Conference paper

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N-alkyl-2-(1,2-diferrocenylvinyl)-4,5-dihydrooxazolinium salts, multi-component synthesis and breaking of their heterocyclic systems

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Abstract: A new multicomponent method for the synthesis of *N*-alkyl-2-(*Z*-1,2-diferrocenylvinyl)-4,5-dihydrooxazolinium salts **3a–f**, 5-(*N*-alkyl-2′,3′-diferrocenyl-acryloylamido)-3-aza-3-alkylpentanols **4a–d**, (*E*)-*N*-alkyl-*N*-(2-morpholinoethyl)-2,3-diferrocenylacrylamides **9a,b,e,f** and (*E*)-*N*-alkyl-*N*-(2-piperidinoethyl)-2,3-diferrocenylacrylamides **10a,c** from reactions of 2,3-diferrocenylcyclopropenone **1** with *bis*-1,4-*N,O*-nucleophiles in the presence of triethyloxonium tetrafluoroborate, alkyl iodides, morpholine, piperidine and Et_3N is described. The characterization of the new compounds was done by IR, ^1H- and ^{13}C-NMR spectroscopy, mass-spectrometry, elemental analysis and X-ray diffraction studies.

Keywords: 2,3-diferrocenylcyclopropenone; 5-(*N*-alkyl-2′,3′-diferrocenylacryloylamido)-3-aza-3-alkylpentanols; (*E*)-2-[(*N*-2′,3′-diferrocenylacryloyl-2-(*N*-alkyl)amino]-ethylheterocycles; *N*-alkyl-2-(*Z*-1,2-diferrocenylvinyl)oxazolinium iodides; POC-16.

Introduction

Nowadays, derivatives of ferrocene are considered to be modular building blocks in organic synthesis and are usually used to introduce a redox-responsive moiety into molecules. Such compounds find many applications in nonlinear optics, molecular electronic devices, redox polymers, ceramics [1], asymmetric catalysis [2–5], biochemistry [6, 9], medicinal [10–14] and bioorganometallic chemistry [15–22], etc. Development of new methods for the synthesis of ferrocenylheterocycles with a conjugated system of double bonds and several heteroatoms in the cycle is of interest for producing novel iron-containing compounds, which are an important category of materials [23–26].

The use of the 2,3-diferrocenylcyclopropenylium salts and *bis*-1,3- or *bis*-1,4-*N,O*-heteronucleophiles as adducts for such synthesis makes it possible to obtain heterocyclic compounds whose structures contain both ferrocene fragments and conjugated multiple bonds with several heteroatoms in the cycles [27, 28]. This served as the basis for the preparation of diferrocenyl-1,2,3-triazines [29], -1,2,4-triazines [30], -pyridazines [31], -pyridines [32], -pyrimidines [33, 34], and -oxazines [35], as well as imidazolines [36].

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The interest in oxazoline compounds bearing ferrocenyl substituents in the molecules can be traced back to the discovery of ferrocene [37]. This is determined by a peculiar chemical behavior of such compounds due to mutual influence of the metallocene and heterocyclic moieties. Little information concerning the synthesis and chemistry of ferrocenyl-4,5-dihydrooxazoles is available. To date, only the preparation of 2-ferrocenyloxazolines has been described [38] together with some of their chemical properties. However, ferrocenyl-substituted oxazolines are still scarcely studied. Investigations of the chemical transformations of such compounds are certainly of interest for theoretical, practical and synthetic organic chemistry, as well as for the search of compounds with favorable practical properties, such as thermal stability, electrical conductivity (even superconductivity), biological activity, nonlinear optical effects, etc. [39]. In this paper we studied the synthesis of ferrocenyl-4,5-dihydrooxazoles and their salts using the condensation of 2,3-diferrocenylcyclopropenone (multicomponent) and of 2,3-diferrocenylcyclopropenylium tetrafluorobarate with the derivatives of 1,2-aminoalcohols. Reactions of this type in the chemistry of cyclopropenylium cations have not yet been studied.

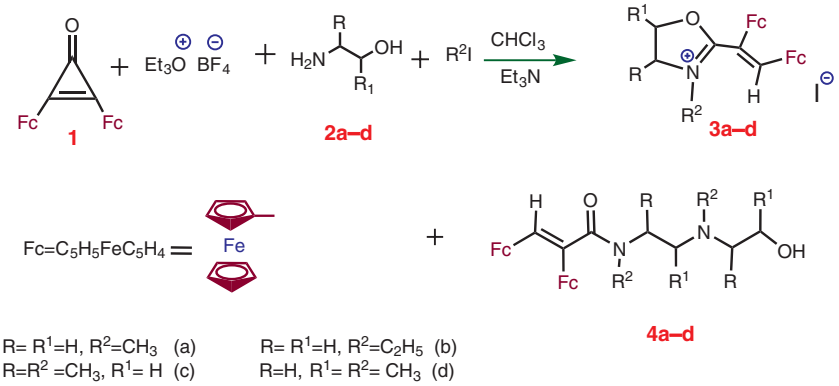
Results and discussion

The initial 2,3-diferrocenylcyclopropenone **1** was prepared from ferrocene and tetrachlorocyclopropene as is described in [40, 41].

We found that 2,3-diferrocenylcyclopropenone **1** interacted with 1,2-aminoalcohols **2a–d** in the presence of triethyloxonium tetrafluoroborate, alkyl iodides and Et_3N during boiling in $CHCl_3$ or CH_3CN with the formation of a mixture of two products: 3-*N*-alkyl-2-(1,2-diferrocenylvinyl)-4,5-dihydrooxazolinium iodides **3a–d** and 2-(*N*-alkyl-2′,3′-diferrocenylacrylamido)ethylmorpholines **4a–d**, whose yields depend on the molar excess of the reagents **2a–d**, temperature, and duration of the reaction (Scheme 1, Table 1).

Individual diferrocenylvinyloxazolinium iodides **3a–d** and 5-(N-alkyl-2′,3′-diferrocenylacryloylamido)-3-aza-3-alkylpentanols **4a–d** were isolated using Al_2O_3 column chromatography (activity grade III, elution with hexane : ether 2 : 1). The compounds obtained are represented by fine crystalline substances of red and orange color, respectively, storage-stable in the solid state. The structures of compounds **3a–d** and **4a–d** were determined on the basis of mass spectrometry, IR, ^1H and ^{13}C NMR spectroscopy and elemental analysis (for **4a–d**).

Treatment of the compound **1** (1 mmol) with 1,2-aminoalcohols **2a–d** (1 mmol) afforded the *N*-alkyl-2-(*Z*-1,2-diferrocenylvinyl)oxazolinium salts **3a–d** (yields ~ 71–78 %) and compounds **4a–d** (yields ~ 8–10 %). The reaction of the cyclopropenone **1** with a two-fold molar excess of *N*-alkylaminoalcohols **2a–d** resulted in the *N*-alkyl-2-(*cis*-1,2-diferrocenylvinyl)oxazolinium salts **3a–d** (~ 30–32 %) and 5-(*N*-alkyl-2′,3′-diferrocenylacryloylamide)-3-aza-3-alkylpentanols **4a–d** (~ 43–45 %); the reaction of the cyclopropenone **1** with a three-fold molar excess of 1,2-aminoalcohols **2a–d** afforded preferentially the 5-(*N*-alkyl-2′,3′-diferrocenylacryloylamide)-3-aza-3-alkylpentanols **4a–d** (yields ~ 71–81 %) (Scheme 1, Table 1).



Scheme 1: Multicomponent reactions of 2,3-diferrocenylcyclopropenone **1** with 1,2-aminoalcohols **2a–f**.

Table 1: Multicomponent reactions of 2,3-diferrocenylcyclopropenone **1** with 1,2-aminoalcohols **2a–d.**

Relations of reagents 1 and 2a,b in mmols	Solvent	Temp. (°C)	Time (h)	Yield 3a/4a or 3b/4b (%)	Time (h)	Yield 3a/4a or 3b/4b (%)
1/2a (1 : 2)	$CHCl_3$	70	6	28/35	12	30/44
1/2b (1 : 2)	$CHCl_3$	70	6	32/40	12	32/43
1/2c (1 : 2)	CH_3CN	80	6	23/34	12	31/45
1/2d (1 : 2)	CH_3CN	80	8	28/39	12	33/44
1/2a (1 : 1)	CH_3CN	80	8	62/4	12	71/8
1/2b (1 : 1)	CH_3CN	80	6	57/3	12	74/10
1/2c (1 : 1)	$CHCl_3$	70	6	54/8	12	75/8
1/2d (1 : 1)	$CHCl_3$	70	6	60/61	12	78/8
1/2a (1 : 3)	$CHCl_3$	70	3	10/31	8	9/71
1/2a (1 : 3)	$CHCl_3$	70	4	11/34	8	10/80
1/2a (1 : 3)	$CHCl_3$	70	5	17/27	8	8/81
1/2a (1 : 3)	$CHCl_3$	70	6	20/24	8	6/79

The structures of compounds **3a–d** and **4a–d** were determined on the basis of mass spectrometry, IR, ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (for **4a–d**). The ^{1}H NMR spectra of oxazolinium salts **3a–d** contain signals from the protons of two ferrocene substituents, singlets from one olefin proton, doublets from the protons of methyl groups (**3c**,**d**), and also the respective numbers of signals from the CH_3–, CH_3–CH_2–, CH_2– and CH-fragments of the oxazolinium rings. The information in the ^{13}C NMR spectra of compounds **3a–d** also confirms the structures of the resultant compounds (see the Experimental section). According to ^{1}H and ^{13}C NMR spectroscopic data, salts **3a–d** are exclusively formed in the form of one geometric isomer with, presumably, *cis*-oriented ferrocene substituents at the double bond in the 1,2-diferrocenylvinyl fragment.

The ^{1}H NMR spectra of compounds **4a–d** contain the necessary numbers of signals from the protons of two ferrocene groups, methyl or ethyl substituents and also the necessary numbers of signals from the protons of methylene and metine fragments, as well as one singlet from olefin protons. The structures of compounds **4a–d** were also derived on the basis of IR spectra, which contain absorption bands characteristic for C=O and OH groups. The ^{13}C NMR spectra of compounds **4a–d** also fully confirm their structures (see the Experimental section).

X-Ray diffraction analysis of single crystals of compound **4a** obtained by crystallization from CH_2Cl_2 confirmed that the structure of **4a** is 2-(*N*-methyl-2′,3′-diferrocenylacrylamido)-3-methyl-3-azapentanol **4a**. The general view of the molecule **4a** and its principal characteristics are given in Fig. 1a. The character of the packing of molecules in the crystals is shown in Fig. 1b; these require no special comments.

The supposed mechanism of the formation of 2-(1,2-diferrocenylvinyl)-4,5-dihydrooxazolinium cations **3a–d** is shown in Scheme 2. The 1,2-aminoalcohol attacks the C(1) carbon atom of the cyclopropenylium cations twice with the formation of intermediate spirane oxazolidines **5a–d**, which subsequently undergo an intramolecular transformation (with the opening of the three-carbon ring) into intermediate vinylcarbenes **6a–d** and allylic carbocations **7a–d**, and then into salts **3a–d**.

We found also that 2,3-diferrocenylcyclopropenone **1** (1 mmol) reacted similarly with 1,2-aminoalcohols **2a,b,e,f** (1 mmol) upon boiling in benzene or acetonitrile in the presence of triethyloxonium tetrafluoroborate (1.2 mmol), alkyl iodides, Et_3N and morpholine **8a** (1 mmol) to form a mixture of two products: **3a,b,e,f** (~ 7–12 %) and (*E*)-*N*-alkyl-*N*-(2-morpholinoethyl)-2,3 diferrocenylacrylamides **9a,b,e,f** (~ 70–75 %) (Scheme 3). The reaction products **3a,b,e,f** and **9a,b,e,f** were separated using Al_2O_3 (activity grade III) column chromatography. Their structures were confirmed using mass spectrometry, elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy.

The ^{1}H NMR spectra of compounds **9a,b,e,f** contained signals of singlets from the protons of the methyl groups of the *N*–Me fragment (δ = 3.20, 2.96 and 2.87 ppm) for compounds **9a, 9e** and **9f**, respectively, singlets from the protons of the olefin CH= fragment (δ = 6.26, 6.42, 7.37 and 7.43 ppm), signals from the protons of the corresponding numbers of the ferrocenyl, *N*-ethyl and phenyl substituents, and also from the CH_2– and

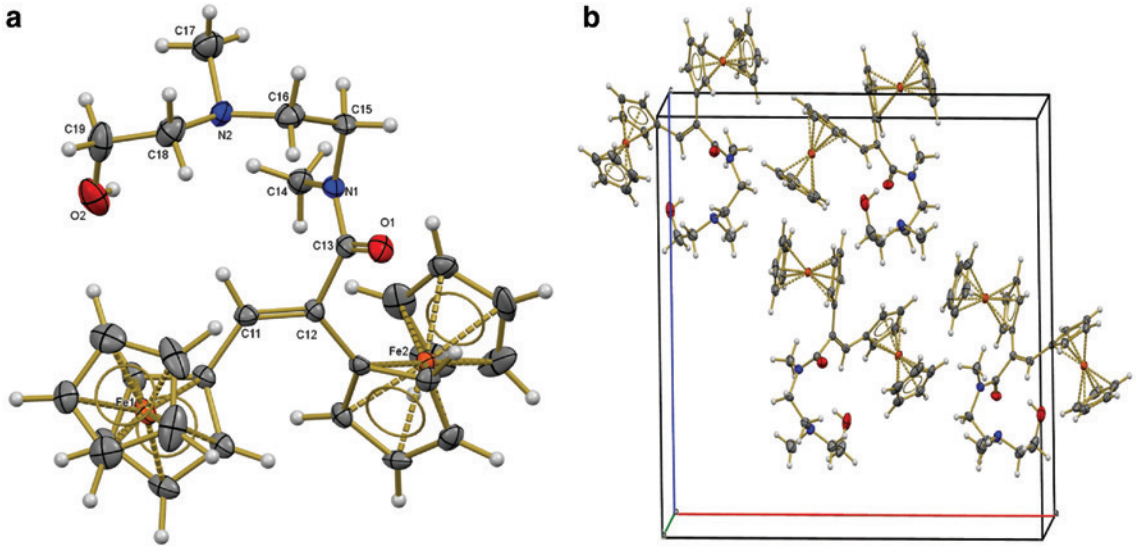
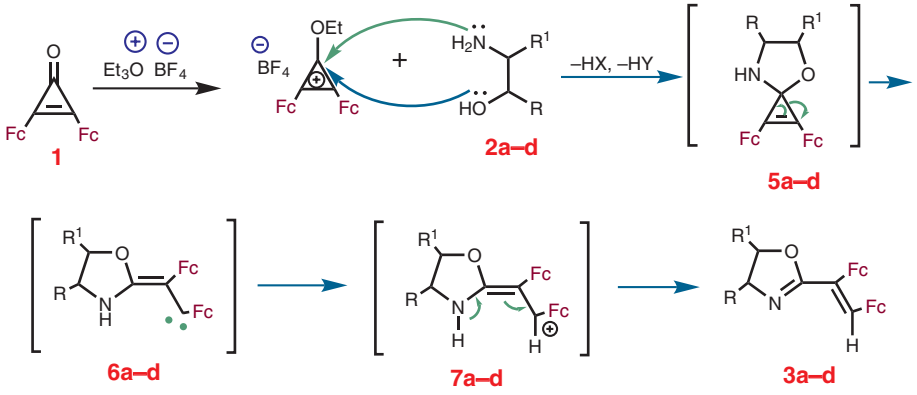
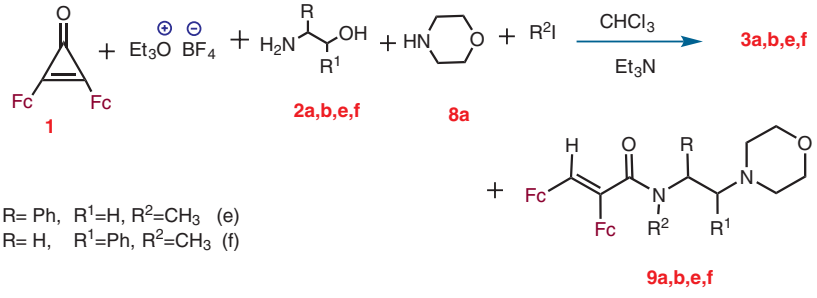


Fig. 1: (a) Crystal structure and (b) crystal packing of compound **4a.** Selected bond lengths (Å) and angles (°): C(11)–C(12) 1.346(5), C(12)–C(13) 1.500(5), C(13)–O(1) 1.246(5), C(13)–N(1) 1.340(5), C(14)–N(1) 1.460(5), C(15)–N(1) 1.468(5), C(16)–N(2) 1.462(5), C(17)–N(2) 1.462(6), C(18)–N(2) 1.461(6), C(18)–C(19) 1.499(7), C(19)–O(2) 1.409(6); C(11)–C(12)–C(13) 116.1(3), O(1)–C(13)–N(1) 121.5(4), O(1)–C(13)–C(12) 118.8(4), N(1)–C(13)–C(12) 119.6(3), N(1)–C(15)–C(16) 110.5(3), N(2)–C(16)–C(15) 112.0(4), N(2)–C(18)–C(19) 114.4(4), O(2)–C(19)–C(18) 114.7(4), C(13)–N(1)–C(14) 124.3(3), C(14)–N(1)–C(15) 117.4(3), C(13)–N(1)–C(15) 117.6(3), C(18)–N(2)–C(16) 110.6(3), C(18)–N(2)–C(17) 110.6(3), C(16)–N(2)–C(17) 110.1(4).



Scheme 2: Plausible mechanism of the formation of 2-(1,2-diferrocenylvinyl)-4,5-dihydrooxazolinium salts **3a–d**.



Scheme 3: Multicomponent reactions of the 2,3-diferrocenylcyclopropenone **1** with 1,2-aminoalcohols **2a,b,e,f** in the presence of morpholine.

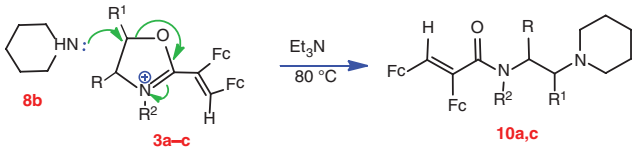
CH-groups of the $-CH_2-CH_2-$ and $-CH_2-$ CH-fragments. The data of the ^{13}C NMR spectra of compounds **9a,b,e,f** confirmed their structure (see the Experimental section).

The formation of products with linear structures **4a–f** and **9a,b,e,f** in the reactions of cyclopropenone **1** with 1,4-*bis*-*N,O*-nucleophiles **2a–f** proceeds, in our opinion, *via* the opening of the five-membered ring in the *N*-alkyloxazolinium cations **3a–f** as a result of the nucleophilic attacks of the nitrogen atoms in the 1,4-*bis*-*N,O*-nucleophiles **2a–f** on the carbon atoms C(5) of the heterocyclic systems of the oxazoliniun salts. This suggestion has been confirmed in studies of the chemical behavior of oxazolinium cations **3a,c** upon reaction with other nucleophiles, as for example, with piperidine **2g** (Scheme 4).

Thus, actually we found that the treatment of *N*-alkyloxazolinium cations **3a**,**c** with piperidine **8b** under similar conditions resulted in (*E*)-*N*-alkyl-*N*-(2-piperidinoethyl)-2,3-diferrocenylacrylamides **10a**,**c** with 70 % and 73 % yields, respectively (Scheme 4). The data of mass spectrometry, elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy confirmed their structure.

X-Ray diffraction analysis of single crystals of compounds **9b, 9e** and **9f** obtained by crystallization from CH_2Cl_2 were undertaken to confirm their structures. The general view of the molecules **9b, 9e** and **9f** and their principal characteristics are given in Figs. 2a, 3a and 4a, respectively; the character of the packing of the molecules in the crystals are shown in Figs. 2b, 3b and 4b.

Following the general procedures (see the Experimental section), treatment of the 2,3-diferrocenylcyclopropenine **1** in the presence of HBF_4, alkyl iodides, Et_3N with *bis*-1,4-*N,O*-nucleophiles **2a–d** or with the mixture of *bis*-1,4-*N,O*-nucleophiles with morpholine (**2a,b,e,f**) or piperidine (**2a,c**) afforded the diferrocenylvinyloxazolinium salts **3a–f** (~ 15–26 %), 5-(*N*-alkyl-2′,3′-diferrocenylacryloylamide)-3-aza-3-alkylpentanols **4a–d** (yields ~ 41–50 %), (*E*)-*N*-alkyl-*N*-(2-morpholinoethyl)-2,3-diferrocenyl-acrylamides **9a,b,e,f** (yields ~ 32–44 %) or (*E*)-*N*-alkyl-*N*-(2-piperidinoethyl)-2,3-diferrocenyl-acrylamides **10a,c** (yields 27 % and 33 %, respectively).



Scheme 4: Plausible mechanism of the ring-opening of oxazolinium salts.

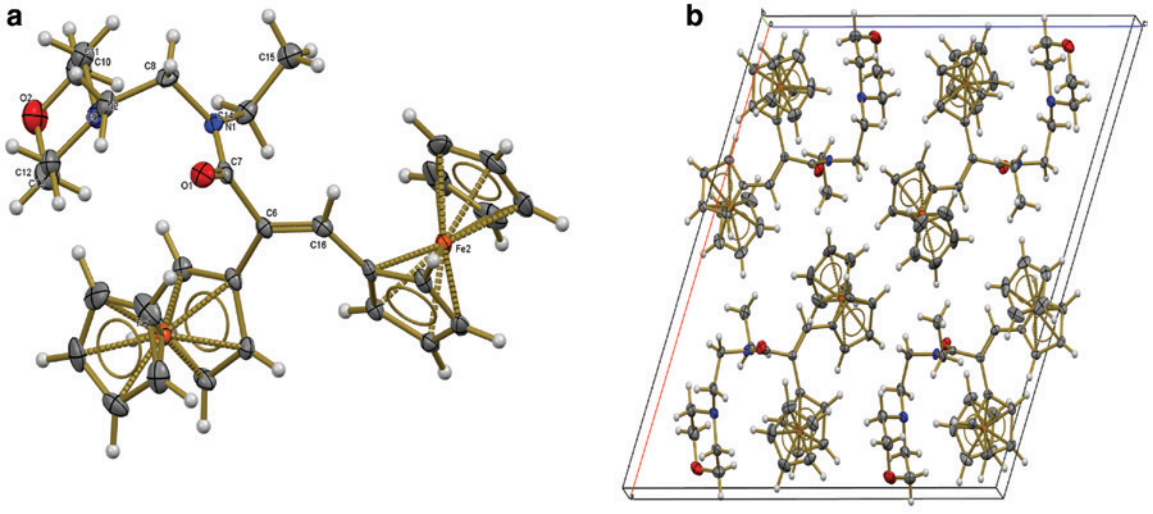


Fig. 2: (a) Crystal structure and (b) crystal packing of compound **9b.** Selected bond lengths (Å) and angles (°): C(6)–C(16) 1.339(4), C(6)–C(7) 1.513(4), C(7)–O(1) 1.229(3), C(7)–N(1) 1.340(5), C(14)–N(1) 1.348(4), C(8)–N(1) 1.465(4), C(9)–N(2) 1.465(4), C(10)–N(2) 1.460(4); C(16)–C(6)–C(7) 118.3(2), O(1)–C(7)–N(1) 121.7(3), O(1)–C(7)–C(6) 120.9(3), N(1)–C(7)–C(6) 117.3(2), N(1)–C(8)–C(9) 111.1(2), N(2)–C(10)–C(11) 109.8(3), C(7)–N(1)–C(8) 118.0(2), C(14)–N(1)–C(7) 124.7(2), C(10)–N(2)–C(9) 112.3(2).

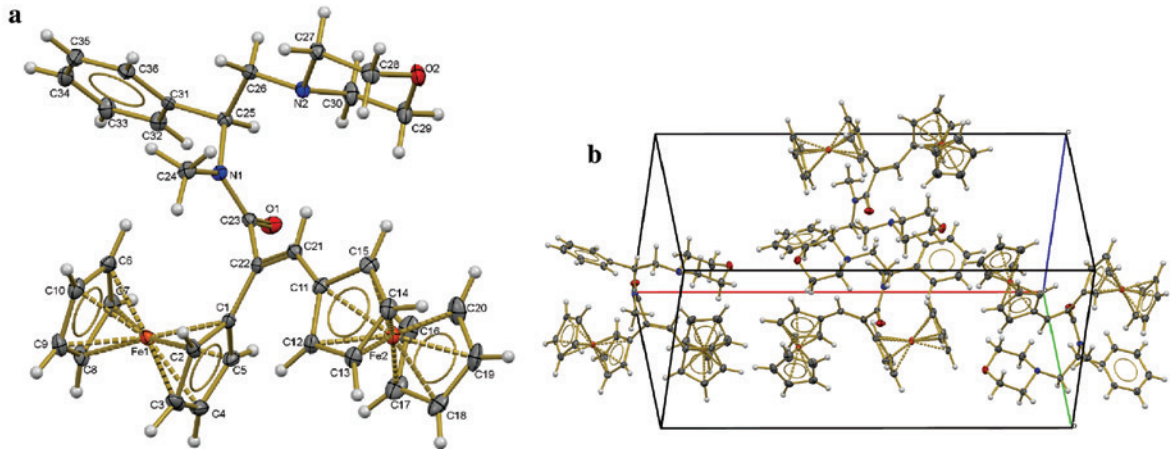


Fig. 3: (a) Crystal structure and (b) crystal packing of compound **9e**. Selected bond lengths (Å) and angles (°): N(1)–C(24) 1.464(5), C(23)–N(1) 1.349(5), O(1)–C(23) 1.231(5), C(25)–N(1) 1.465(5), C(26)–N(2) 1.460(5), C(27)–N(2) 1.453(5), C(28)–O(2) 1.418(6), C(25)–C(26) 1.530(5), N(2)–C(30) 1.462(5); C(23)–N(1)–C(24) 122.2(4), N(1)–C(23)–O(1) 122.9(4), N(1)–C(23)–C(22) 116.4(4), O(1)–C(23)–C(22) 120.6(4), C(23)–N (1)–C(25) 120.2(3), C(27)–N(2)–C(26) 111.5(3), C(28)–O(2)–C(29) 108.9(3), N(1)–C(25)–C(26) 110.6(3),N(2)–C(26)–C(25) 111.9(3).

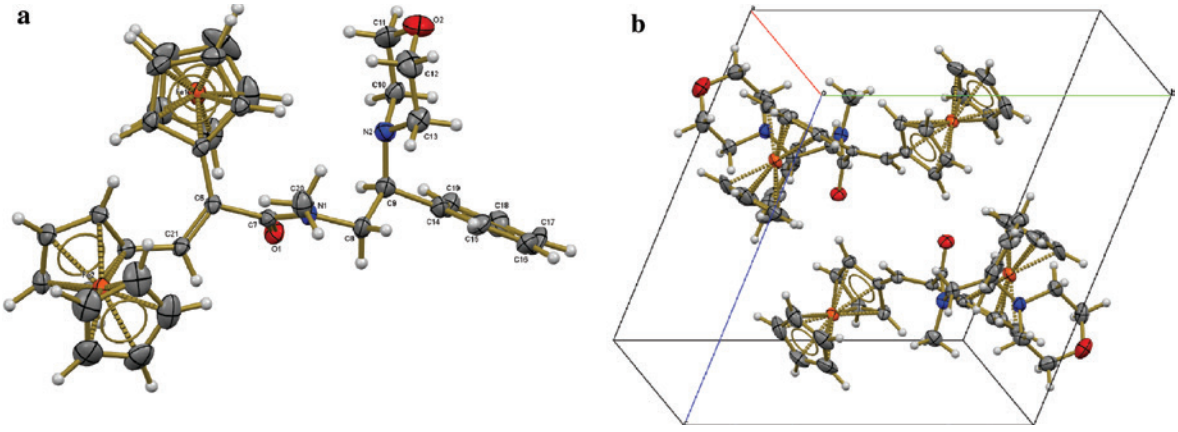


Fig. 4: (a) Crystal structure and (b) crystal packing of compound **9f.** Selected bond lengths (Å) and angles (°) : N(1)–C(7) 1.353(4), C(20)–N(1) 1.449(5), O(1)–C(7) 1.223(4), C(9)–N(2) 1.485(4), C(8)–N(1) 1.467(4), C(14)–C(9) 1.531(5), C (8)–C(9) 1.521(5), C(7)–C(6) 1.531(4); C(7)–N(1)–C(20) 124.4(3), C(7)–N(1)–C(8) 118.6(3), C(13)–N(2)–C(9) 117.7(3), O(1)–C(7)–N(1) 122.3(3), O(1)–C(7)–C(6) 120.2(3), C(21)–C(6)–C(7)115.0(3), C(12)–O(2)–C(11) 110.2(3), N(1)–C(7)–C(6) 117.5(3), N(2)–C(9)-C(8) 112.9(3).

Conclusion

The multicomponent reactions of 2,3-diferrocenylcyclopropenone **1** with *bis*-1,4-*N,O*-nucleophiles **2a–f** in the presence of triethyloxonium tetrafluoroborate, alkyl iodides, morpholine and Et_3N are regioselective. The double nucleophilic attacks of the C(1) atoms of the intermediate 1-ethoxy-2,3-diferrocenylcyclopropenilium tetrafluoroborate **1a** in the presence other reagents to afford *N*-alkyl-2-(*Z*-1,2-diferrocenylvinyl)-4,5-oxazolinium iodides **3a–f**, derivatives of the 5-(*N*-alkyl-2′,3′-diferrocenylacryloylamide)-3-aza-3-alkylpentanols **4a–f** and (*E*)-*N*-alkyl-*N*-(2-morpholinoethyl)-2,3-diferrocenyl-acrylamides **9a,b,e,f**. The interactions of the oxazolinium salts **4a,b,c,e,f** with morpholine or piperidine formed due to the opening of the five-membered heterocycles, giving rise to one type of compounds **9a,b,e,f** or (*E*)-*N*-alkyl-*N*-(2-piperidinoethyl)-2,3-diferrocenyl-acrylamides **10a,c**. The products with linear structures **4a–f**, **9a,b,e,f** and **10a,c** in the reactions of cyclopropenone **1** with 1,4-*bis*-*N,O*-nucleophiles **2a–f** were obtained *via* the opening of the five-membered ring in the *N*-alkyloxazolinium cations **3a–f** as a result of the nucleophilic attacks of the nitrogen atoms in the

1,4-*bis*-*N,O*-nucleophiles **2a–f** on the carbon atoms C(5) of the heterocyclic systems of the oxazoliniun salts. The opening of the five-membered ring in *N*-alkyloxazolinium cations as a result of the nucleophilic attack on the carbon atom C(5) of the heterocyclic system has been described for the first time. Such an opening, in contrast to the opening with the nucleophilic attack on the carbon atom C(2), which was described in the literature [42–45], is apparently due to the influence of the 1,2-diferrocenylvinyl substituent at C(2) in oxazolinium cations. In our opinion, this feature must be of general nature, pertaining to all compounds of a similar structure; thus, they can be used in organic synthesis of macro-molecules as six-atom building blocks.

Experimental section

General

All the solvents were dried according to the standard procedures and were freshly distilled before use [46]. Column chromatography was carried out on alumina (Brockmann activity III). The ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ (**3a–f**, **4a–d**, **10a,c**, **9e,f**), in C_6D_6 (**9b**), in C_6D_6 and $CDCl_3$ (**9a**), with Me_4Si as the internal standard. The IR spectra were measured on a Spectrophotometer FT-IR (Spectrum RXI Perkin Elmer instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementar Analysensysteme LECO CHNS-900 was used for elemental analyses. The unit cell parameters and the X-ray diffraction intensities of **4a, 9b, 9e** and **9f** were recorded on a Gemini (detector Atlas CCD, Cryojet N_2) diffractometer. The structures of compounds **4a, 9b, 9e** and **9f** were solved by the direct method (SHELXS-97) [47–49] and refined using full-matrix least-squares on F^2.

Multicomponent reactions of 2,3-diferrocenylcyclopropenone 1 with 1,2-aminoalcohols 2a–d in the presence of triethyloxonium tetrafluorobo-rate, alkyl iodides and Et_3N

To the solution of 2,3-diferrocenilcyclopropenone **1** (2.5 mmol) in $CHCl_3$, or CH_3CN (50 mL) were added with stirring triethyloxonium tetrafluoroborate (3.0 mL, 1.0 M solution in dichloromethane), 1,2-aminoalcohols (**2a–d**, 5 mmol), methyl or ethyl iodides (0.5 mL) and Et_3N (1.0 mL). After stirring for 3–12 h at 70–80 °C, the volatiles were removed *in vacuo*; chromatography of the residue on Al_2O_3 (hexane-ether, 2 : 1), yielded compounds **3a–d** and **4a–d** (Table 1).

2-(*Z*-2,3-diferrocenylvinyl)-3-methyl-4,5-dihydrooxazol-3-ium iodide (3a)

Red powder, yield 0.46 g (30 %), m.p. 108–109 °C. IR (KBr): ν 467, 478, 731, 808, 905, 953, 1001, 1028, 1044, 1106, 1186, 1204, 1263, 1253, 1284, 1363, 1388, 1420, 1457, 1476, 1604, 1650, 1709, 2869, 2926, 2959, 3054, 3094, 3357 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59 (3H, s, CH_3), 3.07 (2H, t, CH_2, J = 5.4 Hz), 4.05 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.19 (1H, m, C_5H_4), 4.23 (3H, m, C_5H_4), 4.24 (2H, m, C_5H_4), 4.45 (2H, t, CH_2, J = 5.7 Hz), 7.28 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.42 (CH_3), 50.52, 63.89 ($2CH_2$), 69.23, 69.43 ($2C_5H_5$), 69.92 ($2C_{(cpC5H4)}$), 69.59 ($2C_{(cpC5H4)}$), 70.60 ($4C_{(cpC5H4)}$), 79.49, 79.69 ($2C_{ipso}Fc$), 137.00 (CH=), 126.29, 167.70 (2C). $C_{26}H_{26}Fe_2INO$. MS (El, 70 eV): *m/z* 127, 480 $[M]^+$.

2-(*Z*-1,2-diferrocenylvinyl)-3-ethyl-4,5-dihydrooxazol-3-ium iodide (3b)

Red powder, yield 0.5 g (32 %), m.p. 109–110 °C. IR (KBr): ν 469, 480, 727, 777, 814, 899, 1000, 1026, 1040, 1049, 1106, 1146, 1189, 1214, 1253, 1330, 1386, 1411, 1443, 1474, 1605, 1633, 1699, 1787, 2050, 2240, 2821, 2866, 2891,

2961, 3088, 3327 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, t, CH_3, J =7.2 Hz), 2.79 (2H, q, CH_2, J =7.2 Hz), 3.07 (2H, t, CH_2, J = 5.7 Hz), 4.05 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.22 (2H, m, C_5H_4), 4.24 (4H, m, C_5H_4), 4.41 (2H, t, CH_2, J = 5.7 Hz), 4. 45 (2H, m, C_5H_4), 7.29 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.47 (CH_3), 44.08, 48.30, 64.23 ($3CH_2$), 69.28, 69.47 ($2C_5H_5$), 67.96, 69.64, 70.60, 70.62 ($2C_5H_4$), 79.54, 79.72 ($2C_{ipso}$Fc), 137.06 (CH=), 126.45, 167.71 (2C). MS (El, 70 eV): *m/z* 127, 494 $[M]^+$.

2-(*Z*-1,2-diferrocenylvinyl)-3,4-dimethyl-4,5-dihydrooxazol-3-ium iodide (3c)

Red powder, yield 0.48 g (31 %), m.p. 84–85 °C. IR (KBr): ν 478, 641, 710, 732, 807, 833, 879, 992, 1028, 1038, 1104, 1180, 1245, 1291, 1322, 1341, 1371, 1445, 1475, 1596, 1637, 1707, 2880, 2920, 2956, 2970, 3108 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.23 (3H, d, CH_3, J = 6.6 Hz), 2.55 (3H, s, CH_3), 3.05 (1H, m, CH), 4.05 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.17 (1H, dd, CH_2, J = 6.9, 11.1 Hz), 4.22 (2H, m, C_5H_4), 4.27 (4H, m, C_5H_4), 4.31 (1H, dd, CH_2, J = 4.8, 11.1 Hz), 4.45 (1H, m, C_5H_4), 4.48 (1H, m, C_5H_4), 7.29 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.30, 34.06 ($2CH_3$), 54.01 (CH_2), 67.95 (CH), 69.29, 69.48 ($2C_5H_5$), 68.07, 69.68 ($4C_{(cpC5H4)}$) 70.51 ($2C_{(cpC5H4)}$), 70.66, 70.73 ($2C_{(cpC5H4)}$), 79.51, 79.76 ($2C_{ipso}$Fc), 137.07 (CH=), 126.50, 167.67 (2C). $C_{27}H_{28}Fe_2INO$. MS (El, 70 eV): *m/z* 127, 479, 495 $[M]^+$.

2-(*Z*-1,2-diferrocenylvinyl)-3,5-dimethyl-4,5-dihydrooxazol-3-ium iodide (3d)

Red powder, yield 0.51 g (33 %), m.p. 81–82 °C. IR (KBr): ν 478, 491, 649, 725, 811, 817, 832, 900, 972, 999, 1025, 1040, 1104, 1182, 1207, 1240, 1299, 1339, 1391, 1410, 1445, 1454, 1481, 1604, 1621, 1700, 2863, 2924, 2964, 2970, 3072, 3084 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.44 (3H, d, CH_3, J = 6.3 Hz), 2.54 (3H, s, CH_3), 2.82 (1H, dd, CH_2, J = 4.5, 12.6 Hz), 2.98 (1H, dd, CH_2, J = 7.5, 12.6 Hz), 4.06 (5H, s, C_5H_5), 4.07 (5H, s, C_5H_5), 4.20 (1H, m, C_5H_4), 4.24 (4H, m, C_5H_4), 4.28 (1H, m, C_5H_4), 4.46 (1H, m, C_5H_4), 4.50 (1H, m, C_5H_4), 5.27 (1H, m, CH), 7.27 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.40, 36.60 ($2CH_3$), 56.72 (CH_2), 67.89 (CH), 69.35, 69.51 ($2C_5H_5$), 70.48, 70.61, 70.64, 70.89 ($2C_5H_4$), 79.74, 79.85 ($2C_{ipso}$Fc), 136.61 (CH=), 126.85, 167.25 (2C). $C_{27}H_{28}Fe_2INO$. MS (El, 70 eV): *m/z* 127, 480, 495 $[M]^+$.

3,6-Diaza-(*E*-2,3-diferrocenyl)acryloyl-3-methylheptanol (4a)

Orange powder, yield 0.61 g (44 %), m.p. 98–99 °C. IR (KBr): ν 466, 619, 645, 745, 803, 814, 874, 1000, 1025, 1036, 1106, 1161, 1249, 1294, 1312, 1333, 1407, 1448, 1461, 1499, 1572, 1595, 1622, 1769, 2050, 2190, 2240, 2776, 2800, 2875, 2936, 3091, 3415 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.40 (3H, s, CH_3), 2.61 (1H, bs, OH), 2.68 (2H, t, CH_2, J = 5.1 Hz), 2.77 (2H, t, CH_2, J = 6.3 Hz), 3.20 (3H, s, CH_3), 3.66 (4H, m, $2CH_2$), 4.09 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.17 (3H, m, C_5H_4), 4.23 (4H, m, C_5H_4), 4.37 (1H, m, C_5H_4), 6.25 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.78, 44.80 ($2CH_3$), 42.26, 54.86, 58.76, 59.23 ($4CH_2$), 69.11, 69.20 ($2C_5H_5$), 68.13, 68.71, 69.21, 69.65 ($2C_5H_4$), 80.22 ($2C_{ipso}$Fc), 127.28 (CH=), 131.17 (C), 171.53 (C=O). Anal. Calcd. for $C_{29}H_{34}Fe_2N_2O_2$: C, 62.84; H, 6.18; N, 5.05. Found: C, 62.65; H, 6.21; N, 5.09. MS (El, 70 eV): *m/z* 554 $[M]^+$.

3,6-Diaza-(*E*-2,3-diferrocenyl)acryloyl-3-ethyloctanol (4b)

Orange powder, yield 0.63 g (43 %), m.p. 95–96 °C. IR (KBr): ν 465, 481, 743, 764, 806, 821, 900, 999, 1027, 1041, 1083, 1104, 1163, 1187, 1249, 1296, 1350, 1404, 1456, 1498, 1572, 1594, 1616, 2045, 2100, 2230, 2785, 2842, 2875, 2920, 2942, 3088, 3100, 3188, 3437 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.11 (3H, t, CH_3, J = 7.2 Hz), 1.27 (3H, t, CH_3, J = 6.9 Hz), 2.04 (1H, bs, OH), 2.63 (2H, t, CH_2, J = 6.9 Hz), 2.69 (4H, m, $2CH_2$, J = 6.9, 7.2 Hz), 2.74 (2H, t, CH_2, J = 6.9 Hz), 3.54 (2H, t, CH_2, J = 6.9 Hz), 3.65 (2H, t, CH_2, J = 6.9 Hz), 4.08 (5H, s, C_5H_5), 4.12 (5H, s, C_5H_5), 4.18 (4H, m, C_5H_4), 4.22 (4H, m, C_5H_4), 6.60 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.05, 14.40 ($2CH_3$), 42.64, 44.51,

48.12, 51.05, 55.53, 58.95 (6CH_2), 69.18, 69.40 (2C_5H_5), 68.25, 68.72, 69.43, 69.74 (2C_5H_4), 80.41, 81.59 (2C_{ipso}Fc), 126.76 (CH=), 132.14 (C), 171.78 (C=O). Anal. Calcd. for $C_{31}H_{38}Fe_2N_2O_2$: C, 63.93; H, 6.58; N, 4.81. Found: C, 63.79; H, 6.69; N, 4.73. MS (El, 70 eV): *m/z* 582 $[M]^+$.

3,6-Diaza-(*E*-2,3-diferrocenyl)acryloyl-2,3,5-trimethylheptanol (4c)

Orange powder, yield 0.65 g (45 %) m.p. 98–99 °C. IR (KBr): ν 461, 621, 647, 752, 803, 812, 876, 1001, 1026, 1035, 1105, 1161, 1253, 1300, 1315, 1338, 1409, 1444, 1460, 1504, 1578, 1598, 1629, 1756, 2045, 2188, 2242, 2781, 2823, 2867, 2946, 3087, 3435 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.38 (3H, d, CH_3, J = 6.3 Hz), 1.46 (3H, d, CH_3, J = 6.3 Hz), 2.43 (1H, bs, OH), 2.54 (3H, s, CH_3), 2.63 (1H, dd, CH_2, J = 6.6, 12.3 Hz), 2.73 (1H, dd, CH_2, J = 5.1, 11.4 Hz), 2.81 (1H, dd, CH_2, J = 7.2, 11.4 Hz), 2.93 (1H, dd, CH_2, J = 4.5, 12.3 Hz), 3.02 (3H, s, CH_3), 3.78 (2H, m, 2CH), 4.03 (5H, s, C_5H_5), 4.08 (5H, s, C_5H_5), 4.14 (3H, m, C_5H_4), 4.20 (4H, m, C_5H_4), 4.32 (1H, m, C_5H_4), 6.21 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.33, 22.68, 35.52, 39.01 (4CH_3), 41.22, 47.89 (2CH_2), 56.07, 59.73 (2CH), 69.24, 69.28 (2C_5H_5), 68.32, 68.64, 69.37, 69.64 (2C_5H_4), 80.13, 80.22 (2C_{ipso}Fc), 126.37 (CH=), 130.97 (C), 170.85 (C=O). Anal. Calcd. for $C_{31}H_{38}Fe_2N_2O_2$: C, 63.93; H, 6.58; N, 4.81. Found: C, 63.65; H, 6.31; N, 5.02. MS (El, 70 eV): *m/z* 582 $[M]^+$.

4,7-Diaza-(*E*-2,3-diferrocenyl)acryloyl-4,5-dimethyloctan-2-ol (4d)

Orange powder, yield 0.64 g (44 %), m.p. 98–99 °C. IR (KBr): ν 449, 598, 623, 635, 747, 801, 810, 870, 1003, 1027, 1041, 1101, 1165, 1243, 1295, 1325, 1342, 1423, 1454, 1466, 1497, 1578, 1600, 1629, 1751, 2048, 2191, 2244, 2772, 2769, 2877, 2930, 3091, 3422 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.41 (3H, d, CH_3, J = 6.0 Hz), 1.57 (3H, d, CH_3, J = 6.3 Hz), 1.76 (1H, bs, OH), 2.46 (3H, s, CH_3), 2.52 (1H, dd, CH_2, J = 3.6, 10.5 Hz), 2.64 (1H, dd, CH_2, J = 4.2, 11.7 Hz), 2.76 (1H, dd, CH_2, J = 6.3, 10.5 Hz), 3.15 (1H, dd, CH_2, J = 5.4, 11.7 Hz), 3.28 (3H, s, CH_3), 3.85 (2H, m, 2CH), 4.01 (5H, s, C_5H_5), 4.03 (5H, s, C_5H_5), 4.09 (3H, m, C_5H_4), 4.12 (4H, m, C_5H_4), 4.21 (1H, m, C_5H_4), 6.29 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.46, 23.28, 36.15, 39.18 (4CH_3), 45.31, 45.93 (2CH_2), 54.11, 58.64 (2CH), 69.13, 69.21 (2C_5H_5), 68.27, 68.71, 69.42, 69.59 (2C_5H_4), 80.11, 80.18 (2C_{ipso}Fc), 127.04 (CH=), 131.15 (C), 171.32 (C=O). Anal. Calcd. for $C_{31}H_{38}Fe_2N_2O_2$: C, 63.93; H, 6.58; N, 4.81. Found: C, 63.79; H, 6.73; N, 4.67. MS (El, 70 eV): *m/z* 582 $[M]^+$.

Multicomponent reactions of 2,3-diferrocenylcyclopropenone 1 with 1,2-aminoalcohols 2a–c,e,f in the presence of triethyloxonium tetrafluoroborate, morpholine or piperidine, and alkyl iodides

To the solution of 2,3-diferrocenilcyclopropenone **1** (2.5 mmol) in $CHCl_3$, or CH_3CN (50 mL) were added with stirring triethyloxonium tetrafluoroborate (3.0 mL, 1.0 M solution in dichloromethane), 1,2-aminoalcohols **2a–c,e,f**, (2.5 mmol), morpholine or piperidine (2.0 mL), and methyl or ethyl iodides (1.0 mL). After stirring for 3–12 h at 70–80 °C, the volatiles were removed *in vacuo*; chromatography of the residue on Al_2O_3 (hexane-ether, 3 : 1), yielded compounds **3a–c** (7–12 %), **3e,f** (10–11 %), **9a,b,e,f** and **10a,c** (Table 1).

2-(*Z*-1,2-diferrocenylvinyl)-3-methyl-4-phenyl-4,5-dihydrooxazol-3-ium iodide (3e)

Red powder, yield 0.17 g (10 %), m.p. 148–150 °C. IR (KBr): ν 483, 544, 700, 757, 816, 898, 1000, 1015, 1032, 1051, 1106,1174, 1185, 1209, 1243, 1257, 1282, 1332, 1378, 1388, 1436, 1450, 1479, 1491, 1605, 1631, 1712, 2786, 2835, 2890, 2940, 2974, 3093, 3368 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.43 (3H, s, CH_3), 4.03 (5H, s, C_5H_5), 4.05 (5H, s, C_5H_5), 4.21 (1H, dd, CH, J = 5.1, 7.5 Hz), 4.19–4.24 (6H, m,C_5H_4), 4.35 (1H, dd, CH_2, J = 7.5, 10.8 Hz), 4.40 (1H, m, C_5H_4), 4.44 (1H, m, C_5H_4), 4.47 (1H, dd, CH_2, J = 5.1, 10.8 Hz), 7.20 (1H, s, CH=), 7.36–7.49 (5H, m, C_6H_5). ^{13}C

NMR (75 MHz, $CDCl_3$): δ 34.67 (CH_3), 64.14 (CH_2), 70.19 (CH), 69.19, 69.58 ($2C_5H_5$), 68.07, 68.07, 68.52 ($6C_{(cpC5H4)}$), 69.78, 70.68 ($2C_{(cpC5H4)}$), 79.52, 79.5 ($2C_{ipso}Fc$), 137.33 (CH=), 127.78, 127.99, 128.76 (C_6H_5), 126.22, 140.14, 167.44 (3C). $C_{32}H_{30}Fe_2INO$. MS (El, 70 eV): *m/z* 541, 556 $[M]^+$.

2-(*Z*-2,3-diferrocenylvinyl)-3-methyl-5-phenyl-4,5-dihydrooxazol-3-ium iodide (3f)

Red powder, yield 0.19 g (11 %), m.p. 128–129 °C. IR (KBr): ν 480, 593, 757, 812, 886, 1006, 1026, 1045, 1053, 1104, 1146, 1192, 1215, 1265, 1334, 1389, 1419, 1454, 1487, 1608, 1629, 1683, 1775, 2231, 2834, 2879, 2932, 3090, 3328 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.56 (3H, s, CH_3), 3.05 (1H, dd, CH_2, $J = 4.5, 13.5$ Hz), 3.29 (1H, dd, CH_2, $J = 6.0, 13.5$ Hz), 3.95 (5H, s, C_5H_5), 4.05 (5H, s, C_5H_5), 4.16 (1H, m, C_5H_4), 4.24 (4H, m, C_5H_4), 4.32 (1H, m, C_5H_4), 4.43 (1H, m, C_5H_4), 4.51 (1H, m, C_5H_4), 6.12 (1H, dd, CH, $J = 4.5, 6.0$ Hz), 7.39 (1H, s, CH=), 7.32–7.54 (5H, m, C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.49 (CH_3), 51.93 (CH_2), 69.29, 69.48 ($2C_5H_5$), 67.98, 69.65, 70.58, 70.81 ($2C_5H_4$), 70.66 (CH), 79.87, 80.07 ($2C_{ipso}Fc$), 126.67, 128.33, 128.64 (C_6H_5), 140.20 (CH=), 137.09, 157.37, 167.64 (3C). $C_{32}H_{30}Fe_2INO$. MS (El, 70 eV): *m/z* 127, 541, 556 $[M]^+$.

(*E*)-*N*-methyl-*N*-(2-morpholinoethyl)-2,3-diferrocenyl-acrylamide (9a)

Orange powder, yield 1.06 g (75 %), m.p. 125–126 °C. IR (KBr): ν 477, 645, 727, 766, 815, 854, 912, 923, 1001, 1037, 1069, 1105, 1116, 1144, 1257, 1298, 1356, 1397, 1455, 1487, 1629, 1680, 1709, 2807, 2852, 2918, 2953, 3092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.60 (4H, m, CH_2), 2.70 (2H, t, CH_2, $J = 6.0$ Hz), 3.20 (3H, s, CH_3), 3.69 (2H, t, CH_2, $J = 6.0$ Hz), 3.77 (4H, m, $2CH_2$), 4.09 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.19 (2H, m, C_5H_4), 4.25 (4H, m, C_5H_4), 4.44 (2H, m, C_5H_4), 6.26 (1H, s, CH=). ^{13}C NMR (75 MHz, C_6D_6): δ 37.29 (CH_3), 43.14, 56.31 ($2CH_2$), 54.05 ($2CH_2$), 67.14 ($2CH_2$), 69.48, 69.83 ($2C_5H_5$), 68.50, 69.02, 69.71, 70.00 ($2C_5H_4$), 81.09, 81.14 ($2C_{ipso}Fc$), 126.35 (CH=), 132.74 (C), 171.03 (C=O). Anal. Calcd. for $C_{30}H_{34}Fe_2N_2O_2$: C, 63.64; H, 6.05; N, 4.94. Found: C, 63.42; H, 6.14; N, 5.07. MS (El, 70 eV): *m/z* 566 $[M]^+$.

(*E*)-*N*-ethyl-*N*-(2-morpholinoethyl)-2,3-diferrocenyl-acrylamide (9b)

Orange powder, yield 1.03 g (71 %), m.p. 103–105 °C. IR (KBr): ν 471, 618, 651, 766, 788, 805, 822, 844, 852, 923, 972, 1006, 1024, 1086, 1114, 1141, 1243, 1269, 1289, 1343, 1355, 1422, 1437, 1457, 1468, 1564, 1618, 1719, 2754, 2800, 2818, 2947, 2957, 2977, 3094 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 0.99 (3H, t, CH_3, $J = 7.5$ Hz), 2.20 (2H, m, CH_2), 2.33 (4H, m, $2CH_2$), 2.52 (2H, m, CH_2), 3.55 (2H, m, CH_2), 3.66 (4H, m, $2CH_2$), 3.96 (5H, s, C_5H_5), 4.24 (5H, s, C_5H_5), 4.01 (3H, m, C_5H_4), 4.09 (2H, m, C_5H_4), 4.25 (3H, m, C_5H_4), 6.42 (1H, s, CH=). ^{13}C NMR (75 MHz, C_6D_6): δ 13.76 (CH_3), 39.68, 43.33 ($2CH_2$), 53.96, 54.50 ($2CH_2$), 56.43 (CH_2), 66.84, 67.30 ($2CH_2$), 69.18, 69.72 ($2C_5H_5$), 68.21, 68.59, 69.23, 79.74 ($2C_5H_4$), 80.63, 81.35 ($2C_{ipso}Fc$), 125.13 (CH=), 133.67 (C), 170.0 (C=O). Anal. Calcd. for $C_{31}H_{36}Fe_2N_2O_2$: C, 64.16; H, 6.15; N, 4.82. Found: C, 63.93; H, 6.13; N, 4.63. MS (El, 70 eV): *m/z* 580 $[M]^+$.

(*E*)-*N*-methyl-*N*-(2-morpholino-1-phenylethyl)-2,3-diferrocenyl-acrylamide (9e)

Orange powder, yield 1.13 g (70 %), m.p. 115–117 °C. IR (KBr): ν 483, 697, 707, 735, 815, 879, 911, 998, 1029, 1035, 1048, 1105, 1185, 1245, 1268, 1308, 1356, 1386, 1410, 1454, 1480, 1497, 1602, 1636, 1711, 2755, 2854, 2893, 2938, 2964, 3029, 3106 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.57 (2H, m, CH_2), 2.64 (2H, m, CH_2), 2.96 (3H, s, CH_3), 2.90 (2H, m, CH_2), 3.77 (4H, m, $2CH_2$), 3.94 (2H, t, CH_2, $J = 4.5$ Hz), 4.07 (5H, s, C_5H_5), 4.13 (5H, s, C_5H_5), 4.16 (3H, m, C_5H_4), 4.18 (3H, m, C_5H_4), 4.22 (1H, m, C_5H_4), 4.24 (1H, m, C_5H_4), 4.42 (1H, t, CH, $J = 4.5$ Hz), 7.43 (1H, s, CH=), 7.40–7.49 (5H, m, C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.99 (CH_3), 50.95 ($2CH_2$), 67.29 ($2CH_2$), 68.18 (CH_2), 69.15, 69.29 ($2C_5H_5$), 67.79, 68.75, 69.32, 69.60 ($2C_5H_4$), 69.66 (CH), 80.26, 80.30 ($2C_{ipso}Fc$), 127.28 (CH=), 128.00, 128.30,

129.26 (C_6H_5), 131.07, 137.04 (2C), 171.49 (C=O). Anal. Calcd. for $C_{32}H_{38}Fe_2N_2O_2$: C, 67.31; H, 5.96; N, 4.36. Found: C, 67.18; H, 5.71; N, 4.70. MS (El, 70 eV): *m/z* 642 $[M]^+$.

(E)-*N*-methyl-*N*-(2-morpholino-2-phenylethyl)-2,3-diferrocenyl-acrylamide (9f)

Orange powder, yield 1.17 g (72 %), m.p. 102–103 °C. IR (KBr): ν 474, 631, 703, 785, 810, 878, 911, 999, 1019, 1036, 1047, 1104, 1116, 1135, 1250, 1301, 1346, 1384, 1397, 1459, 1478, 1610, 1723, 2755, 2818, 2853, 2955, 2994, 3090 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.49 (2H, m, CH_2), 2.75 (1H, dd, CH_2, *J* = 4.5, 12.3 Hz), 2.87 (3H, s, CH_3), 2.90 (2H, m, CH_2), 3.16 (1H, t, CH_2, *J* = 12.3 Hz), 3.82 (4H, m, $2CH_2$), 4.06 (10H, s, $2C_5H_5$), 4.08 (3H, m, C_5H_4), 4.17 (1H, m, C_5H_4), 4.19 (1H, m, C_5H_4), 4.23 (1H, m, C_5H_4), 4.27 (1H, m, C_5H_4), 4.33 (1H, m, C_5H_4), 6.28(1H, dd, CH, *J* = 4.5, 12.3 Hz), 7.37 (1H, s, CH=), 7.24–7.47 (5H, m, C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.11 (CH_3), 50.21 (CH_2), 53.99 ($2CH_2$), 54.05 ($2CH_2$), 67.79 ($2CH_2$), 69.11, 69.75 ($2C_5H_5$), 68.35, 68.68, 69.41, 69.43 ($2C_5H_4$), 69.93 (CH), 80.79, 80.84 ($2C_{ipso}$Fc), 128.59 (CH=), 127.76, 128.57, 130.15 (C_6H_5), 138.38, 147.45 (2C), 171.96 (C=O). Anal. Calcd. for $C_{32}H_{38}Fe_2N_2O_2$: C, 67.31; H, 5.96; N, 4.36. Found: C, 67.49; H, 5.78; N, 4.35. MS (El, 70 eV): *m/z* 642 $[M]^+$.

(*E*)-*N*-methyl-*N*-(2-piperidinoethyl)-2,3-diferrocenyl-acrylamide (10a)

Orange oil, yield 0.98 g (70 %). IR (KBr): ν 479, 641, 709, 735, 807, 834, 879, 901, 992, 1001, 1028, 1038, 1104, 1180, 1245, 1290, 1340, 1354, 1387, 1410, 1446, 1474, 1597, 1638, 1691, 2879, 2920, 2956, 2970, 3094 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.62 (6H, m, $3CH_2$), 2.51 (4H, m, $2CH_2$), 2.62 (2H, td, CH_2, *J* = 1.2, 6.3 Hz), 2.89 (3H, s, CH_3), 3.42 (1H, m, CH_2, *J* = 6.3 Hz), 3.86 (1H, m, CH_2, *J* = 6.3 Hz), 4.16 (5H, s, C_5H_5), 4.23 (5H, s, C_5H_5), 4.26 (2H, m, C_5H_4), 4.28 (2H, m, C_5H_4), 4.31 (1H, m, C_5H_4), 4.34 (1H, m, C_5H_4), 4.59 (1H, m, C_5H_4), 4.35 (1H, m, C_5H_4), 6.35 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.51 (CH_2), 26.04 ($2CH_2$), 36.56 (CH_2), 43.86 (CH_3), 54.79 ($2CH_2$), 56.07 (CH_2), 69.30, 69.97 ($2C_5H_5$), 68.82, 69.14, 69.44, 70.20 ($2C_5H_4$), 69.93 (CH), 79.93, 81.06 ($2C_{ipso}$Fc), 120.94 (CH=), 131.35 (C), 171.52 (C=O). Anal. Calcd. for $C_{31}H_{36}Fe_2N_2O$: C, 65.97; H, 6.45; N, 4.96. Found: C, 65.68; H, 6.18; N, 4.65. MS (El, 70 eV): *m/z* 564.

(*E*)-*N*-methyl-*N*-(1-methyl-2-piperidinoethyl)-2,3-diferrocenyl-acrylamide (10c)

Orange oil, yield 1.05 g (73 %). IR (KBr): ν 482, 659, 718, 7305, 814, 892, 903, 927, 999, 1027, 1039, 1105, 1179, 1194, 1242, 1253, 1306, 1357, 1389, 1409, 1448, 1477, 1600, 1630, 1680, 2870, 2894, 2935, 3087 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$):): δ 1.52 (3H, d, CH_3, *J* = 6.3 Hz), 1.59 (6H, m, $3CH_2$), 2.47 (4H, m, $2CH_2$), 2.72 (3H, s, CH_3), 3.54 (1H, dd, CH_2, *J* = 7.5, 13.52 Hz), 4.12 (1H, m, CH_2, *J* = 6.0, 13.2 Hz), 4.04 (5H, s, C_5H_5), 4.06 (5H, s, C_5H_5), 4.14 (1H, m, C_5H_4), 4.17 (4H, m, C_5H_4), 4.21 (1H, m, CH), 4.26 (1H, m, C_5H_4), 4.44 (1H, m, C_5H_4), 4.52 (1H, m, C_5H_4), 4.80 (1H, m, CH), 6.38 (1H, s, CH=). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.91, 25.30 ($2CH_3$), 25.93 ($3CH_2$), 53.14 ($2CH_2$), 61.65 (CH), 67.58 (CH_2), 69.29, 69.35 ($2C_5H_5$), 70.14, 70.50, 70.59, 70.85 ($2C_5H_4$), 75.60 (CH), 80.66, 82.79 ($2C_{ipso}$Fc), 123.78 (CH=), 124.01 (C), 178.15 (C=O). Anal. Calcd. for $C_{32}H_{38}Fe_2N_2O$: C, 66.47; H, 6.62; N, 4.84. Found: C, 66.54; H, 6.71; N, 4.72. MS (El, 70 eV): *m/z* 578 $[M]^+$.

Determination of the crystal structure

Suitable X-ray quality crystals of **4a**, **9b**, **9e** and **9f**, were grown by slow evaporation of a saturated dichloromethane solution at room temperature for three days. Data were obtained on an Oxford Difraction Gemini A diffractometer with a CCD area detector, and the CrystAlisPro and CrysAlis RED software packages were used for data collection and data integration [47]. The structures were solved using SHELXS-97 [48] and refined by full-matrix least-squares on F^2 with SHELXL-97 [49]. Weighted *R* factors, R_w, and all goodness-

of-fit indicators, S, were based F^2. The observed criterion of ($F^2 > 2\sigma F^2$) was used only for calculating the R factors. All non-hydrogen atoms were refined with anisotropic thermal parameters in the final cycles on refinement. Hydrogen atoms were placed in idealized positions, with C–H distances of 0.93 and 0.98 Å for aromatic and satured carbon atoms, respectively. The isotropic thermal parameters of the hydrogen atoms were assigned the values of $U_{iso} = 1.2$ times the thermal parameters of the parent non-hydrogen atom. The unit cell parameters and the X-ray diffraction intensities were recorded on a Gemini (detector AtlasCCD, Cryojet N_2) diffractometer.

Crystallographic data for 4a

Crystals of $C_{29}H_{34}Fe_2N_2O_2$ ($M = 554.28$), are orthorhombic, space group $Pca2_1$, at 130(2) K, $a = 21.8387(11)$, $b = 6.0311(3)$, $c = 19.0490(8)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2509.0(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.467$ Mg/cm^3, $\lambda(MoK\alpha) = 0.71073$ Å, $F(000) = 1160$, $\mu = 1.186$ mm^{-1}, index ranges $-30 \le h \le 27$, $-8 \le k \le 8$, $-24 \le l \le 26$, scan range $3.505 \le \theta \le 29.551°$, 6287 independent reflections, $R_{int} = 0.0594$, 26278 total reflections, 321 refinable parameters, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0387$, $wR_2 = 0.0681$; R indices (all data): $R_1 = 0.0560$, $wR_2 = 0.0763$; goodness-of-fit on F^2 1.053, largest difference peak and hole 0.466/– 0.352 e Å^{-3}.

Crystallographic data for 9b

Crystals of $C_{31}H_{36}Fe_2N_2O_2$ ($M = 580.32$), are monoclinic, space group $P2_1/c$, at 130(2) K, $a = 19.5186(16)$, $b = 7.3492(5)$, $c = 19.7752(18)$ Å, $\alpha = 90°$, $\beta = 112.066(9)°$, $\gamma = 90°$, $V = 2628.9(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.466$ Mg/cm^3, $\lambda(MoK\alpha) = 0.71073$ Å, $F(000) = 1216$, $\mu = 1.186$ mm^{-1}, index ranges $-24 \le h \le 26$, $-10 \le k \le 7$, $-24 \le l \le 23$, scan range $3.466 \le \theta \le 29.579°$, 6245 independent reflections, $R_{int} = 0.0498$, 15151 total reflections, 335 refinable parameters, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0487$, $wR_2 = 0.0881$; R indices (all data): $R_1 = 0.0869$, $wR_2 = 0.1077$; goodness-of-fit on F^2 1.076, largest difference peak and hole 0.459/– 0.576 e Å^{-3}.

Crystallographic data for 9e

Crystals of $C_{36}H_{38}Fe_2N_2O_2$ ($M = 642.38$), are orthorhombic, space group $P2_12_12_1$ at 130(2) K, $a = 22.8618(4)$, $b = 11.6301(2)$, $c = 11.2488(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2990.89(9)$ Å^3, $Z = 4$, $d_{calcd} = 1.427$ Mg/cm^3, $\lambda(CuK\alpha) = 0.54184$ Å, $F(000) = 1344$, $\mu = 8.053$ mm^{-1}, scan range $3.867 \le \theta \le 73.451°$, 5931 independent reflections, $R_{int} = 0.0535$, 29921 total reflections, 335 refinable parameters, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0338$, $wR_2 = 0.0786$; R indices (all data): $R_1 = 0.0421$, $wR_2 = 0.0916$; goodness-of-fit on F^2 1.090, largest difference peak and hole 0.501/– 0.289 e Å^{-3}.

Crystallographic data for 9f

Crystals of $C_{36}H_{38}Fe_2N_2O_2$ ($M = 642.38$), are triclinic, space group $P\bar{1}$ at 130(2) K, $a = 10.416(5)$, $b = 12.7864(11)$, $c = 13.0952(12)$ Å, $\alpha = 112.568(8)°$, $\beta = 100.441(5)°$, $\gamma = 104.393(5)°$, $V = 1483.5(39)$ Å^3, $Z = 2$, $d_{calcd} = 1.438$ Mg/cm^3, $\lambda(MoK\alpha) = 0.71073$ Å, $F(000) = 672$, $\mu = 1.014$ mm^{-1}, scan range $3.492 \le \theta \le 29.582°$, 7146 independent reflections, $R_{int} = 0.0417$, 18941 total reflections, 335 refinable parameters, final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0568$, $wR_2 = 0.1244$; R indices (all data): $R_1 = 0.0809$, $wR_2 = 0.1415$; goodness-of-fit on F^2 1.064, largest difference peak and hole 0.782/– 0.838 e Å^{-3}.

CCDC 1474954 (for **4a**), CCDC 1474953 (for **9b**), CCDC 1499096 (for **9e**) and CCDC 1499097 (for **9f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

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