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COMPETITIVE CONDENSATION AND TANDEM CYCLIZATION REACTIONS OF 2-CYANO-3-FERROCENYLACRYLONITRILE WITH AMIDINES IN AN AQUEOUS MEDIUM

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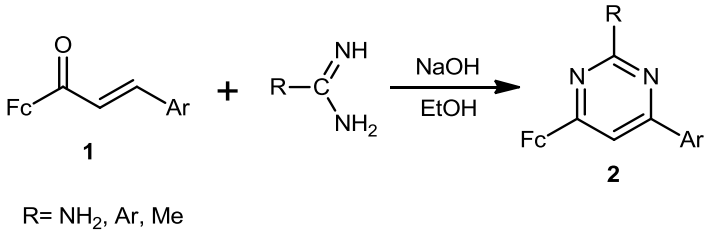
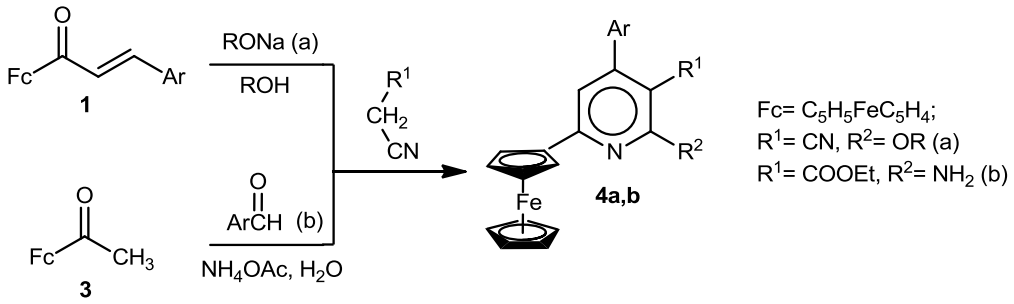
Abstract –The synthesis of a series of ferrocenyl-substituted 2-aminopyridine- and 6-amino-4,5-dihydropyridine-3,5-dicarbonitriles, 4-aminopyrimidine- and 3,4-dihydropyrimidine-5-carbonitriles by reactions of 2-cyano-3-ferrocenyl-acrylonitrile with amidines in aqueous medium is described. New fused 6-amino-2-ethoxy-4-ferrocenyl-5-ferrocenylmethyl-5-ferrocenyl methyl-4,5-dihydropyridine-3,5-dicarbonitrile was prepared in a tricomponent cyclodimerization from 2-cyano-3-ferrocenylacrylonitrile in presence of ethanol. The structures of the obtained compounds were established by IR, ^{1}H and ^{13}C NMR spectroscopy, mass-spectrometry and X-ray diffraction analysis.

Ferrocenyl-substituted organic molecules have been immensely exploited for their potential applications in diverse fields, such as organic synthesis,[1] medicinal chemistry,[2,3] supramolecular chemistry,[4] chemo- and biosensors,[5] materials science,[6] etc. The stability and non toxicity of ferrocenyl group in aqueous and aerobic media has made it an ideal candidate for use in drug designing. Heterocyclic derivatives of ferrocene are the most interesting from the point of view of the biological activity.[6-9] Many ferrocenyl-substituted nitrogen heterocycles, such as pyrazole, triazole, pyridazine, pyrimidine, quinuclidine, pyridine, etc., were reported to pertain to biologically active compounds.[9-14] Their activity depends on the nature of functional groups and of the heterocycle in the molecules. This stimulates the research on new heterocyclic compounds of the ferrocene series with potential practically useful properties. Therefore, the interest in the synthesis of novel ferrocenyl-containing heterocycles is quite justified. The past years have seen a boost in the synthesis of functionalized ferrocenyl-pyrimidines and

pyridines.[15,16] However, the approaches to the synthesis of these compounds and their properties remain largely unexplored so far. Among methods used for the synthesis of such kind of compounds, the most common are reactions of ferrocenyl-α,β-enones (**1**) (Schemes 1 and 2a) or acetylferrocene (**3**) (Scheme 2b) with amidine derivatives (for synthesis of ferrocenylpyrimidines **2**)[15-17] or with malononitrile, ethyl cyanoacetate, or with arylcarboxaldehydes in the presence NH_4OAc (for synthesis of ferrocenylpyridines **4a,b**).[18,19]



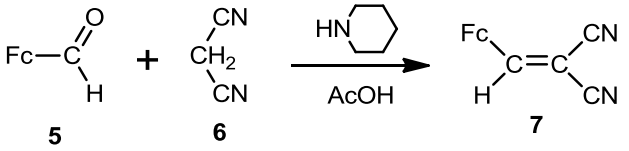
Scheme 1



Schemes 2a,b

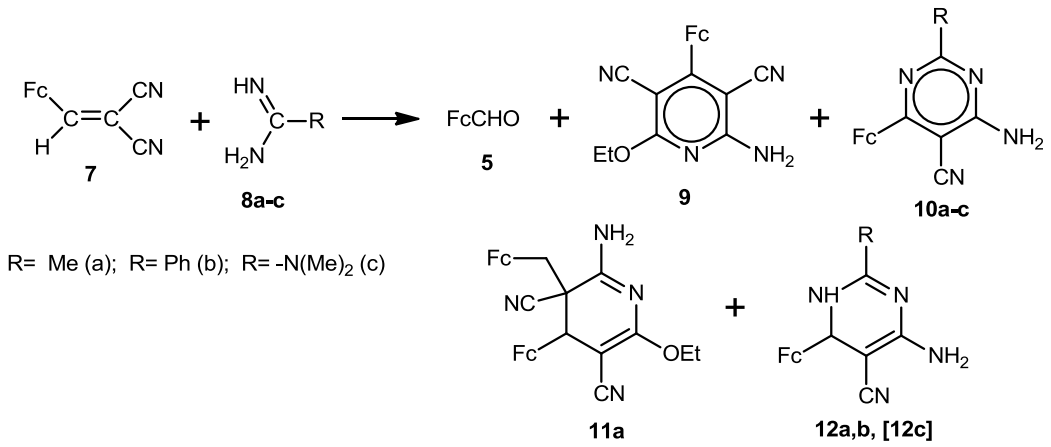
Since the synthetic approach used for obtaining heteryl-ferrocenes plays an important role and is crucial for their possible future application, the aim of our work was to develop a new convenient method of the synthesis of aminocyano(ferrocenyl)pyrimidine and pyridine derivatives by reactions of 2-cyano-3-ferrocenylacrylonitrile with amidines. To the best of our knowledge, the use of 2-cyanoacrylonitniles for the preparation of pyrimidine and pyridine derivatives has not hitherto been documented.

The starting 2-cyano-3-ferrocenylacrylonitrile (**7**) was prepared in 76% yield by condensation of ferrocenecarbaldehyde (**5**) with malononitrile (**6**) (Scheme 3). The physical and ^{1}H NMR spectroscopic characteristics of compound **7** were well in line with the literature data.[20]



Scheme 3

The reaction of 2-cyano-3-ferrocenylacrylonitrile (**7)** with acetamidine hydrochloride (**8a**) and benzamidine hydrochloride (**8b**) was performed in aqueous EtOH in presence of Na_2CO_3 at *ca*. 80-85 °C. It was found that this reaction affords ferrocenecarboxaldehyde(**5)** (~9-10%), 2-amino-6-ethoxy-4-ferrocenylpyridine-3,5-dicarbonitrile (**9**) (~23-27%), 4-amino-2-methyl(or phenyl)-6-ferrocenylpyrimi-dine-5-carbonitriles (**10a**) and (**10b**) (~9-10%), 6-amino-2-ethoxy-4-ferrocenyl-5-ferrocenylmethyl-4,5-dihydropyridine-3,5-dicarbonitrile (**11a**) (~12-15%), 6-amino-4-ferrocenyl-4-ferrocenyl-2-methyl(or phenyl)-3,4-dihydropyrimidine-5-carbonitriles (**12a**) and (**12b**) (~32-33%) (Scheme 4).



Scheme 4

Further we found that the reaction of 2-cyano-3-ferrocenylacrylonitrile (**7**) with 1,1-dimethylguanidinium sulfate (**8c**) under analogous conditions affords, in contrast to condensations of **7** with **8a** and **8b**, only four compounds: **5**, **9**, **10c**, **11a** (Scheme 4), and the product **12c** was not formed in detectable amount. Compounds **5**, **9**, **10a-c**, **11a**, and **12a,b** were isolated by column chromatography on alumina and their structures were established based on the data from IR and NMR sprctroscopy, mass spectrometry, and elemental analysis (see experimental section). The spatial structures of compounds **9**, **11a**, and **12b** were determined by X-ray diffraction analysis of their single crystals.[21] Crystals of **9** and **12b** were obtained by crystallization from $CHCl_3$, and crystals of **11a** were obtained by crystallization from CH_2Cl_2 - MeOH (1:1). The general views of molecules **9**, **11a**, and **12b** are shown in Figures 1-3, respectively. The data from X-ray diffraction analysis confirmed the aromatic pyridine and dihydropyridine structures for

compounds **9** and **11a**, respectively, and the dihydropyrimidine structure for compound **12b**. The central fragment of the molecule **9** is a flat six-membered ring with one nitrogen atom. Data from the X-ray analysis show that the N(1)-C(15) bond in the compound **9** is somewhat shorter [*d* = 1.320(4) Å] than the standard value of 1.338 Å.[22] The C(15)-C(14), C(11)-C(12) and C(12)-C(13) bond lengths are somewhat longer [*d* = 1.413(4) Å, *d* = 1.413(5) Å and *d* = 1.414(5) Å, respectively] than the standard value of 1.339 Å.[23] The lengths of the C-Fe and C-C bonds in the ferrocenyl substituents, as well as the geometric parameters of the ferrocene sandwiches are close to standard values.[24] The central nonplanar fragment of the molecule **11a** is a six-membered ring with one nitrogen atom in the half-chair conformation. The N(1)-C(25), N(1)-C(26), C(23)-C(24) and C(24)-C(25) bond lengths are equal to *d* = 1.377(3) Å, *d* = 1.315(3) Å, *d* = 1.516(3) Å, and *d* = 1.362(3) Å, respectively. The ferrocenyl and ferrocenylmethyl substituents at C-4 and C-5 have *trans*-orientation.

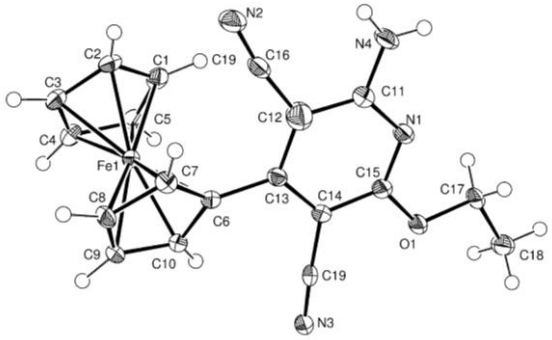


Figure 1. X-Ray crystal structure of compound **9**

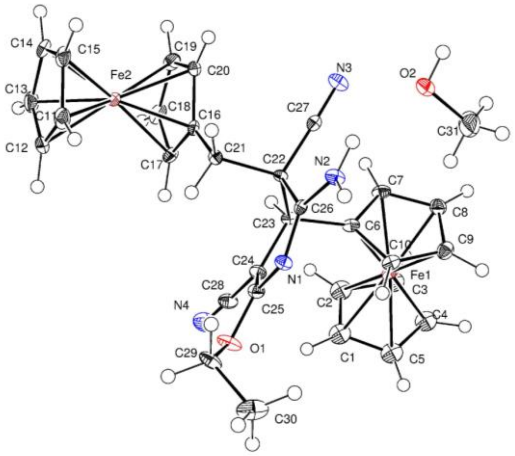


Figure 2. X-Ray crystal structure of compound **11a**

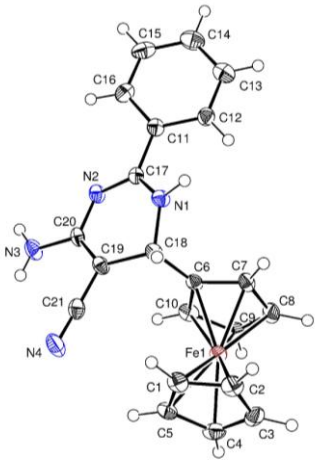
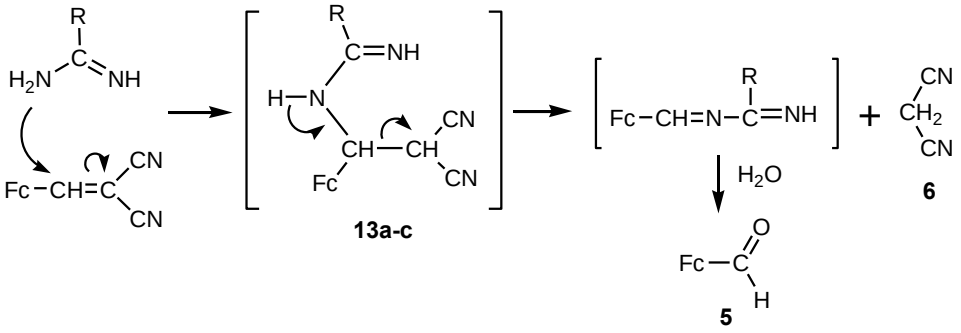


Figure 3. X-Ray crystal structure of dihydropyrimidine **12b**

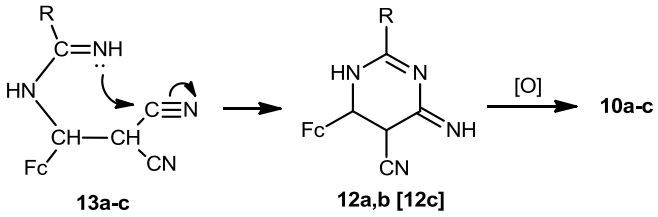
The central nonplanar fragment of the molecule **12b** is a six-membered ring with two nitrogen atoms in the half-chair conformation. Data from the X-ray analysis show that the N(1)-C(17), N(2)-C(17) and N(3)-C(20) bonds in the dihydropyrimidine are somewhat shorter [*d* = 1.335(5) Å, *d* = 1.318(4) Å and *d* =

1.361 Å, respectively] than the corresponding standard values of *d* = 1.387 Å, *d* = 1.355 Å and *d* = 1.394 Å.[23]

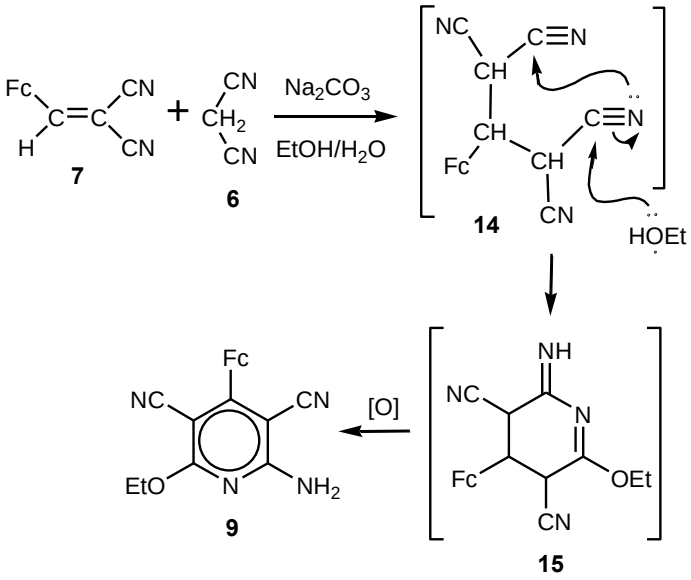
a)



b)



c)

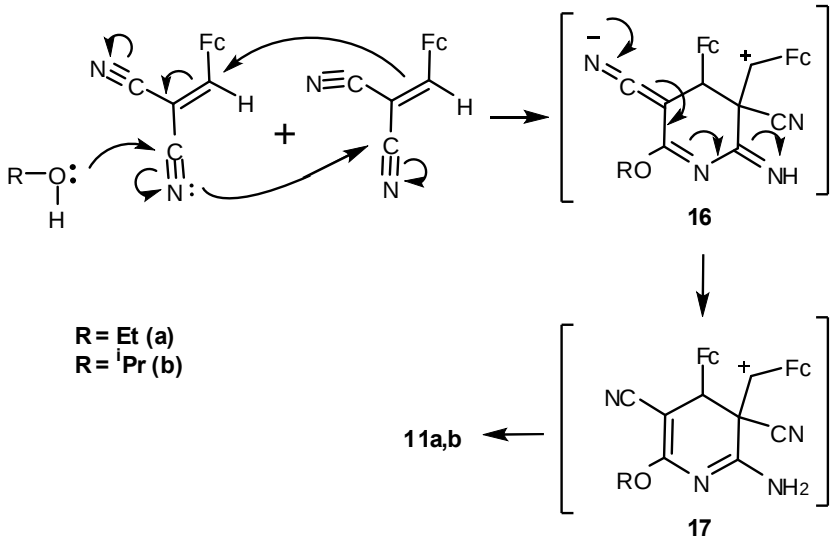


Schemes 5a-c

Although the detailed mechanism of the reaction shown in Scheme 4 requires to be fully clarified, the formation of ferrocenylcarboxaldehyde **5**, 2-amino-6-ethoxy-4-ferrocenylpyridine-3,5-dicarbonitrile **9**, 4-amino-6-ferrocenylpyrimidine-5-carbonitriles **10a-c** and **12a,b** can be explained by possible reaction

sequence presented in Schemes 5a-c. Compound **5** may be formed *via* sequential addition of the amidines **8a-c** at the double bond FcCH=C of the inicial compound **7** (the Michael addition) resulting in intermediate products **13a-c**, further fragmentation of which can lead to aldehyde **5** and malononitrile **6** (Scheme 5a). This type of fragmentation of C_α–C_β bonds in the ferrocenyl-β-dicarbonilic compouds was well documented in previous publications.[35] The intramolecular cyclization of (**13a-c**) gives dihydropyrimidines **12a,b** and aromatic pyrimidines **10a-c** (Scheme 5b). The addition between malononitrile **6** and 2-cyano-3-ferrocenylacrylonitrile **7** affords intermediate (**14**), which upon intramolecular cyclization in the presence of EtOH gives rise to (**15**) and **9** (Scheme 5c). This type of cyclization represents, in reality, a tricomponent reaction.

Tentative mechanism for the formation of the diferrocenyl(dihydro)pyridine-3,5-dicarbonitriles **11a,b** is represented in Scheme 6.



Scheme 6

To prove the mechanism described above, the cyclodimerization of 2-cyano-3-ferrocenylacrylonitrile **1** was carried out under identical conditions in isopropyl alcohol in presence of water and Na_2CO_3. The product of the cyclodimerization, 6-amino-4-ferrocenyl-5-ferrocenylmethyl-2-isopropoxy-4,5-dihydropyridine-3,5-dicarbonitrile **4b**, was obtained with ~ 27% yield. Thus, this cyclodimerization of compound **1** represents a novel type of the three-component *anomalous* reaction of [4+2]-cycloadition, absolutely different from the reaction of Diels-Alder.

Thus, in the present work, a convenient method of obtaining of 6-alkoxy-2-amino-4-ferrocenylpyridine-3,5-dicarbonitriles, 2-alkoxy-6-amino-4-ferrocenyl-5-ferrocenylmethyl-4,5-dihydropyridine-3,5-dicarbonitriles, 6-amino-4-ferrocenyl-2-(alkyl or aryl)-3,4-dihydropyrimidine-5-carbonitriles and 4-amino-6-ferrocenyl-2-(alkyl or aryl)pyrimidine-5-carbonitriles based on accessible 2-cyano-

3-ferrocenylacrylonitrile **7** was developed. This method can be widely used in the synthesis of various ferrocene derivatives. The reactions described in this study will be of interest to synthetic, theoretical and practical organic chemists looking for obtaining functionalized ferrocenylheterocycles.

EXPERIMENTAL

Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$, with Me_4Si as the internal standard. The IR spectra were measured on a Spectrofotometer FT-IR (Spectrum RXI Perkin Elmer instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The unit cell parameters and the X-ray diffraction intensities were recorded on a Gemini (detector AtlasCCD, Cryojet N_2) diffractometer. The structures of compounds **9**, **11a** and **12b** were solved by the direct method (SHELXS-97[25]).

Tipical procedure of the reactions of 2-cyano-3-ferrocenylacrylonitrile (7) with acetamidine (8a), benzamidine (8b) and 1,1-dimethylguanidine (8c). A mixture of compound **7** (2.26 g, 10 mmol), acetamidine hydrochloride **8a** (1.4 g, 15 mmol), benzamidine hydrochloride **8b** (2.34 g, 15 mmol) or 1,1-dimethylguanidinium sulfate **8c** (2.05 g, 15 mmol), EtOH (100 mL), H_2O (10 mL) and 2.0 g Na_2CO_3 was stirred for 8 h at 80 ^{o}C. The solvents were removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (50 mL). The solution was mixed with Al_2O_3 (activity III) (20 g) and the solvent was evaporated in air. This sorbent was applied onto a column with Al_2O_3 (the height of alumina is *ca*. 20 cm) and the reaction products were eluted from the column first with petroleum ether, then with a 1:2 CH_2Cl_2 - petroleum ether and 1:10 CH_2Cl_2 - MeOH solvent system to give compounds **5** (0.09g, 9% from **8a**; 0.11g, 11% from **8b**); 0.1g, 10% from **8c**), **9**, **10a-c**, **11a** and **12a,b**.

2-Amino-6-ethoxy-4-ferrocenylpyridine-3,5-dicarbonitrile (**9)**: yield 0.5g (27.5%, from **8a**), 0.4g (22%, from **8b**) and 0.42g (23%, from **8c**), red crystals, mp 168-169 °C. IR 499, 817, 1006, 1109, 1483, 1555, 1611, 2202, 2218, 2978, 3105, 3226, 3369cm^{-1}; ^{1}H NMR δ 1.43 (t, *J* = 7.08 Hz, 3H), 4.43 (q, *J* = 7.08 Hz, 2H), 4.28 (s, 5H), 4.58 (m, 2H), 5.21 (m, 2H), 5.58 (bs, 2H); ^{13}C NMR δ 14.43, 59.10, 64.12, 70.99, 69.62, 69.85, 70.89, 71.10, 84.99, 116.32, 117.68, 160.12, 161.54, 164.88, 167.18, 170.09; MS: *m/z* 372 $[M]^{+}$. Anal. Calcd for $C_{19}H_{16}FeN_4O$: C, 61.32; H, 4.33; N, 15.05. Found: C, 61.39; H, 4.42; N, 15.07.

4-Amino-6-ferrocenyl-2-methylpyrimidine-5-carbonitrile (**10a)**: yield 0.32 g (10%), red crystals, 182-183 °C. IR 485, 822, 1000, 1100, 1494, 1568, 1595, 1655, 2167, 2930, 3135, 3323, 3377 cm^{-1}; ^{1}H NMR δ 2.53 (s, 3H), 4.18 (s, 5H), 4.56 (m, 2H), 5.32 (m, 2H), 5.52 bs, 1H); ^{13}C NMR δ 26.00, 69.95, 69.21, 71.06, 79.06, 117.09, 164.28, 168.25, 169.21, 171.45; MS: *m/z* 318 $[M]^{+}$. Anal. Calcd. for

$C_{16}H_{14}FeN_4$: C, 60.40; H, 4.44; N, 17.60. Found: C, 60.31; H, 4.53; N, 17.58.

4-Amino-6-ferrocenyl-2-phenylpyrimidine-5-carbonitrile (**10b)**: yield 0.34g (9%), red crystals, mp 197-198 °C. IR 483, 821, 1001, 1106, 1461, 1485, 1531, 1615, 2208, 3093, 3223, 3331 cm^{-1}; ^1H NMR δ 4.18 (s, 5H), 4.58 (m, 2H), 5.44 (m, 2H), 5.63 (bs, 2H), 7.32-7.72 (m, 5H); ^{13}C NMR δ 70.51, 70.04, 71.92, 79.22, 117.50, 128.55, 128.96, 131.65, 137.01, 137.54, 164.42, 164.70,170.83; MS: *m/z* 380 $[M]^+$. Anal. Calcd for $C_{21}H_{16}FeN_4$: C, 66.33; H, 4.24; N, 14.73. Found: C, 66.42; H, 4.17; N, 14.65.

4-Amino-2-dimethylamino-6-ferrocenylpyrimidine-5-carbonitrile (**10c)**: yield 1.46 g (42%), red crystals, mp 156-157 °C. IR 483, 818, 1000, 1104, 1557, 1612, 1633, 2160, 2927, 3094, 3322, 3467 cm^{-1}; ^1H NMR δ 3.21 (bs, 6H), 4.17 (s, 5H), 4.46 (m, 2H), 5.22 (m, 2H), 5.25 (m, 2H); ^{13}C NMR δ 36.95, 70.29, 69.65, 71.02, 80.31, 119.44, 164.81, 170.06, 178.67, 189.72; MS: *m/z* 347 $[M]^+$. Anal. Calcd For $C_{17}H_{17}FeN_5$: C, 58.81; H, 4.93; N, 20.16. Found: C, 58.75; H, 4.81; N, 20.23.

6-Amino-2-ethoxy-4-ferrocenyl-5-ferrocenylmethyl-4,5-dihydropyridine-3,5-dicarbonitrile (**11a)**: yield 0.19g (14%, from **8a**), 0.16g (12%, from **8b**), 0.2 g (15%, from **8c**), yellow crystals, mp dec. *ca*. 273 °C. IR 482, 1001, 1106, 1553, 1595, 1638, 1665, 2194, 2245, 3098, 3325 cm^{-1}; ^1H NMR δ 1.40 (t, *J* = 6.9 Hz, 3H), 2.92 (d, *J* = 14.1 Hz, 1H), 3.11 (d, *J* = 14.1 Hz, 1H), 3.43 (s, 1H), 4.33 (q, *J* = 6.9 Hz, 2H), 4.15 (s, 5H), 4.28 (s, 5H), 3.87 (m, 1H), 4.09 (m, 1H), 4.13 (m, 1H), 4.17 (m, 2H), 4.24 (m, 2H), 4.43 (m, 1H), 5.56 (bs, 2H); ^{13}C NMR δ 15.53, 37.01, 63.55, 41.42, 69.09, 69.60, 66.98, 68.24, 68.60, 68.91, 68.95, 69.17, 69.87, 70.29, 79.33, 83.64, 119.22, 120.51, 51.30, 160.54, 164.30, 165.68, 165.98; MS: *m/z* 572 $[M]^+$. Anal. Calcd for $C_{30}H_{28}Fe_2N_4O$: C, 62.96; H, 4.93; N, 9.79. Found: C, 62.97; H, 4.62; N, 9.55.

6-Amino-4-ferrocenyl-2-methyl-3,4-dihydropyrimidine-5-carbonitrile (**12a)**: yield 1.02 g (32%), yellow crystals, mp 203-204 °C. IR 485, 822, 1000, 1100, 1494, 1568, 1595, 1655, 2167, 2930, 3323, 3377 cm^{-1}; ^1H NMR δ 1.75 (s, 3H), 3.92 (m, 1H), 3.97 (m, 3H), 4.04 (s, 5H), 4.71 (d, *J* = 3.0 Hz, 1H), 5.55 (bs, 1H), 5.64 (bs, 2H); ^{13}C NMR δ 22.01, 52.87, 69.12, 65.74, 65.84, 67.51, 67.99, 95.29, 122.99, 148,94, 159.50, 160.14; MS: *m/z* 320 $[M]^+$. Anal. Calcd for $C_{16}H_{16}FeN_4$: C, 60.02; H, 5.04; N, 17.50. Found: C, 59.91; H, 4.89; N 17.51.

6-Amino-4-ferrocenyl-2-phenyl-3,4-dihydropyrimidine-5-carbonitrile (**12b)**: yield 1.26 g (33%), yellow crystals, mp 218-219 °C. IR 499, 812, 998, 1105, 1573, 1596, 1635, 2168, 3073, 3135, 3255 cm^{-1}; ^1H NMR δ 4.13 (m, 3H), 4.19 (m, 1H), 4.21 (s, 5H), 4.97 (d, *J* = 2.8 Hz, 1H), 5.74 (bs, 1H), 6.01 (bs, 2H), 7.49-7.55 (m, 3H), 7.87 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR δ 54.14, 69.17, 65.73, 65.95, 67.62, 68.24, 95.25, 122.82, 127.88, 128.87, 131.99, 133.93, 157.57, 159.9, 162.41; MS: *m/z* 382 $[M]^+$. Anal. Calcd. for $C_{21}H_{18}FeN_4$: C, 66.00; H, 4.74; N, 14.65. Found: C, 65.97; H, 4.58; N, 14.78.

Tipical procedure of the cyclodimerization of 2-cyano-3-ferrocenylacrylonitrile 7 in the presence 2-PrOH, H_2O and Na_2CO_3. A mixture of compound **7** (1.13 g,5 mmol), 2-PrOH (60 mL), H_2O (10 mL)

and 1.0 g Na_2CO_3 was stirred for 12 h at 80 °C. The reaction mixture was worked up as described above, subsequent chromatography on Al_2O_3 gave 6-amino-4-ferrocenyl-5-ferrocenylmethyl-2-isoprpoxy-4,5-dihydropyridine-3,5-dicarbonitrile **11b**, yield 0.4g (27%), yellow crystals, mp *ca*. 302 °C (decomp). IR 483, 821, 1001, 1106, 1294, 1316, 1355, 1423, 1585, 1629, 2191, 2230, 3095, 3241, 3335 cm^{-1}; ^1H NMR δ 1.39 (d, *J* = 6.0 Hz, 6H), 2.90 (d, *J* = 13.8 Hz, 1H), 3.09 (d, *J* = 13.8 Hz, 1H), 3.81 (s, 1H), 4.13 (s, 5H), 4.28 (s, 5H), 4.08 (m, 1H), 4.16 (m, 2H), 4.23 (m, 2H), 4.28 (m, 2H), 4.42 (m, 1H), 5.07 (m, *J* = 6.0 Hz, 1H), 5.54 (bs, 2H); ^{13}C NMR δ 21.94, 36.96, 41.40, 66.96, 69.04, 69.56, 68.20, 68.54, 68.90, 68.94, 69.09, 69.84, 70.38, 71.52, 79.25, 83.68, 119.16, 120.49, 51.28, 160.43, 161.54, 165.37, 166.82; MS: *m/z* 586 $[M]^+$. Anal. Calcd for $C_{31}H_{30}Fe_2N_4O$: C, 63.51; H, 5.16; N, 9.55. Found: C, 63.67; H, 5.03; N 9.41.

ACKNOWLEDGEMENTS

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21. Crystallographic data for the structure of compounds **9** (CCDC-872988), **11b** (CCDC-873043) and **12b** (CCDC–873044) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge DB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk. These data can be obtained free of charge *via* www.ccdc.com uk/data_request/cif.
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