New Ortho-Directing Group for Lithiation: Use of a Methoxy−Imino Auxiliary for the Synthesis of Chiral Ortho-Substituted Acetyl- and Propionylferrocenes

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Ortho lithiation of acetylferrocene and propionylferrocene followed by addition of chlorosilane and diiodoethane was totally enantioselective when a chiral methoxy−imino auxiliary was used as an easily removable ortho-directing group. Enantiopure (*R*)-*o*-iodoacetylferrocene and (*R*)-*o*-iodopropionylferrocene were obtained. The structure of (*R*)-*o*-iodoacetylferrocene was confirmed by X-ray crystallography.

Introduction

Enantiopure planar chiral ferrocenes have been widely used as chiral ligands in asymmetric syntheses. Because of their synthetic accessibility, most of the chiral ferrocene derivatives have been prepared as the 1,2-disubstituted compounds.

The most important synthetic strategy is based on direct ortho metalation (DoM). Ugi et al. first described the use of a chiral amino group to stabilize a lithium atom at the ortho position (**1**) (Chart 1).[1] Kagan et al. have developed two other approaches, utilizing a dioxane auxiliary (**2**) formed from formylferrocene and a sulfinyl group (**3**).[2,3] Sammakia and Richards used the protection of a carboxylic acid to generate the ortho-directing group in **4**.[4] A chiral alcohol auxiliary (**5**) was studied by Knochel.[5] Recently a chiral hydrazone-SAMP (SAMP = (*S*)-1-aminomethoxymethylpyrrolidine) group (**6**), formed from a keto functionality, has been developed by Enders et al.[6] The hydrazino auxiliary was shown to stabilize a lithium atom at the ortho position by chelation. This stabilization has also been observed for metals other than Li, such as Hg,[7] Pt,[8] and Pd.[9]

Chart 1. Precursors of Planar Chiral Ferrocenes

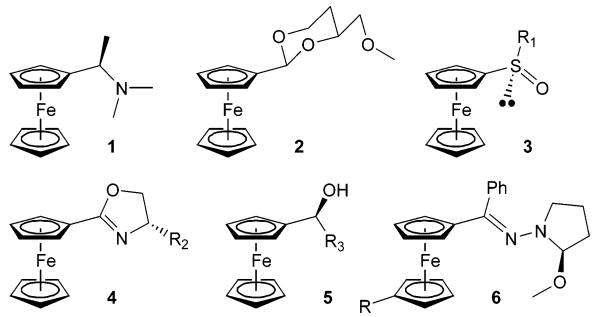
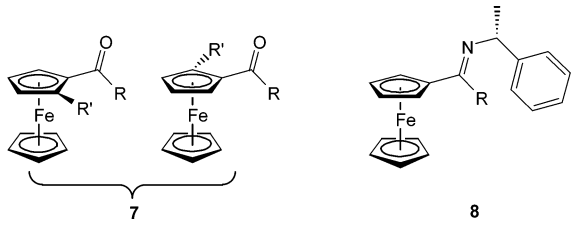


Chart 2



We have recently prepared enantiopure *R* and *S* isomers of 1,2- and 1,3-formyliodoferrocene by using Kagan's dioxane auxiliary.[10] We tried to use this group for the synthesis of the enantiopure disubstituted keto ferrocene **7** (Chart 2). Unfortunately, the protection of the ketone did not give a significant yield of the dioxane compound, the analogue of **2**. This failure forced us to find another ortho-directing group, and we first chose to investigate imino auxiliaries such as **8**. However, the

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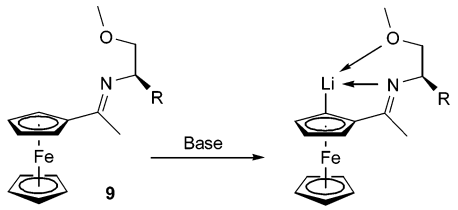
Table 1. Alkylation of Methoxy−Imino Ferrocene

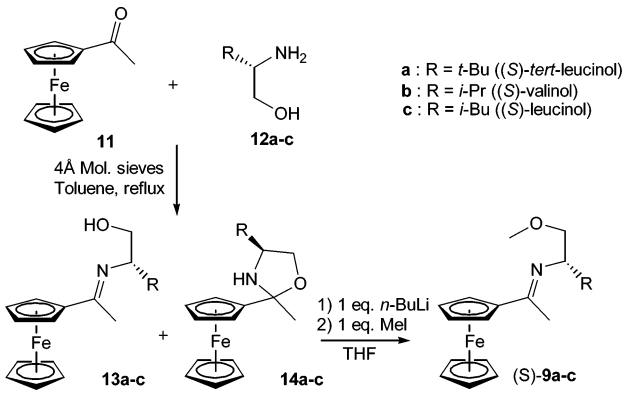
entry	R	EX	precursor	product	cv, %[a]	dr[a]
1	*t*-Bu	$ClSiMe_3$	**9a**	**16a**	100	>95/5
2	*i*-Pr	$ClSiMe_3$	**9b**	**16b**	100	>95/5
3	*i*-Bu	$ClSiMe_3$	**9c**	**16c**	100	89/11
5	*t*-Bu	$ClSiMe_2Ph$	**9a**	**17**	100	>95/5
6	*t*-Bu	$ClSiMePh_2$	**9a**	**18**	100	>95/5
7	*t*-Bu	$ClSiMe_3$	**15**	**20**	100	>95/5
8	*t*-Bu	$C_2H_4I_2$	**9a**	**19**	100	>95/5
9	*t*-Bu	$C_2H_4I_2$	**15**	**21**	100	>95/5

[a] cv (conversion) and dr (diastereoisomer ratio) were determined from ^{1}H NMR spectra of the crude product. dr = R_{Fc}/S_{Fc}.

Scheme 1. Stabilization of Lithium by a Bidentate Group



Scheme 2. Synthesis of Methoxy−Imino Ferrocenes

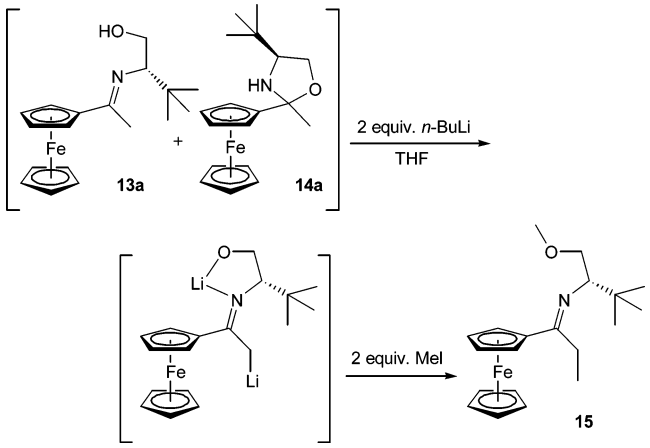


alkylation of **8** with Me_3SiCl did not provide high diastereoselectivity. The use of a hydrazino auxiliary (**6**) developed by Enders et al.[6] was expected to improve the diastereoselectivity. However, the synthesis of hydrazone-SAMP (**6**) from the coupling of the ketone with SAMP utilizes $AlMe_3$ as a reagent, and the removal of the hydrazino auxiliary was achieved with O_3, $TiCl_3$, or $SnCl_2$. These reaction conditions may not be compatible with a large range of compounds. In addition, the high price of SAMP prevents its use in large-scale syntheses. For these reasons we thought it would be worthwhile to develop a new chiral auxiliary that is easy to prepare and to remove and is available at a reasonable price. Thus, we chose to study a bidentate group such as a methoxy−imino group: for example, compound **9** (Scheme 1). The advantage of this group is that these derivatives can be easily prepared from chiral amino−alcohols that are accessible from natural amino acids or commercially available. We found that this strategy was very satisfactory. We now report our results on the diastereoselective ortho substitution of acetylferrocene and propionylferrocene.

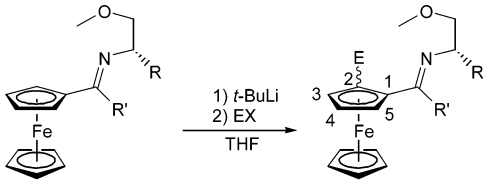
Results and Discussion

The bidentate compounds **9a−c** were prepared from three amino−alcohols, (*S*)-*tert*-leucinol, (*S*)-valinol, and (*S*)-leucinol (Scheme 2). The procedure described for the synthesis of imino−ferrocene[11,12] did not give good yields. Instead, we were able to obtain the hydroxy−imines **13a−c** from the reaction of acetylferrocene **11**, with the amino alcohols **12a−c**, by elimination of the water formed in the toluene solution by allowing the toluene/water azeotrope to pass through Na_2SO_4 solid retained on a dropping funnel. The NMR spectrum showed that each of the imino alcohols obtained were in equilibrium with their oxazolidines **14a−c** in a proportion of 1:1. Both types of compounds, the imino alcohols **13a−c** and oxazolidines **14a−c**, gave the same corresponding lithium alcoholates after deprotonation with 1 equiv of *n*-BuLi at −78 °C. Addition of MeI to the lithium solution at room temperature produced methoxy−imino−ferrocenes (*S*)-**9a−c** in good yields (60−75%).

Scheme 3. Synthesis of the Methoxy−Imino Ferrocene 15.



Scheme 4. Alkylation of Methoxy−Imino Ferrocenes



R = **a**: *t*-Bu, **b**: *i*-Pr, **c**: *i*-Bu

EX = $ClSiMe_3$, $ClSiMe_2Ph$, $ClSiMePh_2$, $C_2H_4I_2$

9a-c	R' = Me	**16a-c, 17, 18, 19**	R' = Me
15	R = *t*-Bu, R' = Et	**20, 21**	R = *t*-Bu, R' = Et

When 2 equiv of *n*-BuLi was added to the solution of the imine derived from *tert*-leucinol, deprotonation also occurred on the methyl group, leading to the formation of compound **15** after addition of MeI (Scheme 3). The ease of the deprotonation of the methyl group may be explained by the formation of the lithium imino−alcoholate chelate that enhances the acidity of the methyl protons.

The cyclopentadienyl rings of imines (*S*)-**9a−c** were deprotonated with *t*-BuLi at −78 °C in THF. After the mixture was stirred for 2 h, trimethylsilyl chloride was added at −78 °C, leading to the formation of ortho-substituted compounds **16a−c** (Scheme 4). Under the same conditions, **15** gave **20** in 47% yield. Table 1 shows the results of all alkylation experiments. Compounds derived from *tert*-leucinol (**16a**) and valinol (**16b**) gave excellent diastereoisomeric excess; only one diastereoisomer was observed by NMR. The diastereoselectivity of **9c**, derived from leucinol (isobutyl group), was lower but still good (dr > 89/11) (**16c**). These results can be explained by the steric effect of the isobutyl group, which is less important than that of auxiliaries derived from valinol or *tert*-leucinol.

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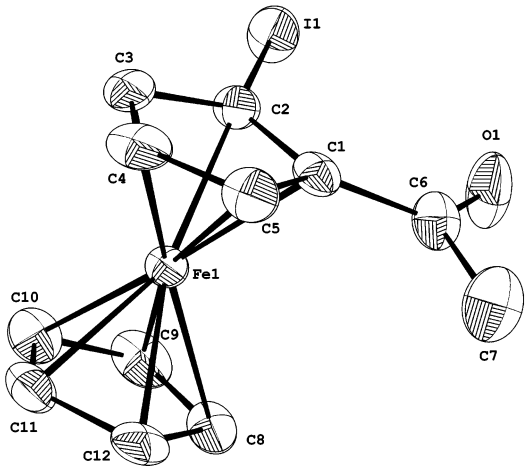


Figure 1. X-ray structure of **22**.

Scheme 5. Deprotection of Methoxy−Imino Ferrocenes 19 and 21

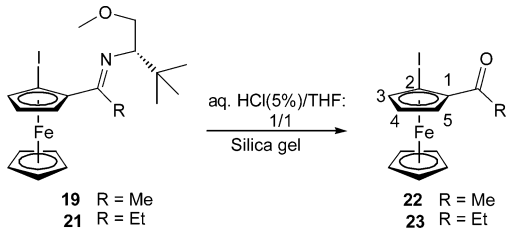
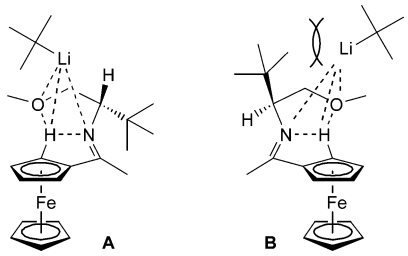


Chart 3. Reagent Approach to Imino Ferrocene



We have also studied the effect of the nature of the silyl group on the diastereoselectivity. Compound **9a** (R = *t*-Bu) was selected for reaction with two different silyl chlorides (Table 1). Compounds **17** and **18** were obtained with excellent diastereoselectivity (dr > 95/5), proving that the size of the silyl group does not play an important role. When, after addition of *t*-BuLi at −78 °C, the lithium intermediate is allowed to stand at room temperature for 1 h before adding a silyl chloride, the proportion of the two diastereoisomers becomes 70/30. It is therefore clear that deprotonation is the key step for the selectivity and that the distribution of the two ortho lithio intermediates is under thermodynamic control at room temperature. When diiodoethane was used to react with the lithium intermediate of **9a**, the iodo compound **19** was obtained, also with excellent diastereoselectivity. The removal of the chiral auxiliary with hydrochloric acid produced (*R*)-*o*-iodoacetylferrocene (**22**) in 73% yield (Scheme 5). The reaction of diiodoethane with **15** produced **21**, also with excellent diastereoselectivity, and *o*-iodopropionylferrocene (**23**) was obtained after the deprotection reaction.

The *R* configuration of **22** has been confirmed by the X-ray structure and Flack parameter (Figure 1).

The formation of the *R* enantiomer may be explained by the reagent approach control, as shown in Chart 3. Only the ortho proton of chelate **A** is accessible to *t*-BuLi, while in **B**, the base cannot attain the proton because of the steric hindrance of the methoxy−imino group. This feature has been observed by Sammakia et al. in the ortho lithiation of **4**.[4] They found that the key step for the selectivity was the base approach to the oxazoline−ferrocene and not the stability of the lithium intermediate.

Conclusion

In conclusion, we have shown in this paper that a methoxy−imino auxiliary, prepared from a chiral amino alcohol, is a fully diastereoselective ortho-directing group, giving access to enantiopure ortho-substituted keto ferrocenes after removal of the auxiliary. In comparison to the hydrazino auxiliary, the methoxy−imino groups are easier to prepare and to remove. Of the three chiral amino alcohols used in this study, valinol is the best reagent; it provides excellent diasteroselectivity and costs 5 times less than SAMP.

Experimental Section

Anhydrous THF and diethyl ether were distilled from sodium/benzophenone. Flash chromatography was performed on silica gel Si 60 (40−63 μM). FT-IR spectra were recorded on a BOMEM Michelson-100 spectrometer. ^{1}H and ^{13}C NMR spectra were acquired on Bruker 300 and 400 spectrometers. Mass spectrometry was performed on a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device.

General Synthetic Procedure for 9a−c. A flask was equipped with a pressure-equalizing dropping funnel filled from the bottom to the top with cotton, molecular sieves, and Na_2SO_4. A condenser was mounted on the top of the funnel. This apparatus was filled with argon, and the ferrocene compound (0.1 M), amino−alcohol (1 equiv), toluene, and 4 Å molecular sieves (20 g) were added into the flask. The mixture was refluxed for several hours by allowing the condensed toluene to drop back into the flask through Na_2SO_4 and molecular sieves in order to retain the water. Then the mixture was filtered through Celite, and the solvent was evaporated under reduced pressure. The crude oil obtained was dissolved in diethyl ether and washed once with water. The oxazolidine and the imine formed were extracted with 5% aqueous HCl. The dark violet aqueous layer was washed once with diethyl ether, and solid K_2CO_3 was added to neutralize the acid. The product was then extracted with diethyl ether, and the organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product obtained was directly used for the synthesis of the methoxy compound.

(*S*)-(*E*)-1-Methoxy-3,3-dimethyl-*N*-(1-ferrocenylethylidenyl)-butan-2-amine (9a). Acetylferrocene (1.94 g, 8.53 mmol) was reacted with (*S*)-*tert*-leucinol (1.00 g, 8.53 mmol) in toluene (90 mL) for 24 h. After workup, a mixture of imine **13a** and oxazolidine **14a** was obtained as a dark red oil in 50% yield (1.46 g). Without any additional purification, 0.500 g (1.44 mmol) of the mixture was dissolved in THF (10 mL) and cooled to −78 °C. *n*-BuLi (0.580 mL, 1.44 mmol) was added dropwise. The mixture was stirred for 15 min at −78 °C and for 1 h at room temperature. Then methyl iodide (0.134 mL, 2.16 mmol) was slowly added, and the mixture was stirred overnight. Solid K_2CO_3 was then added, followed by water and diethyl ether. The organic layer was washed three times with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. A ^{1}H NMR spectrum of the crude product showed only the expected product. The crude product was purified by a silica gel column using 9:1 pentane−triethylamine as eluent. **9a** was obtained as an orange oil which crystallized slowly in a refrigerator (mp <50 °C; 0.330 g, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (s, 9H, CMe_3), 2.03 (s, 3H, $CH_3C{=}N$), 3.19 (s, 3H, OMe), 3.25 (t, 1H, J = 8.4 Hz, CH_2OMe), 3.36 (dd, 1H, J =

2.4 Hz, J = 8.4 Hz, NC*H*), 3.59 (dd, 1H, J = 2.4 Hz, J = 8.4 Hz, CH_2OMe), 4.05 (s, 5H, Cp), 4.20 (t, 2H, J = 1.8 Hz, C_5H_4, H3 and H4), 4.57 (dd, 1H, J = 1.8 Hz, J = 3.3 Hz, C_5H_4, H2 or H5), 4.65 (dd, 1H, J = 1.8 Hz, J = 3.3 Hz, C_5H_4, H2 or H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.2 (*C*H_3C═N), 26.9 (C*Me*$_3$), 33.8 (*C*Me_3), 58.8 (OMe), 67.3 (C_5H_4, C2 or C5), 68.1(C_5H_4, C2 or C5), 68.2 (N*C*H), 68.9 (Cp), 69.5 (C_5H_4, C3 or C4), 69.5 (C_5H_4, C3 or C4), 74.2 (*C*H_2OMe), 86.8 (C_5H_4, C1), 163.6 (C═N). Anal. Calcd for $C_{19}H_{27}FeNO$: C, 66.87; H, 7.97; N, 4.10. Found: C, 67.02; H, 8.34; N, 4.10. $[\alpha]_D^{25}$ = +199° (c = 10.0 g/L, $CHCl_3$).

(*S*)-(*E*)-1-Methoxy-3-methyl-*N*-(1-ferrocenylethylidenyl)-butan-2-amine (9b). Acetylferrocene (2.21 g, 9.69 mmol) was reacted with (*S*)-valinol (1.00 g, 9.69 mmol) in toluene (90 mL) for 48 h. After workup, a mixture of imine **13b** and oxazolidine **14b** was obtained as a dark red oil in 60% yield (1.848 g). Without any additional purification, 1.000 g (3.19 mmol) of the mixture was dissolved in THF (21 mL) and cooled to −78 °C. *n*-BuLi (1.28 mL, 3.19 mmol) was added dropwise. The mixture was stirred for 15 min at −78 °C and for 1 h at room temperature. Then methyl iodide (0.258 mL, 4.15 mmol) was slowly added and the mixture was stirred overnight. Solid K_2CO_3 was then added, followed by water and diethyl ether. The organic layer was washed three times with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. A ^1H NMR spectrum of the crude product showed only the expected product. The crude product was purified by a silica gel column using 9:1 pentane−triethylamine as eluent. **9b** was obtained as an orange oil (mp <50 °C; 0.626 g, 60% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (d, 3H, J = 6.3 Hz, *CHMe*$_2$), 0.94 (d, 3H, J = 6.6 Hz, CH*Me*$_2$), 1.87 (m, 1H, C*H*Me$_2$), 2.17 (s, 3H, C*H*$_3$C═N), 3.32 (s, 3H, OMe), 3.35 (dd, 1H, J = 7.5 Hz, J = 8.7 Hz, C*H*$_2$OMe), 3.50 (m, 1H, NC*H*), 3.56 (dd, 1H, J = 4.0 Hz, J = 8.7 Hz, C*H*$_2$OMe), 4.12 (s, 5H, Cp), 4.29 (t, 2H, J = 2.1 Hz, C_5H_4, H3 and H4), 4.65 (m, 1H, C_5H_4, H2 or H5), 4.68 (m, 1H, C_5H_4, H2 or H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.4 (*C*H_3C═N), 18.5 (CH*Me*$_2$), 20.0 (CH*Me*$_2$), 30.7 (*C*HMe$_2$), 58.9 (OMe), 65.3 (N*C*H), 67.4 (C_5H_4, C2 or C5), 68.2 (C_5H_4, C2 or C5), 69.1 (Cp), 69.8 (C_5H_4, C3 or C4), 69.8 (C_5H_4, C3 or C4), 75.4 (*C*H_2OMe) , 86.1 (C_5H_4, C1), 164.7 (C═N). Anal. Calcd for $C_{18}H_{25}FeNO$: C, 66.07; H, 7.70; N, 4.28. Found: C, 65.20; H, 7.67; N, 3.78. $[\alpha]_D^{25}$ = +90° (c = 18.0 g/L, $CHCl_3$).

(*S*)-(*E*)-1-Methoxy-3-methyl-*N*-(1-ferrocenylethylidenyl)pentan-2-amine (9c). Acetylferrocene (1.94 g, 8.53 mmol) was reacted with (*S*)-leucinol (1.00 g, 8.53 mmol) in toluene (90 mL) for 24 h. After workup, a mixture of imine **13c** and oxazolidine **14c** was obtained as a dark red oil in 27% yield (0.648 g). Without any additional purification, 0.183 g (0.56 mmol) of the mixture was dissolved in THF (4 mL) and cooled to −78 °C. *n*-BuLi (0.22 mL, 0.56 mmol) was added dropwise. The mixture was stirred for 15 min at −78 °C and for 1 h at room temperature. Then methyl iodide (0.045 mL, 0.73 mmol) was slowly added and the mixture was stirred overnight. Solid K_2CO_3 was then added, followed by water and diethyl ether. The organic layer was washed three times with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. A ^1H NMR spectrum of the crude product showed only the expected product. The crude product was purified by a silica gel column using 9:1 pentane−triethylamine as eluent. **9c** was obtained as an orange oil (0.143 g, 75% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.93 (d, 3H, J = 6.6 Hz, CH*Me*$_2$), 0.95 (d, 3H, J = 6.6 Hz, CH*Me*$_2$), 1.12−1.50 (m, 3H, C*H*$_2$C*H*Me$_2$), 2.13 (s, 3H, C*H*$_3$C═N), 3.31 (s, 3H, OMe), 3.31 (m, 1H, C*H*$_2$OMe), 3.35 (dd, 1H, J = 7.5 Hz, J = 8.7 Hz, C*H*$_2$OMe), 3.80 (m, 1H, N═C*H*), 4.13 (s, 5H, Cp), 4.29 (t, 2H, J = 1.8 Hz, C_5H_4, H3 and H4), 4.64 (m, 1H, C_5H_4, H2 or H5), 4.72 (s, 1H, C_5H_4, H2 or H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 16.3 (CH_3C═N), 21.9, 23.7 and 24.7 (*CHMe*$_2$), 42.1 (*C*H_2iPr), 57.9 and 58.9 (N═CH and OMe), 67.5 (C_5H_4, C2 or C5), 68.0 (C_5H_4, C2 or C5), 69.0 (Cp), 69.8 (C_5H_4, C3 and C4), 77.4 (CH_2OMe), 86.1 (C_5H_4, C1), 164.4 (C═N). Anal. Calcd for $C_{19}H_{27}FeNO$: C, 66.87; H, 7.97; N, 4.10. Found: C, 67.02; H, 8.34; N, 4.10. $[\alpha]_D^{25}$ = +17° (c = 12.0 g/L, $CHCl_3$).

(*S*)-(*E*)-1-Methoxy-3,3-dimethyl-*N*-(1-ferrocenylpropylidenyl)-butan-2-amine (15). Acetylferrocene (1.94 g, 8.53 mmol) was reacted with (*S*)-*tert*-leucinol (1.00 g, 8.53 mmol) in toluene (90 mL) for 24 h. After workup, a mixture of imine **13a** and oxazolidine **14a** was obtained as a dark red oil in 50% yield (1.46 g). Without any additional purification, 0.500 g (1.44 mmol) of the mixture was dissolved in THF (10 mL) and cooled to −78 °C. *n*-BuLi (0.72 mL, 2.88 mL) was added dropwise. The mixture was stirred for 15 min at −78 °C and for 1 h at room temperature. Then methyl iodide (0.270 mL, 4.32 mmol) was slowly added and the mixture was stirred overnight. Solid K_2CO_3 was then added, followed by water and diethyl ether. The organic layer was washed three times with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. A ^1H NMR spectrum of the crude product showed only the expected product. The crude product was purified by a silica gel column using 9:1 pentane−triethylamine as eluent. **15** was obtained as an orange oil (0.365 g, 77% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (s, 9H, C*Me*$_3$), 1.17 (t, 3H, J = 7.8 Hz, C*H*$_3$CH$_2$), 2.50 (dd, 1H, J = 7.8 Hz, J = 13.2 Hz, C*H*$_2$CH$_3$), 2.63 (dd, 1H, J = 7.8 Hz, J = 13.2 Hz, C*H*$_2$CH$_3$), 3.28 (s + t, 3H + 1H, OMe + C*H*$_2$OMe), 3.44 (dd, 1H, J = 2.7 Hz, J = 8.1 Hz, NC*H*), 3.67 (dd, 1H, J = 2.7 Hz, J = 8.7 Hz, C*H*$_2$OMe), 4.13 (s, 5H, Cp), 4.28 (m, 2H, C_5H_4, H3 and H4), 4.71 (m, 2H, C_5H_4, H2 and H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 13.0 (*C*H_3CH$_2$), 22.9 (CH$_3$*C*H$_2$C═N), 27.0 (C*Me*$_3$), 33.7 (*C*Me_3), 58.8 (OMe), 67.5 (C_5H_4, C2 or C5), 67.5 (N═*C*H), 68.0 (C_5H_4, C2 or C5), 69.0 (Cp), 69.2 (C_5H_4, C3 or C4), 69.3 (C_5H_4, C3 or C4), 74.2 (*C*H_2OMe), 85.6 (C_5H_4, C1), 168.3 (C═N). Anal. Calcd for $C_{20}H_{29}FeNO$: C, 67.61; H, 8.23; N, 3.94. Found: C, 66.83; H, 8.69; N, 3.58. $[\alpha]_D^{25}$ = +57° (c = 9.0 g/L, $CHCl_3$).

General Procedure for the Ortho Functionalization of Imine Derivatives. Ferrocene (0.4 M) was dissolved under argon in THF and cooled to −78 °C. *t*-BuLi (1.1 equiv) was added dropwise. The mixture was stirred for 2 h at −78 °C. Then the electrophile (1.2 equiv, neat or in THF) was added. The mixture was stirred for 15 min at this low temperature and then at room temperature for 3 h. Solid K_2CO_3 was then added, followed by water and diethyl ether. The organic layer was washed three times with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure.

(*S*)-(*E*)-(R_{Fc})-1-Methoxy-3,3-dimethyl-*N*-[1-(2-(trimethylsilyl)-ferrocenyl)ethylidenyl]butan-2-amine (16a). 9a (0.135 g, 0.38 mmol), THF (1 mL), *t*-BuLi (0.326 mL, 0.49 mmol), and trimethylsilyl chloride (0.06 mL, 0.49 mmol) were used. **16a** was purified by silica gel column using 9:1 pentane−diethyl ether as eluent (orange oil, 0.099 g, 60% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 0.32 (s, 9H, $SiMe_3$), 1.00 (s, 9H, CMe_3), 2.13 (s, 3H, CH_3C═N), 3.22 (s, 3H, OMe), 3.34 (t, 1H, J = 8.5 Hz, J = 9.0 Hz, CH_2-OMe), 3.51 (dd, 1H, J = 2.5 Hz, J = 8.5 Hz, N═CH), 3.66 (dd, 1H, J = 2.5 Hz, J = 9.0 Hz, CH_2OMe), 4.15 (s, 5H, Cp), 4.25 (dd, 1H, J = 1.8 Hz, J = 3.2 Hz, C_5H_3, H3), 4.38 (t, 1H, J = 3.2 Hz, C_5H_3, H4), 4.65 (dd, 1H, J = 1.8 Hz, J = 3.2 Hz, C_5H_3, H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 1.3 ($SiMe_3$), 15.2 (*C*H_3C═N), 27.2 (C*Me*$_3$), 33.7 (*C*Me_3), 58.7 (OMe), 69.0 (Cp), 69.5 (N═CH), 70.0 (C_5H_3, C2), 70.4 (C_5H_3, C4), 73.7 (C_5H_3, C5 or C3), 74.4 (CH_2OMe), 77.2 (C_5H_4, C3 or C5), 92.4 (C1), 165.8 (C═N). HRMS-CI (m/z): calcd for $C_{22}H_{35}FeNOSi$, 413.1838 $[M]^{\bullet+}$; found, 413.1840. $[\alpha]_D^{25}$ = +268° (c = 9.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(R_{Fc})-1-Methoxy-3-methyl-*N*-[1-(2-(trimethylsilyl)-ferrocenyl)ethylidenyl]butan-2-amine (16b). 9b (0.140 g, 0.428 mmol), THF (1 mL), *t*-BuLi (0.370 mL, 0.56 mmol), and trimethylsilyl chloride (0.07 mL, 0.56 mmol) were used. **16b** was purified by a silica gel column using 9:1 pentane−diethyl ether as eluent (orange oil, 0.116 g, 68% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 0.98 (d, 3H, J = 6.9 Hz, *CHMe*$_2$), 1.04 (d,

3H, J = 6.6 Hz, $CHMe_2$), 1.91 (m, 1H, J = 6.9 Hz, CHMe$_2$), 2.14 (s, 3H, CH_3C═N), 3.25 (s, 3H, OMe), 3.39 (dd, 1H, J = 7.5 Hz, J = 8.4 Hz, CH_2OMe), 3.49 (dd, 1H, J = 3.6 Hz, J = 7.5 Hz, NCH), 3.59 (dd, 1H, J = 3.6 Hz, J = 8.4 Hz, CH_2OMe), 4.15 (s, 5H, Cp), 4.29 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H3), 4.41 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.64 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 1.2 ($SiMe_3$), 16.8 (CH_3C═N), 19.4 (Me_2CH), 20.4 (Me_2CH), 30.6 ($CHMe_2$), 58.7 (OMe), 66.7 (NCH), 68.8 (Cp), 70.4 (C_5H_3, C2), 70.9 (C_5H_3, C5 or C3), 73.2 (C_5H_3, C4), 75.5 (CH_2OMe), 79.0 (C_5H_3, C5 or C3), 90.9 (C_5H_3, C1), 165.2 (C═N). Anal. Calcd for $C_{21}H_{33}FeNOSi$: C, 63.15; H, 8.33; N, 3.51. Found : C, 62.53; H, 8.26; N, 3.26. $[\alpha]_D^{25}$ = +545° (c = 5.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3-methyl-*N*-[1-(2-(trimethylsilyl)ferrocenyl)ethylidenyl]pentan-2-amine (16c). 9c (0.080 g, 0.23 mmol), THF (0.8 mL), *t*-BuLi (0.20 mL, 0.30 mmol), and trimethylsilyl chloride (0.04 mL, 0.30 mmol) were used. **16c** was purified by a silica gel column using 9:1 pentane−diethyl ether as eluent (orange oil, 0.063 g, 65% yield). Major diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 9H, $SiMe_3$), 0.99 (d, 6H, J = 6.6 Hz, CHMe_2), 1.20−1.60 (m, 3H, CH_2CHMe_2), 2.15 (s, 3H, CH_3C═N), 3.28 (s, 3H, OMe), 3.43 (m, 2H, CH_2OMe), 3.84 (m, 1H, J = 6.9 Hz, NCH), 4.12 (s, 5H, Cp), 4.28 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H3), 4.40 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.62 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H5); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 0.15 ($SiMe_3$), 16.5 (CH_3C═N), 22.5, 23.5, and 25.0 ($CHMe_2$), 42.3 (CH_2iPr), 58.8 and 59.0 (N═CH and OMe), 69.1 (Cp), 69.9 (C_5H_4, C3 or C5), 70.8 (C_5H_4, C2), 71.3 (C_5H_4, C3), (73.1 (C_5H_4, C3 or C5), 77.5 (CH_2OMe), 90.8 (C_5H_4, C1),-165.0 (C═N). Minor diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 0.88 (d, 6H, J = 7.8 Hz, CHMe_2), 1.20−1.60 (m, 3H, CH_2CHMe_2), 2.41 (s, 3H, CH_3C═N), 3.28 (s, 3H, OMe), 3.43 (m, 2H, CH_2OMe), 3.84 (m, 1H, J = 6.9 Hz, NCH), 4.21 (s, 5H, Cp), 4.46 (dd, 1H, J = 1.5 Hz, J = 2.4 Hz, C_5H_3, H3), 4.60 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.83 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H5). Anal. Calcd for $C_{21}H_{33}FeNOSi$: C, 63.90; H, 8.53; N, 3.39. Found: C, 64.12; H, 8.59; N, 3.49.

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3,3-dimethyl-*N*-[1-(2-(trimethylsilyl)-ferrocenyl)propylidenyl]butan-2-amine (20). 15 (0.090 g, 0.24 mmol), THF (0.8 mL), *t*-BuLi (0.21 mL, 0.31 mmol), and trimethylsilyl chloride (0.04 mL, 0.31 mmol) were used. **20** was purified by a silica gel column using 9:1 pentane−diethyl ether as eluent (red oil, 0.050 g, 47% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.30 (s, 9H, $SiMe_3$), 1.00 (s, 9H, CMe_3), 1.04 (t, 3H, J = 7.5 Hz, CH_3CH_2C═N), 2.50 (m, 2H, CH_2C═N), 3.21 (s, 3H, OMe), 3.34 (dd, 1H, J = 8.1 Hz, J = 8.9 Hz, CH_2OMe), 3.53 (dd, 1H, J = 2.7 Hz, J = 8.9 Hz, NCH), 3.66 (dd, 1H, J = 2.7 Hz, J = 8.9 Hz, CH_2OMe), 4.15 (s, 5H, Cp), 4.22 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H3), 4.35 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.58 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 1.2 ($SiMe_3$), 12.5 (CH_3CH_2), 24.9 (CH_2CH_3), 27.3 (CMe_3), 33.6 (CMe_3), 58.6 (OMe), 68.6 (NCH), 69.1 (Cp), 70.2 (C_5H_4, C3 or C5), 71.1 (C_5H_4, C2), 73.7 (C_5H_4, C4), 74.2 (CH_2-OMe), 76.2 (C_5H_4, C3 or C5), 91.9 (C_5H_4, C1), 171.2 (CN). Anal. Calcd for $C_{23}H_{37}FeNOSi$: C, 64.62; H, 8.72; N, 3.28. Found: C, 64.74; H, 8.74; N, 3.03. $[\alpha]_D^{25}$ = +161° (c = 20.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3,3-dimethyl-*N*-[1-(2-(dimethylphenylsilyl)ferrocenyl)ethylidenyl]butan-2-amine (17). 9a (0.100 g, 0.28 mmol), THF (0.8 mL), *t*-BuLi (0.24 mL, 0.36 mmol), and dimethylphenylsilyl chloride (0.06 mL, 0.362 mmol) were used. **17** was purified by a silica gel column using 8:2 pentane−diethyl ether as eluent (orange oil, 0.092 g, 67% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.67 (s, 3H, SiMe_2), 0.69 (s, 3H, SiMe_2), 0.98 (s, 9H, tBu), 2.09 (s, 3H, CH_3C═N), 3.10 (t, 1H, J = 8.7 Hz, CH_2-OMe), 3.19 (s, 3H, OMe), 3.48 (dd, 1H, J = 2.7 Hz, J = 8.7 Hz, NCH), 3.55 (dd, 1H, J = 2.4 Hz, J = 8.7 Hz, CH_2OMe), 4.03 (m, 1H, C_5H_3, H3), 4.21 (s, 5H, Cp), 4.39 (m, 1H, C_5H_3, H4), 4.75 (m, 1H, C_5H_3, H5), 7.34 (m, 3H, Ph), 7.59 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ −0.6 ($SiMe_2$), 0.9 ($SiMe_2$), 18.4 (CH_3CN), 26.9 ($CHMe_2$), 27.2 (CMe_3), 33.7 (CMe_3), 58.6 (OMe), 69.0 (C_5H_3, C2), 69.2 (Cp), 70.7 (C_5H_3, C4), 73.9 (C_5H_3, C5), 74.3 (CH_2OMe), 78.3 (C_5H_3, C3), 92.5 (C_5H_3, C1), 127.4 (Ph, C_o or C_m), 128.3 (Ph, C_p), 134.0 (Ph, C_o or C_m), 141.0 (Ph, C_p), 165.7 (CN). Anal. Calcd for $C_{27}H_{37}FeNOSi$: C, 68.20; H, 7.84; N, 2.95. Found: C, 68.15; H, 8.22; N, 2.73. $[\alpha]_D^{25}$ = +153° (c = 12.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3,3-dimethyl-*N*-[1-(2-(methyldiphenylsilyl)ferrocenyl)ethylidenyl]butan-2-amine (18). 9a (0.161 g, 0.45 mmol), THF (1.4 mL), *t*-BuLi (0.39 mL, 0.58 mmol), and methyldiphenylsilyl chloride (0.12 mL, 0.583 mmol) were used. **18** was purified by a silica gel column using 8:2 pentane−diethyl ether as eluent (orange oil, 0.140 g, 58% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 0.80 (s, 9H, CMe_3), 1.03 (s, 3H, SiMe), 1.96 (s, 3H, CH_3C═N), 2.29 (dd, 1H, J = 7.5 Hz, J = 9.0 Hz, NCH), 2.93 (s, 3H, OMe), 3.13 (dd, 1H, J = 3.0 Hz, J = 9.0 Hz, CH_2OMe), 3.25 (dd, 1H, J = 3.0 Hz, J = 7.5 Hz, CH_2OMe), 3.68 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H3), 4.12 (s, 5H, Cp), 4.28 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.73 (dd, 1H, J = 1.2 Hz, J = 2.4 Hz, C_5H_3, H5), 7.17 (m, 3H), 7.24 (m, 3H, Ph), 7.32 (m, 2H, Ph), 7.41 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ −0.8 (SiMe), 18.0 (CH_3C═N), 27.2 (CMe_3), 33.6 (CMe_3), 58.4 (OMe), 66.6 (C_5H_3, C2), 69.2 (Cp), 71.0 (C_5H_3, C4), 73.9 (C_5H_3, C5), 74.3 (CH_2OMe), 80.3 (C_5H_3, C3), 91.9 (C_5H_3, C1), 127.2 and 127.4 (Ph, C_o or C_m), 128.3 and 128.6 (Ph, C_p), 134.8 and 135.1 (Ph, C_o or C_m), 138.3 and 139.9 (Ph, C_{ip}), 165.1 (C═N). Anal. Calcd for $C_{32}H_{39}$-FeNOSi: C, 71.19; H, 7.31; N, 2.61. Found: C, 70.42; H, 7.43; N, 2.51. $[\alpha]_D^{25}$ = +315° (c = 10.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3,3-dimethyl-*N*-[1-(2-iodoferrocenyl)-ethylidenyl]butan-2-amine (19) and (*R*$_{Fc}$)-*o*-(Iodoacetyl)ferrocene (22). 9a (0.260 g, 0.72 mmol), THF (1 mL), *t*-BuLi (0.63 mL, 0.94 mmol), and diiodoethane in 1 mL of THF (0.265 g, 0.94 mmol) were used. For stability reasons, **19** was directly transformed to **22** without purification by flash chromatography. ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 9H, CMe_3), 2.24 (s, 3H, CH_3C═N), 3.26 (s, 3H, OMe), 3.32 (dd, 1H, J = 8.4 Hz, J = 9.0 Hz, CH_2OMe), 3.53 (dd, 1H, J = 2.7 Hz, J = 8.4 Hz, NCH), 3.67 (dd, 1H, J = 2.7 Hz, J = 9.0 Hz, CH_2OMe), 4.16 (s, 5H, Cp), 4.32 (t, 1H, J = 2.4 Hz, C_5H_3, H4), 4.52 (dd, 1H, J = 1.5 Hz, J = 2.4 Hz, C_5H_3, H3), 4.58 (dd, 1H, J = 1.5 Hz, J = 2.4 Hz, C_5H_3, H5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): 17.7 (CH_3C═N), 26.9 (CMe_3), 33.9 (CMe_3), 37.6 (C2), 58.9 (OMe), 69.0 and 70.3 (C_5H_3, C3 or C5, NCH), 70.3 (C_5H_3, C4), 72.0 (Cp), 74.3 (CH_2OMe), 78.6 (C_5H_3, C3 or C5), 84.9 (C_5H_3, C1), 162.7 (C═N). **19** (0.200 g) was dissolved in THF (10 mL). A 10 mL portion of 5% HCl aqueous solution and a spatula of silica gel were added, and the mixture was stirred for 3 h at room temperature. K_2CO_3 was added as a solid to neutralize the acid, and then the product was extracted with diethyl ether (30 mL). The organic layer was washed twice with water, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product obtained was purified by filtration through silica gel with 1:1 pentane−diethyl ether. **21** was isolated as a dark red solid (0.186 g, 73% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 2.51 (s, 3H, CH_3CO), 4.22 (s, 5H, Cp), 4.52 (t, 1H, J = 2.7 Hz, C_5H_3, H4), 4.77 (m, 2H, C_5H_3, H3 and H5). NMR ^{13}C NMR (300 MHz, $CDCl_3$): δ 28.8 (CH_3CO), 38.1 (CI), 70.2 (C3), 72.8 (Cp), 73.0 (C4), 80.9 (C5), 85.0 (C1), 212.0 (CO). Anal. Calcd for $C_{12}H_{11}$-FeIO: C, 43.42; H, 3.56. Found: C, 43.59; H, 3.91. IR (cm^{-1}, $CHCl_3$): 3021, 1669 (ν_{CO}). $[\alpha]_D^{25}$ = +31° (c = 10.0 g/L, $CHCl_3$).

(*S*)-(*E*)-(*R*$_{Fc}$)-1-Methoxy-3,3-dimethyl-*N*-[1-(2-iodoferrocenyl)-propylidenyl]butan-2-amine (21) and (*R*$_{Fc}$)-*o*-(Iodopropionyl)-ferrocene (23). 15 (0.280 g, 0.75 mmol), THF (2.5 mL), *t*-BuLi (0.65 mL, 0.97 mmol), diiodoethane in 1 mL of THF (0.280 g, 0.99 mmol). For stability reasons, **21** was directly transformed to **23** without purification by flash chromatography. ^1H NMR (300 MHz, $CDCl_3$): 1.05 (s, 9H, CMe_3), 1.16 (t, 3H, J = 7.5 Hz, CH_3-

$CH_2C{=}N$), 2.64 (m, 2H, $CH_3CH_2C{=}N$), 3.28 (s, 3H, OMe), 3.34 (dd, 1H, $J = 7.8$ Hz, $J = 9.0$ Hz, CH_2OMe), 3.55 (dd, 1H, $J = 3.0$ Hz, $J = 7.8$ Hz, NCH), 3.71 (dd, 1H, $J = 3.0$ Hz, $J = 9.0$ Hz, CH_2OMe), 4.17 (s, 5H, Cp), 4.32 (t, 1H, $J = 2.7$ Hz, C_5H_3, H4), 4.54 (dd 1H, $J = 1.5$ Hz, $J = 2.7$ Hz, C_5H_3, H3), 4.58 (dd, 1H, $J = 1.5$ Hz, $J = 2.7$ Hz, C_5H_3, H5). **21** was dissolved in THF (10 mL). A 10 mL amount of 5% HCl aqueous solution and a spatula of silica gel were added, and the mixture was stirred for 3 h at room temperature. Solid K_2CO_3 was added to neutralize the acid, and then the product was extracted with diethyl ether (30 mL). The organic layer was washed twice with water, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product obtained was purified by filtration through silica gel with 1:1 pentane/diethyl ether. **23** was isolated as a dark red solid (0.175 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, 3H, $J = 7.2$ Hz, CH_3CH_2), 2.84 (m, 2H, CH_3CH_2), 4.21 (s, 5H, Cp), 4.50 (t, 1H, $J = 2.7$ Hz, C_5H_3, H4), 4.77 (m, 2H, C_5H_3, H3 and H5). ^{13}C NMR (300 MHz, $CDCl_3$): δ 8.2 (CH_3CH_2), 33.7 (CH_3CH_2), 38.0 (C−I), 69.7 (C3), 72.7 (Cp), 72.9 (C4), 80.7 (C5), 203.8 (CO). Anal. Calcd for $C_{13}H_{13}$FeIO: C, 40.72; H, 3.13. Found: C, 41.48; H, 3.41. IR (cm^{-1}, $CHCl_3$): 3022, 1672 (ν_{CO}). $[\alpha]_D^{25} = +235°$ ($c = 10.0$ g/L, $CHCl_3$).

Crystal Data for Compound 22: data collections performed on a KAPPACCD Enraf-Nonius area detector diffractometer (Mo Kα, $\lambda = 0.710\,730$ Å, ω scan), CCDC 286837, $C_{12}H_{11}$FeIO, $M_r = 353.97$, orthorhombic, $a = 7.8258(4)$ Å, $b = 8.8461(2)$ Å, $c = 17.3855(7)$ Å, $V = 1203.42(8)$ Å^3, space group $P2_12_12_1$ (No. 19), $Z = 4$, μ(Mo Kα) = 3.788 cm^{-1}, 11 737 reflections measured, 3506 unique ($R_m = 0.038$), which were used in all calculations, final $R_w(F^2) = 0.0508$, Flack parameter $f = 0.08$.

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Supporting Information Available: Tables and a CIF file giving crystal data for compound **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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