SYNTHESIS OF FERROCENYL-SUBSTITUTED HETEROCYCLES: THE BENEFICIAL EFFECT OF THE MICROWAVE IRRADIATION

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The synthesis of ferrocenyl-substituted thiophenes, furans, pyrroles, pyrimidine and pyrazole has been studied. 2-Ferrocenylpyrroles were prepared from ferrocenyl ketoximes and acetylene in DMSO–KOH mixture whereas 3-chloro-3-ferrocenylacrylaldehydes and thioglycolic or glycolic acids were the starting materials for the synthesis of the thiophene and furan derivatives. The yields were significantly enhanced when the reactions were carried out in a microwave oven. The lower stability of 2-ferrocenylfuran in comparison with 2-ferrocenylthiophene is discussed on the basis of semiempirical quantum chemistry calculations.

Only few papers have been published describing ferrocenyl (Fc) derivatives of five-membered heterocycles. 2-Ferrocenylthiophene was prepared from bromoferrocene and potassium tetra(2-thienyl) borate[1]. 2-Ferrocenyl-5-phenylthiophene was obtained from 1-ferrocenyl-4-phenyl-1,3-butadiyne[2], and 2-ferrocenylpyrrole from bromoferrocene and 2-pyrrolemagnesium bromide[1]. No general method for the synthesis of ferrocenyl-substituted heterocycles is described in the literature.

The main aim of this work was to explore some methods which would lead to the synthesis of a broad range of 2-ferrocenyl-substituted heterocycles such as thiophene, furan and pyrrole.

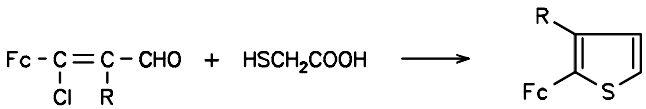
In an analogy to ref.[3], the reactions of 3-chloro-3-ferrocenylacrylaldehydes with glycolic acid, thioglycolic acid, glycine or their derivatives were chosen for the synthesis of ferrocenyl-substituted heterocycles. If successful, this method could be used for the synthesis of a broad range of such compounds due to the variability of substituents, both in the acrylaldehydes and in α-position of carboxylic acids.

The described synthesis of 3-chloro-3-ferrocenylacrylaldehydes[4,5] caused no problems. Schlögl et al.[5] claimed the preparation of 3,3′-(1,1′-ferrocenylene)bis(3-chloroacrylaldehyde) from 1,1′-diacetylferrocene in 70% yield. Repeating the procedure we have found that the structure elucidation, based on elemental analysis and IR spectra, was erroneous. The main product we obtained in 50% yield proved to be (by ^{1}H NMR) 3-chloro-3-[1′-(1-chloroethenyl)ferrocenyl]acrylaldehyde. The desired bisacryl-

aldehyde was unstable; nevertheless, we succeeded in its isolation in 20% yield. Synthesis, structure elucidation, and *E*/*Z* isomerizations of 2-phenyl-3-chloro-3-ferrocenylacrylaldehyde (prepared from (phenylacetyl)ferrocene) and 3,3′-(1,1′-ferrocenylene)bis(3-chloro-2-phenylacrylaldehyde) (from 1,1′-bis(phenylacetylferrocene) will be described elsewhere[6].

Prolonged heating[3] of 3-chloro-3-ferrocenylacrylaldehyde with thioglycolic acid in DMF under Et_3N catalysis afforded a complex mixture of products (TLC) and the desired 2-ferrocenylthiophene was isolated in 20% yield after chromatography on SiO_2 column. This procedure was not hopeful and we decided therefore to repeat this synthesis in a microwave oven, because several papers[7 – 9] described a considerable acceleration of various reactions by microwave irradiation. For this experiment, we used the reactor described in ref.[10]. The reaction proceeded smoothly in 1 : 2 Et_3N–DMF mixture and 87% yield of 2-ferrocenylthiophene was isolated after 2 min heating in a microwave oven. Prolonged heating or using more than 100 mg of the starting acrylaldehyde in one batch caused decomposition. Other ratios of Et_3N–DMF were also used but lower yields of the product were obtained: the ratios 1 : 1 and 1 : 15 gave 62 and 49% yields of the product, respectively. Bose et al.[11] advocated *o*-dichlorobenzene as an excellent solvent for reactions conducted in the microwave oven. However, the use of this solvent instead of DMF gave lower yield (51%) after 5 min of microwave heating. Therefore, all other experiments were carried out in 1 : 2 Et_3N–DMF mixture and in a microwave oven. In all cases, mixtures of *E* and *Z* isomers of 3-chloro-3-ferrocene-acrylaldehydes were used in the reactions.

3-Chloro-3-ferrocenylacrylaldehydes and thioglycolic acid afforded high yields of 2-ferrocenylthiophenes (Scheme 1).

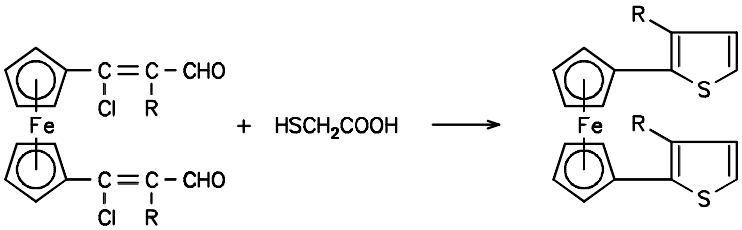


I, R = H
II, R = Ph

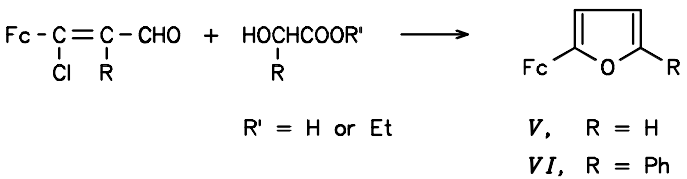
SCHEME 1

We also made attempts at the synthesis of 1,1′-bis(2-thienyl)ferrocenes (Scheme 2). Though the yields were high, they varied considerably due to the instability of the starting material.

To synthesize 2-ferrocenylfuran, we decided to employ ethyl glycolate as the starting material (Scheme 3). The product, ethyl ester of 5-ferrocenyl-2-furancarboxylic acid, should have been then hydrolyzed and decarboxylated. To our surprise, the reaction in a microwave oven yielded directly 2-ferrocenylfuran as a red oil. Hence both the hydrolysis and decarboxylation proceed during the microwave irradiation. Mandelic acid was used for the synthesis of 2-ferrocenyl-3-phenylfuran which was isolated as a red oil.



SCHEME 2

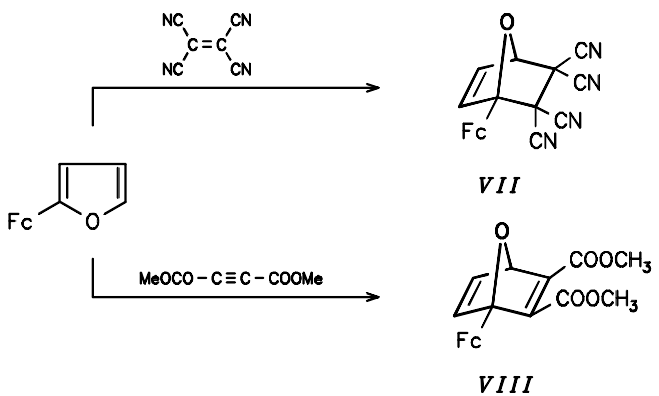


SCHEME 3

The products, 2-ferrocenylfuran (*V*) and 2-ferrocenyl-5-phenylfuran (*VI*), were characterized by ^{1}H NMR spectra.

They were, however, very unstable and, after several hours at room temperature, decomposed.

2-Ferrocenylfuran was fully characterized via Diels–Alder adducts with tetracyanoethylene or dimethyl acetylenedicarboxylate *VII* and *VIII* (Scheme 4).



SCHEME 4

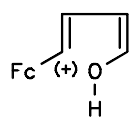
It was of interest to know the reason for the great difference in stability of 2-ferrocenylfuran and 2-ferrocenylthiophene. We tried to estimate the stabilities of 2-ferrocenylthiophene (*I*), 2-ferrocenylfuran (*V*) and 2-ferrocenyl-5-phenylfuran (*VI*) by the extended Hückel (EH) method[12] using the CACAO program[13]. The geometry of the molecules under study was fully optimized using MMX force field implemented in the PCMODEL program package[14]. The MMX force field is specially parametrized for correct description of organometallic molecule structures[15].

The measure of the C–Z bond stability (Z = S or O) in the heterocycle is the reduced overlap population, calculated by the EH method. The values for the free and protonized molecules under study are given in Table I.

The results are in good agreement with the observed stability of the compounds *I* >> *VI* > *V*.

It is just a little confusing that in *V*, according to the calculations, the Z–C bond more distant from ferrocene moiety should be cleaved more easily than that being nearer. If this was the case, the δ-ferrocenylcarbocation should be the intermediate. It is well known, however, that ferrocenyl can stabilize α-carbocation very effectively. To explain the very low stability of *V*, EH calculations of the stability of the protonated *V* and the proposed intermediates were made and the results were compared with the analogous 2-phenylfuran.

It was found that the α-carbocation (*XIII*) is by ca 6 eV more stable than the starting protonated *V*. In the case of 2-phenylfuran the analogous carbocation is only by 0.2 eV more stable than the original protonated heterocycle. We are aware of the fact that the EH method can yield only qualitative data, but even so the high stability of *XIII* is apparent and hence can be responsible for the very low stability of *V*.

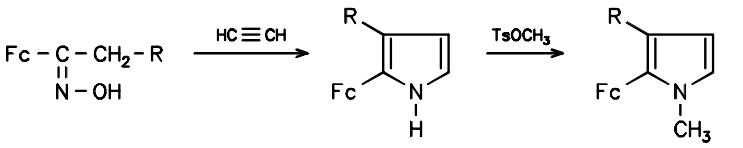


XIII

TABLE I
Calculated reduced overlap populations for C–Z bonds (Z = S or O) in *I*, *V* and *VI*

Compound	**Fc**–**C**–Z–C	Fc–C–**Z**–**C**	**Fc**–**C**–ZH$^+$–C	Fc–C–**ZH**$^+$–**C**
I	0.683	0.675	0.707	0.705
V	0.537	0.520	0.549	0.537
VI	0.622	0.614	0.615	0.610

An attempted synthesis of 2-ferrocenyl-1-methylpyrrole by the same method starting from 3-chloro-3-ferrocenylacrylaldehyde and *N*-methylglycine was little successful: only 5% of the product was isolated after 2.5 min of microwave heating using 1 : 2 Et_3N–DMF mixture as the solvent. The exchange of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine for triethylamine brought no improvement. We decided therefore to explore another method[16,17] using the reaction of oximes with acetylene or 1,2-dichloroethane for the synthesis of pyrrole derivatives (Scheme 5). Ferrocenyl ketoximes were prepared from appropriate acylferrocenes and hydroxylamine hydrochloride in pyridine–ethanol as the solvent in a microwave oven[10]. The reaction of the oximes with acetylene usually yielded a complex mixture from which the products were isolated by column chromatography using different 2-methylpentane–ethyl acetate mixtures as eluent[5].



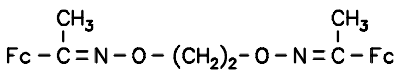
IX, R = H *XI*, R = H
X, R = Ph *XII*, R = Ph

SCHEME 5

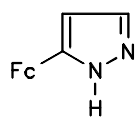
Unfortunately, the pyrrole derivatives were unstable and therefore we prepared their *N*-methyl derivatives using methyl tosylate and sodium hydride (methylation with methyl iodide was not successful). The reaction was smooth when carried out in a ultrasonic bath. *N*-Methyl derivatives were more stable than their precursors.

An attempted synthesis of 2-ferrocenylpyrrole using 1,2-dichloroethane and KOH/DMSO instead of acetylene failed and only an acyclic substitution product *XIV* was isolated.

We also attempted the synthesis of 2-ferrocenyl-5-phenylpyrrole starting from acetylferrocene oxime and phenylacetylene. The experiments, both under classic conditions and in a microwave oven, failed and 80% of acetylferrocene was isolated after the work-up of the reaction mixture.



XIV

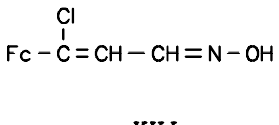


XV

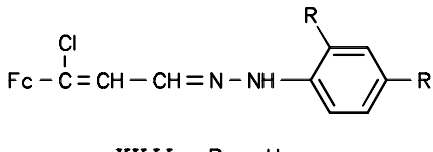
When our work was nearly finished a paper describing the synthesis of 2-ferrocenylisoxazole and 2-ferrocenylpyrazole starting from 3-chloro-3-ferrocenylacrylaldehyde was published[18].

The reaction took 2 – 7 h and the yields varied from 25 to 78%. We decided therefore to perform the reactions in a microwave oven.

Starting from 3-chloro-3-ferrocenylacrylaldehyde and hydrazine, 83% of pyrazole *XV* was isolated (2 min in microwave oven). The reactions with hydroxylamine hydrochloride, phenylhydrazine and 2,4-dinitrophenylhydrazine yielded, after 0.5 – 0.3 min of microwave heating, in contrast to ref.[18], only acyclic condensation products *XVI*, *XVII* and *XVIII*, respectively.

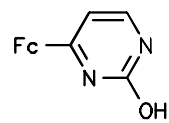


XVI



XVII, R = H

XVIII, R = NO_2



XIX

Two more reactants, urea and thiourea, were also examined. The former gave 49% of 2-hydroxy-4-ferrocenylpyrimidine (*XIX*) after 2 min in microwave oven, the latter afforded a very polar green-blue solid, which we could not characterize.

EXPERIMENTAL

3-Chloro-3-ferrocenylacrylaldehydes were prepared as described in ref.[6], and ferrocenyl ketoximes as described in ref.[10]. All the starting materials and solvents were purified by standard procedures. ^{1}H NMR spectra were measured in $CDCl_3$ solution on a Tesla BS 587 instrument at 80 MHz using tetramethylsilane as an internal standard. Microwave oven DAEWO (500 W) and ultrasonic cleaning bath TESLA UG 160/320 TA (4 l, 20 kHz, 160 W) were used in our experiments. All experiments were carried out under Ar atmosphere.

2-Ferrocenylthiophene (*I*) and 2-Ferrocenyl-3-phenylthiophene (*II*)

A solution of corresponding 3-chloro-3-ferrocenylacrylaldehyde (0.36 mmol) and thioglycolic acid (0.44 mmol) in the mixture of 4 ml dimethylformamide and 2 ml triethylamine, in a reactor[10] was placed in a microwave oven. The course of the reaction was monitored by TLC. When the reaction was over, the mixture was cooled and diethyl ether was added. The ether solution was washed several times with water and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on SiO_2, the mixture of 2-methylpentane and ethyl acetate being the eluent. *I*, m.p. 114 – 115 °C, and *II*, m.p. 130 – 132 °C were isolated in 87 and 79% yields, respectively.

1,1′-Bis(2-thienyl)ferrocene (*III*) and 1,1′-Bis(3-phenyl-2-thienyl)ferrocene (*IV*)

The title compounds were prepared from the corresponding 3,3′-(1,1′-ferrocenylene)bis(3-chloroacrylaldehyde)s (0.33 mmol) and thioglycolic acid (0.8 mmol) in the same way as described above. *III*, m.p. 144 – 147 °C and *IV*, m.p. 147 – 150 °C were isolated in 60 and 55% yields, respectively.

2-Ferrocenylfuran (*V*) and 2-Ferrocenyl-5-phenylfuran (*VI*)

These substances were prepared from corresponding 3-chloro-3-ferrocenylacrylaldehydes (0.36 mmol) and ethyl glycolate or mandelic acid (0.44 mmol), in the same way as described above. *V* and *VI* were isolated as red oils in 35 and 15% yields, respectively.

Diels–Alder Reaction of 2-Ferrocenylfuran with Tetracyanoethylene

2-Ferrocenylfuran (0.39 mmol) and tetracyanoethylene (0.4 mmol) were dissolved in 10 ml of benzene. After 5 min at room temperature, the colour of the solution changed from dark red to yellow. The mixture was left for another 5 min at room temperature and then the solvent was evaporated. The residue was chromatographed on SiO_2. *VII* was isolated in 40% yield.

Diels–Alder Reaction of 2-Ferrocenylfuran with Dimethyl Acetylenedicarboxylate

The solution of 2-ferrocenylfuran (0.6 mmol) and dimethyl acetylenedicarboxylate (0.65 mmol) in 10 ml of benzene was stirred at room temperature for 3 h. After the work-up as above, 35% of *VIII* was isolated.

2-Ferrocenylpyrrole (*IX*) and 2-Ferrocenyl-3-phenylpyrrole (*X*)

Acetylferrocene oxime or (phenylacetyl)ferrocene oxime (4.77 mmol) and KOH (5.35 mmol) were dissolved in 20 ml of DMSO. Acetylene was passed through the solution at 95 °C for 3.5 h. After cooling to room temperature, 150 ml water was added. The mixture was extracted with diethyl ether, the ethereal solution was dried over anhydrous Na_2SO_4, and the solvent evaporated. The residue was chromatographed on SiO_2 column using 2-methylpentane–ethyl acetate as the eluent. *IX*, m.p. 151 – 154 °C and *X*, m.p. 90 – 96 °C were obtained in 40 and 25% yields, respectively.

2-Ferrocenyl-1-methylpyrrole (*XI*) and 2-Ferrocenyl-1-methyl-3-phenylpyrrole (*XII*)

To a solution of corresponding 2-ferrocenylpyrrole (0.79 mmol) in 10 ml of dry benzene, sodium hydride (4 mmol) and methyl *p*-toluenesulfonate (7.9 mmol) were successively added and the mixture was then sonicated for 5 h. After the addition of water and usual work-up, *XI*, m.p. 46 – 48 °C and *XII*, m.p. 94 – 97 °C were isolated in 85 and 50% yields, respectively.

General procedure for Synthesis of *XV*, *XVI*, *XVII*, *XVIII* and *XIX*

To a solution of 3-chloro-3-ferrocenylacrylaldehyde (0.73 mmol) in 5 ml of ethanol and 5 ml of acetic acid, 0.87 mmol of hydrazine, hydroxylamine, phenylhydrazine, 2.4-dinitrophenylhydrazine, or urea was added. The reaction mixture was exposed to microwave irradiation for the given time. After the usual work-up, *XV*, m.p. 149 – 151 °C, *XVI*, m.p. 95 – 97 °C, *XVII*, m.p. 90 – 93 °C, *XVIII*, m.p. 200 – 203 °C and *XIX*, m.p. 210 – 212 °C were obtained in 83, 94, 75, 50, and 49% yields, respectively.

TABLE II
Characteristics of ferrocenyl-substituted heterocycles and related ferrocene compounds

Compound	Time min	M.p., °C Yield, %	Formula (M.w.)	Calculated/Found			
				% C	% H	% Fe	% N
I	2	114 – 115	$C_{14}H_{12}FeS$	62.71	4.51	20.83	–
		87	(268.1)	62.72	4.64	20.78	
II	4	130 – 132	$C_{20}H_{16}FeS$	69.78	4.68	16.22	–
		79	(344.2)	69.24	4.68	15.92	
III	2	144 – 147	$C_{18}H_{14}FeS_2$	61.72	4.02	15.94	–
			(350.3)	61.74	4.01	15.97	
IV	4	147 – 150	$C_{30}H_{22}FeS_2$	71.71	4.41	11.11	–
		55	(502.4)	71.39	5.40	7.95	
V	3	oil	$C_{14}H_{12}FeO$			[a]	
		25 – 35	(252.1)				
VI	7	oil	$C_{20}H_{16}FeO$	73.19	4.91	–	–
		15	(328.2)	73.95	5.40		
VII	10	[a]	$C_{20}H_{12}FeN_4O$	63.20	3.18	–	–
		40	(380.2)	64.01	3.69		
VIII	180	36 – 40	$C_{20}H_{18}FeO_5$	60.96	4.60	14.16	–
		25	(349.2)	61.51	4.75	13.20	
IX	210	151 – 154	$C_{14}H_{13}FeN$	66.96	5.21	22.24	5.57
		40	(251.1)	66.29	5.17	22.25	5.37
X	210	90 – 96	$C_{20}H_{17}FeN$			[a]	
		10 – 25	(372.2)				
XI	300	46 – 48	$C_{15}H_{15}FeN$	67.95	5.70	21.06	5.28
		85	(265.1)	68.36	5.80	20.87	5.21
XII	420	94 – 97	$C_{21}H_{19}FeN$	73.92	5.61	16.36	4.10
		50	(341.2)	73.94	6.01	15.91	3.69
XIV	180	138 – 142	$C_{26}H_{28}Fe_2N_2O_2$	60.97	5.50	21.81	5.47
		54	(512.2)	60.97	5.63	21.53	5.26
XV	2	149 – 151	$C_{13}H_{12}FeN_2$	61.94	4.79	22.15	11.11
		83	(252.1)	61.98	4.82	21.91	10.81
XVI	0.5	95 – 97	$C_{13}H_{12}ClFeNO$	53.92	4.17	19.28	4.83
		94	(289.5)	53.91	4.28	19.40	4.51
XVII	3	90 – 93	$C_{19}H_{17}ClFeN_2$	62.58	4.69	15.31	7.67
		75	(364.6)	62.61	4.54	14.71	7.81
XVIII	1.5	200 – 203	$C_{19}H_{15}ClFeN_4O_4$	50.19	3.32	12.28	12.32
		50	(454.6)	50.28	3.37	11.33	12.34
XIX . H_2O	2	210 – 212	$C_{14}H_{14}FeN_2O_2$	56.40	4.73	18.73	9.39
		49	(298.1)	56.85	4.85	17.80	9.05

[a] Decomposed.

TABLE III

^{1}H NMR chemical shifts (δ in ppm, $CDCl_3$) of ferrocenyl-substituted heterocycles and related ferrocene compounds

Compound	Ferrocene	Heterocycle			Phenyl	Other
		H-3	H-4	H-5		
I	4.09 s (5 H) 4.27 bs (2 H) 4.57 bs (2 H)	6.98 m (2 H)		7.2 m	–	–
II	4.12 – 4.28 m (9 H)	–	6.9 d	7.18 d	7.28 s (5 H)	–
III	4.22 t (4 H) 4.43 t (4 H)	6.89 d (4 H)		7.15 m (2 H)	–	–
IV	4.15 d (8 H)	–	6.9 d (4 H)	7.18 d (2 H)	7.28 s (10 H)	–
V	3.96 s (5 H) 4.06 t (2 H) 4.44 t (2 H)	6.53 m (2 H)		7.15 m	–	–
VI	4.06 s (5 H) 4.24 bs (2 H) 4.61 bs (2 H)	6.28 d	6.54 d	–	7.25 m (3 H) 7.59 m (2 H)	–
VII	3.98 bs (2 H) 4.08 s (5 H) 4.11 bs (2 H)	5.56 m (2 H)		4.39 d	–	–
VIII	4.2 s (5 H) 4.3 bs (2 H) 4.55 bs (2 H)	5.5 d	6.2 d	4.3 bs	–	3.82 s 6 H (OCH_3)
IX	4.08 s (5 H) 4.3 bs (2 H) 4.45 bs (2 H)	6.2 m (2 H)		6.75 d	–	8.0 m 1 H (NH)
X	4.12 s (5 H) 4.25 bs (2 H) 3.36 bs (2 H)	–	6.26 bs	6.65 bs	7.31 m (5 H)	4.12 s 1 H (NH)
XI	4.14 s (5 H) 4.25 bs (2 H) 4.4 bs (2 H)	6.2 m (2 H)		6.58 bs	–	3.71 s 3 H (CH_3)
XII	4.06 s (5 H) 4.19 d (4 H)	–	6.2 d	6.7 bs	7.25 s (5 H)	4.02 s 3 H (CH_3)
XIV	4.35 bs (18 H)	–	–	–	–	2.15 s 6 H (CH_3) 4.3 s 4 H (CH_2)

TABLE III
(*Continued*)

Compound	Ferrocene	Heterocycle			Phenyl	Other
		H-3	H-4	H-5		
XV	4.06 s (5 H)	7.25 d	6.38 d	–	–	–
	4.29 bs (2 H)					
	4.64 bs (2 H)					
XVI	4.19 s (5 H)	–	–	–	–	6.58 d 1 H (CH=C)
	4.39 bs (2 H)					7.24 d 1 H (CH=N)
	4.61 bs (2 H)					8.21 m 1 H (OH)
XVII	4.19 s (5 H)	–	–	–	6.74 – 7.24 m	6.63 d 1 H (=CH–)
	4.34 t (2 H)				(5 H)	7.74 d 1 H (CH=N)
	4.61 t (2 H)					
XVIII	4.23 s (5 H)	–	–	–	8.26 m (2 H)	6.7 d 1 H (=CH–)
	4.47 bs (2 H)				9.11 d (1 H)	7.88 d 1 H (CH=N)
	4.69 bs (2 H)					
XIX	4.19 s (5 H)	–	–	5.8 d	–	5.19 bs 2 H (H_2O)
	4.64 bs (2 H)					7.53 d 1 H (H-6)
	4.88 bs (2 H)					11.29 bs 1 H (OH)

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