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Direct C–C Coupling of Ferrocenyllithium and Azaheterocycles by Nucleophilic Substitution of Hydrogen – Synthesis of Mono- and 1,1′-Diazinylferrocenes

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A versatile synthetic protocol was proposed for the direct C–C coupling of a ferrocene fragment with various azaheterocycles in the absence of metal catalysts on the basis of nucleophilic substitution of hydrogen. Monosubstituted and disubstituted heteroannular azinyl derivatives of ferrocene were prepared in good yields.

Introduction

In the past decades, ferrocene chemistry has experienced a renaissance owing to increasing interest in the catalytic properties of ferrocene-containing compounds. In coordination chemistry, the ferrocene moiety plays a significant role as a backbone or an ancillary substituent in ligands[1] due to the specific and unique geometry provided by ferrocene and has potential application in materials science[2] as molecular devices and electronic sensors because of the electronic (redox-active) properties of such ligands.[3]

The synthesis of hetaryl-containing ferrocenes and, particularly, azinyl derivatives is of considerable interest because of the ability of these compounds to form complexes with various metals.[4] Among these ligands, homoannular di- and polysubstituted derivatives of ferrocene with planar chirality deserve special attention because they are used as auxiliaries in asymmetric synthesis. The mutual arrangement of the electron lone pair of the azine heteroatom and the cyclopentadienyl moiety in azinylferrocenes is responsible for the so-called complex-induced proximity effect (CIPE)[5] as regio- and stereoselective lithiation of this type of compounds. Ferrocene-containing compounds bearing heterocyclic fragments can also be used as ligands for the synthesis of metal complex catalysts.[6]

Two methods are commonly employed to obtain hetarylferrocenes. The first one involves the construction of heterocycles on a ferrocene matrix with functional groups preliminary introduced into the ferrocene structure. Representative examples include the formation of oxazolinylferrocenes from ferrocenecarboxylic acid or its nitrile and amino alcohols,[7] the synthesis of ferrocenyldihydropyrimidines by the reaction of 1-(3-aryl-2-propen-1-oxo-1-yl)ferrocene with thiourea or phenylthiourea,[8] and the synthesis of indol-2-ylferrocene from ethynylferrocene.[9] Another synthetic route to hetarylferrocenes is based on transition metal-catalyzed C–C cross-coupling of heterocyclic derivatives and metallocene. It is known that hetarylferrocenes are formed by Suzuki–Miyaura cross-coupling of 1,1′-ferrocenylenediboronic acid and halogen derivatives of pyridine or pyrimidine[10] as well as by Stille cross-coupling of tributylstannylferrocene with 2-halopyridine or 2-haloquinoline.[11]

Recently, the methodology of nucleophilic aromatic substitution of hydrogen (S_N^H reactions)[12] has received widespread attention, including direct C–C coupling of π-deficient arenes and heteroarenes with various nucleophiles in the absence of catalysis by transition metals. In this paper, we describe a versatile and convenient preparative method for the introduction of the ferrocenyl residue into azines on the basis of S_N^H reactions. This approach has a wide scope and can be applied to various substituted or unsubstituted azines, such as mono-, di-, and triazines containing heteroatoms in different positions of either the nonannelated or benzannelated ring. Well-known analytical reagents, such as 2,2′-bipyridine, 1,10-phenanthroline, 8-hydroxyquinoline, etc., can be involved in this transformation, which opens new possibilities for ligand design.

In the present study, we developed a simple and convenient approach to the synthesis of 1-azinyl- and 1,1′-diazinylferrocenes by C–C coupling of ferrocenes with azines.

Results and Discussion

To the best of our knowledge, practical synthetic approaches to azinylferrocenes are lacking, and available data on this class of compounds are scarce. Nesmeyanov[13] and

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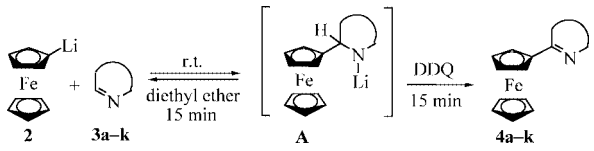
Schlögl[14] were the first to prepare pyridyl- and quinolinylferrocenes by the reactions of ferrocenyllithium with pyridine and quinoline in yields lower than 30%. More recently, 2,2′-bipyridine and 1,10-phenanthroline derivatives were also synthesized according to this method (yields 20–40%).[15]

According to the mechanism accepted for nucleophilic aromatic substitution of hydrogen, this reaction can be considered as a two-step "addition–elimination" process giving **4a**–**k** as the final products (Scheme 1 and Table 1). In the first reversible step, unstable intermediates **A** having a dihydroazine structure are generated under an atmosphere of argon. The second step is rearomatization that formally occurs by elimination of the hydride anion from σ^H adduct **A**, which requires the assistance of an oxidizer. In the absence of a dehydrogenating agent, σ^H adduct **A** can undergo side reactions.[12] The general scheme outlined in Scheme 1 has not been considered as an S_NH process in the cited papers,[13–15] in neither case was the oxidizer specially chosen. In our opinion, this is the main cause for poor yields. As for the oxidation of the σ^H adducts, it occurred spontaneously[13–15] because of the contact of **A** with air. Thus, a natural oxidizer, viz. atmospheric oxygen, performed the rearomatization.



Scheme 1. Synthesis of hetarylferrocenes **4**.

We studied ferrocenyllithium reactions with a series of azaheterocycles, optimized the conditions for the preparation of the starting materials and target products, and determined the factors that allowed us to synthesize mono- and 1,1′-disubstituted azinylferrocenes in good yields. Special experiments aimed towards the search for an appropriate oxidizer were performed. As can be seen from Table 2, DDQ is the oxidizer of choice for this reaction.

Optimization of the reaction conditions showed that the reaction temperature should be 25 °C for the maximum conversion of lithioferrocene to be achieved. The yields of the products decreased with increasing reaction temperature. The use of THF as the solvent in the addition step led to a decrease in the yields of the target products. *n*BuLi is likely to be unstable under these conditions; its half-life is 30 min at room temperature.[16] Diethyl ether is the solvent

Table 1. Yields of compounds **4a**–**k**.

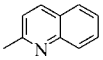
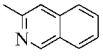
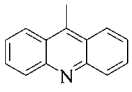
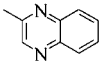
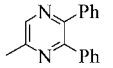
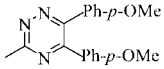
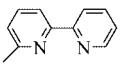
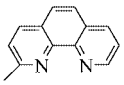
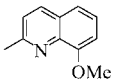
Compound	Azinyl residue		Yield [%]	Lit. Yield [%]
4a	pyridyl-2		67	24[13], 32[14]
4b	quinolin-2-yl		67	2.9[14]
4c	isoquinolin-3-yl		60	
4d	acridin-9-yl		80	
4e	pyrimidin-4-yl		79	
4f	quinoxalin-2-yl		70	
4g	2,3-diphenylpyrazin-5-yl		68	
4h	5,6-di-*p*-methoxyphenyl-1,2,4-triazinyl-3		67	
4i	2,2'-bipyridyl-6		78	35–40[15]
4j	1,10-phenanthrolin-2-yl		80	20–35[15]
4k	8-methoxyquinolin-2-yl		85	

Table 2. Experimental data for the selection of an appropriate oxidizer.

Compound	Yield [%]			
	Method A[a]	Method B[b]	Method C[c]	Method D[d]
4a	tar	38	40	67
4e	–	44	48	79
4j	–	45	52	80

[a] Dry air bubbled through the reaction mixture for 1 h. [b] $FeCl_3$, H_2O (the reaction mixture was added to an aqueous solution of $FeCl_3$). [c] $K_3[Fe(CN)_6]$, H_2O (the reaction mixture was added to an aqueous solution of $K_3[Fe(CN)_6]$). [d] DDQ (a THF solution of DDQ was added to the reaction mixture).

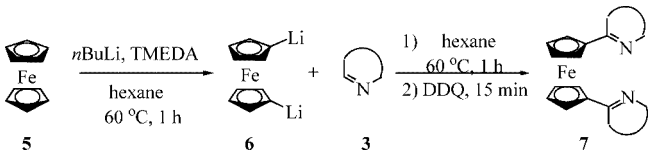
of choice for the synthesis of monosubstituted azinylferrocenes. The use of DDQ and diethyl ether at room temperature allowed us to shorten the reaction time from 16 h[13–15] to 30 min.

It was found that the reaction with the use of bromoferrocene as the starting material instead of ferrocene[13–15] affords only pure monolithiation product **2**, as evidenced by the absence of even trace amounts of disubstituted ferrocenes among the reaction products. Lithioferrocene readily reacts with azines **3** in a molar ratio of ca. 1:1 in diethyl ether at 25 °C under an atmosphere of argon followed by the reaction with DDQ to form hetarylferrocenes **4a**–**k** in 67–85% yields (Table 1). The reaction proceeded without any activation of heteroarene that is commonly used in similar processes.[12] Monolithiated ferrocene is rapidly generated at room temperature; the formation of the product is accompanied by precipitation of a bright orange solid. Upon the addition of a suspension of product **2** to an ethereal solution of azine, the color of the solution immediately became deeper. Dehydrogenation of intermediate **A** by DDQ in a THF solution was followed by a change in the color from orange to green.

We applied this approach to a series of new azaaromatic substrates, such as isoquinoline **3c**, acridine **3d**, pyrimidine **3e**, quinoxaline **3f**, 2,3-diphenylpyrazine **3g**, 5,6-bis-*p*-methoxyphenyl-1,2,4-triazine **3h**, and 8-methoxyquinoline **3k**. In addition, we managed to increase the yields of known[13–15] ferrocene derivatives of pyridine, quinoline, 2,2′-bipyridyl, and 1,10-phenanthroline. Compounds **4a**–**k** are orange-red solids ($\lambda_{max} \approx 450$ nm in methanol).

The above-mentioned techniques that were developed for monosubstituted hetaryl derivatives of ferrocene **4** were slightly modified and used for the synthesis of 1,1′-diazinylferrocenes **7**. The latter are of interest as ligands for complexation with metals.[10] It is known that 1,1′-dilithioferrocene can be prepared by the reaction of ferrocene **5** with *n*BuLi in the presence of TMEDA.[17] 1,1′-Dilithioferrocene smoothly reacts with a twofold excess of azines to give heteroannular-substituted 1,1′-bis-azinylferrocenes **7** (Scheme 2).

As in the synthesis of monoazinylferrocene, the color of the solution became deeper upon the addition of an azine solution to intermediate **6**, the addition of a DDQ solution in THF was also accompanied by a change in the color of

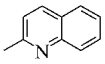
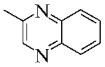
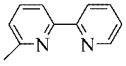
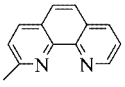
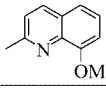


5 6 3 7

Scheme 2. Synthesis of hetarylferrocenes **7**.

the solution. The optimal reaction conditions are as follows: stirring of the reaction mixture in hexane at 60 °C for 1 h. Under these conditions, compounds **7** were prepared in 60–65% yields (Table 3). The yields of compounds **7** significantly decreased as the temperature was lowered to 18 °C and the reaction time was increased to 3 d as well as with the use of THF as the solvent.[15] The formation of small amounts (3–5%) of monosubstituted products was observed but the latter were easily separated from target products **7** by column chromatography. Compounds **7** are deep red stable solids with melting points varying from 160 °C to 300 °C.

Table 3. Yields of compounds **7a**,**b**,**e**,**f**,**i**–**k**.

Compound	Azinyl residue		Yield [%]	Lit. Yield [%]
7a	pyridyl-2		63	3[13,14]
7b	quinolin-2-yl		61	1.1[14]
7e	pyrimidin-4-yl		62	
7f	quinoxalin-2-yl		60	
7i	2,2′-bipyridyl-6		63	20[15]
7j	1,10-phenanthrolin-2-yl		65	14[15]
7k	8-methoxyquinolin-2-yl		64	

The spectral characteristics and elemental analysis data for the resulting mono- and disubstituted hetarylferrocenes agree well with proposed structures **4a**–**k** and **7a**,**b**,**e**,**f**,**i**–**k**. The ^{1}H NMR spectra of compounds **4a**–**k** show characteristic signals of monosubstituted ferrocene, viz. a singlet (5 H intensity) of the unsubstituted cyclopentadienyl fragment of ferrocene at δ = 4.0–4.2 ppm and two multiplets (2 H intensity) of the monosubstituted cyclopentadienyl fragment at δ = 4.3–5.3 ppm, as well as signals of the corresponding heteroaromatic fragments. The ^{1}H NMR spectra of compounds **7a**,**b**,**e**,**f**,**i**–**k** show signals of heteroannular disubstituted ferrocene as two four-proton multiplets of the cyclopentadienyl fragments at δ = 4.2–5.2 ppm and signals of two heteroaromatic fragments. The mass spectra contain molecular ion peaks of **4a**–**k** and **7a**,**b**,**e**,**f**,**i**–**k**.

Most of the resulting compounds were obtained in the crystalline state. The structure of compound **4e** was established by X-ray diffraction (Figure 1). Selected bond lengths and bond angles are listed in Table 4.

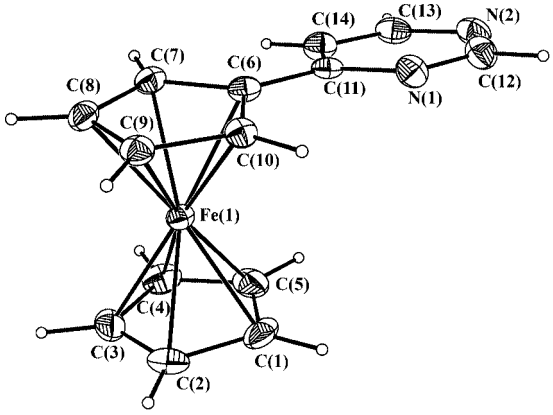


Figure 1. ORTEP representation of the molecular structure of **4e** with thermal ellipsoids drawn at the 40% probability level.

Table 4. Selected bond lengths and bond angles in molecule **4e**.

Bond lengths [Å]			
Fe(1)–C(1)	2.029(3)	Fe(1)–C(10)	2.037(2)
Fe(1)–C(2)	2.037(3)	C(6)–C(11)	1.464(4)
Fe(1)–C(3)	2.042(3)	C(11)–N(1)	1.339(3)
Fe(1)–C(4)	2.042(3)	C(11)–C(14)	1.392(4)
Fe(1)–C(5)	2.034(3)	N(1)–C(12)	1.340(4)
Fe(1)–C(6)	2.030(3)	C(12)–N(2)	1.340(4)
Fe(1)–C(7)	2.026(3)	N(2)–C(13)	1.335(4)
Fe(1)–C(8)	2.042(3)	C(13)–C(14)	1.362(4)
Fe(1)–C(9)	2.052(3)		
Bond angles [°]			
C(6)–C(11)–N(1)	117.4(2)	C(11)–N(1)–C(12)	116.0(2)
C(6)–C(11)–C(14)	122.0(2)	C(13)–N(2)–C(12)	113.6(2)
C(14)–C(11)–N(1)	120.6(2)	N(1)–C(12)–N(2)	128.3(3)
C(11)–C(14)–C(13)	117.2(3)	C(14)–C(13)–N(2)	124.3(3)

The Cp [C(1)–C(5) atoms] and Cp′′ [C(6)–C(10) atoms] rings are coplanar [the angle is 1.9(2)°]. The pyrimidine ring is rotated relative to the Cp′′ ring by 9.5(2)°.

The Fe(1) atom is in the asymmetrical position with respect to the Cp rings. The Cp–Fe(1)–Cp′′ angle is 158.5°. The Fe(1)–Ct and Fe(1)–Ct′′ distances are 1.667 and 1.697 Å, respectively.

In the crystal structure, molecules of **4e** form centrosymmetric dimers (Figure 2) through N···H–C hydrogen bonds and π–π stacking interactions between the pyrimidine rings (Figure 3). The shortest intramolecular N(2)···N(2A) and C(12)···C(13A) distances are 3.451(3) and 3.461(4) Å, respectively.

The parameters of the H bond are as follows: the N(2)···C(5A) and N(2)···H(5AA) distances are 3.409(4) Å and 2.49 Å respectively, and the N(2)–H(5AA)–C(5A) angle is 152°. Because of the formation of this H bond, the C(13)–N(2)–C(12) bond angle is smaller than the C(11)–N(1)–C(12) bond angle (see Table 3).

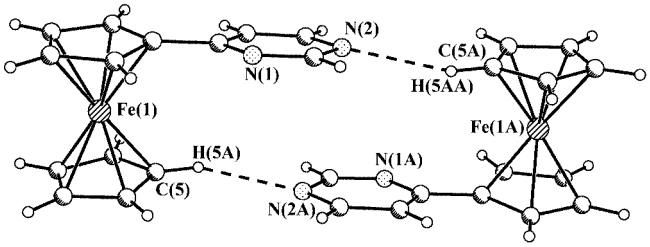


Figure 2. View of the dimer in the crystal structure of **4e**.

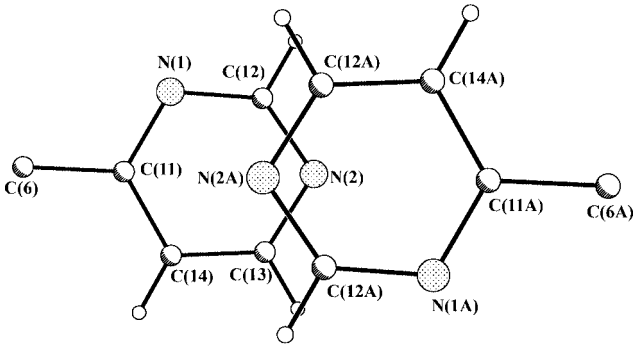


Figure 3. Overlapping of the pyrimidine rings in the intermolecular dimer.

The distance between the mean planes of the pyrimidine rings (Figure 3) in the dimer is 3.38 Å. The shortest intermolecular N(2)···N(2A) distance is 3.451(2) Å.

Conclusions

An improved general method was developed for the synthesis of mono- and disubstituted heterocyclic ferrocene derivatives in the absence of catalysts. This method provides an approach to the synthesis of ferrocene ensembles with various azaheterocycles.

Experimental Section

General: ^{1}H NMR spectra were recorded with a Bruker DRX-400 Avance spectrometer with TMS as the internal standard. The mass spectra were obtained with a Varian MAT-311A instrument, electron beam ionization, ionization energy was 70 eV, direct inlet system, temperature of the ionization chamber was 100–300 °C. Starting heterocycles are commercially available reagents. Bromoferrocene,[18] 2,3-diphenylpyrazine,[19] and 5,6-bis(*p*-methoxyphenyl)-1,2,4-triazine[20] were synthesized according to known procedures. The course of the reactions was monitored and the purity of the reaction products was checked by TLC on Poligram Alox N/UV-254 plates with the use of ethyl acetate as the eluent. The IR spectra were measured with a Perkin–Elmer Spectrum One B FTIR spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400-II instrument. Melting points are not corrected.

X-ray Study of Compound 4e: Single crystals of compounds **4e** suitable for X-ray diffraction study were grown by crystallization from hexane. Crystallographic data: Orange single crystals of **4e**, $C_{14}H_{12}FeN_2$ (*Fw* = 264.11), monoclinic, *a* = 13.974(3) Å, *b* = 7.419(2) Å, *c* = 11.188(2) Å, *β* = 104.058(4)°, *V* = 1125.2(4) Å^3,

space group $P2_1/c$ (No. 14), $Z = 4$, $d_{calcd.} = 1.559\ g\,cm^{-3}$, $\mu = 1.315\ mm^{-1}$, $F(000) = 544$, crystal dimensions $0.15 \times 0.30 \times 0.45$ mm.

A single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD area detector by using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å, ω-scanning technique with a step of 0.3° and the exposure time per frame of 10 s) at 120 K. Low temperature was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated by using the SAINT software[21a] and the semi-empirical SADABS method.[21b] A total of 9481 reflections were measured ($\theta_{max} = 29.0°$, the completeness was 98.0%), and 2928 ($R_{int} = 0.0595$) independent reflections were used in calculations and structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares against F^2_{hkl} with anisotropic displacement parameter for non-hydrogen atoms. All hydrogen atoms were placed in geometrically calculated positions and included in the final refinement by using a riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(C), where U(C) are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. The refinement was converged to $R_1 = 0.0416$ [1833 independent reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0878$ (all 2928 independent reflections), the number of parameters in the refinement was 154, GOOF 0.994, the largest difference peak and hole were 0.783 and –0.357 e Å^{-3}, respectively.

All calculations were performed with a IBM PC/AT by using the SHELXTL program package.[21c]

General Procedure for the Synthesis of 4: A solution of lithioferrocene **2** in diethyl ether obtained from a 2.5 M *n*BuLi solution in hexane (1.59 mL, 4 mmol) and a solution of **1** (3.8 mmol) in dry diethyl ether (20 mL) was added to a solution (or suspension) of the corresponding heterocycle (3.8 mmol) in diethyl ether (10 mL) under an atmosphere of argon at room temperature. After stirring the reaction mixture at room temperature for 15 min, a solution of DDQ (3.8 mmol) in THF (10 mL) was added, and the mixture was stirred for 15 min. Finally, the reaction mixture was filtered through neutral alumina and subjected to alumina column chromatography to obtain a mixture of bromoferrocene and ferrocene (hexane as the eluent) and then the reaction product (ethyl acetate as the eluent). The eluate was concentrated to dryness in vacuo and the residue was recrystallized from an appropriate solvent.

1-(Isoquinolin-3-yl)ferrocene (4c): Orange powder. Yield 0.71 g (60%). M.p. 195 °C (toluene). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.11 (s, 5 H, Cp H), 4.37(m, 2 H, C_5H_4), 4.81 (m, 2 H, C_5H_4), 7.62 (m, 2 H, 6′-H, 7′-H), 7.98 (s, 1 H, 4′-H), 8.16 (m, 1 H, 5′-H), 8.74 (m, 1 H, 8′-H), 9.94 (s, 1 H, 1′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3064, 1599, 1430, 1513, 1280, 1106, 1092, 818, 752 cm^{-1}. EI-MS: *m*/*z* (%) = 313 (100) [M]$^+$. $C_{19}H_{15}FeN$ (313.19): calcd. C 72.87, H 4.83, N 4.47; found C 72.85, H 4.70, N 4.42.

1-(Acridin-9-yl)ferrocene (4d): Red crystals. Yield 1.11 g (80%). M.p. 86 °C (hexane). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.21 (s, 5 H, Cp H), 4.68 (m, 2 H, C_5H_4), 4.86 (m, 2 H, C_5H_4), 7.55 (m, 2 H, 2′-H, 7′-H), 7.73 (m, 2 H, 3′-H, 6′-H), 8.10 (d, ^3J = 8.8 Hz, 2 H, 1′-H, 8′-H), 9,05 (d, ^3J = 8.8 Hz, 2 H, 4′-H, 5′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3075, 1626, 1517, 1405, 1335, 1105, 1030, 812, 752 cm^{-1}. EI-MS: *m*/*z* (%) = 363 (100) [M]$^+$. $C_{23}H_{17}FeN$ (363.25): calcd. C 76.05, H 4.72, N 3.86; found C 76.15, H 4.83, N 3.95.

1-(Pyrimidin-4-yl)ferrocene (4e): Orange crystals. Yield 0.79 g (79%). M.p. 85 °C (hexane). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.02 (s, 5 H, Cp H), 4.50 (m, 2 H, C_5H_4), 5.04 (m, 2 H, C_5H_4), 7.50 (m, 1 H, 6′-H), 8.51 (d, ^3J = 5.8 Hz, 1 H, 5′-H), 8.88 (d, ^4J = 1.0 Hz, 1 H, 2′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3100, 1576, 1490, 1388, 1287, 1106, 1016, 813, 781 cm^{-1}. EI-MS: *m*/*z* (%) = 264 (100) [M]$^+$. $C_{14}H_{12}FeN_2$ (264.11): calcd. C 63.67, H 4.58, N 10.61; found C 63.78, H 4.39, N 10.68.

1-(Quinoxalin-2-yl)ferrocene (4f): Red crystals. Yield 0.83 g (70%). M.p. 130 °C (hexane). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.07 (s, 5 H, Cp H), 4.56 (m, 2 H, C_5H_4), 5.19 (m, 2 H, C_5H_4), 7.70 (m, 2 H, 5′-H, 8′-H), 7.95 (m, 2 H, 6′-H, 7′-H), 9.07 (s, 1 H, 3′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3075, 1544, 1498, 1291, 1110, 1087, 1023, 814, 756 cm^{-1}. EI-MS: *m*/*z* (%) = 314 (100) [M]$^+$. $C_{18}H_{14}FeN_2$ (314.17): calcd. C 68.82, H 4.49, N 8.92; found C 68.86, H 4.33, N 9.17.

1-(2,3-Diphenylpyrazin-5-yl)ferrocene (4g): Orange crystals. Yield 1.07 g, (68%). M.p. 115 °C (hexane).^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.10 (s, 5 H, Cp H), 4.48 (m, 2 H, C_5H_4), 5.08 (m, 2 H, C_5H_4), 7.31 (m, 6 H, Ph), 7.42 (m, 4 H, Ph), 8.77 (s, 1 H, 6′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3093, 1554, 1410, 1373, 1296, 1120, 1025, 818, 700 cm^{-1}. EI-MS: *m*/*z* (%) = 416 (100) [M]$^+$. $C_{26}H_{20}FeN_2$ (416.31): calcd. C 75.01, H 4.84, N 6.73; found C 75.03, H 4.73, N 6.42.

1-(5,6-Bis-*p*-methoxyphenyl-1,2,4-triazinyl-3)ferrocene (4h): Orange crystals. Yield 1.03 g, (67%). M.p. 170 °C (ethyl acetate).^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.83 (s, 6 H, OMe), 4.12 (s, 5 H, Cp H), 4.56 (m, 2 H, C_5H_4), 5.21 (m, 2 H, C_5H_4), 6.92 (m, 4 H, C_6H_4), 7.46–7.58 (m, 4 H, C_6H_4) ppm. IR (KBr): $\tilde{\nu}$ = 2959, 1504, 1479, 1370, 1250, 1177, 1025, 831, 731 cm^{-1}. EI-MS: *m*/*z* (%) = 477 (74) [M]$^+$. $C_{27}H_{23}FeN_3O_2$ (477.35): calcd. C 67.94, H 4.86, N 8.80; found C 67.93, H 4.93, N 8.90.

1-(8-Methoxyquinolin-2-yl)ferrocene (4k): Red crystals. Yield 0.68 g, (85%). M.p. 135 °C (hexane). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.00 (s, 5 H, Cp H); 4.05 (s, 3 H, OMe); 4.41 (m, 2 H, C_5H_4); 5.13 (m, 2 H, C_5H_4); 7.05 (m, 1 H, 7′-H); 7.37 (m, 2 H, 5′-H, 6′-H); 7.66 (d, ^3J = 8.5 Hz, 1 H, 3′-H); 8.09 (d, ^3J = 8.5 Hz, 1 H, 4′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 1558, 1460, 1327, 1258, 1109, 995, 839, 738 cm^{-1}. EI-MS: *m*/*z* 343 (100) [M]$^+$. $C_{20}H_{17}FeNO$ (343.21): calcd. C 69.99, H 4.99, N 4.08; found C 70.03, H 5.15, N 4.18.

General Procedure for Synthesis of 7: A suspension of 1,1′-bislithioferrocene **6** in dry hexane (25 mL), which was prepared by heating ferrocene (1 g, 5.4 mmol) with a 2.5 M *n*BuLi solution in hexane (4.5 mL, 11.3 mmol) and TMEDA (1.69 mL, 11.3 mmol) at 60 °C for 1 h, was added to a stirred solution (or a suspension) of the corresponding heterocycle (10.8 mmol) in dry THF (10 mL) under an atmosphere of argon at room temperature. The reaction mixture was heated at 60 °C for 1 h, a solution of DDQ (11.3 mmol) in THF (10 mL) was added, and the mixture was stirred for 15 min. Finally, the reaction mixture was filtered through neutral alumina and subjected to alumina column chromatography to successively obtain ferrocene (hexane as the eluent), a small amount of monosubstituted hetarylferrocene (ethyl acetate), and finally product **7** (ethyl acetate). The eluate was concentrated to dryness in vacuo and the residue was recrystallized from an appropriate solvent.

1,1′-Bis(quinolin-2-yl)ferrocene (7b): Red crystals. Yield 1.44 g, (61%). M.p. 204 °C (toluene/hexane). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 4.38 (m, 4 H, C_5H_4), 5.00 (m, 4 H, C_5H_4), 7.17 (d, ^3J = 8.5 Hz, 2 H, 3′-H), 7.39–7.59 (m, 8 H, 5′-H, 6′-H, 7′-H, 8′-H), 7.73 (d, ^3J = 8.5 Hz, 2 H, 4′-H) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2854, 1600, 1513, 1465, 1426, 1282, 1093, 821, 750 cm^{-1}. EI-MS: *m*/*z* (%) = 440 (100) [M]$^+$. $C_{28}H_{20}FeN_2$ (440.33): calcd. C 76.38, H 4.58, N 6.36; found C 76.35, H 4.58, N 6.41.

1,1′-Bis(pyrimidin-4-yl)ferrocene (7e): Red crystals. Yield 1.12 g, (62%). M.p. 181 °C (toluene/hexane). ^{1}H NMR (400 MHz, [D$_6$]-

DMSO): δ = 4.43 (m, 4 H, C_5H_4), 4.96 (m, 4 H, C_5H_4), 7.16 (m, 2 H, 6′-H), 8.34 (m, 2 H, 5′-H), 8.74 (s, 2 H, 2′-H) ppm. IR (KBr): $\tilde{\nu}$ = 3099, 2922, 1584, 1496, 1388, 1287, 1106, 1019, 987, 835 cm^{-1}. EI-MS: *m*/*z* (%) = 342 (100) $[M]^+$. $C_{18}H_{14}FeN_4$ (342.19): calcd. C 63.18, H 4.12, N, 16.37; found C 63.08, H 3.95, N 16.04.

1,1′-Bis(quinoxalin-2-yl)ferrocene (7f): Red crystals. Yield 1.5 g (60%). M.p. 225 °C (toluene/hexane). ^1H NMR (400 MHz, [D_6]-DMSO): δ = 4.55 (m, 4 H, C_5H_4), 5.19 (m, 4 H, C_5H_4), 7.53 (m, 8 H, 5′-H, 8′-H, 6′-H, 7′-H), 8.65 (s, 2 H, 3′-H) ppm. IR (KBr): $\tilde{\nu}$ = 2933, 2855, 1574, 1548, 1499, 1295, 1088, 909, 825, 758 cm^{-1}. EI-MS: *m*/*z* (%) = 442 (100) $[M]^+$. $C_{26}H_{18}FeN_4$ (442.31): calcd. C 70.60, H 4.10, N 12.67; found C 70.42, H 4.15, N 12.40.

1,1′-Bis(8-methoxyquinolin-2-yl)ferrocene (7k): Red crystals. Yield 1.77 g (64%). M.p. 201 °C (toluene/hexane). ^1H NMR (400 MHz, [D_6]DMSO): δ = 3.98 (s, 6 H, OMe); 4.35 (m, 4 H, C_5H_4); 4.99 (m, 4 H, C_5H_4); 7.00 (m, 2 H, 7′-H); 7.10 (m, 2 H, 5′-H); 7.22 (d, ^3J = 8.5 Hz, 2 H, 3′-H); 7.31 (m, 2 H, 6′-H); 7.48 (d, ^3J = 8.5 Hz, 2 H, 4′-H) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2856, 1557, 1456, 1326, 1256, 1108, 993, 841, 752 cm^{-1}. EI-MS: *m*/*z* (%) = 500 (100) $[M]^+$. $C_{30}H_{24}FeN_2O_2$ (500.39): calcd. C 72.01, H 4.83, N 5.60; found C 72.01, H 4.75, N 5.88.

CCDC-282124 contains 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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