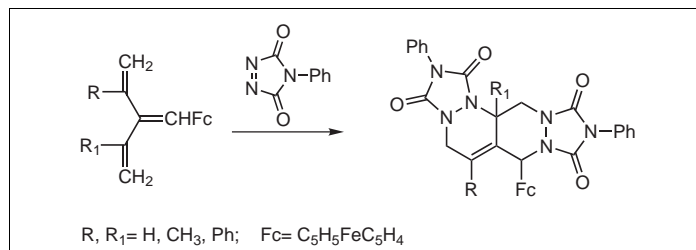


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Cross-conjugated monoferrocenyltrienes react with 4-phenyl-1,2,4-triazoline-3,5-dione to give mono- and bis-[4+2]-cycloaddition products. Nonsubstituted and 2,4-disubstituted 3-ferrocenylmethylidenepenta-1,4-dienes afford respective pyridazine and pyridazino[4,5-*c*]pyridazine derivatives. Their structures were established based on <sup>1</sup>H and <sup>13</sup>C NMR data and X-ray diffraction analysis.

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## Introduction.

Introduction of ferrocenyl substituents into organic compounds enhances, as a rule, biological activities of the resulting substances and diminishes their toxicities compared with those of analogous compounds without ferrocene fragments [1-4]. Biologically active compounds include various ferrocenyl-substituted nitrogen heterocycles, such as triazoles, pyrazolines, pyrazoles, pyrimidones, tetrahydropyridazines, *etc.* [5-9].

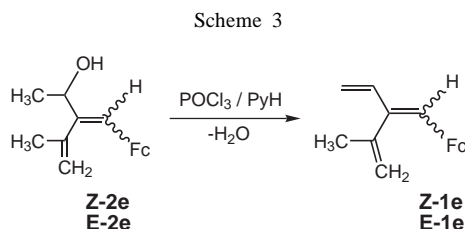
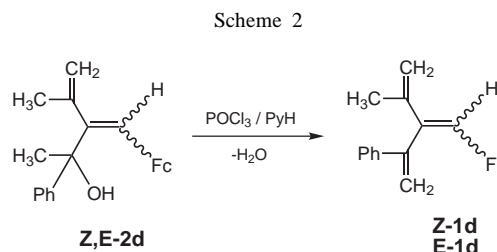
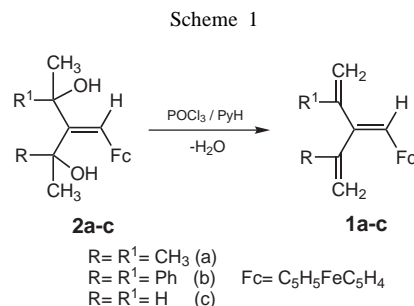
The most common route to tetrahydropyridazine derivatives involves [4+2]-cycloaddition reaction of azodicarboxylic acid derivatives with 1,3-dienes [6,10]. Reactions of cross-conjugated trienes with 4-phenyl-1,2,4-triazoline-3,5-dione should occur in a stepwise manner to give ultimately bis-Diels - Alder adducts containing four nitrogen atoms in a bicyclic structure – pyridazino[4,5-*c*]pyridazine derivatives. One can expect that this type of products will possess a wide spectrum of useful biological characteristics. In particular, these compounds with ferrocenyl substituents are interesting as potential bio-receptor ligands [11-13].

In the present work, we studied the [4+2]-cycloaddition reactions of recently synthesized **1a** [14] and previously unknown **1b-e** 3-ferrocenylmethylidenepenta-1,4-dienes with 4-phenyl-1,2,4-triazoline-3,5-dione.

## Results and Discussion.

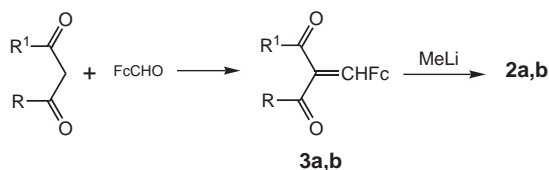
The starting cross-conjugated monoferrocenyltrienes **1a-e** were prepared by dehydration of ferrocenylmethylidenepentane-1,4-diol **2a-c** and *Z*- and *E*-3-ferrocenylmethylidene-4-

methyl-2-phenyl- and 3-ferrocenylmethylidene-4-methyl-4-penten-2-ols **2d**, **2e** under the action of POCl<sub>3</sub> in pyridine according to the following schemes (Schemes 1, 2 and 3).

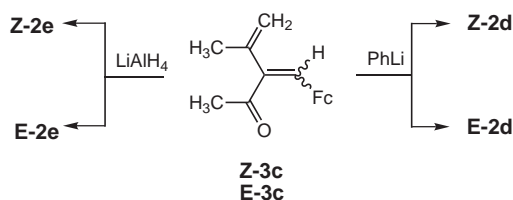


3-Ferrocenylmethylidenepentane-2,4-diols **2a,b** were obtained by addition of MeLi in benzene to 3-ferrocenylmethylidenepentane-2,4-diones (**3a,b**) (Scheme 4), compounds **2c**, *Z*-**2e** and *E*-**2e** were prepared by reduction of ketones **3a**, *Z*-**3c** and *E*-**3c** [15] under the action of LiAlH<sub>4</sub> (Schemes 4 and 5), pentenols *Z*-**2d** and *E*-**2d** were obtained by addition of PhLi to *Z*- and *E*-2-acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes **3c** (Scheme 5).

Scheme 4



Scheme 5



The compounds **2a-e** were isolated in 40-82% yield following chromatographic purification on alumina. The structures of compounds **2a-e** were established on the basis of <sup>1</sup>H and <sup>13</sup>C NMR spectra (Tables 1 and 2). <sup>1</sup>H NMR spectral data suggest that compounds **2a-c** were formed as mixtures of two diastereomers in *ca.* 2:1, 1.5:1 and 1:1 ratios, respectively. The yields of the trienes **1a-e** (storage - stable orange crystals) were 23-65%.

The newly synthesized alcohols **2b-e** and trienes **1b-e** were identified based on <sup>1</sup>H and <sup>13</sup>C NMR data, elemental analysis and the known spatial structures for the starting non-symmetrical enones *Z*-**3c**, *E*-**3c** [15].

The ferrocenyltrienes **1a-e** obtained are orange crystalline compounds. 3-Ferrocenylmethylidenepenta-1,4-diene **1c** was the least stable, it polymerized within several hours when stored under ordinary conditions. 2,4-Diphenyl-3-ferrocenylmethylidenepenta-1,4-diene **1b** was the most stable and remained unchanged for a prolonged time.

These trienes react with 4-phenyl-1,2,4-triazoline-3,5-dione at 20 °C to afford a mixture of mono and bis Diels-Alder adducts or only bis-adducts (Scheme 6).

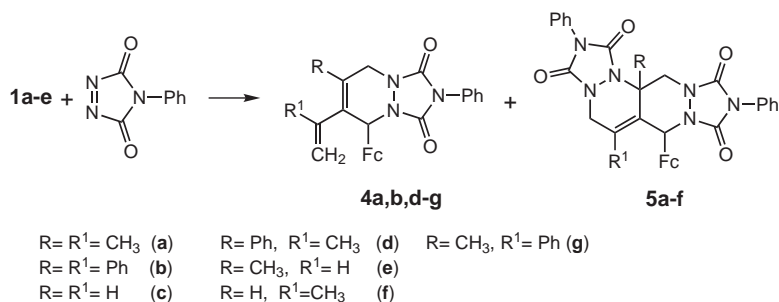
Obviously, the formation of bis-adducts **5a-f** occurs in two steps: the primary mono-adduct of the type **4** contains a system of conjugated multiple bonds and reacts further with the second molecule of the dienophile to give compounds **5**.

The structures of the adducts **4a,b,d-g** and **5a-f** were established based on elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR data (see Experimental). According to the <sup>1</sup>H NMR data, bis-pyridazines **5a-f** are formed stereospecifically. Despite the presence of two chiral centers in the molecules **5a-f**, they were isolated as single diastereomers.

The spatial structures of the bis-adducts **5d** (Figure 1) were based on X-ray diffraction analysis of single crystals obtained with crystallization from chloroform. X-ray data show that **5d** corresponds to *N,N*-diphenyl-5-ferrocenyl-4-methyl-9-phenyl-1,2,3,5,6,7,8,9-octahydro-pyridazino[4,5-*c*]pyridazine-1,2,6,7-tetracarboxydiimide with *cis*-orientation of the ferrocenyl and phenyl substituents.

Thus, the reaction described may be regarded as a convenient method for the synthesis of *N,N,N,N*-tetrasubstituted pyridazino[4,5-*c*]pyridazines with ferrocenyl fragment in the six-membered ring of the bicyclic framework together with other groups.

Scheme 6



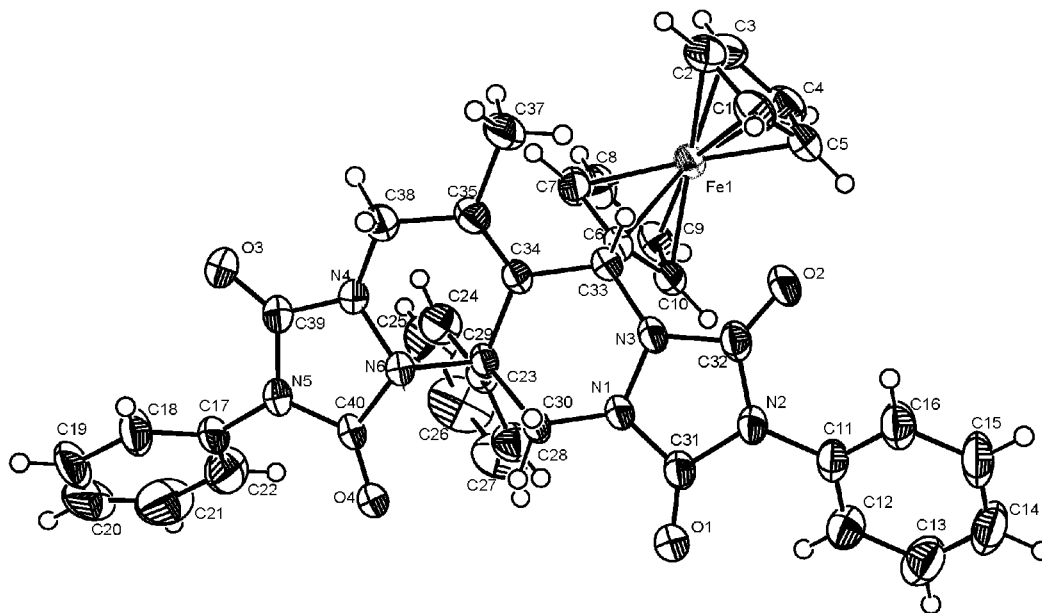


Figure 1. Crystal structure of **5d**. Selected bond lengths (Å): N(1)-N(3) = 1.412(3); N(4)-N(6) = 1.420(3); N(1)-C(30) = 1.462(3); N(6)-C(29) = 1.506(3); C(29)-C(30) = 1.544(4); C(29)-C(34) = 1.539(4); C(33)-C(34) = 1.524(4); N(3)-C(33) = 1.466(4); C(35)-C(34) = 1.338(4); C(35)-C(38) = 1.495(4); N(4)-C(38) = 1.432(4); N(6)-C(29) = 1.506(3); O(1)-C(31) = 1.204(4); N(2)-C(31) = 1.410(4). Selected bond angles (°): C(30)-N(1)-N(3) = 114.8(2); N(1)-N(3)-C(33) = 118.3(2); N(3)-C(33)-C(34) = 108.6(2); N(6)-N(4)-C(38) = 118.1(2); C(31)-N(2)-C(32) = 110.8(2); N(4)-N(6)-C(29) = 112.5(2); C(33)-C(34)-C(35) = 120.3(2); O(1)-C(31)-N(1) = 127.3(3).

Table 1  
<sup>1</sup>H NMR Spectral Data of Compounds **1b-e**; **2b-e**; **4a,b,d,g**; **5a-f** ( $\delta$ , J/Hz)

Compound	C <sub>5</sub> H <sub>5</sub> (s)	C <sub>5</sub> H <sub>4</sub> (m)	CH <sub>3</sub> , CH, CH=	CH <sub>2</sub> ,CH <sub>2</sub> =	Ar, OH
<b>1b</b>	4.02 (5H)	4.12 (2H), 4.28 (2H)	6.21 s (1H)	5.04 bs (1H), 5.23 d (1H), <i>J</i> = 1.2; 5.25 d (1H), <i>J</i> = 1.5; 5.89 d (1H), <i>J</i> = 1.5	7.28 - 7.67 m (10H)
<b>1c</b>	4.14 (5H)	4.27 (2H), 4.42 (2H)	6.21 s (1H), 6.46 ddd (1H), <i>J</i> = 1.5, 10.5, 17.3; 6.75 ddd (1H), <i>J</i> = 1.8, 11.7, 17.3	5.11 dd (1H), <i>J</i> = 1.5, 10.5; 5.33 dm (1H), <i>J</i> = 1.5, 10.5; 5.38 dd (1H), <i>J</i> = 1.8, 11.7; 5.44 dd (1H), <i>J</i> = 1.8, 11.7	-
<b>1d</b>	4.08 (5H)	4.19 (2H), 4.41 (2H)	2.00 dd (3H), <i>J</i> = 0.9, 1.2; 5.91 s (1H)	4.97 m (1H); 5.12 m (1H); 5.23 m (1H); 5.31 m (1H)	7.30 - 7.46 m (5H)
<b>Z-1e</b>	4.09 (5H)	4.22 (2H), 4.48 (2H)	1.94 dd (3H), <i>J</i> = 1.2, 1.8; 6.03 s (1H); 6.38 dd (1H), <i>J</i> = 10.2, 17.1	4.85 m (1H); 5.0 dm (1H), <i>J</i> = 1.5, 10.2; 5.14 dm (1H), <i>J</i> = 1.5, 17.1; 5.25 m (1H)	-
<b>E-1e</b>	4.12 (5H)	4.24 (2H), 4.40 (2H)	1.95 dd (3H), <i>J</i> = 0.9, 1.5; 6.19 s (1H); 6.72 dd (1H), <i>J</i> = 11.1, 17.4	4.98 m (1H); 5.03 dm (1H), <i>J</i> = 2.7, 11.1; 5.10 dm (1H), <i>J</i> = 2.7, 17.4; 5.30 m (1H)	-
<b>2b</b> (2 diastereomers, ~1.5:1)	3.98 (5H); 4.05 (5H)	3.88 (2H), 3.96 (1H), 4.13 (1H); 3.19 (1H), 3.49(2H), 4.24 (1H)	1.87s (3H), 1.96 s (3H); 1.71 s (3H), 1.79 s (3H); 6.44 s (1H); 6.69 s (1H)	-	<b>1.93</b> bs (1H), <b>2.10</b> bs (1H); 7.19 - 7.60 m (10H); 7.40 - 7.92 m (10H)
<b>2c</b> (2 diastereomers, ~2:1)	4.10 (5H), 4.11 (5H)	4.22 (2H), 4.4.25 (2H), 4.28 ((2H), 4.32 (2H)	1.49 d (3H), <i>J</i> = 6.6; 1.52 d (3H), <i>J</i> = 6.6; 1.40 d (3H), <i>J</i> = 6.9; 1.44 d (3H), <i>J</i> = 6.9; 5.12 q (1H), <i>J</i> = 6.6; 4.58 q (1H), <i>J</i> = 6.9; 6.16 s (1H); 6.23 s (1H).	-	1.82 bs (1H), 2.04 bs (1H)
<b>Z-2d</b>	4.06 (5H)	4.10 (2H), 4.21 (2H)	1.67 dd (3H), <i>J</i> = 1.2, 1.5; 1.84 s (3H); 6.28 s (1H)	4.54 dd (1H), <i>J</i> = 1.2, 2.4; 4.92 dd (1H), <i>J</i> = 1.5, 2.4	2.50 s (1H); 7.23 - 7.45 m (5H)
<b>E-2d</b>	4.09 (5H)	4.18 (2H), 4.45 (2H)	1.60 dd (3H), <i>J</i> = 0.9, 1.2; 1.75 s (3H); 6.31 s (1H)	4.65 dd (1H), <i>J</i> = 0.9, 2.1; 5.09 dd (1H), <i>J</i> = 1.2, 2.1	2.44 s (1H); 7.32 - 7.61 m (5H)
<b>Z-2e</b>	4.02 (5H)	4.07 (2H), 4.19 (2H)	1.64 dd (3H), <i>J</i> = 1.2, 1.5; 1.80 d (3H), <i>J</i> = 6.6; 6.21 s (1H)	4.50 dd (1H), <i>J</i> = 1.2, 2.1; 4.89 dd (1H), <i>J</i> = 1.5, 2.1	2.40 s (1H)

Table 1 (continued)

Compound	C <sub>5</sub> H <sub>5</sub> (s)	C <sub>5</sub> H <sub>4</sub> (m)	CH <sub>3</sub> , CH, CH=	CH <sub>2</sub> ,CH <sub>2</sub> =	Ar, OH
<b>E-2e</b>	4.10 (5H)	4.15 (2H), 4.40 (2H)	1.58 dd (3H), <i>J</i> = 0.9, 1.2; 1.70 d (3H), <i>J</i> = 6.3; 6.27 s (1H)	4.56 dd (1H), <i>J</i> = 0.9, 1.8; 5.09 dd (1H), <i>J</i> = 1.2, 1.8	2.47 s (1H)
<b>4a</b>	4.14 (5H)	4.04 (2H), 4.39 (2H)	1.85 dd (3H), <i>J</i> = 0.9, 1.2; 2.01 s (3H); 5.55 s (1H)	3.93 d (1H), <i>J</i> = 16.5; 4.24 d (1H), <i>J</i> = 16.5; 4.98 bs (1H); 5.35 bs (1H)	7.32 – 7.47 m (5H)
<b>4b</b>	4.05 (5H)	4.15 (3H), 4.34 (1H)	5.68 s (1H)	4.23 dd (1H), <i>J</i> = 1.2, 17.1; 4.77 d (1H), <i>J</i> = 17.1; 5.06 d (1H), <i>J</i> = 0.6; 5.62 d (1H), <i>J</i> = 0.6	7.19 – 7.52 m (15H)
<b>4d</b>	4.12 (5H)	4.08 (2H), 4.18 (1H), 4.42 (1H)	1.75 dd (3H), <i>J</i> = 0.9, 1.5; 5.78 s (1H)	4.06 d (1H), <i>J</i> = 16.8; 4.65 dd (1H), <i>J</i> = 1.5, 16.8; 5.10 bs (1H); 5.18 bs (1H)	7.25 – 7.51 m (10H)
<b>4e</b>	4.10 (5H)	4.06 (2H), 4.35 (2H)	1.87 s (3H); 5.63 s (1H); 6.39 dd (1H), <i>J</i> = 7.8, 16.3	3.85 d (1H), <i>J</i> = 15.3; 4.24 d (1H), <i>J</i> = 15.3; 5.08 dd (1H), <i>J</i> = 1.2, 7.8; 5.51 dd (1H), <i>J</i> = 1.2, 16.3	7.31 – 7.67 m (5H)
<b>4f</b>	4.15 (5H)	4.13 (2H), 4.21 (2H)	1.90 dd (3H), <i>J</i> = 0.6, 1.2; 5.83 s (1H); 6.72 dd (1H), <i>J</i> = 10.8, 17.4	3.94 d (1H), <i>J</i> = 15.3; 4.35 (1H), <i>J</i> = 15.3; 5.43 dd (1H), <i>J</i> = 0.9, 10.8; 5.52 dd (1H), <i>J</i> = 0.9, 17.4	7.34 – 7.53 m (5H).
<b>4g</b>	4.08 (5H)	4.14 (2H), 4.36 (2H)	1.75 bs (3H); 5.54 s (1H)	4.03 d (1H), <i>J</i> = 16.2; 4.27 d (1H), <i>J</i> = 16.2; 5.08 bs (1H); 5.60 bs (1H)	7.29 – 7.57 m (10H)
<b>5a</b>	4.25 (5H)	3.95 (1H), 3.98 (1H), 4.15 (2H)	1.20 s (3H), 2.19 s (3H), 6.61 s (1H)	3.36 d (1H), <i>J</i> = 11.7; 4.01 d (1H), <i>J</i> = 16.8; 4.36 d (1H), <i>J</i> = 16.8; 5.02 d (1H), <i>J</i> = 11.7	7.35 – 7.63 m (10H)
<b>5b</b>	3.79 (5H)	3.31 (1H), 3.46 (1H), 3.62 (2H)	6.39 s (1H)	3.74 d (1H), <i>J</i> = 12.9; 4.35 d (1H), <i>J</i> = 17.1; 4.96 d (1H), <i>J</i> = 17.1; 6.11 d (1H), <i>J</i> = 12.9	7.09 – 7.68 m (20H), 7
<b>5c</b>	4.21 (5H)	4.13 (2H), 4.32 (2H)	3.19 t (1H), <i>J</i> = 10.8; 5.97 s (1H); 6.32 dd (1H), <i>J</i> = 3.6, 4.8	4.23 dd (1H), <i>J</i> = 4.8, 17.1; 4.35 dd (1H), <i>J</i> = 3.6, 17.1; 4.83 m (1H); 5.10 dd (1H), <i>J</i> = 5.4, 10.8	7.36 – 7.53 m (10H)
<b>5d</b>	4.12 (5H)	3.34 (1H), 3.47 (1H), 3.77 (1H), 3.79 (1H)	2.29 s (3H), 6.42 s (1H)	3.60 d (1H), <i>J</i> = 12.6; 4.14 d (1H), <i>J</i> = 17.1; 4.57 d (1H), <i>J</i> = 17.1; 6.10 d (1H), <i>J</i> = 12.6	7.01 – 7.62 m (15H)
<b>5e</b>	4.18 (5H)	3.87 (2H), 4.10 (2H)	1.89 s (3H), 6.08 dd (1H), <i>J</i> = 10.5, 16.5; 6.48 s (1H)	3.69 d (1H), <i>J</i> = 12.9; 4.21 d (1H), <i>J</i> = 12.9; 4.63 dd (1H), <i>J</i> = 9.6, 10.5; 5.98 dd (1H), <i>J</i> = 9.6, 16.5	7.30 – 7.49 m (10H).
<b>5f</b>	4.24 (5H)	4.07 (2H), 4.17 (2H)	2.16 bs (3H), 3.13 t (1H), <i>J</i> = 10.5; 6.38 s (1H)	4.19 dd (1H), <i>J</i> = 1.5, 9.9; 4.22 dd (1H), <i>J</i> = 3.9; 9.9; 4.75 dm (1H), <i>J</i> = 10.5; 4.96 dd (1H), <i>J</i> = 5.1, 10.5	7.36 – 7.56 m (10H).

Table 2

<sup>13</sup>C-NMR Spectral Data of Compounds **1b-e**; **2b,c**; **4a,b,d-f**; **5a-f** (δ, ppm)

Comp.	C <sub>5</sub> H <sub>5</sub>	C <sub>5</sub> H <sub>4</sub>	C <sub>ipso</sub> Fc	CH <sub>3</sub>	CH, CH=	Ar	CH <sub>2</sub> =, CH <sub>2</sub>	C
<b>1b</b>	69.05	69.11, 69.90	81.52	-	129.34	127.25 (2C), 127.82 (4C), 128.69 (4C)	114.54, 116.33	139.98, 140.75, 140.21, 140.46, 144.88
<b>1c</b>	69.11	69.18, 69.87	81.48	-	128.21, 133.75, 138.05	-	113.97, 116.98	134.98
<b>1d</b>	69.04	68.96, 69.37	81.39	22.42	127.43	127.16 (1C), 127.93 (2C), 128.87 (2C)	114.14, 116.20	141.09, 142.11, 143.83, 150.11
<b>Z-1e</b>	69.15	69.01, 69.22	81.02	22.43	127.47, 139.59	-	112.32, 115.46	140.35, 142.53
<b>E-1e</b>	69.09	68.92, 69.82	81.84	22.19	125.63, 133.93	-	114.23, 117.77	139.39, 145.16
<b>2b</b> (1.5:1)	68.76, 68.98	67.98, 68.23, 68.47, 69.24	81.12, 81.23	22.31, 22.45, 23.45, 24.12	127.68, 127.89	128.31, 128.44, 128.83, 128.97, 129.32, 129.67	-	140.24, 140.28, 140.47, 140.65, 140.88, 141.36, 141.93, 143.39, 144.65, 144.87
<b>2c</b> (2:1)	68.99; 69.13	67.41, 69.05, 70.11, 71.43	80.43, 80.61	22.30, 22.36, 23.29, 24.03	66.87, 67.13, 122.79, 123.47	-	-	142.70, 143.44
<b>4a</b>	69.96	66.48, 67.78, 68.90, 68.92	88.01	17.52, 22.59	53.89	125.53, 128.07, 129.13	48.18, 118.31	123.43, 131.37, 133.32, 140.94, 150.68, 153.04
<b>4b</b>	69.90	66.25, 67.15, 68.23, 69.12	86.95	-	55.05	125.56, 126.67, 127.87, 128.43, 128.99, 129.15	48.36, 119.81	131.35, 132.84, 134.15, 137.79, 138.44, 144.24, 151.04, 152.84

Table 2 (continued)

Comp.	C <sub>5</sub> H <sub>5</sub>	C <sub>5</sub> H <sub>4</sub>	C <sub>ipso</sub> Fe	CH <sub>3</sub>	CH, CH=	Ar	CH <sub>2</sub> =, CH <sub>2</sub>	C
<b>4d</b>	69.42	65.99, 67.30, 68.21, 68.61	86.52	22.27	55.95	128.09, 128.15, 128.20, 128.57, 129.08, 129.17	48.18, 125.54	118.72, 131.31, 135.07, 138.10, 141.93, 151.08, 153.10
<b>4e</b>	69.24	66.85, 67.56, 67.59, 67.94	87.24	16.43	51.56, 125.46	128.09, 129.17, 131.27	47.89, 116.14	128.23, 129.00, 130.49, 131.34, 140.88, 150.41, 152.36
<b>4f</b>	69.49	65.67, 66.23, 67.36, 68.74	84.58	17.89	52.39, 124.76	128.79, 129.31, 133.64	47.91, 117.32	129.41, 137.56, 142.72, 150.59, 153.11
<b>5a</b>	69.94	65.95, 66.33, 67.49, 68.43	84.96	17.37, 21.28	53.03	125.28, 125.47, 128.36, 128.39, 129.15, 129.33	47.06, 52.56	59.65, 124.99, 127.89, 130.63, 131.21, 150.25, 152.32, 152.43, 153.71
<b>5b</b>	69.59	63.15, 65.21, 66.40, 68.23	86.12	-	53.18	125.38, 125.57, 127.27, 127.88, 128.38, 128.60, 129.05, 129.28, 129.56	47.32, 50.74	58.98, 128.00, 130.87, 131.20, 133.08, 133.89, 136.08, 150.14, 152.06, 152.74, 154.03
<b>5c</b>	69.63	65.87, 66.23, 66.57, 68.13	85.47	-	48.73, 52.23, 126.42	125.09, 125.68, 127.43, 127.89, 128.42, 129.11	47.85, 50.32	58.57, 128.69, 128.94, 129.73, 130.58, 152.14, 153.23
<b>5d</b>	69.75	65.46, 66.42, 66.44, 67.94	85.86	17.76	52.51	125.34, 125.64, 127.27, 127.79, 128.29, 128.38, 128.45, 128.99, 129.36	46.53, 50.21	62.84, 127.13, 130.47, 131.29, 132.80, 149.41, 151.13, 152.42, 153.44, 154.12
<b>5e</b>	69.55	66.35, 67.32, 68.21, 68.50	84.20	17.01	49.80, 53.37	125.34, 125.45, 128.37, 128.45, 129.26, 129.28	46.74, 46.83	58.31, 123.64, 125.20, 130.63, 150.11, 150.30, 151.91, 152.04
<b>5f</b>	69.61	65.88, 66.24, 67.47, 68.23	84.46	18.36	48.73, 52.81	126.34, 127.78, 128.21, 128.45, 128.94, 131.23	47.18, 49.89	125.36, 126.44, 131.45, 132.54, 150.19, 150.53, 153.61, 153.68

Table 3

Yields, mp., Elemental Analysis and MS Data for the Synthesized Compounds

Compound	Yield, %	M.p., °C	Found, %				Molecular formula	MS, (M <sup>+</sup> )	m/z
			Calculated, %						
			C	H	Fe	N			
<b>1b</b>	65	125-126	<u>80.65</u> 80.77	<u>5.94</u> 5.81	<u>13.51</u> 13.42	-	C <sub>28</sub> H <sub>24</sub> Fe	416	
<b>1c</b>	54	34-35	<u>72.64</u> 72.75	<u>6.19</u> 6.11	<u>21.29</u> 21.14	-	C <sub>16</sub> H <sub>16</sub> Fe	264	
<b>Z-1d</b>	34	94-95	<u>77.81</u> 77.98	<u>6.31</u> 6.26	<u>15.63</u> 15.76	-	C <sub>23</sub> H <sub>23</sub> Fe	354	
<b>E-1d</b>	23	77-78	<u>78.11</u> 77.98	<u>6.13</u> 6.26	<u>15.82</u> 15.76	-	C <sub>23</sub> H <sub>22</sub> Fe	354	
<b>Z-1e</b>	27	37-38	<u>73.21</u> 73.40	<u>6.61</u> 6.52	<u>20.17</u> 20.08	-	C <sub>17</sub> H <sub>18</sub> Fe	287	
<b>E-1e</b>	38	44-45	<u>73.56</u> 73.40	<u>6.46</u> 6.52	<u>20.13</u> 20.08	-	C <sub>17</sub> H <sub>18</sub> Fe	287	
<b>2b</b>	82	183-184	<u>74.51</u> 74.34	<u>6.29</u> 6.21	<u>12.48</u> 12.35	-	C <sub>28</sub> H <sub>28</sub> FeO <sub>2</sub>	452	
<b>2c</b>	80	oil	<u>64.17</u> 64.02	<u>6.81</u> 6.72	<u>18.47</u> 18.60	-	C <sub>16</sub> H <sub>20</sub> FeO <sub>2</sub>	300	
<b>Z-2d</b>	40	142-143	<u>74.11</u> 74.20	<u>6.57</u> 6.49	<u>14.82</u> 15.00	-	C <sub>23</sub> H <sub>24</sub> FeO	372	
<b>E-2d</b>	72	178-179	<u>74.03</u> 74.20	<u>6.53</u> 6.49	<u>15.03</u> 15.00	-	C <sub>23</sub> H <sub>24</sub> FeO	372	
<b>Z-2e</b>	68	oil	<u>68.79</u> 68.93	<u>6.72</u> 6.81	<u>18.74</u> 18.86	-	C <sub>17</sub> H <sub>20</sub> FeO	296	
<b>E-2e</b>	74	oil	<u>69.14</u> 68.93	<u>6.90</u> 6.81	<u>18.91</u> 18.86	-	C <sub>17</sub> H <sub>20</sub> O	296	

Table 3 (continued)

Compound	Yield, %	M.p., °C	Found, % Calculated, %				Molecular formula	MS, (M <sup>+</sup> )	m/z
			C	H	Fe	N			
<b>4a</b>	25	150-151	<u>66.68</u>	<u>5.42</u>	<u>11.88</u>	<u>9.10</u>	C <sub>26</sub> H <sub>25</sub> FeN <sub>3</sub> O <sub>2</sub>	467	
			66.83	5.39	11.94	9.00			
<b>4b</b>	28	195-196	<u>73.19</u>	<u>5.08</u>	<u>9.51</u>	<u>7.18</u>	C <sub>36</sub> H <sub>29</sub> FeN <sub>3</sub> O <sub>2</sub>	591	
			73.11	4.95	9.43	7.10			
<b>4d</b>	18	162-163	<u>70.45</u>	<u>5.17</u>	<u>10.63</u>	<u>8.04</u>	C <sub>31</sub> H <sub>27</sub> FeN <sub>3</sub> O <sub>2</sub>	529	
			70.33	5.14	10.55	7.93			
<b>4e</b>	11	145-146	<u>70.21</u>	<u>5.06</u>	<u>10.44</u>	<u>7.84</u>	C <sub>31</sub> H <sub>27</sub> FeN <sub>3</sub> O <sub>2</sub>	529	
			70.33	5.14	10.55	7.93			
<b>4f</b>	10	153-154	<u>66.21</u>	<u>5.04</u>	<u>12.44</u>	<u>9.21</u>	C <sub>25</sub> H <sub>23</sub> FeN <sub>3</sub> O <sub>2</sub>	453	
			66.24	5.11	12.32	9.27			
<b>4g</b>	15	141-143	<u>66.35</u>	<u>5.19</u>	<u>12.19</u>	<u>9.38</u>	C <sub>25</sub> H <sub>23</sub> FeN <sub>3</sub> O <sub>2</sub>	453	
			66.24	5.11	12.32	9.27			
<b>5a</b>	61	213-214	<u>63.68</u>	<u>4.80</u>	<u>8.64</u>	<u>13.23</u>	C <sub>34</sub> H <sub>30</sub> FeN <sub>6</sub> O <sub>4</sub>	642	
			63.56	4.71	8.70	13.07			
<b>5b</b>	66	248-250	<u>69.11</u>	<u>4.38</u>	<u>7.41</u>	<u>10.87</u>	C <sub>44</sub> H <sub>34</sub> FeN <sub>6</sub> O <sub>4</sub>	767	
			68.94	4.47	7.29	10.96			
<b>5c</b>	74	229-230	<u>62.70</u>	<u>4.31</u>	<u>8.98</u>	<u>13.76</u>	C <sub>32</sub> H <sub>26</sub> FeN <sub>6</sub> O <sub>4</sub>	614	
			62.56	4.27	9.09	13.67			
<b>5d</b>	60	211-213	<u>66.39</u>	<u>4.49</u>	<u>7.84</u>	<u>12.03</u>	C <sub>39</sub> H <sub>32</sub> FeN <sub>6</sub> O <sub>4</sub>	704	
			66.49	4.58	7.93	11.92			
<b>5f</b>	15	204-205	<u>63.02</u>	<u>4.39</u>	<u>11.91</u>	<u>8.95</u>	C <sub>33</sub> H <sub>28</sub> FeN <sub>6</sub> O <sub>4</sub>	628	
			63.07	4.49	11.80	8.89			
<b>5g</b>	42	179-180	<u>63.15</u>	<u>4.57</u>	<u>11.59</u>	<u>8.77</u>	C <sub>33</sub> H <sub>28</sub> FeN <sub>6</sub> O <sub>4</sub>	628	
			63.07	4.49	11.80	8.89			

## EXPERIMENTAL

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as the internal standard. The NMR spectroscopic data are listed in Tables 1 and 2. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elemental Analysis system GmbH was used for determination of elemental analyses. The mass spectrometric data, data from elemental analyses, yields, and melting points of the compounds obtained are given in Table 3. Column chromatography was carried out on alumina (Brockmann activity III).

The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; 2,4-pentanedione, 99+%; dibenzoylmethane, 98%; methyllithium, 1.6 M solution in diethyl ether; phenyllithium, 1.9 M solution in cyclohexane-ether; 4-phenyl-1,2,4-triazoline-3,5-dione, 98%; lithium aluminium hydride, powder, 98%; phosphorus oxychloride, 99%; pyridine, anhydrous, 99.8%; piperidine, 99%.

3-Ferrocenylmethylidene-2,4-pentanedione (**3a**) and 3-Ferrocenylmethylidene-1,3-diphenyl-1,3-propanedione (**3b**).

Compounds **3a** and **3b** were prepared by condensation of ferrocenecarbaldehyde with pentane-2,4-dione or dibenzoylmethane in benzene in the presence of piperidinium acetate. The yield of compound **3a** was 72%, m.p. 141-142 °C (ref. [14,15]: mp 142 °C). The yield of compound **3b** was 81%, mp 203-204 °C (ref. [16]: mp 203-204 °C).

Synthesis of 3-Ferrocenylmethylidene-2,4-dimethylpentane-2,4-diol (**2a**).

A 1.6 M solution of methyllithium in diethyl ether (30.0 ml) was added dropwise in an inert atmosphere to a stirred solution of the diketone **3a** (2.86 g, 0.01 mol) in dry benzene (100 ml) for 30 min at 20 °C. The mixture was stirred for an additional 2 h and the excess of methyllithium was quenched by addition of water (50 ml). The organic layer was separated, dried with Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed *in vacuo*, and the residue was chromatographed on alumina (hexane-diethyl ether, 2:1) to give the diol **2a** (2.2 g, 67%), orange powder, mp 75-77 °C (ref. [14]: mp 75-77 °C).

3-Ferrocenylmethylidene-2,4-diphenylpentane-2,4-diol (**2b**) was obtained similarly.

Z- and E-2-Acetyl-1-ferrocenyl-3-methylbuta-1,3-dienes (Z-**3c** and E-**3c**).

Compounds Z- and E-**3c** were prepared by reaction of 3-(ferrocenylmethylidene)pentane-2,4-dione **3a** with methyllithium in tetrahydrofuran. The yield of Z-**3c** was 27%, orange crystals, mp 58-60 °C. (ref.[15] mp 58 -60 °C), MS: m/z 294 [M]<sup>+</sup>. The yield of E-**3c** was 46%; red crystals, mp 84-85 °C. (ref.[15] mp 84 -85 °C), MS: m/z 294 [M]<sup>+</sup>.

Reaction of Diene **3c** with Phenyllithium.

A solution of PhLi (1.9 M solution in cyclohexane-diethyl ether, 15 ml) was added to a stirred solution of compound Z-**3c** (1.47 g, 5 mmol) in dry benzene (100 ml), the mixture was stirred for additional 30 min at 20 °C and the excess of phenyllithium was quenched by addition of water (50 ml). The organic layer was separated, washed with water (2 × 20 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed *in vacuo* and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (hexane – ether, 2:1) to

give 0.74 g (40%) of 3-ferrocenylmethylidene-4-methyl-2-phenyl-4-pentene-2-ol **Z-2d**, yellow crystals, mp 142-143 °C.

3-Ferrocenylmethylidene-4-methyl-2-phenyl-4-pentene-2-ol **E-2d** was obtained similarly.

Synthesis of 3-Ferrocenylmethylidene-2,4-pentanediol (**2c**).

LiAlH<sub>4</sub> (0.19 g, 5 mmol) was added to a stirred solution of compound **3a** (1.48 g, 5 mmol) in abs. diethyl ether (100 ml), the mixture was stirred for additional 40 min at 20 °C and the excess of LiAlH<sub>4</sub> was quenched by addition of ethyl acetate (10 ml) and water (50 ml). The organic layer was separated, washed with water (2 × 20 ml), and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed *in vacuo* and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (hexane - ether, 2:1) to give 1.2 g (80%) of 3-ferrocenylmethylidene-2,4-pentanediol **2c**, yellow oil.

**Z-** and **E-**3-ferrocenylmethylidene-4-methyl-4-pentane-2-ols (**Z-2e** and **E-2e**) were obtained similarly.

Dehydration of the Alcohols **2a-e** with POCl<sub>3</sub>/PyH.

The alcohols **2a - 2e** (0.01 mol) were added to a mixture of dry pyridine (100 ml) and POCl<sub>3</sub> (1.0 ml) and stirred at 30 - 40 °C for 3 h (TLC control). The reaction mixture was treated with water (100 ml) and benzene (100 ml), the organic layer was separated, washed with water (3 × 50 ml) and concentrated *in vacuo*. The residue was chromatographed on a column with Al<sub>2</sub>O<sub>3</sub> in hexane to yield trienes **1a - 1e**.

Condensation of Trienes **1a - 1e** with 4-Phenyl-1,2,4-triazoline-3,5-dione.

4-Phenyl-1,2,4-triazoline-3,5-dione (0.2 g, 1.22 mmol) was added portionwise to a stirred solution of the triene **1a** (or **1b-e**) (0.37 g, 1 mmol) in benzene (30 ml) at 20-25 °C and the solution discolored. Stirring was continued for an additional 1 h and the solvent was evaporated. Column chromatography of the residue on Al<sub>2</sub>O<sub>3</sub> (hexane - dichloromethane, 2:1) afforded *N*-phenyl-3-ferrocenyl-4-isopropenyl-5-methyl-1,2,3,6-tetrahydropyridazine-1,2-dicarboximide **4a** (0.12 g, 25%) and *N,N*-diphenyl-5-ferrocenyl-4,9-dimethyl-1,2,3,5,6,7,8,9-octahydro-pyridazino[4,5-*c*]pyridazine-1,2,6,7-tetracarboxdiimide **5a** (0.39 g, 61%).

Tetrahydropyridazine-1,2-dicarboximides **4b,d-g** and octahydro-pyridazino[4,5-*c*]pyridazine-1,2,6,7-tetracarboxdiimides **5a-f** were obtained similarly.

Determining the Crystal Structure.

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The structure of compound **5d** was solved by the direct method (SHELXS) and refined using full-matrix least-squares on *F*<sup>2</sup>.

Crystal data for C<sub>29</sub>H<sub>25</sub>Fe<sub>2</sub>N<sub>3</sub> (**5d**): *M* = 704.56 gmol<sup>-1</sup>, triclinic *P*-1, *a* = 11.135(4), *b* = 11.895(3), *c* = 11.300(4) Å, α = 76.416(19), β = 87.78(3), γ = 70.93(2)°, *V* = 1617.0(8) Å<sup>3</sup>, *T* = 298(2) K, *Z* = 2, ρ = 1.447 Mg/m<sup>3</sup>, λ (Mo - Kα) = 0.71073 Å, *F*(000) = 732, absorption coefficient 0.520 mm<sup>-1</sup>, index ranges -1 ≤ *h* ≤ 13, -14 ≤ *k* ≤ 14, -16 ≤ *l* ≤ 16, scan range 1.58 ≤ θ ≤ 27.00°, 7045 independent reflections, *R*<sub>int</sub> = 0.0241, 8061 total

reflections, 394 refinable parameters, final *R* indices [*I* > 2σ(*I*)] *R*<sub>1</sub> = 0.0586, *wR*<sub>2</sub> = 0.1526, *R* indices (all data) *R*<sub>1</sub> = 0.0800, *wR*<sub>2</sub> = 0.1666, largest difference peak and hole 0.607/-0.764 e-Å<sup>-3</sup>.

Supplementary material CCDC-285845 (for **5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/const/retrieving.html](http://www.ccdc.cam.ac.uk/const/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, UK; Fax: (internat.) +44-1223/336-0333; E-mail: [deposit@ccdc.cam.ac.uk].

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