

# Synthesis of Ferrocenyl-1-(4-pyridylmethyl)- and Ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazoles

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**Abstract:** Pyridine-4-carbaldehyde reacts with ferrocenyl-4,5-dihydropyrazoles to yield ferrocenyl-1-(4-pyridylmethyl)pyrazoles and ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazoles. The structures of the compounds obtained were established based on spectroscopic (IR, mass, <sup>1</sup>H and <sup>13</sup>C NMR) data. X-ray diffraction data for 4-[3-(*p*-bromophenyl)-5-ferrocenyl-1-(4-pyridyl)methyl]pyrazole corroborate its structure.

**Key words:** *α,β*-unsaturated ketones, ferrocenylpyrazolines, ferrocenyl-1-(4-pyridylmethyl)pyrazoles, ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazoles

Studies of pharmacological properties and metabolism of biologically active heterocyclic compounds are currently focused on pyrazole derivatives. Being non-steroidal pharmaceuticals, these often possess a complex of valuable medicinal characteristics and do not injure living organisms.<sup>1–5</sup> Medicines of the pyrazole series manifest anti-inflammatory, analgesic, antiviral, antithrombotic and anti-psychotic activities and are also favorable for cardiovascular and gastrointestinal systems.

It is known that the introduction of ferrocene substituents into molecules of organic compounds leads to an enhancement (or to the appearance) of biological activity of the resulting compounds and to a decrease in their toxicity compared to the initial compounds.<sup>6</sup> Thus ferrocenyl-substituted 4,5-dihydropyrazoles also belong to pharmacologically active compounds. In particular, 4-acetyl-3-ferrocenyl-2,4,5-triazatricyclo[5.2.2.0<sup>2,6</sup>]undec-5-ene exhibits high antiviral activity.<sup>7</sup> One would expect that the introduction of additional ferrocenilic fragments into molecules of pyrazoles of this class will afford products possessing a broader spectrum of useful biological characteristics.

Pyrazoles with ferrocenyl substituents are virtually unexplored, since ferrocenyl 1,3-diketones, which are the starting compounds for their synthesis, are usually hardly accessible.<sup>8</sup> Ferrocenyl-4,5-dihydropyrazoles, which can easily be prepared from ferrocene-containing *α,β*-enones and hydrazine,<sup>8,9</sup> are the most available compounds of the ferrocene series suitable for the access to ferrocenylpyra-

zoles. However, the use of conventional oxidation procedures is inapplicable in this case, as it can result in destruction of the metallocene structure of ferrocene.

In this connection, it is of interest to develop procedures for the synthesis of pyrazoles with ferrocenyl substituents and to study their chemical and pharmacological properties. The aim of the present study was the study of an intramolecular redox process that takes place in the reaction of ferrocenyl-4,5-dihydropyrazoles with pyridine-4-carbaldehyde.

Ferrocenyl-4,5-dihydropyrazoles **1a–d** and **2a–e** were used as the starting compounds (Figure 1).

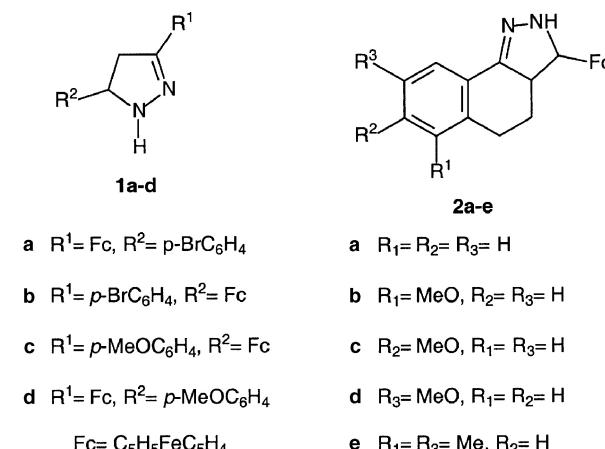


Figure 1

Compounds **1a–d** and **2a–e** were prepared by condensation of hydrazine hydrate with ferrocenyl *α,β*-enones **3a–d** and **4a–e**, respectively (Figure 2).

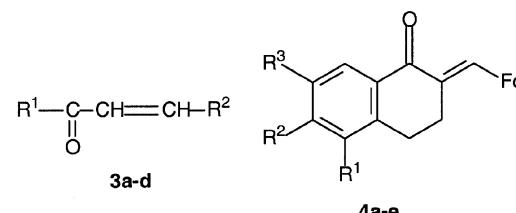


Figure 2

Dihydropyrazoles **1a–d** and **2a–e** are yellow or orange crystalline compounds that are sufficiently stable in the dry state. We have found that dihydropyrazoles react with pyridine-4-carbaldehyde (ca 120 °C, ca 20 min) to yield mixtures of two types of products, namely, **5a–d + 6a–d** and **7a–e + 8a–e** (Scheme 1).

The structures of compounds **5–8** were established based on the data from mass spectrometry, IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and elemental analysis (see experimental section).

The spatial structure of one of the reaction products, viz., compounds **5b**, was determined using X-ray diffraction analysis of a single crystal prepared by crystallization from CHCl<sub>3</sub>. The general view of the molecule **5b** is given in Figure 3a, the crystal packing is shown in Figure 3b.

The five-membered ring in the molecule **5b** is a planar and virtually equilateral pentagon, the ferrocenyl substituent being in the eclipsed conformation. According to <sup>1</sup>H NMR data, compounds **6a–d** and **8a–e** were formed as single diastereomeric forms. We could not elucidate their spatial structures because no crystals suitable for the X-ray diffraction analysis could be prepared.

Thus, the reaction of 4,5-dihydropyrazoles **1** and **2** with pyridine-4-carbaldehyde proceeds with intramolecular oxidation of the pyrazoline ring ( $\rightarrow$  pyrazole) and concomitant reduction of an exocyclic functionality into the methylene group.

A putative reaction scheme may be suggested, which gives a rationale for the transformations observed. Initially, the dihydropyrazole with a free 1-NH group adds to pyridine-4-carbaldehyde to yield a cation **9** (Scheme 2).

Presumably, this is followed by an intramolecular shift of the electron pairs leading to a bipolar mesomeric intermediate **10** and then to a carbanion **11**. The latter is stabilized

by abstracting a proton from water (to yield compounds **5** and **7**) or by reacting with the second molecule of pyridine-4-carbaldehyde (to yield compounds **6** and **8**). The formation of double addition products **6** and **8** is in favor of the suggested scheme.

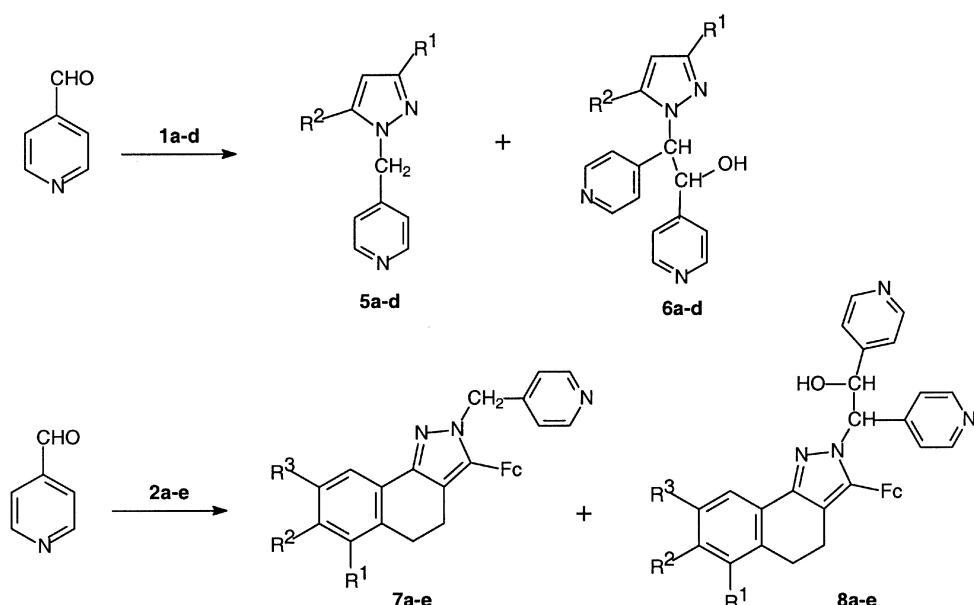
An alternative mechanism involving a 1,3-hydride shift from the carbon atom 5 in the cation **9** was ruled out experimentally (Scheme 3).

Thus we have found that the reaction product of deuterated 3-phenyl-4,5-dihydro-2*H*-benzo[*g*]indazole (**2f–D**) with pyridine-4-carbaldehyde contained virtually no deuterium atoms.

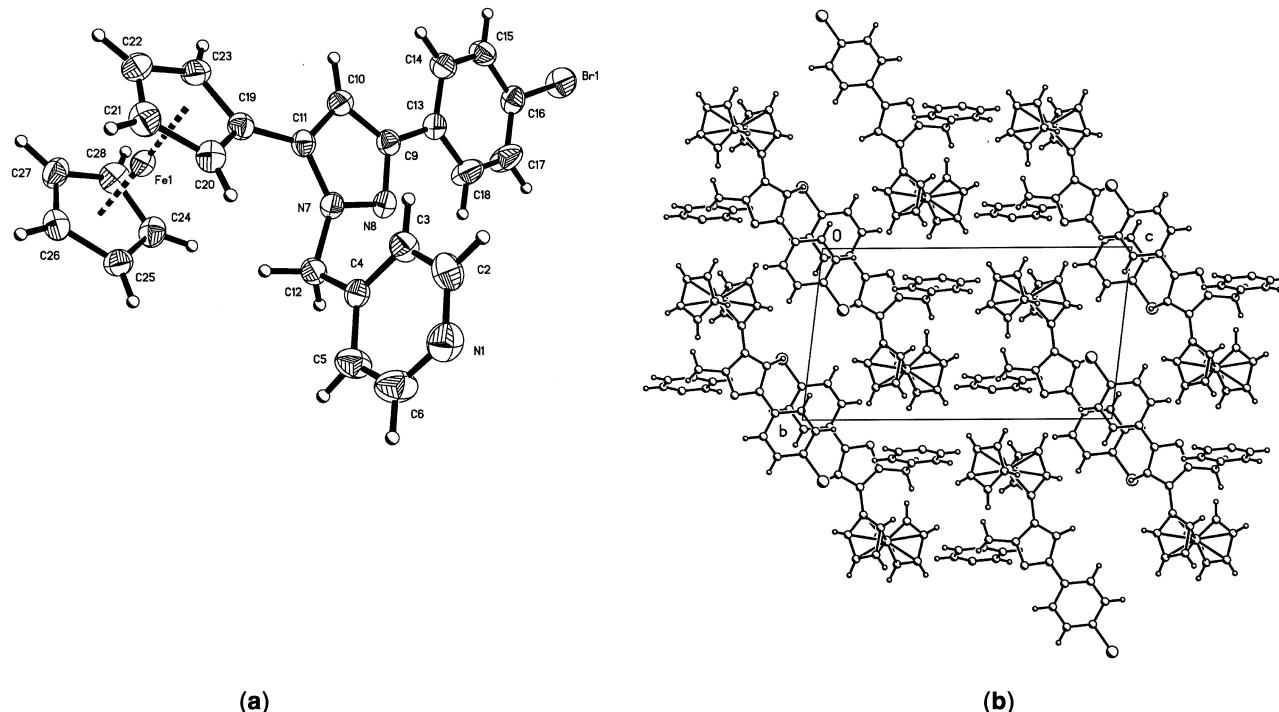
The biological activity of compounds **5–8** is being researched.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Unity Inova Varian spectrometer (at 300 MHz and 75 MHz, respectively) for solutions in CDCl<sub>3</sub> with tetramethylsilane as the internal standard. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elemental Analysis system GmbH was used for elemental analyses. IR spectra were obtained for KBr pellets on a Specord IR-75 instrument. Chromatographic separations were carried out on columns with alumina (Brockmann activity III). The unit cell parameters and the X-ray diffraction intensities were recorded on a Bruker Smart Apex CCD diffractometer. The principal geometrical parameters of the molecule **5b** are listed in the legend to Figure 1. The structure of compound **5b** was solved by the direct method (SHELXS) and refined using full-matrix least-squares on F<sup>2</sup>.

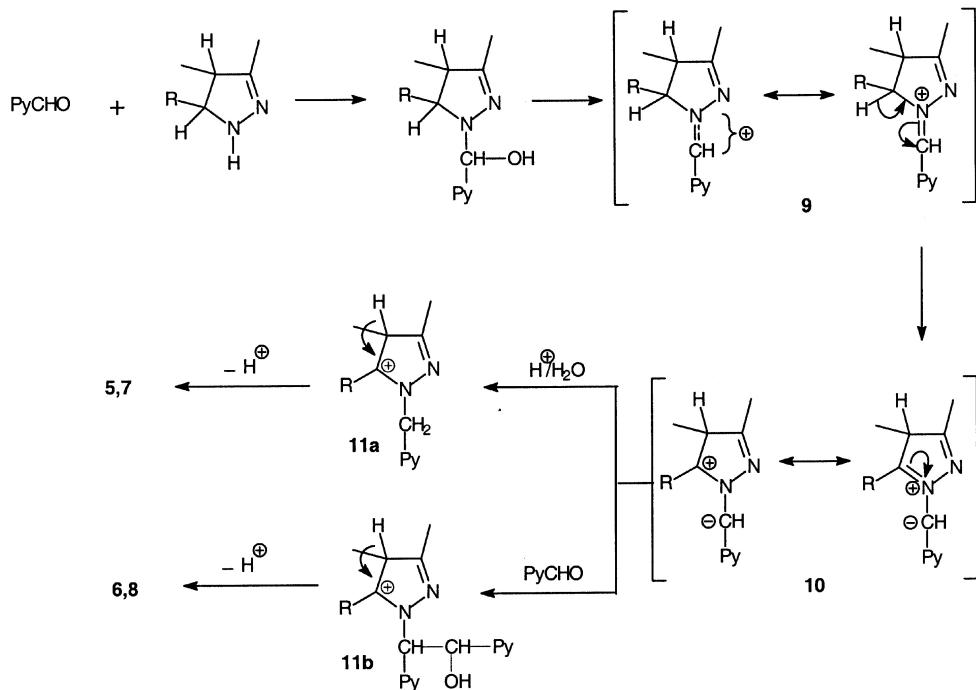
The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; acetylferrocene, 98%; 4-bromobenzaldehyde, 99%; 4-bromoacetophenone, 98%; *p*-anisaldehyde, 98%; 4-methoxyacetophenone, 99%;  $\alpha$ -tetralone, 98%; 5-methoxy-1-tetralone, 97%; 6-methoxy-1-tetralone, 99%; 7-methoxy-1-tetralone, 99%; 5,7-dimethyl-1-tetralone, 97%; 4-pyridinecarboxaldehyde, 97%; benzaldehyde-*d*, 98 atom% D.



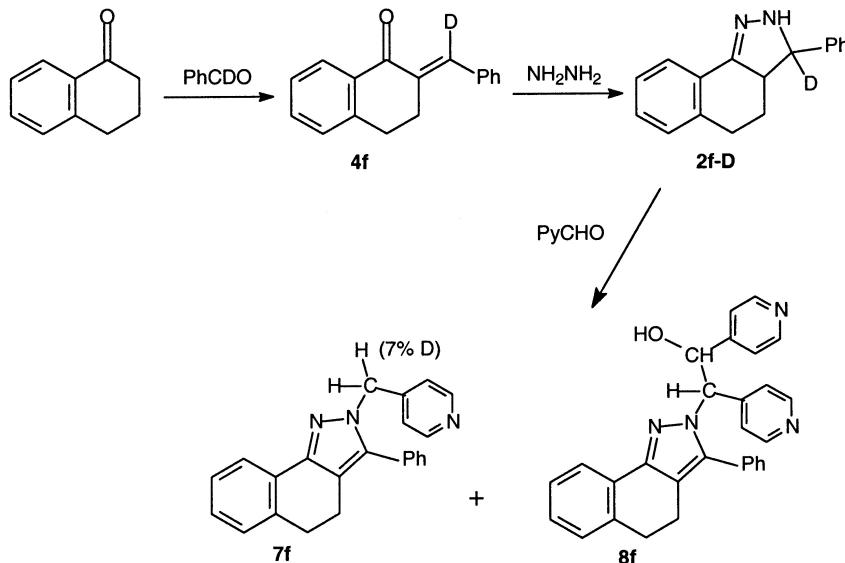
**Scheme 1**



**Figure 3** (a) Molecular structure of **5b**. Selected bond lengths ( $\text{\AA}$ ): N(7)–N(8) = 1.356(3); N(7)–C(11) = 1.361(3); C(10)–C(11) = 1.363(4); N(7)–C(12) = 1.448(3); C(9)–C(10) = 1.399(4); C(9)–N(8) = 1.330(3); C(9)–C(13) = 1.473(4); C(11)–C(19) = 1.463(4); C(16)–Br(1) = 1.901(3). Selected bond angles ( $^{\circ}$ ): C(11)–N(7)–N(8) = 112.1(2); N(8)–N(7)–C(12) = 117.5(2); N(8)–C(9)–C(10) = 110.5(2); N(8)–C(9)–C(13) = 119.8(3); C(11)–N(7)–C(12) = 130.4(2); C(9)–N(8)–N(7) = 105.1(2); C(11)–C(10)–C(9) = 106.5(3); N(7)–C(11)–C(10) = 105.8(2); N(7)–C(11)–C(19) = 125.7(2). (b) Crystal packing of **5b**.



**Scheme 2**



Scheme 3

### 3-Aryl-1-ferrocenylprop-2-enones 3a,d and 3b,c; General Procedure

These compounds were prepared by condensation of acetylferrocene with arenecarbaldehydes or acetophenones with ferrocene-carbaldehyde in aqueous-ethanolic alkali.<sup>9–11</sup>

### 2-Ferrocenylmethylidenetetralones 4a–e and 2-Benzylidene-tetralone 4f; General Procedure

These compounds were prepared by condensation of ferrocenecarbaldehyde and benzaldehyde-*d* with tetralones in aqueous-ethanolic alkali.<sup>13</sup> The physical and <sup>1</sup>H NMR spectroscopic characteristics of compounds 3a–d and 4a–e were in accord with the literature data.<sup>12,13</sup>

### Ferrocenyl-4,5-dihydropyrazoles 1a–d and 2a–f; General Procedure

These compounds were obtained according to the known procedure<sup>10,11</sup> by reactions of the enones 3a–d and 4a–f, respectively, with hydrazine hydrate in EtOH. The reaction products that precipitated (1a–d and 2a–f) were filtered off, washed with EtOH and dried in vacuo. Their yields ranged from 60% to 70% and the melting points corresponded to the literature data.<sup>11–13</sup>

### Reaction of Pyridine-4-carbaldehyde with Ferrocenyl-4,5-dihydropyrazoles 1a–d; General Procedure

The dihydropyrazole 1a–d (2.0 mmol) was added with stirring to pyridine-4-carbaldehyde (0.32 g, 3.0 mmol) at 120 °C. The mixture was stirred at 100–120 °C for 20 min, and excess of pyridinecarbaldehyde was steam-distilled. The residue was chromatographed on alumina (hexane–CH<sub>2</sub>Cl<sub>2</sub>, 4:1) to yield ferrocenyl-1-(4-pyridylmethyl)pyrazoles 5a–d and ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazoles 6a–d.

### 5-(4-Bromophenyl)-3-ferrocenyl-1-(4-pyridylmethyl)pyrazole (5a)

Yield: 35%; mp 165–166 °C.

IR (KBr): 3090, 3026, 2954, 1654, 1598, 1561, 1472, 1447, 1409, 1379, 1317, 1295, 1103, 1068, 1031, 968, 873, 828, 779 cm<sup>–1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.10 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.30 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.72 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.31 (br s, 2 H, CH<sub>2</sub>), 6.43 (s, 1 H, CH=), 6.93 (d,

$J$  = 6.0 Hz, 2 H, ArH), 7.17 (d,  $J$  = 8.4 Hz, 2 H, ArH), 7.53 (d,  $J$  = 8.4 Hz, 2 H, ArH), 8.53 (d,  $J$  = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 51.93 (CH<sub>2</sub>), 66.61, 68.68 (C<sub>5</sub>H<sub>4</sub>), 69.60 (C<sub>5</sub>H<sub>5</sub>), 77.80 (C<sub>ipso</sub>Fc), 104.55 (CH=), 121.21, 130.09, 132.00, 150.06 (ArH), 123.16, 129.04, 144.09, 146.73, 151.27 (C).

MS: *m/z* = 498 [M]<sup>+</sup>.

Anal. Calcd for C<sub>25</sub>H<sub>20</sub>BrFeN<sub>3</sub>: C, 60.28; H, 4.04; Br, 16.04; Fe, 11.21; N, 8.43. Found: C, 60.46; H, 3.91; Br, 16.21; Fe, 11.40; N, 8.27.

### 3-(4-Bromophenyl)-5-ferrocenyl-1-(4-pyridylmethyl)pyrazole (5b)

Yield: 40%; mp 172–173 °C.

IR (KBr): 3082, 3031, 2936, 1650, 1599, 1562, 1464, 1444, 1413, 1357, 1310, 1219, 1105, 1070, 1006, 956, 882, 831, 787 cm<sup>–1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 4.13 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.29 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.31 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.54 (br s, 2 H, CH<sub>2</sub>), 6.69 (s, 1 H, CH=), 7.00 (d,  $J$  = 6.0 Hz, 2 H, ArH), 7.54 (d,  $J$  = 8.7 Hz, 2 H, ArH), 7.72 (d,  $J$  = 8.7 Hz, 2 H, ArH), 8.57 (d,  $J$  = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 52.36 (CH<sub>2</sub>), 68.30, 69.19 (C<sub>5</sub>H<sub>4</sub>), 69.68 (C<sub>5</sub>H<sub>5</sub>), 74.01 (C<sub>ipso</sub>Fc), 103.32 (CH=), 121.20, 127.17, 131.69, 150.14 (ArH), 121.69, 132.08, 143.50, 146.79, 146.84 (C).

MS: *m/z* = 498 [M]<sup>+</sup>.

Anal. Calcd for C<sub>25</sub>H<sub>20</sub>BrFeN<sub>3</sub>: C, 60.28; H, 4.04; Br, 16.04; Fe, 11.21; N, 8.43. Found: C, 60.35; H, 4.23; Br, 15.85; Fe, 11.02; N, 8.62.

### 3-(4-Methoxyphenyl)-5-ferrocenyl-1-(4-pyridylmethyl)pyrazole (5c)

Yield: 34%; mp 163–165 °C.

IR (KBr): 3077, 2934, 2835, 1601, 1566, 1531, 1462, 1437, 1359, 1292, 1253, 1173, 1107, 1032, 997, 957, 832, 828, 789 cm<sup>–1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 3.85 (s, 3 H, CH<sub>3</sub>), 4.13 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.28 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.31 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.54 (br s, 2 H, CH<sub>2</sub>), 6.65 (s, 1 H, CH=), 6.96 (d,  $J$  = 9.0 Hz, 2 H, ArH), 7.01 (d,  $J$  = 6.0 Hz, 2 H, ArH), 7.78 (d,  $J$  = 9.0 Hz, 2 H, ArH), 8.56 (d,  $J$  = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 52.24 (CH<sub>2</sub>), 55.31 (CH<sub>3</sub>), 68.29, 69.09 (C<sub>5</sub>H<sub>4</sub>), 69.68 (C<sub>5</sub>H<sub>5</sub>), 74.35 (C<sub>ipso</sub>Fc), 102.97 (CH=), 114.02,

121.24, 126.88, 150.12 (ArH), 125.92, 143.09, 147.16, 151.12, 159.44 (C).

MS:  $m/z = 449$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>26</sub>H<sub>23</sub>FeN<sub>3</sub>O: C, 69.50; H, 5.16; Fe, 12.43; N, 9.35. Found: C, 69.71; H, 5.32; Fe, 12.64; N, 9.16.

### 5-(4-Methoxyphenyl)-3-ferrocenyl-1-[4-pyridylmethyl]pyrazole (5d)

Yield: 36%; mp 135–136 °C.

IR (KBr): 3083, 2936, 2837, 1601, 1562, 1538, 1485, 1413, 1348, 1295, 1251, 1173, 1101, 1069, 1028, 996, 945, 830, 779, 720 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 3.83$  (s, 3 H, CH<sub>3</sub>), 4.10 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.29 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.72 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.32 (br s, 2 H, CH<sub>2</sub>), 6.39 (s, 1 H, CH=), 6.91 (d,  $J = 8.7$  Hz, 2 H, ArH), 6.94 (d,  $J = 6.6$  Hz, 2 H, ArH), 7.24 (d,  $J = 8.7$  Hz, 2 H, ArH), 8.52 (d,  $J = 6.6$  Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 51.82$  (CH<sub>2</sub>), 55.34 (CH<sub>3</sub>), 66.62, 68.59 (C<sub>5</sub>H<sub>4</sub>), 69.48 (C<sub>5</sub>H<sub>5</sub>), 78.23 (C<sub>ipso</sub>Fc), 104.14 (CH=), 114.19, 121.33, 129.22, 150.01 (ArH), 122.13, 145.12, 147.18, 150.63, 160.46 (C).

MS:  $m/z = 449$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>26</sub>H<sub>23</sub>FeN<sub>3</sub>O: C, 69.50; H, 5.16; Fe, 12.43; N, 9.35. Found: C, 69.29; H, 5.03; Fe, 12.28; N, 9.49.

### 5-(4-Bromophenyl)-3-ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazole (6a)

Yield: 22%; mp 235–237 °C.

IR (KBr): 3500–3040, 2861, 2723, 1913, 1599, 1563, 1474, 1412, 1352, 1315, 1219, 1101, 1069, 999, 877, 816, 805, 714 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 4.14$  (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.37 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.77 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.16 (d,  $J = 3.6$  Hz, 1 H, CH), 5.64 (d,  $J = 3.6$  Hz, 1 H, CH), 6.18 (br s, 1 H, OH), 6.36 (s, 1 H, CH=), 6.88 (d,  $J = 6.0$  Hz, 2 H, ArH), 6.92 (d,  $J = 8.1$  Hz, 2 H, ArH), 7.07 (d,  $J = 5.4$  Hz, 2 H, ArH), 7.50 (d,  $J = 8.1$  Hz, 2 H, ArH), 8.43 (d,  $J = 5.4$  Hz, 2 H, ArH), 8.48 (d,  $J = 6.0$  Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 66.40$  (CH), 66.70, 66.85, 68.98, 69.00 (C<sub>5</sub>H<sub>4</sub>), 69.54 (C<sub>5</sub>H<sub>5</sub>), 74.59 (C<sub>ipso</sub>Fc), 74.61 (CHOH), 104.37 (CH=), 121.35, 123.19, 130.38, 132.07, 149.48, 149.76 (ArH), 123.70, 128.30, 144.38, 144.51, 148.32, 151.30 (C).

MS:  $m/z = 605$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>31</sub>H<sub>25</sub>BrFeN<sub>4</sub>O: C, 61.52; H, 4.16; Br, 13.20; Fe, 9.23; N, 9.25. Found: C, 61.37; H, 4.25; Br, 13.05; Fe, 9.37; N, 9.44.

### 3-(4-Bromophenyl)-5-ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazole (6b)

Yield: 20%; mp 224–225 °C.

IR (KBr): 3419, 3084, 2938, 2720, 1943, 1599, 1563, 1458, 1415, 1376, 1311, 1223, 1187, 1104, 1067, 1003, 885, 805, 713 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 4.09$  (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.02 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.29 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.46 (dd,  $J = 4.0$ , 8.1 Hz, 1 H, CH), 5.71 (d,  $J = 4.0$  Hz, 1 H, CH), 6.10 (d,  $J = 8.1$  Hz, 1 H, OH), 6.60 (s, 1 H, CH=), 7.05 (d,  $J = 8.7$  Hz, 2 H, ArH), 7.12 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.26 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.90 (d,  $J = 8.7$  Hz, 2 H, ArH), 8.47 (d,  $J = 6.3$  Hz, 2 H, ArH), 8.65 (d,  $J = 6.3$  Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, D<sub>2</sub>O):  $\delta = 4.08$  (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.02 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.30 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.44 (d,  $J = 4.0$  Hz, 1 H, CH), 5.71 (d,  $J = 4.0$  Hz, 1 H, CH), 6.60 (s, 1 H, CH=), 7.04 (d,  $J = 8.5$  Hz, 2 H, ArH), 7.12 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.27 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.90 (d,  $J = 8.5$  Hz, 2 H, ArH), 8.47 (d,  $J = 6.3$  Hz, 2 H, ArH), 8.61 (d,  $J = 6.3$  Hz, 2 H, ArH).

MS:  $m/z = 605$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>31</sub>H<sub>25</sub>BrFeN<sub>4</sub>O: C, 61.52; H, 4.16; Br, 13.20; Fe, 9.23; N, 9.25. Found: C, 61.74; H, 4.01; Br, 13.41; Fe, 9.39; N, 9.12.

### 3-(4-Methoxyphenyl)-5-ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazole (6c)

Yield: 25%; mp 179–181 °C.

IR (KBr): 3333, 3081, 2956, 2835, 1941, 1599, 1563, 1531, 1465, 1415, 1384, 1292, 1249, 1177, 1107, 1069, 1031, 1003, 959, 835, 790 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 3.89$  (s, 3 H, CH<sub>3</sub>), 4.08 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.94 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.25 (m, 3 H, C<sub>5</sub>H<sub>4</sub>), 5.40 (dd,  $J = 4.2$ , 9.0 Hz, 1 H, CH), 5.60 (d,  $J = 4.2$  Hz, 1 H, CH), 6.08 (d,  $J = 9.0$  Hz, 1 H, OH), 6.55 (s, 1 H, CH=), 7.02 (d,  $J = 8.7$  Hz, 2 H, ArH), 7.06 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.20 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.81 (d,  $J = 8.7$  Hz, 2 H, ArH), 8.45 (d,  $J = 6.3$  Hz, 2 H, ArH), 8.61 (d,  $J = 6.3$  Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 55.40$  (CH<sub>3</sub>), 65.01 (CH), 68.18, 69.12, 69.20, 69.30 (C<sub>5</sub>H<sub>4</sub>), 69.75 (C<sub>5</sub>H<sub>5</sub>), 73.86 (C<sub>ipso</sub>Fc), 75.91 (CHOH), 103.17 (CH=), 114.21, 121.14, 122.15, 127.00, 149.73, 150.21 (ArH), 121.60, 123.30, 125.03, 145.04, 147.01, 159.93 (C).

MS:  $m/z = 556$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>33</sub>H<sub>28</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 69.07; H, 5.07; Fe, 10.04; N, 10.07. Found: C, 68.87; H, 4.89; Fe, 10.19; N, 10.23.

### 5-(4-Methoxyphenyl)-3-ferrocenyl-1-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]pyrazole (6d)

Yield: 18%; mp 172–173 °C.

IR (KBr): 3335, 3082, 2935, 2837, 1940, 1654, 1599, 1563, 1538, 1489, 1412, 1349, 1288, 1250, 1178, 1105, 1062, 1032, 998, 877, 825, 792, 721 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 3.83$  (s, 3 H, CH<sub>3</sub>), 4.12 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.29 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.74 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.12 (dd,  $J = 3.2$ , 8.1 Hz, 1 H, CH), 5.53 (d,  $J = 3.2$  Hz, 1 H, CH), 6.15 (d,  $J = 8.1$  Hz, 1 H, OH), 6.30 (s, 1 H, CH=), 6.84 (d,  $J = 6.0$  Hz, 2 H, ArH), 6.90 (d,  $J = 8.7$  Hz, 2 H, ArH), 7.03 (d,  $J = 6.3$  Hz, 2 H, ArH), 7.35 (d,  $J = 8.7$  Hz, 2 H, ArH), 8.43 (d,  $J = 6.3$  Hz, 2 H, ArH), 8.51 (d,  $J = 6.0$  Hz, 2 H, ArH).

MS:  $m/z = 556$  [M]<sup>+</sup>.

Anal. Calcd for C<sub>33</sub>H<sub>28</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 69.07; H, 5.07; Fe, 10.04; N, 10.07. Found: C, 69.24; H, 4.92; Fe, 9.87; N, 9.86.

### Reaction of Pyridine-4-carbaldehyde with 3-Ferrocenyl-3,3a,4,5-tetrahydro-2H-benzol[g]indazoles 2a–e; General Procedure

The condensation of compound 4a–e (2 mmol) with pyridine-4-carbaldehyde (0.53 g, 5 mmol) was carried out at 110–120 °C for 30 min. Subsequent work-up of the reaction mixture as described above and column chromatography (Al<sub>2</sub>O<sub>3</sub>, hexane–CH<sub>2</sub>Cl<sub>2</sub>, 4:1) afforded 3-ferrocenyl-2-(4-pyridylmethyl)-4,5-dihydro-2H-benzol[g]indazoles 7a–e and 3-ferrocenyl-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2H-benzol[g]indazole 8a–e.

### 3-Ferrocenyl-2-(4-pyridylmethyl)-4,5-dihydro-2H-benzol[g]indazole (7a)

Yield: 37%; mp 162–163 °C.

IR (KBr): 3078, 2923, 2843, 1946, 1626, 1594, 1554, 1495, 1462, 1414, 1371, 1307, 1233, 1103, 1066, 1030, 991, 884, 813, 793, 767, 726 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 3.00$  (m, 4 H, CH<sub>2</sub>), 4.14 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.30 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.71 (br s, 2 H, CH<sub>2</sub>), 7.02 (d,  $J = 6.0$  Hz, 2 H, ArH), 7.65 (d,  $J = 6.3$  Hz, 1 H, ArH), 7.73 (m, 1 H, ArH), 7.85 (d,  $J = 6.6$  Hz, 2 H, ArH), 8.43 (d,  $J = 6.0$  Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 20.46, 29.76 (CH<sub>2</sub>), 52.49 (CH<sub>2</sub>), 67.74, 68.89 (C<sub>5</sub>H<sub>4</sub>), 69.40 (C<sub>5</sub>H<sub>5</sub>), 74.38 (C<sub>ipso</sub>Fc), 121.12, 122.13, 150.16, 156.59 (ArH), 129.60, 136.44, 137.13, 140.59, 147.73, 160.45 (C).

MS: *m/z* = 445 [M]<sup>+</sup>.

Anal. Calcd for C<sub>27</sub>H<sub>23</sub>FeN<sub>3</sub>: C, 72.82; H, 5.20; Fe, 12.55; N, 9.43. Found: C, 72.61; H, 5.37; Fe, 12.36; N, 9.24.

### 3-Ferrocenyl-6-methoxy-2-(4-pyridylmethyl)-4,5-dihydro-2*H*-benzo[g]indazole (7b)

Yield: 33%; mp 188–189 °C.

IR (KBr): 3084, 2929, 2831, 1949, 1607, 1593, 1528, 1461, 1415, 1360, 1308, 1248, 1229, 1158, 1101, 1067, 1033, 975, 869, 814, 790 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.97 (m, 4 H, CH<sub>2</sub>), 3.87 (s, 3 H, CH<sub>3</sub>), 4.18 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.35 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 4.41 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.75 (br s, 2 H, CH<sub>2</sub>), 6.90 (dd, *J* = 0.9, 8.1 Hz, 1 H, ArH), 7.11 (d, *J* = 6.0 Hz, 2 H, ArH), 7.21 (t, *J* = 8.1 Hz, 1 H, ArH), 7.43 (dd, *J* = 0.9, 8.1 Hz, 1 H, ArH), 8.56 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 20.47, 22.55 (2 × CH<sub>2</sub>), 53.26 (CH<sub>2</sub>), 55.81 (CH<sub>3</sub>), 68.50, 69.59 (C<sub>5</sub>H<sub>4</sub>), 70.16 (C<sub>5</sub>H<sub>5</sub>), 75.44 (C<sub>ipso</sub>Fc), 110.33, 115.51, 122.10, 150.90, 151.00 (ArH), 115.75, 125.11, 127.83, 131.96, 141.58, 148.84, 157.83 (C).

MS: *m/z* = 475 [M]<sup>+</sup>.

Anal. Calcd for C<sub>28</sub>H<sub>25</sub>FeN<sub>3</sub>O: C, 70.75; H, 5.30; Fe, 11.75; N, 8.84. Found: C, 70.93; H, 5.08; Fe, 11.93; N, 8.99.

### 3-Ferrocenyl-7-methoxy-2-(4-pyridylmethyl)-4,5-dihydro-2*H*-benzo[g]indazole (7c)

Yield: 31%; mp 206–207 °C.

IR (KBr): 3025, 2929, 2831, 1946, 1625, 1607, 1593, 1528, 1461, 1439, 1415, 1360, 1308, 1248, 1232, 1158, 1109, 1033, 1003, 869, 814, 790 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.98 (m, 4 H, CH<sub>2</sub>), 3.84 (s, 3 H, CH<sub>3</sub>), 4.13 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.30 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.67 (br s, 2 H, CH<sub>2</sub>), 6.83 (d, *J* = 2.7 Hz, 1 H, ArH), 6.85 (d, *J* = 1.5 Hz, 1 H, ArH), 7.02 (d, *J* = 6.0 Hz, 2 H, ArH), 7.70 (dd, *J* = 1.5, 2.7 Hz, 1 H, ArH), 8.75 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 19.94, 21.65 (2 × CH<sub>2</sub>), 53.44 (CH<sub>2</sub>), 55.51 (CH<sub>3</sub>), 67.85, 68.69 (C<sub>5</sub>H<sub>4</sub>), 69.38 (C<sub>5</sub>H<sub>5</sub>), 74.86 (C<sub>ipso</sub>Fc), 109.48, 115.04, 125.90, 127.17, 128.71 (ArH), 124.54, 127.05, 130.99, 136.75, 138.56, 147.66, 156.76 (C).

MS: *m/z* = 475 [M]<sup>+</sup>.

Anal. Calcd for C<sub>28</sub>H<sub>25</sub>FeN<sub>3</sub>O: C, 70.75; H, 5.30; Fe, 11.75; N, 8.84. Found: C, 70.57; H, 5.49; Fe, 11.57; N, 8.67.

### 3-Ferrocenyl-8-methoxy-2-(4-pyridylmethyl)-4,5-dihydro-2*H*-benzo[g]indazole (7d)

Yield: 24%; mp 226–227 °C.

IR (KBr): 3084, 3021, 2937, 2846, 1943, 1597, 1569, 1503, 1478, 1451, 1427, 1372, 1301, 1244, 1207, 1163, 1104, 1039, 1007, 905, 823, 800, 748 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.96 (m, 4 H, CH<sub>2</sub>), 3.85 (s, 3 H, CH<sub>3</sub>), 4.13 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.31 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.71 (br s, 2 H, CH<sub>2</sub>), 6.82 (dd, *J* = 2.7, 8.1 Hz, 2 H, ArH), 7.02 (dd, *J* = 1.5, 6.0 Hz, 1 H, ArH), 7.18 (d, *J* = 8.1 Hz, 1 H, ArH), 7.42 (d, *J* = 2.7 Hz, 1 H, ArH), 8.58 (dd, *J* = 1.5, 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 20.71, 28.95 (2 × CH<sub>2</sub>), 52.51 (CH<sub>2</sub>), 55.53 (CH<sub>3</sub>), 67.76, 68.90 (C<sub>5</sub>H<sub>4</sub>), 69.41 (C<sub>5</sub>H<sub>5</sub>), 74.38 (C<sub>ipso</sub>Fc), 106.50, 114.52, 121.10, 129.24, 150.21 (ArH), 115.71, 128.69, 130.52, 137.23, 147.71, 148.39, 158.72 (C).

MS: *m/z* = 475 [M]<sup>+</sup>.

Anal. Calcd for C<sub>28</sub>H<sub>25</sub>FeN<sub>3</sub>O: C, 70.75; H, 5.30; Fe, 11.75; N, 8.84. Found: C, 70.61; H, 5.38; Fe, 12.00; N, 8.71.

### 3-Ferrocenyl-6,8-dimethyl-2-(4-pyridylmethyl)-4,5-dihydro-2*H*-benzo[g]indazole (7e)

Yield: 27%; mp 235–237 °C.

IR: 3078, 3019, 2936, 2917, 2836, 1944, 1641, 1597, 1571, 1505, 1466, 1413, 1380, 1314, 1302, 1264, 1216, 1161, 1102, 1063, 1033, 991, 912, 850, 827, 797, 743 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.32 (s, 3 H, CH<sub>3</sub>), 2.34 (s, 3 H, CH<sub>3</sub>), 2.97 (m, 4 H, CH<sub>2</sub>), 4.05 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.30 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.70 (br s, 2 H, CH<sub>2</sub>), 6.96 (br s, 1 H, ArH), 7.00 (d, *J* = 6.3 Hz, 2 H, ArH), 7.60 (br s, 1 H, ArH), 8.57 (d, *J* = 6.3 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 19.98, 29.31 (2 × CH<sub>2</sub>), 20.87, 25.13 (2 × CH<sub>3</sub>), 52.51 (CH<sub>2</sub>), 67.72, 68.85 (C<sub>5</sub>H<sub>4</sub>), 69.41 (C<sub>5</sub>H<sub>5</sub>), 74.54 (C<sub>ipso</sub>Fc), 120.74, 121.12, 130.47, 150.17 (ArH), 115.19, 129.26, 131.68, 135.56, 135.79, 136.92, 147.80, 148.75 (C).

MS: *m/z* = 473 [M]<sup>+</sup>.

Anal. Calcd for C<sub>29</sub>H<sub>27</sub>FeN<sub>3</sub>: C, 73.58; H, 5.75; Fe, 11.80; N, 8.87. Found: C, 73.74; H, 5.52; Fe, 11.59; N, 8.67.

### 3-Phenyl-2-(4-pyridylmethyl)-4,5-tetrahydro-2*H*-benzo[g]indazole (7f)

Yield: 35%; mp 143–145 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.90–3.21 (m, 4 H, CH<sub>2</sub>), 5.75 (br s, 1.86 H, CH<sub>2</sub>), 7.10 (d, *J* = 6.0 Hz, 2 H, ArH), 7.35–7.64 (m, 5 H, ArH), 7.72 (m, 2 H, ArH), 7.85 (d, *J* = 6.6 Hz, 2 H, ArH), 8.43 (d, *J* = 6.0 Hz, 2 H, ArH).

MS: *m/z* = 337 [M]<sup>+</sup>.

Anal. Calcd for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>: C, 81.88; H, 5.68; N, 12.44. Found: C, 81.51; H, 5.97; N, 12.17.

### 3-Ferrocenyl-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8a)

Yield: 24%; mp 222–223 °C.

IR (KBr): 3334, 3082, 2931, 2845, 1949, 1647, 1598, 1562, 1464, 1415, 1344, 1299, 1217, 1164, 1104, 1067, 1003, 952, 876, 817, 777, 731 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, D<sub>2</sub>O): δ = 2.92 (m, 2 H, CH<sub>2</sub>), 3.01 (m, 2 H, CH<sub>2</sub>), 4.07 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.03 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.16 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.26 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.31 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.45 (dd, *J* = 4.5, 8.7 Hz, 1 H, CH), 5.89 (d, *J* = 4.5 Hz, 1 H, CH), 6.02 (d, *J* = 8.7 Hz, 1 H, OH), 7.07 (d, *J* = 6.0 Hz, 2 H, ArH), 7.22 (d, *J* = 6.0 Hz, 2 H, ArH), 7.20–7.39 (m, 4 H, ArH), 8.44 (d, *J* = 6.0 Hz, 2 H, ArH), 8.62 (d, *J* = 6.0 Hz, 2 H, ArH).

MS: *m/z* = 552 [M]<sup>+</sup>.

Anal. Calcd for C<sub>33</sub>H<sub>28</sub>FeN<sub>4</sub>O: C, 71.75; H, 5.11; Fe, 10.11; N, 10.14. Found: C, 71.49; H, 4.95; Fe, 10.30; N, 9.97.

### 3-Ferrocenyl-6-methoxy-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8b)

Yield: 19%; mp 235 °C (decomp.).

IR (KBr): 3399, 3081, 3023, 2931, 2832, 1945, 1612, 1596, 1567, 1499, 1453, 1414, 1375, 1343, 1301, 1260, 1212, 1101, 1044, 1002, 925, 876, 821, 793, 727 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.90 (m, 2 H, CH<sub>2</sub>), 3.11 (m, 2 H, CH<sub>2</sub>), 3.90 (s, 3 H, CH<sub>3</sub>), 4.05 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.03 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.16 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.26 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.30 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.44 (dd, *J* = 4.2, 9.0 Hz, 1 H, CH), 5.89 (d, *J* = 4.2 Hz, 1 H, CH), 6.07 (d, *J* = 9.0 Hz, 1 H, OH), 6.90 (dd, *J* = 0.9, 8.4 Hz, 1 H, ArH), 7.08 (d, *J* = 6.0 Hz, 2 H, ArH), 7.21 (d, *J* = 6.0 Hz, 2 H, ArH), 7.32 (t, *J* = 8.4 Hz, 1 H, ArH), 7.58 (dd, *J* = 0.9, 8.4, Hz, 1 H, ArH), 8.45 (d, *J* = 6.0 Hz, 2 H, ArH), 8.62 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 19.59, 21.44 (2 × CH<sub>2</sub>), 55.59 (CH<sub>3</sub>), 65.50 (CH), 67.09, 68.40, 68.77, 69.09 (C<sub>5</sub>H<sub>4</sub>), 69.42 (C<sub>5</sub>H<sub>5</sub>), 73.72 (CHOH), 76.18 (C<sub>ipso</sub>Fc), 110.23, 115.05, 121.28, 122.23, 127.31, 149.70, 150.25 (ArH), 114.97, 125.0, 129.97, 139.18, 147.43, 148.51, 149.60, 156.95 (C).

MS: *m/z* = 582 [M]<sup>+</sup>.

Anal. Calcd for C<sub>34</sub>H<sub>30</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 70.11; H, 5.19; Fe, 9.59; N, 9.61. Found: C, 70.28; H, 5.40; Fe, 9.38; N, 9.49.

### 3-Ferrocenyl-7-methoxy-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8c)

Yield: 23%; mp 271 °C (decomp.).

IR (KBr): 3426, 3089, 2937, 2834, 1940, 1614, 1589, 1529, 1464, 1433, 1371, 1347, 1304, 1257, 1152, 1106, 1032, 1004, 864, 820, 759 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.90 (m, 2 H, CH<sub>2</sub>), 2.97 (m, 2 H, CH<sub>2</sub>), 3.86 (s, 3 H, CH<sub>3</sub>), 4.03 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.01 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.25 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.28 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.33 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.63 (t, *J* = 6.0 Hz, 1 H, CH), 5.95 (d, *J* = 6.0 Hz, 1 H, CH), 6.27 (d, *J* = 6.0 Hz, 1 H, OH), 6.87 (m, 2 H, ArH), 7.15 (d, *J* = 4.5 Hz, 2 H, ArH), 7.25 (d, *J* = 6.0 Hz, 2 H, ArH), 7.85 (d, *J* = 8.1 Hz, 1 H, ArH), 8.43 (d, *J* = 6.0 Hz, 2 H, ArH), 8.52 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 19.33, 29.03 (2 × CH<sub>2</sub>), 54.34 (CH<sub>3</sub>), 65.08 (CH), 67.20, 68.34, 68.81, 69.12 (C<sub>5</sub>H<sub>4</sub>), 69.39 (C<sub>5</sub>H<sub>5</sub>), 73.19 (CHOH), 73.23 (C<sub>ipso</sub>Fc), 111.38, 112.85, 120.42, 122.83, 137.43, 148.32, 148.37 (ArH), 113.22, 121.43, 122.62, 136.86, 145.69, 146.08, 149.40, 158.37 (C).

MS: *m/z* = 582 [M]<sup>+</sup>.

Anal. Calcd for C<sub>34</sub>H<sub>30</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 70.11; H, 5.19; Fe, 9.59; N, 9.61. Found: C, 69.97; H, 5.02; Fe, 9.76; N, 9.45.

### 3-Ferrocenyl-8-methoxy-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8d)

Yield: 20%; mp 268 °C (decomp.).

IR (KBr): 3369, 3078, 2924, 2848, 1945, 1612, 1597, 1563, 1500, 1467, 1411, 1297, 1267, 1209, 1167, 1103, 1035, 1001, 876, 811, 750 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.87 (m, 4 H, 2 × CH<sub>2</sub>), 3.89 (s, 3 H, CH<sub>3</sub>), 4.18 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.20 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.32 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.36 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.38 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.71 (t, *J* = 6.6 Hz, 1 H, CH), 6.02 (d, *J* = 6.6 Hz, 1 H, CH), 6.25 (d, *J* = 6.6 Hz, 1 H, OH), 6.82 (dd, *J* = 2.7, 8.4 Hz, 1 H, ArH), 7.20 (d, *J* = 6.3 Hz, 2 H, ArH), 7.23 (d, *J* = 6.3 Hz, 2 H, ArH), 7.46 (d, *J* = 2.7 Hz, 1 H, ArH), 7.51 (d, *J* = 8.4 Hz, 1 H, ArH), 8.40 (d, *J* = 6.3 Hz, 2 H, ArH), 8.47 (d, *J* = 6.3 Hz, 2 H, ArH).

MS: *m/z* = 582 [M]<sup>+</sup>.

Anal. Calcd for C<sub>34</sub>H<sub>30</sub>FeN<sub>4</sub>O<sub>2</sub>: C, 70.11; H, 5.19; Fe, 9.59; N, 9.61. Found: C, 70.29; H, 5.39; Fe, 9.80; N, 9.79.

### 3-Ferrocenyl-6,8-dimethyl-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8e)

Yield: 18%; mp 254–255 °C.

IR (KBr): 3337, 3090, 3034, 2937, 2858, 1944, 1645, 1600, 1563, 1506, 1417, 1372, 1300, 1197, 1169, 1106, 1073, 1036, 1001, 961, 881, 851, 813, 745 cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.35 (s, 3 H, CH<sub>3</sub>), 2.40 (s, 3 H, CH<sub>3</sub>), 2.93 (m, 4 H, 2 × CH<sub>2</sub>), 4.05 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.02 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.15 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.26 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.29 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.45 (dd, *J* = 4.2, 8.7 Hz, 1 H, CH), 5.87 (d, *J* = 4.2 Hz, 1 H, CH), 6.18 (d, *J* = 8.7 Hz, 1 H, OH), 7.03 (s, 1 H, ArH), 7.07 (d, *J* = 6.0 Hz, 2 H, ArH), 7.22 (d, *J* = 6.0 Hz, 2 H, ArH), 7.64 (s, 1 H, ArH), 8.43 (d, *J* = 6.0 Hz, 1 H, ArH), 8.62 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, D<sub>2</sub>O): δ = 2.35 (s, 3 H, CH<sub>3</sub>), 2.40 (s, 3 H, CH<sub>3</sub>), 2.93 (m, 4 H, 2 × CH<sub>2</sub>), 4.06 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.02 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.14 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.26 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 4.30 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.45 (d, *J* = 4.2 Hz, 1 H, CH), 5.87 (d, *J* = 4.2 Hz, 1 H, CH), 7.03 (s, 1 H, ArH), 7.08 (d, *J* = 6.0 Hz, 2 H, ArH), 7.21 (d, *J* = 6.0 Hz, 2 H, ArH), 7.64 (s, 1 H, ArH), 8.42 (d, *J* = 6.0 Hz, 1 H, ArH), 8.63 (d, *J* = 6.0 Hz, 2 H, ArH).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 19.95 (CH<sub>3</sub>), 20.01 (CH<sub>3</sub>), 21.04, 24.96 (2 × CH<sub>2</sub>), 65.38 (CH), 67.06, 68.37, 68.76, 69.08 (C<sub>5</sub>H<sub>4</sub>), 69.41 (C<sub>5</sub>H<sub>5</sub>), 73.81 (CHOH), 76.20 (C<sub>ipso</sub>Fc), 114.67, 120.88, 121.27, 122.24, 149.70, 150.25 (ArH), 128.31, 128.59, 131.07, 131.97, 135.85, 135.95, 139.08, 147.50, 148.99 (C).

MS: *m/z* = 580 [M]<sup>+</sup>.

Anal. Calcd for C<sub>35</sub>H<sub>32</sub>FeN<sub>4</sub>O: C, 72.42; H, 5.56; Fe, 9.62; N, 9.65. Found: C, 72.56; H, 5.36; Fe, 9.49; N, 9.88.

### 3-Phenyl-2-[2-hydroxy-1,2-bis(4-pyridyl)ethyl]-4,5-dihydro-2*H*-benzo[g]indazole (8f)

Yield: 32%; mp 199–202 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.97 (m, 2 H, 2 × CH<sub>2</sub>), 3.10 (m, 2 H, CH<sub>2</sub>), 5.49 (dd, *J* = 4.8, 9.0 Hz, 1 H, CH), 5.98 (d, *J* = 4.8 Hz, 1 H, CH), 6.11 (d, *J* = 9.0 Hz, 1 H, OH), 7.12 (d, *J* = 6.3 Hz, 2 H, ArH), 7.20 (d, *J* = 6.3 Hz, 2 H, ArH), 7.22–7.79 (m, 9 H, ArH), 8.41 (d, *J* = 6.3 Hz, 2 H, ArH), 8.64 (d, *J* = 6.3 Hz, 2 H, ArH).

MS: *m/z* = 444 [M]<sup>+</sup>.

Anal. Calcd for C<sub>29</sub>H<sub>24</sub>N<sub>4</sub>O: C, 78.36; H, 5.44; N, 12.60. Found: C, 78.60; H, 5.22; N, 12.38.

### 3-Phenyl-3,3a,4,5-tetrahydro-2*H*-benzo[g]indazole (2f)

Yield: 74%; mp 121–123 °C.

<sup>1</sup>H NMR (acetone-d<sub>6</sub>): δ = 3.07 (m, 4 H, 2 × CH<sub>2</sub>), 3.61 (t, *J* = 4.8 Hz, 1 H, CH), 6.99 (br s, 1 H, NH), 7.16–7.49 (m, 9 H, ArH).

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 234759 for compound 5b. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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