Notes

Copper(I)-Catalyzed Synthesis of Ferrocenyl Aryl Ethers

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Summary: Ferrocenyl aryl ether can be synthesized in good yields by CuI/2,2,6,6-tetramethylheptane-3,5-dione (TMHD)-catalyzed coupling reactions from iodoferrocene or 1,1′-diiodoferrocene and various phenols in NMP solvent using Cs_2CO_3 or K_3PO_4 bases.

Ferrocenes constitute an important class of organometallic compounds, which has found numerous applications as ligands in homogeneous catalysis,[1] for molecular recognition,[2] in polymer sciences,[3] and as biolabels,[4] sensors,[5] NLO materials,[6] and molecular switches.[7]

Nonetheless, several deficits in the preparative chemistry of ferrocenes are still obvious. As an example, the synthetic availability of heteroatom (oxygen, nitrogen)-substituted ferrocenes is rather limited, as the synthetic routes traditionally used to introduce such heteroatoms on benzenes are not suitable for ferrocenes. The main entries into this chemistry are 1,1′-diaminoferrocene and 1,1′-dihydroxyferrocene or the respective monosubstituted ferrocenes, which can be functionalized via simple nucleophilic substitutions with alkyl halides to result in secondary or tertiary ferrocenylamines or in ferrocenyl alkyl ethers.[8]

Related compounds with additional substituents on ferrocene are less easily obtained. Basically, substituted ferrocenyl alkyl ethers are accessible primarily via the stable trialkylsilyl-protected hydroxyferrocenes, which can be obtained in good yields from the respective lithiated cyclopentadienyl silyl ethers and $FeCl_2$.[9] On the contrary, ferrocenyl aryl ethers are almost unknown; the only synthesis of such compounds dates back to the early 1960s when Rausch[10] and Nefedova[11] described Ullmann type coupling reactions at elevated temperatures to produce ferrocenyl phenyl ethers in modest yields of around 10−25%.

Consequently, we wish to describe here a reliable and high-yielding synthesis of ferrocenyl aryl ethers from bromo- or iodoferrocenes and phenols mediated by copper(I)-based catalysts.[12]

To synthesize ferrocenyl aryl ethers, we first tested the Pd-catalyzed Buchwald−Hartwig ether synthesis[13] using various phenols and iodo- or bromoferrocenes. Unfortunately, all our attempts using different phosphine ligands and palladium sources as catalysts did not lead to the formation of the desired products. Following this, we evaluated several copper-based catalysts,[14] which were demonstrated to work efficiently for the synthesis of aryl ethers by Buchwald et al. (CuI/1,10-phenanthroline, Cs_2CO_3),[15] Venkataraman et al. [Cu(neocup)(PPh_3) and Cu(PPh_3)$_3$Br],[16] and Song et al. [CuCl/THMD].[17] Among these, the CuI/1,10-phenanthroline catalyst (Table 1, entries 1−4) and the Cu(PPh_3)$_3$Br complex resulted in the formation of modest amounts of ferrocenyl aryl ethers. In test reactions of iodoferrocene and 1,4-*tert*-butylphenol up to 16% yield of coupling products were formed with the CuI/1,10-phenanthroline system (10 mol % CuI and 20 mol % phen) after 24 h at 110 °C.

Significantly improved yields were obtained with the Venkataraman catalyst Cu(PPh_3)$_3$Br. However, instead of using a preformed copper-phosphine complex, we considered it more practical to in situ generate the respective catalyst. Consequently, we evaluated the

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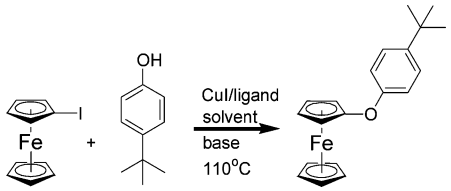
Table 1. Ligand Screening for the Coupling of Iodoferrocene and 1,4-*tert*-Butylphenol[a]



entry	solvent	ligand	base	yield[e] [%]
1	toluene	1,10-phen[b]	Cs_2CO_3	9
2	toluene	1,10-phen[b]	K_3PO_4	16
3	toluene	1,10-phen[b]	DABCO	<5
4	toluene	1,10-phen[b]	Et_3N	<5
5	toluene	Cy_2PBn[c]	Cs_2CO_3	94
6	toluene	$(1\text{-Ad})_2PBn$[c]	Cs_2CO_3	84
7	toluene	P(*o*-tolyl)$_3$[c]	Cs_2CO_3	64
8	toluene	PPh_3[c]	Cs_2CO_3	85
9	toluene	PPh_3[c]	K_3PO_4	99
10	NMP	PPh_3[d]	Cs_2CO_3	28
11	NMP	$BnPAd_2$[d]	Cs_2CO_3	37
12	NMP	TMHD[d]	Cs_2CO_3	54
13	toluene	TMHD[d]	Cs_2CO_3	30

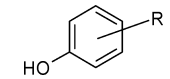
[a] Conditions: iodoferrocene (0.125 mmol), base (0.25 mmol), 1,4-*tert*-butylphenol (0.25 mmol). [b] CuI (10 mol %), 1,10-phenanthroline (20 mol %), 110 °C, 24 h. [c] CuI (10 mol %), ligand (20 mol %), 110 °C, 30 h. [d] CuI (5 mol %), ligand (12.5 mol %), 110 °C; 5 h. [e] Yields determined by GC.

suitability of several different phosphines (PPh_3, $(1\text{-Ad})_2$-PBn, Cy_2PBn, P(*o*-tolyl)$_3$) in combination with CuI (10 mol %) as the copper source, utilizing different Cu:P ratios and several different bases in toluene solvent. Among the bases, Cs_2CO_3 and K_3PO_4 turned out to be the best ones. Concerning the influence of the phosphines, neither the nature of the substituents nor the ratio Cu:P appears to be critical. As can be seen in Table 1, copper complexes with various phosphines result in the formation of **1** in roughly the same yields (entries 5−9). Consequently, we decided to use PPh_3 as the cheapest one of the phosphines studied together with equimolar amounts of CuI. While the yields of the ferrocenyl aryl ethers are satisfactory, the large amounts of catalysts needed as well as extended reaction times obviously render this route less attractive.

Recently another protocol for an improved Ullmann type coupling for diaryl ether synthesis was published by Song et al., which utilizes 2,2,6,6-tetramethylheptane-3,5-dione (TMHD) as a ligand in combination with CuCl as the copper source, Cs_2CO_3 as the base, and NMP as the solvent.[17]

Consequently, we tested NMP as the solvent for the coupling reactions, applying the improved conditions from the first screen to the catalysts CuI/PPh_3 and CuI/TMHD. The results (Table 1, entries 10−13) clearly show that NMP is a more suitable solvent, especially for the CuI/TMHD system (entry 12). Consequently, we decided to study this catalytic system in more detail. A second set of screening experiments was performed focusing on the CuI/THMD and the CuI/PPh_3 catalysts. From the results presented in Table 2 it is quite clear that the combination of CuI/TMHD gives much better results than CuI/PPh_3. Furthermore, with CuI/THMD the catalyst activity is consistently higher when using Cs_2CO_3 as a base instead of K_3PO_4. However, with a view to the drastically lower price of K_3PO_4 the phosphate should still be considered as an alternative.

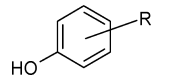
Table 2. Ligand/Base Screening for the Coupling of Iodoferrocene and Phenols in NMP[a]



entry		ligand	base	yield[b] [%]
1	2-*t*-Bu, 4-Me	PPh_3	Cs_2CO_3	21
2	2-*t*-Bu, 4-Me	PPh_3	K_3PO_4	13
3	2-*t*-Bu, 4-Me	TMHD	Cs_2CO_3	84
4	2-*t*-Bu, 4-Me	TMHD	K_3PO_4	72
5	3-*t*-Bu	PPh_3	Cs_2CO_3	53
6	3-*t*-Bu	PPh_3	K_3PO_4	68
7	3-*t*-Bu	TMHD	Cs_2CO_3	96
8	3-*t*-Bu	TMHD	K_3PO_4	83
9	4-*t*-Bu	PPh_3	Cs_2CO_3	52
10	4-*t*-Bu	PPh_3	K_3PO_4	71
11	4-*t*-Bu	TMHD	Cs_2CO_3	99
12	4-*t*-Bu	TMHD	K_3PO_4	81
13	2,4-Me_2	PPh_3	Cs_2CO_3	41
14	2,4-Me_2	PPh_3	K_3PO_4	56
15	2,4-Me_2	TMHD	Cs_2CO_3	80
16	2,4-Me_2	TMHD	K_3PO_4	75

[a] Conditions: iodoferrocene (0.125 mmol), CuI (5 mol %), ligand (12.5 mol %), base (0.25 mmol), phenol (0.25 mmol), T = 110 °C, NMP. Samples taken after 17 h. [b] Yields determined by GC.

Table 3. Coupling of Iodoferrocene and 1,1′-Diiodoferrocene in the Presence of 2,2,6,6-Tetramethylheptane-3,5-dione (TMHD)[a]

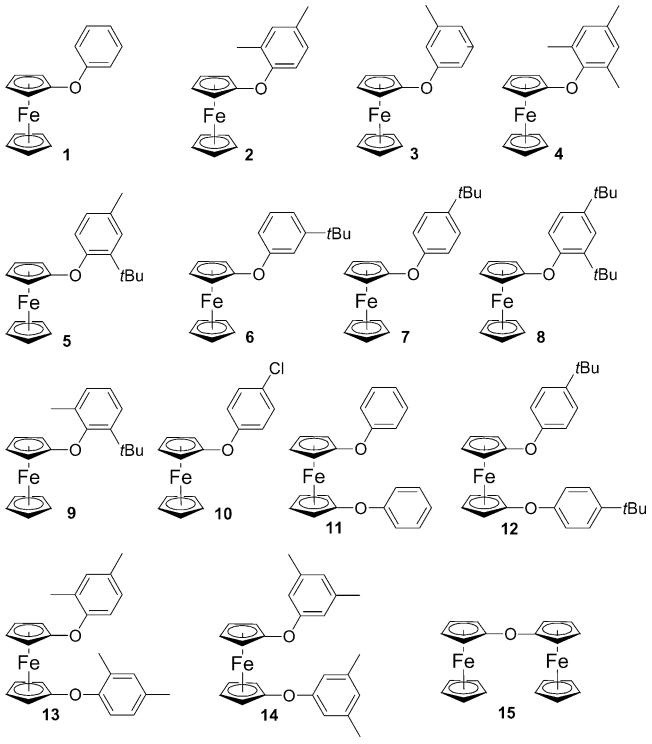


entry		ferrocene	yield[b] [%]	isolated yield[c] [%]
1	H	FcI	62	42
2	2,4-Me_2	FcI	89	81
3	3,5-Me_2	FcI	>95	86
4	2,4,6-Me_3	FcI	44	30
5	2-*t*-Bu, 4-Me	FcI	93	77
6	3-*t*-Bu	FcI	>95	89
7	4-*t*-Bu	FcI	>95	87
8	2,4-*t*-Bu	FcI	86	65
9	2-*t*-Bu, 6-Me	FcI	33	24
10	4-Cl	FcI	>95	90
11	H	1,1′-FcI_2		40
12	4-*t*-Bu	1,1′-FcI_2	75	65
13	2,4-Me_2	1,1′-FcI_2	70	27
14	3,5-Me_2	1,1′-FcI_2	60	30
15	FcOH	FcI		22
16	2-NO_2	FcI	<5	none
17	4-OMe, 2-NO_2	FcI	<5	none
18	4-Cl, 2-NO_2	FcI	<5	none

[a] Conditions: iodoferrocene (0.125 mmol) or 1,1′-diiodoferrocene (0.062 mmol), CuI (5 mol %), TMHD (12.5 mol %), Cs_2CO_3 (0.25 mmol), phenol (0.25 mmol), T = 110 °C, NMP, reaction time 20 h. [b] Yields determined by GC. [c] Yields based on isolated material after chromatographic purification.

The optimized reaction conditions [CuI (5 mol %), TMHD (12.5 mol %), Cs_2CO_3 (0.25 mmol), T = 110 °C, solvent NMP] for the synthesis of ferrocenyl aryl ethers were now applied to the synthesis of several ferrocenyl aryl ethers (Table 3). Most coupling reactions now result in the formation of the respective ferrocenyl aryl ethers in very good yields. Steric bulk (Me or *t*-Bu) ortho to the oxygen atom does not reduce the yields of the coupling products significantly (entries 2, 5, 8), while for phenols with substituents in both the 2- and the 6-position respectable coupling yields are observed. Somewhat unexpectedly the reaction fails completely with strongly electron-withdrawing substituents on the phenol, since none of the $-NO_2$-substituted phenols can be coupled successfully. Interestingly, instead of ether formation, a hydro-dehalogenation takes place, to generate ferrocene from the corresponding ferrocenyl ha-

lides. Such a transformation is known to be a typical side-reaction in transition metal-catalyzed cross-coupling reactions.[18] The respective 1,1′-substituted ferrocenyl aryl ethers were also synthesized in good yields from 1,1′-diiodoferrocene (entries 11−14). The modest yields observed after isolation of the respective ferrocene diethers are most likely due to significant decomposition (oxidation) during chromatographic purifications of the small amounts of material synthesized. It should be noted that the diferrocenyl ether (entry 15) is a simple metallocene compound that has not been described in the literature before. The compound is formed in a modest yield (22%) with the Cu(I)-catalyzed methodology since it is accompanied by the reduction of Cu(I) to Cu(0).



For all of the reactions described in Tables 1−3 we have used iodoferrocene or 1,1′-diiodoferrocene as the organometallic building blocks. The reason for this was the expectation that the lower bond energy of the carbon−iodine bond would render more active substrates than with the carbon−bromine bond in brominated ferrocenes. However, since only bromoferrocene and 1,1′-dibromoferrocene are commercially available, we considered it useful to also evaluate coupling reactions of brominated ferrocenes. Using the same catalyst it is also possible to couple bromoferrocene; however, the activity of the catalyst is roughly half of that for iodoferrocenes. Consequently, much higher catalyst loadings are required to effect the coupling reactions.

Summary. We have presented here a simple and high-yielding synthesis of various ferrocenyl aryl ethers by a Ullmann type coupling of halogenated ferrocenes (FcI, 1,1′-FcI_2, FcBr, 1,1′-$FcBr_2$) and different phenols using a catalyst composed of CuI and 2,2,6,6-tetramethylheptane-3,5-dione (TMHD). Unhindered and sterically demanding phenols can be coupled efficiently, while reactions of electron-deficient nitrophenols do not yield the respective aryl ethers but result in the formation of dehalogenated ferrocenes instead.

Experimental Section

General Methods. Phenols, bases, CuI, and ligands were used as received. All reactions and experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Column chromatography: Silica MN60 (63−200 μm), TLC on Merck plates coated with silica gel 60, F254. Gas chromatography: Perkin-Elmer Autosystem with a Varian CP-SIL-8 column; ferrocene samples were applied to the column using the sandwich technique to obtain reproducible results. NMR spectroscopy: spectra recorded at 293 K with a Bruker Avance 500 (^{1}H NMR 500 MHz, ^{13}C NMR 125 MHz), a Bruker AC 300 (^{1}H NMR 300 MHz, ^{13}C NMR 75 MHz), or a Bruker AC 200 (^{1}H NMR 200 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual protonated impurities in the solvent ($CDCl_3$ 7.24 ppm), ^{13}C NMR to the solvent signal ($CDCl_3$ 77.0 ppm). Starting materials were commercially available or prepared according to literature procedures: iodoferrocene,[19,20] 1,1′-diiodoferrocene,[21] 1,1′-dibromoferrocene.[22] The coupling products obtained were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. For phenoxyferrocene (**1**)[23] and 1,1′-diphenoxyferrocene (**11**)[23] spectroscopic data were found to be identical with those reported in the literature.

General Procedure for the Screening of Coupling Reactions. In a Schlenk tube CuI (2.4 mg, 12.5 μmol, 10 mol %), the respective ligand (25 μmol, 20 mol %), the respective ferrocenyl halide (0.125 mmol), the respective phenol (0.25 mmol), and bases (0.25 mmol) were dissolved in NMP or toluene (7.5 mL), and the reaction was stirred at 110 °C for a given time. In the case of NMP solvent after completion of the reaction, diethyl ether was added (35 mL) and the mixture was extracted with water (3 × 15 mL). After evaporation of the volatiles the crude product was purified by column chromatography (*n*-heptane).

Optimized Procedure for Synthesis of Ferrocenyl Phenyl Ethers. In a Schlenk tube CuI (2.4 mg, 12.5 μmol, 5.0 mol %), TMHD (6.4 μL, 31.2 μmol), iodoferrocene (78 mg, 0.25 mmol) (or half the molar amount of 1,1′-diiodoferrocene), the respective phenol (0.50 mmol), and Cs_2CO_3 (163.2 mg, 0.50 mmol) were dissolved in NMP (15 mL), and the reaction was stirred at 110 °C for the given time. After completion, diethyl ether was added (50 mL) and the mixture was extracted with water (3 × 25 mL). After evaporation of the organic solvent the crude product was purified by column chromatography (*n*-heptane) to obtain the respective pure products.

2,4-Dimethylphenoxyferrocene (2). R_f = 0.26 [*n*-heptane]. ^{1}H NMR ($CDCl_3$): 2.23 (s, 3H, *o*-CH_3), 2.26 (s, 3H, *p*-CH_3), 3.87 ("t", 2H, J = 2.0 Hz, C_5H_4), 4.14 (t, 2H, J = 2.0 Hz, C_5H_4), 4.23 (s, 5H, C_5H_5), 6.86 (s, 2H, C_6H_3), 6.97 (s, 1H, C_6H_3). ^{13}C NMR ($CDCl_3$): 16.2 (Ar*C*H$_3$), 20.7 (Ar*C*H$_3$), 59.1 (*C*$_5$H$_4$), 62.6 (*C*$_5$H$_4$), 69.3 (*C*$_5$H$_5$), 117.0 (Ar*C*), 127.1 (Ar*C*), 128.1 (*C*(C$_5$H$_4$)O), 131.7 (Ar*C*), 132.3 (H$_3$C-Ar*C*), 154.5 (O-Ar*C*).

3,5-Dimethylphenoxyferrocene (3). R_f = 0.19 [*n*-heptane]. ^{1}H NMR ($CDCl_3$): 2.26 (s, 6H, CH_3), 3.93 ("t", 2H, J = 1.9 Hz, C_5H_4), 4.21 (t, 2H, J = 1.9 Hz, C_5H_4), 4.26 (s, 5H, C_5H_5), 6.60 (s, 2H, C_6H_3), 6.65 (s, 1H, C_6H_3). ^{13}C NMR ($CDCl_3$): 21.5

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(Ar*C*H$_3$), 60.2 (*C*$_5$H$_4$), 63.0 (*C*$_5$H$_4$), 69.4 (*C*$_5$H$_5$), 114.7 (*o*-Ar*C*), 122.0 (*C*(C$_5$H$_4$)O), 124.2 (*p*-Ar*C*), 139.2 (H$_3$C-Ar*C*), 159.1 (O-Ar*C*).

2,4,6-Trimethylphenoxyferrocene (4). $R_f{}' = 0.185$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 2.18 (s, 6H, *o*-C*H*$_3$), 2.22 (s, 3H, *p*-C*H*$_3$), 3.77 ("t", 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.02 (t, 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.22 (s, 5H, C$_5$*H*$_5$), 6.78 (s, 2H, C$_6$*H*$_3$). ^{13}C NMR (CDCl$_3$): 16.8 (Ar*C*H$_3$), 20.7 (Ar*C*H$_3$), 59.2 (*C*$_5$H$_4$), 61.7 (*C*$_5$H$_4$), 69.3 (*C*$_5$H$_5$), 129.5 (Ar*C*), 122.4 (*C*(C$_5$H$_4$)O), 134.2 (H$_3$C-Ar*C*), 142.1 (H$_3$C-Ar*C*), 154.3 (O-Ar*C*). Anal. Calcd for C$_{19}$H$_{20}$FeO (320.21): C, 71.27; H, 6.30. Found: C, 71.19; H, 6.31.

2-*tert*-Butyl-4-methylphenoxyferrocene (5). $R_f = 0.29$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 1.46 (s, 9H, *t*-Bu*H*), 3.94 (t, 2H, $J = 2.0$ Hz, C$_5$*H*$_4$), 4.21 ("t", 2H, $J = 2.0$ Hz, C$_5$*H*$_4$), 4.28 (s, 5H, C$_5$*H*$_5$), 6.69 (t, 1H, $J = 8.2$ Hz, C$_6$*H*$_3$), 6.84 (d, 1H, $J = 8.2$ Hz, C$_6$*H*$_3$), 7.07 (s, 1H, $J = 8.2$ Hz, C$_6$*H*$_3$). ^{13}C NMR (CDCl$_3$): 21.0 (Ar*C*H$_3$), 30.1 (*C*H$_3$), 34.8 (*C*CH$_3$), 61.1 (*C*$_5$H$_4$), 63.2 (*C*$_5$H$_4$), 69.4 (*C*$_5$H$_5$), 115.9 (Ar*C*), 121.7 (*C*(C$_5$H$_4$)O), 127.1 (Ar*C*), 127.4 (Ar*C*), 130.9 (H$_3$C-Ar*C*), 138.3 (*t*-Bu-Ar*C*), 156.5 (O-Ar*C*).

3-*tert*-Butylphenoxyferrocene (6). $R_f = 0.18$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 1.31 (s, 9H, *t*-Bu*H*), 3.98 ("t", 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.25 (t, 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.30 (s, 5H, C$_5$*H*$_5$), 6.78−6.74 (m, 1H, Ar*H*), 7.23−7.04 (m, 3H, Ar*H*). ^{13}C NMR (CDCl$_3$): 31.4 (*C*H$_3$), 34.9 (*C*CH$_3$), 59.8 (*C*$_5$H$_4$), 63.1 (*C*$_5$H$_4$), 69.6 (*C*$_5$H$_5$), 113.1 (Ar*C*), 115.0 (Ar*C*), 119.6 (Ar*C*), 123.0 (*C*(C$_5$H$_4$)O), 128.9, 153.1 (*t*-Bu-Ar*C*), 158.6 (O-Ar*C*).

4-*tert*-Butylphenoxyferrocene (7). $R_f = 0.17$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 1.22 (s, 9H, *t*-Bu*H*), 3.86 ("t", 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.13 (t, 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.19 (s, 5H, C$_5$*H*$_5$), 6.85 (d, 2H, $J = 8.8$ Hz, C$_6$*H*$_4$), 7.21 (d, 2H, $J = 8.8$ Hz, C$_6$*H*$_4$). ^{13}C NMR (CDCl$_3$): 31.6 (*C*H$_3$), 34.3 (*C*CH$_3$), 59.8 (*C*$_5$H$_4$), 62.9 (*C*$_5$H$_4$), 69.4 (*C*$_5$H$_5$), 116.7 (*o*-Ar*C*), 126.2 (*m*-Ar*C*), 141.6 (*C*(C$_5$H$_4$)O), 145.3 (*t*-Bu-Ar*C*), 156.5 (O-Ar*C*). Anal. Calcd for C$_{20}$H$_{22}$FeO (334.24): C, 71.87; H, 6.63. Found: C, 71.37; H, 6.78.

2,4-Di-*tert*-butylphenoxyferrocene (8). $R_f = 0.28$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 1.27 (s, 9H, 4-*t*-Bu*H*), 1.47 (s, 9H, 2-*t*-Bu*H*), 3.95 ("t", 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.23 (t, 2H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.29 (s, 5H, C$_5$*H*$_5$), 6.71 (d, 1H, $J = 8.6$ Hz, C$_6$*H*$_3$), 7.05 (d, 1H, $J = 8.6$ Hz, C$_6$*H*$_3$), 7.30 (s, 1H, C$_6$*H*$_3$). ^{13}C NMR (CDCl$_3$): 30.1 (*o*-C(*C*H$_3$)$_3$), 31.7 (*p*-C(*C*H$_3$)$_3$), 34.4 (*C*CH$_3$), 35.1 (*C*CH$_3$), 61.2 (*C*$_5$H$_4$), 63.2 (*C*$_5$H$_4$), 69.4 (*C*$_5$H$_5$), 115.0 (Ar*C*), 121.3 (*C*(C$_5$H$_4$)O), 123.3 (Ar*C*), 123.8 (Ar*C*), 137.5 (*o*-*t*-Bu-Ar*C*), 144.1 (*p*-*t*-Bu-Ar*C*), 156.3 (O-Ar*C*).

2-*tert*-Butyl-6-methylphenoxyferrocene (9). $R_f = 0.11$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 1.42 (s, 9H, *t*-Bu*H*), 2.25 (s, 3H, *o*-C*H*$_3$), 3.72 ("t", 2H, $J = 2.0$ Hz, C$_5$*H*$_4$), 3.95 (t, 2H, $J = 2.0$ Hz, C$_5$*H*$_4$), 4.17 (s, 5H, C$_5$*H*$_5$), 6.79 (t, 1H, $J = 7.6$ Hz, C$_6$*H*$_3$), 7.12 (d, 1H, $J = 7.6$ Hz, C$_6$*H*$_3$), 7.16 (d, 1H, $J = 7.6$ Hz, C$_6$*H*$_3$).

4-Chlorophenoxyferrocene (10). $R_f = 0.11$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 3.94 ("t", 2H, $J = 2.2$ Hz, C$_5$*H*$_4$), 4.12 ("t", d, 2H, $J = 2.2$ Hz, C$_5$*H*$_4$), 4.18 (s, 5H, C$_5$*H*$_5$), 6.86 (d, 2H, $J = 8.6$ Hz), 7.23 (d, 2H, $J = 8.6$ Hz).

1,1′-Di(phenoxy)ferrocene (11). $R_f = 0.55$ [cyclohexane]. ^{1}H NMR (CDCl$_3$): 3.89 ("t", 4H, $J = 2.0$ Hz, C$_5$*H*$_4$), 4.15 (t, 4H, $J = 2.0$ Hz, C$_5$*H*$_4$), 6.91−6.96 (m, 4H, Ar*H*), 7.03−7.04 (m, 2H, Ar*H*), 7.18−7.23 (m, 4H, Ar*H*). ^{13}C NMR (CDCl$_3$): 58.9 (*C*$_5$H$_4$), 61.9 (*C*$_5$H$_4$), 117.4 (Ar*C*), 122.8 (Ar*C*), 129.8 (Ar*C*), 123.1 (*C*(C$_5$H$_4$)O), 159.3 (O-Ar*C*). Anal. Calcd for C$_{22}$H$_{18}$FeO$_2$ (370.23): C, 71.37; H, 4.90. Found: C, 70.94, H, 5.02.

1,1′-Di(4-*tert*-butylphenoxy)ferrocene (12). $R_f = 0.58$ [cyclohexane/ethyl acetate (20:1)]. ^{1}H NMR (CDCl$_3$): 1.22 (s, 18H, *t*-Bu*H*), 3.95 ("t", 2H, $J = 2.2$ Hz, C$_5$*H*$_4$), 4.21 (t, 4H, $J = 2.2$, C$_5$*H*$_4$), 6.91 (d, 4H, $J = 8.6$ Hz, C$_6$*H*$_4$), 7.23 (d, 4H, $J = 8.6$ Hz, C$_6$*H*$_4$). ^{13}C NMR (CDCl$_3$): 31.6 (*C*H$_3$), 34.3 (*C*(CH$_3$)$_3$), 60.8 (*C*$_5$H$_4$), 64.2 (*C*$_5$H$_4$), 117.0 (Ar*C*), 126.2 (Ar*C*), 141.7 (*C*(C$_5$H$_4$)O), 145.4 (*t*-Bu-Ar*C*), 156.4 (Ar*C*).

1,1′-Di(2,4-dimethylphenoxy)ferrocene (13). $R_f = 0.57$ [cyclohexane]. ^{1}H NMR (CDCl$_3$): 2.17 (s, 6H, *o*-C*H*$_3$), 2.22 (s, 6H, *p*-C*H*$_3$), 3.85 ("t", 4H, $J = 2.0$ Hz, C$_5$*H*$_4$), 4.11 (t, 4H, $J = 2.0$ Hz, C$_5$*H*$_4$) 6.77−6.84 (m, 4H, C$_6$*H*$_3$), 6.98 (br s, 2H, C$_6$*H*$_3$). ^{13}C NMR (CDCl$_3$): 18.8 (Ar*C*H$_3$), 23.4 (Ar*C*H$_3$), 58.8 (*C*$_5$H$_4$), 63.0 (*C*$_5$H$_4$), 115.8 (Ar*C*), 125.8 (Ar*C*), 129.6 (Ar*C*), 130.5 (*C*(C$_5$H$_4$)O), 131.3 (Ar*C*), 134.4 (Ar*C*), 155.6 (O-Ar*C*).

1,1′-Di(3,5-dimethylphenoxy)ferrocene (14). $R_f = 0.56$ [cyclohexane]. ^{1}H NMR (CDCl$_3$): 2.24 (s, 12H, C*H*$_3$), 3.93 ("t", 4H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.16 (t, 4H, $J = 1.9$ Hz, C$_5$*H*$_4$), 6.55 (s, 4H, C$_6$*H*$_3$), 6.66 (s, 2H, C$_6$*H*$_3$). ^{13}C NMR (CDCl$_3$): 20.3 (Ar*C*H$_3$), 59.0 (*C*$_5$H$_4$), 64.7 (*C*$_5$H$_4$), 113.7 (*o*-Ar*C*), 123.1 (*C*(C$_5$H$_4$)O), 124.7 (*p*-Ar*C*), 138.1 (H$_3$C-Ar*C*), 153.2 (O-Ar*C*).

Diferrocenyl Ether (15). $R_f = 0.49$ [*n*-heptane]. ^{1}H NMR (CDCl$_3$): 3.78 ("t", 4H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.08 (t, 4H, $J = 1.9$ Hz, C$_5$*H*$_4$), 4.20 (s, 10H, C$_5$*H*$_5$). ^{13}C NMR (CDCl$_3$): 62.9 (*C*$_5$H$_4$), 65.3 (*C*$_5$H$_4$), 68.4 (*C*$_5$H$_5$), 124.9 (*C*(C$_5$H$_4$)O). EI-MS: *m*/*z* 330 (M^+).

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