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Electrophilic Substitutions on some Ferrocenylheteroarenes

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Abstract: Friedel-Crafts acetylation, Vilsmeier-Haack formylation and BuLi metallation followed by DMF quenching of 2-ferrocenylthiophene, 2-ferrocenyl-3-phenylthiophene, 2-ferrocenyl-5-phenylthiophene, 2-ferrocenyl-1-methylpyrrole and 2-ferrocenyl-1-methyl-3-phenylpyrrole have been studied. The ferrocene behaved as a strong electron donor and electrophilic substitution took place at the heteroarene ring, the only exception being the Friedel-Crafts acetylation of 2-ferrocenyl-1-methylpyrrole. The course of formylation of 2-ferrocenyl-5-phenylthiophene was dependent on the applied method. Vilsmeier-Haack formylation gave 3-formyl-, and BuLi/DMF gave 4-formyl derivative. The product of 2-ferrocenylthiophene dimerization was isolated as the side product of its Friedel-Crafts acetylation.

INTRODUCTION

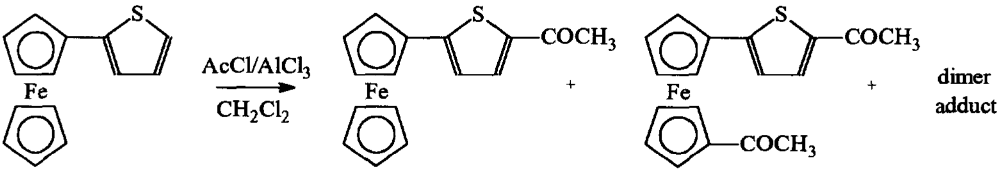
The reactivity of ferrocene, thiophene and furan and some derivatives having ferrocene and heteroarene connected by the bridge have been studied several years ago. The competitive experiments proved[1] that ferrocene is more reactive than thiophene and approximately as reactive as furan (Ferrocene is more than 10^6 times more reactive than benzene towards to Friedel-Crafts acetylation[2]). In the case of ketones Fc-CO-Ar, the Friedel-Crafts acetylation took place only at the ferrocene moiety[3]. When the methylene bridge was inserted between the ferrocene and arene (Fc-CH_2-Ar), the ferrocene moiety was more reactive than benzene, but less reactive than thiophene and furan towards to Friedel-Crafts acetylation[3,4]. In the case of stilbene analogues (Fc-CH=CH-Ar) the Friedel-Crafts acetylation took place at the double bond when the aryl was phenyl [3,5], but at the heteroarene when Ar was 2-thienyl or 2-furyl[3]. In the case of chalcone analogues the course of Friedel-Crafts acetylation was very dependent on their structure. In the case of chalcones Fc-CH=CH-CO-Ar the substitution took place predominantly at the unsubstituted cyclopentadienyl ring of ferrocene and at the double bond (Ar=phenyl, 2-furyl, 2-thienyl)[1,6]. When Ar=2-(1-methylpyrrolyl) the main products were those of acetylation at the double bond and at pyrrole moiety[7]. In the case of the chalcones Fc-CO-CH=CH-Ar the substitution took place at the ferrocene moiety if Ar=phenyl, but at the heteroarene moiety in all other cases. The reactivity of phenylferrocene was studied by Rosenblum[8] who found that Friedel-Crafts acetylation with the Perrier complex took place mainly at the ferrocene moiety, but some product of the benzene acetylation was isolated too. We have studied[9] Friedel-Crafts acetylation (Ac_2O/H_3PO_4) as well as Vilsmeier-Haack formylation of several substituted phenylferrocenes and found that the mixture of 1,1′-, 1,2- and 1,3- monoacetylated phenylferrocenes is formed. The substitution in 1′-position is dominant. Only in the case of 3-methoxyphenylferrocene substitution took place at the 4-position of the benzene ring exclusively.

The main goal of this work was to study electrophilic substitution on ferrocenylheteroarenes and our second aim was to find out if the Vilsmeier-Haack formylation (method A), and BuLi metallation followed with DMF quenching (method B) would result in the same products.

RESULTS

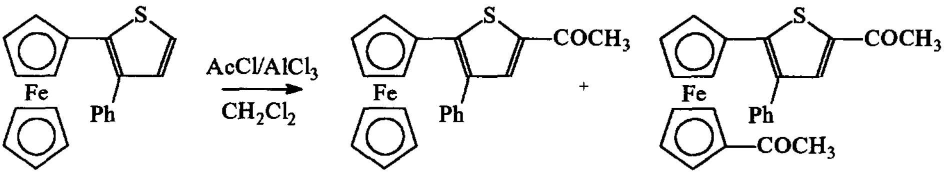
The original aim of our work was study electrophilic substitutions not only on the 2-ferrocenylthiophene and 2-ferrocenyl-1-methylpyrrole derivatives but also on the 2-ferrocenylfurane derivatives. All these derivatives have been prepared[10], but 2-ferrocenylfuran derivatives proved to be very unstable and therefore were omitted from this study. For the sake of comparison all Friedel-Crafts acetylations of ferrocenylheteroarenes have been carried out under the same conditions. The same was valid for Vilsmeier-Haack formylations and BuLi/DMF formylations, respectively.

The results of Friedel-Crafts acetylations of heteroarylferrocenes are depicted on the schemes 1- 4.



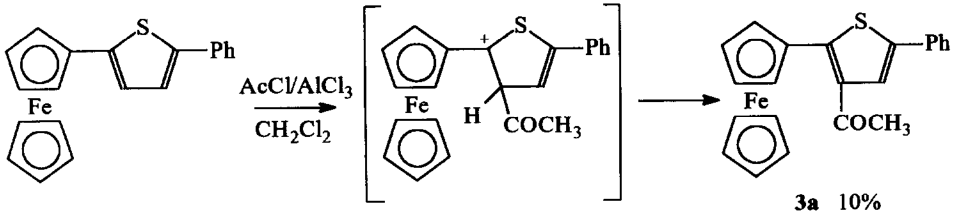
1a 21% **1b** 6% **A** 24%

Scheme n.1



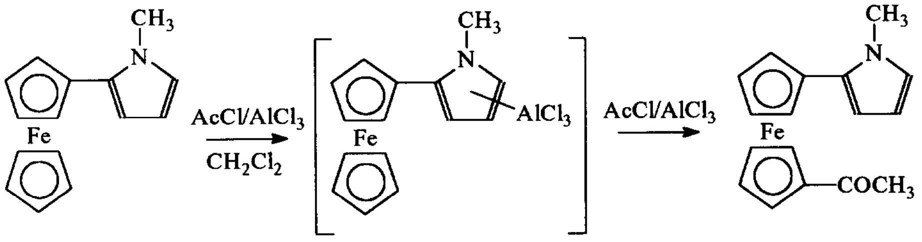
2a 14% **2b** 4%

Scheme n.2



3a 10%

Scheme n.3



Scheme n.4

4a 8%

From the results given in the Schemes 1-3 it follows that in all 2-ferrocenylthiophenes, the thiophene ring acetylation took place preferentially, as we can assume that diacetylated products (**1b**, **2b**) were formed via the monoacetylated products. No green colour of the reaction mixture, that would indicate the oxidation of ferrocene to ferricinium cation, was observed at acetylation. The structure elucidation of the products was straightforward from their ^{1}H NMR spectra. The only problem was to prove the structure of **3a**. If two possible intermediate σ-complexes are compared, the one given on the Scheme 3 should be more stable as it can be directly stabilised by the ferrocenyl group. The extraordinary strong stabilising effect of ferrocene on the α-carbenium ion is well documented[11,12]. Our assumption was proved indirectly by the NOE experiments done on formylderivative (see below).

It is of interest to note that the acetylation of 2-ferrocenylthiophene gave a by-product with R_F value very close to that of the starting material. Crystallisation from petroleum ether-benzene afforded a yellow substance with m. p. 135-137 °C. The inspection of ^{1}H NMR spectra and MS of this material revealed that it was a product of dimerization of 2-ferrocenylthiophene. The simplified picture of its MS is given on Chart 1. As it follows from Chart 1, the main process of degradation of the mother ion is aromatization of the thiophene moiety, but the product of retro-Diels-Alder reaction was observed in MS .

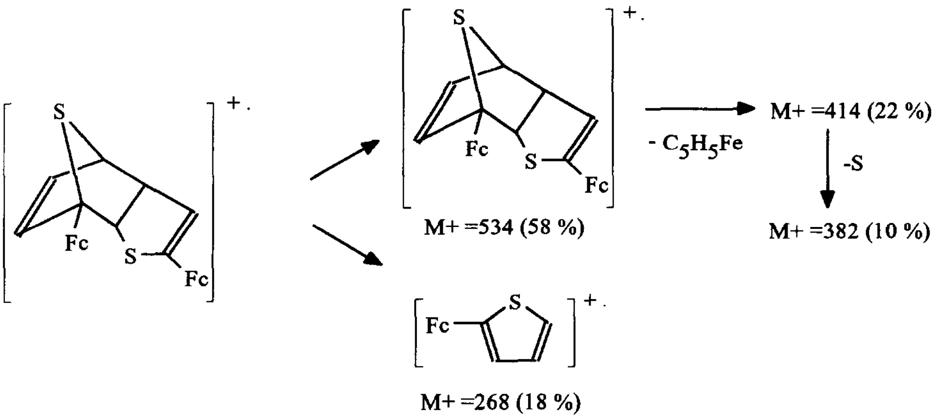
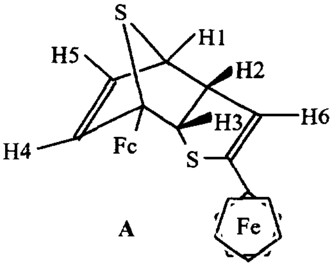


Chart 1

If we assume that the dimer A was formed via Diels-Alder reaction then pairs (endo, exo) of four regioisomers could be formed. ^{1}H NMR spectra (250 MHz) of the crude dimer as well as crystalline material were measured. The spectrum of the crude material revealed that it was a mixture of isomers, but the spectrum of crystalline material proved that it was a pure single isomer. The relative configuration given on the Chart 2 follows from the chemical shifts and multiplicity of the ^{1}H NMR signals. The attribution of the signals follows:



H2	3.726	(dd, $^3J_{2,3}$=11.1Hz, $^3J_{2,1}$=8.7 Hz)
H3	3.327	(dd, $^3J_{2,3}$=11.1 Hz, $^4J_{3,1}$=6.2 Hz)
H4	6.894	(d, $^3J_{4,5}$=3.6 Hz)
H5	6.697	(d, $^3J_{4,5}$=3.6 Hz)
H6	5.750	(d, $^4J_{6,1}$=2.9 Hz)
Hα	4.518	(t, 2H)
Hβ	4.242	(t, 2H)
HCp	4.096	(s, 5H)
HFc	4.27	(m,7H),4.45(m,1H),4.55(m,2H)

Chart 2

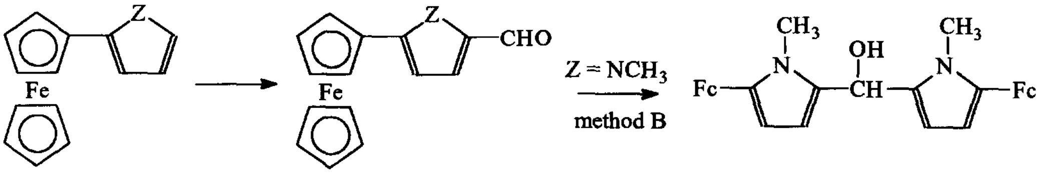
Because the chemical shift of the H1 proton was not possible to ascribe directly from 1D spectrum, a COSY experiment has been made which proved that the signal of H1 proton is covered by the signal of a ferrocenyl proton. (All ferrocenyl protons bonded to the chiral bridgehead carbon atom are not equivalent.) The COSY spectrum unanimously proved the interaction of H1 proton with protons H2, H3 and H6.

The endo configuration of the fused thiophene rings follows from the observed coupling constants. The great vicinal interaction between H1 and H2 (8.7 Hz) proved their cis configuration. Unusually great value of long-range interaction between H1 and H6 (6.2 Hz) proved that bonds between these protons have form which is possible only in the endo configuration. The observed long-range interaction between H1 and H6 ($^4J_{1,6}$ =2.9 Hz) excludes the exo configuration as well as the assumption of the structure having S atoms closer to each other (S atom bonded to the C2) as in that case a much smaller (if any) ^5J coupling constant should be observed.

This is to our best knowledge the first example of the dimerization of the thiophene derivative under such mild conditions (0-30 °C). The possibility of the Diels-Alder addition of 2-ferrocenylthiophene is therefore being studied more closely in our laboratory.

The result of the acetylation of 2-ferrocenyl-1-methylpyrrole is seemingly surprising as pyrrole is usually more reactive than ferrocene. We assume that acetylation of the ferrocene moiety was caused by deactivation of the pyrrole by complexation with $AlCl_3$. The low yield of the acetylated product can be caused by the same reason. Similar deactivation (blocking) of the pyrrole by $SnCl_4$ was described [13,14].

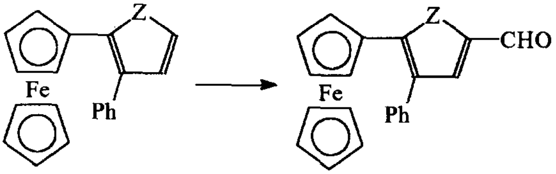
The results of formylation of heteroarylferrocenes are given in the Schemes 5-7. Method A is the typical Vilsmeier-Haack formylation (N-methylformanilide/ $POCl_3$), method B consists of BuLi metallation and DMF quenching.



6b 10%

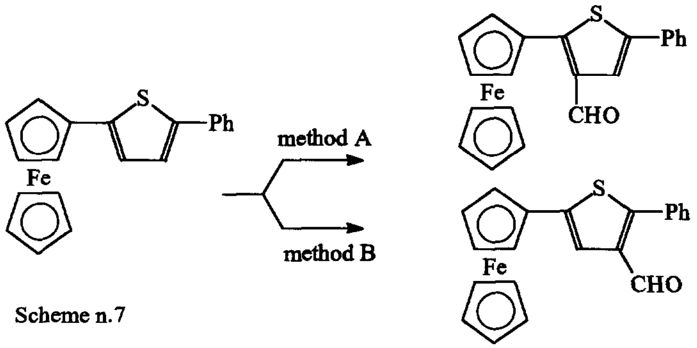
Z = S	method A	**5**	23 %
	method B	**5**	54 %
Z = NCH_3	method A	**6a**	18%

Scheme n.5



Z = S	method A	**7**	19%
	method B	**7**	46%
Z = NCH_3	method A	**8**	14%
	method B	**8**	9%

Scheme n.6



9a 11%

9b 9%

Scheme n.7

Formylation of 2-ferrocenylthiophene as well as 2-ferrocenyl-1-methylpyrrole derivatives under the conditions used at Vilsmeier-Haack formylation of ferrocene resulted in low yields of aldehydes; starting ferrocenylheteroarenes were recovered. No optimisation of the experiments was carried out. Applying the conditions used at classical Vilsmeier-Haack formylation would most probably give a complicated mixture of products. Substitution took place at the same positions as the Friedel-Crafts acetylation of the same substrate. Structure elucidation of the products caused no problems. Our assumption that formylation of 2-ferrocenyl-5-phenylthiophene took place on the position 3- is based on the following.

On the ^{1}H NMR spectra of the aldehyde isolated from the Vilsmeier-Haack reaction the chemical shift of -CHO proton was found very downfield, at 10.137 ppm, which is caused by the ring-current effect of cyclopentadienyl ring of ferrocene. The -CHO proton is close enough to display a NOE enhancement on the Hα of Cp ring and H,H homonuclear 5 % NOE enhancement of these protons was observed. This could not be possible if the -CHO was bonded to the position 4 of the thiophene ring. On the other hand the -CHO chemical shift of the aldehyde isolated from BuLi metallation/DMF quenching procedure was found at 9.83 ppm and no NOE enhancement of the Cp ring protons was observed in this case.

Metallation of ferrocenylthiophenes went smoothly using the arene-BuLi ratio 1:2 at -65 °C. Quenching of the lithioderivative with 4 molar excess of DMF yielded the same aldehydes as the Vilsmeier-Haack formylation. The exception was the reaction product from 2-ferrocenyl-5-phenylthiophene. In this case the isomeric 4-formyl- derivative was isolated. That means that Vilsmeier-Haack formylation as well as Friedel-Crafts acetylation is governed by the stability of the σ-complex, which is stabilised by the adjacent ferrocenyl group. Metallation, on the other hand, is governed by the hydrogen acidity, and hydrogen adjacent to phenyl group should be more acidic than that adjacent to ferrocenyl group.

Metallation of 2-ferrocenyl-1-methylpyrrole derivatives did not work under the conditions given for thiophene derivatives. To get positive results the BuLi-arene ratio had to be raised to 1:4 and 8 molar excess of DMF was used for the quenching. In spite of that only poor yields of the aldehyde were isolated and in one case (Scheme 5) we did not succeed in isolation of aldehyde, and the product of the subsequent addition of the lithio-intermediate to the aldehyde was isolated instead.

EXPERIMENTAL

Synthesis of 2-ferrocenyl-5-phenylthiophene was carried out according to[15], all other heteroaryl-ferrocenes were prepared according to[10]. All experiments were carried out in carefully purified solvent in dry N_2 atmosphere.

^1H NMR spectra were measured in $CDCl_3$ solution on Tesla BS 587 (80 MHz) or Bruker (250 MHz) instruments using tetramethylsilane as an internal standard. The ^1H NMR spectra of the dimer A, as well as 2-ferrocenylthiophenealdehydes were measured on Varian VXR-300, working frequency 300 MHz at the same conditions. The COSY experiment was performed using the standard Varian supplied pulse sequence. Data were acquired with 256 increments. The sweep width was 2100 Hz, 1024 data points and relaxation delay was 4s.

A general procedure for Friedel-Crafts acetylation of ferrocenylheteroarenes.

Acetyl chloride (0.7 mmol) was added dropwise to a stirred solution of 0.7 mmol of the appropriate ferrocenylheteroarene (0.7 mmol) in 5 ml of dry dichloromethane cooled to 0 °C. Aluminium chloride (0.75 mmol) was added to the stirred reaction mixture during 0.5 hour. Reaction mixture was stirred for another 0.5 hour at 0 °C, and 5 hour at room temperature. Reaction mixture was poured into water and product was extracted into chloroform. Chloroform solution was washed with water and dried over anhydrous Na_2SO_4. The residue left after evaporation of the solvent was chromatographed on SiO_2 column, isohexane-ethyl acetate 20:1 solution was used as the eluent. The results are given in the order of elution.

Acetylation of 2-ferrocenylthiophene yielded 37 mg (20%) of the starting material, 90 mg (24%) of the dimer product A as yellow crystals, m.p. 135-137 °C (petroleum ether-benzene). Calcd. for $C_{28}H_{24}Fe_2S_2$: C, 62.70; H, 4.51; Fe, 20.82; Found: C, 61.70; H, 4.49; Fe, 18.08. ^1H NMR: δ 3.327 (dd, 1H, H3, $^3J_{2,3}$=11.1Hz, $^4J_{3,1}$=6.2Hz), 3.726 (dd, 1H, H2, $^3J_{2,3}$=11.1Hz, $^3J_{2,1}$=8.7Hz), 4.096 (s, 5H, Cp), 4.242 (t, 2H, Hβ'), 4.518 (t, 2H, Hα'), 4.27 (m, 7H, Fc), 4.45 (m, 1H, Fc), 4.55 (m, 2H, Fc, H1), 5.750 (d, 1H,H6, $^4J_{6,1}$=2.9Hz), 6.697 (d, 1H, H5, $^3J_{4,5}$=3.6Hz), 6.894 (d, 1H, $^3J_{4,5}$=3.6Hz). MS spectrum: m/z 536, m/z 414 (CpFe), m/z 268 (monomer). 45 mg (21%) of **1a** as red crystals, m. p. 148-151 °C (petroleum ether). Calcd. for $C_{16}H_{14}FeOS$: C, 61.95; H, 4.55; Found: C, 61.85; H, 4.75. ^1H NMR: δ 2.52 (s, 3H, $COCH_3$), 4.09 (s, 5H, Cp), 4.38 (bs, 2H, Hβ), 4.65 (bs, 2H, Hα), 7.00 (d, 1H, H4), 7.50 (d, 1H, H3). 15 mg (6 %) of **1b** as a red crystals, m. p. 116-118 °C (petroleum ether). Calcd. for $C_{18}H_{16}FeO_2S$: C, 61.38; H, 4.58; Found: C, 61.75; H, 5.17. ^1H NMR: δ 2.22 (s, 3H, Fc-$COCH_3$), 2.53 (s, 3H, Het-$COCH_3$), 4.39 (m, 4H, Hβ), 4.63 (m, 4H, Hα), 7.01 (d, 1H, H4), 7.53 (d, 1H, H3).

Acetylation of 2-ferrocenyl-3-phenylthiophene yielded 168 mg (70 %) of the starting material, 37 mg (14 %) of **2a** as red crystals, m. p. 125-127 °C (petroleum ether). Calcd. for $C_{22}H_{18}FeOS$: C, 68.40; H, 4.70; Found: C, 68.95; H, 4.94. ^1H NMR: δ 2.54 (s, 3H, $COCH_3$), 4.09 (s, 5H, Cp), 4.26 (bs, 4H, Hαβ), 7.34 (bs, 5H, Ph), 7.42 (bs, 1H, H3). 12 mg (4 %) of **2b** as a red oil. Calcd. for $C_{24}H_{20}FeO_2S$: C, 67.30; H,4.71; Found: C, 67.95; H, 5.12. ^1H NMR: δ 2.25 (s, 3H, Fc-$COCH_3$), 2.55 (s, 3H, Het-$COCH_3$), 4.28 (m, 4H, Hβ), 4.40 (bs, 2H, Hα), 4.65 (bs, 2H, Hα), 7.30 (m, 5H, Ph), 7.47 (s, 1H, H3).

Acetylation of 2-ferrocenyl-5-phenylthiophene yielded 100 mg (40 %) of the starting material, 27 mg (10 %) of **3** as a red oil. Calcd. for $C_{22}H_{18}FeOS$: C, 68.40; H, 4.70; Found: C, 69.31; H, 5.23. ^1H NMR: δ 2.30 (s, 3H, $COCH_3$), 4.27 (s, 5H, Cp), 4.37 (t, 2H, Hβ), 4.69 (t, 2H, Hα), 7.35 (m, 3H, Ph), 7.44 (s, 1H, H4), 7.55 (m, 2H, Ph).

Acetylation of 2-ferrocenyl-1-methylpyrrole yielded 90 mg (50 %) of the starting material, 17 mg (8 %) of **4** as a red oil. Calcd. for $C_{17}H_{17}FeNO$: C, 66.47; H, 5.58; Found: C, 67.25; H, 5.93. ^1H NMR: δ 2.19 (s, 3H, $COCH_3$), 4.21 (m, 4H, Hβ), 4.47 (bs, 2H, Hα), 4.73 (bs, 2H, Hα), 5.90-6.25 (m, 2H, H3,4), 6.55 (m, 1H, H5).

A general procedure of Vilsmeier-Haack formylation of ferrocenylheteroarenes (method A)

To the cooled (0 °C) N-methylformanilide (0.7 mmol) was added 0.7 mmol of $POCl_3$ with stirring and the mixture was stirred at 0 °C for 30 min. Heteroarylferrocene (0.7 mmol) in 5 ml of dry chloroform was added to the reaction mixture during 15 min. The mixture was stirred for 1 hour at 0 °C and for 20 hours at room temperature. The reaction mixture was then poured into 30 ml of 20 % solution of sodium acetate cooled to 0 °C, and the mixture was stirred for 2 hours. Organic material was extracted into chloroform, washed with water and dried over anhydrous Na_2SO_4. The residue left after evaporation of the solvent was chromatographed on SiO_2 column using isohexane-ethyl acetate 20:1 solution as an eluent.

Vilsmeier-Haack formylation of 2-ferrocenylthiophene yielded 75 mg (40 %) of the starting material, 47 mg (23 %) of **5** as red crystals, m.p. 99-101 °C (petroleum ether). Calcd. for $C_{15}H_{12}FeOS$: C, 60.83; H, 4.08; Fe, 18.86; Found: C, 61.00; H, 4.08; Fe, 18.87. ^1H NMR: δ 4.11 (s, 5H, Cp), 4.22 (t, 2H, Hβ), 4.67 (t, 2H, Hα), 7.07 (d, 1H, H4), 7.58 (d, 1H, H3), 9.83 (s, 1H, CHO).

Vilsmeier-Haack formylation of 2-ferrocenyl-1-methylpyrrole yielded a small amount of the starting material, 37 mg (18 %) of **6a** as a red crystals, m. p. 82-84 °C (petroleum ether). Calcd. for $C_{16}H_{15}FeNO$: C, 65.56; H, 5.16; Fe, 19.05; N, 4.79; Found: C, 66.22; H, 5.26; Fe, 18.89; N, 4.61. ^1H NMR: δ 4.07 (s, 3H, CH_3), 4.16 (s, 5H, Cp), 4.39 (t, 2H, Hβ), 4.53 (t, 2H, Hα), 6.35 (d, 1H, H4), 6.86 (d, 1H, H3), 9.46 (s, 1H, CHO).

Vilsmeier-Haack formylation of 2-ferrocenyl-3-phenylthiophene yielded 144 mg (60 %) of the starting material, 50 mg (19 %) of **7** as a red crystals, m.p. 150-152 °C (petroleum ether). Calcd. for $C_{21}H_{16}FeOS$: C, 67.74; H, 4.33; Fe, 15.04; Found: C, 67.78; H, 4.58; Fe, 14.85. ^1H NMR: δ 4.09 (s, 7H, Cp, Hβ), 4.29 (bs, 2H, Hα), 7.35 (bs, 5H, Ph), 7.54 (s, 1H, H3), 9.85 (s, 1H, CHO).

Vilsmeier-Haack formylation of 2-ferrocenyl-3-phenyl-1-methylpyrrole yielded small amount of the starting material, 36 mg (14 %) of **8** as a orange crystals, m.p. 187-189 °C (petroleum ether). Calcd. for $C_{22}H_{19}FeNO$: C, 71.53; H,5.19; Fe, 15.16; N, 3.79; Found: C, 71.11; H, 5.31; Fe, 15.06; N, 3.59. ^1H NMR: δ 4.09 (s, 5H, Cp), 4.22 (t, 2H, Hβ), 4.30 (t, 2H, Hα), 4.38 (s, 3H, CH_3), 6.89 (s, 1H, H3), 7.28 (m, 5H, Ph), 9.54 (s, 1H, CHO).

Vilsmeier-Haack formylation of 2-ferrocenyl-5-phenylthiophene yielded 145 mg (60 %) of the starting material, 28 mg (11 %) of **9a** as a red crystals, m.p. 120-122 °C (petroleum ether-ether). Calcd. for

$C_{21}H_{16}FeOS$: C, 67.74; H, 4.33; Fe, 15.04; Found: C, 67.82; H, 4.60; Fe, 14.95. ^1H NMR: δ 4.22 (s, 5H, Cp), 4.46 (t, 2H, Hβ), 4.68 (t, 2H, Hα), 7.38 (m, 5H, Ph), 7.57 (s, 1H, H4), 10.14 (s, 1H, CHO).

A general procedure of formylation of ferrocenylheteroarenes via BuLi metallation and DMF quenching (method B).

Formylation of 2-ferrocenylthiophenes

To the solution of 0.7 mmol of ferrocenylthiophene in 4 ml of dry THF cooled to -65 °C was added 2 drops of TMEDA under stirring and then 1.4 mmol of n-BuLi. Reaction mixture was stirred at -65 °C for 2 hours. DMF (2.8 mmol) was then added during 15 min into the reaction mixture, stirring continued for another 1 hour at -65 °C, and then was warmed to the room temperature. Reaction mixture was poured on ice and the product was extracted into diethyl ether.

Formylation of 2-ferrocenylthiophene yielded 84 mg (45 %) of the starting material, 110 mg (54 %) of **5** as a red crystals, m. p. 99-101 °C (petroleum ether). Calcd. for $C_{15}H_{12}FeOS$: C, 60.83; H, 4.08; Fe 18.86; Found: C, 61.00; H, 4.08; Fe, 18.87. ^1H NMR: δ 4.11 (s, 5H, Cp), 4.22 (t, 2H, Hβ), 4.67 (t, 2H, Hα), 7.07 (d, 1H, H4), 7.58 (d, 1H, H3), 9.83 (s, 1H, CHO).

Formylation of 2-ferrocenyl-3-phenylthiophene yielded 36 mg (15 %) of the starting material, 120 mg (46 %) of **7** as a red crystals, m.p. 151-152 °C (petroleum ether). Calcd. for $C_{21}H_{16}FeOS$: C, 67.74; H, 4.33; Fe, 15.04; Found: C, 67.78; H, 4.58; Fe, 14.85. ^1H NMR: δ 4.09 (s, 7H, Cp, Hβ), 4.29 (bs, 2H, Hα), 7.35 (bs, 5H, Ph), 7.54 (s, 1H, H3), 9.85 (s, 1H, CHO).

Formylation of 2-ferrocenyl-5-phenylthiophene yielded 150 mg (62 %) of the starting material, 23 mg (9 %) of **9b** as a violet oil. Calcd. for $C_{21}H_{16}FeOS$: C, 67.74; H, 4.33; Found: C, 68.12; H, 4.69. ^1H NMR: δ 4.22 (s, 5H, Cp), 4.63 (t, 2H, Hβ), 5.07 (t, 2H, Hα), 7.38 (m, 3H, Ph), 7.50 (s,1H, H3), 7.60 (m, 2H, Ph), 9.52 (s, 1H, CHO).

Formylation of 2-ferrocenyl-1-methylpyrroles

Reaction was carried out as described above with the exception that BuLi-arene ratio was 4:1, reaction temperature was -35 °C, and 8 mol excess of DMF was used for quenching.

Formylation of 2-ferrocenyl-1-methylpyrrole yielded 120 mg (65 %) of the starting material, 19 mg (10 %) of **6b**, as yellow very unstable crystals, by heating decomposed. Calcd. for $C_{31}H_{30}FeN_2O$: C, 66.69; H, 5.41; Found: C, 67.52; H, 5.68. ^1H NMR: δ 3.53 (s, 6H, CH_3), 3.71 (s, 1H, CH), 4.12 (s, 10H, Cp), 4.22 (bs, 4H, Hβ), 4.33 (bs, 4H, Hα), 5.85 (bs, 4H, H3,4).

Formylation of 2-ferrocenyl-1-methyl-3-phenylpyrrole yielded 130 mg (55 %) of the starting material, 23 mg (9 %) of **8** as an orange crystals, m.p. 187-189 °C (petroleum ether). Calcd. for $C_{22}H_{19}FeNO$: C, 71.53; H,5.19; Found: C, 71.11; H, 5.31. ^1H NMR: δ 4.09 (s, 5H, Cp), 4.22 (t, 2H, Hβ), 4.30 (t, 2H, Hα), 4.38 (s, 3H, CH_3), 6.89 (s, 1H, H3), 7.28 (m, 5H, Ph), 9.54 (s, 1H, CHO).

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