_2CH_2), 26.3 ($NCH_2CH_2CH_2$), 41.9 (NCH_2), 67.4 ($C_{Cp}H$), 69.5 ($C_{Cp}H$), 70.1 (5 $C_{Cp}H$), 80.4 ($C_{Cp}C$), 108.9 ($NCH_2CH_2CH_2CCH$), 120.8 ($NCH_2CH_2CH_2C$), 123.4 (H_2NC), 125.8 ($H_2NCCHCCO$), 128.6 ($H_2NCCHCH$), 133.6 ($H_2NCCHCCO$), 141.1 ($H_2NCCHCH$), 144.6 ($H_2NCCHCHCN$), 148.8 (NCO), 161.9 (NCN) ppm. ESI-HRMS: m/z calcd. for $C_{23}H_{21}FeN_3O$ 411.1034, found 411.1030.

N*-{(*E*)-6-(Ferrocenylmethylene)-11-oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl}acetamide (14).** ***Method A: Ferrocenecarbaldehyde (**9**; 0.214 g, 1.0 mmol) was added to *N*-(11-oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl)acetamide (**7**; 0.256 g, 1.0 mmol) in glacial acetic acid (5 mL). The mixture was heated at 100 °C for 4 h and then allowed to stand at 25 °C for 2 h. After addition of water (15 mL) the formed precipitate was filtered off, washed with water (3 × 15 mL) and dried at 25 °C in the air. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:1 to 2:1). After crystallization from ethanol, **14** (0.326 g, 0.72 mmol, 72 %) was obtained as a Bordeaux red solid; m.p. > 275 °C (dec.); R_f = 0.4 in ethyl acetate/hexanes (10:1). Crystal structure analysis: CCDC 1402243.[74] ***Method B:*** Ferrocenecarbaldehyde (**9**; 0.214 g, 1.0 mmol) was added to 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.215 g, 1.0 mmol) in glacial acetic acid (3 mL). The mixture was heated by reflux for 3–4 h and then allowed to stand at 25 °C for 2 h. After addition of water (15 mL), the mixture was stirred at 25 °C for 0.5 h, and the formed precipitate was filtered off, washed with water (3 × 15 mL), and dried at 25 °C in the air. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:1 to 2:1). After crystallization from ethanol, **14** (0.294 g, 0.65 mmol, 65 %) was obtained as a Bordeaux red solid; m.p. > 275 °C (dec.); R_f = 0.4 in ethyl acetate/hexanes (10:1). IR: $\tilde{\nu}$ = 3326 (m, NH), 2950 (w, CpH), 2860 (w, CpH), 1676 (s, CO), 1645 (s, CO), 1589 (m), 1523 (s), 1489 (s), 1280 (s), 1174 (w), 1037 (w), 921 (m), 788 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.06 (m, 2H, NCH_2CH_2), 2.27 (s, 3H, CH_3), 2.83 (t, J = 5.2 Hz, 2H, $NCH_2CH_2CH_2$), 4.18 (t, J = 5.6 Hz, 2H, NCH_2), 4.20 (s, 5H, CpH), 4.45 (s, 2H, CpH), 4.59 (s, 2H, CpH), 7.72 [d, J = 8.8 Hz, 1H, C(NHAc)CHCH], 7.85 (br. s, 1H, NH), 7.98 (br. s, 1H, C(NHAc)CHCH), 8.07 (br. s, 1H, $NCH_2CH_2CH_2CCH$), 8.34 (d, J = 7.6 Hz, 1H, OCCCH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8 (CH_3), 26.2 (NCH_2CH_2), 42.1 ($NCH_2CH_2CH_2$), 53.4 (NCH_2), 67.3 ($C_{Cp}H$), 70.4 ($C_{Cp}H$), 70.8 (5 $C_{Cp}H$), 80.0 ($C_{Cp}C$), 115.7 ($NCH_2CH_2CH_2CCH$), 119.9 ($NCH_2CH_2CH_2C$), 125.2 (HNCCH), 127.2 (HNCCHCCO), 128.2 (HNCCHCH), 135.4 (HNCCH), 136.0 (HNCO), 144.7 (HNCCHCHC), 151.0 (HNCCHCH), 162.0 (NCO), 168.4 (NCN) ppm. MS (70 eV): m/z (%) = 453 (53) $[M]^+$, 488 (100) $[M - Cp]^+$, 331 (11) $[M - CpH\text{-}NCOMe]^+$. EI-HRMS calcd. for $C_{25}H_{23}FeN_3O_2$: 453.1140, found 453.1132.

***N*-{(*E*)-6-(Ferrocenylmethylene)-11-oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl}propionamide (15):** *Method A:* Ferrocenecarbaldehyde (**9**; 0.214 g, 1.0 mmol) was added to *N*-(11-oxo-6,8,9,11-tetrahydro-7*H*-pyrido[2,1-*b*]quinazolin-2-yl)propionamide (**8**; 0.271 g, 1.0 mmol) in glacial acetic acid (5 mL). The mixture was heated at 100 °C for 4 h and then allowed to stand at 25 °C for 2 h. After addition of water (15 mL) the formed precipitate was filtered off, washed with water (3 × 15 mL) and dried at 25 °C in the air. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:1 to 3:2 with 2 % triethylamine). After crystallization from toluene **15** (0.28 g, 0.6 mmol, 60 %) was obtained as orange-red crystals; m.p. > 233 °C (dec.); R_f = 0.75 (ethyl acetate/methanol, 10:1). *Method B:* Ferrocenecarbaldehyde (**9**; 0.428 g, 2.0 mmol) was added to 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.215 g, 1.0 mmol) in propionic acid (3 mL). The mixture was heated by reflux for 3–4 h and then allowed to stand at 25 °C for 2 h. After addition of water (15 mL), the mixture was stirred at 25 °C for 0.5 h, and the formed precipitate was filtered off, washed with water (3 × 15 mL) and dried at 25 °C in the air. The crude product was purified by column chromatography [30 × 3 cm; SiO_2, ethyl acetate/petroleum ether, 1:1 to 3:2 (with 2 % triethylamine)]. After crystallization from toluene, **15** (0.27 g, 0.58 mmol, 58 %) was obtained as orange-red crystals; m.p. > 233 °C (dec.); R_f = 0.75 (ethyl acetate/methanol, 10:1). IR: $\tilde{\nu}$ = 3329 (m, NH), 2954 (w, CpH), 2867 (w, CpH), 1651, 1635 (m, CO), 1529 (s), 1492 (s), 1421 (w), 1384 (w), 1230 (m), 1153 (w), 1076 (w), 935 (m), 788 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.6 Hz, 3H, CH_3), 2.03–2.08 (m, 2H, NCH_2CH_2), 2.48 (q, J = 7.2 Hz, 2H, CH_3CH_2), 2.82 (t, J = 6.4 Hz, 2H, $NCH_2CH_2CH_2$), 3.96 (s, 1H, NH), 4.17 (t, J = 5.6 Hz, 2 H, NCH_2), 4.18 (s, 5H, CpH), 4.45 + 4.60 (AA′BB′, 2 × 2H, CpH), 7.19 (dd, 1H, J = 2.8 Hz, J = 7.6 Hz, NHCCHCH), 7.59 (t, J = 4.0 Hz, 1H, $NCH_2CH_2CH_2CCH$), 7.73 (d, J = 8.8 Hz, 1H, HNCCHCH), 8.05 (d, J = 2.4 Hz, 1H, HNCCHCCO) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.7 (CH_3), 21.5 (CH_3CH_2), 22.0 (NCH_2CH_2), 26.3 ($NCH_2CH_2CH_2$), 42.0 (NCH_2), 69.3 ($C_{Cp}H$), 69.4 ($C_{Cp}H$), 70.8 (5 $C_{Cp}H$), 80.0 ($C_{Cp}C$), 109.0 ($NCH_2CH_2CH_2CCH$), 115.1 ($NCH_2CH_2CH_2C$), 119.9 (HNCCH), 123.4 (HNCCHCO), 125.3 (HNCCHCH), 128.2 (HNCCHCCO), 128.2 (HNCCHCH), 129.1 (HNCO), 137.7 (HNCCHCHC), 145.4 (NCO), 161.9 (NCN) ppm. MS (70 eV): m/z (%) = 468 (9.4) $[M + H]^+$, 467 (62.5) $[M]^+$, 411 (35.6) $[M - (CH_2)_2CO]^+$, 402 (100) $[M - Cp]^+$, 346 (70.6) $[M - Cp - Fe]^+$, 120 (8.1). EI-HRMS calcd. for $C_{26}H_{25}FeN_3O_2$: 467.1296, found 467.1296.

(6*E*,6′*E*)-6,6′-[1,1′-Ferrocenylenebis(methanylylidene)]bis-(6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one) (18): Ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol), and 6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**4**; 0.4 g, 2.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (5 mL). The mixture was heated at reflux for 8 h and then allowed to stand at 25 °C for 1 h. After addition of water (10 mL), the mixture was stirred at 25 °C for 1 h and the formed precipitate was filtered off, washed with water (3 × 10 mL) and dried at 25 °C in the air. The crude product was purified by column chromatography (30 × 3 cm SiO_2, ethyl acetate/petroleum ether, 2:1 with 0.3 % of triethylamine). After recrystallization of from dioxane, **18** (0.97 g, 0.80 mmol, 80 %) was obtained as dark violet crystals; m.p. > 275 °C (dec.); R_f = 0.45 (ethyl acetate/petroleum ether, 4:1). Crystal Structure Analysis: CCDC 1985959.[74] IR: $\tilde{\nu}$ = 3080 (w), 2951 (w, CpH), 2891 (w, CpH), 1660 (s, CO), 1608 (w, CO), 1571 (w), 1489 (s), 1390 (s), 1207 (m), 1165 (w), 1039 (m), 929 (m), 756 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.98 (m, 4H, NCH_2CH_2), 2.78 (t, J = 7.6 Hz, 4H, $NCH_2CH_2CH_2$), 3.92 (t, 4H, J = 5.6 Hz, NCH_2), 4.46 + 4.70 (AA′BB′, 2 × 4H, CpH), 7.37 (t, J = 8.0 Hz, 2H, OCCCHCH), 7.53 (d, J = 8.4 Hz, 2H, OCCCHCHCHCH), 7.67 (dt, J = 1.6 Hz, J = 8.4 Hz, 4H,

OCCCHCHC*H*), 7.91 (s, 2H, $NCH_2CH_2CH_2CCH$), 8.08 (dd, *J* = 1.2, 8.0 Hz, 2H, OCCC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.4 (NCH_2CH_2), 26.3 ($NCH_2CH_2CH_2$), 41.7 (NCH_2), 71.2 ($C_{Cp}H$), 72.0 ($C_{Cp}H$), 81.3 (*C*CpC), 119.5 ($NCH_2CH_2CH_2CCH$), 125.7 ($NCH_2CH_2CH_2C$), 126.5 (OCCCH*C*H), 126.6 (OCCC*C*H), 133.9 (OCCCHCHCH*C*H), 134.0 (OCCCHCH*C*H), 147.4 (OCCCHCHCH*C*N), 151.2 (OC), 161.6 (NCN) ppm. MS (70 eV): *m/z* (%) = 606 (26.3) $[M]^+$, 331 (100) [M – mackinazolinone – CH – CpH]$^+$, 275 (37.5) [M – mackinazolinone – CH – CpH – Fe]$^+$. EI-HRMS: *m/z* calcd. for $C_{36}H_{30}FeN_4O_2$ 606.1718, found 606.1711.

6-{(*E*)-2-[(*E*)-(9-Oxo-1,2-dihydropyrrolo[2,1-*b*]quinazolin-3(9*H*)-ylidene)methyl]ferrocenylidene}-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (19): Ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) and 6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]-quinazolin-11-one (**4**; 0.2 g, 1.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (5 mL). The mixture was heated at reflux for 3.5 h. Then 2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**1**; 0.186 g, 1.0 mmol) was added, the reaction mixture was heated at reflux for 3.5 h and then allowed to stand at 25 °C for 1 h. After addition of water (10 mL), the mixture was stirred at 25 °C for 0.5 h and the formed precipitate was filtered off, washed with water (3 × 10 mL), and dried at 25 °C in the air. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 7:1 with 0.3 % of triethylamine). After recrystallization from toluene **19** (0.44 g, 0.73 mmol, 74 %) was obtained as dark violet crystals; m.p. > 295 °C (dec.); R_f = 0.21 (ethyl acetate/petroleum ether, 4:1).

Abbreviation for "mackinazolinone part": *M*; abbreviation for "deoxyvasicinone part": *D*. IR: $\tilde{\nu}$ = 2954 (w, CpH), 2893 (w, CpH), 1682 (m, CO), 1610 (m, CO), 1585 (s), 1465 (s), 1382 (w), 1186 (m), 1078 (w), 927 (m), 759 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (t, *J* = 6.4 Hz, 2H, *M*, $NCH_2CH_2CH_2$), 2.72 (t, *J* = 5.6 Hz, 2H, *D*, NCH_2CH_2), 2.95 (quin, 2H, *M*, NCH_2CH_2), 3.93 (t, *J* = 5.6 Hz, 2H, *D*, NCH_2), 4.00 (t, *J* = 7.2 Hz, 2H, *M*, NCH_2), 4.46 (m, 2H, CpH), 4.69 (s, 2H, CpH), 4.73 (s, 2H, CpH), 7.35 (m, 3H, *D*, OCCCHCHCHC*H* + *M*, OCCC*H*CHCHCH + *M*, $NCH_2CH_2CH_2CCH$), 7.43 (t, *J* = 8.8 Hz, 2H, *D*, OCCCHC*H* + *M*, OCCCHC*H*), 7.67 (dt, *J* = 1.2, 8.0 Hz, 2H, *D*, OCCCHCHC*H* + *M*, OCCCHCHC*H*), 7.82 (s, 1H, *D*, NCH_2CH_2CCH), 7.87 (dd, *J* = 1.2, 8.0 Hz, 1H, *M*, OCCC*H*), 7.93 (dd, *J* = 1.2, 8.0 Hz, 1H, *D*, OCCC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.1 (*M*, NCH_2CH_2), 24.9 (*D*, NCH_2CH_2), 26.4 (*M*, $NCH_2CH_2CH_2$), 41.6 (*D*, NCH_2), 43.6 (*M*, NCH_2), 71.0 ($C_{Cp}H$), 71.1 ($C_{Cp}H$), 71.2 ($C_{Cp}H$), 71.9 ($C_{Cp}H$), 81.1 ($C_{Cp}C$), 81.6 ($C_{Cp}C$), 119.2 (*M*, $NCH_2CH_2CH_2CCH$), 120.2 (*D*, NCH_2CH_2CCH), 125.58 (*M*, $NCH_2CH_2CH_2CCH$), 125.62 (*D*, NCH_2CH_2CCH), 126.1 (*M*, OCCCHCH), 126.2 (*D*, OCCCHCH), 126.4 (*M*, OCCCH), 126.7 (*D*, OCCCH), 126.8 (*M*, OCCCHCHCHCH), 128.2 (*D*, OCCCHCHCHCH), 129.7 (*M*, OCCCHCHCH), 132.6 (*D*, OCCCHCHCH), 134.13 (*M*, OCCCHCHCHCN), 134.16 (*D*, OCCCHCHCHCN), 147.1 (*M*, OCC), 149.3 (*D*, OCC), 151.0 (*M*, NCO), 155.1 (*D*, NCO), 160.3 (*M*, NCN), 161.2 (*D*, NCN) ppm. MS (70 eV): *m/z* (%) = 592 (85) $[M]^+$, 331 (90) [M – deoxyvasicinone – CH – CpH]$^+$, 316 (100) [M – mackinazolinone – CH – CpH]$^+$, 275 (10), 261 (6.7). ESI-HRMS: *m/z* calcd. for $C_{35}H_{28}FeN_4O_2$ 592.1562, found 592.1559.

Reaction of Ferrocene-1,1′-dicarbaldehyde (16) with Deoxyvasicinone (1) and Mackinazolinone (4): Ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol), 2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**1**, deoxyvasicinone; 0.186 g, 1.0 mmol) and 6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**4**, mackinazolinone; 0.2 g, 1.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (5 mL). The mixture was heated at reflux for 7 h and then allowed to stand at 25 °C for 1 h. After addition of water (15 mL), the mixture was stirred at 25 °C for 0.5 h and the formed precipitate was filtered off, washed with water (3 × 10 mL), and dried at 25 °C in air. The crude product was purified by column chromatography [30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 2:1 (for **18**), 7:1 (for **19**), 20:1 (for **17**), with 0.3 % of triethylamine].

I: **18** (0.24 g, 0.40 mmol, 40 %). R_f = 0.45 (ethyl acetate/petroleum ether, 4:1) dark violet crystals (recrystallization from dioxane); m.p.> 275 °C (dec.).

II: **19** (0.059 g, 0.10 mmol, 10 %). R_f = 0.21 (ethyl acetate/petroleum ether, 4:1), dark violet crystals (recrystallization from toluene); m.p. > 295 °C (dec.).

III: **17**,[21] (0.087 g, 0.15 mmol, 15 %). R_f = 0.10 (ethyl acetate/petroleum ether, 4:1), red crystals (recrystallization from dioxane); m.p. > 346 °C (dec.).

(*E*)-1′-{[7-Nitro-9-oxo-1,2-dihydropyrrolo[2,1-*b*]quinazolin-3(9*H*)-ylidene]methyl}ferrocenecarbaldehyde (20): Ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) and 7-nitro-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**2**; 0.462 g, 2.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (10 mL). The mixture was heated at reflux for 7 h and then allowed to stand at 25 °C for 14 h. After addition of water (50 mL), the mixture was extracted with dichloromethane (3 × 50 mL), and the combined organic layers dried with anhydrous $MgSO_4$. After solvent removal the obtained crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:1 to 2:1). After recrystallization from dioxane, **20** (0.53 g, 0.80 mmol, 80 %) was obtained as dark-purple crystals; m.p. > 318 °C (dec.); R_f = 0.4 (ethyl acetate/petroleum ether, 2:1). IR: $\tilde{\nu}$ = 3076 (w), 2954 (w), 2878 (w), 1678 (s, CO), 1614 (m, CO), 1554 (w), 1521 (m, NO_2), 1469 (m), 1390 (w), 1261 (s), 1168 (m), 1060 (m), 921 (m), 786 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD, 7:1): δ = 2.95 (t, *J* = 6.0 Hz, 2H, NCH_2CH_2), 4.29 (t, 2H, *J* = 7.2 Hz, NCH_2), 4.57 + 4.80 (AA′BB′, 2 × 2H, CpH), 4.64 (dt, 4H, *J* = 2.0, 4.0 Hz, $C_{Cp}H$), 7.58 (t, *J* = 2.8 Hz, NCH_2CH_2CCH), 7.77 (d, *J* = 9.2 Hz, 1H, OCCCHCCHCH), 8.48 (dd, *J* = 2.8 Hz, *J* = 9.2 Hz, 1H, OCCCHCCH), 9.09 (d, *J* = 2.4 Hz, 1H, OCCCH), 9.76 (s, 1H, CHO) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$/CD_3OD, 7:1): δ = 24.8 (NCH_2CH_2), 44.3 (NCH_2), 70.9 ($C_{Cp}H$), 71.6 ($C_{Cp}H$), 74.4 ($C_{Cp}H$), 77.3 ($C_{Cp}H$), 80.3 ($C_{Cp}C$), 80.6 ($C_{Cp}C$), 120.5 (NCH_2CH_2CCH), 123.10 (NCH_2CH_2C), 128.20 ($O_2NCCHCH$), 128.90 ($O_2NCCHCHC$), 131.6 ($O_2NCCHCH$), 144.7 ($OCCCHCNO_2$), 154.0 (OCCCH), 158.4 (OCN), 160.4 (NCN), 193.4 (O_2NC) ppm. ESI-HRMS: *m/z* calcd. for $C_{23}H_{17}FeN_3O_4$ $[M + H]^+$ 456.0568, found 456.0570.

(*E*)-2{[2-Nitro-11-oxo-8,9-dihydro-7*H*-pyrido[2,1-*b*]quinazolin-6(11*H*)-ylidene]methyl}ferrocenecarbaldehyde (21): Ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) and 2-nitro-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**5**; 0.490 g, 2.0 mmol) were added to sodium hydroxide (0.040 g, 1.0 mmol) in ethanol (10 mL). The mixture was heated at reflux for 7 h and then allowed to stand at 25 °C for 14 h. After addition of water (50 mL), the mixture was extracted with dichloromethane (3 × 50 mL), and the combined organic phases dried with anhydrous $MgSO_4$. After solvent removal the obtained crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/petroleum ether, 1:1 to 2:1). After recrystallization from toluene, **21** (0.60 g, 0.87 mmol, 87 %) was obtained as dark-purple crystals; m.p. > 270 °C (dec.); R_f = 0.5 (ethyl acetate/petroleum ether, 2:1). IR: $\tilde{\nu}$ = 3093 (m), 2956 (w, CpH), 2875 (w, CpH), 1674 (s, CO), 1608 (s, CO), 1579 (w), 1506 (s, NO_2), 1429 (m), 1371 (m), 1203 (m), 1143 (s), 1047 (w), 921 (m), 790 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07–2.12 (m, 2H, NCH_2CH_2), 2.74 (t, *J* = 6.0 Hz, 2H, $NCH_2CH_2CH_2$), 4.24 (t, 2H, *J* = 6.0 Hz, NCH_2), 4.59 + 4.66 + 4.72 + 4.85 (AA′BB′, 4 × 2H, CpH),

7.8 (d, J = 8.8 Hz, 1H, OCCCHCCHC*H*), 8.03 (s, 1H, =CH), 8.51 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H, OCCCHCC*H*), 9.15 (d, J = 2.4 Hz, 1H, OCCC*H*), 9.87 (s, 1H, C*H*O) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 21.4 (NCH_2CH_2), 26.0 ($NCH_2CH_2CH_2$), 42.0 (NCH_2), 70.1 ($C_{Cp}H$), 74.0 ($C_{Cp}H$), 81.3 ($C_{Cp}C$), 119.5 ($NCH_2CH_2CH_2CCH$), 123.8 ($NCH_2CH_2CH_2C$), 126.5 ($O_2NCCHCH$), 128.1 ($O_2NCCHCHC$), 136.1 ($O_2NCCHCH$), 144.6 ($OCCCHCNO_2$), 151.8 (OCCCH), 154.7 (OCN), 161.2 (NCN), 192.9 (O_2NC) ppm. ESI-HRMS: m/z calcd. for $C_{24}H_{19}FeN_3O_4$ $[M + H]^+$ 470.0725, found 470.0727.

7-(*N*-2-Aza[3]ferrocenophanyl)-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (22) and 7,7′-{[1,1′-Ferrocenylenebis(methylene)]bis(azanediyl)}bis[2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one] (23): *Method A:* 7-amino-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**3**; 0.201 g, 1.0 equiv.) was added to ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) in 1,2-dichloroethane (20 mL), and the mixture was stirred at 25 °C for 3 h. To this suspension sodium triacetoxyborohydride (0.636 g, 3.0 equiv., 6.5 mmol) was added, and the mixture was stirred at 25 °C for 48 h. The reaction mixture was hydrolyzed by addition of 1 M NaOH (15 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layers were dried with $MgSO_4$, and solvents were removed at reduced pressure. The crude product was purified by column chromatography on silica gel (30 × 3 cm, SiO_2, ethyl acetate/methanol, 20:1 to 15:1).

I: After recrystallization from toluene, **22** (0.226 g, 0.55 mmol, 55 %) was obtained as yellow crystals; m.p. > 280 °C (dec.); R_f = 0.8 (dichloromethane/methanol, 15:1).

II: **23** (0.17 g, 0.28 mmol, 28 %) was obtained as yellow crystals; m.p. > 260 °C (dec.); R_f = 0.26 (dichloromethane/methanol, 15:1).

Method B: 7-amino-2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (**3**; 0.402 g, 2.0 equiv.) was added to ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) in 1,2-dichloroethane (30 mL), and the mixture was stirred at 25 °C for 3 h. To this suspension sodium triacetoxyborohydride (0.636 g, 3.0 equiv., 6.5 mmol) was added, and the mixture was stirred at 25 °C for 28 h. The reaction mixture was hydrolyzed by addition of 1 M NaOH (15 mL), the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layers were dried with $MgSO_4$, and the solvents were removed at reduced pressure. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, dichloromethane/methanol, 20:1 to 15:1) to give **23** (0.49 g, 0.80 mmol, 80 %) as yellow crystals; m.p. > 260 °C (dec.); R_f = 0.26 (dichloromethane/methanol, 15:1).

22: IR: $\tilde{\nu}$ = 3055 (w), 2978 (w, CpH), 2875 (w, CpH), 1664 (s, CO), 1548 (w), 1465 (w), 1379 (s), 1219 (w), 1153 (w), 1060 (m), 923 (s), 767 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25–2.33 (m, 2H, NCH_2CH_2), 3.17 (t, J = 7.6 Hz, 2H, $NCH_2CH_2CH_2$), 3.99 (s, 4H, CH_2NCH_2), 4.08 + 4.20 (AA′BB′, 2 × 4H, CpH), 4.22 (t, 2H, J = 7.2 Hz, NCH_2), 7.44 (dd, J = 3.2 Hz, J = 9.2 Hz, 1H, OCCCHCC*H*), 7.60 (d, J = 8.8 Hz, 1H, OCCCHCCHC*H*), 7.74 (d, J = 2.8 Hz, 1H, OCCC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.8 (NCH_2CH_2), 32.2 ($NCH_2CH_2CH_2$), 46.35 (NCH_2), 46.43 (CH_2NCH_2), 69.3 ($C_{Cp}H$), 70.0 ($C_{Cp}H$), 83.81 ($C_{Cp}C$), 107.0 (OCCCHCCHCH), 121.4 (OCCCHCCH), 121.6 (OCCCH), 128.0 (OCCCHCCHCHC), 140.9 (OCCCHC), 147.8 (OCCCH), 155.7 (NCO), 161.1 (NCN) ppm. MS (70 eV): m/z (%) = 411 (100) $[M]^+$, 333 (49.3) $[M - CpH\text{-}CH_2]^+$, 276 (5.3) $[M - CpH\text{-}FeHCH_2]^+$, 201 (69) $[M - Fc - (CH)_2]^+$. EI-HRMS: m/z calcd. for $C_{23}H_{21}FeN_3O$ 411.1034, found 411.1031.

23: IR: $\tilde{\nu}$ = 3367 (m, NH), 3342 (m, NH), 3074 (w), 2953 (w, CpH), 2871 (w, CpH), 1649 (s, CO), 1618 (s, CO), 1564 (w), 1490 (w), 1363 (s), 1249 (w), 1155 (w), 1070 (m), 923 (s), 783 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 7:1): δ = 2.20 (m, 4H, NCH_2CH_2), 3.05 (t, J = 8.0 Hz, 4H, $NCH_2CH_2CH_2$), 4.02 + 4.22 (AA′BB′, 2 × 4H, CpH), 4.09 (d, J = 5.6 Hz, 4H, CH_2NH), 4.10 (t, 4H, J = 6.0 Hz, NCH_2), 7.01 (dd, J = 2.8 Hz, J = 8.8 Hz, 2H, OCCCHCC*H*), 7.26 (d, J = 2.8 Hz, 2H, OCCC*H*), 7.36 (d, J = 8.8 Hz, 2H, OCCCHCCHC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 7:1): δ = 19.5 (NCH_2CH_2), 31.7 ($NCH_2CH_2CH_2$), 43.1 (NCH_2), 46.5 ($NHCH_2$), 68.6 ($C_{Cp}H$), 68.8 ($C_{Cp}H$), 85.9 (*C*CpC), 104.5 (OCCCHCCHCH), 121.1 (OCCCHCCH), 122.3 (OCCCH), 127.2 (OCCCHCCHCHC), 140.7 (OCCCHC), 146.8 (OCCCH), 155.6 (NCO), 161.3 (NCN) ppm. MS (ESI, ES$^+$): m/z (%) = 613 (100) $[M + H^+]$, 612 (24) $[M^+]$, 611 (10.5) $[M^+ - H]$, 491 (5.3) $[M + H^+ - CpH\text{-}Fe - 2H]$. HRMS (ESI): m/z calcd. For $C_{34}H_{33}FeN_6O_2$ $[M + H]^+$ 613.2014, found 613.2015.

2-Aza[3]ferrocenophanyl-*N*-(6,7,8,9-tetrahydro-11*H*-pyrido-[2,1-*b*]quinazolin-11-one) (24) and 2,2′-[(1,1′-Ferrocenylenebis(methylene))bis(azanediyl)]bis(6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one) (25): *Method A:* To a solution of ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) in 1,2-dichloroethane (20 mL) 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.215 g, 1 equiv.) was added, and the mixture was stirred at 25 °C for 3 h. To this suspension sodium triacetoxyborohydride (0.636 g, 3 equiv., 6.54 mmol) was added, and the mixture was stirred at 25 °C for 48 h. Aqueous 1 M NaOH (15 mL) was added, the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layers were dried with $MgSO_4$, and the solvents were removed at reduced pressure. The crude product was purified by column chromatography (30 × 3 cm, SiO_2, ethyl acetate/methanol, 25:1 to 15:1).

I: **24** (0.272 g, 0.6 mmol, 64 %) was obtained as yellow crystals (recrystallized from ethyl acetate); m.p. > 245 °C (dec.); R_f = 0.64 (ethyl acetate/methanol, 15:1).

II: **25** (0.160 g, 0.3 mmol, 25 %) was obtained as yellow crystals; m.p. > 248 °C (dec.); R_f = 0.27 (ethyl acetate/methanol, 15:1).

Method B: To a solution of ferrocene-1,1′-dicarbaldehyde (**16**; 0.242 g, 1.0 mmol) in 1,2-dichloroethane (30 mL) was added 2-amino-6,7,8,9-tetrahydro-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**; 0.430 g, 2 equiv.), and the suspension was stirred at 25 °C for 3 h. Sodium triacetoxyborohydride (0.636 g, 3 equiv., 6.5 mmol) was added, and the mixture was stirred at 25 °C for 28 h. After addition of 1 M NaOH (15 mL) the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layers were dried with $MgSO_4$, and the solvents were removed at reduced pressure. The crude product was purified by column chromatography (30 × 3 cm, SiO_2 ethyl acetate/methanol, 15:1) to give **25** (0.540 g, 0.9 mmol, 85 %) as yellow crystals; m.p. > 248 °C (dec.); R_f = 0.27 (ethyl acetate/methanol, 15:1).

24: Crystal structure analysis: CCDC 1992993.[74] IR: $\tilde{\nu}$ = 3078 (w), 2947 (m, CpH), 2870 (w, CpH), 1660 (s, CO), 1583 (s), 1460 (m), 1382 (s), 1220 (w), 1170 (w), 1031 (s), 920 (s), 783 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95–2.05 (m, 4H, $NCH_2CH_2CH_2$), 2.99 (t, J = 6.8 Hz, 2H, $NCH_2CH_2CH_2CH_2$), 3.97 (s, 4H, CH_2NCH_2), 4.08 + 4.20 (AA′BB′, 2 × 4H, CpH), 4.11 (t, J = 6.0 Hz, 2H, NCH_2), 7.45 (dd, J = 3.2 Hz, J = 9.2 Hz, 1H, OCCCHCC*H*), 7.56 (d, J = 9.2 Hz, 1H, OCCCHCCHC*H*), 7.73 (d, J = 2.8 Hz, 1H, OCCC*H*) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.5 ($NCH_2CH_2CH_2$), 22.3 (NCH_2CH_2), 31.7 ($NCH_2CH_2CH_2CH_2$), 42.3 (NCH_2), 46.4 (CH_2NCH_2), 69.3 ($C_{Cp}H$), 70.0 ($C_{Cp}H$), 83.8 (*C*CpC), 107.1 (OCCCHCCHCH), 121.5 (OCCCHCCH), 121.8 (OCCCH), 127.7 (OCCCHCCHCHC), 139.4 (OCCCHC), 147.7 (OCCCH), 151.1 (NCO), 162.2 (NCN) ppm. MS (70 eV): m/z (%) = 425 (3.3) $[M]^+$, 219 (29.6), 209 (74.3), 135 (100), 69 (9.2). EI-HRMS: m/z calcd. for $C_{24}H_{23}FeN_3O$ 425.1191, found 425.1187.

25: IR: $\tilde{\nu}$ = 3269 (m, NH), 3076 (w), 2943 (m, CpH), 2870 (w, CpH), 1658 (s, CO), 1618 (s, CO), 1583 (s), 1490 (s), 1375 (s), 1188 (w), 1053 (w), 920 (m), 785 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3/CD_3OD$, 1.5:1): δ = 1.92–2.06 (m, 8H, $NCH_2CH_2CH_2CH_2$), 2.95 (t, J = 6.8 Hz, 4H, $NCH_2CH_2CH_2CH_2$), 4.07 (t, J = 6.0 Hz, 4H, NCH_2), 4.1 (s, 4H, CH_2NH), 4.17 + 4.30 (AA'BB', 2 × 4H, CpH), 7.14 (dd, J = 2.8 Hz, J = 8.8 Hz, 2H, OCCCHCCH), 7.29 (d, J = 3.6 Hz, 2H, OCCCH), 7.39 (d, J = 8.8 Hz, 2H, OCCCHCCHCH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3/CD_3OD$, 1.5:1): δ = 19.1 ($NCH_2CH_2CH_2$), 22.0 (NCH_2CH_2), 31.0 ($NCH_2CH_2CH_2CH_2$), 42.5 (NCH_2), 43.0 ($NHCH_2$), 68.6 ($C_{Cp}H$), 68.9 ($C_{Cp}H$), 84.7 (CCpC), 104.1 (OCCCHCCHCH), 121.0 (OCCCHCCH), 123.0 (OCCCH), 126.6 (OCCCHCCHCHC), 138.9 (OCCCHC), 147.2 (OCCCH), 151.1 (NCO), 162.5 (NCN) ppm. MS (ESI, ES^+): m/z (%) = 641 (100) [M + H^+], 640 (16.5) [M^+], 321 (58). ESI-HRMS: m/z calcd. for $C_{36}H_{37}FeN_6O_2$ [M + $H]^+$ 641.2327, found 641.2330.

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