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Diferrocenyl(hydroxy)oxazepines and diferrocenyl-4-*aza*-1,3-dienes in the reactions of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide with aromatic and aliphatic *bis*-1,4-*N,O*-nucleophiles

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ABSTRACT

A novel method for the synthesis of 3,4-diferrocenyl-2-methylthio-2,3-dihydrobenzo[*b*]-1,4-oxazepin-3-ols **7a–e** (23–30%), 3,4-diferrocenylquinolin-8-ols **8b–d** (9–16%), 1-*E*-2,3-diferrocenyl-4-(2-hydroxyphenyl)-1-methylthio-4-aza-1,3-dienes **9a–e** (24–30%), *cis*-/*trans*-2,3-diferrocenyl-3-methylthioacroleins **10a,b** (7–19%), *S,R*-5,6-diferrocenyl-7-methylthio-2,3,6,7-tetrahydro-1,4-oxazepin-6-ols **13b,d,e** (28–33%) and *E,Z*- and *Z,E*-2,3-diferrocenyl-6-hydroxy-1-methylthio-4-aza-1,3-alkadienes **14a–e** (29–34%) and **15a–e** (10–13%) by reactions of 2,3-diferrocenyl-1-sulfanyl-cyclopropenylium iodide **2** with aromatic and aliphatic *bis*-1,4-*N,O*-nucleophiles (1,2-aminophenols **3a–e** and 1,2-aminoalcohols **11a–e**) in the presence of Et_3N is presented. A new reaction for the transformation of the intermediate products of the addition of *bis*-1,4-*N,O*-nucleophiles **3a–e** and **11a–e** to the diferrocenylcyclopropenilium cation **2** in the positions C(1) and C(2) is found. The characterization of the new compounds was conducted by IR, ^1H and ^{13}C NMR spectroscopy, mass-spectrometry, elemental analysis, and X-ray diffraction.

1. Introduction

Bi- and *poly*nuclear ferrocenyl compounds containing conjugated π systems and functional groups in their molecules have recently attracted much interest in organometallic chemistry [1]. This interest is due to the unique physicochemical properties of these compounds [2], which make them promising components for the synthesis of catalytic [3], photochemical, electrochemical [4], pharmacological [5], and other systems on their basis. The synthesis of many organic compounds of the ferrocene series is based on a fairly high availability of functionalized ferrocene derivatives [6], such as ferrocenyl carbaldehyde, acetylferrocene, ferrocenyllithium, diaminomethylferrocene, α,β-enones with ferrocenyl substituents in their molecules [7]. On the basis of these initial compounds, different methods of synthesis have been developed for many polyene, carbo- and heterocyclic products with ferrocene groups in their molecules. These products have various useful properties, e.g., thermal stability [8], magnetic behavior [9], electric conductivity (even superconductivity) [10], nonlinear optical effects [11], bioactivity [12].

In the last two decades, diferrocenylcyclopropenylium salts have been studied as possible initial compounds in the synthesis of diferrocenyl-substituted organic compounds [13]. This methodology is based on the capacity of diferrocenylcyclopropenylium cations for the opening of the three-carbon cycle in the reactions with mono *C*-, *N*-, *O*-nucleophiles and di-*N,N*-, di-*N,O*-nucleophiles, leading to the formation of polyene, carbo- and heterocyclic products with several ferrocene groups. The latter property makes it possible to use these cations for introducing the 1,2-diferrocenylpropene fragment as a three-carbon building block into organic compounds. In addition, the functional groups (OR, NR_2, SR) at the C(1) carbon atom of the three-membered cycle of diferrocenylcyclopropenylium have been found to affect the regioselectivity of the processes in the interactions with nucleophiles, which is expressed in the nucleophilic attacks of the reagents predominantly on the carbon atom C(1) or C(2) and in subsequent transformations of the intermediates [14]. This phenomenon has been insufficiently studied until now, although it is of interest for the

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synthesis of polyferrocenyl-substituted organic compounds of various classes that cannot be obtained using other methods [15].

It is already known that much attention is paid to the synthesis of novel derivatives of mono- and polycyclic heterocycles containing several heteroatoms in a cycle, since such heterocycles are often present as important structural elements in many natural and medicinal compounds. Ferrocenyl-substituted heterocycles of these types are of special interest in the search for bioactive substances. These compounds include ferrocenyl derivatives of pyrazolines [16], pyrazoles [17], thiazoles [18], oxazoles [19], quinuclidines [20], pyrimidines [21], triazines [22], imidazole [23], etc.

This study investigates the interaction of *bis*-1,4-*N*,*O*-nucleophiles of the aliphatic and aromatic series with 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide with the aim of developing a novel method for the synthesis of hydroxyl-1,3-diene systems and heterocyclic products, like 1,4-oxazines or 1,4-oxazepines.

2. Experimental

2.1. Materials and physical measurements

All the solvents were dried according to the standard procedures and freshly distilled before use. 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 (400-MHz and 100 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard. Chemical shifts (δ, ppm) were reported with respect to residual solvent peaks as internal standard (^{1}H: $CDCl_3$, δ = 7.26 ppm, ^{13}C: $CDCl_3$, δ = 77.2 ppm), δ values were measured with precision 0.01 ppm. The IR spectra were measured on a Spectrophotometer FT-IR (Spectrum RXI Perkin Elmer 400 instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). An Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses.

The following reagents were purchased from Aldrich: ferrocene, 98%; aluminum chloride, 99.99%; tetrachlorocyclopropene, 98%; Lawesson reagent, 97%; triethylamine, 99.5%; iodomethane, 99.5%; 2-aminophenol, 99%; 2-amino-4-methylphenol, 97%; 2-amino-4-*tert*-butylphenol, 98%; 2-amino-4-chlorophenol, 97%; 2-amino-4-nitrophenol, 96%; ethanolamine, 99.5+%; 2-amino-2-phenylethanol, 98%; 2-amino-3-phenylpropanol, 98%; 2-amino-1-phenylethanol, 98%; 2-amino-3-methyl-1-butanol, 97%.

The starting material 2,3-diferrocenylcyclopropenone was obtained from the ferrocene and tetrachlorocyclopropene in the presence of $AlCl_3$. 2,3-Diferrocenyl-1-methylthiocyclopropenylium iodide **2** was obtained from 2,3-diferrocenylcyclopropenthione **1** and methyl iodide according to the standard procedures [24–27], respectively. The physical and ^{1}H NMR spectroscopic characteristics of 2,3-diferrocenylcyclopropenone and 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **2** were in accord with the literature data [24].

2.2. Synthesis

2.2.1. Synthesis of the 2,3-diferrocenylcyclopropenthione (*1*)

A mixture of the 2,3-diferrocenylcyclopropenone 3.4 g (8 mmol), Lawesson reagent 3.0 g (8.2 mmol) in 15 mL of the dry benzene was heated to refluxed (80 °C) in an argon atmosphere ~6–8 h. The organic layer was concentrated, and the residue was chromatographed on alumina (Brockmann activity III, hexane–dichloromethane, 1:1) to give 2,3-diferrocenylcyclopropenthione **1**, yield 3.15 g (7 mmol), 92%, m.p. 208–209 °C. (Lit. [24] m.p. 208–209 °C.)

2.3. Reaction of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide (*2*) with 1,2-aminophenols (*3a–e*) or 1,2-aminoalcohols (*11a–e*) (general procedure)

1,2-Aminophenol **3a** [or **3b–e**, or 1,2-aminoalcohols **11a–e**] (2.5 mmol) and Et_3N (1.0 mL) was added to a stirring solution of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **2** (3.0 mmol) in dry benzene (70 mL) under a nitrogen atmosphere. The reaction mixture was heated to refluxing conditions (6–8 h), the solvent was removed *in vacuo* and the residue was dissolved in dichloromethane (30 mL). The solution was mixed with (Al_2O_3, Brockmann activity III) (20 g) and the solvent was evaporated in air. This material was placed on the top of a column with Al_2O_3 (the height of alumina is *ca.* 20 cm) and the elution was performed first with hexane and then with hexane–ether (3:1), hexane–dichloromethane (4:1) to afford compounds **4**, **5a**, **6a**, **7a**, **9a**, **10a**,**b** [or (**4**, **5b–e**, **6b–e**, **7b–e**, **8b–d**, **9b–e**, **10a**,**b**), or (**4**, **12a–e**, **13b-e**, **14a–e** + **15a–e**, **10a**,**b**)]. *cis*-**14a–e** and *trans*-**15a–e** isomers were isolated by thin-layer chromatography (TLC) on Al_2O_3 or silica in a solvent system hexane–ether (4:1). The physicochemical characteristics of compounds **4**, **5a–e**, **6a–e**, **8c**,**d** and **12a–e** were in accordance with the literature data (See Supplementary material) [27–29].

2.3.1. S,R-3,4-Diferrocenyl-2-methylthio-2,3-dihydrobenzo[b]-1,4-oxazepin-3-ol (*7a*)

Orange powder, yield 0.370 g (26%), m.p. 158–160 °C. IR (KBr): ν 810, 825, 1001, 1102, 1179, 1244, 1285, 1342, 1422, 1431, 1457, 1492, 1589, 1600, 1658, 2867, 2883, 2946, 2986, 3098, 3176, 3430 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (3H, s, CH_3), 3.87 (1H, bs, OH), 4.02 (5H, s, C_5H_5), 4.28 (5H, s, C_5H_5), 4.12, 4.14, 4.16, 4.24, 4.32, 4.67, 4.90, 5.01 ($2C_5H_4$), 5.43 (1H, s, CH), 7.35 (2H, bs, C_6H_4), 7.41 (2H, bs, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.05 (CH_3), 68.94, 69.99 ($2C_5H_5$), 67.22, 67.81, 68.12, 68.25, 69.35, 70.33, 70.80, 71.20 ($2C_5H_4$), 79.76, 84.20 ($2C_{ipso}$Fc), 91.02 (CH), 128.77, 130.87 (C_6H_4), 92.17, 127.93, 134.13, 167.76 (4C). *Anal.* Calc. for $C_{30}H_{27}Fe_2NO_2S$ (577.22): C, 62.42; H, 4.72; N, 2.43; S, 5.54. Found: C, 62.50; H, 4.79; N, 2.42, S, 5.52%. MS (El, 70 eV): *m*/*z* 577 [M]$^{+}$.

2.3.2. S,R-3,4-Diferrocenyl-7-methyl-2-methylthio-2,3-dihydrobenzo[b]-1,4-oxazepin-3-ol (*7b*)

Orange powder, yield 0.440 g (30%), m.p. 157–158 °C. IR (KBr): ν 806, 821, 930, 999, 1027, 1104, 1249, 1296, 1323, 1351, 1404, 1457, 1498, 1572, 1594, 1616, 2842, 2941, 2980, 3088, 3188, 3437 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (3H, s, CH_3), 2.36 (3H, s, CH_3), 3.99 (1H, s, OH), 4.12 (5H, s, C_5H_5), 4.26 (5H, s, C_5H_5), 3.86, 4.08, 4.17, 4.23, 4.38, 4.42, 5.10, 5.13 ($2C_5H_4$), 5.46 (1H, s, CH), 6.90 (1H, d, J = 6.0 Hz, C_6H_3), 7.02 (1H, d, J = 6.0 Hz, C_6H_3), 7.45 (1H, s, C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.87, 20.32 ($2CH_3$), 68.91, 69.84 ($2C_5H_5$), 65.53, 66.97, 67.70, 68.82, 69.75, 70.30, 70.55, 70.65 ($2C_5H_4$), 79.62, 83.73 ($2C_{ipso}$Fc), 90.93 (CH), 120.16, 129.28, 135.32 (C_6H_3), 92.51, 132.10, 135.39, 143.53, 167.22 (5C). *Anal.* Calc. for $C_{31}H_{29}Fe_2NO_2S$ (591.24): C, 62.97; H, 4.94; N, 2.37; S, 5.41. Found: C, 62.77; H, 4.78; N, 2.42, S, 5.50%. MS (El, 70 eV): *m*/*z* 592 [M]$^{+}$.

2.3.3. S,R-7-Chloro-3,4-diferrocenyl-2-methylthio-2,3-dihydrobenzo[b]-1,4-oxazepin-3-ol (*7c*)

Orange powder, yield 0.380 g (25%), m.p. 178–179 °C. IR (KBr): ν 802, 827, 1000, 1103, 1245, 1261, 1388, 1445, 1479, 1551, 1604, 1616, 2864, 2924, 2958, 3094, 3447 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28 (3H, s, CH_3), 3.80 (1H, bs, OH), 4.10 (5H, s, C_5H_5), 4.25 (5H, s, C_5H_5), 3.82, 3.95, 4.16, 4.22, 4.41, 4.45, 5.11, 5.16 ($2C_5H_4$), 5.45 (1H, s, CH), 7.13 (1H, bs, C_6H_3), 7.53 (1H, bs, C_6H_3), 7.70 (1H, s, C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.06 (CH_3), 68.93, 69.97 ($2C_5H_5$), 67.22, 68.13, 69.38, 70.33 ($2C_5H_4$), 79.76,

83.01 ($2C_{ipso}$Fc), 91.01 (CH), 128.77, 130.87, 134.14 (C_6H_3), 92.17, 127.93, 132.25, 144.54, 167.78 (5C). *Anal.* Calc. for $C_{30}H_{26}ClFe_2NO_2S$ (611.70): C, 58.90; H, 4.30; N, 2.20; S, 5.23. Found: C, 59.10; H, 4.50; N, 2.35, S, 5.48%. MS (El, 70 eV): *m*/*z* 612 $[M]^+$.

*2.3.4. S,R-3,4-Diferrocenyl-7-nitro-2-methylthio-2,3-dihydrobenzo [b]-1,4-oxazepin-3-ol (**7d**)*

Orange powder, yield 0.360 g (23%), m.p. 172–173 °C. IR (KBr): *ν* 814, 868, 1001, 1106, 1253, 1272, 1296, 1357, 1377, 1421, 1457, 1627, 2852, 2893, 2933, 2958, 3092, 3452 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.31 (3H, s, CH_3), 3.79 (1H, s, OH), 4.08 (5H, s, C_5H_5), 4.28 (5H, s, C_5H_5), 4.01, 4.02, 4.06, 4.13, 4.46, 4.51, 5.18, 5.21 ($2C_5H_4$), 5.50 (1H, s, CH), 7.03 (1H, d, *J* = 6.6 Hz, C_6H_3), 8.03 (1H, dd, *J* = 2.1, 6.6 Hz, C_6H_3), 8.51 (1H, d, *J* = 2.1 Hz, C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 15.12 (CH_3), 68.99, 70.15 ($2C_5H_5$), 64.77, 67.51, 67.96, 69.09, 70.37, 70.60, 70.87, 71.91 ($2C_5H_4$), 79.91, 82.97 ($2C_{ipso}$Fc), 91.81 (CH), 121.09, 122.84, 130.63 (C_6H_3), 91.65, 128.76, 135.69, 151.34, 171.66 (5C). *Anal.* Calc. for $C_{30}H_{26}Fe_2N_2O_4S$ (622.21): C, 57.91; H, 4.21; N, 4.50; S, 5.14. Found: C, 57.80; H, 4.28; N, 4.50, S, 5.35%. MS (El, 70 eV): *m*/*z* 622 $[M]^+$.

*2.3.5. S,R-7-tert-Butyl-3,4-diferrocenyl-2-methylthio-2,3-dihydrobenzo[b]-1,4-oxazepin-3-ol (**7e**)*

Orange powder, yield 0.400 g (25%), m.p. 168–169 °C. IR (KBr): *ν* 814, 833, 1000, 1107, 1116, 1258, 1276, 1317, 1385, 1412, 448, 1499, 1651, 2918, 3091, 3395, 3412 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.35 (9H, s, $3CH_3$), 2.30 (3H, s, CH_3), 4.03 (1H, s, OH), 4.15 (5H, s, C_5H_5), 4.29 (5H, s, C_5H_5), 3.95, 4.05, 4.07, 4.14, 4.24, 4.38, 4.40, 5.11 ($2C_5H_4$), 5.50 (1H, s, CH), 6.95 (1H, d, *J* = 6.0 Hz, C_6H_3), 7.25 (1H, d, *J* = 6.0 Hz, C_6H_3), 7.85 (1H, s, C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.88 (CH_3), 31.43 ($3CH_3$), 68.92, 69.79 ($2C_5H_5$), 65.86, 66.82, 67.61, 68.82, 69.78, 69.84, 70.41, 70.83 ($2C_5H_4$), 79.58, 83.74 ($2C_{ipso}$Fc), 91.05 (CH), 119.75, 125.90, 131.95 (C_6H_3), 34.03, 92.62, 135.00, 143.47, 145.35, 166.86 (6C). *Anal.* Calc. for $C_{34}H_{35}Fe_2NO_2S$ (633.32): C, 64.48; H, 5.57; N, 2.21; S, 5.06. Found: C, 64.37; H, 5.40; N, 2.32 %, S, 5.08. MS (El, 70 eV): *m*/*z* 633 $[M]^+$.

*2.3.6. 3,4-Diferrocenyl-5-methylquinolin-8-ol (**8b**)*

Orange powder, yield 0.400 g (25%), m.p. 168–169 °C. IR (KBr): *ν* 480, 806, 821, 999, 1027, 1041, 1104, 1162, 1249, 1295, 1350, 1404, 1456, 1498, 1572, 1594, 2785, 2941, 2980, 3058, 3435 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.32 (3H, s, CH_3), 4.02 (1H, s, OH), 4.14 (5H, s, C_5H_5), 4.28 (5H, s, C_5H_5), 3.95, 4.07, 4.14, 4.24, 4.38, 4.60, 4.80, 5.11 (C_5H_4), 5.50 (1H, s, CH), 6.95 (1H, d, *J* = 6.0 Hz, C_6H_3), 7.25 (1H, d, *J* = 6.0 Hz, C_6H_3), 7.85 (1H, s, C_6H_3). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.91 (CH_3), 31.43 ($3CH_3$), 68.92, 69.79 ($2C_5H_5$), 65.86, 66.82, 67.61, 68.82, 69.78, 69.84, 70.41, 70.83 ($2C_5H_4$), 79.58, 83.74 ($2C_{ipso}$Fc), 91.05 (CH), 119.75, 125.90, 131.95 (C_6H_3), 34.03, 92.62 135.00, 143.47, 145.35, 166.86 (6C). *Anal.* Calc. for $C_{34}H_{35}Fe_2NO_2S$ (633.32): C, 64.48; H, 5.57; N, 2.21; S, 5.06. Found: C, 61.99; H, 4.50; N, 11.46%. MS (El, 70 eV): *m*/*z* 633 $[M]^+$.

*2.3.7. E,Z-2,3-Diferrocenyl-4-(2-hydroxyphenyl)-1-methylthio-4-aza-1,3-butadiene (**9a**)*

Orange powder, yield 0.290 g (21%), m.p. 147–148 °C. IR (KBr): *ν* 814, 827, 886, 924, 1001, 1105, 1156, 1230, 1266, 1254, 1284, 1325, 1374, 1388, 1408, 1420, 1447, 1532, 1621, 2928, 3081, 3099, 3120, 3366 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.50 (3H, s, CH_3), 4.18 (5H, s, C_5H_5), 4.19 (5H, s, C_5H_5), 4.27, 4.47, 4.68, 4.73 ($2C_5H_4$), 7.05 (1H, s, CH), 7.53 (2H, bs, C_6H_4), 7.70 (2H, bs, C_6H_4), 8.10 (1H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.04 (CH_3), 69.38, 70.12 ($2C_5H_5$), 68.33, 68.80, 71.36, 71.86 ($2C_5H_4$), 79.22, 80.06 ($2C_{ipso}$Fc), 128.77, 130.87 (C_6H_4), 135.22, (HC═), 129.45, 132.38, 135.56, 167.76 (4C). *Anal.* Calc. for $C_{30}H_{27}Fe_2NOS$ (561.28): C, 64.19; H, 4.85; N, 2.49; S, 5.71. Found: C, 64.10; H, 4.52; N, 2.40; S, 5.52%. MS (El, 70 eV): *m*/*z* 561 $[M]^+$

*2.3.8. E,Z-2,3-Diferrocenyl-4-(2-hydroxy-5-methylphenyl)-1-methylthio-4-aza-1,3-butadiene (**9b**)*

Orange powder, yield 0.390 g (27%), m.p. 152–154 °C. IR (KBr): *ν* 465, 480, 539, 642, 759, 806, 821, 868, 899, 953, 999, 1027, 1041, 1084, 1104, 1162, 1187, 1249, 1296, 1350, 1403, 1456, 1498, 1572, 1594, 1615, 1736, 2785, 2842, 2874, 2941, 2980, 3088, 3435 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.48 (3H, s, CH_3), 2.53 (3H, s, CH_3), 4.17 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 4.50, 4.77, 5.07, 5.55 ($2C_5H_4$), 7.47 (1H, s, HC═), 7.35 (2H, m, C_6H_3), 7.58 (1H, d, *J* = 6.3 Hz, C_6H_3), 7.71 (1H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 21.51, 30.15 ($2CH_3$), 69.82, 70.55 ($2C_5H_5$), 69.37, 70.12, 70.91, 71.98 ($2C_5H_4$), 79.23, 80.06 ($2C_{ipso}$Fc), 119.06, 125.11, 129.17 (C_6H_3), 135.45, (HC═), 121.66, 134.07, 142.45, 148.66, 166.32 (5C). *Anal.* Calc. for $C_{31}H_{29}Fe_2NOS$ (575.24): C, 64.72; H, 5.08; N, 2.43; S, 5.56. Found: C, 64.70; H, 5.15; N, 2.40; S, 5.40%. MS (El, 70 eV): *m*/*z* 575 $[M]^+$.

*2.3.9. E,Z-2,3-Diferrocenyl-4-(2-hydroxy-5-chlorophenyl)-1-methylthio-4-aza-1,3-butadiene (**9c**)*

Orange powder, yield 0.360 g (24%), m.p. 165–167 °C. IR (KBr): *ν* 465, 480, 541, 642, 743, 764, 806, 821, 868, 900, 930, 954, 999, 1027, 1041, 1083, 1104, 1163, 1187, 1249, 1296, 1323, 1351, 1404, 1457, 1498, 1572, 1594, 1616, 2785, 2842, 2875, 2921, 2941, 2980, 3088, 3100, 3188, 3437 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.27 (3H, s, CH_3), 4.10 (5H, s, C_5H_5), 4.25 (5H, s, C_5H_5), 3.82, 4.07, 4.45, 5.16 ($2C_5H_4$), 7.14 (1H, s, HC═), 6.92 (1H, s, C_6H_3), 7.53 (1H, bs, C_6H_3), 7.70 (1H, bs, C_6H_3), 8.09 (1H, bs, OH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 23.70 (CH_3), 68.84, 69.99 ($2C_5H_5$), 65.19, 67.22, 67.81, 68.12, 70.04, 70.57, 70.67, 71.20 ($2C_5H_4$), 79.76, 83.96 ($2C_{ipso}$Fc), 135.45 (HC═), 128.77, 130.87, 134.17 (C_6H_3), 125.37, 125.67, 132.36, 144.54, 167.76 (5C). *Anal.* Calc. for $C_{30}H_{26}ClFe_2NOS$ (595.66): C, 60.50; H, 4.40; N, 2.35; S, 5.37. Found: C, 60.62; H, 4.62; N, 2.45; S, 5.49%. MS (El, 70 eV): *m*/*z* 596 $[M]^+$.

*2.3.10. E,Z-2,3-Diferrocenyl-4-(2-hydroxy-5-nitrophenyl)-1-methylthio-4-aza-1,3-butadiene (**9d**)*

Orange powder, yield 0.390 g (26%), m.p. 160–162 °C. IR (KBr): *ν* 480, 642, 764, 806, 821, 868, 930, 999, 1027, 1041, 1083, 1104, 1163, 1187, 1249, 1296, 1323, 1351, 1404, 1457, 1498, 1572, 1594, 1616, 2842, 2921, 2941, 2980, 3088, 3100, 3188, 3437 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 2.41 (3H, s, CH_3), 4.04 (5H, s, C_5H_5), 4.17 (5H, s, C_5H_5), 4.27, 4.35, 4.50, 4.95 ($2C_5H_4$), 7.36 (2H, m, C_6H_3), 7.41 (1H, s, C_6H_3), 7.88 (1H, s, HC═), 8.12 (1H, bs, OH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 18.70 (CH_3), 68.92, 70.01 ($2C_5H_5$), 69.82, 70.01, 70.34, 71.20 ($2C_5H_4$), 79.96, 82.54 ($2C_{ipso}$Fc), 91.02 135.58 (HC═), 128.61, 131.73, 134.01 (C_6H_3), 125.24, 125.45, 132.61, 144.49, 167.81 (5C). *Anal.* Calc. for $C_{30}H_{26}Fe_2N_2O_3S$ (606.21): C, 59.44; H, 4.32; N, 4.62; S, 5.28. Found: C, 61.99; H, 4.50; N, 11.46%. MS (El, 70 eV): *m*/*z* 606 $[M]^+$.

*2.3.11. E,Z-7-4-(2-Hydroxy-5-tert-butylphenyl)-2,3-diferrocenyl-1-methylthio-4-aza-1,3-butadiene (**9e**)*

Orange powder, yield 0.460 g (30%), m.p. 171–173 °C. IR (KBr): *ν* 483, 594, 693, 735, 814, 899, 934, 1000, 1023, 1039, 1107, 1116, 1145, 1178, 1258, 1276, 1317, 1385, 1412, 1434, 1448, 1499, 1651, 2918, 3091, 3395 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): *δ* 1.28 (9H, s, $3CH_3$), 2.31 (3H, s, CH_3), 4.08 (5H, s, C_5H_5), 4.28 (5H, s, C_5H_5), 3.82, 4.01, 4.13, 4.18, 4.17, 4.22, 4.45, 5.19 ($2C_5H_4$), 6.52 (1H, s, HC═), 7.53 (2H, m, C_6H_3), 7.70 (1H, bs, C_6H_3), 8.52 (1H, s, OH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.11 (CH_3), 30.38 ($3CH_3$), 31.47 (C), 68.18, 70.22 ($2C_5H_5$), 64.79, 67.58, 68.02, 69.39, 70.45, 70.63, 70.95, 71.97 ($2C_5H_4$), 79.95, 83.01 ($2C_{ipso}$Fc), 128.83, 130.93 (C_6H_3), 132.45 (HC═), 121.17, 124.01, 129.55, 130.72,

167.81 (5C). *Anal.* Calc. for $C_{34}H_{35}Fe_2NOS$ (617.32): C, 66.15; H, 5.72; N, 2.27; S, 5.18. Found: C, 61.99; H, 4.50; N, 11.46%. MS (El, 70 eV): *m*/*z* 617 $[M]^+$.

*2.3.12. trans-2,3-Diferrocenyl-3-methylthioacrylaldehyde (**10a**)*

Orange powder, yield 0.056 g (4.7%), m.p. 153–155 °C. IR (KBr): *v* 485, 522, 688, 742, 809, 822, 870, 960, 1003, 1026, 1043, 1101, 1220, 1270, 1355, 1372, 1412, 1443, 1454, 1565, 1637, 1734, 2928, 2920, 2956, 3006, 3028, 3079, 3100 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.97 (3H, s, CH_3), 4.19 (5H, s, C_5H_5), 4.35 (5H, s, C_5H_5), 4.37, 4.57, 4.68, 4.84 ($2C_5H_4$), 9.41 (1H, s, C═O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.96 (CH_3), 69.83, 70.39 ($2C_5H_5$), 69.71, 70.39, 71.64, 72.04 ($2C_5H_4$), 82.37, 83.90 ($2C_{ipso}Fc$), 188.06 (C═O), 134.55, 165.10 (2C). *Anal.* Calc. for $C_{24}H_{22}Fe_2OS$ (470.12): C, 61.31; H, 4.72; S, 6.81. Found: C, 61.01; H, 4.26; S, 6.51%. MS (El, 70 eV): *m*/*z* 470 $[M]^+$.

*2.3.13. cis-2,3-Diferrocenyl-3-methylthioacrylaldehyde (**10b**)*

Orange powder, yield 0.028 g (2.7%), m.p. 145–147 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.55 (3H, s, CH_3), 4.06 (5H, s, C_5H_5), 4.14 (5H, s, C_5H_5), 4.11, 4.16, 4.31, 4.38 ($2C_5H_4$), 10.15 (1H, s, HC═O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.80 (CH_3), 68.50, 69.43 ($2C_5H_5$), 68.05, 69.38, 69.54, 70.72 ($2C_5$ H_4), 82.79, 83.98 ($2C_{ipso}Fc$), 189.13 (HC═O), 132.44, 162.50 (2C).

*2.3.14. S,R-5,6-Diferrocenyl-7-methylthio-2-phenyl-2,3,6,7-tetrahydro-1,4-oxazepin-6-ol (**13b**)*

Orange powder, yield 0.42 g (28%), m.p. 182–183 °C. IR (KBr): *v* 470, 632, 731, 764, 812, 871, 923, 1000, 1028, 1103, 1119, 1138, 1164, 1205, 1239, 1276, 1304, 1353, 1387, 1420, 1443, 1634, 1711, 2819, 2867, 2939, 2961, 3092, 3357, 3411 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (1H, bs, OH), 2.05 (3H, s, CH_3), 3.76 (2H, m, CH_2), 4.03 (5H, s, C_5H_5), 4.29 (5H, s, C_5H_5), 4.12, 4.19, 4.21, 4.26, 4.32, 4.68, 4.80, 5.03 ($2C_5H_4$), 4.91 (1H, m, CH), 5.44 (1H, s, CH), 7.28 (1H, m, C_6H_5), 7.36 (2H, t, *J* = 7.2 Hz, C_6H_5), 7.42 (2H, d, *J* = 7.2 Hz, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.31 (CH_3), 67.04 (CH_2), 69.08, 69.27 ($2C_5H_5$), 67.38, 68.61, 68.74 69.03 ($2C_5H_4$), 69.48, 71.00 (2CH), 82.10, 83.60 ($2C_{ipso}Fc$), 126.97, 127.32, 128.46 (C_6H_5), 81.70, 130.84, 167.73 (3C). *Anal.* Calc. for $C_{32}H_{31}Fe_2NO_2S$ (605.33): C, 63.49; H, 5.16; N, 2.31; S, 5.30. Found: C, 63.90; H, 4.80; N, 2.46, S, 5.50%. MS (El, 70 eV): *m*/*z* 605 $[M]^+$.

*2.3.15. S,R-5,6-Diferrocenyl-7-methylthio-3-phenyl-2,3,6,7-tetrahydro-1,4-oxazepin-6-ol (**13d**)*

Orange powder, yield 0.48 g (32%), m.p. 181–183 °C. IR (KBr): *v* 475, 645, 727, 764, 815, 868, 912, 1001, 1026, 1105, 1116, 1144, 1160, 1208, 1253, 1272, 1296, 1357, 1377, 1421, 1456, 1627, 1709, 2808, 2852, 2893, 2933, 2958, 3092, 3374, 3401 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.05 (3H, s, CH_3), 2.65 (1H, bs, OH), 3.89 (2H, m, CH_2), 4.04 (5H, s, C_5H_5), 4.30 (5H, s, C_5H_5), 4.18 (4H, m, C_5H_4) 4.26 (1H, m, C_5H_4) , 4.34 (1H, m, C_5H_4), 4.68 (1H, m, C_5 H_4), 5.02 (1H, m, C_5H_4), 4.92 (1H, dd, *J* = 4.2, 7,2 Hz , CH), 5.45 (1H, s, CH), 7.28 (1H, m, C_6H_5), 7.37 (2H, t, *J* = 7.2 Hz, C_6 H_5), 7.45 (2H, d, *J* = 7.2 Hz, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.38 (CH_3), 67.45 (CH_2), 69.24, 69.34 ($2C_5H_5$), 67.09, 68.12, 68.61, 68.68, 68.81, 69.10, 69.52, 69.90 ($2C_5H_4$), 70.02, 71.06 (2CH), 81.76, 83.70 ($2C_{ipso}Fc$), 127.02, 127.38, 128.53 (C_6H_5), 130.28, 143.66, 172.02 (3C). *Anal.* Calc. for $C_{32}H_{31}Fe_2NO_2S$ (605.27): C, 63.49; H, 5.16; N, 2.48; S, 5.29. Found: C, 63.38; H, 5.22, N, 2.28, S, 5.50%. MS (El, 70 eV): *m*/*z* 605 $[M]^+$.

*2.3.16. S,R-3-Benzyl-5,6-diferrocenyl-7-methylthio-2,3,6,7-tetrahydro-1,4-oxazepin-6-ol (**13e**)*

Orange powder, yield 0.52 g (33%), m.p. 178–180 °C. IR (KBr): *v* 475, 519, 761, 815, 827, 886, 924, 966, 1001, 1028, 1045, 1061, 1105, 1155, 1230, 1254, 1283, 1326, 1374, 1387, 1408, 1420, 1447, 1532, 1621, 1738, 2883, 2970, 2981, 3080, 3099, 3120, 3363 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (1H. bs, OH), 2.26 (3H, s, CH_3), 2.93 (1H, dd, *J* = 6.0, 9.9 Hz, CH_2), 3.02 (1H, dd, *J* = 4.2, 9.9 Hz, CH_2), 3.61 (2H, m, CH_2), 3.81 (1H, m, CH), 4.03 (5H, s, C_5H_5), 4.21 (5H, s, C_5H_5), 4.16 (1H, m, C_5H_4), 4.27 (1H, m, C_5H_4), 4.32 (3H, m, C_5H_4), 4.55 (2H, m, C_5H_4), 4.84 (1H, m, C_5H_4) ($2C_5H_4$), 5.50 (1H, s, CH), 7.29–7.35 (5H, m, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.51 (CH_3), 30.35, 39.77 ($2CH_2$), 64.70, 70.88 (2CH), 69.16, 69.31 ($2C_5H_5$), 65.93, 67.16, 67.20, 68.06, 68.39, 69.53, 69.59, 69.81 ($2C_5H_4$), 82.56, 84.59 ($2C_{ipso}Fc$), 126.04, 128.38, 129.38 (C_6H_5), 125.95, 139.65, 170.12 (3C). *Anal.* Calc. for $C_{33}H_{33}Fe_2NO_2S$ (619.36): C, 64.00; H, 5.37; N, 2.26; S, 5.18. Found: C, 64.10; H, 5.40; N, 2.36, S, 5.40%. MS (El, 70 eV): *m*/*z* 620 $[M]^+$.

*2.3.17. E,Z-2,3-Diferrocenyl-6-hydroxy-1-methylthio-4-aza-1,3-hexadiene (**14a**)*

Orange powder, yield 0.38 g (30%), m.p. 145–147 °C. IR (KBr): *v* 817, 1001, 1039, 1106, 1117, 1188, 1249, 1266, 1289, 1326, 1353, 1397, 1451, 1488, 1631, 3027, 3086, 3405 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.84 (1H, bs, OH), 2.50 (3H, s, CH_3), 3.57 (2H, m, CH_2), 3.84 (2H, m, CH_2), 4.10 (5H, s, C_5H_5), 4.21, 4.23, 4.27, 4.33, 4.35, 4.37, 4.55, 4.80 ($2C_5H_4$), 6.14 (1H, s, HC═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.78 (CH_3), 55.15, 62.81 ($2CH_2$), 69.38, 69.60 ($2C_5H_5$), 68.28, 68.41, 68.61, 69.70, 69.85, 69.94, 70.14, 71.10 ($2C_5H_4$), 81.85, 84.08 ($2C_{ipso}Fc$), 126.55, (HC═), 131.05, 171.53 (2C). *Anal.* Calc. for $C_{26}H_{27}Fe_2NOS$ (513.18): C, 60.85; H, 5.30; N, 2.73; S, 6.23. Found: C, 61.12; H, 5.42; N, 3.05; S, 6.41%. MS (EI, 70 eV): *m*/*z* 514 $[M]^+$.

*2.3.18. E,Z-2,3-Diferrocenyl-6-hydroxy-1-methylthio-5-phenyl-4-aza-1,3-hexadiene (**14b**)*

Orange powder, yield 0.43 g (29%), m.p. 173–174 °C. IR (KBr): *v* 817, 898, 912, 1000, 1106, 1177, 1210, 1275, 1343, 1377, 1435, 1451, 1485, 1599, 2867, 2919, 2951, 3026, 3086, 3418, 3565 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70 (1H, bs, OH), 2.41 (3H, s, CH_3), 3.73 (2H, m, CH_2), 4.04 (5H, s, C_5H_5), 4.17 (5H, s, C_5H_5), 4.20, 4.27, 4.55, 4.94 ($2C_5H_4$), 4.35 (1H, m, CH), 5.87 (1H, s, HC═), 7.36 (3H, m, C_6H_5), 7.43 (2H, m, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.57 (CH_3), 38.71 (CH_2), 69.20, 69.40 ($2C_5H_5$), 60.45 (CH), 67.44, 68.11, 68.15, 68.47, 69.82, 70.07, 70.63, 72.94 ($2C_5H_4$), 81.52, 81.79 ($2C_{ipso}Fc$), 125.93, 126.52, 128.26 (C_6H_5), 130.85, (HC═), 130.94, 143.06, 167.73 (3C). *Anal.* Calc. for $C_{32}H_{31}$-Fe_2NOS (589.27): C, 65.22; H, 5.30; N, 2.38; S, 5.43. Found: C, 65.35; H, 5.48; N, 2.30; S, 5.57%. MS (El, 70 eV): *m*/*z* 590 $[M]^+$.

*2.3.19. E,Z-2,3-Diferrocenyl-6-hydroxy-5-isopropyl-1-methylthio-4-aza-1,3-hexadiene (**14c**)*

Orange powder, yield 0.44 g (32%), m.p. 159–160 °C. IR (KBr): *v* 803, 814, 1000, 1025, 1036, 1106, 1161, 1249, 1292, 1313, 1322, 1407, 1499, 1572, 1595, 1622, 2875, 2936, 3091, 3415 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (3H, d, *J* = 5.1 Hz, CH_3), 1.02 (3H, d, *J* = 5.1 Hz, CH_3), 1.64 (1H, bs, OH), 2.49 (3H, s, CH_3), 3.43 (1H, m, *J* = 2.7, 5.4, Hz, CH), 3.54 (1H, dd, *J* = 3.0, 8.1 Hz, CH_2), 3.72 (1H, dd, *J* = 3.0, 8.1 Hz, CH_2), 3.81 (1H, m, CH), 4.14 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 4.28, 4.34, 4.38, 4.40, 4.44, 4.45, 4.47, 4.87 ($2C_5$ H_4), 6.17 (1H, s, HC═). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.68 (CH_3), 19.26, 20.14 ($2CH_3$), 29.67 (CH), 30.65 (CH_2), 67.55 (CH), 69.20, 69.25 ($2C_5H_5$), 67.87, 68.29, 68.46, 69.91 ($2C_5H_4$), 82.62, 82.74 ($2C_{ipso}Fc$), 126.78 (HC═), 131.04, 169.18 (2C). *Anal.* Calc. for $C_{29}H_{33}Fe_2NOS$ (555.25): C, 62.73; H, 6.00; N, 2.52; S, 5.76. Found: C, 62.47; H, 5.50; N, 2.47, S, 5.43%. MS (El, 70 eV): *m*/*z* 555 $[M]^+$.

*2.3.20. E,Z-2,3-Diferrocenyl-6-hydroxy-1-methylthio-6-phenyl-4-aza-1,3-hexadiene (**14d**)*

Orange powder, yield 0.49 g (34%), m.p. 167–168 °C. IR (KBr): *v* 488, 522, 759, 791, 816, 889, 947, 1000, 1022, 1046, 1087, 1106,

1174, 1207, 1248, 1296, 1307, 1339, 1374, 1388, 1409, 1451, 1492, 1589, 1607, 2809, 2886, 2923, 3022, 3057, 3088, 3202 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (1H, bs, OH), 2.36 (3H, s, CH_3), 3.68 (1H, dd, J = 6.9, 10.5 Hz, CH_2), 3.86 (1H, dd, J = 2.7, 10.5 Hz, CH_2), 3.96 (5H, s, C_5H_5), 3.99 (5H, s, C_5H_5), 3.94, 4.26, 4.30, 4.47 ($2C_5$ H_4), 5.01 (1H, dd, J = 2.4, 6.9 Hz, CH), 6.48 (1H, s, HC=), 7.27 (1H, t, J = 3.0 Hz, C_6H_5), 7.37 (2H, td, J = 3.0, 5.4 Hz, C_6H_5), 7.50 (2H, d, J = 3.0 Hz, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.70, (CH_3), 61.90 (CH_2), 69.52, 69.55 ($2C_5H_5$), 66.95, 66.98, 68.10, 68.17 ($2C_5$ H_4), 73.59 (CH), 82.81, 84.50 ($2C_{ipso}$Fc), 124.56, 126.13, 128.30 (C_6H_5), 127.43, (HC=), 128.76, 142.51 167.73 (3C). *Anal.* Calc. for $C_{32}H_{31}Fe_2NOS$ (589.27): C, 65.22; H, 5.30; N, 2.38; S, 5.43. Found: C, 65.41; H, 5.20; N, 2.10, S, 5.60%. MS (El, 70 eV): m/z 590 $[M]^+$.

2.3.21. E,Z-2,3-Diferrocenyl-6-hydroxy-1-methylthio-7-phenyl-4-aza-1,3-heptadiene (**14e**)

Orange powder, yield 0.47 g (31%), m.p. 175–176 °C. IR (KBr): ν 816, 868, 979, 1001, 1034, 1079, 1106, 1276, 1343, 1379, 1432, 1452, 1490, 1582, 1600, 2861, 2918, 3081, 3094, 3345, 3552 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (1H, s, OH), 2.46 (3H, s, CH_3), 3.52 (1H, m, CH_2), 3.74 (2H, m, CH_2), 3.83 (1H, m, CH_2), 4.07 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.23, 4.32 , 4.36, 4.44, 4.56, 4.65, 4.80, 4.85 ($2C_5H_4$), 4.95 (1H, m, CH), 6.01 (1H, s, HC=), 7.34–7.50 (5H, m, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.64 (CH_3), 61.07, 67.75 ($2CH_2$), 69.23, 69.41 ($2C_5H_5$), 67.45, 68.33, 70.24, 72.93 ($2C_5H_4$), 73.82 (CH), 83.77, 83.87 ($2C_{ipso}$Fc), 126.14, 127.20 (C_6H_5), 127.46, (HC=), 126.34, 130.93, 142.64 (3C). *Anal.* Calc. for $C_{33}H_{33}Fe_2NOS$ (603.29): C, 65.69; H, 5.51; N, 2.32; S, 5.31. Found: C, 61.99; H, 4.50; N, 11.46%. MS (El, 70 eV): m/z 603 $[M]^+$.

2.3.22. Z,E-2,3-Diferrocenyl-6-hydroxy-1-methylthio-4-aza-1,3-hexadiene (**15a**)

Orange powder, yield 0.13 g (10%), m.p. 145–147 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.84 (1H, bs, OH), 2.41 (3H, s, CH_3), 3.54 (2H, m, CH_2), 3.82 (2H, m, CH_2), 4.07 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.15, 4.18, 4.22, 4.25, 4.38, 4.40, 4.55, 4.70 ($2C_5H_4$), 6.48 (1H, s, HC=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.23 (CH_3), 55.17, 62.81 ($2CH_2$), 69.38, 69.60 ($2C_5H_5$), 68.28, 68.41, 68.61, 69.70, 69.85, 69.94, 70.14, 71.10 ($2C_5$ H_4), 81.85, 84.08 ($2C_{ipso}$Fc), 124.48, (HC=), 131.05, 171.53 (2C).

2.3.23. Z,E-2,3-Diferrocenyl-6-hydroxy-1-methylthio-5-phenyl-4-aza-1,3-hexadiene (**15b**)

Orange powder, yield 0.16 g (11%), m.p. 162–163 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70 (1H, bs, OH), 2.47 (3H, s, CH_3), 3.52 (1H, m, CH_2), 3.80 (1H, m, CH_2), 4.07 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.35 (1H, m, CH), 4.22, 4.32, 4.38, 4.80 ($2C_5H_4$), 6.02 (1H, s, HC=), 7.30–7.46 (5H, m, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.64 (CH_3), 30.35 (CH_2), 61.08 (CH), 69.23, 69.45 ($2C_5H_5$), 67.38, 67.88, 68.33, 68.43, 69.87, 70.01, 70.23, 73.83 ($2C_5H_4$), 83.80, 83.89 ($2C_{ipso}$Fc), 126.13, 127.46, 128.30 (C_6H_5), 130.45 (HC=), 132.42, 142.64, 171.29 (3C).

2.3.24. Z,E-2,3-Diferrocenyl-6-hydroxy-5-isopropyl-1-methylthio-4-aza-1,3-hexadiene (**15c**)

Orange oil, yield 0.14 g (10%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.75 (3H, d, J = 5.1 Hz, CH_3), 0.89 (3H, d, J = 5.1 Hz, CH_3), 1.64 (1H, bs, OH), 2.50 (3H, s, CH_3), 3.57 (2H, m, CH_2), 3.84 (2H, m, CH_2), 4.13 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.12, 4.20, 4.28, 4.37, 4.40, 4.47, 4.37, 4.94 ($2C_5$ H_4), 6.28 (1H, s, HC=). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.78 (CH_3), 55.15, 62.81 ($2CH_2$), 69.38, 69.60 ($2C_5H_5$), 67.64, 67.78, 68.15, 68.28, 68.77, 69.94, 70.17, 70.63 ($2C_5H_4$), 81.85, 84.08 ($2C_{ipso}$Fc), 126.55 (HC=), 131.48, 171.53 (2C).

2.3.25. Z,E-2,3-Diferrocenyl-6-hydroxy-1-methylthio-6-phenyl-4-aza-1,3-hexadiene (**15d**)

Orange powder, yield 0.19 g (13%), m.p. 180–181 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.65 (1H, bs, OH), 2.39 (3H, s, CH_3), 3.56 (1H, dd, J = 6.6, 10.5 Hz, CH_2), 3.78 (1H, dd, J = 2.4, 10.5 Hz, CH_2), 4.10 (10H, s, $2C_5H_5$), 3.94, 4.04, 4.20, 4.32 ($2C_5$ H_4), 6.31 (1H, bs, OH), 5.09 (1H, dd, J = 2.4, 6.9 Hz, CH), 6.47 (1H, s, HC=), 7.27 (1H, t, J = 6.0 Hz, C_6H_5), 7.36 (2H, td, J = 3.0, 6.0 Hz, C_6H_5), 7.49 (2H, d, J = 6.0 Hz, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.65 (CH_3), 61.44 (CH_2), 69.71 ($2C_5$ H_5), 66.81, 66.92, 67.88, 68.01, 68.52 ($2C_5$ H_4), 73.59 (CH), 84.49, 82.81 ($2C_{ipso}$Fc), 124.81, 125.99, 128.30 (C_6H_5), 127.35 (HC=), 130.84, 142.66, 167.73 (3C).

2.3.26. Z,E-2,3-Diferrocenyl-6-hydroxy-1-methylthio-7-phenyl-4-aza-1,3-heptadiene (**15e**)

Orange powder, yield 0.15 g (10%), m.p. 183–185 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (1H, s, OH), 2.41 (3H, s, CH_3), 3.49 (1H, m, CH_2), 3.76 (2H, m, CH_2), 3.81 (1H, m, CH_2), 4.04 (5H, s, C_5H_5), 4.17 (5H, s, C_5H_5), 4.20, 4.27, 4.35, 4.54 ($2C_5$ H_4), 4.94 (1H, m, CH), 5.88 (1H, s, HC=), 7.34–7.50 (5H, m, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.58 (CH_3), 60.43, 67.38 ($2CH_2$), 69.31, 69.41 ($2C_5H_5$), 68.15, 68.33, 68.44, 69.84, 69.89, 70.03, 70.09, 70.65 ($2C_5H_4$), 73.82 (CH), 81.52, 81.79 ($2C_{ipso}$Fc), 125.94, 128.26 (C_6H_5), 128.30, (HC=), 126.65, 130.43, 143.06 (3C).

2.4. Single-crystal X-ray diffraction data

Suitable single crystals of the compounds **7b**, **14a**, **14c** and **14d** were studied by single-crystal X-ray diffraction. Each crystal was mounted on a glass fiber and crystallographic data were collected with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector (λ Mo Kα = 0.71073 Å) at 130 K. Unit cell parameters were determined with a set of three runs of 15 frames (1° in ω). The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CRYSALISPRO and CRYSALIS RED software packages [30] were used for data collection and integration. Analysis of the integrated data did not reveal any decay. Final cell parameters were determined by a global refinement of 3995, 5415, 4481 and 3897 reflections for **7b**, **14a**, **14c** and **14d** respectively. Collected data were corrected for absorption effects by analytical numeric absorption correction [31] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections. Structure solution and refinement were carried with the programs SHELXS-2014 [32] and SHELXL-2014 respectively [33], WINGX V2018.3 [34], and MERCURY CSD 4.1.0 [35] were used to prepare the material for publication. Full-matrix least-squares refinement was carried out by minimizing (Fo^2 - – Fc^2)^2. All nonhydrogen atoms were refined anisotropically. For H atoms of the hydroxy groups were located in a difference map and refined isotropically with U_{iso}(H) = –1.5 for H—O. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H = 0.95–1.00 Å with U_{iso}(H) = 1.2 U_{eq}(C) for aromatic, methylene and methyne groups, and U_{iso}(H) = 1.5 U_{eq}(C) for methyl group. Crystal data and experimental details of the structure determination are listed in Table 1. Select bond lengths and angles are presented in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as Supplementary Materials CCDC 1909613 (**7b**), CCDC 1909614 (**14d**), CCDC 1909615 (**14a**) and CCDC 1909616 (**14c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

Table 1
Crystal data and structure refinement parameters for compounds **7b** and **14a**,**c**,**d**.

Identification code	**7b**	**14a**	**14c**	**14d**
Empirical formula	$C_{31}H_{29}Fe_2NO_2S$	$C_{26}H_{27}Fe_2NOS$	$C_{29}H_{33}Fe_2NOS$	$C_{32}H_{31}Fe_2NOS$
Formula weight	591.31	513.24	555.32	589.34
Temperature (K)	130(2)	130(2)	130(2)	130(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\,2_1/n$	$P\bar{1}$	$P\,2_1\,2_1\,2_1$
Unit cell dimensions				
a (Å)	10.6889(8)	10.1262(9)	9.8440(8)	11.0566(5)
b (Å)	11.1538(10)	10.1375(9)	11.3703(8)	13.5327(5)
c (Å)	11.4826(9)	22.1983(18)	12.0747(7)	17.7647(7)
α (°)	85.299(7)	90	112.950(6)	90
β (°)	78.789(7)	102.186(8)	98.569(6)	90
γ (°)	70.111(8).	90	91.359(6)	90
V (Å^3)	1262.57(19)	2227.4(3)	1225.66(16)	2658.05(19)
Z	2	4	2	4
$D_{Calc.}$ mg m^3)	1.555	1.531	1.505	1.473
Absorption coefficient	1.263 mm^{-1}	1.415 mm^{-1}	1.292 mm^{-1}	1.197 mm^{-1}
F(0 0 0)	612	1064	580	1224
Crystal size (mm)	0.570 × 0.440 × 0.150	0.250 × 0.190 × 0.130	0.510 × 0.360 × 0.150	0.250 × 0.200 × 0.060
θ range for data collection	3.569–30.088°	3.460–29.474°	3.445–29.504°	3.530–29.511°
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 15$, $-16 \le l \le 15$	$-13 \le h \le 12$, $-13 \le k \le 12$, $-30 \le l \le 29$	$-12 \le h \le 11$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-8 \le h \le 14$, $-12 \le k \le 18$, $-22 \le l \le 24$
Reflections collected	13 404	19 029	11 540	9309
Independent reflections	6317 [R_{int} = 0.0326]	5474 [R_{int} = 0.0362]	5758 [R_{int} = 0.0339]	5839 [R_{int} = 0.0275]
Maximum and minimum transmission	0.838 and 0.641	0.847 and 0.767	0.420 and 0.149	0.930 and 0.773
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	6317/685/344	5474/4/298	5758/1/313	5839/1/338
Goodness-of-fit on F^2	1.058	1.056	1.077	1.036
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0424, wR_2 = 0.0810	R_1 = 0.0391, wR_2 = 0.0800	R_1 = 0.0458, wR_2 = 0.1150	R_1 = 0.0300, wR_2 = 0.0594
R indices (all data)	R_1 = 0.0645, wR_2 = 0.0941	R_1 = 0.0588, wR_2 = 0.0900	R_1 = 0.0573, wR_2 = 0.1271	R_1 = 0.0362, wR_2 = 0.0627
Largest diff. peak and hole (e Å^{-3})	0.496 and −0.503	0.679 and −0.685	1.516 and −0.835	0.277 and −0.330

3. Results and discussion

The initial 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **2** was synthesized via the methylation of 2,3-diferrocenylcyclopropenethione **1** using methyl iodide (Scheme 1):

Cyclopropenethione **1** was obtained in this study using direct sulfonation of 2,3-diferrocenylcyclopropenone by Lawesson's reagent [36,37] with a yield of ~90–95%. In earlier work we published a method for synthesizing diferrocenylcyclopropenethione **1** using a three-stage synthesis according to Scheme 2 [25]:

We found that cyclopropropenylium iodide **2** interacts with 1,2-aminophenols **3a**–**e** in dry benzene upon boiling (about 6–8 h) in the presence of Et_3N, forming the following products: 1,1-dimethylthio-2,3-diferrocenylcyclopropene **4**, 2-ferrocenylbenzoxazoles **5a**–**e**, 2-(*cis*/*trans*-1,2-diferrocenylvinyl)oxazoles **6a**–**e**, 3,4-diferrocenyl-2-methylthio-2,3-dihydro-benzo[*b*]-1,4-oxazepin-3-oles **7a**–**e**, 3,4-diferrocenylquinolin-8-ols **8b**–**c**, *E*-/*Z*-2,3-diferrocenyl-4-(2-hydroxy-phenyl)-1-methylthio-4-aza-1,3-dienes **9a**–**e** and *cis*-/*trans*-2,3-diferrocenyl-3-methylthiopropanal **10a**,**b** (Scheme 3).

All the compounds were separated using column and thin-layer chromatography (Al_2O_3, Brockmann activity III), and their structures were established using IR, ^{1}H and ^{13}C NMR spectroscopy, as well as elemental analysis. The physicochemical characteristics of compounds **4**, **5a**–**e**, **6a**–**e** and **8c**,**d**, which have been described earlier[28], fully match the literature data. According to the ^{1}H NMR spectra of novel compounds **7a**–**e**, despite the presence of two chiral centers in the molecules, they were formed as a single diastereomers, which suggests the stereospecificity of the process.

The IR spectra of compounds **7a**–**e** contain the corresponding numbers of characteristic absorption bands of the Ferrocenyl, Ar, C═N, OH, and other fragments. The ^{1}H NMR spectra of compounds **7a**–**e** contain the signals for two ferrocenyl substituents, a signal for the methylsulfanyl groups, multiplet protons of the CH_2, CH, Ar fragments, as well as the signals from the hydrogen atoms of the hydroxyl groups. An important feature of the ^{1}H NMR spectra of compounds **7a**–**e** is the presence of the signals from the hydrogen atoms of the methine groups (CH—SMe) shifted upfield (δ = 5.44–5.50 ppm).

The spatial structure of oxazepine **7b** was also determined by X-ray diffraction analysis of single crystals obtained using crystallization from CH_2Cl_2. The perspective view of molecule **7b** is shown in Fig. 1a; the crystal packing shows in Fig. 1b; and the main geometrical parameters of the compound are listed in Table 1. The seven-membered ring in molecule **7b** is stabilized in a boat conformation, with two heteroatoms *N* and *O* occupying positions 1 and 4 in the heterocycle. X-ray analysis showed that compound **7b** has the structure of *S*,*R*/*R*,*S*-5,6-diferrocenyl-6-hydroxy-7-methylthio-3-phenyl-6,7-dihydro-1,4-oxazepine, where the ferrocene and methylthio substituents occupy the axial–equatorial positions.

Data from the X-ray analysis show that the C═N bond in the oxazepine ring is somewhat longer (1.279(3) Å) than the standard value of 1.23 Å [38]. 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 [39].

2,3-Diferrocenyl-4-(2-hydroxyphenyl)-1-methylthio-4-aza-1,3-dienes **9a**–**e** was also isolated using column chromatography and thin-layer chromatography (Al_2O_3, Brockmann activity III). 4-Aza-1,3-dienes **9a**–**e** are orange crystalline compounds, which during storage decompose fairly quickly. The structures of compounds **9a**–**e** were established based on the data obtained from IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spec-

Table 2
Selected bond lengths and bond angles for compounds **7b** and **14a**,**c**,**d**.

Selected bond lengths (Å)		Selected bond angles (°)	
7b			
C(6)—O(1)	1.428(3)	C(11)—C(6)—C(7)	110.8(2)
C(6)—C(11)	1.535(3)	O(2)—C(7)—S(1)	113.67(17)
C(6)—C(7)	1.547(3)	O(2)—C(9)—C(10)	127.2(2)
C(7)—O(2)	1.409(3)	C(22)—C(10)—N(1)	112.5(2)
C(7)—S(1)	1.813(3)	C(9)—C(10)—N(1)	130.6(2)
C(9)—O(2)	1.382(3)	N(1)—C(11)—C(12)	115.3(2)
C(9)—C(10)	1.407(3)	N(1)—C(11)—C(6)	124.8(2)
C(10)—N(1)	1.409(3)	C(11)—N(1)—C(10)	128.4(2)
C(11)—N(1)	1.279(3)	C(9)—O(2)—C(7)	121.90(19)
		C(8)—S(1)—C(7)	101.6(7)
14a			
C(11)—C(21)	1.473(3)	C(25)—C(21)—C(11)	126.9(2)
C(21)—C(25)	1.337(3)	C(25)—C(21)—C(22)	119.5(2)
C(21)—C(22)	1.506(3)	C(11)—C(21)—C(22)	113.62(19)
C(22)—N(1)	1.281(3)	N(1)—C(22)—C(21)	124.5(2)
C(23)—N(1)	1.467(3)	C(1)—C(22)—C(21)	115.21(19)
C(23)—C(24)	1.509(3)	N(1)—C(23)—C(24)	111.16(19)
C(24)—O(1)	1.414(3)	O(1)—C(24)—C(23)	110.8(2)
C(25)—S(1)	1.735(3)	C(22)—N(1)—C(23)	119.1(2)
C(26)—S(1)	1.790(11)	C(25)—S(1)—C(26)	102.8(2)
14c			
C(6)—N(1)	1.282(3)	N(1)—C(6)—C(5)	120.1(2)
C(7)—N(1)	1.475(3)	N(1)—C(6)—C(12)	123.7(2)
C(7)—C(8)	1.527(3)	N(1)—C(7)—C(8)	109.72(19)
C(7)—C(9)	1.554(4)	N(1)—C(7)—C(9)	108.3(2)
C(8)—O(1)	1.417(3)	C(8)—C(7)—C(9)	112.1(2)
C(9)—C(10)	1.522(4)	O(1)—C(8)—C(7)	111.0(2)
C(12)—C(23)	1.347(4)	C(12)—C(23)—S(1)	126.8(2)
C(23)—S(1)	1.735(3)	C(6)—N(1)—C(7)	117.9(2)
C(24)—S(1)	1.798(4)	C(23)—S(1)—C(24)	100.92(16)
14d			
C(6)—N(1)	1.274(4)	N(1)—C(6)—C(1)	118.6(2)
C(6)—C(15)	1.512(4)	N(1)—C(6)—C(15)	125.5(3)
C(7)—N(1)	1.475(4)	C(1)—C(6)—C(15)	115.9(2)
C(7)—C(9)	1.509(4)	N(1)—C(7)—C(9)	111.4(2)
C(7)—C(8)	1.521(4)	N(1)—C(7)—C(8)	106.6(2)
C(8)—O(1)	1.424(4)	C(9)—C(7)—C(8)	110.8(3)
C(15)—C(26)	1.342(4)	O(1)—C(8)—C(7)	111.7(3)
C(26)—S(1)	1.741(3)	C(15)—C(26)—S(1)	127.2(2)
C(27)—S(1)	1.807(4)	C(6)—N(1)—C(7)	118.8(2)
		C(26)—S(1)—C(27)	99.21(16)

trometry, and confirmed that dienes **9a–e** were obtained in the form of single geometric isomers.

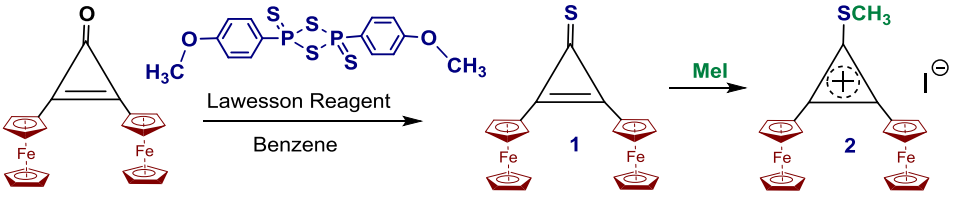
The ^{1}H NMR spectra of compounds **9a–e** contain one singlet for the methylthio fragments, characteristic signals for two ferrocenyl substituents, one singlet for the olefinic proton and signals from the protons of the aryl groups. The characteristic singlets of the olefinic protons and protons of the hydroxyl groups of compounds **9a–e** are located downfield (δ = 7.05–7.47 and 7.71–8.10 ppm, respectively). The ^{13}C NMR spectra of compounds **9a–e** contain the necessary numbers of signals from the carbon atoms of the ferrocenylic, arylic, olefinic fragments of the molecules **9a–e**, as well as from the quaternary carbons, and the signals from the two C_{ipso}-Fc atoms, confirming their diene structure. In addition, the IR spectra of compounds **9a–e** contain bands at ~3400 cm^{-1}, which are characteristic of OH groups. Presumably, 4-(2-hydroxyphenyl)-4-aza-1,3-dienes **9a–e** have an 1-*E*-configuration analogous to those of *E*-2,3-diferrocenyl-1-methylthio-1,3-diene [21].

Optimal results in the synthesis of compounds **7a–e** (23–30%) and **9a–e** (24–30%) were obtained when the reaction mixtures (**2** + **3a–e** = 1:1.3) were heated to ~80–82 °C for 8 h in benzene (Table 3). The highest results of the benzoxazoles **6a–e** (32–38%) [28] and 2,3-diferrocenylacroleins **10a** + **10b** (16–19%) were obtained when the reaction mixtures were boiled (6–8 h) in acetonitrile.

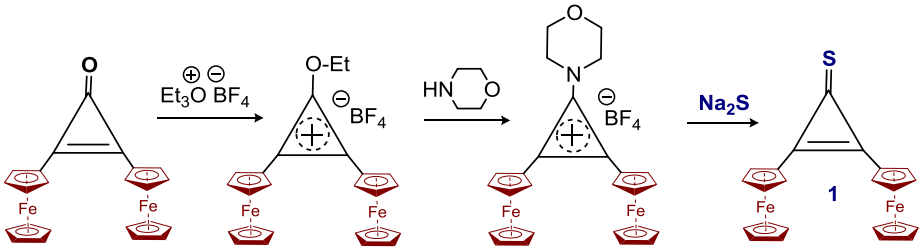
The side products **4**, **5a–e**, and **8b–d** have been described earlier. The physical and ^{1}H and ^{13}C NMR spectroscopic characteristics of compounds **4**, **5a–e**, and **8b–d** were in accordance with the literature data [28,29,40].

We also found that aliphatic 1,4-*N*,*O*-nucleophiles **11a–e** interact with 2,3-diferrocenyl-1-methylthio-cyclopropenylium iodide **2** under similar conditions (benzene, 80 °C, Et_3N), forming a mixture of the principal products **13b**,**d**,**e**, **14a–e**, **15a–e**. In addition, 1,1-dimethylthio-2,3-diferrocenylcyclopropene **4**, **10a–b** and 2-(*cis*-1,2-diferrocenylvinyl)-4,5 dihydrooxazoles **12a–e** [41] were also isolated from the reaction mixture (Scheme 4).

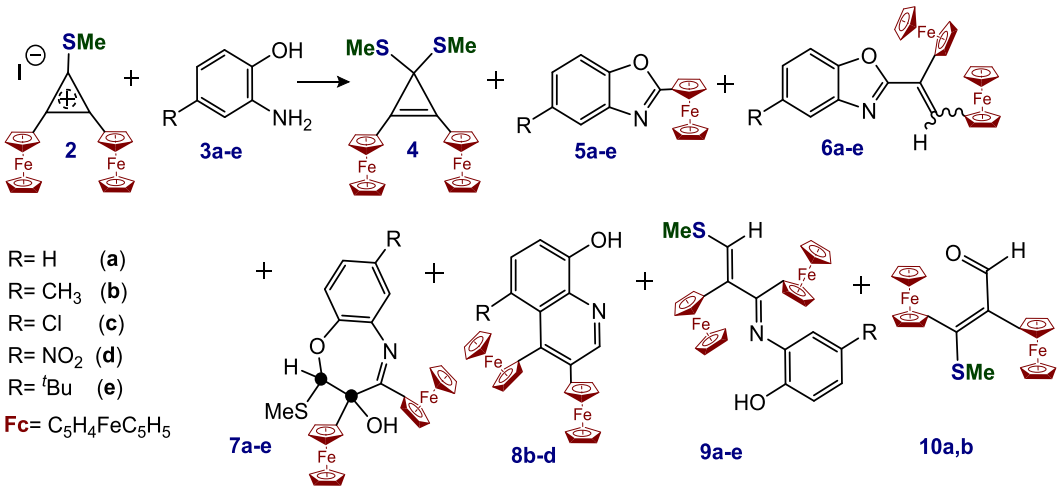
All the resultant compounds were separated using chromatography on (Al_2O_3, Brockmann activity III) and dry TLC on silica gel. Analysis of the ^{1}H and ^{13}C NMR spectra showed that compounds **13b**,**d**,**e** are individual diastereomers of 5,6-diferrocenyl-tetrahydro-1,4-oxazepines, whereas compounds **14a–e** and **15a–e** are isolated as a mixture of geometric isomers of the 2,3-diferrocenyl-6-hydroxy-4-aza-1,3-alkadienes, compounds **10a**,**b** – *cis*- and *trans*-2,3-diferrocenylacroleins. The data obtained from IR, ^{1}H and ^{13}C NMR analysis, mass spectra analysis, and elemental analysis confirm the structures attributed to them.



Scheme 1. Synthesis of the 2,3-diferrocenylcyclopropenthione **1** and 2,3-diferrocenyl-1-methylsulfonyl-cyclopropenylium iodide **2**.



Scheme 2. Synthesis of the 2,3-diferrocenylcyclopropenthione.



Scheme 3. Reactions of the 2,3-diferrocenyl-1-methylsulfonylcyclopropenylium iodide **2** with 1,2-aminophenols **3a–e**.

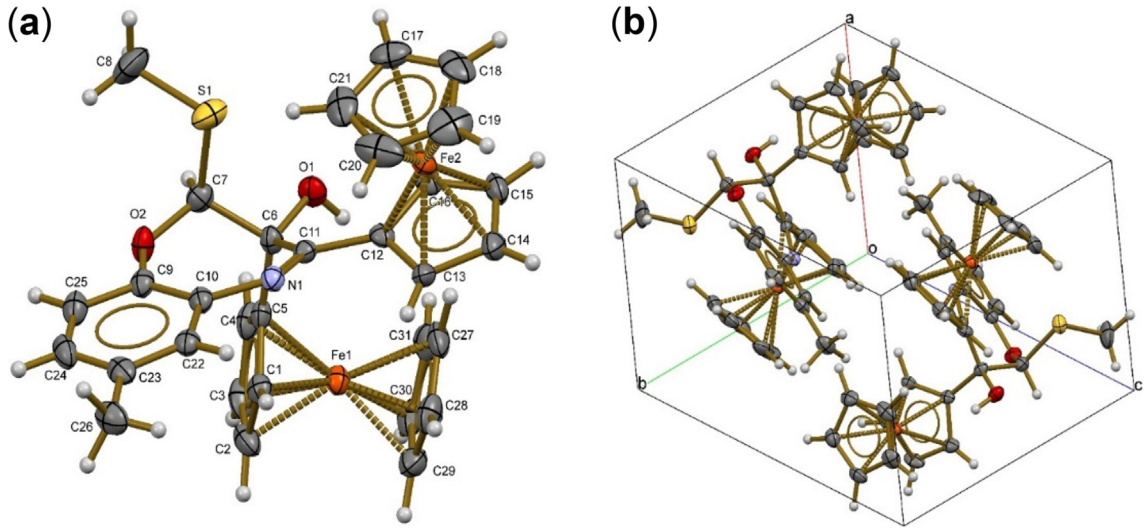


Fig. 1. (a) Crystal structure of **7b**; (b) crystal packing of **7b**.

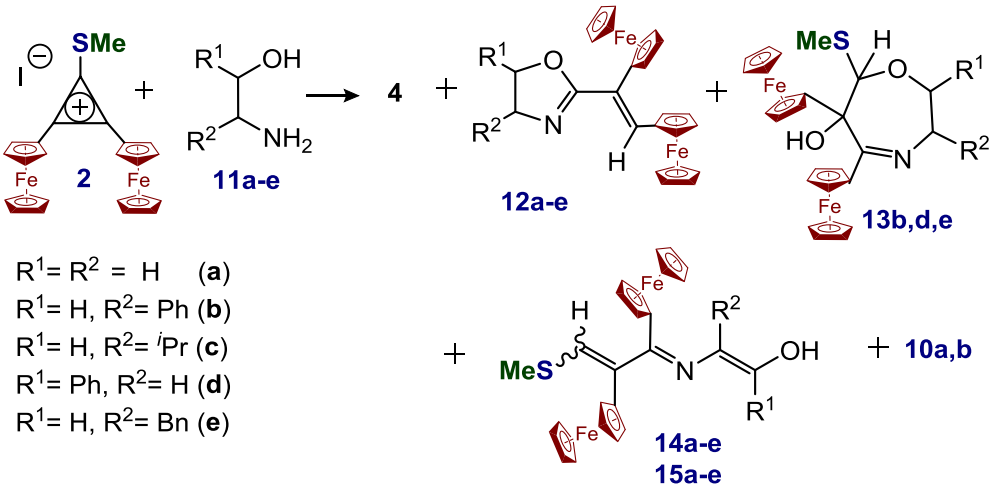
Table 3
Optimal reaction conditions for the synthesis of the representative compounds **6a–e**, **7a–e**, **8b–d**, **9a–e**, and **10a + b**.

Entry	Solvent	**2 + 3a–e (1:1.3)**	**4 (%)**	**5a–e (%)**	**6a–e (%)**	**7a–e (%)**	**8b-d (%)**	**9a–e (%)**	**10a + 10b (%)**
1	Benzene	**2 + 3a**	5.0	8.0	17.0	26.0	–	24.0	7.0
2	Benzene	**2 + 3b**	3.5	6.0	14.0	30.0	10.0	27.0	9.0
3	Benzene	**2 + 3c**	4.0	6.0	16.0	25.0	11.0	24.0	7.0
4	Benzene	**2 + 3d**	3.5	7.0	14.0	23.0	9.0	26.0	8.0
5	Benzene	**2 + 3e**	4.2	6.5	18.0	25.0	–	30.0	7.0
6	CH_3CN	**2 + 3a**	7.0	9.0	35.0	–	–	–	17.0
7	CH_3CN	**2 + 3b**	7.5	11.0	32.0	–	11.0	–	19.0
8	CH_3CN	**2 + 3c**	6.8	10.0	37.0	–	12.0	–	16.0
9	CH_3CN	**2 + 3d**	7.2	12.0	38.0	–	16.0	–	17.0
10	CH_3CN	**2 + 3e**	6.5	11.0	35.0	–	–	–	17.5

The 5,6-diferrocenyl-6-hydroxy-7-methylthio-2,3,6,7-tetrahydro-1,4-oxazepines **13b**,**d**,**e** were characterized by their ^1H and ^{13}C NMR spectral data, elemental analysis data and coincidence of their physicochemical properties with those for compounds **7a–e**. The ^1H NMR spectra of products **13b**,**d**,**e** contain the characteristic singlets from CH protons of CHSMe fragments and protons of OH groups with the chemical shift values δ = 5.45–5.50 ppm and δ = 1.65–1.75 ppm, respectively. The presence of the corresponding numbers of the signals from the quaternary carbon atoms, methyl, methylene, methine, aryl and ferrocenyl groups in the ^{13}C NMR spectra confirms the cyclic 1,4-oxazepine structure of each diastereomer **13b**,**d**,**e**.

The ^1H and ^{13}C NMR spectroscopic data of the aliphatic hydroxydienes suggest that they were formed in mixture of two isomeric

forms: **14a–e** + **15a–e** in *a* ~2:1 ratio. Our attempts to separate the isomeric dienes by chromatography were unsuccessful, however they were easily identified by spectroscopy because the positions of all the signals in the ^{1}H and ^{13}C NMR spectra, their multiplicities, and integral intensities are distinctly different. The isomers **14a**,**c**,**d** were separated partially by TLC on silica gel. The crystal structures



Scheme 4. Reactions of the 2,3-diferrocenyl-1-methylsulfonylcyclopropenylium iodide **2** with 1,2-aminoalcohols **11a–e**.

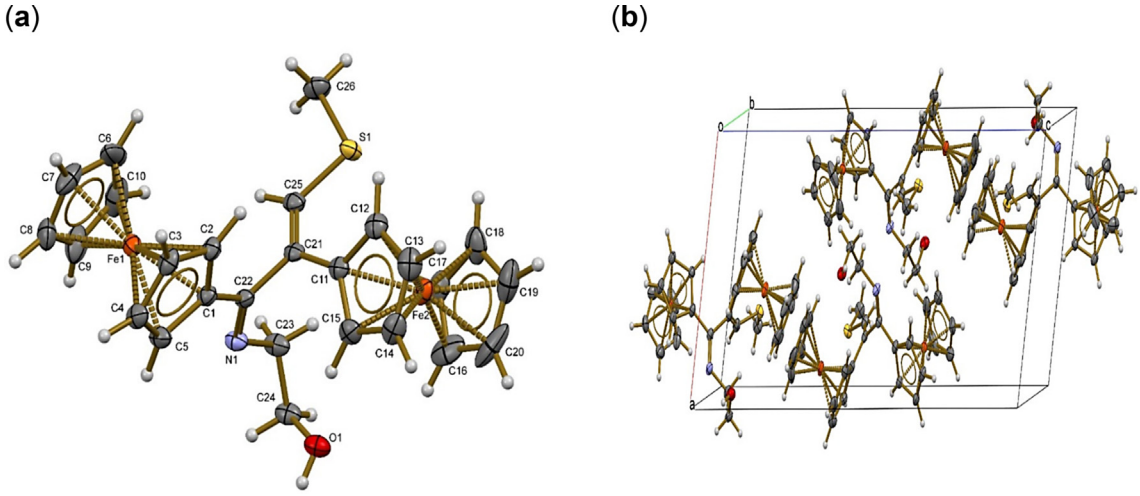


Fig. 2. (a) Crystal structure of *E*-**14a**. (b) Crystal packing of *E*-**14a**.

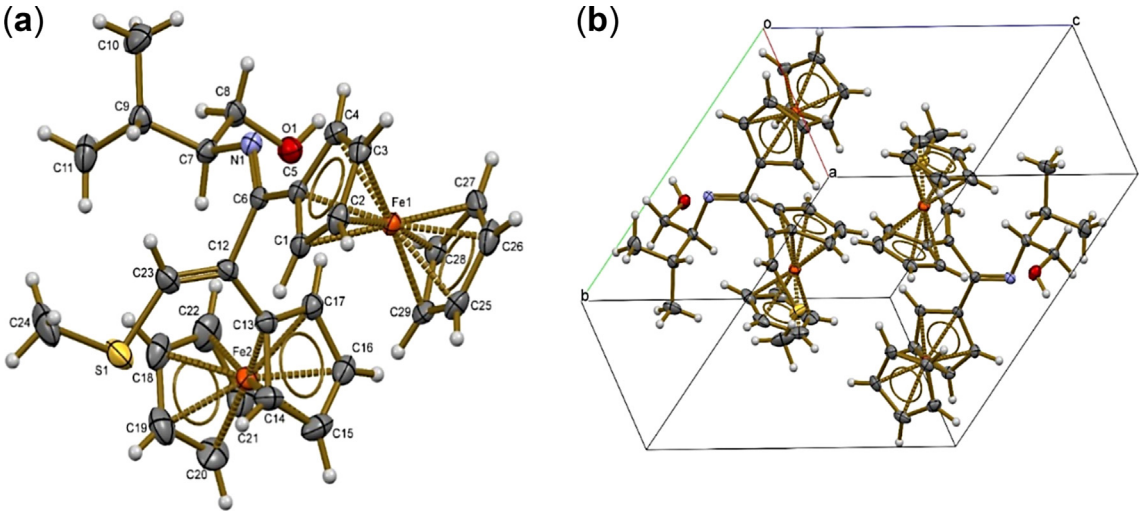


Fig. 3. (a) Crystal structure of *E*-**14c**. (b) Crystal packing of *E*-**14c**.

of compounds **14a**,**c**,**d** were established by X-ray diffraction analysis of a single crystals of these compounds, which were prepared by crystallization in diethyl ether. The perspective views of molecules **14a**,**c**,**d** are shown in Figs. 2a, 3a, 4a, crystal packing views of **14a**,**c**,**d** are displayed in Figs. 2b, 3b, 4b; selected bond lengths and angles are given in Table 1.

The compounds **14a**,**c**,**d** have the structures of (1-*E*)-2,3-diferrocenyl-1-methylthio-6-hydroxy-4-aza-1,3-dienes. Obviously, hydroxydienes **14b**,**e** have an (1-*E*) configurations analogous to those of **14a**,**c**,**d**; isomeric dienes **15a**–**e** have an (1-*Z*) configurations with trans-orientation of the MeS and Fc substituents in the FcC═CSMe fragments of the dienic systems.

Data from the X-ray analysis show that the C═C bonds in the compounds **14a**,**c**,**d** are somewhat shorter [1.337(3) (**14a**), 1.347 (4) (**14c**), 1.342(4) Å (**14d**)] than the standard value of 1.38 Å [40] and the C═N bond in the azadienes **14a**,**c**,**d** are somewhat longer [1.281(3) (**14a**), 1.282(3) (**14c**), 1.274(4) Å (**14d**)] than the standard value of 1.23 Å. [40] According to the X-ray diffraction data, the crystal structure of the molecule **14a** has a *S-trans*-configuration for the double bonds, whereas the crystal structures of the molecules **14c** and **14d** have *s-cis*-configurations for the double bonds.

Compounds **10a** and **10b** were isolated from the reactions of aromatic and aliphatic *bis*-1,4-*N,O*-nucleophiles **3a**–**e** and **11a**–**e** with 2.3-diferrocenyl-1-methyltiocyclopropenylium iodide **2** as a mixture of two geometric isomers in *ca.* 2:1 ratios (**10a** and **10b** represent *cis*- and *trans*-2,3-diferrocenyl-3-methylthio-acroleins), the ^{1}H NMR spectroscopic data, shows the signs for ferrocenyl and methylsulfanyl substituents, two low field singlets [δ = 10.15 (**10a**) and 9.41 (**10b**) ppm] for the CH protons of the HC═O fragments. The ^{13}C NMR spectra of compounds **10a** and **10b** contained signals for the carbon atoms of two ferrocenyl units with two sig-

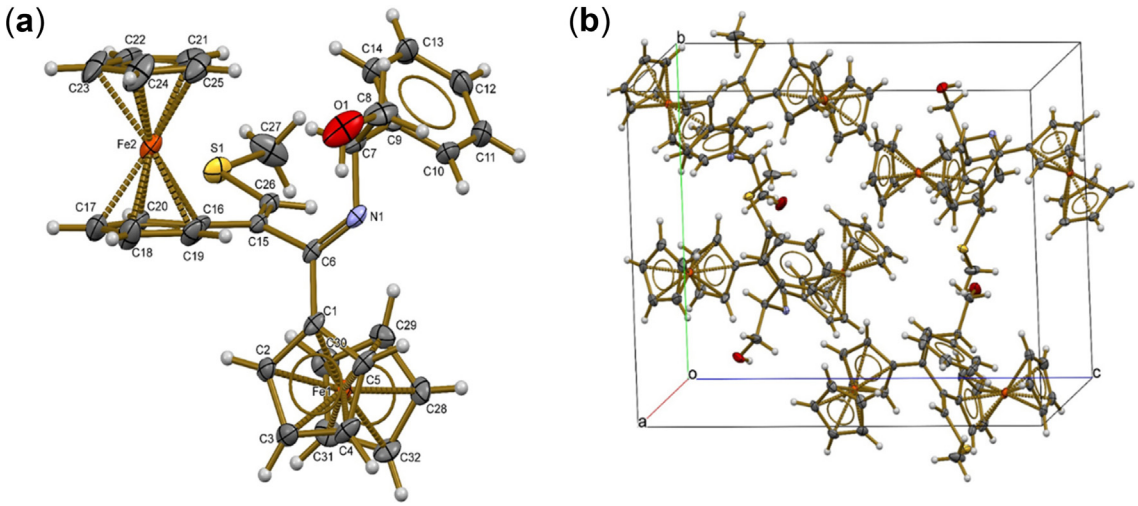
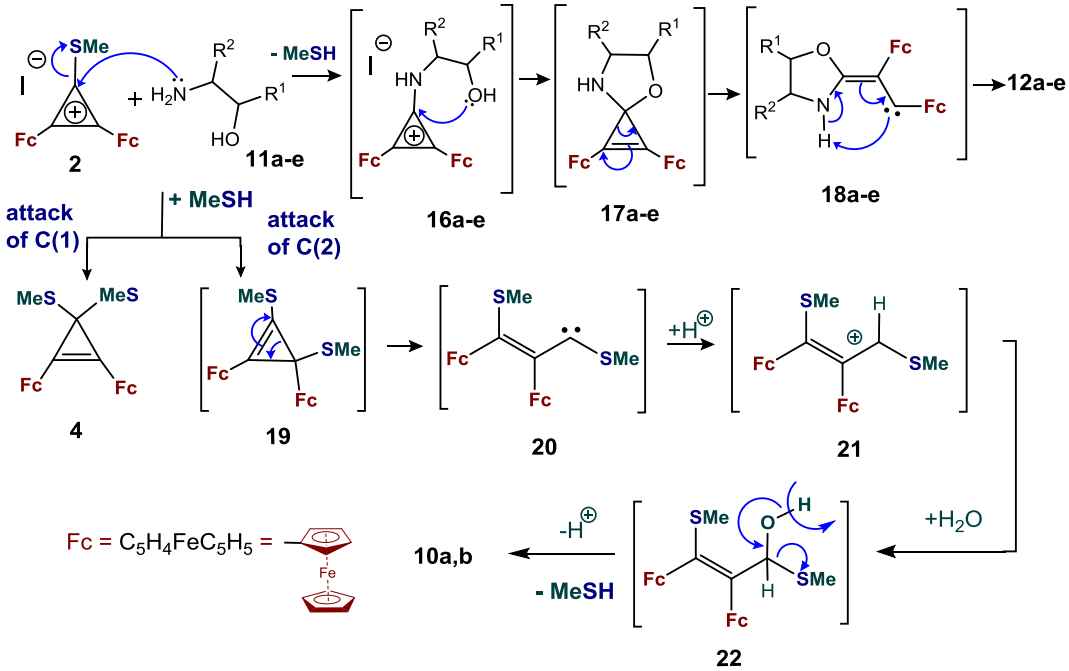


Fig. 4. (a) Crystal structure of *E*-**14d**. (b) Crystal packing of *E*-**14d**.

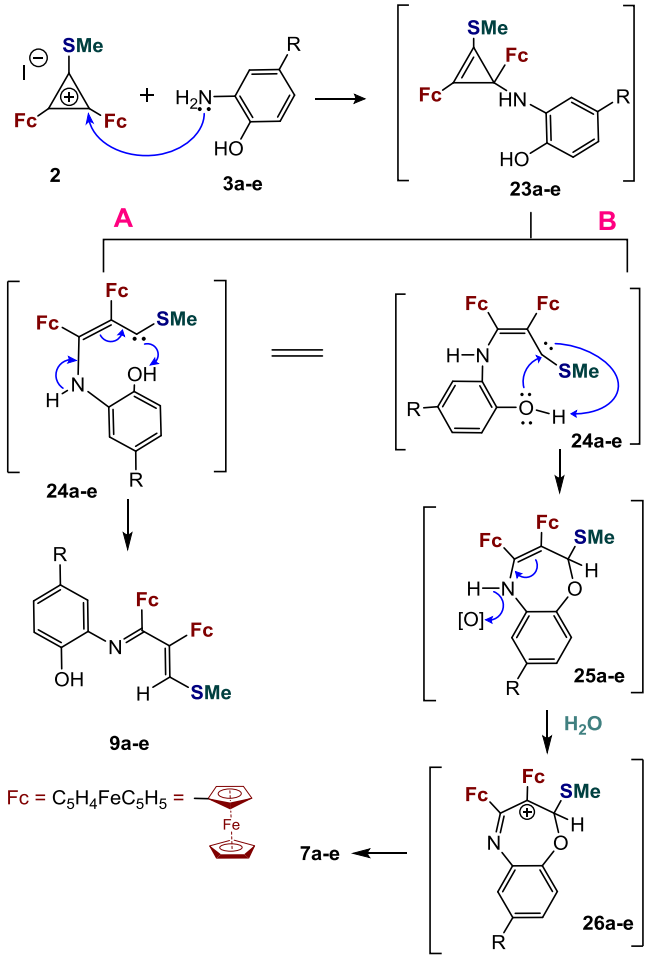


Scheme 5. Plausible mechanism of the formation of compounds **4**, **10a**,**b** and **12a**–**e**.

nals for C_{ipsoFc}, one signal for MeS substituent, one signal for HC═O fragment, two signals for the quaternary carbon atoms.

The presumable mechanism describing the formation of the derivatives of oxazoles **12a**–**e**, 2,3-diferrocenyl-1-methylthioacroleins **10a**,**b** and 2,3-diferrocenyl-1,1-dimethylthio-cyclopropene **4** is shown in Scheme 5. The nitrogen atoms of *bis*-1,4-*N,O*-nucleophiles, for example **11a**–**e**, attacks atom C-1 of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **2** and substitutes the MeS group with the formation of 1-aminocyclopropenylium cations **16a**–**e** and MeSH. The repeated attack of another oxygen atom on the C-1 carbon atom in cations **16a**–**e** yield the spirane tetrahydrooxazoles **17a**–**e**. The opening of the small cycle ring in the cyclopropene fragments of **17a**–**e** with the formation of vinylcarbene intermediates **18a**–**e** and subsequent intramolecular cyclic transformation of the carbenes lead to the formation of oxazoles **12a**–**e**. The sulfur atoms of methanethiol attacks the C-1 carbon atoms of salt **2** with the obtention of 2,3-diferrocenyl-1-methylthio-cyclopropene **4**; which attacks the C-2 carbon atoms of compound **2** by sulfur atoms of methanethiol are formed tetrasubstituted cyclopropenes **19**. The opening of the small cycle ring in the cyclopropene **19** into 2,3-diferrocenyl-3-methylthiovinylcarbene **20** with subsequent intramolecular transformation of **20** in the presence of the water result to *cis*- and *trans*-2,3-diferrocenyl-1-methylthioacroleins **10a**,**b**.

The formation of diferrocenylbenz-1,4-oxazepines **7a**–**e** and N-(2-hydroxyphenyl)-4-aza-1,3-dienes **9a**–**e** may be rationalized as being due to the nucleophilic contacts of the nitrogen atoms of the *bis*-1,4-*N,O*-nucleophiles, for example **3a**–**e**, with C-2 carbon atoms of 2,3-diferrocenyl-1-methylthiocyclopropenylium iodide **2** (Scheme 6) with obtention cyclopropane intermediates **23a**–**e**. The diferrocenylbenzoxazepines **7a**–**e** and N-aryl-4-aza-1,3-dienes **9a**–**e** are formed *via* a three-membered ring opening giving rise to carbenes **24a**–**e** and following pathway A and B, respectively. Evidently, compounds **13b**,**c**,**d**, **14a**–**e** and **15a**–**e** were obtained by analogy with Scheme 6.



Scheme 6. Plausible mechanism for the formation of compounds **7a**–**e**, **9a**–**e**.

4. Conclusions

The results of the present study support our previous conclusion [24,28,29,42], that depending on whether the nucleophile attacks of C(1) or C(2) on the cation **2** of the initially formed intermediates **16a**–**e**,**17a**–**e**, **19**, or **23a**–**e** (see Schemes 5 and 6**)** usually form the products that either retain the original three-membered ring or undergo C—C cleavage to give ring-opened products. The reactions of 2,3-diferroceny-1-methylthiocyclopropenylium iodide **2** with aromatic and aliphatic *bis*-1,4-*N,O*-nucleophiles **3a**–**e** and **11a**–**e**, respectively, in a benzene medium in the presence of Et_3N affords products of the nucleophile attacks C(1) and C(2) atoms of the three-membered **2** giving non-regioselectivity mixtures of the seven (from **3a**–**e**) and five (from **11a**–**e**) compounds. However, in the main were obtained derivatives of the diferrocenyl-1,4-oxazepines and diferrocenyl-hydroxy-4-aza-1,3-dienes **7a**–**e** + **9a**–**e** (∼49–57%), **13b**,**c**,**d** (∼28–33%), **14a**–**e** + **15a**–**e** (∼40–47%). These were formed by nucleophilic attacks of the C(2) atoms of the cyclopropenylium cations with nitrogen atoms of the nucleophiles **3a**–**e** or **11a**–**e**. This novel method of synthesis of 1,4-oxazepines and hydroxy-4-aza-1,3-dienes, obviously, requires more detailed studies aimed at the extension of its potential for the application in organic synthesis, further investigations in the fields of theoretical and synthetic organic chemistry, the search for new methods for an access to practically valuable materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Appendix A. Supplementary data

CCDC 1909613, 1909614, 1909615 and 1909616 contains the supplementary crystallographic data for **7b**, **14d**, **14a** and **14c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.07.019.

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