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SYNTHESIS OF FERROCENYL-3,4-DIHYDRO-1*H*-PYRIMIDIN-2-ONES

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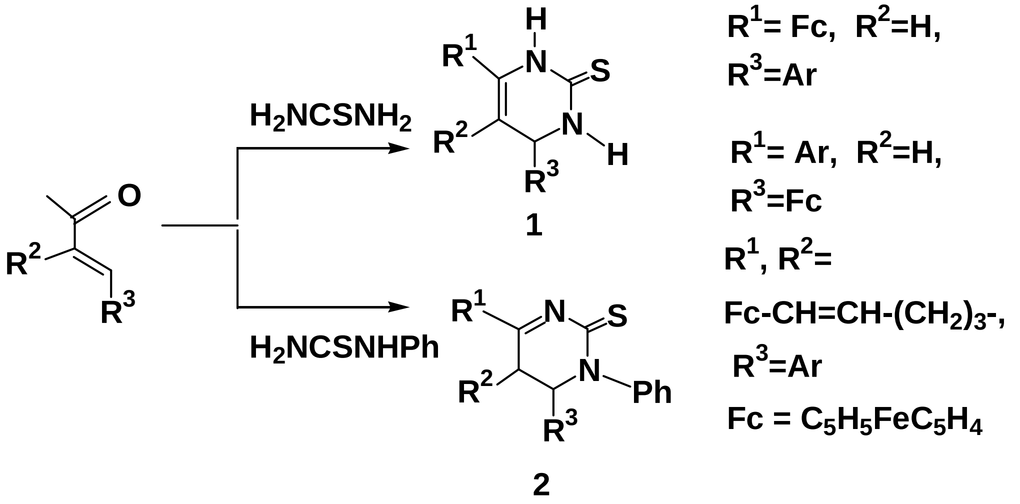
Abstract –Methylurea reacts with linear and cyclic α,β-enones of the ferrocene series to yield ferrocenyl-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-ones characterized by IR and ^{1}H and ^{13}C NMR spectroscopical data. The structure of 4-ferrocenyl-6-(4-methoxyphenyl)-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one is confirmed by X-Ray diffraction analysis.

INTRODUCTION

Urea, thiourea, and their derivatives are employed in the synthesis of pyrimidines which often serve as fragments of many biologically active compounds and represent nucleic acid components.[1-3] The use of these reagents in the chemistry of metallocenes has been described by the examples of the reactions of α,β-enones of the ferrocene series with thiourea and phenylthiourea.[4-9] The reactions were carried out in boiling alcohols in the presence of sodium alkoxides[5,6,8,9] or with sonication.[7] The structures of tetrahydropyrimidine-2-thiones (**1**) with a C=C double bond at positions 5,6 of the heterocycle were ascribed to the condensation products with thiourea,[5-8] while the structures of tetrahydropyrimidine-2-thiones (**2**) with a C=N double bond in the molecule were obtained by the condensation with phenylthiourea[9] (Scheme 1).

The use of urea and its analogues in similar condensations has not hitherto been studied. The potential possibility of the practical use of the expected reaction products, *e.g.*, as physiologically active compounds, explains the interest in the synthesis of ferrocenyl-substituted tetrahydropyrimidin-2-ones and in the detailed investigations into their structures and chemical properties.

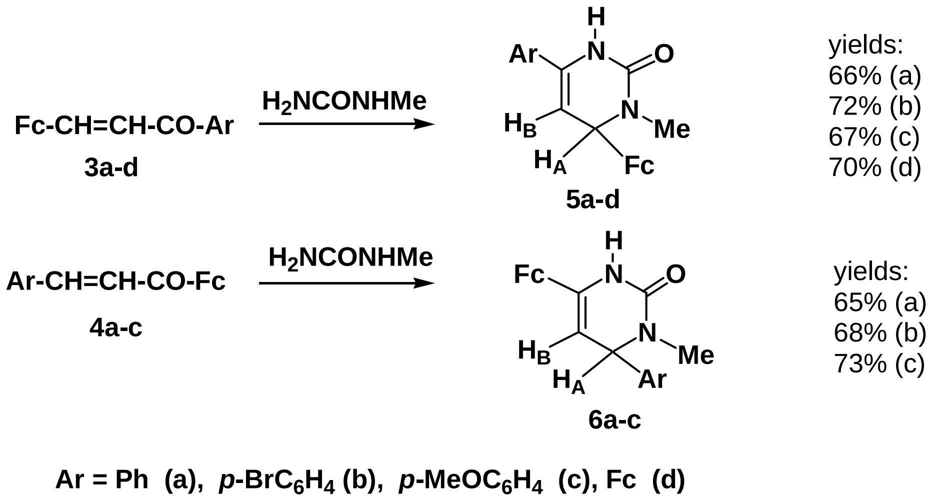


Scheme 1. Synthesis of tetrahydropyrimidine-2-thiones (**1**) and (**2**)

In the present paper, we report the reactions of methylurea with α,β-enones with a ferrocene substituent in the molecule.

RESULTS AND DISCUSSION

We have found that methylurea reacts with the chalcones (**3a-d**) and (**4a-c**) on boiling in anhydrous isopropyl alcohol in the presence of *t*-BuOK to give 3,4-dihydro-1*H*-pyrimidin-2-ones (**5a-d**) and (**6a-c**), respectively, in yields of 60-75% (Scheme 2).



Scheme 2. Reaction of linear enones with methylurea

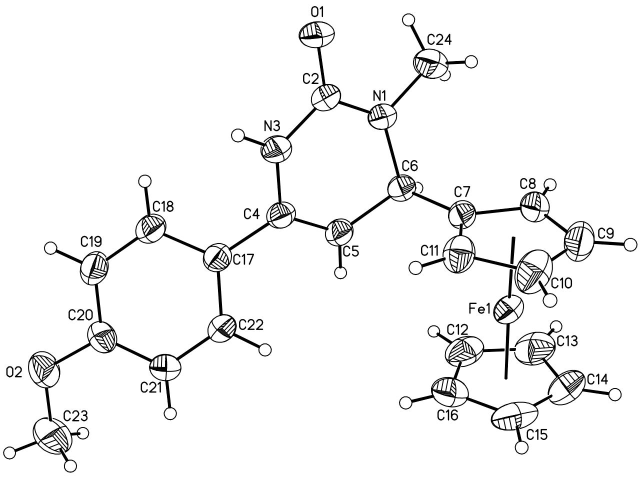
Ferrocenyldihydropyrimidin-2-ones (**5**) and (**6**) are the only reaction products isolated. Compounds (**5a-c**) are finely crystalline, pale yellow substances, compounds (**5d**) and (**6a-c**) are orange colored. In solid state, these products are storage-stable, but decompose gradually when stored as solutions in the majority of common solvents (chloroform, dichloromethane, ethyl acetate, acetone, benzene, etc.). It can be noted that compounds (**5a-d**) are more stable in solutions than compounds (**6a-c**).

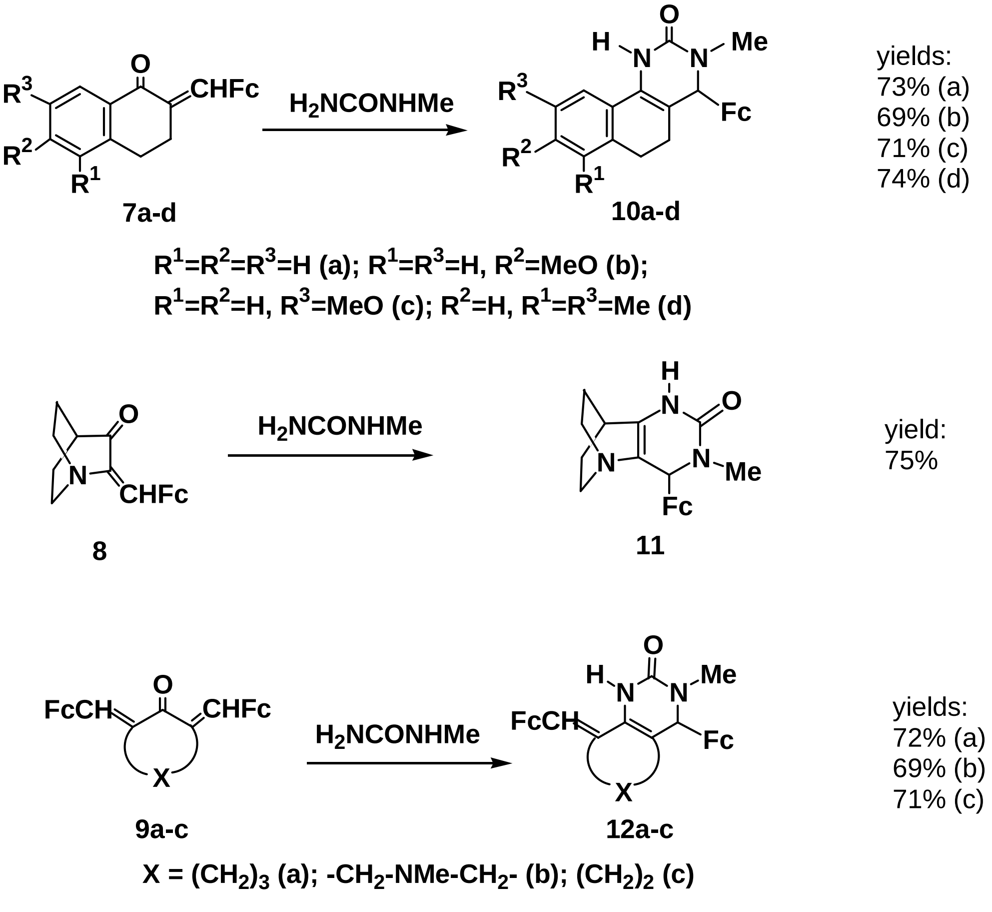
Data from IR and ^1H and ^{13}C NMR spectroscopy and elemental analysis (see EXPERIMENTAL) confirm their structures. The ^1H NMR spectra of compounds (**5a-d**) and (**6a-c**) contain singlets for the protons of the methyl groups, signals for the protons of the imino groups (-NH-), and AB-spin systems of H(5) and H(6) typical of 3,4-dihydro-1*H*-pyrimidin-2-ones. The spectral patterns depend substantially on the position of the ferrocenyl substituent in the heterocycle. Thus for the 3,6-dihydro-1*H*-pyrimidin-2-ones (**5a-d**) with the ferrocenyl group at position 4, the signals for the protons H_A appear at δ 4.62-4.86 and those for H_B, at δ 5.21-5.57, the difference $\Delta\delta = \delta_A$-δ_B lying in the range 0.56-0.71 ppm. For the tetrahydropyrimidin-2-ones (**6a-c**) with the ferrocenyl group at position 6, the signals for the protons H_A and H_B appear at δ 4.82-5.02 and differ insignificantly [$\Delta\delta$ = 0.08 (**6a**), –0.03 (**6b**), and 0.00 ppm (**6c**)].

The chemical shifts for the protons of the ferrocenyl groups in the isomers are affected by the position of this group. Thus for 6-ferrocenyldihydropyrimidin-2-ones (**6a-c**), all of the signals for the protons of the substituted cyclopentadienyl ring are down-field shifted as compared with the signals for the protons of the nonsubstituted cyclopentadienyl ring. Hence, the effect of the tetrahydropyrimidin-2-one fragment of the molecule is analogous to that of a strong electron-withdrawing substituent,[10] probably, owing to the interaction of the ferrocene electronic π system with the π electrons of the C=C bond of the dihydro-1*H*-pyrimidin-2-one. In the case of 4-ferrocenyldihydropyrimidin-2-ones (**5a-d**) with ferrocenyl substituents at the sp^3-hybridized carbon atoms, a portion of the protons of the substituted cyclopentadienyl ring resonate at the higher field than the signals for the protons of the C_5H_5 group. The observed differences between the spectral patterns of 4- and 6-ferrocenyldihydropyrimidin-2-ones may apparently be employed for spectroscopic identification of the isomeric ferrocenyldihydropyrimidin-2-ones.

The structure of one of the products obtained, namely, compound (**5c**), was established by X-Ray diffraction analysis of a single crystal prepared by crystallization from benzene. According to X-Ray diffraction data, compound (**5c**) is indeed 4-ferrocenyl-6-(4-methoxyphenyl)-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one (**5c**). The general view of the molecule (**5c**) is shown in Figure 1 and deserve no special comments.

We also studied the reactions of methylurea with certain conjugated mono- and bisferrocenylmethylidene ketones (**7a-d**, **8**), and (**9a-c**) of the carbocyclic and heterocyclic series. In all cases, the reactions are fast and result in the corresponding polycyclic ferrocenyldihydropyrimidin-2-ones (**10a-d**, **11**), and (**12a-c**) in high yields (Scheme 3).





Scheme 3. Reaction of mono- and bisferrocenylmethylidene ketones with methylurea

The structures of compounds (**10a-d**, **11**, and **12a-c**) were established unequivocally based on the data from IR and ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The positions of the double bonds in compounds (**10-12**) followed from the multiplicities and chemical shifts of the protons of the substituted cyclopentadienyl ring of the Fc-fragments at positions 4 of the pyrimidine moieties: some of the protons are up-field shifted as compared with the singlets for the protons of the C_5H_5-ring, as was the case for compounds (**5a-d**). The presence of the appropriate amount of signal for carbon atoms bearing no hydrogen atoms in the ^{13}C NMR spectra serves as an additional evidence in favor of the structures discussed.

In the reactions studied, high regioselectivity of the formation of compounds (**5, 6**, **10-12)** worth noting. These compounds have been isolated as single enamide forms. The formation of minor amounts of isomers of the type (**2**) cannot be completely ruled out, but their low percentage (if at all) precludes unambiguous identification.

EXPERIMENTAL

The IR spectra were measured on a Specord IR-75 instruments for KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $(CD_3)_2CO$, $CDCl_3$, and CD_3CN with Me_4Si as the internal standard. The chromatographic separations were carried out on columns with alumina (Brockmann activity III) using a hexane–ether mixture (1:2, v/v) as an eluent.

The following reagents from Aldrich were employed: ferrocenecarbaldehyde, 99%; acetylferrocene, 95%; acetophenone, 99%; *p*-bromoacetophenone, 98%; *p*-methoxyacetophenone, 99%; benzaldehyde, 99%; *p*-bromobenzaldehyde, 99%; *p*-anisaldehyde, 98%; cyclohexanone, 99%; 1-methyl-4-piperidone, 97%; cyclopentanone, 99%; 3-quinuclidone hydrochloride, 97%; α-tetralone, 98%; 6-methoxy-1-tetralone, 99%; 7-methoxy-1-tetralone, 99%; 5,7-dimethyl-1-tetralone, 97%; methylurea, 97%.

The unit cell parameters and intensities of reflections were measured on a Siemens P4/PC/ω diffractometer.

The chalcones (**3a-d**, **7a-d**, **8**, and **9a-c**) were prepared from ferrocenecarbaldehyde and the corresponding ketones in aqueous-ethanolic NaOH,[11-15] compounds (**4a-c**) were prepared from acetylferrocene and aromatic aldehydes under analogous conditions.

Synthesis of ferrocenyl-3,4-dihydro-1*H*-pyrimidin-2-ones. General procedure

A mixture of a chalcone (**3**, **4**, **7-9)**[11-15] (5 mmol), methylurea (949 mg, 12 mmol) and *t*-BuOK (1120 mg, 10 mmol) in anhydrous *i*-PrOH (100 mL) was boiled under reflux for 2-4 h with stirring until the bright-red color of the chalcone faded resulting in the appearance of a yellow- or orange-colored solution. The reaction mixture was rapidly poured in water (200 mL), the precipitate that formed was filtered off, washed with water on a filter, and dried *in vacuo*. Additional purification was achieved by chromatography on a column with alumina or recrystallization from morpholine or benzene.

4-Ferrocenyl-3-methyl-6-phenyl-3,4-dihydro-1*H*-pyrimidin-2-one (**5a**), yield 1.22 g (66%), pale yellow crystals, mp 209-211 °C. [Anal. Calcd for $C_{21}H_{20}N_2OFe$: C, 67.76; H, 5.42; N, 7.52; Fe, 15.00. Found: C, 67.64; H, 5.61; N, 7.35; Fe, 15.20.]; ν_{max} (KBr)/cm^{-1}: 766, 816, 1030, 1105, 1222, 1285, 1337, 1399, 1447, 1490, 1525, 1570, 1600, 1660, 2830, 2933, 3095, 3234, 3429; δ_H ($(CD_3)_2CO$) : 2.82 (3H, s, CH_3), 4.16 (1H, m, C_5H_4), 4.20 (1H, m, C_5H_4), 4.22 (1H, m, C_5H_4), 4.25 (5H, s, C_5H_5), 4.35 (1H, m, C_5H_4), 4.86 (1H, d, *J* = 5.1 Hz, CH), 5.57 (1H, dd, *J* = 2.0, 5.1 Hz, CH=), 7.52 (1H, d, *J* = 2.0 Hz, NH,), 7.43-7.50, 7.63-7.75 (5H, m, C_6H_5); δ_C ($(CD_3)_2CO$): 32.95 (CH_3), 58.3 (CH), 67.8, 68.8, 69.2, 69.3 (C_5H_4), 69.5 (C_5H_5), 88.65 (C_{ipso}Fc), 98.8 (CH=), 126.4, 127.0, 129.5 (C_6H_5), 135.8 (C_{ipso}), 137.4 (=C–N), 153.9 (C=O).

6-(4-Bromophenyl)-4-ferrocenyl-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one (**5b**), yield 1.63 g (72%), pale yellow crystals, mp 258-260 °C. [Anal. Calcd for $C_{21}H_{19}N_2OBrFe$: C, 55.90; H, 4.24; N, 6.20; Fe, 12.38. Found: C, 56.02; H, 4.09; N, 6.33; Fe, 12.47.]; ν_{max} (KBr)/cm^{-1}: 717, 822, 1008, 1105, 1299, 1464, 1655, 1711, 1771, 2838, 2924, 3095, 3251, 3420; δ_H ($CDCl_3$): 2.91 (3H, s, CH_3), 4.17 (2H, m, C_5H_4), 4.20 (5H, s, C_5H_5), 4.22 (2H, m, C_5H_4), 4.77 (1H, d, *J* = 5.0 Hz, CH), 5.40 (1H, dd, *J* = 2.1, 5.0 Hz, CH=), 6.73 (1H, br s, NH), 7.40 (2H, d, *J* = 9.0 Hz, C_6H_4), 7.57 (2H, d, *J* = 9.0 Hz, C_6H_4); δ_C ($CDCl_3$): 32.9 (CH_3), 58.0 (CH), 67.2, 67.5, 68.2, 68.4 (C_5H_4), 68.6 (C_5H_5), 86.9 (C_{ipso}Fc), 98.35 (CH=), 126.7, 132.2 (C_6H_4), 133.4, 136.6 (C_{ipso}); 135.1 (=C–N), 156.7 (C=O).

4-Ferrocenyl-6-(4-methoxyphenyl)-3-methyl-3,4-dihydropyrimidin-2-one (**5c**), yield 1.35 g (67%), pale yellow crystals, mp 197-198 °C. [Anal. Calcd for $C_{22}H_{22}N_2O_2Fe$: C, 65.68; H, 5.52; N, 6.96; Fe, 13.88. Found: C, 65.51; H, 5.72; N, 7.08; Fe, 13.67.]; ν_{max} (KBr)/cm^{-1}: 780, 833, 1033, 1105, 1250, 1435, 1520, 1610, 1654, 1708, 2837,2933, 3095, 3234, 3429; δ_H ($CDCl_3$): 2.90 (3H, s, CH_3), 3.85 (3H, s, CH_3), 4.14 (1H, m, C_5H_4), 4.19 (5H, s, C_5H_5), 4.20 (1H, m, C_5H_4), 4.21 (2H, m, C_5H_4), 4.75 (1H, d, *J* = 5.1 Hz, CH), 5.31 (1H, dd, *J* = 2.1, 5.1 Hz, CH=), 6.52 (1H, br s, NH), 6.96 (2H, d, *J* = 9.0 Hz, C_6H_4), 7.45 (2H, d, *J* = 9.0 Hz, C_6H_4); δ_C ($CDCl_3$): 32.85 (CH_3), 55.4 (CH_3), 58.0 (CH); 67.3, 68.0, 68.3, 68.6 (C_5H_4), 68.7 (C_5H_5), 87.4 (C_{ipso}Fc), 96.45 (CH=), 114.3, 126.4 (C_6H_4), 127.0, 153.4 (C_{ipso}), 135.5 (=C–N), 160.2 (C=O).

4,6-Diferrocenyl-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one (**5d**), yield 1.18 g (70%), pale yellow crystals, mp 181-182 °C. [Anal. Calcd for $C_{25}H_{24}N_2O\ Fe_2$: C, 62.53; H, 5.04; N, 5.83; Fe 23.26. Found: C, 62.38; H, 4.87; N, 6.03; Fe, 23.17.]; ν_{max} (KBr)/cm^{-1}: 756, 818, 1001, 1107, 1294, 1484, 1594, 1654, 1718, 2874, 2928, 3091, 3218, 3422; δ_H ($CDCl_3$): 2.89 (3H, s, CH_3), 4.15 (1H, m, C_5H_4), 4.17 (1H, m, C_5H_4), 4.19 (2H, m, C_5H_4), 4.20 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5), 4.32 (1H, m, C_5H_4), 4.34 (1H, m, C_5H_4), 4.43 (1H, m, C_5H_4), 4.50 (1H, m, C_5H_4), 4.62 (1H, d, *J* = 4.8 Hz, CH), 5.21 (1H, dd, *J* = 2.1, 4.8 Hz, CH=), 6.41 (1H, br s, NH); δ_C ($CDCl_3$): 32.86 (CH_3), 58.0 (CH), 67.2, 67.9, 68.3, 68.5, 68.7, 68.8, 69.1, 69.2 ($2C_5H_4$), 68.6, 69.3 ($2C_5H_5$), 79.9, 87.2 ($2C_{ipso}$Fc), 94.85 (CH=), 133.5 (=C–N), 153.5 (C=O).

6-Ferrocenyl-3-methyl-4-phenyl-3,4-dihydro-1*H*-pyrimidin-2-one (**6a**), yield 1.21 g (65%), pale yellow crystals, mp 256-257 °C. [Anal. Calcd for $C_{21}H_{20}N_2OFe$: C, 67.76; H, 5.42; N, 7.52; Fe, 15.00. Found: C, 67.92; H, 5.33; N, 7.67; Fe, 14.84.]; ν_{max} (KBr)/cm^{-1}: 757, 822, 1026, 1109, 1281, 1483, 1585, 1657, 1698, 2830, 2927, 3026, 3091, 3222, 3424; δ_H (($(CD_3)_2CO$): 2.75 (3H, s, CH_3), 4.20 (5H, s, C_5H_5), 4.28 (2H, m, C_5H_4), 4.64 (1H, m, C_5H_4), 4.71 (1H, m, C_5H_4), 4.94 (1H, d, *J* = 4.8 Hz, CH), 5.02 (1H, dd, *J* = 2.0, 4.8 Hz, CH=), 7.25 (1H, d, *J* = 2.0 Hz, NH), 7.29-7.42 (5H, m, C_6H_5); δ_C ($(CD_3)_2CO$): 32.8 (CH_3), 64.2 (CH), 66.1, 66.2, 69.8, 69.9 (C_5H_4), 70.2 (C_5H_5), 80.4 (C_{ipso}Fc), 96.4 (CH=), 127.7, 128.0, 129.7 (C_6H_5), 134.6 (C_{ipso}), 144.1 (=C–N), 153.7 (C=O).

4-(4-Bromophenyl)-6-ferrocenyl-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one (**6b**), yield 1.50 g (68%), pale yellow crystals, mp 248-250 °C. [Anal. Calcd for $C_{21}H_{19}N_2OBrFe$: C, 55.90; H, 4.24; N, 6.20; Fe, 12.38. Found: C, 55.73; H, 4.43; N, 6.03; Fe, 12.54.]; ν_{max} (KBr)/cm^{-1}: 757, 818, 1006, 1108, 1282, 1483, 1568, 1658, 2820, 2958, 3091, 3220, 3422; δ_H ($CDCl_3$): 2.83 (3H, s, CH_3), 4.19 (5H, s, C_5H_5), 4.27 (2H, m, C_5H_4), 4.35 (2H, m, C_5H_4), 4.82 (1H, d, *J* = 4.5 Hz, CH), 4.84 (1H, dd, *J* = 1.8, 4.5 Hz, CH=), 6.32 (1H, br s, NH), 7.20 (2H, d, *J* = 8.4 Hz, C_6H_4), 7.51 (2H, d, *J* = 8.4 Hz, C_6H_4).

6-Ferrocenyl-4-(4-methoxyphenyl)-3-methyl-3,4-dihydro-1*H*-pyrimidin-2-one (**6c**), yield 1.45 g (73%), pale yellow crystals, mp 238-239 °C. [Anal. Calcd for $C_{22}H_{22}N_2O_2Fe$: C, 65.68; H, 5.52; N, 6.96; Fe, 13.88. Found: C, 65.79; H, 5.38; N, 7.05; Fe, 13.64.]; ν_{max} (KBr)/cm^{-1}: 754, 825, 1031, 1110, 1243, 1482, 1508, 1610, 1656, 2835, 2956, 3091, 3219, 3426; δ_H ($CDCl_3$): 2.83 (3H, s, CH_3), 3.81 (3H, s, CH_3), 4.20 (5H, s, C_5H_5), 4.25 (2H, m, C_5H_4), 4.39 (2H, m, C_5H_4), 4.85 (2H, br s, CH, CH=), 6.58 (1H, br s, NH), 6.90 (2H, d, *J* = 7.4 Hz, C_6H_4), 7.25 (2H, d, *J* = 7.4 Hz, C_6H_4); δ_C ($CDCl_3$): 32.7 (CH_3), 55.3 (CH_3), 63.3 (CH), 64.95, 65.2, 69.0, 69.1 (C_5H_4), 69.3 (C_5H_5), 79.1 (C_{ipso}Fc), 96.3 (CH=), 114.2, 128.1 (C_6H_4), 132.7, 153.3 (C_{ipso}), 134.3 (=C–N), 159.4 (C=O).

4-Ferrocenyl-3-methyl-3,4,5,6-tetrahydro-1*H*-benzo[*h*]quinazolin-2-one (**10a**), yield 1.45 g (73%), pale yellow crystals, mp 234-235 °C. [Anal. Calcd for $C_{23}H_{22}N_2OFe$: C, 69.36; H, 5.57; N, 7.03; Fe, 14.02. Found: C, 69.18; H, 5.73; N, 7.15; Fe, 13.89.]; ν_{max} (KBr)/cm^{-1}: 761, 822, 1030, 1278, 1484, 1550, 1654, 1720, 2839, 2895, 3101, 3230, 3425; δ_H ($CDCl_3$): 2.36 (1H, m, CH_2), 2.58 (1H, m, CH_2), 2.87 (2H, m, CH_2), 3.16 (3H, s, CH_3), 4.08 (1H, m, C_5H_4), 4.13 (1H, m, C_5H_4), 4.15 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.59 (1H, s, CH), 6.93 (1H, s, NH), 7.21 (4H, m, C_6H_4); δ_C ($CDCl_3$): 22.3, 28.5 ($2CH_2$), 34.5 (CH_3), 61.6 (CH), 66.2, 66.3, 67.6, 67.6 (C_5H_4), 68.8 (C_5H_5), 88.2 (C_{ipso}Fc), 119.5, 126.7, 127.7, 127.9 (C_6H_4), 108.6, 128.1, 128.6 (3C), 135.7 (=C–N), 154.9 (C=O).

4-Ferrocenyl-8-methoxy-3-methyl-3,4,5,6-tetraahydro-1*H*-benzo[*h*]quinazolin-2-one (**10b**), yield 1.48 g (69%), pale yellow crystals, mp 311-314 °C. [Anal. Calcd for $C_{24}H_{24}N_2O_2Fe$: C, 67.30; H, 5.65; N, 6.54; Fe, 13.04. Found: C, 67.43; H, 5.39; N, 6.34; Fe, 13.20.]; ν_{max} (KBr)/cm^{-1}: 768, 819, 1028, 1265, 1478, 1584, 1657, 1700, 2824, 2944, 3095, 3230, 3425; δ_H ($CDCl_3$): 2.35-2.80 (4H, m, CH_2), 3.15 (3H, s, CH_3), 3.94 (3H, s, CH_3), 4.06 (1H, m, C_5H_4), 4.09 (1H, m, C_5H_4), 4.15 (5H, s, C_5H_5), 4.18 (2H, m, C_5H_4), 4.58 (1H, s, CH), 6.77 (1H, br s, NH), 7.18 (1H, dd, *J* = 2.4, 6.3 Hz, C_6H_3), 7.23 (1H, d, *J* = 2.4, C_6H_3), 7.36 (1H, d, *J* = 6.3, C_6H_3).

4-Ferrocenyl-9-methoxy-3-methyl-3,4,5,6-tetrahydro-1*H*-benzo[*h*]quinazolin-2-one (**10c**), yield 1.52 g (71%), pale yellow crystals, mp 260-262 °C. [Anal. Calcd for $C_{24}H_{24}N_2O_2Fe$: C, 67.30; H, 5.65; N, 6.54; Fe, 13.04. Found: C, 67.23; H, 5.71; N, 6.43; Fe, 12.87.]; ν_{max} (KBr)/cm^{-1}: 765, 819, 1042, 1105, 1221, 1292, 1475, 1579, 1610, 1653, 1757, 2834, 2934, 3097, 3236, 3447; δ_H ($CDCl_3$): 2.34 (1H, m, CH_2), 2.56 (1H, m, CH_2), 2.82 (2H, m, CH_2), 3.15 (3H, s, CH_3), 3.81 (3H, s, CH_3), 4.09 (1H, m, C_5H_4), 4.12 (1H, m, C_5H_4), 4.14 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.59 (1H, s, CH), 6.75 (1H, dd, *J* = 2.4, 8.1 Hz, C_6H_3), 6.83 (1H, d, *J* = 2.4, C_6H_3), 7.10 (1H, d, *J* = 8.1, C_6H_3), 7.23 (1H, br s, NH); δ_C ($CDCl_3$): 25.7, 27.6 ($2CH_2$), 34.6, 55.5 ($2CH_3$), 61.6 (CH), 66.3, 66.35, 67.6, 67.7 (C_5H_4), 68.8 (C_5H_5), 88.2 (C_{ipso}Fc), 105.9, 113.0, 128.6 (C_6H_3), 109.2, 127.6, 128.3, 154.8 (4C), 129.7 (=C–N), 158.6 (C=O).

4-Ferrocenyl-3,7,9-trimethyl-3,4,5,6-tetrahydro-1*H*-benzo[*h*]quinazolin-2-one (**10d**), yield 1.58 g (74%), pale yellow crystals, mp 276-278 °C. [Anal. Calcd for $C_{25}H_{26}N_2OFe$: C, 70.43; H, 6.15; N, 6.57; Fe, 13.10. Found: C, 70.62; H, 6.01; N, 6.32; Fe, 13.37.]; ν_{max} (KBr)/cm^{-1}: 765, 818, 1050, 1291, 1485, 1594, 1655, 1705, 2825, 2915, 3099, 3243, 3431; δ_H ($CDCl_3$): 2.28 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.37 (1H, m, CH_2), 2.56 (1H, m, CH_2), 2.81 (2H, m, CH_2), 3.15 (3H, s, CH_3), 4.08 (1H, m, C_5H_4), 4.12 (1H, m, C_5H_4), 4.15 (5H, s, C_5H_5), 4.16 (2H, m, C_5H_4), 4.59 (1H, s, CH), 6.20 (1H, br s, NH), 6.85 (1H, s, C_6H_2), 6.94 (1H, s, C_6H_2); δ_C ($CDCl_3$): 19.6, 21.1 ($2CH_3$), 24.0, 25.1 ($2CH_2$), 34.6 (CH_3), 61.6 (CH), 66.3, 66.35, 67.6, 67.7 (C_5H_4), 68.8 (C_5H_5), 88.2 (C_{ipso}Fc), 118.2, 130.6 (C_6H_2), 107.9, 128.2, 128.4, 130.8, 135.4 (5C), 135.5 (=C–N), 154.6 (C=O).

3-Ferrocenyl-4-methyl-1,4,6-triazatricyclo[6.2.2.$0^{2,7}$]dodec-2(7)-en-5-one (**11**), yield 1.41 g (75%), pale yellow crystals, mp 253-255 °C. [Anal. Calcd for $C_{20}H_{23}N_3OFe$: C, 63.67; H, 6.14; N, 11.13; Fe, 14.81. Found: C, 63.78; H, 6.25; N, 10.98; Fe, 15.03.]; ν_{max} (KBr)/cm^{-1}: 754, 804, 1022, 1262, 1454, 1657, 1702, 2869, 2955, 3096, 3216, 3393; δ_H ($CDCl_3$): 2.68 (4H, m, CH_2), 2.61 (2H, m, CH_2), 2.99 (2H, m, CH_2), 3.09 (1H, m, CH), 3.19 (3H, s, CH_3), 4.07 (2H, m, C_5H_4), 4.14 (2H, m, C_5H_4), 4.20 (5H, s, C_5H_5), 4.80 (1H, s, Fc-CH), 7.50 (1H, br s, NH); δ_C ($CDCl_3$): 28.1 (2C), 29.0 (2C) ($4CH_2$), 35.4 (CH_3), 50.6, 51.3 (2CH), 65.5, 67.4 (C_5H_4), 69.1 (C_5H_5), 88.3 (C_{ipso}Fc), 136.6 (C), 136.7 (=C–N), 154.3 (C=O).

4-Ferrocenyl-8-ferrocenylmethylidene-3-methyl-3,4,5,6,7,8-hexahydro-1*H*-quinazolin-2-one (**12a**), yield 1.46 g (72%), pale yellow crystals, mp 232-233 °C. [Anal. Calcd for $C_{30}H_{30}N_2O\ Fe_2$: C, 65.96; H, 5.54; N, 5.13; Fe, 20.45. Found: C, 65.78; H, 5.71; N, 5.28; Fe, 20.31.]; ν_{max} (KBr)/cm^{-1}: 772, 818, 1001, 1106, 1285, 1490, 1578, 1653, 1708, 2862, 2929, 3092, 3240, 3430; δ_H ($CDCl_3$): 1.75 (1H, m, CH_2), 1.86 (1H, m, CH_2), 2.15 (1H, dt, *J* = 5.1, 17.0, CH_2), 2.36-2.55 (2H, m, CH_2), 2.74 (1H, dt, *J* = 5.1, 15.0, CH_2), 3.15 (3H, s,

CH_3), 4.10 (1H, m, C_5H_4), 4.11 (5H, s, C_5H_5), 4.13 (1H, m, C_5H_4), 4.15 (1H, m, C_5H_4), 4.16 (1H, m, C_5H_4), 4.17 (5H, s, C_5H_5), 4.26 (2H, m, C_5H_4), 4.34 (2H, m, C_5H_4), 4.43 (1H, s, Fc-CH), 6.08 (1H, s, CH=), 6.32 (1H, s, NH); δ_C ($CDCl_3$): 22.9, 26.9, 27.6 ($3CH_2$), 34.6 (CH_3), 62.1 (CH), 66.1, 66.2, 67.5, 67.5, 68.8, 69.4, 69.6, 69.7 ($2C_5H_4$), 68.8, 69.1 ($2C_5H_5$), 81.5, 88.4 ($2C_{ipso}$Fc), 118.4 (CH=), 111.2, 127.0 (2C), 128.7 (=C–N), 154.6 (C=O).

4-Ferrocenyl-8-ferrocenylmethylidene-3,6-dimethyl-3,4,5,6,7,8-hexahydropyrido-1*H*-pyrido[4,3-*d*]pyrimidin-2-one (**12b**), yield 1.44 g (69%), pale yellow crystals, mp 162-163 °C. [Anal. Calcd for $C_{30}H_{31}N_3OFe_2$: C, 64.19; H, 5.57; N, 7.48; Fe, 19.90. Found: C, 64.27; H, 5.37; N, 7.32; Fe, 20.10.]; ν_{max} (KBr)/cm^{-1}: 759, 820, 1121, 1258, 1470, 1591, 1692, 2881, 2939, 3101, 3264, 3473; δ_H (CD_3CN): 2.45 (3H, s, CH_3), 3.08 (3H, s, CH_3), 3.35 (2H, d, $J = 13.8$, CH_2), 3.58 (2H, d, $J = 13.8$, CH_2), 4.15 (2H, m, C_5H_4), 4.16 (1H, m, C_5H_4), 4.18 (1H, m, C_5H_4), 4.20 (5H, s, C_5H_5), 4.21 (2H, m, C_5H_4), 4.26 (5H, s, C_5H_5), 4.35 (1H, m, C_5H_4), 4.42 (1H, m, C_5H_4), 4.60 (1H, br s, Fc-CH), 6.38 (1H, s, CH=), 7.23 (1H, br s, NH).

4-Ferrocenyl-7-ferrocenylmethylidene-3-methyl-1,3,4,5,6,7-hexahydrocyclopentano[*d*]pyrimidin-2-one (**12c**), yield 1.38 g (71%), pale yellow crystals, mp 164-165 °C. [Anal. Calcd for $C_{29}H_{28}N_2O\ Fe_2$: C, 65.44; H, 5.30; N, 5.26; Fe, 21.00. Found: C, 65.63; H, 5.09; N, 5.11; Fe, 21.12.]; ν_{max} (KBr)/cm^{-1}: 759, 818, 1001, 1105, 1286, 1403, 1459, 1570, 1659, 1725, 2852, 2927, 3091, 3221, 3406; δ_H (CD_3CN): 2.42-2.85 (4H, m, CH_2), 3.14 (3H, s, CH_3), 4.06 (2H, m, C_5H_4), 4.10 (5H, s, C_5H_5), 4.13 (2H, m, C_5H_4), 4.15 (5H, s, C_5H_5), 4.18 (1H, m, C_5H_4), 4.24 (1H, m, C_5H_4), 4.35 (1H, m, C_5H_4), 4.38 (1H, m, C_5H_4), 4.79 (1H, br s, Fc-CH), 5.92 (1H, s, CH=), 7.02 (1H, br s, NH).

Crystal structure determination

The unit cell parameters and the X-Ray diffraction intensities were recorded on a Siemens P4/PC/ω diffractometer. The structure of compound (**5c**) was solved by the direct method (SHELXS) and refined using full-matrix least-squares on F^2. Crystal data for $C_{22}H_{22}N_2O_2Fe$ with $^1/_2$ of C_6H_6, Mr = 441.32 $gmol^{-1}$, triclinic P-1, a = 9.5124(8), b = 10.2885(10), c = 12.4859(12) Å, $\alpha = 73.178(7)$, $\beta = 77.771(8)$, $\gamma = 66.558(7)^o$, V = 1066.62(17) $Å^3$, T = 293 K, Z = 2, $\rho = 1.374$ g cm^{-3}, λ (Mo-Kα) = 0.71073 Å, F(000) = 462, index ranges $0 \le h \le 11$, $-10 \le k \le 11$, $-14 \le l \le 14$, scan range $1.71 \le \theta \le 25.00^o$, 3732 independent reflections, $R_{int} = 0.0502$, 3977 total reflections, 273 refinable parameters, final R indices [I > 2σ(I)] $R_1 = 0.0493$, $wR_2 = 0.1188$, R indices (all data) $R_1 = 0.0710$, $wR_2 = 0.1279$, largest difference peak and hole 0.497/-0.319 e $Å^{-3}$.

CCDC reference number 202754 for compound (**5c**). See http://www.rsc.org/suppdata/ for crystallographic data in .cif or other electronic format.

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