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PII: S0040-4020(14)00856-4
DOI: 10.1016/j.tet.2014.06.010
Reference: TET 25675

To appear in: *Tetrahedron*

Received Date: 11 February 2014
Revised Date: 19 May 2014
Accepted Date: 2 June 2014

Please cite this article as: Trofimov BA, Oparina LA, Tarasova OA, Artem’ev AV, Kobychev VB, Gatilov YV, Albanov AI, Gusarova NK, Tuneable superbase-catalyzed vinylation of α-hydroxyalkylferrocenes with alkynes, *Tetrahedron* (2014), doi: 10.1016/j.tet.2014.06.010.

Graphical Abstract

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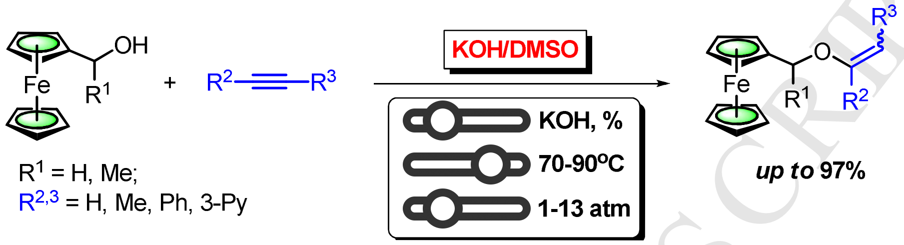

Tetrahedron
journal homepage: www.elsevier.com

Tuneable superbase-catalyzed vinylation of α-hydroxyalkylferrocenes with alkynes

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Alkynes
Enol Ethers
Ferrocene
Regioselectivity
Superbase systems

ABSTRACT

Superbase-catalyzed (KOH/DMSO suspension as a catalyst) vinylation of hydroxymethyl- and α-hydroxyethylferrocenes with terminal and internal alkynes (acetylene, propyne, phenylacetylene, 3-ethynylpyridine, 1-propyn-1-yl-benzene, diphenylacetylene) affords hitherto unknown vinyl ethers of ferrocene in 30-93% yields depending on the alkyne structure and the tuneable ratio of reactants/KOH/DMSO. The vinylation smoothly proceeds under mild conditions (70-90 °C 0.25-13 h). With unsubstituted acetylene the process is readily realized under atmospheric pressure (yield of the corresponding vinyl ethers is 81-90%) though under pressure (initial pressure at room temperature is 10-13 atm, maximum pressure is 13-16 atm at the reaction temperature) the yield is close to quantitative (93%). The synthesized compounds were characterized using ^{1}H and ^{13}C NMR, and IR spectroscopy, as well as X-ray diffraction analysis.

1. Introduction

Currently, the chemistry of ferrocene compounds continues to progress rapidly.[1] This is due to the fact that ferrocene and its numerous derivatives are widely used in various fields such as catalysis,[2] materials science,[2,3] organometallic and bio-organometallic chemistry,[4] medicine,[5] organic synthesis.[6] Moreover, ferrocene derivatives have been extensively investigated as reversible redox couples for design of molecular sensors.[7]

The modification of ferrocene derivatives by diverse reactive, especially polymerizable functions, considerably increases their possible for applications in advanced technologies. An attractive functionalization of the ferrocene scaffold might be introduction of the enol ether moiety which possesses versatile and rich reactivity.[8] Surprisingly, until now, vinyl ethers of ferrocene alcohols remain essentially unknown, except for the single incomplete report on the synthesis of (vinyloxymethyl)ferrocene.[9] The latter was claimed to be synthesized in small yield by the reaction of hydroxymethylferrocene with acetylene in the presence of KOH (28 mol %) at 130-140 °C in the absence of solvent or by trans-vinylation of this ferrocene alcohol with butyl vinyl ether catalyzed by $Hg(OAc)_2$ (50-55% yield). The liquid product was characterized by incomplete description of the IR spectra, providing no reliable structural proofs.[9]

Meanwhile, the superbase catalytic systems of the type alkali metal hydroxide (alkoxide) / polar aprotic solvent (DMSO, HMPA) have allowed substantial improvements in the vinylation of alcohols, i.e. carrying out the process at much lower temperature and under atmospheric pressure (in the case of unsubstituted acetylene and propyne).[8,10] An advantage of these catalysts is their tuneability, i.e. the alteration of their basicity and hence catalytic activity depending on the nature and content of the alkali metal hydroxide or alkoxide and polar aprotic solvent passing through true solutions to two-phase systems (suspensions).[10] The successful adaptation of this methodology to the vinylation of ferrocene alcohols stays unclear, particularly having in mind the specific organometallic feature of the substrates.

Here we report the efficient superbase-catalyzed direct vinylation of ferrocene alcohols (hydroxymethyl- and α-hydroxyethylferrocenes) with diverse alkynes (acetylene, propyne, phenylacetylene, 3-ethynylpyridine, 1-propyn-1-yl-benzene, diphenylacetylene).

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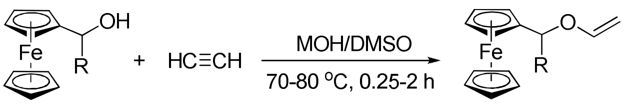
2. Results and Discussion

Vinylation with acetylene

Ferrocene alcohols **1a**,**b** react with acetylene in the KOH/DMSO system under elevated pressure in autoclave (the initial pressure at room temperature 10-13 atm, maximum pressure at the reaction temperature 13-16 atm) at 70-80 °C to afford vinyl ethers **2a**,**b** in up to 93% yield (Table 1).

Table 1 Vinylation of ferrocenylalkanols **1a**,**b** with acetylene[a]



1a,b

2a,b
36-93%

R = H (**1a, 2a**), Me (**1b, 2b**)

Entry	Alcohol	MOH (mol%)	T, °C	Time, h	Product, yield (%)[b]
1	**1a**	KOH (100)	80	0.25	**2a**, 58
2	**1a**	KOH (100)	70-74	2	**2a**, 65
3	**1a**	KOH (50)	70	1	**2a**, 70
4	**1a**	KOH (10)	70	1	**2a**, 81
5	**1b**	KOH (10)	70	0.75	**2b**, 93
6	**1b**	NaOH (10)	70	1	**2b**, 36[c]

[a] Reactions were carried out on 30-mmol scale (0.6 mol/L), with the mentioned amount of MOH in DMSO (50 mL); initial pressure of acetylene at ambient temperature was 10-13 atm.
[b] Isolated yields after chromatographic purification.
[c] Conversion of alcohol **1b** being 41%.

The best results were achieved with 10 mol% KOH at 70 °C (81% and 93% yields for **2a** and **2b**, respectively). Noteworthy, the progressive increase of the KOH content to 100 mol% decreases the yields of the target products (Entries 1-3 in Table 1), apparently due to the resinification processes (tar formation). Under similar conditions, the less basic NaOH/DMSO system allows vinyl ether **2b** to be synthesized in 36% yield only, conversion of the starting alcohol **1b** being 41% (Entry 6 in Table 1).

It is well-known that for safety reasons and engineering complications, pressure is a major challenge for the widespread application of acetylene-based syntheses both in laboratories and industry. Therefore, we have spent a lot of efforts to accomplish the vinylation of ferrocene alcohols at atmospheric pressure. Eventually, we have elaborated the synthetically and technologically feasible procedure for the synthesis of vinyl ethers **2a**,**b** in a flow reactor avoiding the neat for pressurized acetylene. According to this protocol, acetylene is passed through a suspension of KOH/DMSO containing ferrocenyl alcohol (**1a**,**b**: KOH molar ratio = 1:1, concentration of **1a**,**b** and KOH = 0.5 mol/L) at 80 °C for 2 h. The yields were 81 and 90% for **2a** and **2b**, respectively.

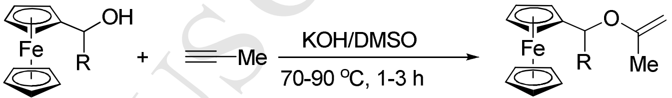
It should be underlined that ferrocene alcohols **1a**,**b** (Table 1) are vinylated at a lower temperature and faster than other alcohols, e.g. methanol,[11] prop-2-en-1-ol[12] and furan-2-ylmethanol.[13] Another interesting feature of the vinylation of ferrocene alcohols is that normally, secondary alcohols add to acetylene in the presence of bases much slower than primary alcohols.[14] In the case of ferrocene alcohols **1a**,**b** the opposite is true.

As for vinylation of tertiary ferrocene alcohols, we have shown that the heating of (1-hydroxy-1-methylethyl)ferrocene with pressured acetylene in the KOH/DMSO system (autoclave, 12 atm, 70 °C, 2 h) does not lead to the expected vinyl ether (97% of initial alcohol is recovered along with trace amounts of dehydratation product, i.e. isopropenylferrecene).

Vinylation with propyne

We have found that ferrocene alcohols **1a**,**b** react with propyne in the KOH/DMSO suspension (80 °C, 2 h) under atmospheric pressure to give 2-propenyl ethers **2c**,**d** with 100% regioselectivity, the best yields being 65 and 58%, respectively (Entries 1, 4, Table 2). The exclusive formation of 2-propenyl ethers is a common feature of nucleophilic vinylation of alcohols with propyne[15] is explained by the destabilization of the alternative carbanionic center adjacent to the electron-donating methyl substituent. However, in this case the regioselectivity is astonishing because it occurs despite obvious steric hindrance towards the nucleophilic attack of internal acetylenic carbon atom by voluminous ferrocene alkoxide anions.

Table 2 Vinylation of ferrocenylalkanols **1a**,**b** with propyne[a]



1a,b

2c,d
25-65%

R = H (**1a, 2c**), Me (**1b, 2d**)

Entry	Alcohol	KOH (mol%)	T, °C	Time, h	Conversion of **1a,b** (%)	Product, yield (%)[b]
1	**1a**	100	80	2	84	**2c**, 65
2	**1a**	50	90	3	94	**2c**, 47
3	**1a**	50	70	1	ndt	**2c**, traces
4	**1b**	100	80	2	74	**2d**, 58
5	**1b**	50	90	3	65	**2d**, 25

[a] Reactions were carried out on 5-mmol scale, with the mentioned amount of KOH in DMSO (30 mL); propyne flow rate ~ 0.5 L/h).
[b] Isolated yields after chromatographic purification.

As expected for nucleophilic addition to acetylenes, propyne displays lower reactivity than unsubstituted acetylene owing to the electron-donating effect of the methyl group. For example, under conditions of almost quantitative vinylation of alcohol **1a** with acetylene (80 °C, 2 h), the reaction with propyne is incomplete (conversion of the starting alcohol is 84%, Entry 1 in Table 2). Decreasing the amount of catalyst (from 100 to 50 mol%) and carrying out the reaction at 90 °C results in a substantial drop of the yield (47% for 3 h, Entry 2 in Table 2). At a lower reaction temperature (70 °C, 1 h, Entry 3 in Table 2), ferrocene alcohol **1a** reacts with propyne to afford the expected adduct **2d** in trace amounts (the reaction mixture contains mainly initial reagents).

Similar results have been obtained for the reaction of ferrocene alcohol **1b** with propyne (Entries 4, 5 in Table 2). However, when the reaction is performed in a closed system (0.3-L Parr-reactor, 70 °C, 1 h), ether **2d** is formed in 51% isolated yield (conversion of **1b** is 63%).

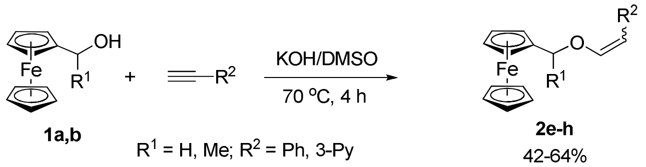
Like the vinylation of ferrocene alcohols **1a**,**b** with acetylene, their reaction with propyne is accompanied by the formation of considerable amounts of polymers containing iron, up to 12%, the content of which increases with the reaction temperature.

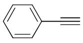
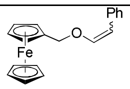
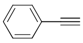
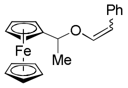
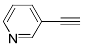
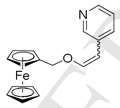
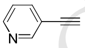
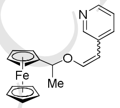
Other terminal alkyl acetylenes are found to be inactive in the reaction with the ferrocene alcohols. For example, when alcohol **1a** is heated with 1-octyne in KOH/DMSO system under close conditions (70 °C, 4 h), the formation of 1,3H-isomerization product, i.e. 2-octyne, is observed, while alcohol **1a** remains unchanged (^{13}C NMR data). The inertness of the formed 2-octyne toward alcohol **1a** can be explained by lower electrophilicity of the former in conjunction with its steric hindrance.

Vinylation with phenyl- and 3-pyridylacetylenes

In the superbase suspension KOH/DMSO, ferrocene alcohols **1a**,**b** regioselectively add to phenylacetylene and 3-ethynylpyridine (70 °C, 4 h) to deliver vinyl ethers **2e-h** (as mixtures of *E*- and *Z*-isomers) in 42-64% yields (Table 3). Like in other cases, during the reaction with phenylacetylene and 3-ethynylpyridine, considerable amounts of brown iron-containing (up to 18 mass% Fe) polymers are formed.

Table 3 Regioselective vinylation of ferrocenylalkanols **1a**,**b** with arylacetylenes[a]



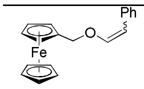
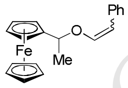
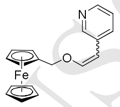
Entry	Alcohol (conversion, %)	Alkyne	Product	*Z/E* ratio[b]	Yield (%)[c]
1	**1a** (85)		 (**2e**)	68:32	64
2	**1b** (80)		 (**2f**)	68:32	58
3	**1a** (90)		 (**2g**)	57:43	56
4	**1b** (68)		 (**2h**)	56:44	42

[a] Reaction conditions: alkohol **1a**,**b** (5 mmol), alkyne (5 mmol), $KOH \cdot 0.5H_2O$ (2.5 mmol) in DMSO (10 mL), 70 °C, 4 h.
[b] Determined by ^{1}H NMR analysis of the crude reaction mixtures.
[c] Isolated yields after chromatographic purification.

The regioselectivity observed can be explained by fact that the Fukui function [calculated by B3LYP/6-31G(d,p)] f^+ for phenylacetylene C^β atom (0.1802) is larger than that for C^α atom (0.0599). Similarly, the Fukui functions for triple bonded atoms of 3-ethynylpyridine, $f^+_{C^\beta} = 0.1597$ and $f^+_{C^\alpha} = 0.0475$, predicts the preferred nucleophilic attack at the terminal position of this alkyne.

Normally, nucleophilic addition to monosubstituted acetylenes is a *trans*-selective process leading to *Z*-adducts.[16] As stated above, vinyl ethers **2e-h** are formed as the *Z*/*E*-mixtures. The isomer ratio does not noticeably depend on the reactants structure, though always being in favor of the *Z*-isomer. In this case, violation of the expected *Z*-selectivity probably results from steric encumbrance in the *Z*-isomers, i.e. bears the thermodynamic character. Indeed, heating of the *Z*- and *E*-isomers **2e** (80 °C, 3 h) does not lead to change of their ratio. Moreover, the theoretical calculations [MP2/6-311++G(d,p)//B3LYP/6-31G(d,p)] predict that the isomer ratios for products **2e-g** are close to those observable (Table 4).

Table 4 The energy differences between *Z*- and *E*-isomers and their ratios for products **2e-f** [MP2/6-311++G(d,p)//B3LYP/6-31G(d,p)][a]

Product	Δ*G*, kcal/mol	*Z/E* ratio
 (**2e**)	0.78	80:20
 (**2f**)	1.20	88:12
 (**2g**)	0.51	70:30

[a] The values are referred to 298 K, 1 atm.

For evaluation of the relative reactivity of hydroxymethylferrocene (**1a**) and methanol in their reaction with phenylacetylene, the alternative reaction method was used. It has been found that heating (70 °C, 3 h) of alcohol **1a** and methanol with phenylacetylene (1:1:1 molar ratio) in KOH(50 mol%)/DMSO system gives, according to ^{1}H NMR spectrum, adduct **2e** (*Z/E* ratio 60:40) and 1-(2-methoxyethenyl)benzene (*Z/E* ratio 55:45) in molar ratio of 59:41. This result clearly demonstrates that hydroxymethylferrocene (**1a**), despite the presence of the bulky ferrocene moiety, appears to be more reactive then methanol. In order to understanding this issue, we have calculated the HOMO energies of potassium methoxide and ferrocenylmethoxide (actual intermediates in vinylation reactions) as appropriate[17] descriptors of reactivity of the corresponding alcohols in the reaction with phenylacetylene. Following our theoretical model[17] of KOH/DMSO reactive center, we have considered complexes of potassium alcoholates with one DMSO molecule within the PCM solvation model. In the optimized complex of potassium ferrocenylmethoxide with DMSO (Figure 1), the potassium ion is coordinated to one of cyclopentadienyl rings. The HOMO energy for this complex is, by 0.24 eV, higher than that for MeOK•DMSO (–9.03 eV).[17] Consequently, considering this difference in HOMO energy between these model complexes, we suggest that alcohol **1a** should display increased reactivity with respect to metanol.

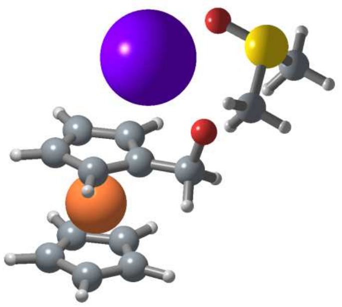
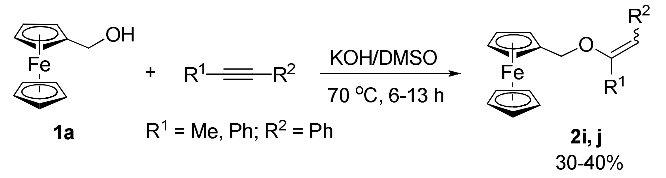


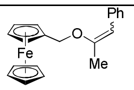
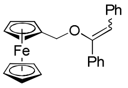
Fig. 1. Model complex of potassium ferrocenylmethoxide with one DMSO molecule [B3LYP/6-31G(d,p)].

Vinylation with 1-propyn-1-yl-benzene and diphenylacetylene

To extend the scope of the developed protocol over the aryl(alkyl)- and diarylacetylenes, we have checked vinylation of alcohol **1a** with 1-propyn-1-yl-benzene and diphenylacetylene under conditions, optimized for reaction with arylacetylenes (70 ^{o}C, 50 mol% KOH, DMSO). To our surprise, superbase system KOH/DMSO successfully catalyzes this reaction despite of sterical hindrance caused by bulky substituents within both reactants (Table 5). The vinyl ethers **2i,j** are isolated as *Z*/*E* isomer mixtures after column chromatography in 30-40% yields (non-optimized) along with unreacted alcohol **1a** (72-75% conversion).

Table 5 Regioselective vinylation of ferrocenylalkanol **1a** with disubstituted alkynes[a]



Entry	Alkyne	Product	Conversion of alcohol, %	*Z/E* ratio[b]	Yield (%)[c]
1	Ph—≡—Me	 **(2i)**	72	70:30	40
2	Ph—≡—Ph	 **(2j)**	75	52:48	30

[a] Reaction conditions: alcohol **1a** (2 mmol), alkyne (2 mmol), KOH·0.5H_2O (1 mmol) in DMSO (5 mL), 70 ^{o}C, 6-13 h.

[b] Determined by ^{1}H NMR analysis of the crude reaction mixtures.

[c] Isolated yields after chromatographic purification.

To our knowledge, the formation of ethers **2i,j** is the first example of the alcohol addition to internal alkynes under basic conditions. Now, such synthetic challenge is usually solved by using of noble metal-based catalysts, which are often too expensive. Therefore, the result obtained significantly compliments the existing conceptions on base-catalyzed addition of alcohols to C≡C bonds.

*X-ray structure of ferrocenes **2a**,**c***

The molecular structures of the (vinyloxymethyl)ferrocene (**2a**) and (prop-1-en-2-yloxymethyl)ferrocene (**2c**) have been determined by X-ray diffraction analysis (Figures 2 and 3).[18] The Cp (cyclopentadienyl) cycles in the ferrocene moieties are nearly eclipsed with twist angles of *ca.* 8.85° (**2a**) and 0.09° (**2c**). The Fe atom is coordinated to the free and substituted Cp rings at an average Cg···Fe distance of 1.65 Å, with Cg(1)···Fe···Cg(2) angles of *ca.* 179°. The lengths of the C-C and C-Fe bonds in the ferrocene sandwich fall close to standard values.[19]

Within molecule **2a** the vinyloxy fragment, OCH=CH_2, attached to methylene carbon (C6) is almost planar and adopts an s-*cis* conformation: the dihedral angle C(6)-O(1)-C(7)-C(8) takes the value -0.1(6)°. The C(7)-O(1)-C(6)-C(4) side-chain exists in the s-*trans* conformation [torsion angle of -179.2(3)°]. Finally, the dihedral angle between the average plane of the C(8)-C(7)-O(1)-C(6) chain and Cp ring is 77.50(15)°. The crystal structure of **2a** displays C-H···π and C-H···O interactions (Figure 2). In particular, intermolecular C-H···Cp short contacts between the cyclopentadienyl hydrogen, C(5)H, and the cyclopentadienyl carbon C(2), on the one hand, and between the methylene hydrogen, C(6)H, and the oxygen (O1), on the other, have been observed. These short interactions contribute to the formation of supramolecular chains between adjacent molecules along the *c* axis.

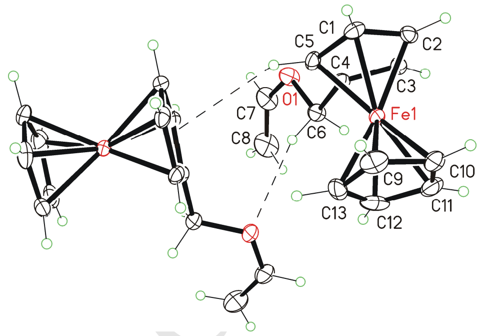


Fig. 2. Molecular structure of **2a** (30% probability thermal ellipsoids) showing the intermolecular C-H···O and C-H···π interactions. Selected bond distances (Å) and angles (°): C(7)-C(8) 1.302(6), O(1)-C(6) 1.442(4), O(1)-C(7) 1.363(5), C(4)-C(6) 1.492(4). The parameters of intermolecular interactions: C(6)···O(1) 3.506(4), H(6)···O(1) 2.57, C(5)···Cg(1) 3.777(4), H(2)···Cg(1) 2.94, C(6)-H(6)···O(1) 159, C(5)-H(2)···Cg(1) 149.

Compound **2c** shows a similar structural motif. In this structure the non-hydrogen atoms of the chain linked to the ferrocene unit are essentially coplanar. The mean plane formed by C(7), O(1), C(8), C(9) and C(10) atoms is orthogonal (90°) with respect to adjacent Cp ring. Interestingly, despite the presence of hydrogen bond donors and acceptors in **2c**, there are no short contacts within the crystal packing of the latter.

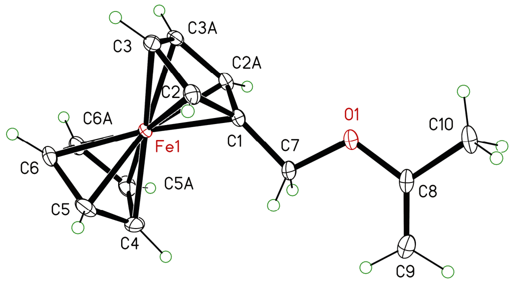


Fig. 3. Molecular structure of **2c** (30% probability thermal ellipsoids). The atoms C2A, C3A, C5A and C6A were generated by mirror plane x, 0.5-y, z. Selected bond distances (Å) and angles (°): C(8)-C(9) 1.326(3), C(8)-C(10) 1.497(3), O(1)-C(8) 1.369(2), O(1)-C(7) 1.441(2), C(7)-O(1)-C(8) 116.87, C(9)-C(8)-C(10) 125.1.

3. Conclusion

In summary, a simple, general and efficient synthesis of vinyloxy group-containing ferrocenes has been developed. Superbase systems like “alkali metal hydroxide/DMSO” have been successfully used for direct vinylation of ferrocene-based alcohols with various terminal and internal acetylenes, both under elevated and atmospheric pressure. The vinyloxy-functionalized ferrocenes thus synthesized are prospective building blocks for organic and organometallic synthesis as well as promising monomers and co-monomers for the creation of redox active polymeric materials. The synthesized ferrocenes **2a-**

j are currently being successfully employed by us for the synthesis of ferrocene-containing phosphines and phosphine chalcogenides *via* free-radical addition of diverse P-H addends to the vinyloxy groups. The detailed results of these investigations will be published elsewhere.

4. Experimental section

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX-400 spectrometer (20-25 ^{o}C) in $CDCl_3$ solution using HMDS as an internal standard. The FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer in the region of 400-4000 cm^{-1}. The electron ionization mass spectra were obtained by using Agilent 5975C MSD instrument. Samples were introduced into the source by means of the gas chromatograph Agilent 6890N through capillary column HP-5MS (30 m x 0.25 mm x 0.25 mm), the helium being the gas-carrier. The source temperature was approximately 190 °C. The elemental analyses were carried out on a Flash EA 1112 elemental analyzer. The content of iron in the reaction products was determined by energy dispersive X-ray analysis (TM 3000 Hitachi microscope equipped with SDD X-flash 430-m detector). Melting points (uncorrected) were determined on a Kofler micro-hot stage apparatus. The high-pressure experiments were carried out in a stainless steel, high-pressure batch reactor (Parr 4572, Parr Instrument Co.) equipped with an electrical heating jacket, a gas inlet, a mechanical stirrer and 4848A temperature controller. TLC analyses were carried out on Silica gel 60 F_{254} plates. Commercially available $KOH\cdot 0.5H_2O$, DMSO (with content of water up to 0.5%) were used without further purification. The alcohol **1a** was prepared from (ferrocenylmethyl)dimethylamine according to improved method.[20] The alcohol **1b** was synthesized by acylation of ferrocene (Aldrich) with acetic anhydride in presence of $BF_3\cdot Et_2O$[21] followed by reduction of the resulting acetylferrocene with $NaBH_4$.[22]

4.2. Crystallography

The crystallographic data were obtained on a Bruker Kappa Apex II CCD diffractometer using φ,ω-scans of narrow (0.5°) frames with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares method against all F^2 in anisotropic approximation using the *SHELX-97* programs set.[23] The hydrogen atoms positions were calculated with the riding model.

4.3. Theoretical calculations

All computations were performed using the Gaussian-09 package.[24] The equilibrium geometries and Gibbs free energy corrections were calculated within a density functional theory with a hybrid Becke's three-parameter exchange functional[25] and Lee, Yang, and Parr gradient-corrected correlation functional[26] using the 6-31G(d,p) basis set. The energy of most stable conformers of *Z*- and *E*-isomers was refined using the extended 6-311++G(d,p) basis set with the correlation effects included in the Møller–Plesset second order perturbation theory.

4.4. Synthesis

*4.4.1. General procedure for vinylation of ferrocenylalkanols **1a**,**b** with acetylene*

Method A (Table 1, entries 4, 5). A mixture of alcohol **1a**,**b** (30 mmol) and $KOH\cdot 0.5H_2O$ (0.20 g, 3 mmol) in DMSO (50 mL) was placed into a 0.3-L Parr reactor. The latter was fed with acetylene and then decompressed to atmospheric pressure to remove air. The autoclave was fed with acetylene again (initial pressure at ambient temperature was 13 atm) and heated (70 ^{o}C) upon stirring for 0.75 or 1 h. The reaction mixture, after cooling to room temperature, was diluted with an aqueous 1% solution of NH_4Cl (50 ml). The aqueous layer was extracted with diethyl ether (20 mL x 6), the extracts were washed with water (15 mL x 3) and dried (Na_2SO_4). Column chromatography (basic Al_2O_3, eluent hexane/diethyl ether with gradient from 1:0 to 1:1) of the crude residue after removal of the solvent gave the pure adducts **2a**,**b** and unreacted alcohols **1a**,**b**.

Method B. $KOH\cdot 0.5H_2O$ (3.25 g, 50 mmol) and DMSO (100 mL) were placed into a 3-neck flask equipped with a mechanical stirrer, reflux condenser and a tube for acetylene feeding. The suspension was vigorously stirred at 120 ^{o}C for 1 h and cooled to 80 ^{o}C. Then alcohol **1a**,**b** (50 mmol) was added and pure dry acetylene was fed into the reaction mixture at a rate of ~ 1 L/h for 2 h (the reaction was monitored by TLC). Further treatment was performed in the same way as described in method A.

*4.4.2. General procedure for the reaction of ferrocenylalkanols **1a**,**b** with propyne in the KOH/DMSO system*

Method A (Table 2, entries 1, 4). Into a glass 50-mL flask equipped with a stirrer, a reflux condencer, a thermometer, a bubbler for propyne supply and a gas outlet, alcohol **1a**,**b** (5.0 mmol), $KOH\cdot 0.5H_2O$ (0.16 g, 2.5 mmol) and DMSO (30 mL) were placed. Propyne was passed on stirring for 2 h through the reaction mixture heated up to 80 ^{o}C. After cooling to room temperature the reaction mixture was diluted with an aqueous 1% solution of NH_4Cl (50 ml) and extracted with ether (5 x 30 mL), the extracts were washed from DMSO by water (2 x 30 mL), dried over Na_2SO_4. Column chromatography (basic Al_2O_3, eluent hexane/diethyl ether with gradient from 1:0 to 3:1) of the crude residue after removal of the solvent gave the pure adducts **2c,d** and unreacted alcohols **1a**,**b**.

Method B. A 0.3-L Parr reactor was charged with alcohol **1b** (2.30 g, 10 mmol), $KOH\cdot 0.5H_2O$ (0.16 g, 2.5 mmol), and propyne (2.12 g, 53 mmol) dissolved at room temperature in DMSO (50 mL). The reaction mixture was heated at 70 ^{o}C for 1 h. Further treatment was performed in the same way as described in method *A.* As a result, 1.37 g (yield 51%) of **2d** and 0.86 g of **1b** (63% conversion) were isolated.

*4.4.3. General procedure for the reaction of ferrocenylalkanols **1a**,**b** with phenylacetylene and 3-ethynylpyridine in the KOH/DMSO system*

A mixture of alcohol **1a**,**b** (5 mmol), arylacetylene (5 mmol) and $KOH\cdot 0.5H_2O$ (0.163 g, 2.5 mmol) in DMSO (10 mL) was heated (70 ^{o}C) and stirred for 4 h. The reaction mixture, after cooling (20-25 ^{o}C), was diluted with H_2O (20 mL), neutralized with aqueous NH_4Cl and extracted with Et_2O (10 mL x 6). The organic extract was washed with H_2O (10 mL x 3) and dried (Na_2SO_4). Column chromatography (basic Al_2O_3, eluent hexane/diethyl ether with gradient from 1:0 to 1:1) of the crude residue after removal of the solvent gave the pure adducts **2e-h** and unreacted alcohols **1a**,**b**.

*4.4.4. General procedure for the reaction of ferrocenylalkanol **1a** with disubstituted alkynes in the KOH/DMSO system*

A mixture of alcohol **1a** (0.432 g, 2 mmol), 1-propyn-1-yl-benzene (0.224 g, 2 mmol) or diphenylacetylene (0.356 g, 2 mmol), $KOH\cdot 0.5H_2O$ (0.065 g, 1.0 mmol) in DMSO (5 mL) was heated (70 ^{o}C) and stirred for 6 h (in case of 1-propyn-1-yl-benzene) or 13 h (in case of diphenylacetylene). The reaction mixture, after cooling (20-25 ^{o}C), was diluted with H_2O (5 mL), neutralized with aqueous NH_4Cl and extracted with Et_2O (5 mL x 6). The organic extract was washed with H_2O (5 mL x 3) and dried (Na_2SO_4). Column chromatography (basic Al_2O_3, eluent hexane/diethyl ether with gradient from 1:0 to 1:1) of the crude residue after removal of the solvent gave the pure adducts **2i,j** and unreacted alcohol **1a** (0.120 and 0.110 g, conversion 72 and 75%, respectively).

4.5. Characterization data for compounds 2a-h

*4.5.1. Vinyloxymethylferrocene (**2a**)*

Yellow-orange solid, mp 32 °C (hexane). Yield: 5.91 g, 81% (*method A*), 9.81 g, 81% (*method B*). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 6.46 (dd, ^3J = 14.3, ^3J = 6.7 Hz, 1H, CH=), 4.46 (s, 2 H, CH_2O), 4.23 (d, ^3J = 14.3 Hz, 1H, CH_2=), overlapped with 4.22 (br. s, 2 H, 2H_α in Fc), 4.13-4.12 (m, 7H, 2H_β in Fc, C_5H_5), 3.99 (d, ^3J = 6.7 Hz, 1H, CH_2=). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 151.6 (CH=), 86.6 (CH_2=), 82.3 (C_i in Fc), 68.9 (C_β in Fc), 68.45 (C_α in Fc), 68.4 (C_5H_5), 66.6 (OCH_2). IR (KBr) 3120, 3105, 3090, 3031, 2928, 2883, 1660 sh, 1636, 1612, 1408, 1397, 1382, 1315, 1242, 1192, 1146, 1105, 1045 sh, 1039, 1027, 998, 984, 953, 928, 867, 828, 813, 749, 509, 500, 482 cm^{-1}. EI-MS: *m/z* 242 [M$^+$], 100%. Anal. Calcd for $C_{13}H_{14}FeO$ (242.09): C, 64.50; H, 5.83; Fe, 23.07. Found: C, 64.74; H, 5.86; Fe, 23.13.

*4.5.2. 1-(Vinyloxy)ethylferrocene (**2b**)*

Orange syrup. Yield: 7.12 g, 93% (*method A*), 11.51 g, 90% (*method B*). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 6.36 (dd, ^3J = 14.3, ^3J = 6.7 Hz, 1H, CH=), 4.71 (q, ^3J = 6.4 Hz, 1H, CH), 4.31 (d, ^3J = 14.3 Hz, 1H, CH_2=), 4.19-4.18 (m, 2 H, 2H_α in Fc), 4.13-4.12 (m, 7H, 2H_β in Fc, C_5H_5), 3.98 (d, ^3J = 6.7 Hz, 1H, CH_2=), 1.53 (d, ^3J = 6.4 Hz, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 150.7 (CH=), 89.1 (C_i in Fc), 88.3 (CH_2=), 74.3 (CH), 68.7 (C_5H_5), 68.0, 67.9 (C_β in Fc), 67.8, 65.9 (C_α in Fc), 20.4 (Me). IR (film) 3096, 2979, 2935, 2891, 2870, 1632, 1611, 1444, 1412, 1404, 1391, 1371, 1330, 1314, 1240, 1201 sh, 1187, 1153, 1106, 1073, 1045, 1027, 1001, 971, 948, 911, 819, 720, 697, 482 cm^{-1}. EI-MS: *m/z* 256 [M$^+$], 90%. Anal. Calcd for $C_{14}H_{16}FeO$ (256.12): C, 65.65; H, 6.30; Fe, 21.80. Found: C, 65.50; H, 6.18; Fe, 21.89.

*4.5.3. 2-(Propenyloxy)methyl]ferrocene (**2c**)*

Orange solid, mp 92-94 °C (hexane). Yield: 0.88 g, 65% (*method A*). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 4.44 (s, 2H, OCH_2), 4.25 (br. t, ^3J = 1.7 Hz, 2H, H_α in Fc), 4.14-4.13 (m, 7H, 2H_β in Fc, C_5H_5), 3.90 and 3.87 (br. s, each 1H, CH_2=), 1.81 (s, 3H, *Me*C). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 160.0 (OC=), 82.9 (C_i in Fc), 81.2 (CH_2=), 69.2 (C_α in Fc), 68.6 (C_5H_5), 68.5 (C_β in Fc), 65.8 (OCH_2), 21.2 (*Me*C). IR (film) 3114, 3101, 3083, 2991, 2956, 2922, 2850, 1655, 1648 sh, 1595, 1482, 1462, 1449, 1430, 1406, 1398, 1376, 1357, 1277, 1240, 1106, 1055, 1041, 1024, 992, 952, 931, 879, 841, 827, 798, 732, 514, 497, 485, 449 cm^{-1}. EI-MS: *m/z* 256 [M$^+$], 100%. Anal. Calcd for $C_{14}H_{16}FeO$ (256.12): C, 65.65; H, 6.30; Fe, 21.80. Found: C, 65.27; H, 6.69; Fe, 21.36.

*4.5.4. 2-[1-(Propenyloxy)ethyl]ferrocene (**2d**)*

Yellow solid, mp 83-84 °C (hexane). Yield: 0.79 g, 58% (*method A*), 1.37 g, 51% (*method B*). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 4.92 (q, ^3J = 6.2 Hz, 1H, C*H*Me), 4.21-4.20 (m, 2H, H_α in Fc), 4.13 (s, 5H, C_5H_5), 4.11-4.10 (m, 2H, H_β in Fc), 3.92 (s, 2H, CH_2=), 1.80 (s, 3H, *Me*C), 1.51 (d, ^3J = 6.2 Hz, 3H, *Me*CH). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 158.6 (OC=), 90.4 (C_i in Fc), 81.6 (CH_2=), 68.5 (C_5H_5), 70.4 (C_α in Fc), 67.8, 67.6 (C_β in Fc), 66.3 (OCHMe), 21.8 (*Me*CH), 19.4 (*Me*C). IR (film) 3113, 3102, 3090, 2989, 2981, 2941, 2922, 1649, 1584, 1478, 1443, 1430, 1408, 1373, 1318, 1274, 1241, 1207, 1105, 1098, 1069, 1046, 1027, 1002, 979, 916, 893, 832, 816, 794, 712, 545, 506, 482, 445 cm^{-1}. EI-MS: *m/z* 270 [M$^+$], 100%. Anal. Calcd for $C_{15}H_{18}FeO$ (270.15): C, 66.69; H, 6.72; Fe, 20.67. Found: C, 66.64; H, 6. 68; Fe, 20.47.

*4.5.5. 2-(Phenylethenyl)oxymethylferrocene (**2e**)*

A mixture of *Z/E* isomers in a 68:32 ratio (after chromatographic purification). Yellow powder, mp 45-47 °C (hexane). Yield: 1.02 g (64%). IR (KBr) 3096, 3083, 3049, 3021, 2976, 2925, 1650, 1641, 1597, 1492, 1460, 1446, 1419, 1382, 1347, 1322, 1306, 1283, 1240, 1219, 1199, 1162, 1127, 1104, 1078, 1028, 998, 980, 924, 821, 812, 758, 746, 713, 694, 531, 511, 481, 412, 403 cm^{-1}. EI-MS: *m/z* 318 [M$^+$], two picks (100%). Anal. Calcd for $C_{19}H_{18}FeO$ (318.19): C, 71.72; H, 5.70; Fe, 17.55. Found: C, 71.64; H, 5.86; Fe, 17.43. **(*Z*)-2e:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2 H, H_o), 7.27-7.20 (m, 2H, H_m), 7.12-6.99 (m, 1H, H_p), 6.28 (d, ^3J = 7.1 Hz, 1H, =CHO), 5.20 (d, ^3J = 7.1 Hz, 1H, =C*H*Ph), 4.71 (s, 2H, CH_2), 4.27 (t, ^3J = 1.8 Hz, 2H, H_α in Fc), 4.16 (t, ^3J = 1.8 Hz, 2H, H_β in Fc), 4.16 (s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 146.4 (OCH=), 136.1 (C_i, Ph), 128.3, 128.2 ($C_{o,m}$, Ph), 125.7 (C_p, Ph), 105.6 (Ph*C*H=), 83.1 (C_i in Fc), 71.7 (OCH_2), 69.1 (C_α in Fc), 68.8 (C_β in Fc), 68.6 (C_5H_5). **(*E*)-2e:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2 H, H_o), 7.27-7.20 (m, 2H, H_m), 7.12-6.99 (m, 1H, H_p), 7.00 (d, ^3J = 12.7 Hz, 1H, =CHO), 5.89 (d, ^3J = 12.7 Hz, 1H, =C*H*Ph), 4.64 (s, 2H, CH_2), 4.22 (t, ^3J = 1.8 Hz,, 2H, H_α in Fc), 4.16 (t, ^3J = 1.8 Hz,, 2H, H_β in Fc), 4.16 (s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 147.8 (OCH=), 136.5 (C_i, Ph), 128.6, 128.2 ($C_{o,m}$, Ph), 125.1 (C_p, Ph), 106.4 (Ph*C*H=), 82.3 (C_i in Fc), 69.1 (C_α in Fc), 68.8 (C_β in Fc), 68.7 (C_5H_5), 68.6 (OCH_2).

*4.5.6. 2-(1-[2-Phenylethenyl]oxyethyl)ferrocene (**2f**)*

A mixture of *Z/E* isomers in a 68:32 ratio (after chromatographic purification). Brown honey-like substance. Yield 0.96 g (58%). IR (film) 3086, 3056, 3023, 2979, 2930, 2856, 1648, 1599, 1573, 1493, 1448, 1413, 1391, 1373, 1329, 1318, 1264, 1241, 1219, 1200, 1152, 1106, 1096, 1062, 1043, 1025, 1001, 954, 923, 893, 820, 779, 751, 695, 557, 512, 483, 436, 403 cm^{-1}. EI-MS: *m/z* 332 [M$^+$], two picks (100%). Anal. Calcd for $C_{20}H_{20}FeO$ (332.22): C, 72.31; H, 6.07; Fe, 16.81. Found: C, 72.44; H, 5.96; Fe, 17.13. **(*Z*)-2f:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.64-7.63 (m, 2H, H_o), 7.29-7.25 (m, 2H, H_m), 7.20-7.18 (m, 1H, H_p), 6.34 (d, ^3J = 7.1 Hz, 1H, =CHO), 5.21 (d, ^3J = 7.1 Hz, 1H, =C*H*Ph), 4.73 (q, ^3J = 6.5 Hz, 1H, MeC*H*), 4.24 (br. s, 2H, H_α), 4.16 (br.s, 7H, H_β in Fc, C_5H_5), 1.62 (d, ^3J = 6.5 Hz, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 145.7 (OCH=), 136.4 (C_i, Ph), 128.2, 128.2 ($C_{o,m}$, Ph), 125.6 (C_p, Ph), 105.3 (Ph*C*H=), 89.9 (C_i in Fc), 77.8 (OCH), 68.8 (C_5H_5), 68.0 (C_β in Fc), 67.4, 66.0 (C_α in Fc), 21.6 (Me). **(*E*)-2f:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.22-7.20 (m, 2H, H_o), 7.12-7.09 (m, 3H, $H_{m,p}$), 6.94 (d, ^3J = 12.7 Hz, 1H, =CHO), 5.93 (d, ^3J = 12.7 Hz, 1H, =C*H*Ph), 4.81 (q, ^3J = 6.5 Hz, 1H, MeC*H*), 4.21 (br. s, 2H, H_α in Fc), 4.15 (br. s, 7H, H_β in Fc, C_5H_5), 1.60 (d, ^3J = 6.5 Hz, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 146.9 (OCH=), 136.7 (C_i, Ph), 128.6, 125.6 (C_p, Ph), 125.1 ($C_{o,m}$, Ph), 107.8 (Ph*C*H=), 88.9 (C_i in Fc), 76.1 (OCH), 68.8 (C_5H_5), 68.3, 68.2 (C_β in Fc), 68.0, 66.0 (C_α in Fc), 20.8 (Me).

*4.5.7. 3-{2-[(Ferrocenyl)methoxy]ethenyl}pyridine (**2g**)*

A mixture of *Z/E* isomers in a 57:43 ratio (after chromatographic purification). Reddish-brown oil, yield 0.89 g (56%). IR (film) 3091, 3040, 3031, 3022, 2987, 2933, 2873, 2858, 1649, 1633, 1586, 1566, 1480, 1457, 1425, 1413, 1382, 1353, 1348, 1332, 1286, 1239, 1196, 1146, 1124, 1104, 1077, 1040, 1023, 1001, 986 sh, 945, 932, 876, 831, 816, 800 sh, 776, 751, 710, 511, 500, 491, 484, 438 cm^{-1}. EI-MS: *m/z* 320 [M$^+$], two picks (80%). Anal. Calcd for $C_{18}H_{17}FeNO$ (319.18): C, 67.73; H, 5.37; Fe, 17.50; N, 4.39. Found: C, 67.70; H, 5.46; Fe, 17.13; N, 4.20. **(*Z*)-2g:** ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.68-8.67 (m, 1H, H-2, Py), 8.32 (dd, ^{3}J = 4.7, ^{4}J = 1.8 Hz, 1H, H-6, Py), 7.97 (dt, ^{3}J = 7.6, $^{4}J \approx {}^{4}J$ = 1.8, Hz, 1H, H-4, Py), 7.17 (dd, ^{3}J = 7.6, ^{3}J = 5.0 Hz, 1H, H-5, Py), 6.40 (d, ^{3}J = 6.9 Hz, 1H, =CHO), 5.18 (d, ^{3}J = 6.9 Hz, 1H, =C*H*Py), 4.75 (s, 2H, OCH_2), 4.27 (br. s, 2H, H_{α} in Fc), 4.20-4.19 (m, 2H, H_{β} in Fc), 4.16 (br. s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 149.4 (C-2, Py), 148.1 (C-6, Py), 146.4 (OCH=), 134.8 (C-4, Py), 132.1 (C-3, Py), 123.1 (C-5, Py), 102.0 (Py*C*H=), 101.7 (C_i in Fc), 72.0 (OCH_2), 68.9 (C_{β} in Fc), 68.6 (C_5H_5), 68.5 (C_{α} in Fc). **(*E*)-2g:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.46-4.44 (m, 1H, H-2, Py), 8.34 (dd, ^{3}J = 5.0, ^{4}J = 1.7 Hz, 1H, H-6, Py), 7.50 (br. d, ^{3}J = 7.0 Hz, 1H, H-4, Py), 7.15 (dd, ^{3}J = 7.08, ^{3}J = 5.0 Hz, 1H, H-5, Py), 7.03 (d, ^{3}J = 12.7 Hz, 1H, =CHO), 5.83 (d, ^{3}J = 12.7 Hz, 1 H, =C*H*Py), 4.67 (s, 2H, OCH_2), 4.27 (br. s, 2H, H_{α} in Fc), 4.20-4.19 (m, 2H, H_{β} in Fc), 4.16 (br. s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 149.0 (C-2, Py), 147.0 (C-6, Py), 146.8 (OCH=), 132.4 (C-3, Py), 131.5 (C-4, Py), 123.4 (C-5, Py), 102.8 (Py*C*H=), 101.7 (C_i in Fc), 69.2 (C_{β} in Fc), 69.0 (OCH_2), 68.8 (C_5H_5), 68.3 (C_{α} in Fc).

*4.5.8. 3-{2-[1-(2-Ferrocenyl)ethoxy]ethenyl}pyridine (**2h**)*

A mixture of *Z/E* isomers in a 82:18 ratio (after chromatographic purification). Reddish-brown oil, yield 0.70 g (42%). IR (film) 3094, 3036, 2979, 2935, 2896, 2869, 1647, 1586, 1564, 1477, 1428, 1404, 1375, 1330, 1315, 1276, 1241, 1221, 1198, 1153, 1126, 1106, 1098, 1069, 1042, 1024, 1002, 947, 923, 893, 816, 710, 751, 629, 511, 483, 436 cm^{-1}. EI-MS: *m/z* 333 [M^{+}], two picks (100%). Anal. Calcd for $C_{19}H_{19}FeNO$ (333.20): C, 68.49; H, 5.75; Fe, 16.76; N, 4.20. Found: C, 68.30; H, 5.59; Fe, 16.62; N, 4.12. **(*Z*)-2h:** ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.73 (br. s, 1H, H-2, Py), 8.32 (br. d, ^{3}J = 4.7 Hz, 1H, H-6, Py), 8.00 (br. d, ^{3}J = 7.9 Hz, 1H, H-4), 7.18 (dd, $^{3}J_{5\text{-}4}$ = 7.9, $^{3}J_{5\text{-}6}$ = 4.7 Hz, 1H, H-5, Py), 6.46 (d, ^{3}J = 6.3 Hz, 1H, =CHO), 5.17 (d, ^{3}J = 6.9 Hz, 1H, =C*H*Py), 4.79 (q, ^{3}J = 6.3 Hz, 1H, MeC*H*), 4.21 and 4.23 (br. s, each 1H, H_{α} in Fc), 4.17 (br. s, 2H, H_{β} in Fc), 4.15 (s, 5H, C_5H_5), 1.64 (d, ^{3}J = 6.3 Hz, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 149.4 (C-2, Py), 147.4 (C-6, Py), 146.4 (OCH=), 134.7 (C-4, Py), 131.5 (C-3, Py), 123.1 (C-5, Py), 101.7 (Py*C*H=), 89.2 (C_i in Fc), 78.3 (OCH), 68.8 (C_5H_5), 68.2 (C_{β} in Fc), 67.5, 66.0 (C_{α} in Fc), 21.5 (Me). **(*E*)-2h:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 8.44 (br. s, 1H, H-2, Py), 8.32 (d, ^{3}J = 4.9 Hz, 1H, H-6, Py), 7.47 (br. d, ^{3}J = 7.8 Hz, 1H, H-4, Py), 7.13 (dd, ^{3}J = 7.8, ^{3}J = 4.9, Hz, 1H, H-5, Py), 6.97 (d, ^{3}J = 12.7 Hz, 1H, =CHO), 5.85 (d, ^{3}J = 12.7 Hz, 1H, =C*H*Py), 4.85 (q, ^{3}J = 6.3 Hz, 1H, MeC*H*), 4.21 and 4.23 (br. s, each 1H, H_{α} in Fc), 4.17 (br. s, 2H, H_{β} in Fc), 4.15 (s, 5H, C_5H_5), 1.62 (d, ^{3}J = 6.3 Hz, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 148.10 (C-2, Py), 146.8 (OCH=), 146.7 (C-6, Py), 132.5 (C-3, Py), 132.3 (C-4, Py), 123.4 (C-5, Py), 104.1 (Py*C*H=), 88.5 (C_i in Fc), 76.6 (OCH), 68.8 (C_5H_5), 68.4, 68.3 (C_{β} in Fc), 68.0, 66.0 (C_{α} in Fc), 20.7 (Me).

*4.5.9. 1-{[(1-methyl-2-phenylethenyl)oxy]methyl}ferrocene (**2i**)*

A mixture of *Z*/*E* isomers in a 70:30 ratio (after chromatographic purification). Yellow powder, mp 44-59 ^{o}C (hexane). Yield: 0.26 g (40%). IR (KBr) 3086, 3055, 3021, 2996, 2950, 2919, 2872, 1649, 1598, 1573, 1493, 1463, 1438, 1411, 1391, 1380, 1352, 1339, 1313, 1289, 1271, 1240, 1179, 1157, 1106, 1075, 1046, 1025, 1001, 963, 913, 818, 752, 736, 698, 639, 523, 504, 486 cm^{-1}. EI-MS: *m/z* 332 [M^{+}], two picks (100%). Anal. Calcd for $C_{20}H_{20}FeO$ (322.22): C, 72.31; H, 6.07; Fe, 16.81. Found: C, 71.41; H, 5.99; Fe, 16.20. **(*Z*)-2i:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.58-7.08 (m, 5 H, Ph), 5.67 (s, 1H, =C*H*Ph), 4.59 (s, 2H, CH_2), 4.29 (br. s, 2H, H_{α} in Fc), 4.17 (br. s, 2H, H_{β} in Fc), 4.16 (s, 5H, C_5H_5), 2.00 (s, 3 H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.8 (OC=), 137.9 (C_i, Ph), 128.7, 128.2 ($C_{o,m}$, Ph), 125.1 (C_p, Ph), 100.1 (Ph*C*H=), 82.8 (C_i in Fc), 69.2 (C_{α} in Fc), 68.6 (C_5H_5), 68.5 (C_{β} in Fc), 65.6 (OCH_2), 18.2 (Me). **(*E*)-2i:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.58-7.08 (m, 5H, Ph), 5.33 (s, 1H, =C*H*Ph), 4.72 (s, 2H, CH_2), 4.27 (br.s, 2H, H_{α} in Fc), 4.16 (br.s, 2H, H_{β} in Fc), 4.14 (s, 5H, C_5H_5), 2.07 (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 152.7 (OC=), 136.7 (C_i, Ph), 128.0 ($C_{o,m}$, Ph), 125.2 (C_p, Ph), 107.6 (Ph*C*H=), 83.7 (C_i in Fc), 68.6 (C_5H_5), 68.5 (C_{β} in Fc), 68.3 (C_{α} in Fc), 66.2 (OCH_2), 19.6 (Me).

*4.5.10. 1-{[(1,2-diphenylethenyl)oxy]methyl}ferrocene (**2j**)*

A mixture of *Z*/*E* isomers in a 52:48 ratio (after chromatographic purification). Yellow powder, mp 68-81 ^{o}C (hexane). Yield: 0.235 g (30%). IR (KBr) 3109, 3080, 3060, 3018, 2997, 2925, 2877, 2857, 1668, 1633, 1623, 1596, 1570, 1492, 1446, 1410, 1392, 1378, 1330, 1317, 1277, 1242, 1224, 1201, 1181, 1103, 1098, 1073, 1042, 1024, 1000, 969, 952, 934, 920, 910, 889, 863, 842, 828, 815, 773, 750, 728, 695, 646, 574, 503, 480 cm^{-1}. EI-MS: *m/z* 394 [M^{+}], two picks (90%). Anal. Calcd for $C_{25}H_{22}FeO$ (394.29): C, 76.15; H, 5.62; Fe, 14.16. Found: C, 76.04; H, 5.55; Fe, 13.89. **(*Z*)-2j:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.71-7.16 (m, 10 H, Ph), 6.10 (s, 1H, =C*H*Ph), 4.73 (s, 2H, CH_2), 4.30 (br. s, 2H, H_{α} in Fc), 4.13 (br.s, 2H, H_{β} in Fc), 4.12 (s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 156.6 (OC=), 137.2, 136.1 (C_i, Ph), 128.4, 126.7 (C_p, Ph), 129.0, 128.4, 128.3, 128.1 ($C_{o,m}$, Ph), 113.9 (Ph*C*H=), 83.08 (C_i in Fc), 69.2 (C_{α} in Fc), 68.8 (C_5H_5, OCH_2), 68.6 (C_{β} in Fc), 65.6 (OCH_2). **(*E*)-2j:** ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.33-6.96 (m, 10 H, Ph), 5.91 (s, 1H, =C*H*Ph), 4.55 (s, 2H, CH_2), 4.20 (br.s, 2H, H_{α} in Fc), 4.15 (br. s, 2H, H_{β} in Fc), 4.04 (s, 5H, C_5H_5). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ 155.1 (OC=), 137.1, 136.3 (C_i, Ph), 129.6, 128.9, 128.7, 126.8 ($C_{o,m}$, Ph), 128.7, 125.4 (C_p, Ph), 103.3 (Ph*C*H=), 82.8 (C_i in Fc), 69.5 (C_{α} in Fc), 68.9 (C_{β} in Fc), 68.6 (C_5H_5), 67.0 (OCH_2).

Acknowledgments

This work was supported by the President of the Russian Federation (program for the support of leading scientific schools, grant NSh-156.2014.3).

Supplementary Material

Copies of NMR spectra for compounds **2a-j**; crystallographic data for compounds **2a**,**c**; structural and thermochemical data for compounds **2e-g** from DFT and MP2 calculations can be found in the online version, at … .

References and notes

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18. CCDC 942726 (**2a**) and 973903 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
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Supporting Information

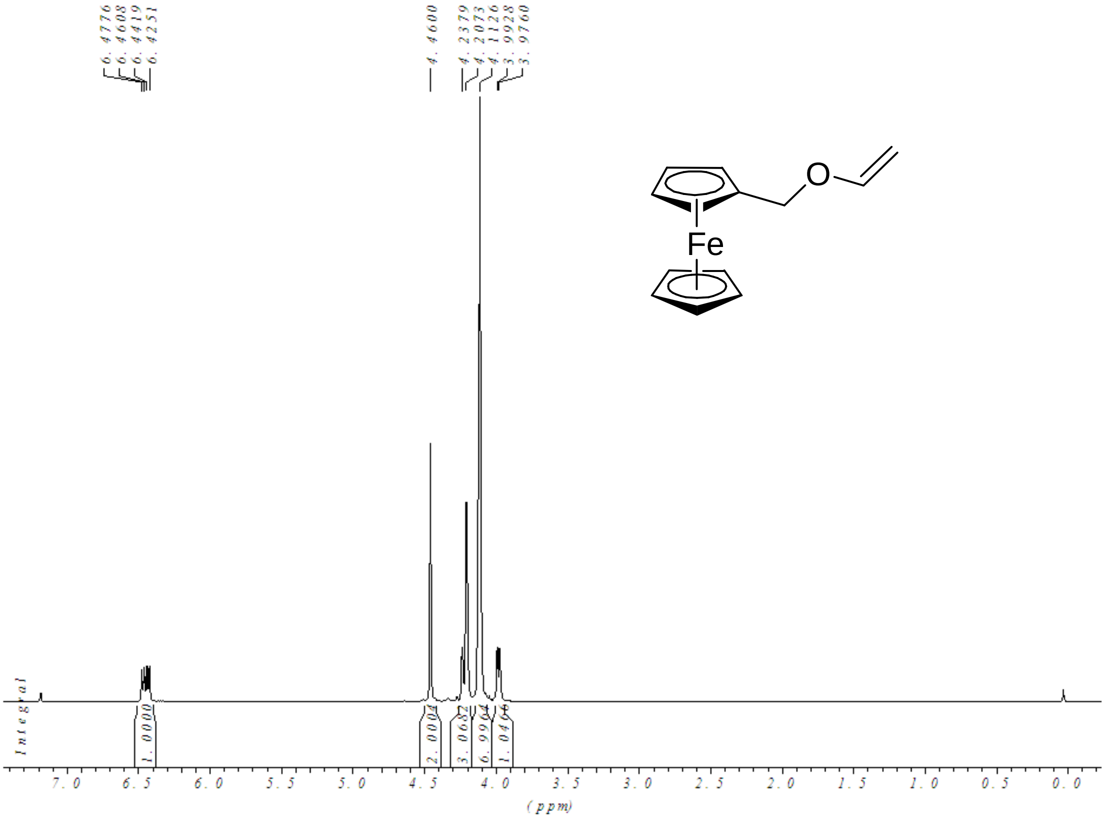
Table of Contents

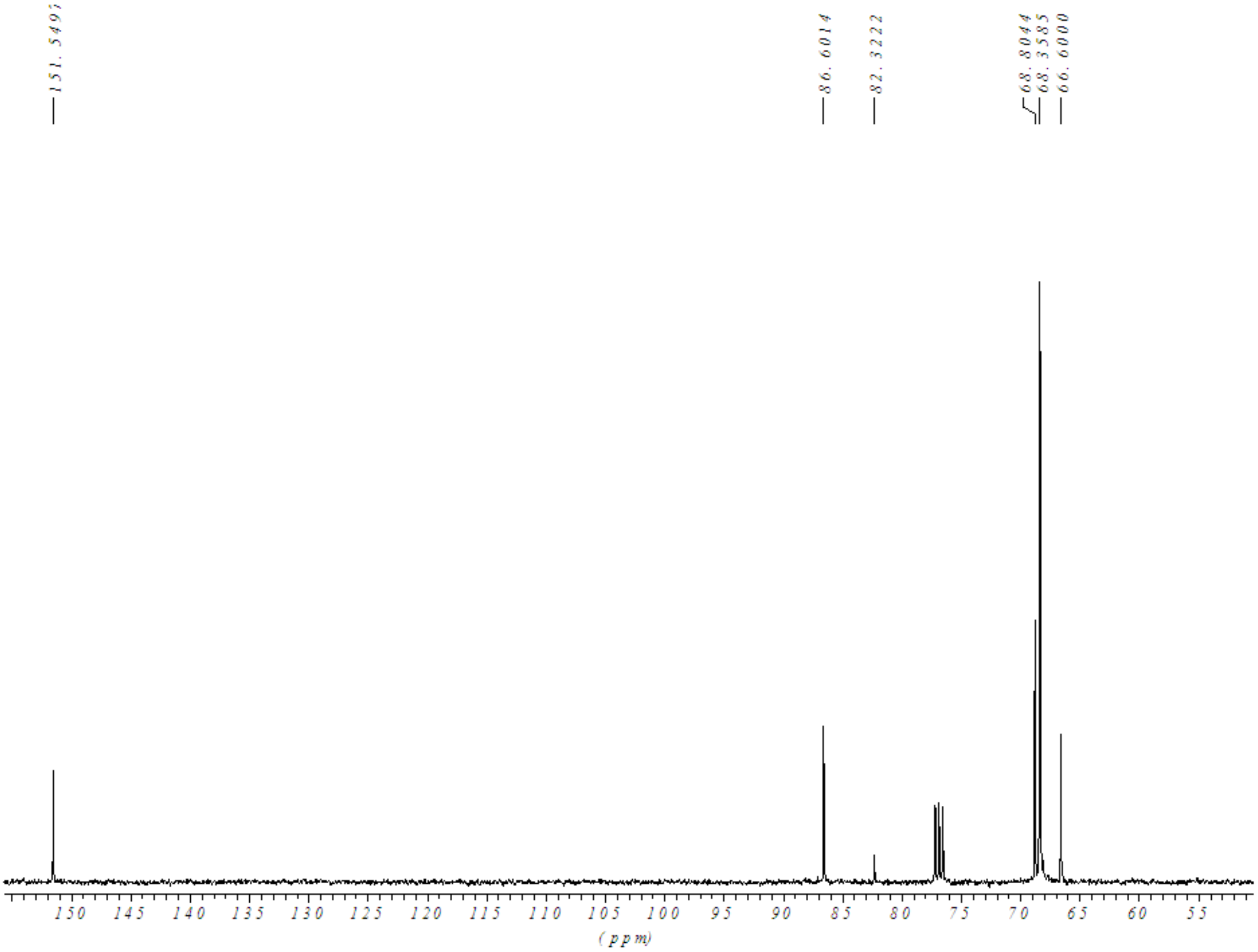
Crystallographic data for compounds 2a,c

Compound	**2a**	**2c**
Empirical formula	$C_{13}H_{14}FeO$	$C_{14}HFeO$
Formula weight	242.09	241.00
Temperature/K	223(2)	200(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	Pnma
a/Å	13.976(3)	11.4876(3)
b/Å	9.967(2)	8.2377(2)
c/Å	8.0699(14)	12.4947(3)
α/°	90.00	90.00
β/°	93.419(7)	90.00
γ/°	90.00	90.00
Volume/Å^3	1122.1(4)	1182.39(5)
Z	4	4
ρ_{calc}mg/mm^3	1.433	1.354
m/mm^{-1}	1.312	1.246
F(000)	504.0	476.0
Crystal size/mm^3	0.16 × 0.14 × 0.02	0.58 × 0.35 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection	2.92 to 54.98°	4.82 to 60.12°
Reflections collected	11203	26802
Independent reflections	2576 [R_{int} = 0.0519, R_{sigma} = 0.0478]	1847 [R_{int} = 0.0426, R_{sigma} = 0.0157]
Data/restraints/parameters	2576/0/136	1847/7/94
Goodness-of-fit on F^2	1.033	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1209	R_1 = 0.0267, wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0650, wR_2 = 0.1517	R_1 = 0.0289, wR_2 = 0.0905
Largest diff. peak/hole / e Å^{-3}	0.54/-0.49	0.61/-0.60

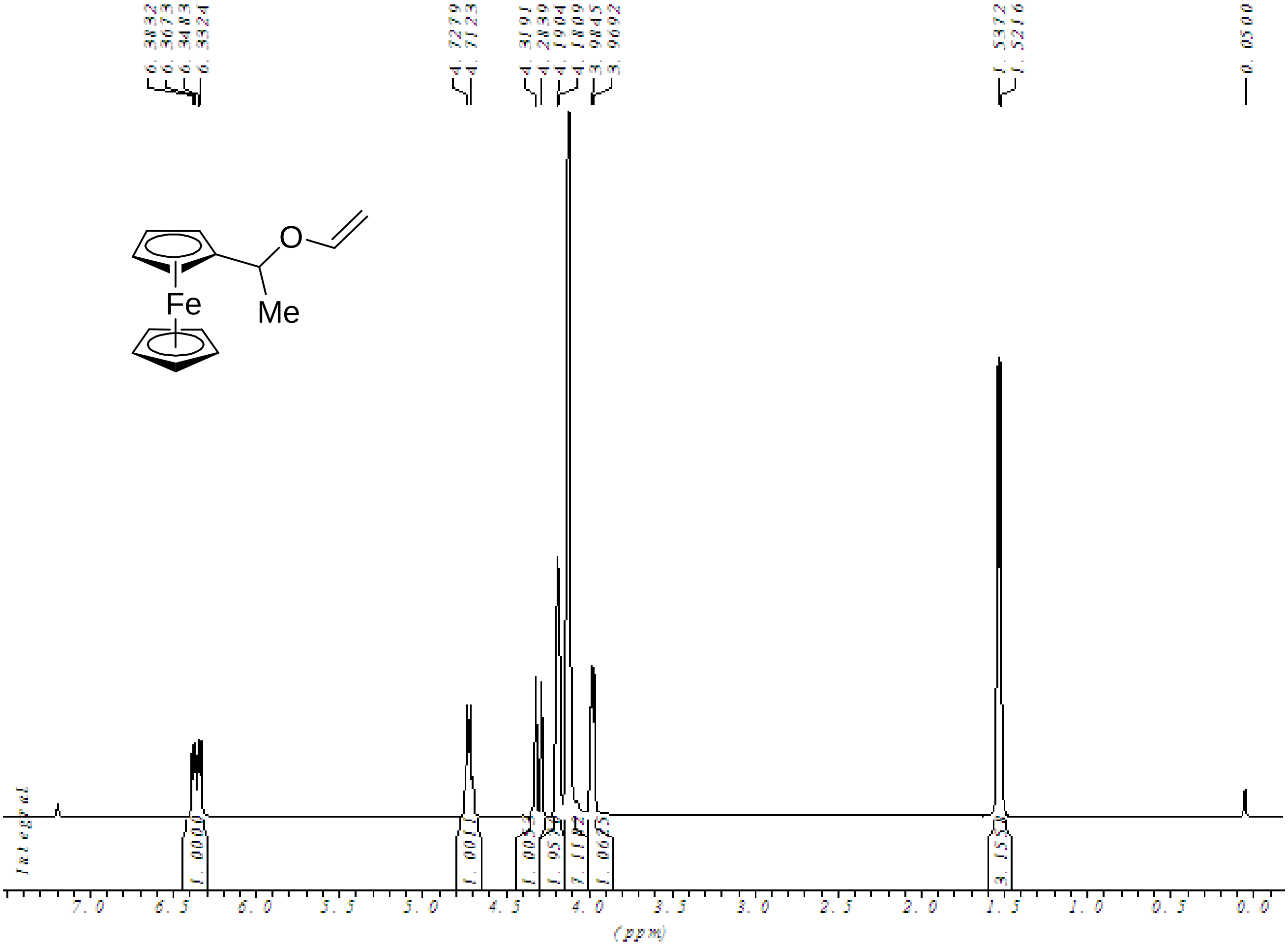
Copies of ^{1}H and ^{13}C NMR spectra of the synthesized products

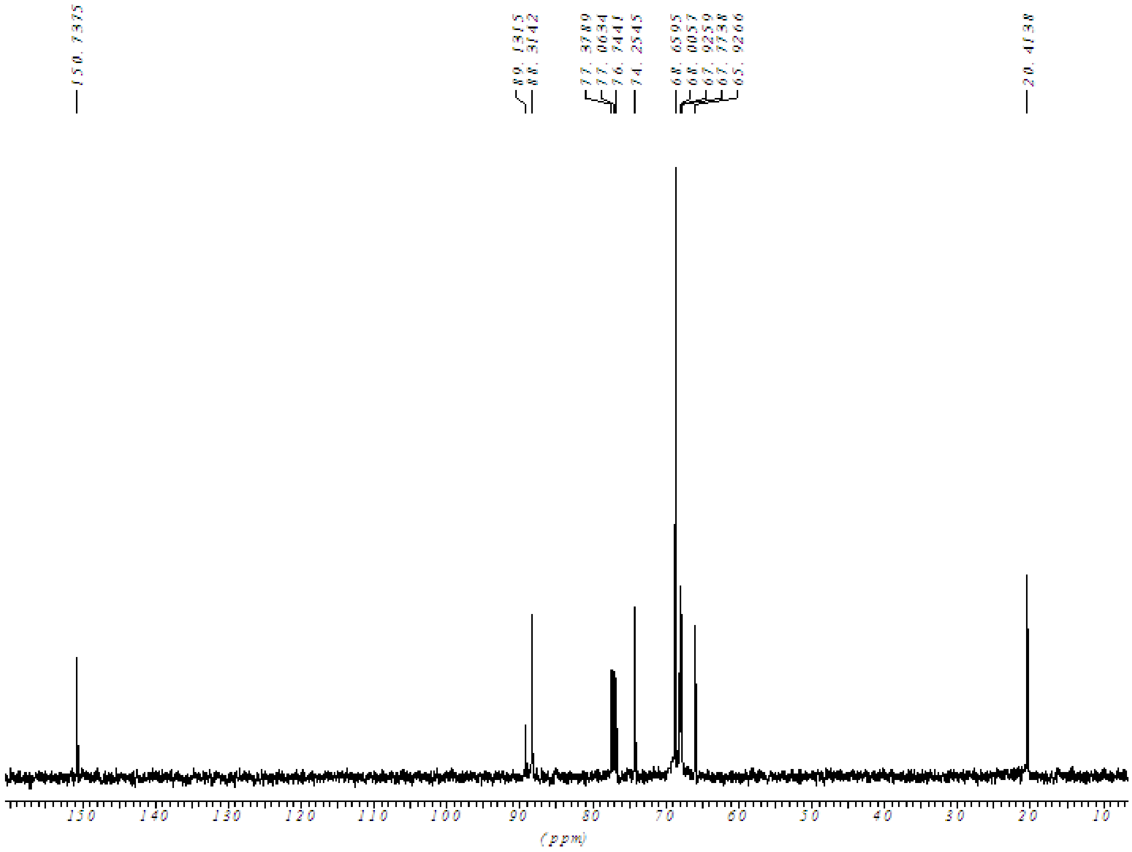
Vinyloxymethylferrocene (2a).





1-(Vinyloxy)ethylferrocene (2b).





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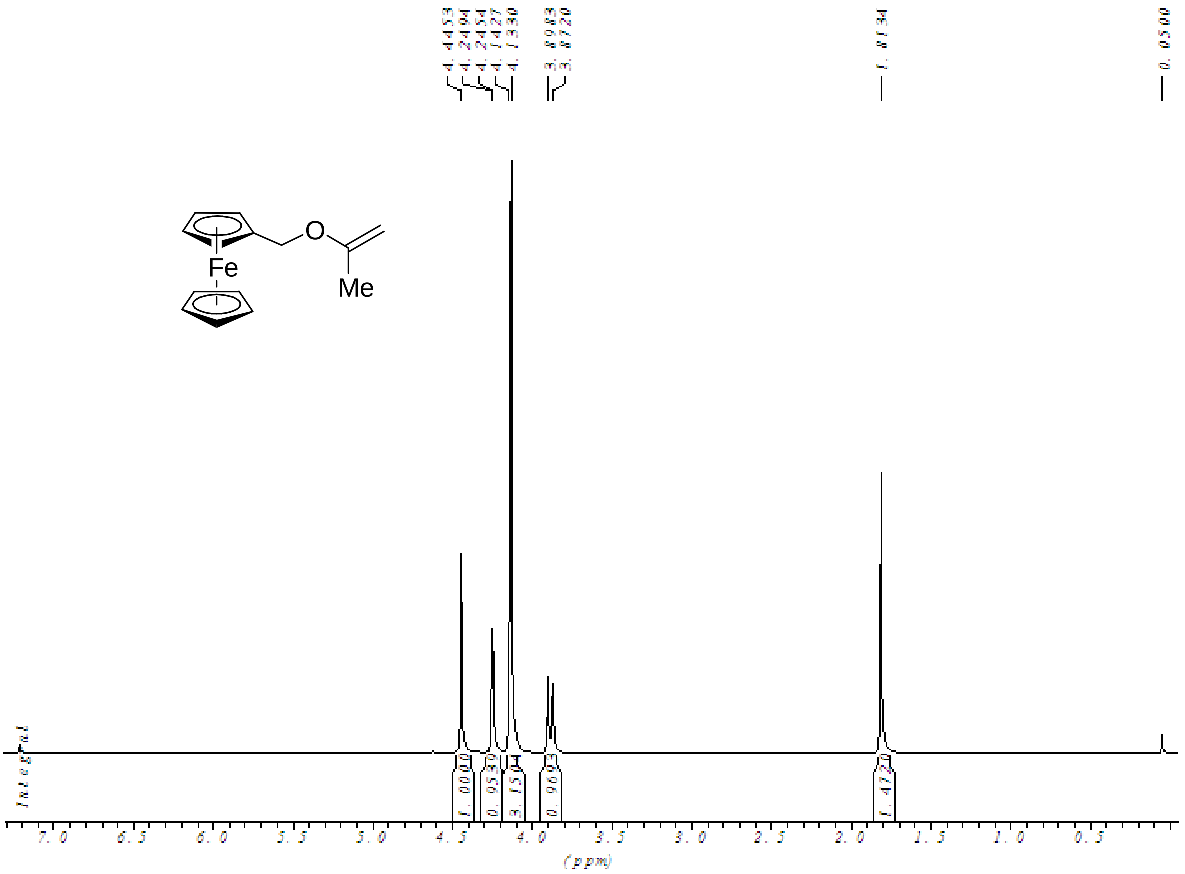

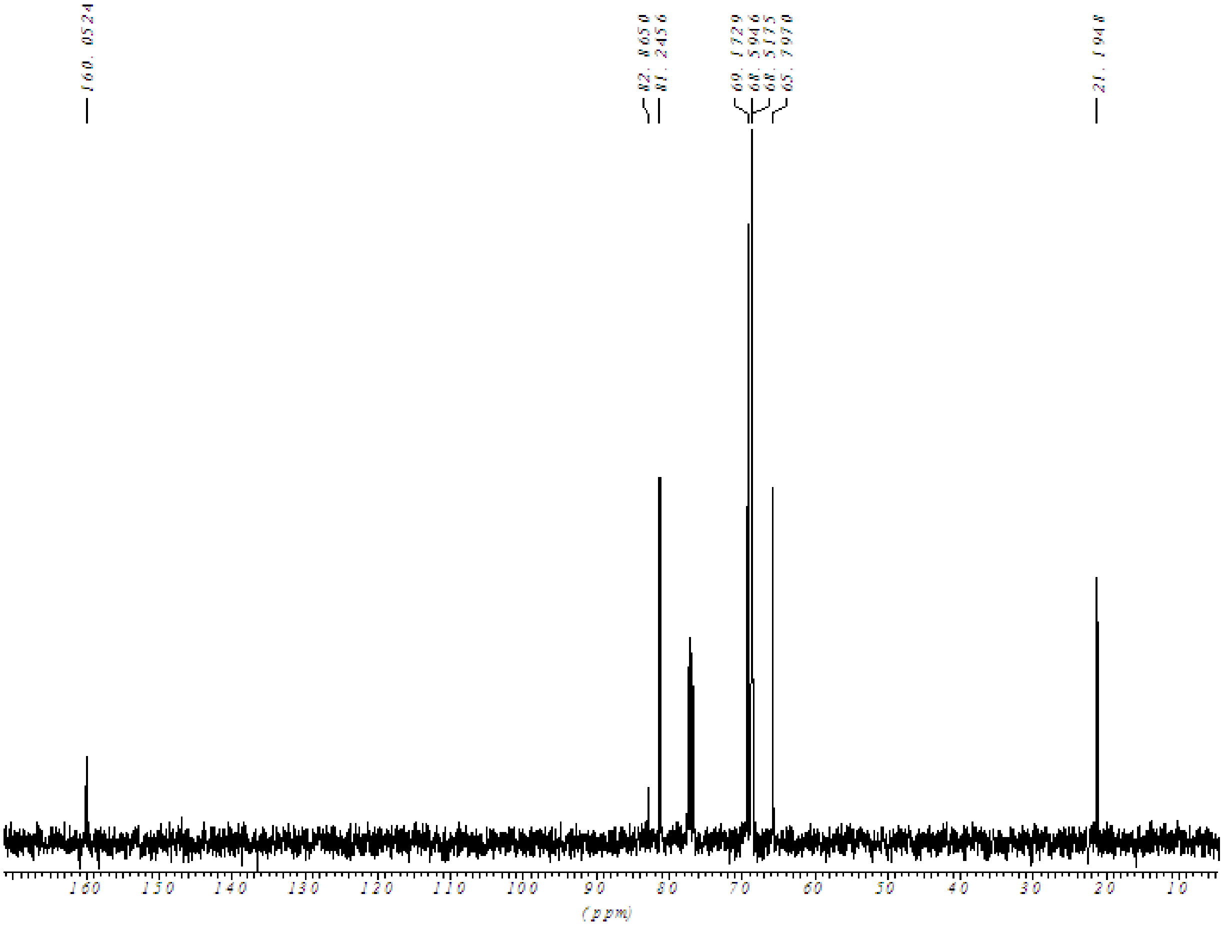

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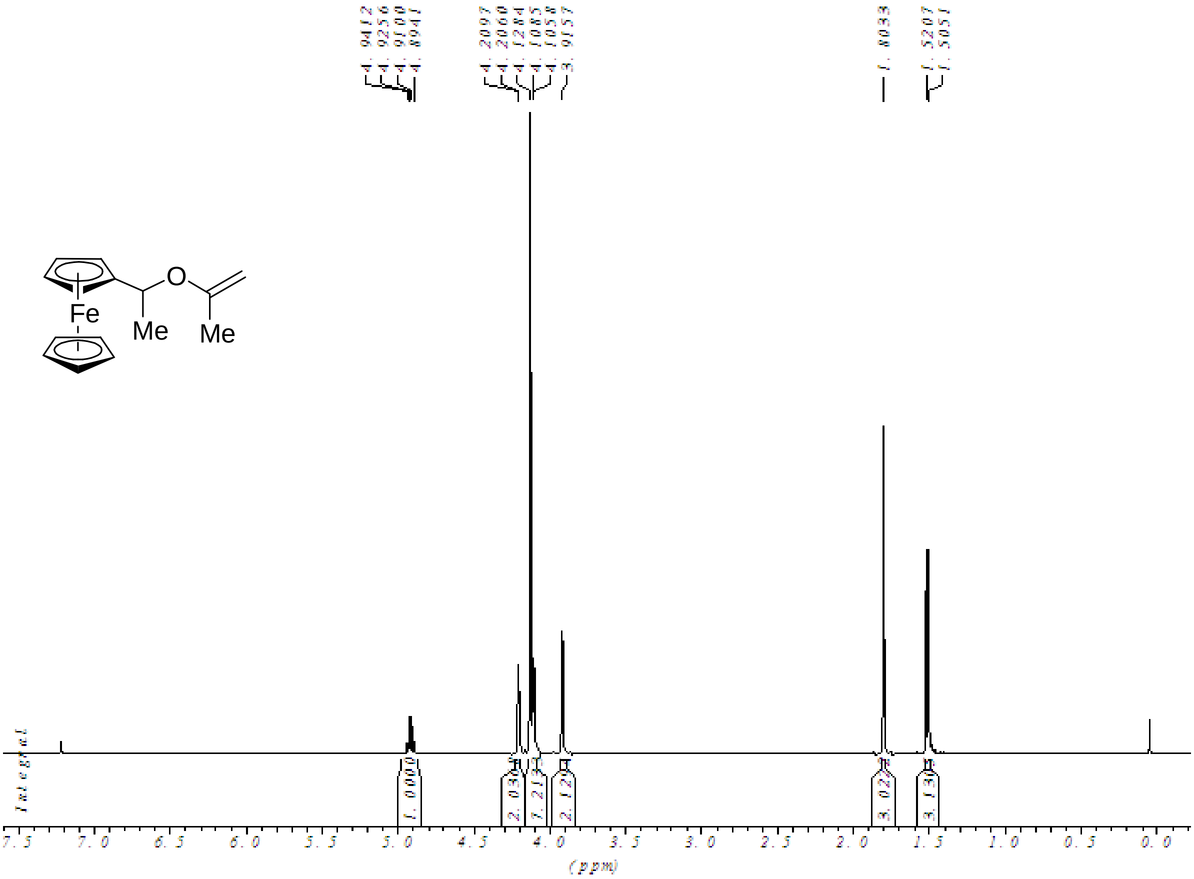
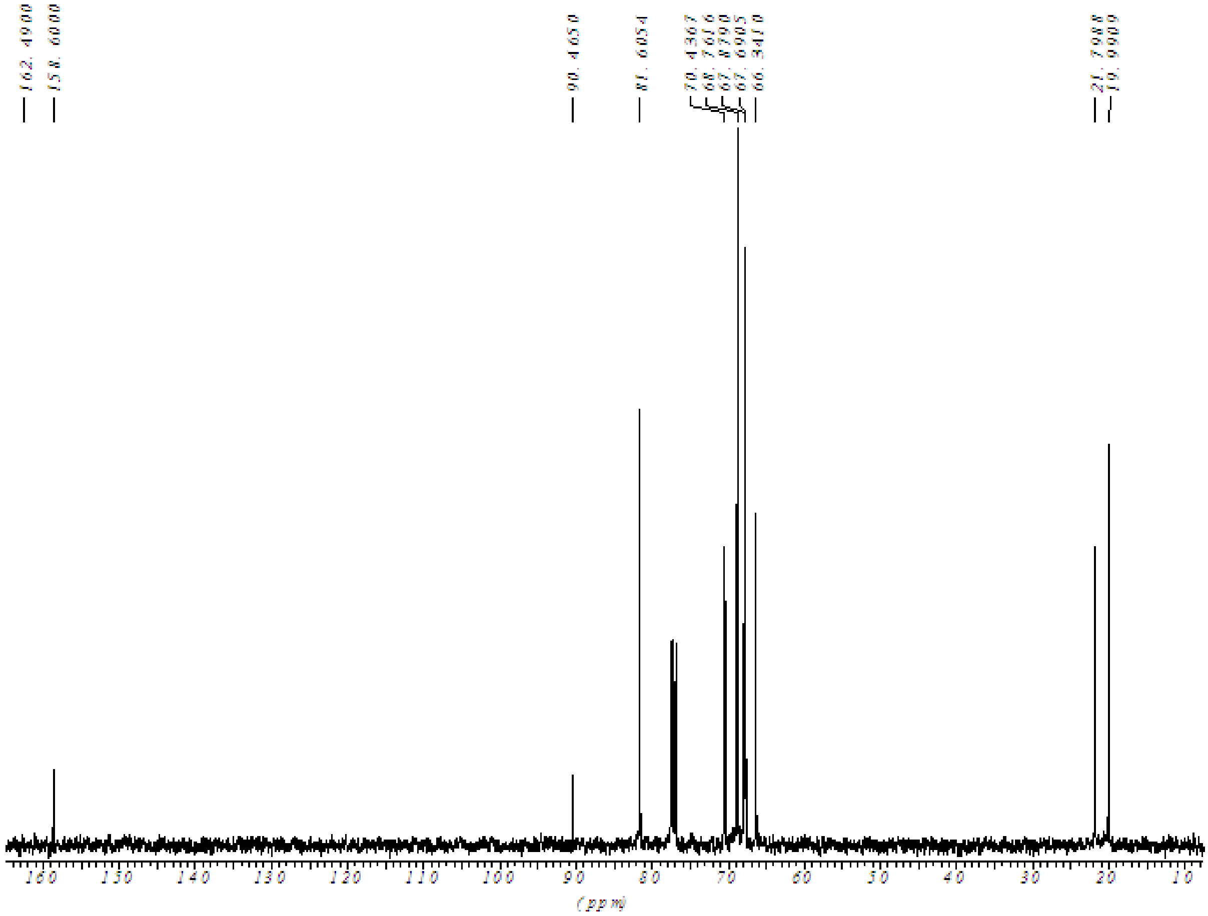
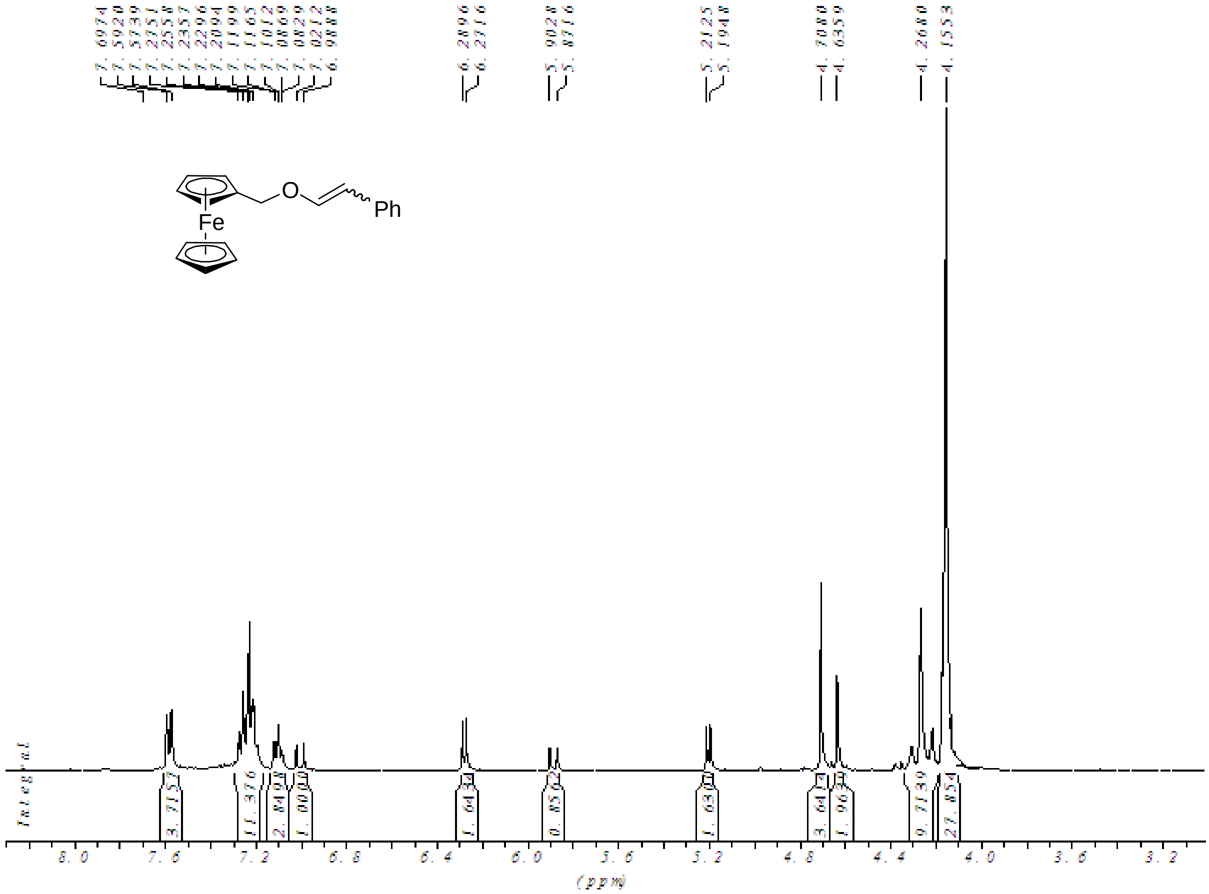
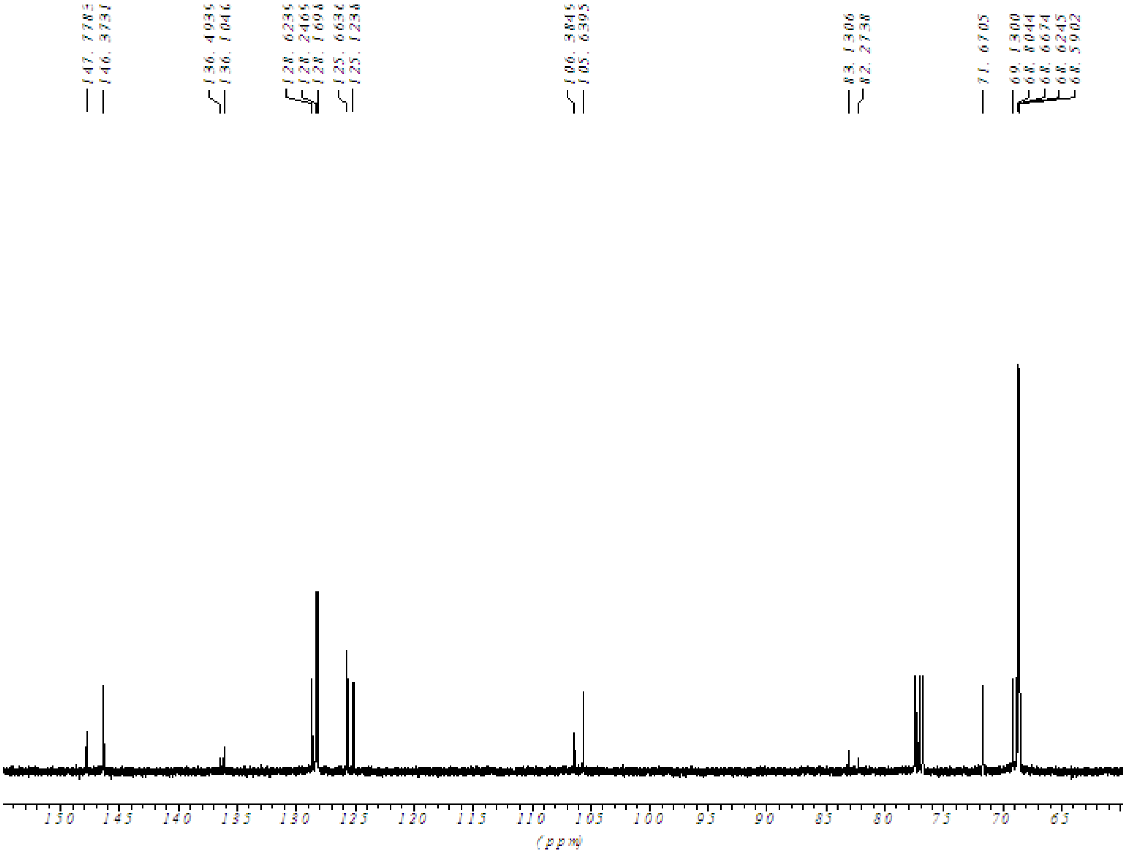


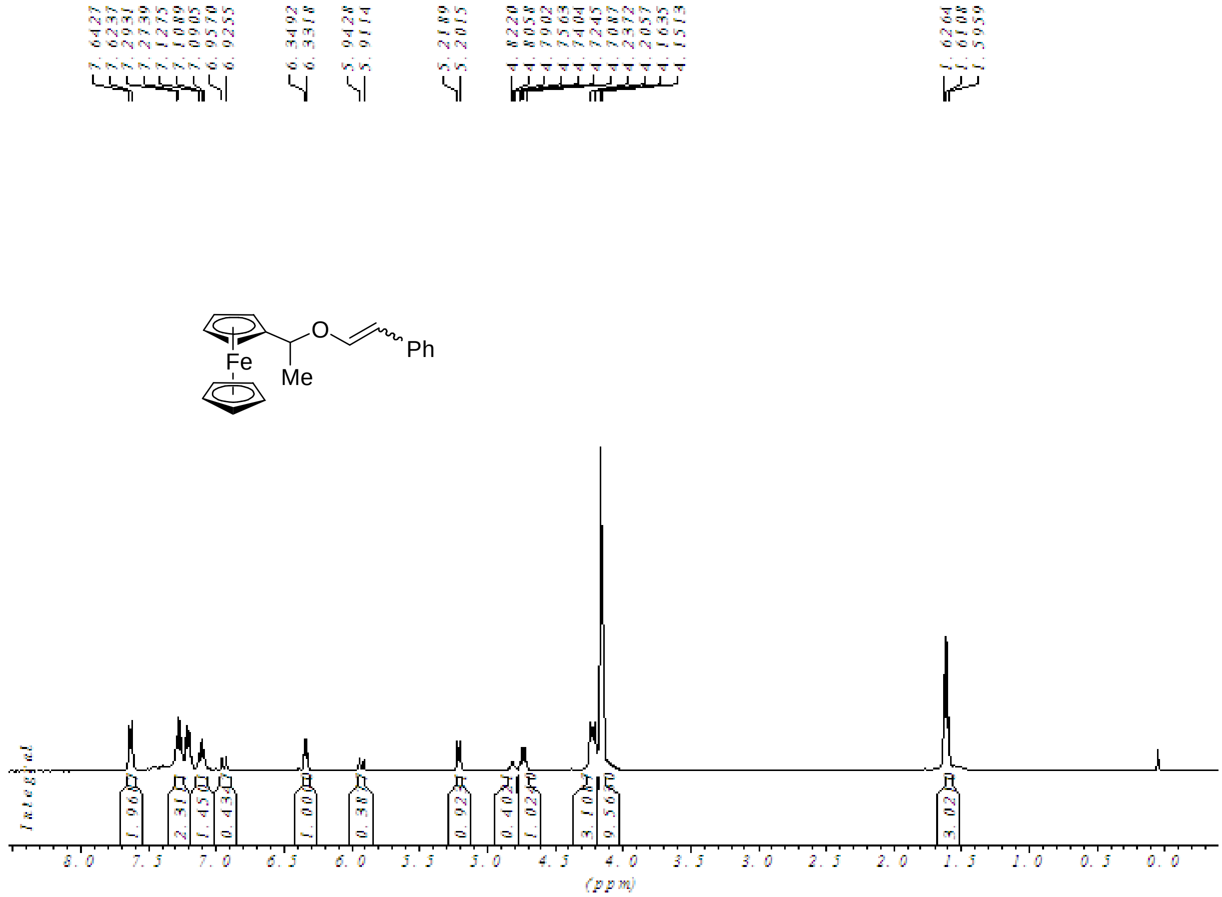


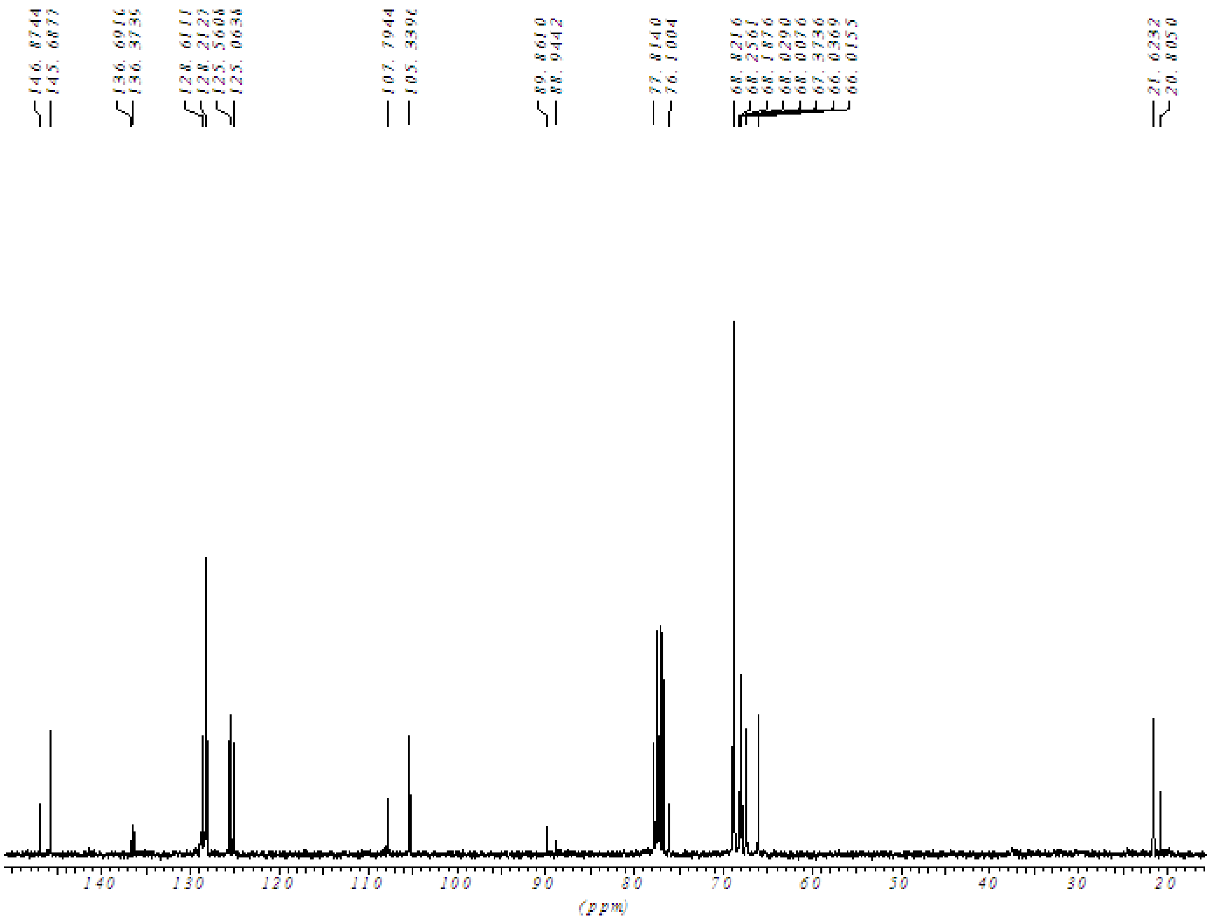
2-(Phenylethenyl)oxymethylferrocene (2e).



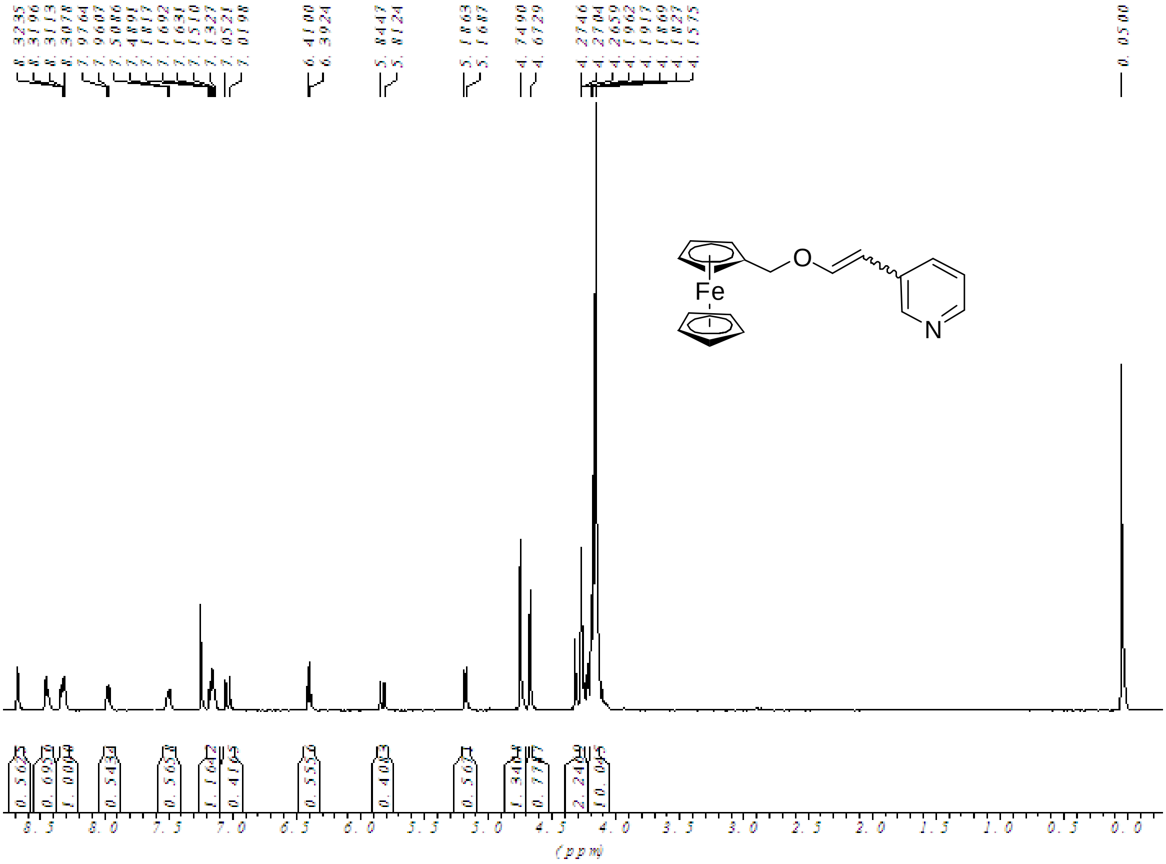


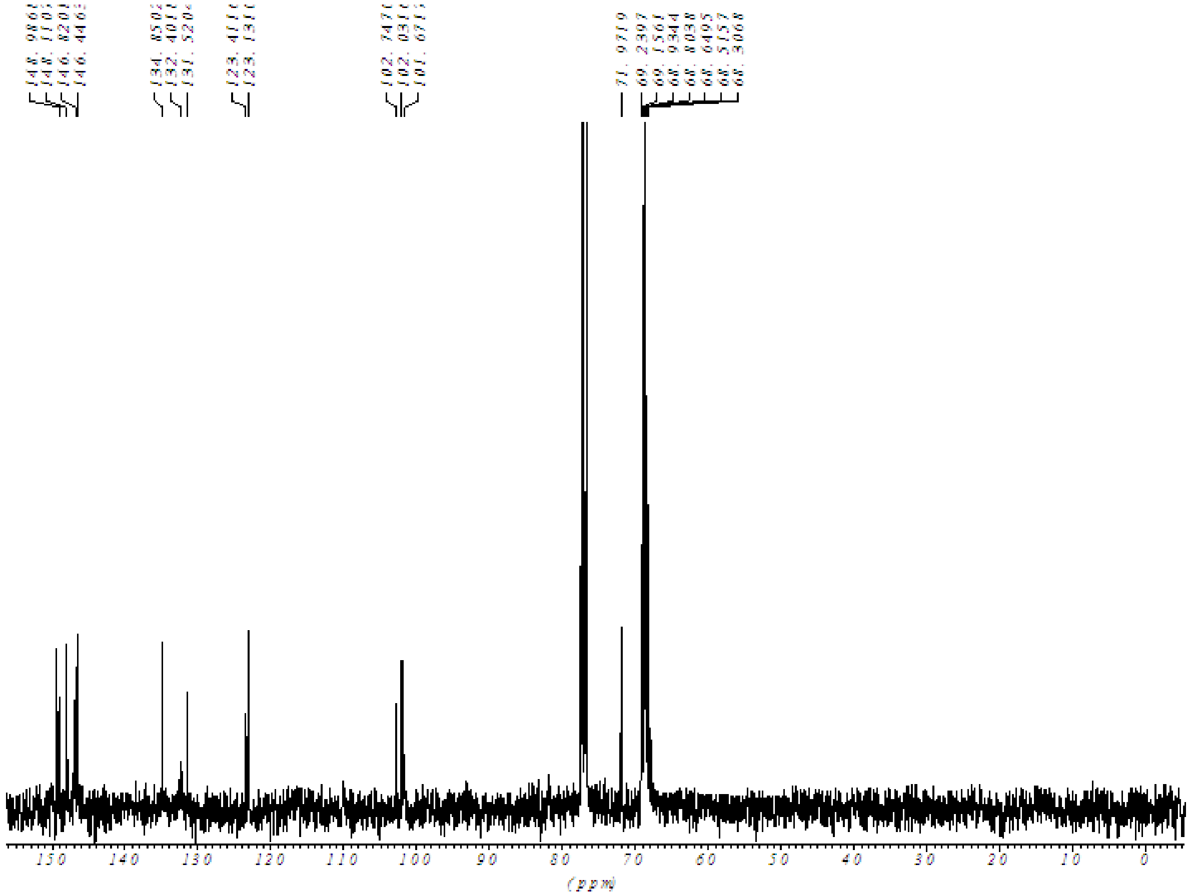
2-(1-[2-Phenylethenyl]oxyethyl)ferrocene (2f).



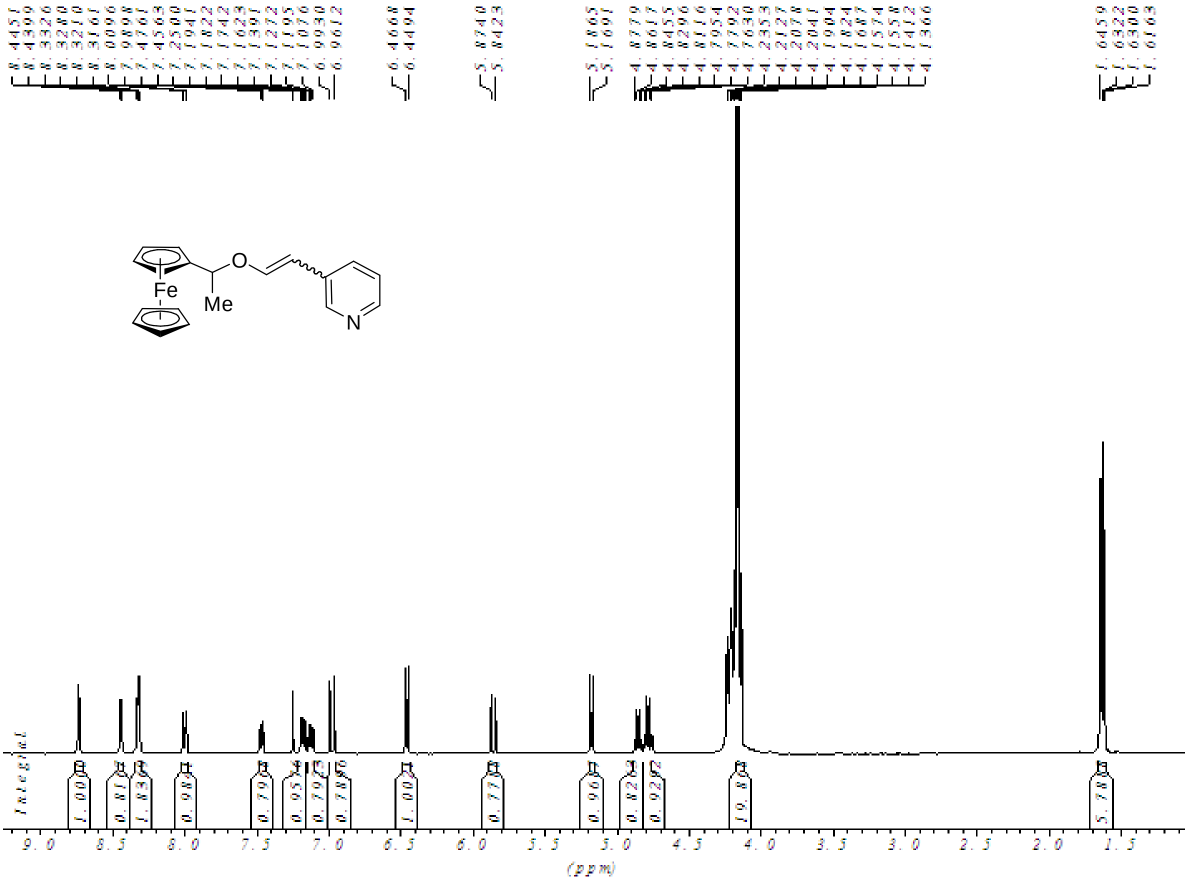


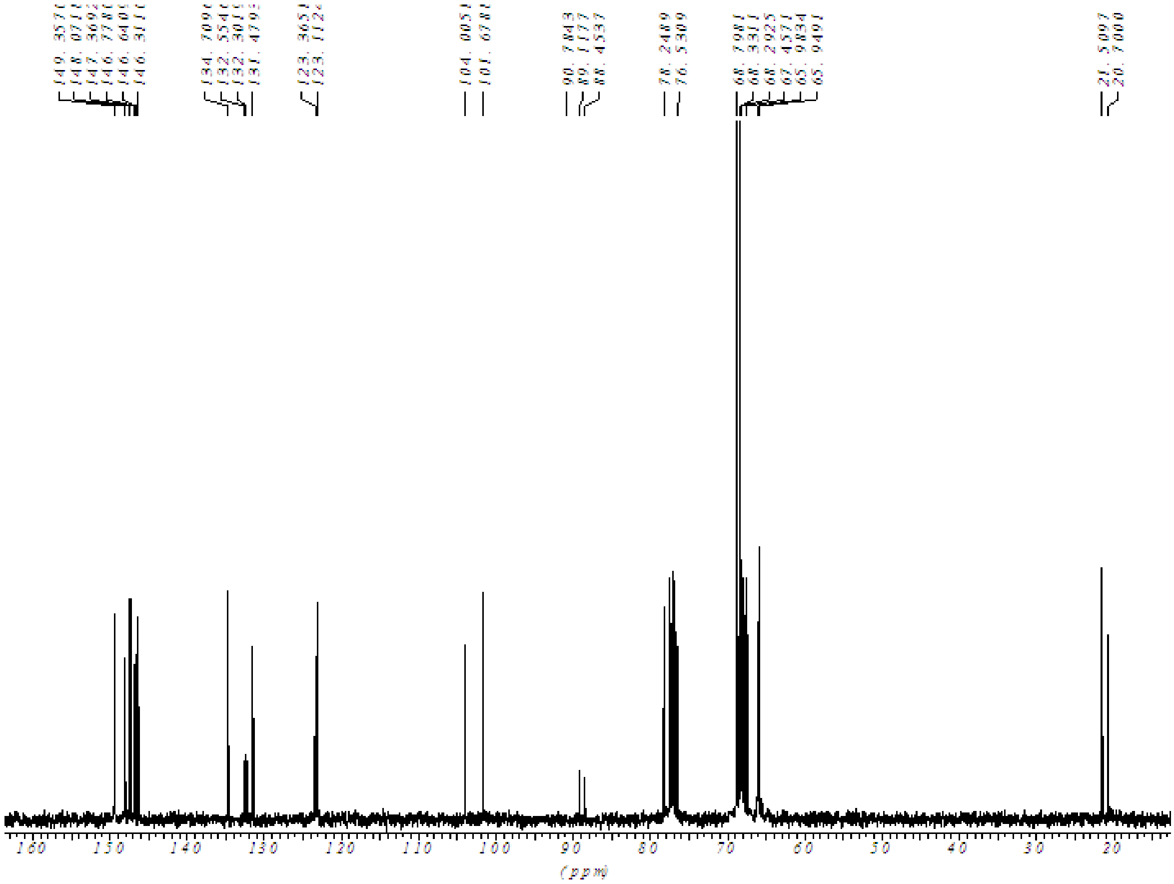
3-{2-[(ferrocenyl)methoxy]ethenyl}pyridine (2g)



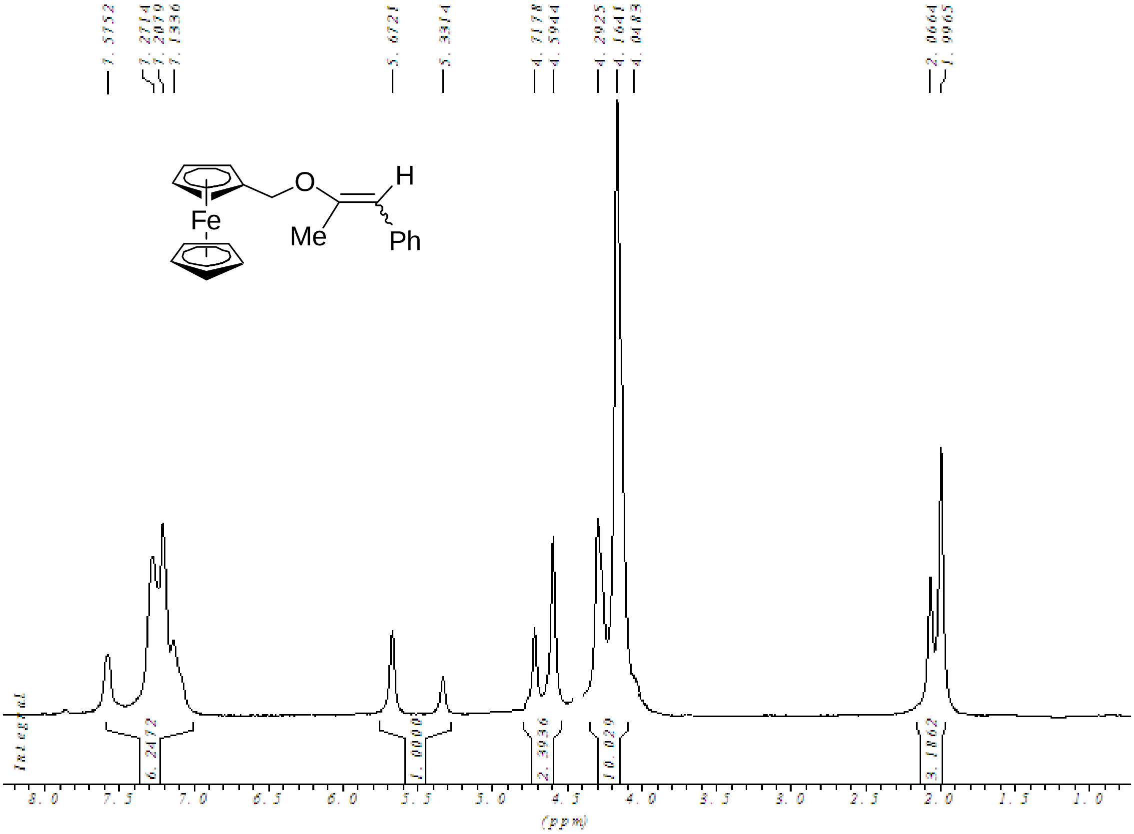


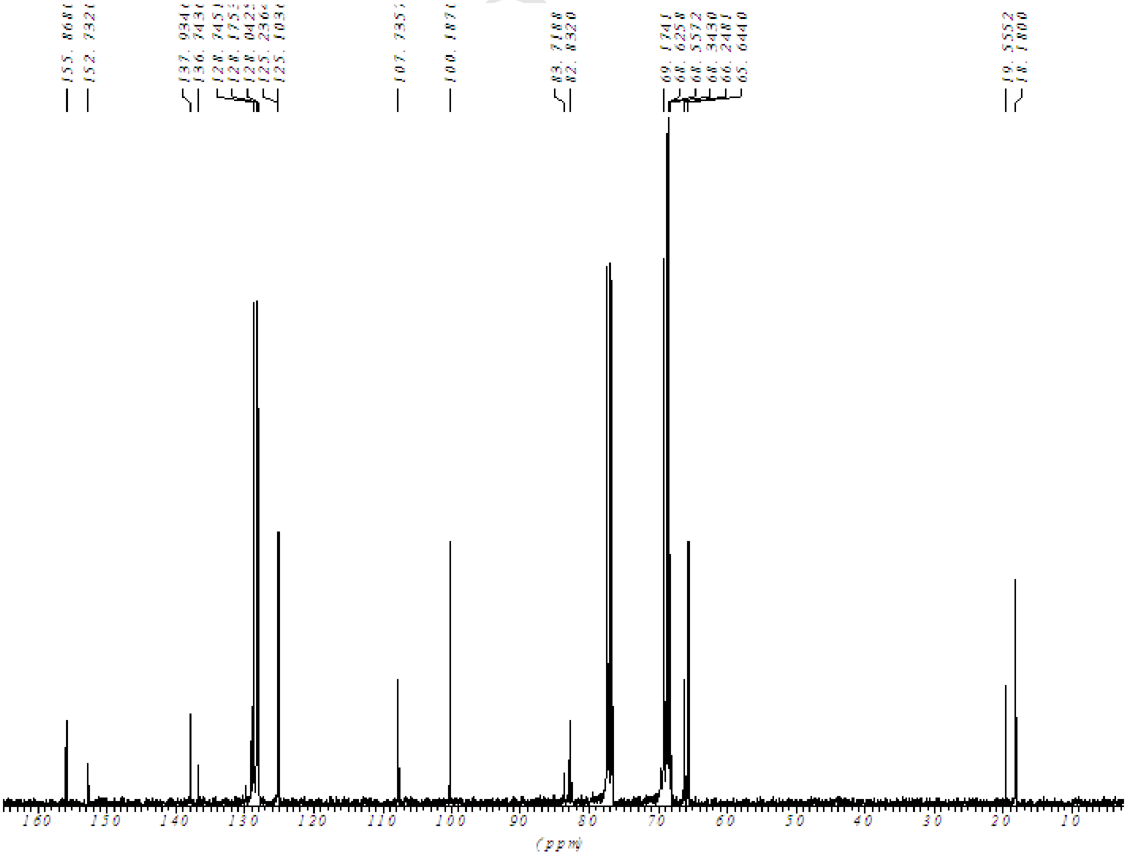
3-{2-[1-(2-ferrocenyl)ethoxy]ethenyl}pyridine (2h)



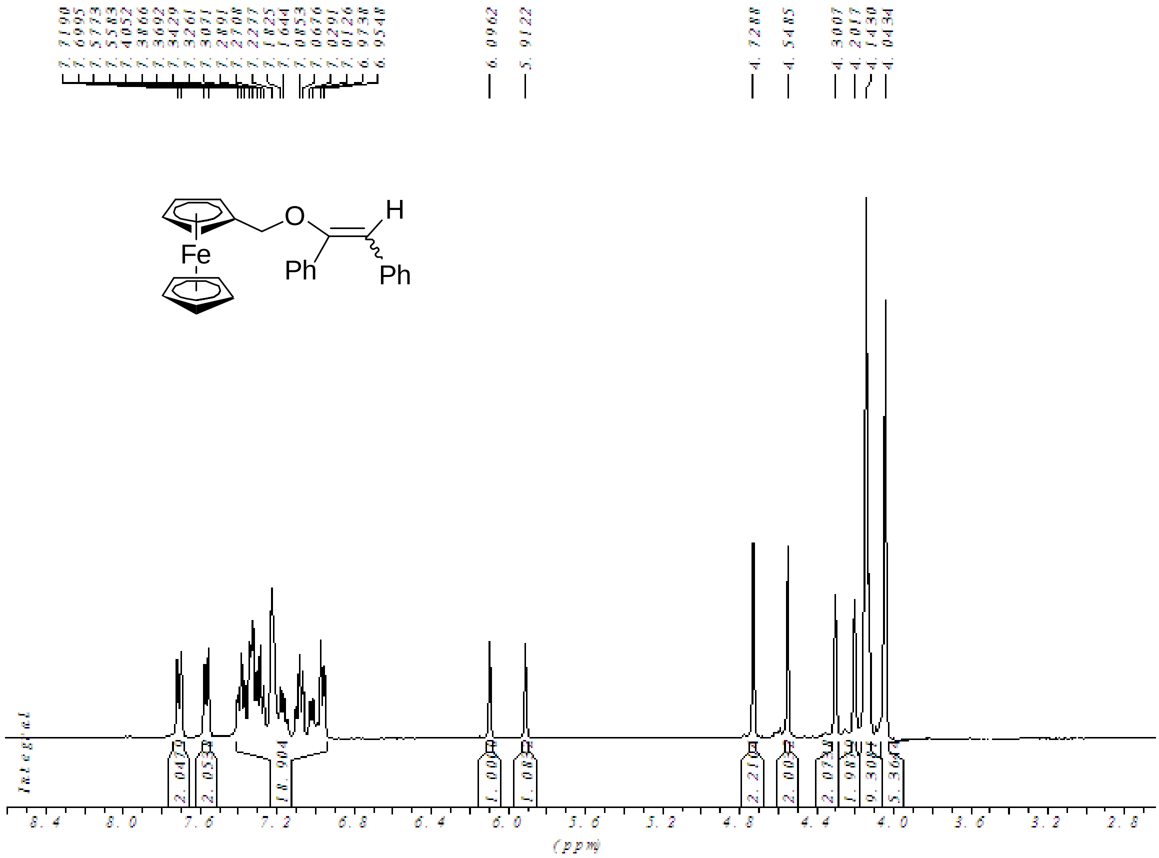


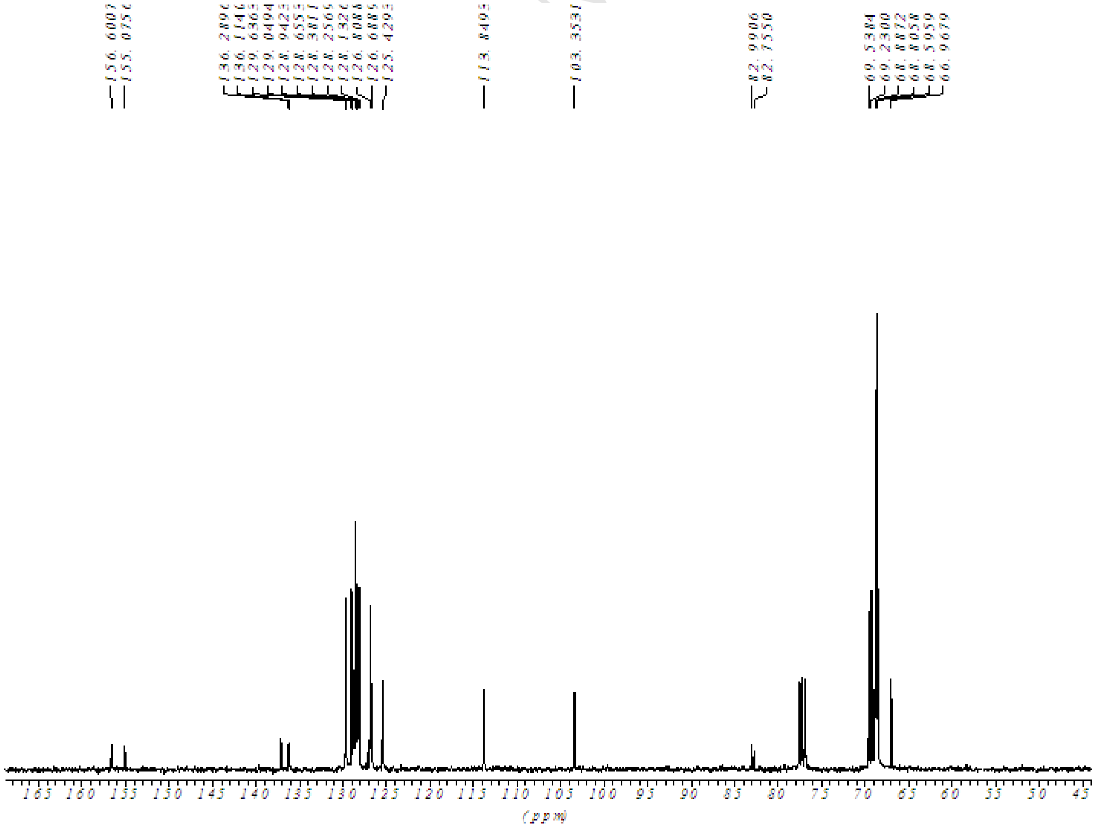
1-{[(1-methyl-2-phenylethenyl)oxy]methyl}ferrocene (2i)





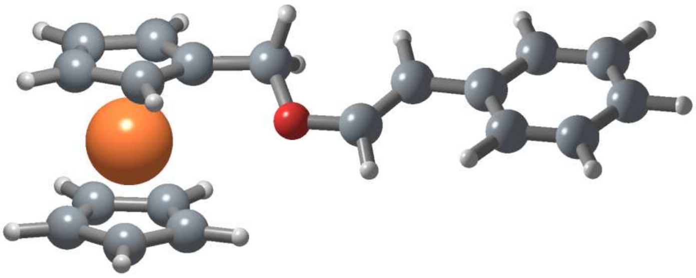
1-{[(1,2-diphenylethenyl)oxy]methyl}ferrocene (2j)





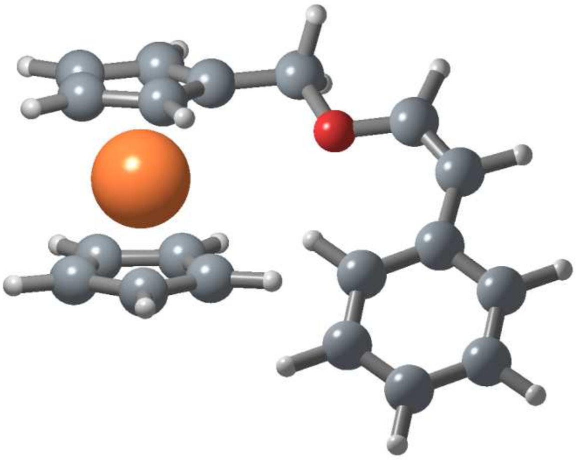
Structural and thermochemical data for compounds 2e-g from DFT and MP2 calculations

The B3LYP/6-31G(d,p) optimized structures, the MP2/6-311++G(d,p)//B3LYP/6-31G(d,p) energies (E_{MP2}) and the B3LYP/6-31G(d,p) corrections to Gibbs free energy (G_{corr}) of **2e – g**



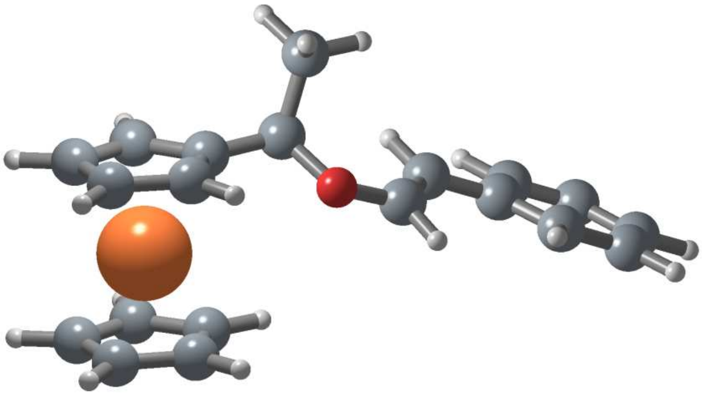
E_{MP2} = – 2070.4468811 a.u.
G_{corr} = 0.268319 a.u.

C	0.082704	-0.021953	-0.069911
C	0.240303	-0.128534	1.325579
C	1.528883	-0.407075	1.817074
C	2.616637	-0.552874	0.958574
C	2.445361	-0.425673	-0.420161
C	1.170657	-0.160810	-0.927147
C	-0.865972	0.025737	2.280373
C	-2.056099	0.584341	1.996976
O	-3.119472	0.751651	2.823791
C	-3.018943	0.220617	4.148555
C	-4.322682	0.393620	4.861499
C	-4.468480	0.631204	6.266475
C	-5.860780	0.628565	6.578023
C	-6.580474	0.390102	5.368806
C	-5.633893	0.237652	4.312441
Fe	-5.431511	2.081758	5.194390
C	-6.047061	3.499483	3.842062
C	-4.638726	3.591639	4.050971
C	-4.415350	3.848915	5.437075
C	-5.686000	3.914788	6.084838
C	-6.694704	3.699249	5.098208
H	-7.656468	0.348681	5.267451
H	-5.859371	0.063203	3.269778
H	-3.659101	0.793879	6.966217
H	-5.854872	4.088514	7.138954
H	-7.761891	3.681118	5.273528
H	-6.536413	3.296793	2.899149
H	-3.876018	3.449871	3.298617
H	-3.452325	3.963352	5.916069
H	-6.292912	0.795578	7.555202
H	-2.211005	0.727045	4.694149
H	-2.289169	0.992678	1.018609
H	-0.663557	-0.322079	3.288657
H	-0.902588	0.151867	-0.492019
H	1.020204	-0.074340	-1.999699
H	3.290421	-0.540168	-1.092319
H	3.599898	-0.765613	1.368793
H	1.675083	-0.502417	2.890200
H	-2.757009	-0.845981	4.079465



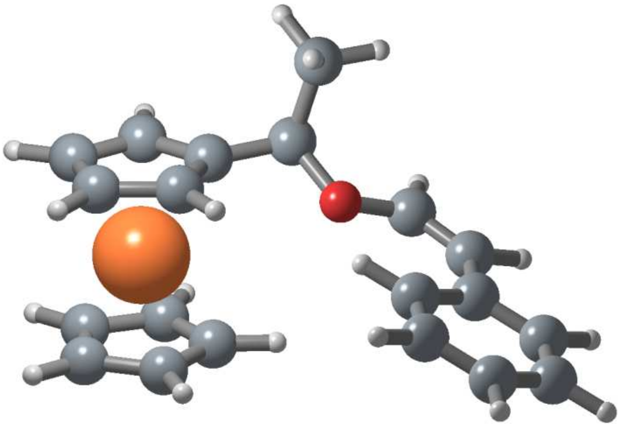
E$_{MP2}$ = –2070.4486162 a.u.
G$_{corr}$ = 0.268813a.u.

C	0.137643	0.318899	0.113291
C	0.061986	0.186350	1.513967
C	1.081924	-0.542052	2.160828
C	2.120319	-1.113899	1.428550
C	2.175311	-0.977372	0.039904
C	1.176390	-0.254581	-0.614760
C	-1.062260	0.814403	2.209975
C	-1.421345	0.759746	3.504457
O	-0.747367	0.068697	4.464791
C	-1.383050	0.035827	5.749447
C	-0.464415	-0.567720	6.762764
C	0.955071	-0.414910	6.840644
C	1.407637	-1.061048	8.029126
C	0.271004	-1.605278	8.698587
C	-0.884274	-1.303258	7.917973
Fe	0.438534	-2.405232	6.816571
C	-0.571561	-3.958372	5.928627
C	0.276876	-4.446507	6.967922
C	1.618662	-4.077838	6.649865
C	1.597527	-3.362106	5.415175
C	0.244472	-3.287852	4.968827
H	2.435688	-1.139422	8.355879
H	1.572559	0.083064	6.106537
H	-1.902553	-1.586355	8.150698
H	-0.041379	-4.990756	7.846786
H	2.495563	-4.292863	7.245450
H	2.455457	-2.936762	4.912562
H	-0.101147	-2.784765	4.076869
H	-1.646524	-4.069550	5.882412
H	0.282878	-2.165241	9.623721
H	-2.317125	-0.539262	5.689925
H	-2.304329	1.294699	3.851141
H	-1.719476	1.417411	1.588851
H	1.056967	-0.647720	3.237810
H	2.896011	-1.670063	1.948192
H	2.987348	-1.426434	-0.524333
H	1.206521	-0.136523	-1.694369
H	-0.635565	0.880057	-0.405749
H	-1.640744	1.065444	6.042101



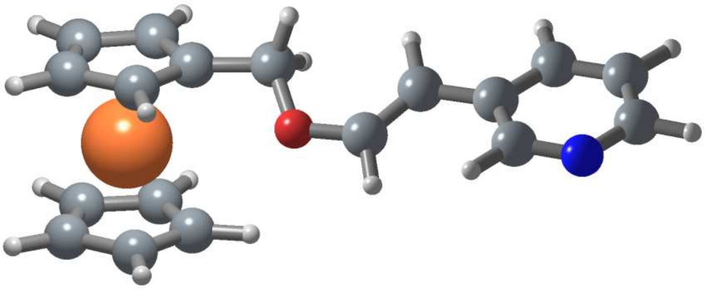
E_{MP2} = –2109.6507017 a.u.
G_{corr} = 0.294375 a.u.

C	-0.382396	0.111216	0.470188
C	0.127147	0.104624	1.803744
C	1.545972	-0.038092	1.734098
C	1.912963	-0.121771	0.356871
C	0.721419	-0.029138	-0.423425
Fe	0.949664	1.652505	0.731265
C	0.426018	3.398973	1.656373
C	-0.041044	3.389628	0.302562
C	1.101461	3.251110	-0.546724
C	2.262337	3.163989	0.278439
C	1.846238	3.257922	1.640523
C	-1.465603	3.608435	-0.124915
C	-1.782210	5.095278	-0.321426
O	-1.655041	2.897701	-1.365730
C	-2.903390	2.534307	-1.750022
C	-4.073100	2.701681	-1.106264
C	-5.376600	2.243530	-1.607380
C	-6.453913	2.140961	-0.707974
C	-7.707602	1.698710	-1.125180
C	-7.921311	1.348413	-2.458644
C	-6.866904	1.456776	-3.368858
C	-5.616110	1.904721	-2.953427
H	3.278408	3.032872	-0.068343
H	1.074912	3.193003	-1.625398
H	-0.194830	3.487963	2.538404
H	2.223930	-0.069675	2.576262
H	2.918432	-0.227214	-0.027403
H	0.664686	-0.045309	-1.503016
H	-1.419800	0.218889	0.184334
H	-0.457670	0.200141	2.708588
H	2.489961	3.215562	2.508529
H	-2.130035	3.179115	0.635551
H	-2.811706	5.238495	-0.659431
H	-1.645132	5.634959	0.620186
H	-1.104663	5.523738	-1.064970
H	-2.847905	2.030531	-2.710556
H	-4.090416	3.180136	-0.131795
H	-4.822963	2.010428	-3.687529
H	-7.023293	1.202439	-4.413558
H	-8.897356	1.004778	-2.787696
H	-8.518595	1.627099	-0.405770
H	-6.297219	2.404791	0.335080



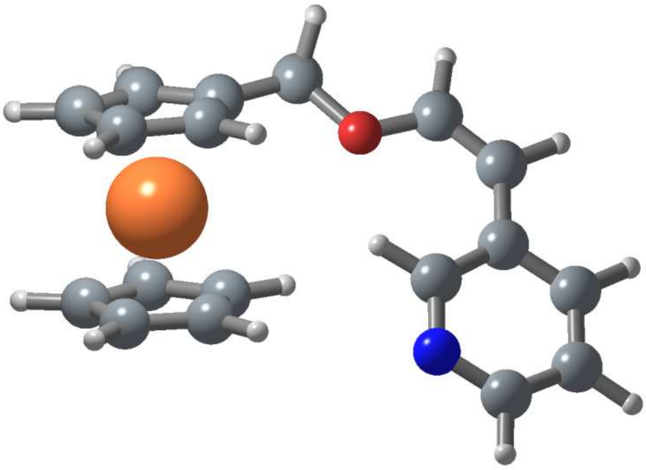
E_{MP2} = – 2109.6523318 a.u.
G_{corr} = 0.294094 a.u.

C	0.099534	-0.046306	-0.096795
C	0.013669	-0.186075	1.320516
C	1.329132	-0.046072	1.864518
C	2.223737	0.191448	0.771577
C	1.464983	0.190535	-0.436774
Fe	1.274609	-1.605168	0.538191
C	2.251190	-3.039057	-0.559758
C	0.839585	-3.239679	-0.627575
C	0.358052	-3.437666	0.701318
C	1.470352	-3.360817	1.591187
C	2.640556	-3.115192	0.811844
C	1.711158	-0.010230	3.316804
O	0.877811	-0.947283	4.031063
C	1.549551	1.388739	3.919739
H	-0.724305	-0.125356	-0.793118
H	-0.882574	-0.391651	1.888394
H	3.293356	0.336098	0.851740
H	2.908085	-2.853010	-1.398656
H	0.238830	-3.230650	-1.526945
H	-0.671655	-3.601418	0.987989
H	1.426577	-3.444723	2.667992
H	3.646215	-2.998554	1.192838
H	1.859777	0.327284	-1.434315
H	2.757648	-0.333859	3.416387
H	1.833391	1.391874	4.976783
H	2.180431	2.106476	3.387254
H	0.508948	1.714105	3.836976
C	1.365162	-1.398584	5.217936
C	0.648836	-2.073805	6.134568
H	2.426043	-1.210172	5.382381
H	1.223052	-2.399831	6.997986
C	-0.768807	-2.439558	6.147196
C	-1.685852	-2.080945	5.137589
C	-3.023452	-2.460088	5.224598
C	-3.485678	-3.205781	6.311262
C	-2.590912	-3.569272	7.319097
C	-1.253949	-3.190106	7.236549
H	-1.340558	-1.500735	4.291749
H	-3.711976	-2.169958	4.435400
H	-4.529591	-3.499244	6.371632
H	-2.934731	-4.148440	8.171608
H	-0.565208	-3.477472	8.027278



E_{MP2} = – 2086.47317741 a.u.
G_{corr} = 0.255562 a.u.

C	-0.173514	0.098584	0.027025
C	-0.107169	0.075711	1.452831
C	1.263911	-0.055444	1.829077
C	2.044534	-0.114714	0.635177
C	1.155884	-0.018716	-0.477971
Fe	0.990752	1.645377	0.711589
C	0.250746	3.369447	1.524887
C	0.114273	3.389352	0.099021
C	1.425132	3.273066	-0.461634
C	2.360302	3.170275	0.610628
C	1.635939	3.234167	1.838836
C	-1.164732	3.620035	-0.640734
O	-1.169745	2.844966	-1.845301
C	-2.212673	3.005731	-2.693706
C	-3.307248	3.770960	-2.526611
C	-4.387700	3.893716	-3.511495
C	-5.661907	4.332223	-3.116105
C	-6.682439	4.432350	-4.056247
C	-6.407390	4.089387	-5.379693
N	-5.197322	3.689456	-5.793729
C	-4.225932	3.610207	-4.882796
H	-1.270803	4.681857	-0.908841
H	3.430229	3.049374	0.509333
H	1.654619	3.242453	-1.517458
H	-0.560506	3.438595	2.237755
H	1.644815	-0.095887	2.840534
H	3.120951	-0.206333	0.583968
H	1.440054	-0.017544	-1.521229
H	-1.067738	0.214041	-0.568843
H	-0.946812	0.152816	2.130317
H	2.058773	3.174851	2.832340
H	-2.025974	3.344811	-0.017106
H	-2.063236	2.394094	-3.578123
H	-3.446394	4.321670	-1.601318
H	-3.248159	3.320470	-5.263929
H	-7.182888	4.146420	-6.140892
H	-7.674894	4.766459	-3.769759
H	-5.846193	4.583337	-2.074452



E_{MP2} = – 2086.476448 a.u
G_{corr} = 0.258022 a.u.

C	0.086563	0.055571	0.177232
C	-0.016378	0.062036	1.579272
C	0.991511	-0.634068	2.281762
N	1.996970	-1.296126	1.701355
C	2.056952	-1.293662	0.363041
C	1.129339	-0.627849	-0.438523
C	-1.124360	0.766375	2.223845
C	-1.482573	0.773799	3.521075
O	-0.814546	0.098613	4.489678
C	-1.417693	0.085285	5.791886
H	-1.643602	1.121646	6.085978
C	-0.475115	-0.541292	6.768812
C	0.943782	-0.365697	6.825420
C	1.430695	-1.053145	7.976290
C	0.317242	-1.647108	8.642869
C	-0.858925	-1.333398	7.898712
Fe	0.462370	-2.362007	6.725349
C	-0.485038	-4.063758	6.076510
C	0.654309	-4.399546	6.868892
C	1.807039	-3.838741	6.240186
C	1.382142	-3.157822	5.060225
C	-0.034322	-3.295886	4.960768
H	2.465981	-1.124063	8.280912
H	1.538715	0.178822	6.105745
H	-1.867368	-1.643783	8.139081
H	0.644545	-4.969748	7.788031
H	2.824716	-3.911076	6.599313
H	2.017355	-2.636477	4.356675
H	-0.654217	-2.875265	4.181679
H	-1.509675	-4.337187	6.289869
H	0.357750	-2.244837	9.543120
H	-2.363713	-0.471230	5.759345
H	-2.349071	1.343649	3.853889
H	-1.759028	1.356369	1.568209
H	0.973624	-0.649689	3.364448
H	2.882661	-1.843602	-0.084423
H	1.223481	-0.647662	-1.519962
H	-0.654663	0.581321	-0.419848