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PII: S0040-4020(17)31151-1

DOI: 10.1016/j.tet.2017.11.015

Reference: TET 29095

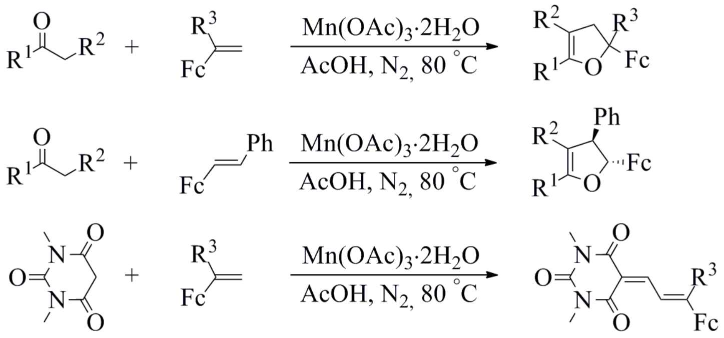
To appear in: *Tetrahedron*

Received Date: 10 August 2017

Revised Date: 20 October 2017

Accepted Date: 6 November 2017

Please cite this article as: Aslan H, Öktemer A, Dal H, Hökelek T, Synthesis of ferrocene substituted dihydrofuran derivatives via manganese(III) acetate mediated radical addition-cyclization reactions, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.11.015.


Mn(OAc)$_3$·2H$_2$O
AcOH, N$_2$, 80 °C
R^1
R^2
R^3
Fc
Ph
O
N

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Synthesis of ferrocene substituted dihydrofuran derivatives via manganese(III) acetate mediated radical addition-cyclization reactions

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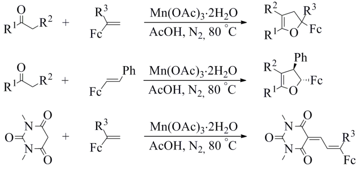

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Manganese(III) acetate
Ferrocene
Trans-dihydrofuran
Allylidene derivatives
Benzofuran

ABSTRACT

In this study, the manganese(III) acetate mediated radical addition-cyclization reactions of ferrocene substituted alkenes and active methylene compounds were carried out. The regio- and stereoselective radical cyclization reactions of (E)-styrylferrocene (**1a**) and active methylene compounds (**2a-g**) gave trans-5-ferrocenyl-4-phenyl-4,5-dihydrofuran compounds as the sole products. The reactions of 1-ferrocenyl-1-aryl(heteroaryl)ethenes (**1b-e**) and active methylene compounds (**2a-f**) via Mn(OAc)$_3$ led to furan and benzofuran derivatives (**10-33**) in mid-good yields (up to 75 %). Surprisingly, ferrocene substituted allylidene derivatives were obtained from the Mn(OAc)$_3$ mediated reactions of 1-aryl-1-ferrocenylethene (**1b-d**) and 1,3-dimethylbarbituric acid (**2g**). The uses of ferrocene substituted alkenes in manganese(III) acetate mediated radical reactions is the first example in this field as far as we know.

1. Introduction

Ferrocene has attracted much attention due to it having both organic and inorganic properties, high thermal stability, good solubility in organic solvents, easy synthesis,[1] and reversible redox properties.[2] Ferrocene derivatives are used as homogeneous catalysts,[3] chemosensors,[4] asymmetric ligands,[5] non-linear optical materials,[6] conductive polymers,[7] liquid crystals[8] and biosensors.[9] In addition, ferrocene compounds[10] and ferrocenium salts[10c, 11] have strong antitumor activities.

Furan and benzofuran derivatives form the basic structure of many natural compounds and show a wide range of biological activities.[12] In addition, these compounds are used as substrates for the synthesis of many polyfunctional organic compounds.[13]

There are only a few studies that include both ferrocene and furan groups. These studies are concentrated on synthesis of ferrocenylfurans,[14] furan and ferrocene containing conjugates and their electrochemical behaviour,[15] applications of nonlinear optical materials,[6] and cytotoxic investigations of ferrocenylfurans.[16]

Furan compounds can easily be prepared by the oxidative cyclization reaction of an active methylene compound and an unsaturated system mediated by transition metal salts (Mn^{3+},[17] Ce^{4+},[18] Cu^{2+},[19]). Manganese(III) acetate has introduced differences in the field of free radical chemistry, due to its selectivity, specificity, mild and efficient reaction conditions.[20]

The first study of the Mn(OAc)$_3$ mediated oxidation reactions of ferrocene compounds was made in 1976.[21] It was reported that diferrocenylmethane derivatives were obtained by the oxidation and aromatic electrophilic substitution reactions of methylferrocene without the presence of any cyclization product. Following this study, we have not been able to find any research dealing with Mn(OAc)$_3$ mediated reactions of ferrocene compounds until the present.

In this study, manganese(III) acetate mediated oxidative cyclization reactions of ferrocene substituted alkene and active methylene compounds have been carried out. As a result, ferrocene substituted dihydrofuran, benzofuran and pyrimidine derivatives with the potential of showing biological activity were obtained. The use of ferrocene substituted alkenes in manganese(III) acetate mediated radical reactions is the first example in this field as far as we know.

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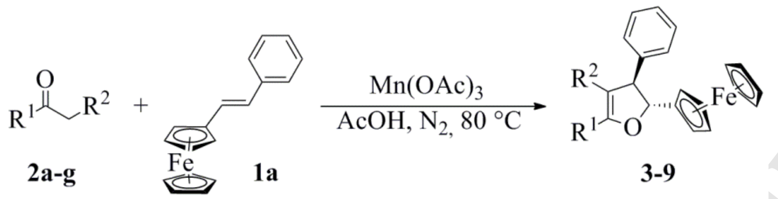
2. Results and Discussion

Initially, the reactions of (E)-styrylferrocene (**1a**) and active methylene compounds (**2a-g**) via Mn(OAc)$_3$ were studied. Although two regioisomers and two stereoisomers may form in these reactions, trans-5-ferrocenyl-4-phenyl-dihydrofuran compounds (**3-9**) were obtained as the sole product (**Table 1**).

Table 1 Products of the oxidative cyclization reactions of **1a** with **2a-g** via Mn(OAc)$_3$[a].

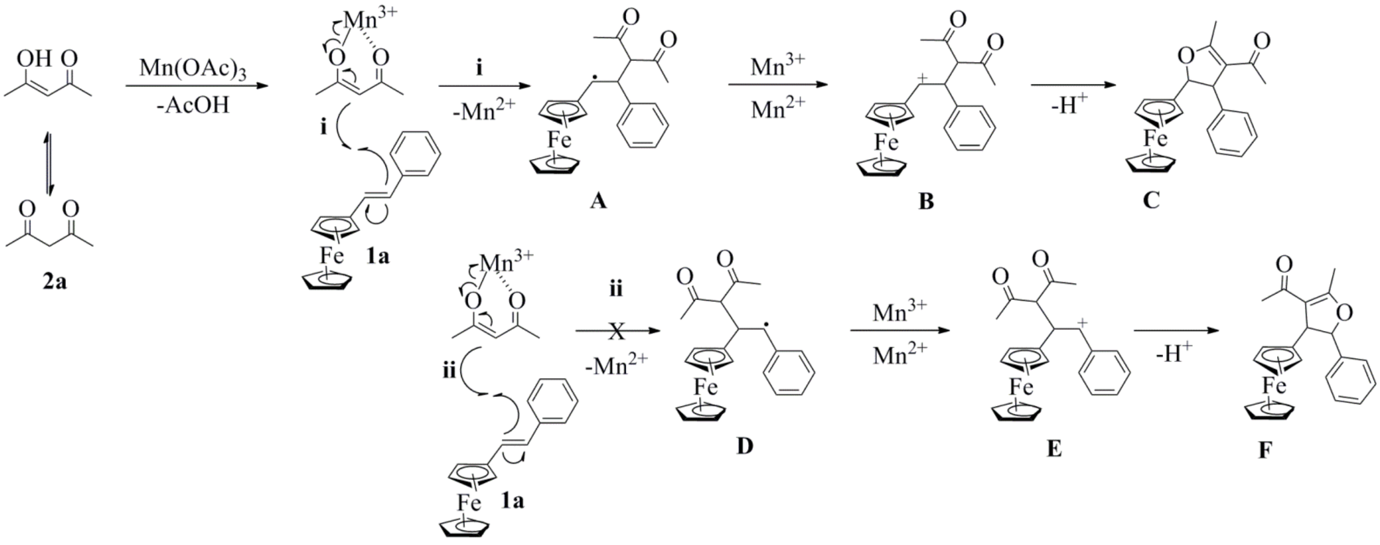


Entry	Active Methylene	Time (min)	Product		Yield, %[b]
			R^1	R^2	
1	**2a**	20	CH_3	$COCH_3$	10 (**3**)
2	**2b**	25	CH_3	COOEt	30 (**4**)
3	**2c**	14	$CH_2C(CH_3)_2CH_2CO$		50 (**5**)
4	**2d**	20	$CH_2CH_2CH_2CO$		28 (**6**)
5	**2e**	27	C_6H_5	CN	24 (**7**)
6	**2f**	32	Thien-2-yl	CN	25 (**8**)
7	**2g**	22	$N(CH_3)CON(CH_3)CO$		15 (**9**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1a-e**), active methylene (**2a-f**) and Mn(OAc)$_3$ in AcOH at 80 °C;

[b] : Isolated yield based on alkene

The proposed mechanism of these reactions is shown in **Scheme 1**. The trans-5-ferrocenyl-4-phenyl-dihydrofuran compounds (**3-9**) are probably formed by following the commonly accepted route.[22] According to this mechanism, a Mn(III)-enolate complex is formed through the interaction of Mn(OAc)$_3$ and the enol form of the active methylene compound. Interaction of the Mn(III)-enolate complex and alkene (**1a**) affords a radical carbon intermediate (**A**) via pathway **i**. **A** is then oxidized by Mn(OAc)$_3$ to form a carbocation (**B**). 5-Ferrocenyl-4-phenyl-dihydrofuran (**C**) is produced through the cyclization of **B**. Similarly, the radical carbon intermediate (**D**), carbocation (**E**) and 4-Ferrocenyl-5-phenyl-dihydrofuran (**F**) can also be attained respectively via pathway **ii**. Only one product with the skeletal structure of compound **C** was obtained from the related reactions.



Scheme 1 Proposed mechanism for the formation of ferrocenyl substituted dihydrofurans

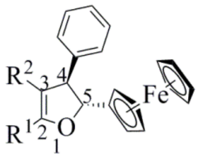


Figure 1 Enumerated structure of **3-9**

The structure of the product was identified using HSQC, HMBC and NOESY spectra. Due to being adjacent to the oxygen atom, H5 and C5 resonate at a lower field than H4 and C4, respectively. The H4-H5 protons and C4-C5 carbons were determined using HSQC spectra. HMBC spectra show that H5 correlates with the ortho-carbons of the ferrocenyl group, and doesn't correlate with ortho-carbons of the phenyl group. Similarly, H4 correlates with the ortho-carbons of the phenyl group, and doesn't correlate with ortho-carbons of the ferrocenyl group. These results prove that the ferrocenyl group is attached to the C5 carbon and the obtained product is **C** by pathway **i**. As the ferrocenyl group possesses considerably more electron donating properties than the phenyl group,[23] **A** and **B** are more stable than **D** and **E**, respectively. For this reason, reaction path **ii** doesn't proceed to form **F**. Moreover, in the NOESY spectra of products **3-9**, there is either no correlation or weak correlation between the H4 and H5 protons which shows that these protons are in the trans configuration. To ensure that the product (**3-9**) structures are in the trans configuration, the structure of one of these compounds (**8**) was confirmed by X-ray crystallography.[24] It can clearly be seen from the ORTEP view that **6** is a trans-dihydrofuran (**Figure 2**).

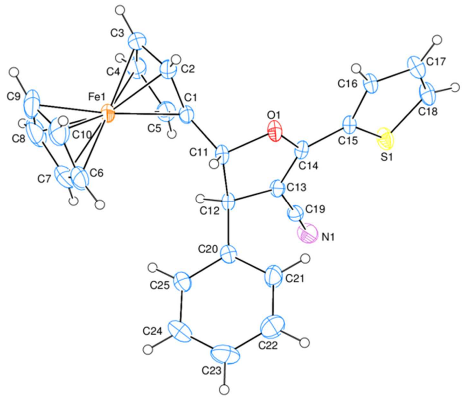
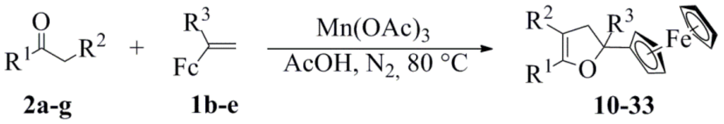


Figure 2 The molecular entities of compound **8**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

$Mn(OAc)_3$ mediated reactions of 1-ferrocenyl-1-aryl(heteroaryl)ethenes (**1b-e**) and active methylene compounds (**2a-f**) lead to the formation of furan and benzofuran derivatives (**10-33**) in mid-good yields up to 75 % (**Table 2**). The ^{1}H-NMR spectra of almost all products revealed the dihydrofuran $H_2C(4)$ protons to be diastereotopic, exhibiting doublets between 3.34 and 4.02 ppm. The coupling constant of these protons is between $^2J_{H\text{-}H}$ = 13.6-14.8.

Table 2 Products of the oxidative cyclization reactions of **1b-e** with **2a-f** via $Mn(OAc)_3$[a].

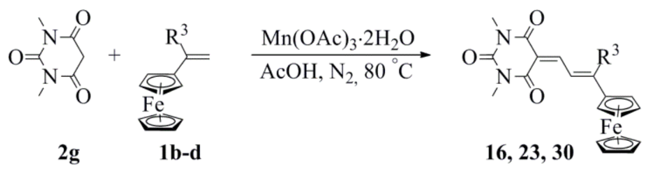


Entry	Active Methylene	Alkene	Time (min)	Product R^1	R^2	R^3	Yield, %[b]
1	**2a**	**1b**	5	CH_3	$COCH_3$	C_6H_5	44 (**10**)
2	**2b**	**1b**	8	CH_3	COOEt	C_6H_5	47 (**11**)
3	**2c**	**1b**	5	$CH_2C(CH_3)_2CH_2CO$		C_6H_5	75 (**12**)
4	**2d**	**1b**	5	$CH_2CH_2CH_2CO$		C_6H_5	67 (**13**)
5	**2e**	**1b**	5	C_6H_5	CN	C_6H_5	52 (**14**)
6	**2f**	**1b**	8	Thien-2-yl	CN	C_6H_5	58 (**15**)
7	**2a**	**1c**	20	CH_3	$COCH_3$	4-CH_3-C_6H_4	48 (**17**)
8	**2b**	**1c**	20	CH_3	COOEt	4-CH_3-C_6H_4	52 (**18**)
9	**2c**	**1c**	10	$CH_2C(CH_3)_2CH_2CO$		4-CH_3-C_6H_4	50 (**19**)
10	**2d**	**1c**	10	$CH_2CH_2CH_2CO$		4-CH_3-C_6H_4	41 (**20**)
11	**2e**	**1c**	17	C_6H_5	CN	4-CH_3-C_6H_4	46 (**21**)
12	**2f**	**1c**	20	Thien-2-yl	CN	4-CH_3-C_6H_4	37 (**22**)
13	**2a**	**1d**	14	CH_3	$COCH_3$	4-F-C_6H_4	55 (**24**)
14	**2b**	**1d**	14	CH_3	COOEt	4-F-C_6H_4	57 (**25**)
15	**2c**	**1d**	10	$CH_2C(CH_3)_2CH_2CO$		4-F-C_6H_4	66 (**26**)
16	**2d**	**1d**	10	$CH_2CH_2CH_2CO$		4-F-C_6H_4	52 (**27**)
17	**2e**	**1d**	9	C_6H_5	CN	4-F-C_6H_4	45 (**28**)
18	**2f**	**1d**	9	Thien-2-yl	CN	4-F-C_6H_4	43 (**29**)
19	**2c**	**1e**	45	$CH_2C(CH_3)_2CH_2CO$		Thien-2-yl	50 (**31**)
20	**2e**	**1e**	44	C_6H_5	CN	Thien-2-yl	54 (**32**)
21	**2f**	**1e**	28	Thien-2-yl	CN	Thien-2-yl	52 (**33**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1a-e**), active methylene (**2a-f**) and $Mn(OAc)_3$ in AcOH at 80 °C; [b] : Isolated yield based on alkene; Fc: Ferrocenyl

Furopyrimidine derivatives were not formed from the $Mn(OAc)_3$ mediated reactions of 1-ferrocenyl-1-aryl(heteroaryl)ethenes (**1b-e**) and 1,3-dimethylbarbituric acid (**2g**). Unexpectedly, acyclic and one-carbon extended allylidene compounds were obtained from these reactions (**Table 3**).

Table 3 Products of the oxidative cyclization reactions of **1b-d** with **2g** via $Mn(OAc)_3$[a].



Entry	Alkene	Time (min)	R^3	Yield, %[b]
1	**1b**	4	C_6H_5	14 (**16**)
2	**1c**	20	$4\text{-}CH_3\text{-}C_6H_4$	17 (**23**)
3	**1d**	10	$4\text{-}F\text{-}C_6H_4$	15 (**30**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1b-d**), active methylene (**2g**) and $Mn(OAc)_3$ in AcOH at 80 °C; [b] : Isolated yield based on alkene

The structures of these compounds (**16, 23, 30**) were identified with various spectroscopic methods. Unlike the spectra of other cyclic products (**8-31**), there weren't any diastrotopic protons resonated between 3.3-4.0 ppm in the ^{1}H-NMR spectra of these products. The synthesized compound seems to posses one extra carbon than expected and the molecular weight is 12 g.mol^{-1} more than expected. The alkene protons exhibited doublets at about 8.0 and 8.5 ppm. Some NMR chemical shifts of **16**, **23** and **30** are shown in **Table 4**. At the same time, the structure of compound **23** was confirmed by X-ray crystallography[24] and an the ORTEP view is given in **Figure 3**.

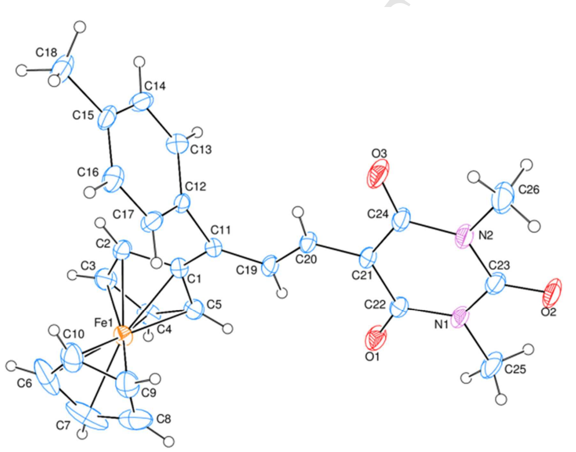
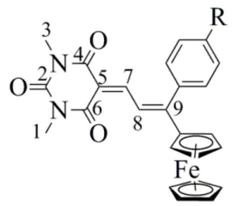
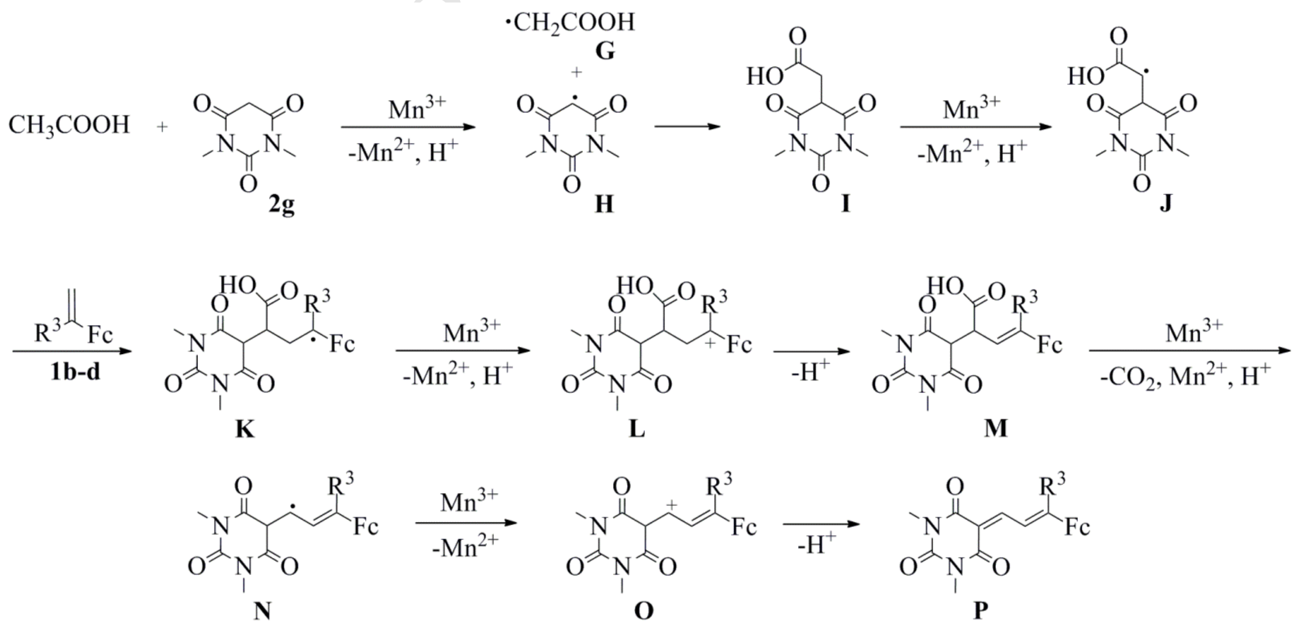


Figure 3 The molecular entities of compound **23**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 4 NMR chemical shifts of enumerated atoms of **16, 23, 30**

	Compound	R	Atom Numbers									
			^{1}H-NMR (δ)			^{13}C-NMR (δ)						
			1/3	7	8	1/3	2	4/6	5	7	8	9
	**16**	H	3.31 3.40	7.98	8.51	27.96 28.46	170.93	162.33 163.01	110.48	154.09	121.64	151.74
	23	CH_3	3.31 3.40	8.01	8.48	27.92 28.43	171.32	162.34 163.08	110.22	154.35	121.70	151.75
	30	F	3.31 3.40	7.94	8.50	27.97 28.48	169.43	162.10 162.97	110.77	153.51	121.89	151.68



Scheme 2 Proposed mechanism for the formation of allylidene derivatives

The proposed mechanism of the reactions of 1-aryl-1-ferrocenylethene (**1b-d**) and 1,3-dimethylbarbituric acid (**2g**) via $Mn(OAc)_3$ is shown in **Scheme 2**. Acyclic and one-carbon extended allylidene compounds (**16, 23, 30**) are likely to occur by various reaction steps that are commonly accepted.[25] According to this mechanism, the radical intermediates **G** and **H** are formed from acetic acid and **2g** respectively via $Mn(OAc)_3$. **G** and **H** produce a new carboxylic acid (**I**). The radical intermediate **J** is formed form **I** via $Mn(OAc)_3$. The interaction of an alkene and **J** results in the formation radical intermediate **K** which is subsequently oxidized with $Mn(OAc)_3$ to carbocation **L**. Elimination of a proton gives the intermediate product (**M**). **M** is oxidized with $Mn(OAc)_3$ to give radical intermediate (**N**) and carbocation (**O**), respectively. After the elimination reaction, conjugated product (**P**) is formed.

3. Conclusions

Manganese(III) acetate mediated oxidative cyclization reactions of 1,1- and 1,2- disubstituted aryl-ferrocenyl alkenes and active methylene compounds were carried out. We have synthesized a series of ferrocenyl substituted dihydrofuran derivatives, which have biological activity potential. The radical cyclization reactions of (E)-styrylferrocene (**1a**) and active methylene compounds (**2a-g**), which are regio- and stereoselective, produced trans-5-ferrocenyl-4-phenyl-4,5-dihydrofurans as the sole product. The reaction mechanism was proposed for the formation of these products. The reactions of 1-ferrocenyl-1-aryl(heteroaryl)ethenes (**1b-e**) and active methylene compounds (**2a-f**) gave dihydrofuran and benzofuran derivatives (21 examples, up to 75 % yields). Ferrocene substituted allylidene compounds were obtained from the reactions of 1-aryl-1-ferrocenylethene (**1b-d**) and 1,3-dimethylbarbituric acid (**2g**) via $Mn(OAc)_3$, surprisingly. The oxidative cyclization reactions of ferrocenyl-aryl substituted alkenes and various active methylene compounds via $Mn(OAc)_3$ and biological activity studies are currently under investigation.

4. Experimental

General information

Active methylene compounds **2a-d** and **2g** were available as commercial products and used in highest purity. **2e-f**[26] and **1a**[27] were synthesized according to the literature by the condensation reaction and Wittig reaction, respectively. **1b-e** were synthesized by dehydration reaction of the carbinoles formed from the Grignard reactions of acetylferrocene and arylmagnesium bromide. $Mn(OAc)_3{\cdot}2H_2O$ was prepared from $Mn(OAc)_2{\cdot}4H_2O$ electrochemically.[28] Thin layer chromatography (TLC) was performed on Merck aluminium-packed silica gel plates. Purification of products was performed by column chromatography (cc) on silica gel (Merck silica gel 60, 40–60 mm) or prep. TLC on silica gel Merck (PF254–366 nm). M.p. were determined on an electrothermal capillary melting point apparatus. IR spectra (ATR, ν/cm) were obtained with a Perkin-Elmer Spectrum 100 FT-IR in the 600-4000 cm^{-1} range with 4 cm^{-1} resolution. NMR spectra were recorded on a Varian Mercury-400 High performance Digital FT-NMR spectrophotometer. The mass spectra were measured on a Waters 2695 Alliance Micromass ZQ LC/ESI-MS spectrometer and an Agilent 6530 Accurate-Mass Q-TOF LC–MS instrument; m/z (rel. %). Elemental analyses were performed on a Leco CHNS-932 instrument; in %. Crystallographic data were recorded on a Bruker Kappa APEXII CCD area-detector diffractometer using Mo K_α radiation (λ=0.71073 Å) at T=296(2) K. Absorption correction by multi-scan was applied. [29] Structure was solved by direct methods and refined by full-matrix least squares against F^2 using all data. [30]

Substrates

3-Oxo-3-phenyl-propanenitrile (2e).

yield 84 %. Yellow solid, mp : 80-82 °C (lit.[31] mp: 75-76 °C). IR (ATR, ν/cm): 3072 (ArH), 2954-2924 (RH), 2256 (CN), 1685 (CO); ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 4.09 (2H, s, CH_2), 7.52 (2H,t, *J* = 7.2 Hz, Ph-H), 7.66 (1H, t, *J* = 7.2 Hz, Ph-H), 7.92 (2H, d, *J* = 7.2 Hz, Ph-H). Same to that previously reported. [31]

3-Oxo-3-(thiene-2-yl)-propanenitrile (2f).

yield 81%. Brown solid, mp : 114-115 °C (lit.[31] mp: 123-126 °C). IR (ATR, ν/cm): 3113-3091 (ArH), 2949-2918 (RH), 2256 (CN), 1664 (CO); ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 4.00 (2H, s, CH_2), 7.20 (1H, dd, *J* = 4.8, 4.4 Hz, thienyl H-4), 7.78-7.80 (2H, m, thienyl H-3 and H-5). Similar to that previously reported. [31]

(E)-Styrylferrocene (1a).
yield 76 %. Red solid, mp : 122-124 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 4.13 (5H, s), 4.27 (2H, t, J=1.6 Hz), 4.45 (2H, t, J=1.6 Hz), 6.69 (1H, d, J=16.4 Hz), 6.87 (1H, d, J=16.0 Hz), 7.19-7.23 (1H, m), 7.30-7.33 (2H, m), 7.41-7.44 (2H, m). Similar to that previously reported.[27]; HRMS (m/z): calculated for $C_{18}H_{16}Fe$ $[M]^+$: 288.06014; found: 288.06016.

General procedure for the synthesis of 1b-e

A freshly dried flask was capped with a septum and cooled under nitrogen atmosphere. Arylmagnesium bromide (1M, 10 ml) was added to the flask with a syringe. A solution of acetylferrocene (5 mmol; 1.14 g) in 10 mL THF was added dropwise to the flask, then the mixture was stirred overnight. The reaction was then, hydrolysed with saturated NH_4Cl solution in an ice-salt bath, and the solution was extracted with Et_2O (3×20 mL). The alkene was formed by dehydration of the carbinoles by HCl/water solution (2/3, v/v). The combined organic layers were neutralized with saturated $NaHCO_3$ solution, washed with H_2O, and brine. They were then dried over anhydrous Na_2SO_4, and evaporated. The product was purified by cc with hexane.

(1-Phenyl-vinyl)-ferrocene (1b).
yield 88 %. ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 4.10 (5H, s), 4.24 (2H, s), 4.35 (2H, s), 5.17 (1H, s), 5.53 (1H, s), 7.32-7.38 (3H, m), 7.47 (2H, d, J=6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 67.79(CH*2), 68.74(CH*2), 69.67(CH*5), 84.88(C), 111.54(CH_2), 127.38(CH*2), 127.98(CH*2), 128.11(CH), 142.02(C), 147.62(C). Similar to that previously reported.[32]; HRMS (m/z): calculated for $C_{18}H_{16}Fe$ $[M]^+$: 288.06014; found: 288.06026.

[1-(4-Methyl-phenyl)-vinyl]-ferrocene (1c).
yield 83 %. IR (KBr, ν/cm^{-1}): 3086, 2922, 2860, 1700, 1574, 1408, 1368, 792; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.39 (3H, s), 4.10 (5H, s), 4.24 (2H, s), 4.35 (2H, s), 5.15 (1H, s), 5.50 (1H, s), 7.16 (2H, d, J=7.6 Hz), 7.37 (2H, d, J=7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.16(CH_3), 67.78(CH*2), 68.61(CH*2), 69.61(CH*5), 84.98(C), 111.08(CH_2), 127.93(CH*2), 128.60(CH*2), 137.02(C), 139.06(C), 147.34(C); HRMS (m/z): calculated for $C_{19}H_{18}Fe$ $[M]^+$: 302.07579; found: 302.07585

[1-(4-Fluorophenyl)-vinyl]-ferrocene (1d).
yield 56 %. IR (KBr, ν/cm^{-1}): 3096, 2922, 2862, 1684, 1594, 1456, 920, 786; ^{1}H-NMR (400 MHz, CDCl$_3$, δ) : 4.10 (5H, s), 4.25 (2H, s), 4.32 (2H, s), 5.14 (1H, s), 5.52 (1H, s), 7.00-7.10 (2H, m), 7.40-7.47 (2H, m); ^{13}C-NMR (100 MHz, Acetone-D$_6$, δ) : 68.41(CH*2), 69.67(CH*2), 70.40(CH*5), 85.50(C), 112.03(CH$_2$), 115.57(CH*2, d, ^{2}J=21.3 Hz), 130.72(CH*2, d, ^{3}J=7.6 Hz), 139.16 (C, d, ^{4}J=3.8 Hz), 147.66(C), 163.15(C, d, ^{1}J=242.3 Hz); ^{19}F-NMR (376 MHz, Acetone-D$_6$, δ): -116.71; HRMS (m/z): calculated for $C_{18}H_{15}FFe$ [M]$^+$: 306.05072; found: 306.05088.

[1-(Thiene-2-yl)-vinyl]-ferrocene (1e).
yield 79 %. IR (KBr, ν/cm): 3092, 2914, 2856, 1698, 1416, 1360, 1030, 820, 710; ^{1}H-NMR (400 MHz, CDCl$_3$, δ) : 4.20 (5H, s), 4.31 (2H, t, J=2.0 Hz), 4.51 (2H, t, J=2.0 Hz), 5.43 (1H, d, J=0.8 Hz), 5.48 (1H, d, J=0.8 Hz), 7.06 (1H, dd, J=4.8; 3.6 Hz), 7.27 (1H, dd, J=4.8; 0.8 Hz), 7.33 (1H, dd, J=3.6; 1.2 Hz) ; ^{13}C-NMR (100 MHz, CDCl$_3$, δ) : 67.67(CH*2), 68.68(CH*2), 69.73(CH*5), 84.82(C), 111.92(CH$_2$), 124.28(CH), 125.51(CH), 126.80(CH), 140.06(C), 143.83(C); LC-MS m/z (%) : 294 (M$^+$, % 100); HRMS (m/z): calculated for $C_{16}H_{14}FeS$ [M]$^+$: 294.01656; found: 294.01660.

General procedure for the reactions between alkenes (1a-e) and active methylene compounds (2a-g) via Mn(OAc)$_3$·2H$_2$O

A solution of Mn(OAc)$_3$·2H$_2$O (0.804 g, 3 mmol) in glacial AcOH (7.5 mL) was heated under N$_2$ at 80° C until it dissolved. Then a solution of active methylene compound (2 mmol) and alkene (1 mmol) in glacial AcOH (5 mL) was added to the mixture. Reaction was monitored by TLC. When the reaction was complete, H$_2$O was added to the mixture and extracted with CHCl$_3$ (3×20 mL). The combined organic layers were neutralized with saturated NaHCO$_3$ solution, washed with H$_2$O, dried over anhydrous Na$_2$SO$_4$, and evaporated. The products were purified by cc on silica gel or preparative layer chromatography on silica gel, eluating with hexane: AcOEt mixtures.

Physical and spectral data of products

1-[5-Ferrocenyl-2-methyl-4-phenyl-4,5-dihydrofuran-3-yl]ethanone (3)
Brown oil; yield 10 %; IR (ATR, ν/cm^{-1}): 3082, 2963, 1664, 1589, 1257, 1074, 1014, 796, 700; ^{1}H-NMR: 1.94 (3H, s), 2.39 (3H, d, J=0.8 Hz), 4.15 (5H, s), 4.16-4.23 (4H, m), 4.35 (1H, d, J=4.8 Hz), 5.22 (1H, d, J=4.8 Hz), 7.26-7.39 (5H, m); ^{13}C-NMR: 15.42(CH$_3$), 29.84(CH$_3$CO), 56.25(C4), 66.13(CH), 66.78(CH), 68.69(CH), 68.81(CH), 68.87(CH*5), 87.46(C), 89.74(C5), 116.26(C3), 127.38(CH), 127.64(CH*2), 129.12(CH*2), 143.89(C), 168.24(C2), 195.02(CO); LC-MS m/z (%) : 386 (M$^+$, % 74), 387 (MH$^+$, % 100); HRMS (m/z): calculated for $C_{23}H_{22}FeO_2$ [M]$^+$: 386.09692; found: 386.09726.

Ethyl 5-ferrocenyl-2-methyl-4-phenyl-4,5-dihydrofuran-3-carboxylate (4)
Yellow solid; yield 30 %; IR (ATR, ν/cm^{-1}): 3074, 3024, 2939, 1625, 1602, 1392, 1064, 1024, 819; ^{1}H-NMR: 1.09 (3H, t, J=7.6 Hz), 2.33 (3H, d, J=1.2 Hz), 3.96-4.08 (2H, m), 4.13 (5H, s), 4.19-4.26 (4H, m), 4.36 (1H, dd, J=5.2; 1.2 Hz), 5.29 (1H, d, J=5.2 Hz), 7.23-7.37 (5H, m); ^{13}C-NMR: 14.12(CH$_3$), 14.38(CH$_3$), 55.10(C4), 59.30(CH$_2$), 65.98(CH), 67.18(CH), 68.59(CH), 68.64(CH), 68.68(CH*5), 87.36(C), 89.15(C5), 106.91(C3), 126.80(CH), 127.51(CH*2), 128.49(CH*2), 144.23(C), 165.70(C), 167.55(C); LC-MS m/z (%) : 416 (M$^+$, % 52), 417 (MH$^+$, % 47), 399 ([MH$^+$]-H$_2$O, % 100); HRMS (m/z): calculated for $C_{24}H_{24}FeO_3$ [M]$^+$: 416.10749; found: 416.10878.

2-Ferrocenyl-6,6-dimethyl-3-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (5)
Yellow-orange solid; mp : 147.5-148.4 °C; yield 50 %; IR (ATR, ν/cm^{-1}): 3084, 2916, 2870, 1622, 1396, 823, 731; ^{1}H-NMR: 1.12 (3H, s), 1.14 (3H, s), 2.21 (2H, d, J=2.4 Hz), 2.36 (1H, dd, J=17.6; 2.0 Hz), 2.43 (1H, d, J=17.6 Hz), 4.13 (5H, s), 4.21-4.24 (4H, m), 4.44 (1H, d, J=4.8 Hz), 5.47 (1H, d, J=4.8 Hz), 7.23-7.37 (5H, m); ^{13}C-NMR: 28.74(CH$_3$), 29.22(CH$_3$), 34.42(C6), 38.28(C7), 51.42(C3), 51.61(C5), 66.12(CH), 67.90(CH), 68.92(CH*5), 69.16(CH), 69.25(CH), 86.55(C), 93.11(C2), 116.00(C), 127.25(CH), 127.47(CH*2), 129.04(CH*2), 143.16(C), 175.30(C), 194.04(CO); LC-MS m/z (%) : 426 (M$^+$, % 70), 427 (MH$^+$, % 100); HRMS (m/z): calculated for $C_{26}H_{26}FeO_2$ [M+H]$^+$: 427.1355; found: 427.13572.

2-Ferrocenyl-3-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (6)
Pale brown solid; mp : 143-144 °C; yield 28 %; IR (ATR, ν/cm^{-1}): 3074, 2937, 1689, 1625, 821, 700; ^{1}H-NMR: 2.04-2.11 (2H, m), 2.35 (2H, td, J=6.8; 2.8 Hz), 2.48 (1H, dtd, J=18.0; 6.4; 1.6 Hz), 2.60 (1H, dt, J=17.6; 5.6 Hz), 4.13 (5H, s), 4.24 (4H, m), 4.45 (1H, d, J=4.4 Hz), 5.46 (1H, d, J=5.2 Hz), 7.23-7.37 (5H, m); ^{13}C-NMR: 21.80(C6), 24.26(C7), 36.86(C5), 51.35(C3), 65.93(CH), 67.69(CH), 68.69(CH*5), 68.96(CH*2), 86.22(C), 92.57(C2), 117.15(C), 127.02(CH), 127.27(CH*2), 128.78(CH*2), 142.84(C), 176.22(C), 194.55(CO); LC-MS m/z (%) : 398 (M$^+$, % 77), 399 (MH$^+$, % 100); HRMS (m/z): calculated for $C_{24}H_{22}FeO_2$ [M+H]$^+$: 399.10420; found: 399.10740.

5-Ferrocenyl-2,4-diphenyl-4,5-dihydrofuran-3-carbonitrile (7)
Yellow-orange solid; mp : 108-109 °C; yield 24 %; IR (ATR, ν/cm): 3084, 3034, 2926, 2852, 2204, 1620, 1348, 1222, 829, 744, 702; ^{1}H-NMR: 4.13 (5H, s), 4.20-4.26 (4H, m), 4.44 (1H, d, J=6.8 Hz), 5.50 (1H, d, J=6.0 Hz), 7.30-7.41 (5H, m), 7.43-7.49 (3H, m), 8.04 (2H, dd, J=8.4, 2.0); ^{13}C-NMR: 57.21(C4), 66.35(CH), 66.78(CH), 68.87(CH*5), 68.90(CH), 69.02(CH), 84.86(C3), 86.24(C), 89.90(C5), 117.38(CN), 127.34(CH*2), 127.63(CH*2), 128.01(C), 128.14(CH), 128.85(CH*2), 129.30(CH*2), 131.70(CH), 140.45(C), 166.01(C2); LC-MS m/z (%) : 431 (M$^+$, % 100), 432 (MH$^+$, % 69); HRMS (m/z): calculated for $C_{27}H_{21}FeNO$ [M]$^+$: 431.09726; found: 431.10038.

(4R,5R)-5-Ferrocenyl-4-phenyl-2-(thiene-2-yl)-4,5-dihydrofuran-3-carbonitrile (8)
Yellow solid; mp : 143.4-143.7 ; yield 25 %; IR (ATR, ν/cm^{-1}): 3099, 2920, 2851, 2199, 1606, 1095, 1041, 815, 719, 700; ^{1}H-NMR: 4.17 (5H, s), 4.23-4.27 (4H, m), 4.41 (1H, d, J=6.0 Hz), 4.47 (1H, d, J=6.8 Hz), 7.18 (1H, dd, J=5.2; 4.0 Hz), 7.31-7.35 (3H, m), 7.39-7.42 (2H, m), 7.55 (1H, dd, J=5.2; 1.2 Hz), 7.96 (1H, dd, J=4.0, 1.2); ^{13}C-NMR: 57.15(C4), 66.38(CH), 66.65(CH), 68.74(CH), 68.89(CH*5), 69.00(CH), 82.97(C3), 86.08(C), 90.67(C5), 116.98(CN), 127.53(CH*2), 128.01(CH), 128.26(CH), 129.25(CH*2), 129.97(CH), 130.13(C), 130.25(CH), 140.21(C), 161.40(C2); LC-MS m/z (%) : 437 (M$^+$, % 100), 438 (MH$^+$, % 65); HRMS (m/z): calculated for $C_{25}H_{19}FeNOS$ [M]$^+$: 437.05368; found: 437.05764.

6-Ferrocenyl-1,3-dimethyl-7-phenyl-6,7-dihydrofuro[3,2-d]pyrimidin-2,4(1H,3H)-dione (9)
Brown solid; mp : 145 °C; yield 15 %; IR (ATR, ν/cm^{-1}): 3084, 2954, 1703, 1641, 819, 707; ^{1}H-NMR: 3.27 (3H, s), 3.38 (3H, s),

4.11 (5H, s), 4.23-4.29 (4H, m), 4.67 (1H, d, J=4.0 Hz), 5.69 (1H, d, J=4.0 Hz), 7.27-7.40 (5H, m); ^{13}C-NMR: 26.91(CH_3), 28.48(CH_3), 50.34(C7), 65.36(CH), 66.95(CH), 67.78(CH*5), 68.32(CH), 68.42(CH), 83.27(C), 90.00(C), 93.45(C6), 126.25(CH*2), 126.58(CH), 127.99(CH*2), 140.57(C), 150.86(C), 159.89(C); LC-MS m/z (%) : 442 (M^+, % 54), 443 (MH^+, % 100); HRMS (m/z): calculated for $C_{24}H_{22}FeN_2O_3$ $[M+H]^+$: 443.10526; found: 443.10902.

1-(5-Ferrocenyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)ethanone (10)

Brown solid; mp : 116.4-117 °C; yield 44%; IR (ATR, ν/cm^{-1}): 3007, 2933, 2873, 1641, 1226, 815; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 2.25 (3H, s), 2.40 (3H, s), 3.42 (1H, d, J=13.6 Hz), 3.74 (1H, d, J=14.0 Hz), 4.03 (1H, s), 4.13 (5H, s), 4.17 (3H, s), 7.20-7.34 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 14.17(CH_3CO), 28.46(CH_3), 44.63(C4), 65.15(CH), 65.88(CH), 66.91(CH), 67.48(CH), 67.71(CH*5), 88.54(C), 93.91(C5), 111.12(C3), 123.78(CH), 126.34(CH*2), 127.03(CH*2), 144.72(C), 165.05(C2), 193.00(CO); MS m/z (%) : 386 (M^+, % 100), 387 (MH^+, % 65); HRMS (m/z): calculated for $C_{23}H_{22}FeO_2$ $[M+H]^+$: 387.1042; found: 387.1044.

Ethyl 5-ferrocenyl-2-methyl-phenyl-4,5-dihydrofuran-3-carboxylate (11)

Yellow solid; mp : 102 °C; yield 47%; IR (ATR, ν/cm^{-1}): 3111, 2960, 2927, 1699, 1639, 1240, 1080, 808, 773; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 1.33 (3H, t, J=7.2 Hz), 2.43 (3H, s), 3.41 (1H, dd, J=14.4, 0.8 Hz), 3.74 (1H, dd, J=14.4, 0.8 Hz), 4.09 (1H, d, J=0.8 Hz), 4.20-4.26 [10H (2H, O-$\underline{CH_2}$-CH_3; 8H, Ferrocene C-H), m], 7.23-7.40 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 14.33(CH_3), 14.59(CH_3), 45.08(C4), 59.59(CH_2), 66.27(CH), 67.01(CH), 67.90(CH), 68.78(CH), 68.81(CH*5), 89.45(C), 95.18(C5), 101.53(C3), 124.90(CH), 127.32(CH*2), 128.07(CH*2), 146.14(C), 165.99(C), 166.46(C); MS m/z (%) : 416 (M^+, % 100); HRMS (m/z): calculated for $C_{24}H_{24}FeO_3$ $[M+H]^+$: 417.11476; found: 417.11653.

2-Ferrocenyl-6,6-dimethyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (12)

Yellow solid, mp : 133-134 °C; yield 75%; IR (ATR, ν/cm^{-1}): 3094, 2954, 2870, 1636, 1402, 1238, 820; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 1.15 (3H, s), 1.19 (3H, s), 2.30 (2H, s), 2.48 (2H, s), 3.41 (1H, d, J= 14.0 Hz), 3.71 (1H, d, J= 14.0 Hz), 3.96 (1H, s), 4.15 (6H, s), 4.20 (1H, s), 4.21 (1H, s), 7.25-7.36 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 29.11(CH_3*2), 34.35(C6), 38.28(C7), 41.35(C3), 51.29(C5), 66.41(CH), 67.60(CH), 68.41(CH), 69.07(CH), 69.13(CH*5), 91.94(C), 94.49(C2), 125.23(CH*2), 127.84(CH), 128.34(CH*2), 145.29(C), 175.05(C), 195.12(CO); MS m/z (%): 426 (M^+, % 78), 427 (MH^+, % 100); HRMS (m/z): calculated for $C_{26}H_{26}FeO_2$ $[M+H]^+$: 427.1355; found: 427.13744.

2-Ferrocenyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (13)

Yellow solid; mp : 162-163 °C; yield 67%; IR (ATR, ν/cm^{-1}): 3096, 2952, 2880, 1630, 1400, 1248, 818, 754; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 2.13 (2H, m), 2.42 (2H, td, J=6.8, 3.2 Hz), 2.60 (2H, tt, J=6.8, 1.6 Hz), 3.38 (1H, dt, J=14.0, 1.6 Hz), 3.67 (1H, dt, J=14.0, 1.6 Hz), 3.96-3.97 (1H, m), 4.14 (5H, s), 4.17-4.18 (1H, m), 4.19-4.20 (1H, m), 4.22-4.23 (1H, m), 7.25-7.35 (5H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 21.89(C6), 24.11(C7), 36.50(C5), 41.14(C3), 66.08(CH*2), 67.34(CH), 68.14(CH), 68.83(CH*5), 93.94(C), 94.26(C), 112.90(C), 125.00(CH), 127.61(CH*2), 128.11(CH*2), 145.08(C), 175.84(C), 195.47(CO); LC-MS m/z (%) : 398 (M^+, % 100), 399 (MH^+, % 93); Anal. Calcd for $C_{24}H_{22}FeO_2$: C % 72.38, H 5.57; found: C % 72.88, H 5.31.

5-Ferrocenyl-2,5-diphenyl-4,5-dihydrofuran-3-carbonitrile (14)

Orange solid; mp : 156 °C; yield 52%; IR (ATR, ν/cm^{-1}): 3105, 3066, 2202, 1624, 1259, 823, 767; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 3.53 (1H, d, J=14.4 Hz), 3.87 (1H, d, J=14.4 Hz), 4.09-4.10 (1H, m), 4.16 (5H, s), 4.22-4.23 (1H, m), 4.235-4.244 (2H, m), 7.25-7.38 (5H, m), 7.51-7.54 (3H, m), 8.12-8.14 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 46.76(C4), 66.37(CH), 66.80(CH), 68.19(CH), 68.76(CH), 68.90(CH*5), 78.67(C), 90.94(C), 93.93(C), 117.64(CN), 124.78(CH*2), 127.15(CH*2), 127.83(CH), 128.04(C), 128.29(CH*2), 128.90(CH*2), 131.52(CH), 144.86(C), 165.52(C2); LC-MS m/z (%) : 430 (M^+, % 57), 431 (MH^+, % 100); HRMS (m/z): calculated for $C_{27}H_{21}FeNO$ $[M]^+$: 431.09726; found: 431.10186.

5-Ferrocenyl-5-phenyl-2-(thien-2-yl)-4,5-dihydrofuran-3-carbonitrile (15)

Brown solid; mp : 154-155 °C; yield 48%, IR (ATR, ν/cm^{-1}): 3105, 2920, 2850, 2198, 1620, 1261, 819; ^{1}H-NMR (400 MHz, $CDCl_3$, δ) : 3.47 (1H, d, J=14.8 Hz), 3.79 (1H, d, J=14.8 Hz), 4.07-4.08 (1H, m), 4.15-4.16 (6H, m), 4.19-4.21 (2H, m), 7.16 (1H, dd, J=5.2, 4.0 Hz), 7.25-7.36 (5H, m), 7.52 (1H, dd, J=5.2, 0.8 Hz), 7.98 (1H, dd, J=4.0, 0.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ) : 46.54(C4), 66.69(CH), 66.71(CH), 68.33(CH), 68.79(CH), 69.01(CH*5), 77.126(C), 91.99(C), 93.66(C), 117.35(CN), 124.86(CH*2), 127.92(CH), 128.34(CH*2), 128.42(CH), 129.85(CH), 130.03(CH), 130.18(CH), 144.56(CH), 160.92(CH); MS m/z (%): 437 (M^+, % 100); HRMS (m/z): calculated for $C_{25}H_{19}FeNOS$ $[M+H]^+$: 438.06095; found: 438.0639.

5-[3-(Ferrocenyl)-3-phenylallyliden]-1,3-dimethyl-pyrimidin-2,4,6(1H,3H,5H)-trione (16)

yield 14 %; IR (KBr, ν/cm^{-1}): 3084, 2955, 2886, 1707, 1662, 1542, 1426, 1223, 1085, 830, 772; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 3.31 (3H, s), 3.40 (3H, s), 4.21 (5H, s), 4.63 (2H, t, J=2.0 Hz), 4.67 (2H, t, J=2.0 Hz), 7.30-7.33 (2H, m), 7.47-7.48 (3H, m), 7.98 (1H, d, J=12.8 Hz), 8.51 (1H, d, J=12.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 27.96(CH_3), 28.46(CH_3), 70.40(CH*2), 70.98(CH*5), 73.24(CH*2), 83.23(C), 110.48(C), 121.64(CH), 128.16(CH*2), 129.33(CH), 129.59(CH*2), 136.97(CH), 151.74(C), 154.09(CH), 162.33(CO), 163.01(CO), 170.93(CO); HRMS (m/z): calculated for $C_{25}H_{22}FeN_2O_3$ $[M+H]^+$: 455.10526; found: 455.10770.

1-[5-Ferrocenyl-2-methyl-5-(4-methyl-phenyl)-4,5-dihydrofuran-3-yl]ethanone (17)

Yellow-orange solid; mp : 76.2 °C; yield 48 %; IR (ATR, ν/cm^{-1}): 3095, 3010, 2924, 2866, 1668, 1597, 1244, 1141, 933, 817, 750; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.26 (3H, s), 2.31 (3H, s), 2.40 (3H, d, J=1.6 Hz), 3.42 (1H, dd, J=14.0; 1.6 Hz), 3.73 (1H, dd, J=14.0; 1.6 Hz), 4.02 (1H, d, J=1.2 Hz), 4.15 (5H, s), 4.19 (3H, s), 7.10 (2H, d, J=8.0 Hz), 7.22 (2H, d, J=8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 15.24(CH_3), 21.00(CH_3Ph), 29.49(CH_3CO), 45.60(C4), 66.22(CH), 66.98(CH), 67.93(CH), 68.52(CH), 68.76(CH*5), 89.61(C), 95.07(C5), 112.19(C3), 124.80(CH*2), 128.73(CH*2), 137.11(C), 142.87(C), 166.19(C2), 194.14(CO); HRMS (m/z): calculated for $C_{24}H_{24}FeO_2$ $[M+H]^+$: 401.11985; found: 401.12131.

Ethyl 5-ferrocenyl-2-methyl-5-(4-methyl-phenyl)-4,5-dihydrofuran-3-carboxylate (18)

Yellow-orange solid; mp : 135.9 °C; yield 52 %; IR (ATR, ν/cm^{-1}): 3099, 2980, 2872, 1697, 1649, 1510, 1232, 1159, 1097, 972, 812, 763, 752; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.29 (3H, t, J=7.2 Hz), 2.31 (3H, s), 2.37 (3H, t, J=1.6 Hz), 3.35 (1H, dd, J=14.0, 1.6 Hz), 3.67 (1H, dd, J=14.0, 1.6 Hz), 4.03 (1H, d, J=1.2 Hz), 4.16-4.22 [10H (2H, O-$\underline{CH_2}$-CH_3; 8H, Ferrocene C-H), m], 7.09 (2H, d, J=8.0 Hz), 7.22 (2H, d, J=8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 14.29(CH_3), 14.51(CH_3), 20.99(CH_3CO), 44.92(C4), 59.54(CH_2), 66.25(CH), 67.01(CH), 67.84(CH), 68.42(CH), 68.78(CH*5), 89.40(C), 95.26(C5), 101.45(C3), 124.81(CH*2), 128.68(CH*2), 136.95(C), 143.19(C), 166.06(C), 166.47(C); LC-MS m/z (%) : 430 (M^+, % 82), 431 (MH^+, % 100); HRMS (m/z): calculated for $C_{25}H_{26}FeO_3$ $[M]^+$: 430.12314; found: 430.12770.

2-Ferrocenyl-2-(4-methyl-phenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (19)

Yellow solid; mp : 167.5 °C; yield 50 %; IR (ATR, ν/cm^{-1}): 3103, 2927, 2866, 1624, 1508, 1402, 1236, 812, 738; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.14 (3H, s), 1.19 (3H, s), 2.29 (2H, s), 2.32 (3H, s), 2.44 (2H, s), 3.38 (1H, d, J= 14.0 Hz), 3.67 (1H, dt, J= 14.0, 1.6 Hz), 3.94-3.95 (1H, m), 4.15 (5H, s), 4.18-4.22 (3H, m), 7.11 (2H, d, J=8.0 Hz), 7.22 (2H, d, J=8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.00(CH_3Ph), 28.84(CH_3*2), 34.10(C6), 38.03(C7), 40.99(C3), 50.97(C5), 66.13(CH), 67.38(CH), 68.13(CH), 68.79(CH), 68.85(CH*5), 94.27(C), 94.36(C), 111.34(C), 124.94(CH/2), 128.75(CH*2), 137.34(C), 142.13(C), 174.81(C), 194.74(CO); LC-MS m/z (%) : 440 (M^+, % 44), 441 (MH^+, % 100); HRMS (m/z): calculated for $C_{27}H_{28}FeO_2$ $[M+H]^+$: 441.15115; found: 441.15551.

2-Ferrocenyl-2-(4-methyl-phenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (20)

Yellow solid; mp : 140-141 °C; yield 41 %; IR (ATR, ν/cm^{-1}): 3101, 2974, 2870, 1625, 1510, 1402, 1180, 815, 752; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.09-2.15 (2H, m), 2.32 (3H, s), 2.42 (2H, td, J=6.4; 2.8 Hz), 2.58 (2H, t, J=6.4 Hz), 3.38 (1H, d, J=14.0 Hz), 3.66 (1H, dt, J=14.0; 2.0 Hz), 3.95-3.96 (1H, m), 4.14 (5H, s), 4.17-4.19 (2H, m), 4.21-4.23 (1H, m), 7.11 (2H, d, J=8.4 Hz), 7.22 (2H, d, J=8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.00(C6), 21.89(CH_3), 24.14(C7), 36.50(C5), 41.06(C3), 66.09(CH), 67.34(CH), 68.11(CH), 68.78(CH), 68.81(CH*5), 93.98(C), 94.38(C), 112.93(C), 124.98(CH*2), 128.75(CH*2), 137.36(C), 142.17(C), 175.86(C), 195.47(CO); HRMS (m/z): $C_{25}H_{24}FeO_2$ calculated for $[M+H]^+$: 413.11985; found: 413.12185.

5-Ferrocenyl-2-phenyl-5-(4-methyl-phenyl)-4,5-dihydrofuran-3-carbonitrile (21)

Yellow-orange solid; mp : 145.8 °C; yield 46 %; IR (ATR, ν/cm^{-1}): 3089, 3026, 2964, 2922, 2200, 1625, 1575, 1259, 1103, 1026, 812, 759; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.32 (3H, s), 3.52 (1H, d, J=14.4 Hz), 3.85 (1H, d, J=14.8 Hz), 4.07-4.08 (1H, m), 4.16 (5H, s), 4.22-4.24 (3H, m), 7.12 (2H, d, J=8.0 Hz), 7.24 (2H, d, J=7.6 Hz), 7.50-7.53 (3H, m), 8.10-8.13 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.03(CH_3), 46.73(C4), 66.38(CH), 66.79(CH), 68.14(CH), 68.70(CH), 68.87(CH*5), 78.64(C), 90.97(C5), 94.04(C3), 117.69(CN), 124.75(CH*2), 127.15(CH*2), 128.11(C), 128.85(CH*2), 128.91(CH*2), 131.45(CH), 137.60(C), 141.97(C), 165.52(C2); HRMS (m/z): $C_{28}H_{23}FeNO$ calculated for $[M+H]^+$: 446.12018; found: 446.12274.

5-Ferrocenyl-5-(4-methyl-phenyl)-2-(thien-2-yl)-4,5-dihydrofuran-3-carbonitrile (22)

Yellow solid; mp : 135.2 °C; yield 37 %; IR (ATR, ν/cm^{-1}): 3092, 2974, 2918, 2198, 1616, 1510, 1423, 1261, 1107, 817, 732, 711; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2. 32 (3H, s), 3.48 (1H, d, J=14.4 Hz), 3.79 (1H, d, J=14.0 Hz), 4.07-4.08 (1H, m), 4.16-4.17 (6H, m), 4.21-4.22 (2H, m), 7.12 (2H, d, J=7.6 Hz), 7.18 (1H, dd, J=5.2, 3.6 Hz), 7.24 (2H, d, J=8.0 Hz), 7.54 (1H, dd, J=5.2, 1.2 Hz), 7.98 (1H, dd, J=3.6, 0.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.01(CH_3), 46.45(C4), 66.63(CH), 66.65(CH), 68.18(CH), 68.63(CH), 68.89(CH*5), 91.94(C3), 93.70(C5), 117.31(CN), 124.74(CH*2), 128.26(CH), 128.87(CH*2), 129.63(CH), 129.88(CH), 130.21(C), 137.58(C), 141.60(C), 160.86(C2); HRMS (m/z): $C_{26}H_{21}FeNOS$ calculated for $[M+H]^+$: 452.0766; found: 452.07951.

5-[3-(Ferrocenyl)-3-(p-tolyl)allyliden]-1,3-dimethyl-pyrimidin-2,4,6(1H,3H,5H)-trione (23)

Purple solid, mp : 274-275 °C; yield 17 %; IR (ATR, ν/cm^{-1}): 3101, 2960, 2926, 1716, 1656, 1539, 1409, 1303, 1222, 1083, 821, 785, 750; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.43 (3H, s), 3.31 (3H, s), 3.40 (3H, s), 4.20 (5H, s), 4.63-4.64 (2H, m), 4.66-4.67 (2H, m), 7.20 (2H, d, J=8.4 Hz), 7.26 (2H, d, J=7.6 Hz), 8.01 (1H, d, J=12.8 Hz), 8.48 (1H, d, J=13.2 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 21.39(CH_3Ph), 27.92(NCH_3), 28.43(NCH_3), 70.50(CH*2), 70.99(CH*5), 73.16(CH*2), 83.28(C), 110.22(C), 121.70(CH), 128.86(CH*2), 129.68(CH*2), 134.09(C), 139.53(C), 151.75(C), 154.35(CH), 162.34(C), 163.08(C), 171.32(C); LC-MS m/z (%) : 468 (M^+, %100), 469 (MH^+, %65); Anal. Calcd for $C_{26}H_{24}FeN_2O_3$: C % 66.68, H 5.17, N 5.98; found: C % 66.61, H 5.13, N 6.12.

1-[5-Ferrocenyl-2-methyl-5-(4-fluoro-phenyl)-4,5-dihydrofuran-3-yl]ethanone (24)

Yellow-orange solid; mp : 74.9-76.0 °C; yield 55 %; IR (ATR, ν/cm^{-1}): 3019, 1620, 1605, 1244, 1215, 934, 821; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 2.28 (3H, s), 2.41 (3H, t, J=1.2 Hz), 3.38 (1H, dd, J=14.0; 1.2 Hz), 3.74 (1H, dd, J=14.0; 1.2 Hz), 4.01 (1H, d, J=1.6 Hz), 4.13 (1H, d, J=1.6 Hz), 4.15 (5H, s), 4.19-4.21 (2H, m), 6.96-7.01 (2H, m), 7.28-7.32 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 15.19(CH_3), 29.48(CH_3CO), 45.68(C4), 66.15(CH), 66.87(CH), 68.06(CH), 68.65(CH), 68.78(CH*5), 89.20(C), 94.79(C5), 112.20(C3), 114.86 (CH*2, d, ^{2}J=21.3 Hz), 126.65 (CH*2, d, ^{3}J=8.4 Hz), 141.65 (C, d, ^{4}J=3.9 Hz), 161.93 (C, d, ^{1}J=245.3 Hz), 165.93(C2), 194.05(CO); ^{19}F-NMR (376 MHz, $CDCl_3$, δ): -115.20; HRMS (m/z): $C_{23}H_{21}FFeO_2$ calculated for $[M+H]^+$: 405.09478; found: 405.09600.

Ethyl 5-ferrocenyl-5-(4-fluoro-phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (25)

Yellow solid; mp : 97.5 °C; yield 57 %; IR (ATR, ν/cm^{-1}): 3095, 2970, 2928, 1697, 1645, 1508, 1271, 1155, 1146, 1085, 1072, 968, 833, 808, 754; ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 1.31 (3H, t, J=7.2 Hz), 2.39 (3H, s), 3.32 (1H, dd, J=14.4, 1.6 Hz), 3.69 (1H, dd, J=14.4, 1.6 Hz), 4.03 (1H, d, J=1.6 Hz), 4.14-4.24 [10H (2H, O-$\underline{CH_2}$-CH_3; 8H, Ferrocene C-H), m], 6.94-7.00 (2H, m), 7.28-7.33 (2H, m); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 14.26(CH_3), 14.50(CH_3), 45.05(C4), 59.65(CH_2), 66.17(CH), 66.90(CH), 67.96(CH), 68.55(CH), 68.79(CH*5), 89.02(C), 94.94(C5), 101.49(C3), 114.79 (CH*2, d, ^{2}J=21.4 Hz), 126.66 (CH*2, d, ^{3}J=7.6 Hz), 141.97 (C, d, ^{4}J=3.1 Hz), 161.89 (C, d, ^{1}J=244.6 Hz), 165.92(C), 166.28(C); ^{19}F-NMR (376 MHz, $CDCl_3$, δ): -115.45; LC-MS (m/z): 434.30 (M^+, % 100); Anal. Calcd for $C_{24}H_{23}FFeO_3$: C % 66.38, H 5.34; found: C % 66.38, H 5.034

2-Ferrocenyl-2-(4-fluoro-phenyl)-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (26)

Yellow solid; mp : 136.0 °C; yield 66 %; IR (ATR, ν/cm^{-1}): 3107, 2959, 2930, 1627, 1602, 1506, 1402, 1236, 1161, 821, 742; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 1.15 (3H, s), 1.19 (3H, s), 2.30 (2H, s), 2.45 (2H, t, J=2.0 Hz), 3.34 (1H, dt, J= 14.4, 2.0 Hz), 3.67 (1H, dt, J= 14.4, 2.0 Hz), 3.92-3.94 (1H, m), 4.13-4.15 (6H, m), 4.20-4.215 (1H, m), 4.224-4.24 (1H, m), 6.97-7.02 (2H, m), 7.28-7.33 (2H, m); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 28.81(CH$_3$), 28.83(CH$_3$), 34.12(C6), 37.98(C7), 41.15(C3), 50.94(C5), 66.09(CH), 67.24(CH), 68.26(CH), 68.88(CH*5), 68.93(CH), 93.80(C), 94.06(C), 111.26(C), 114.92 (CH*2, d, ^{2}J=21.4 Hz), 126.78 (CH*2, d, ^{3}J=7.6 Hz), 140.95 (C, d, ^{4}J=3.1 Hz), 162.03 (C, d, ^{1}J=245.4 Hz), 174.60(C), 194.70(CO); ^{19}F-NMR (376 MHz, CDCl$_3$, δ): -114.83; HRMS (m/z): C$_{26}$H$_{25}$FFeO$_2$ calculated for [M+H]$^+$: 445.12608; found: 445.12631.

2-Ferrocenyl-2-(4-fluoro-phenyl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (27)

Yellow solid; mp : 134.8 °C; yield 52 %; IR (ATR, ν/cm^{-1}): 3092, 2943, 2895, 1734, 1651, 1626, 1508, 1402, 1240, 1225, 1166, 1020, 937, 924, 812, 775; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 2.11-2.17 (2H, m), 2.43 (2H, td, J=6.8; 1.6 Hz), 2.59 (2H, t, J=6.4 Hz), 3.34 (1H, dt, J=14.4, 1.6 Hz), 3.66 (1H, dt, J=14.0; 1.6 Hz), 3.945-3.953 (1H, m), 4.14 (5H, s), 4.15-4.20 (1H, m), 4.21-4.23 (1H, m), 4.24-4.25 (1H, m), 6.96-7.01 (2H, m), 7.28-7.32 (2H, m); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 21.87(C6), 24.09(C7), 36.49(C5), 41.22(C3), 66.05(CH), 67.24(CH), 68.26(CH), 68.85(CH*5), 68.93(CH), 93.50(C), 94.12(C), 112.85(C), 114.92 (CH*2, d, ^{2}J=21.4 Hz), 126.83 (CH*2, d, ^{3}J=7.6 Hz), 141.00 (C, d, ^{4}J=3.8 Hz), 162.04 (C, d, ^{1}J=245.4 Hz), 175.65(C), 195.42(CO); ^{19}F-NMR (376 MHz, CDCl$_3$, δ): -114.83; HRMS (m/z): C$_{24}$H$_{21}$FFeO$_2$ calculated for [M+H]$^+$: 417.09478; found: 417.09613.

5-Ferrocenyl-5-(4-fluoro-phenyl)-2-phenyl-4,5-dihydrofuran-3-carbonitrile (28)

Yellow solid; mp : 159.8 °C; yield 45 %; IR (ATR, ν/cm^{-1}): 3084, 2922, 2854, 2201, 1606, 1607, 1508, 1258, 1215, 1153, 974, 910, 823, 789, 768; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.48 (1H, d, J=14.8 Hz), 3.87 (1H, d, J=14.4 Hz), 4.07-4.08 (1H, m), 4.16 (5H, s), 4.20-4.21 (1H, m), 4.25-4.26 (2H, m), 6.97-7.02 (2H, m), 7.30-7.34 (2H, m), 7.50-7.54 (3H, m), 8.01-8.12 (2H, m); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 46.77(C4), 66.31(CH), 66.75(CH), 68.30(CH), 68.89(CH), 68.93(CH*5), 78.69(C), 90.57(C5), 93.75(C3), 115.13 (CH*2, d, ^{2}J=22.1 Hz), 117.46(CN), 126.67 (CH*2, d, ^{3}J=7.6 Hz), 127.12(CH*2), 127.91(C), 128.94(CH*2), 131.61(CH), 140.78 (C, d, ^{4}J=3.0 Hz), 162.16 (C, d, ^{1}J=246.2 Hz), 165.41(C2); ^{19}F-NMR (376 MHz, CDCl$_3$, δ): -114.39; HRMS (m/z): C$_{27}$H$_{20}$FFeNO calculated for [M+H]$^+$: 450.09511; found: 450.09711.

5-Ferrocenyl-5-(4-fluoro-phenyl)-2-(thien-2-yl)-4,5-dihydrofuran-3-carbonitrile (29)

Yellow solid; mp : 103.0 °C; yield 43 %; IR (ATR, ν/cm^{-1}): 3101, 3076, 2199, 1612, 1510, 1423, 1261, 1217, 947, 833, 815, 783; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.45 (1H, d, J=14.4 Hz), 3.81 (1H, d, J=14.4 Hz), 4.07-4.08 (1H, m), 4.14-4.16 (6H, m), 4.23-4.24 (2H, m), 6.98-7.02 (2H, m), 7.19 (1H, dd, J=4.8, 4.0 Hz), 7.30-7.34 (2H, m), 7.56 (1H, dd, J=5.2, 1.2 Hz), 7.99 (1H, dd, J=4.0, 1.2 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 46.52 (C4), 66.57(CH), 66.65(CH), 68.37(CH), 68.84(CH), 68.97(CH*5), 91.57(C), 93.45(C), 115.14 (CH*2, d, ^{2}J=21.4 Hz), 117.12(CN), 126.69 (CH*2, d, ^{3}J=8.4 Hz), 128.40(CH), 129.85(CH), 130.01(C), 130.06(CH), 140.46 (C, d, ^{4}J=3.0 Hz), 160.79(C2), 162.18 (C, d, ^{1}J=245.4 Hz); ^{19}F-NMR (376 MHz, CDCl$_3$, δ): -114.26; HRMS (m/z): C$_{25}$H$_{18}$FFeNOS calculated for [M+H]$^+$: 456.0515; found: 456.0527.

5-[3-Ferrocenyl-3-(4-fluorophenyl)-allyliden)-1,3-dimethylpyrimidin-2,4,6(1H,3H,5H)-trione (30)

yield 15 %; IR (KBr, ν/cm^{-1}): 3074, 3016, 2952, 1670, 1596, 1516, 1432, 1376, 1088, 834, 756; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.31 (3H, s), 3.40 (3H, s), 4.20 (5H, s), 4.60 (2H, d, J=2.0 Hz), 4.68 (2H, d, J=2.0 Hz), 7.15-7.19 (2H, m), 7.26-7.33 (2H, m), 7.94 (1H, d, J=12.8 Hz), 8.50 (1H, d, J=12.8 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 27.97(CH$_3$), 28.48(CH$_3$), 70.33(CH*2), 70.99(CH*5), 73.29(CH*2), 83.19(C), 110.77(C), 115.41 (CH*2, d, ^{2}J=22.1 Hz), 121.89(CH), 131.44 (CH*2, d, ^{3}J=8.3 Hz), 132.98(C), 151.68(C), 153.51(CH), 162.10(CO), 162.97(CO), 163.43 (C, d, ^{1}J=231.6 Hz), 169.43(CO); LC-MS m/z (%) : 472 (M$^+$, %100), 473 (MH$^+$, %72); Anal. Calcd for C$_{25}$H$_{21}$FFeN$_2$O$_3$: C % 63.58, H 4.48, N 5.93; found: C % 63.05, H 4.21, N 5.67.

2-Ferrocenyl-6,6-dimethyl-2-(thien-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (31)

Brown solid; mp : 78.0 °C; yield 50 %; IR (ATR, ν/cm^{-1}): 3095, 2956, 2868, 1737, 1629, 1398, 1228, 817, 750, 700; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 1.17 (6H, s), 2.31 (2H, s), 2.44 (2H, s), 3.65 (2H, s), 4.20-4.26 (9H, m), 6.88-6.92 (2H, m), 7.21 (1H, d, J= 4.4 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 28.87(CH$_3$*2), 34.13(C6), 38.09(C7), 42.15(C3), 51.45(C5), 67.03, 68.70, 69.01(CH*5), 92.31(C), 93.14(C), 124.24(CH), 124.93(CH), 126.39(CH), 148.94(C), 174.52(C), 194.02(CO); HRMS (m/z): C$_{24}$H$_{24}$FeO$_2$S calculated for [M+H]$^+$: 433.09192; found: 433.09318.

5-Ferrocenyl-2-phenyl-5-(thien-2-yl)-4,5-dihydrofuran-3-carbonitrile (32)

Orange solid; mp : 108.0 °C; yield 54 %; IR (ATR, ν/cm^{-1}): 3088, 3012, 2929, 2202, 1622, 1255, 975, 819,750; ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 3.63 (1H, d, J=14.8 Hz), 3.90 (1H, d, J=14.8 Hz), 4.08-4.09 (1H, m), 4.18 (5H, s), 4.23-4.25 (1H, m), 4.25-4.27 (1H, m), 4.32-4.34 (1H, m), 6.90-6.93 (2H, m), 7.21 (1H, dd, J=4.8; 1.2 Hz), 7.45-7.50 (3H, m), 8.04-8.07 (2H, m); ^{13}C-NMR (100 MHz, CDCl$_3$, δ): 47.45(C4), 66.64(CH), 66.88(CH), 68.49(CH), 68.81(CH), 69.06(CH*5), 78.23(C), 89.32(C5), 92.85(C3), 117.44(CN), 124.34(CH), 125.19(CH), 126.55(CH), 127.24(CH*2), 127.97(C), 128.85(CH*2), 131.56(CH), 148.43(C), 165.23(C2); HRMS (m/z): C$_{25}$H$_{19}$FeNOS calculated for [M]$^+$: 437.05368; found: 437.05688.

5-Ferrocenyl-2,5-di(thien-2-yl)-4,5-dihydrofuran-3-carbonitrile (33)

Orange solid; mp : 63.1-64.0 °C; yield 52 %; IR (ATR, ν/cm^{-1}): 3097, 2970, 2927, 2198, 1614, 1215, 819, 702; ^{1}H-NMR (400 MHz, Acetone-D$_6$, δ): 3.72 (1H, d, J=14.8 Hz), 4.02 (1H, d, J=14.8 Hz), 4.13-4.18 (1H, m), 4.24 (5H, s), 4.28-4.30 (1H, m), 4.31-4.32 (1H, m), 4.40-4.41 (1H, m), 6.99 (1H, dd, J=5.2; 3.6 Hz), 7.10 (1H, dd, J=3.2; 1.2 Hz), 7.28 (1H, dd, J=5.2; 4.0 Hz), 7.41 (1H, dd, J=5.2; 1.6 Hz), 7.81 (1H, dd, J=5.2; 0.8 Hz), 7.94 (1H, dd, J=4.0; 1.2 Hz); ^{13}C-NMR (100 MHz, Acetone-D$_6$, δ): 47.34(C4), 67.51(CH), 68.01(CH), 69.32(CH), 69.66(CH), 69.85(CH*5), 78.70(C), 91.39(C), 93.34(C), 117.28(CN), 125.49(CH), 126.27(CH), 127.46(CH), 129.23(CH), 130.72(CH), 130.85(C), 131.33(CH), 149.01(C), 160.72(C2); HRMS (m/z): C$_{23}$H$_{17}$FeNOS$_2$ calculated for [M]$^+$: 443.0101; found: 443.01301.

Acknowledgements

We gratefully acknowledge financial support from the Scientific and Technical Research Council of Turkey (TUBITAK) (No: 115Z079).

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24) **CCDC**-1565371 and 1565372 contain the supplementary crystallographic data for the structures **8** and **23**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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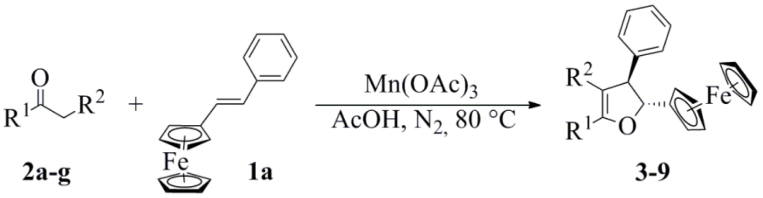
Supplementary Material

NMR spectra of synthesized compounds; ORTEP view, crystallographic data and explanations for compounds **8** and **23** (PDF)

TABLES

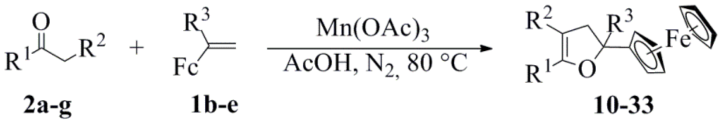
Table 5 Products of the oxidative cyclization reactions of **1a** with **2a-g** via $Mn(OAc)_3$[a].



Entry	Active Methylene	Time (min)	Product R^1	Product R^2	Yield, %[b]
1	**2a**	20	CH_3	$COCH_3$	10 (**3**)
2	**2b**	25	CH_3	COOEt	30 (**4**)
3	**2c**	14	$CH_2C(CH_3)_2CH_2CO$		50 (**5**)
4	**2d**	20	$CH_2CH_2CH_2CO$		28 (**6**)
5	**2e**	27	C_6H_5	CN	24 (**7**)
6	**2f**	32	Thien-2-yl	CN	25 (**8**)
7	**2g**	22	$N(CH_3)CON(CH_3)CO$		15 (**9**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1a-e**), active methylene (**2a-f**) and $Mn(OAc)_3$ in AcOH at 80 °C;
[b] : Isolated yield based on alkene

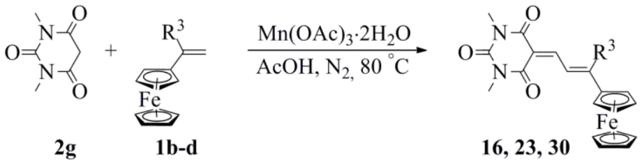
Table 6 Products of the oxidative cyclization reactions of **1b-e** with **2a-f** via $Mn(OAc)_3$[a].



Entry	Active Methylene	Alkene	Time (min)	Product R^1	Product R^2	Product R^3	Yield, %[b]
1	**2a**	**1b**	5	CH_3	$COCH_3$	C_6H_5	44 (**10**)
2	**2b**	**1b**	8	CH_3	COOEt	C_6H_5	47 (**11**)
3	**2c**	**1b**	5	$CH_2C(CH_3)_2CH_2CO$		C_6H_5	75 (**12**)
4	**2d**	**1b**	5	$CH_2CH_2CH_2CO$		C_6H_5	67 (**13**)
5	**2e**	**1b**	5	C_6H_5	CN	C_6H_5	52 (**14**)
6	**2f**	**1b**	8	Thien-2-yl	CN	C_6H_5	58 (**15**)
7	**2a**	**1c**	20	CH_3	$COCH_3$	$4-CH_3-C_6H_4$	48 (**17**)
8	**2b**	**1c**	20	CH_3	COOEt	$4-CH_3-C_6H_4$	52 (**18**)
9	**2c**	**1c**	10	$CH_2C(CH_3)_2CH_2CO$		$4-CH_3-C_6H_4$	50 (**19**)
10	**2d**	**1c**	10	$CH_2CH_2CH_2CO$		$4-CH_3-C_6H_4$	41 (**20**)
11	**2e**	**1c**	17	C_6H_5	CN	$4-CH_3-C_6H_4$	46 (**21**)
12	**2f**	**1c**	20	Thien-2-yl	CN	$4-CH_3-C_6H_4$	37 (**22**)
13	**2a**	**1d**	14	CH_3	$COCH_3$	$4-F-C_6H_4$	55 (**24**)
14	**2b**	**1d**	14	CH_3	COOEt	$4-F-C_6H_4$	57 (**25**)
15	**2c**	**1d**	10	$CH_2C(CH_3)_2CH_2CO$		$4-F-C_6H_4$	66 (**26**)
16	**2d**	**1d**	10	$CH_2CH_2CH_2CO$		$4-F-C_6H_4$	52 (**27**)
17	**2e**	**1d**	9	C_6H_5	CN	$4-F-C_6H_4$	45 (**28**)
18	**2f**	**1d**	9	Thien-2-yl	CN	$4-F-C_6H_4$	43 (**29**)
19	**2c**	**1e**	45	$CH_2C(CH_3)_2CH_2CO$		Thien-2-yl	50 (**31**)
20	**2e**	**1e**	44	C_6H_5	CN	Thien-2-yl	54 (**32**)
21	**2f**	**1e**	28	Thien-2-yl	CN	Thien-2-yl	52 (**33**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1a-e**), active methylene (**2a-f**) and $Mn(OAc)_3$ in AcOH at 80 °C; [b] : Isolated yield based on alkene; Fc: Ferrocenyl

Table 7 Products of the oxidative cyclization reactions of **1b-d** with **2g** via $Mn(OAc)_3$[a].

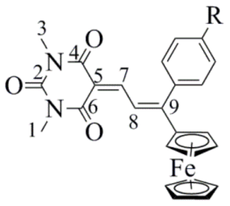


2g **1b-d** **16, 23, 30**

Entry	Alkene	Time (min)	R^3	Yield, %[b]
1	**1b**	4	C_6H_5	14 (**16**)
2	**1c**	20	$4\text{-}CH_3\text{-}C_6H_4$	17 (**23**)
3	**1d**	10	$4\text{-F-}C_6H_4$	15 (**30**)

[a] : All the reactions were carried out in a 1 : 2 : 3 molar ratio of alkene (**1b-d**), active methylene (**2g**) and $Mn(OAc)_3$ in AcOH at 80 °C; [b] : Isolated yield based on alkene

Table 8 NMR chemical shifts of enumerated atoms of **16, 23, 30**

	Compound	R	Atom Numbers									
			^{1}H-NMR (δ)			^{13}C-NMR (δ)						
			1/3	7	8	1/3	2	4/6	5	7	8	9
	**16**	H	3.31 3.40	7.98	8.51	27.96 28.46	170.93	162.33 163.01	110.48	154.09	121.64	151.74
	23	CH_3	3.31 3.40	8.01	8.48	27.92 28.43	171.32	162.34 163.08	110.22	154.35	121.70	151.75
	30	F	3.31 3.40	7.94	8.50	27.97 28.48	169.43	162.10 162.97	110.77	153.51	121.89	151.68

FIGURES

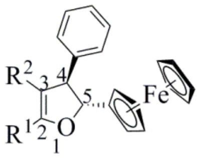


Figure 4 Enumerated structure of **3-9**

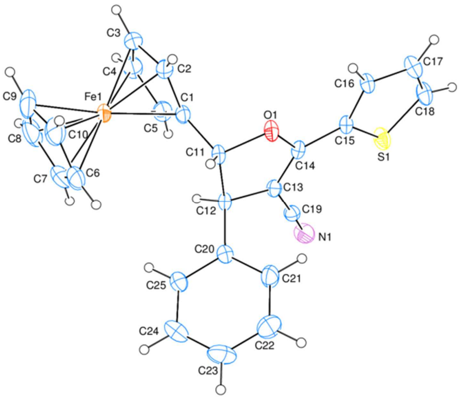


Figure 5 The molecular entities of compound **8**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

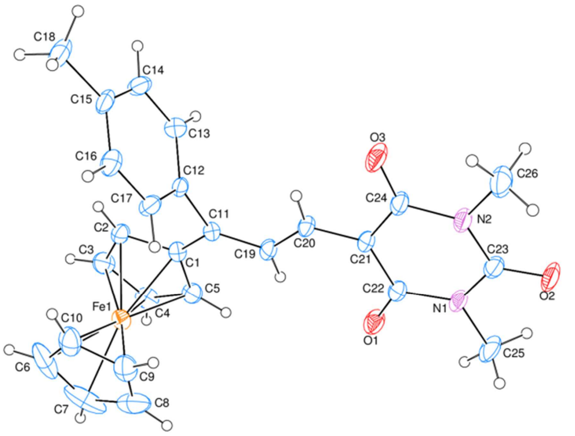
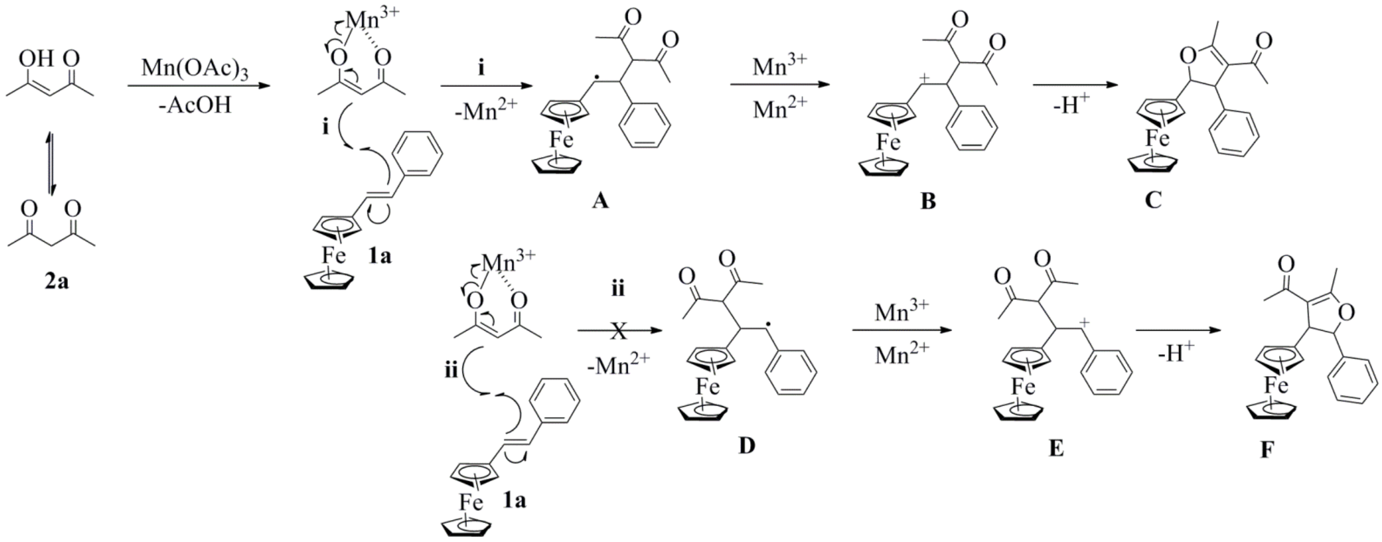
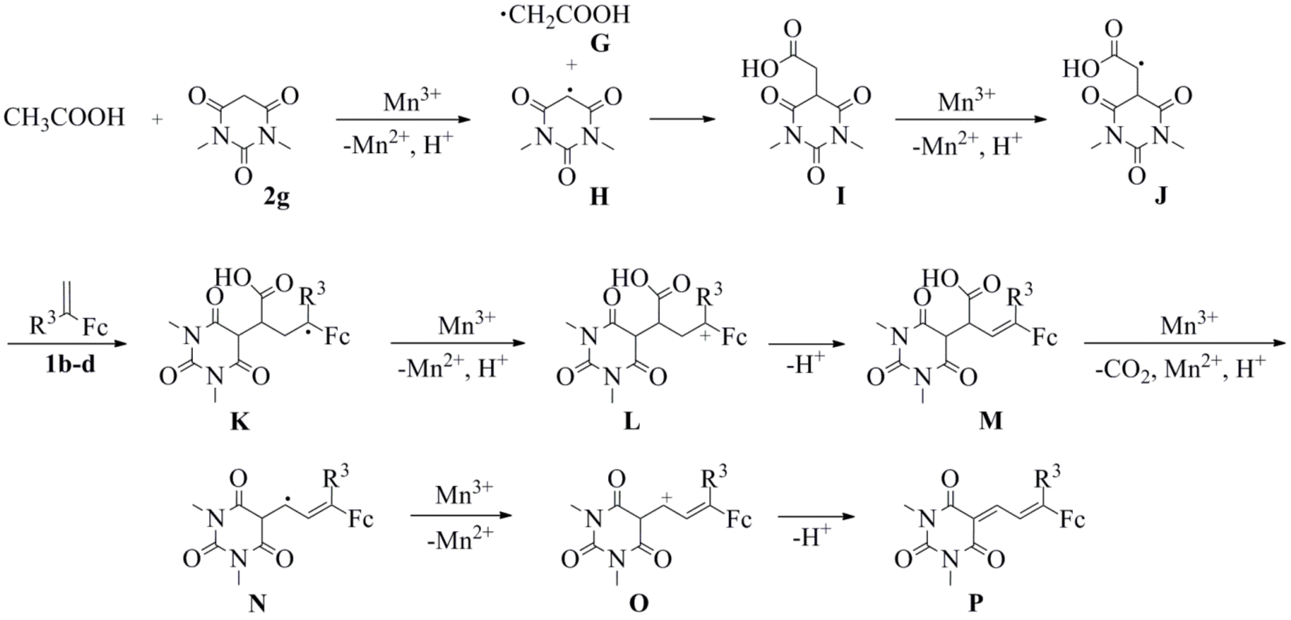


Figure 6 The molecular entities of compound **23**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

SCHEMES



Scheme 3 Proposed mechanism for the formation of ferrocenyl substituted dihydrofurans



Scheme 4 **Proposed mechanism for the formation of allylidene derivatives**