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Low Pressure Asymmetric Hydrogenation of Quinolines using an Annulated Planar Chiral *N*-Ferrocenyl NHC-Iridium Complex

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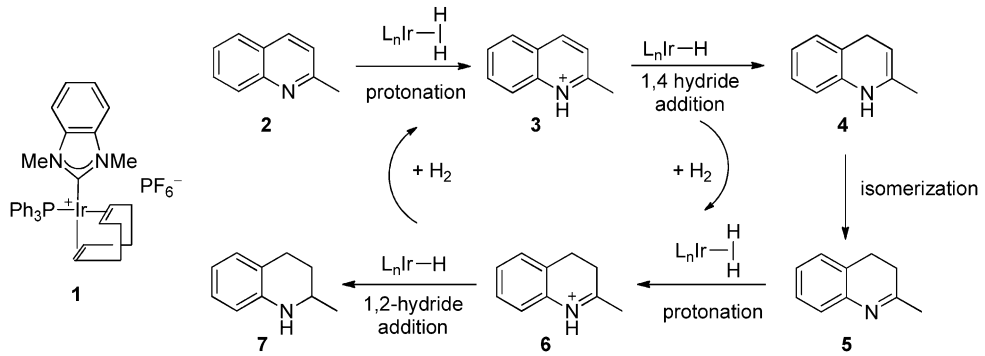
Abstract: Annulated planar chiral *N*-ferrocenylimidazolones, obtained by acid-mediated cyclization of diphenylmethanol derivatives, may be reduced with diisobutylaluminium hydide (DIBAL-H) to afford a series of surprisingly stable and isolable hemiaminal ether aminals. Two of these derivatives can be oxidized with triphenylcarbenium tetrafluoroborate to imidazolinium salt precursors of N-heterocyclic carbenes (NHCs). Deprotonation of these salts in the presence of (cyclooctadiene)iridium chloride dimer {[Ir(COD)Cl]$_2$} provides chiral coordination complexes bearing *N*-ferrocenyl NHCs with unique rigid tetracyclic frameworks. Cationic analogues of these complexes catalyze the asymmetric hydrogenation of 2-substituted quinolines under very mild conditions (1 mol% complex, 1 mol% PPh_3, 1–5 atm H_2, toluene, 25 °C) in appreciable enantioselectivity (up to 90:10 *er*). The sensitivity of the hydrogenation process to changes in the phosphine additive suggests that an outer-sphere reaction mechanism may be involved, as proposed for a related achiral NHC-Ir complex reported by Crabtree and co-workers.

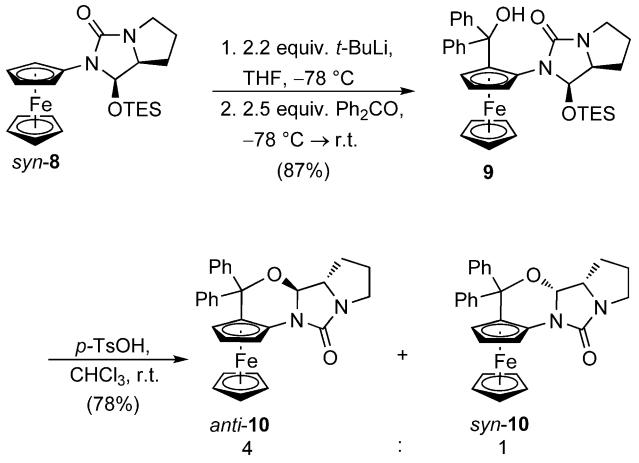
Keywords: ferrocenes; hydrogenation; imidazolones; iridium; lithiation; N-heterocyclic carbenes; quinolines

Introduction

Optically active tetrahydroquinolines display diverse biological activity,[1] and have been investigated as chiral ligands for asymmetric synthesis.[2] Iridium-catalyzed asymmetric hydrogenations of 2-substituted quinolines offer convenient accesses to these compounds,[3] especially when the reactions are supported by chiral diphosphine,[3,4] diphosphinite,[5] diphosphonite,[6] phosphoramidite,[7] phosphite,[8] diamine,[9] and P,N[10] ligands. Almost all of these catalyst systems require elevated hydrogen pressures or elevated temperatures to achieve good coversions. A recent notable exception has been reported by Crabtree and co-workers[11] wherein Ir complex **1** (Scheme 1), which contains an achiral monodentate benzimidazolylidene ligand, has been found to catalyze the reduction of substituted quinolines under exceptionally mild conditions (1 mol% **1**, 1 mol% PPh_3, 1–5 atm H_2, 35 °C). The atypical reactivity of **1** has been explained by in-



Scheme 1. Outer-sphere quinoline hydrogenation with **1**.



Scheme 2. Synthesis and acid-mediated annulation of **9**.

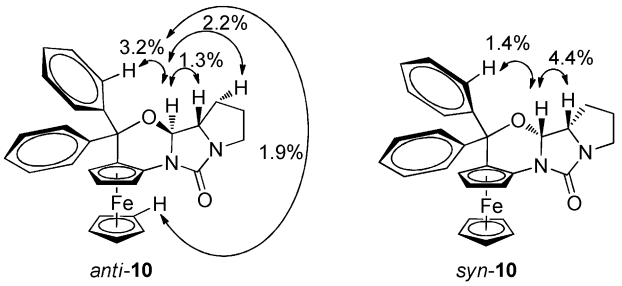


Figure 1. Difference nOes from selective irradiation of hemianinal ether methine hydrogens of *anti*- and *syn*-**10**.

voking an outer-sphere reaction mechanism[11] wherein an iridium dihydrogen complex protonates substrate **2** and key intermediate **5**, the latter preceding final hydride addition to prochiral iminium species **6**.[12]

As part of our ongoing studies of NHC-Ir complexes,[13,14] we were interested in investigating whether an analogue of **1** bearing a chiral NHC ligand would be capable of catalyzing the hydrogenation of quinolines in appreciable enantioselectivity, but also under similarly mild conditions. Described in this paper are the syntheses of two unusual monodentate planar chiral *N*-ferrocenyl NHC ligands, prepared by established stereoselective lithiation of *syn*- and *anti*-**8** (Scheme 2 and Scheme 4).[15] The derived ferrocenyl NHC-Ir complexes were characterized crystallographically and/or spectroscopically, and found to promote the asymmetric hydrogenation of 2-substituted quinolines under mild conditions (1–5 atm H_2, 25 °C) in up to 90:10 *er*.

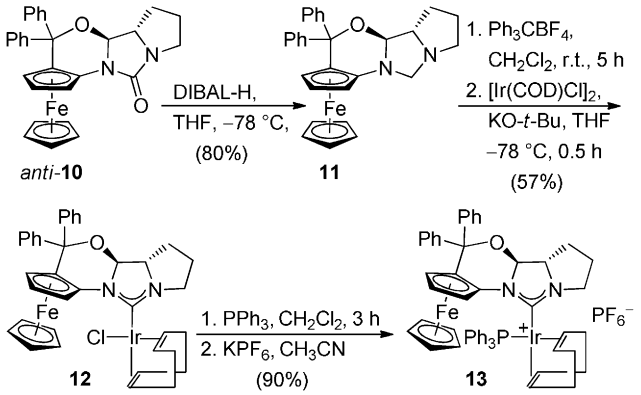
Results and Discussion

Having established that epimeric imidazolones *syn*- and *anti*-**8** induce opposite planar chirality in lithiation–substitution reactions,[15] attention turned to applications of products such as diphenylmethanol adducts **9** and **14** in ligand synthesis (Scheme 2 and Scheme 4). A potential entry into a new ligand motif was discovered when alcohol **9** underwent acid-mediated cyclization to give a 4:1 mixture of *anti*- and *syn*-**10**, rather than elimination to the unsaturated imidazolone.[15] Repetition of this experiment on a larger scale (1.2 g) afforded exclusively *anti*-**10**, presumably because the longer reaction time allowed for equilibration of the stereoisomers.

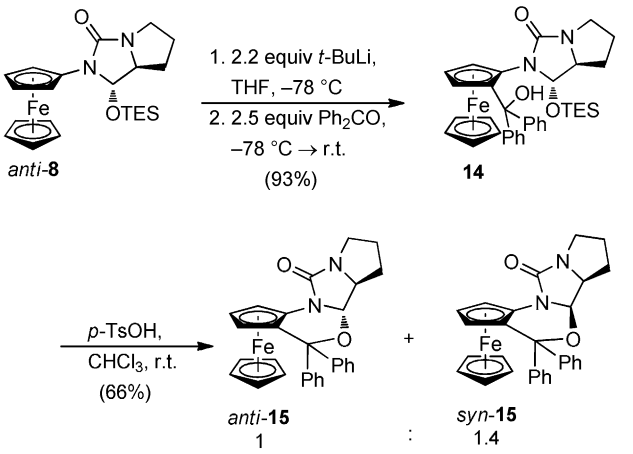
The relative stereochemistries of *anti*- and *syn*-**10** were established by nOe difference spectroscopy, obtained by selective irradiation of the respective methine hydrogens α to oxygen (Figure 1).[16] In the case of *syn*-**10**, the α to oxygen methine signal at $\delta = 4.93$ was observed to be a doublet ($^3J = 7.5$ Hz) as a result of coupling to the neighbouring pyrrolidine methine hydrogen. The magnitude of this coupling constant is similar to that of the starting material *syn*-**8** ($^3J = 6.3$ Hz). Selective irradiation of the $\delta = 4.93$ doublet of *syn*-**10** produced a 4.4% nOe for the neighbouring pyrrolidine methine at $\delta = 3.97$, along with a 1.4% nOe for a phenyl ring hydrogen at $\delta = 7.18$. In the case of *anti*-**10**, the analogous α to oxygen methine signal at $\delta = 5.46$ is a singlet as a result of its near orthogonal dihedral angle with respect to the neighbouring pyrrolidine methine. This lack of observable coupling has been seen in other derivatives with established *anti*-stereochemistry (e.g., *anti*-**8**). Irradiation of the $\delta = 5.46$ singlet resulted in only 1.3% nOe for the neighbouring pyrrolidine methine at $\delta = 3.90$. Additional nOes were observed for the unsubstituted Cp ring protons at $\delta = 3.72$ (1.9%), the methylene hydrogen at $\delta = 1.57$ (2.2%), and for a phenyl ring proton at $\delta = 7.76$ (3.2%).

Reduction of *anti*-**10** with four equivalents of DIBAL-H afforded the unusual hemiaminal ether aminal **11** (Scheme 3). This compound was surprisingly robust and indefinitely stable in a freezer (−15 °C) under an inert atmosphere. Oxidation of **11** with triphenylcarbenium tetrafluoroborate gave an imidazolinium salt, which was not isolated due to its instability.[17] Instead, deprotonation of this NHC precursor with KO-*t*-Bu in the presence of 0.5 equivalents of $[Ir(COD)Cl]_2$ afforded Ir(I) complex **12**. Coordination of this atypical NHC ligand to iridium was determined initially by ^{13}C NMR, where a characteristic ylidene carbon signal was observed at $\delta = 206$. Exposure of **12** to triphenylphosphine in dichloromethane gave the cationic iridium complex **13** upon anion exchange with potassium hexafluorophosphate.

The structure of **12** was confirmed by X-ray diffraction studies on a single crystal grown from acetonitrile solution. The complex was found to crystallize in the chiral triclinic space group *P*1 as two independent molecules. The absolute stereochemistry was assigned



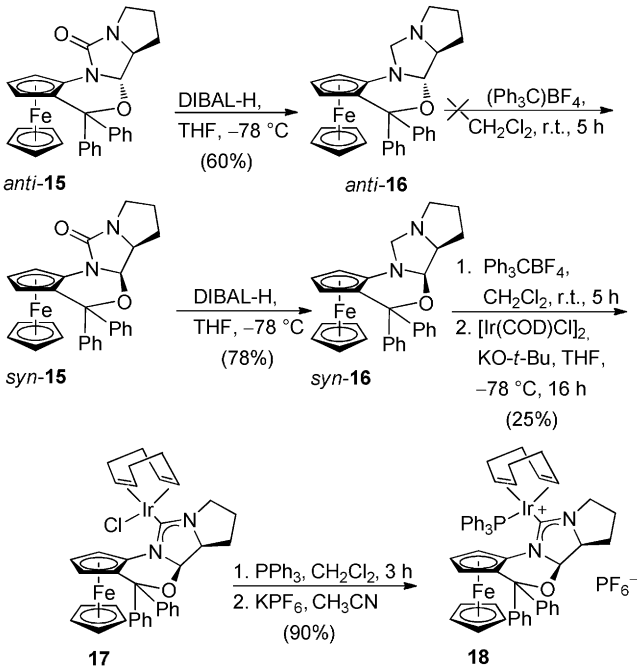
Scheme 3. Synthesis of Ir(I) complexes **12** and **13**.



Scheme 4. Synthesis and acid-mediated annulation of **14**.

on the basis of a Flack value of −0.024(5), which corroborates the known lithiation stereochemistry of starting material *syn*-**8**.[15] The NMR-assigned *anti* stereochemistry of methine hydrogens H-5a and H-6a was also affirmed. Each independent molecule is four-coordinate with square-planar geometry at iridium and $C_{ylidine}$–Ir bond lengths of 1.999(7) Å [Ir(1A)–C(1A)] and 2.001(7) Å [Ir(1B)–C(1B)], respectively. Due to the broad similarity of the two complexes, the remaining crystallographic metrics refer solely to complex A, depicted in Figure 2. This complex is characterized by ferrocenyl Cp rings that are virtually eclipsed. Despite the rigid annulated structure of the C_1-symmetric NHC ligand, the torsion angle defined by N-2a–C-1a–Ir-1a–C-l1a [98.6(3)°] is closer to that observed in related Ir(COD)Cl complexes bearing non-annulated[18] chiral NHCs [96.9(3)°] rather than those containing annulated chiral NHCs [104.0(2) and 112.89(18)°].[13a]

An analogous synthetic route was used for the synthesis of an Ir(I) complex **18** (Scheme 5). Thus, diastereoselective lithiation of *anti*-**8** followed by benzophenone quench gave carbinol **14** (Scheme 4). Acid-mediated cyclization of this intermediate furnished a 1:1.4 mixture of ureas *anti*- and *syn*-**15**, which were separable by column chromatography.



Scheme 5. Synthesis of Ir(I) complexes **17** and **18** from *syn*-**15**.

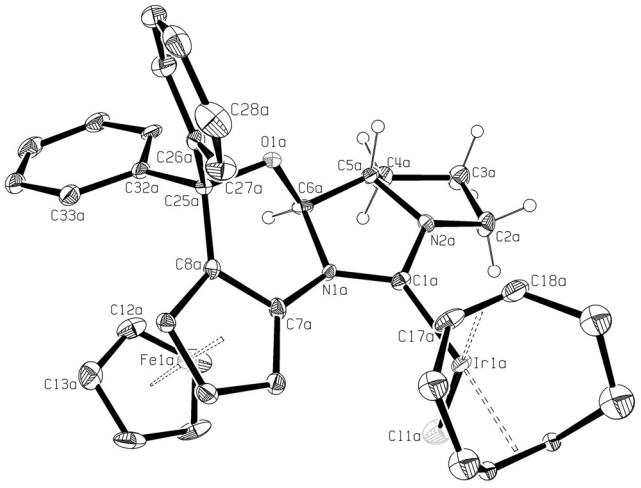


Figure 2. ORTEP depiction of **12** at 30% probability. Most hydrogens have been omitted for clarity.[19]

As in the case of *anti*/*syn*-**10**, the stereochemistries of *anti*- and *syn*-**15** were assigned by selective irradiation of the respective methine hydrogens α to oxygen, and by ^3J coupling constants. For *syn*-**15**, the methine signal at $\delta = 5.58$ was found to be a doublet with a ^3J coupling constant of 6.3 Hz, similar to *syn*-**8** and *syn*-**10** (*vide supra*). Irradiation of the $\delta = 5.58$ doublet induced a 3.8% nOe for the neighbouring pyrrolidine methine at $\delta = 4.21$, a 2.9% nOe for a phenyl ring hy-

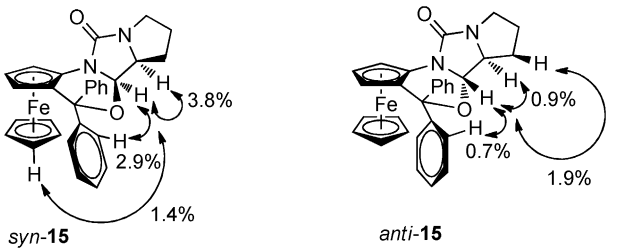


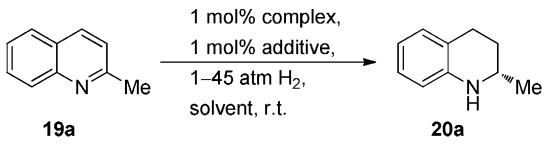
Figure 3. Difference nOes from selective irradiation of hemianinal ether methine hydrogens of *syn*- and *anti*-**15**.

drogen at $\delta = 7.75$, and a 1.4% nOe for the Cp ring hydrogens at $\delta = 3.77$ (Figure 3). For *anti*-**15**, the methine signal at $\delta = 4.60$ was found to be a doublet with a typically much smaller coupling constant ($^3J = 1.5$ Hz). Difference nOe spectroscopy obtained by irradiation of the $\delta = 4.60$ signal revealed a much smaller 0.9% nOe for the neighbouring pyrrolidine methine at $\delta = 4.01$, along with a 0.7% nOe for one of the phenyl ring protons at $\delta = 7.21$. In addition, a 1.9% nOe was observed for one methylene hydrogen of the pyrrolidine ring (Figure 3).

Reduction of ureas *anti*- and *syn*-**15** with DIBAL-H gave the hemiaminal ether aminals *anti*-**16** (60%) and *syn*-**16** (78%), respectively. Of these products, only aminal *syn*-**16** was found to undergo oxidation with triphenylcarbenium tetrafluoroborate to give the required imidazolinium salt, which was cooridinated to Ir(I) without purification. Iridium complex **17** thus obtained was converted to cationic complex **18** by treatment with PPh_3, and isolated as the hexafluorophospate salt upon anion exchange.

Based on the work by Crabtree and co-workers wherein benzimidazolylidenes were employed as ancillary ligands for the first time in the iridium-catalyzed hydrogenation of quinolines (e.g., complex **1**),[11] chiral NHC-Ir complexes **13** and **18** were investigated in the asymmetric hydrogenation of 2-substituted quinolines. Initial experiments focused on identifying optimum conditions for the enantioselective reduction of 2-methylquinoline (**19a**) with complex **13** (Scheme 6). Hydrogenation of **19a** (1 mol% **13**, 1 mol% PPh_3, PhMe, room temperature) at 45 atm of hydrogen for 6 h afforded the desired tetrahydroquinoline **20a** in 91% yield and 70:30 *er* favouring the *S*-enantiomer. Complex **13** retained significant activity at 1 atm of hydrogen, as reported by Crabtree for **1**, but provided **20a** in lower yield (56%) and marginally better selectivity (73:27 *er*) after 16 h. The best reaction outcome was obtained at 5 atm of hydrogen pressure, where **20a** was isolated in 94% yield and 79:21 *er* after 6 h.

Unlike **13**, complex **18** was found to catalyze hydrogenation of **19a** only at 45 atm of hydrogen, requiring longer reaction times (16 h) to give **20a** in 84% yield and 68:32 *er* (again favouring the *S*-enantiomer).

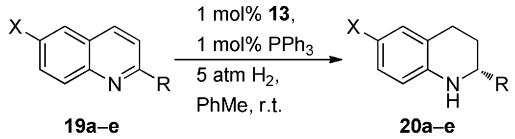


complex	solvent	pressure [atm]	additive	time [h]	yield [%] **20a**	*er* (*S*:*R*) **20a**
13	PhMe	45	PPh_3	6	91	70:30
13	PhMe	5	PPh_3	6	94	79:21
13	PhMe	1	PPh_3	16	56	73:27
18	PhMe	45	PPh_3	16	84	68:32
13	MeOH	5	PPh_3	16	47	55:45
13	CH_2Cl_2	5	PPh_3	16	71	69:31
13	THF	5	PPh_3	16	86	72:28
13	PhMe	5	none	24	76	61:39
13	PhMe	5	$P(o\text{-tol})_3$	18	90	67:33
13	PhMe	5	$P(2\text{-fur})_3$	18	53	50:50
13	PhMe	5	I_2	24	0	-

Scheme 6. Optimization of the asymmetric reduction of 2-methylquinoline (**19a**).

Lowering the hydrogen pressure to 5 atm resulted in no turnover for the **18**-catalyzed reaction. These results seem to indicate that the *anti versus syn* stereochemistry of the imidazoinylidene ligand framework is more important than the planar chirality in determining the reactivity and sense of enantio-induction in asymmetric hydrogenations mediated by complexes **13** or **18**. Based on the preceding observations, the remaining optimization experiments were conducted solely with complex **13** at 5 atm of hydrogen. Reaction outcomes with **13** were found to be solvent dependent, with good yields of **20a** being observed only in toluene (94%) and THF (86%) (Scheme 6). Methanol was found to be poor a solvent for this reaction, both in terms of yield (47%), and enantioselectivity (55:45 *er*). Dichloromethane also led to some erosion of yield (71%) and selectivity (69:31 *er*) in comparision to the reactions conducted in toluene.

The role of additives was also explored. Exclusion of the 1 mol% of PPh_3 from the reaction mixture was notably detrimental to the outcome, resulting in diminished yield and selectivity (76% yield, 61:39 *er*) and greater reaction time (24 h). The reaction also responded to the nature of the phosphine additive. Whereas the use of 1 mol% of $P(o\text{-tol})_3$ gave similar results as PPh_3 (90% yield, 67:33 *er*), the use of 1 mol% of $P(2\text{-furyl})_3$ afforded **20a** as a racemate in 53% yield. In contrast to some other catalysts that are expected to operate by an inner-sphere mechanism,[20,26] the use of iodine as an additive in hydrogenation with **13** led to complete inhibition of the reaction. The sensitivity of complex **13** to changes in phosphine additives or iodine, and its marked activity at low H_2 pressures (1–5 atm) in the presence of PPh_3, is



19a–e 20a–e

substrate (**19a–e**)	time [h]	yield [%] **20a–e**	*er* (*S*:*R*) **20a–e**
19a (X = H, R = Me)	6	94	79:21
19b (X = OMe, R = Me)	24	78	79:21
19c (X = F, R = Me)	10	93	90:10
19d (X = H, R = *n*-Pr)	24	78	69:31
19e (X = H, R = Ph)	36	25	25:75

Scheme 7. Asymmetric hydrogenation of 2-substituted quinolines mediated by precatalyst **13**.

consistent with an outer-sphere mechanism as proposed by Crabtree for achiral complex **1**.

Several additional 2-substituted quinolines were subjected to hydrogenation with complex **13** (Scheme 7). Reduction of 6-methoxy-2-methylquinoline (**19b**) under optimized conditions (1 mol% **13**, 1 mol% PPh_3, 5 atm H_2, PhMe, r.t.) gave **20b** in 78% yield and 79:21 *er* within 24 h. Better results were obtained for 2-fluoro-2-methylquinoline (**19c**), which afforded **20c** in 93% yield and 90:10 *er* within 10 h. Notably, **20c** is a key intermediate in the synthesis of antibacterial agent (*S*)-flumequine.[21] The higher enantioselectivity observed for **19c** seems to imply that enhanced electrophilicity of iminium species **6** (Scheme 1) may be important in differentiating enantiomers during the final hydride addition. This observation, in turn, may provide additional cursory support for an outer-sphere reaction mechanism (*vide supra*). Sterically hindered substrates gave somewhat poorer results. 2-Propylquinoline (**19d**) was reduced less selectively than **19a**, **b** (69:31 *er*), while hydrogenation of more sterically encumbered 2-pheylquinoline **19e** was sluggish, providing **20e** in 25% yield and 75:25 *er*. Attempts to extend this method to hydrogenation of 2,3-dimethylquinoline resulted in a low yield (18%) of racemic product (*syn* stereochemistry). Additional heterocycles such as 1- and 3-methylisoquinoline, and 2-methyl-7,8-dihydroquinolin-5(6*H*)-one, were inert to hydrogenation with complex **13**.[22]

Conclusions

Diphenylmethanol derivatives **9** and **14**, prepared stereoselectively by lithiation of *syn*- and *anti*-**8**, undergo acid-mediated cyclization to give unusual annulated imidazolones. These ureas may be reduced with DIBAL-H to give surprisingly stable and isolable hemiaminal ether aminals, two of which (**11** and *syn*-**16**) are amenable to oxidation with triphenylcarbenium tetrafluoroborate. The rigid tetracyclic and planar chiral imidazolinium salts thus obtained may be coordinated to $[Ir(COD)Cl]_2$ in the presence of *t*-BuOK to afford neutral complexes **12** and **17**. Exposure of **12** and **17** to triphenylphosphine furnished cationic complexes **13** and **18**, which are chiral analogues of complex **1**. Of these two precatalysts, **13** was found to mediate low pressure enantioselective hydrogenation (1–5 atm H_2) of prochiral 2-substituted quinolines in up to 90:10 *er* (**19c**). Changes in reactivity that were observed by altering the additive from PPh_3 to P(*o*-tol)$_3$, P(2-furyl)$_3$ or I_2, and the similarity of reaction conditions with complex **1**, point to the likelihood that this process operates under an outer-sphere mechanism (Scheme 1). As such, this procedure represents a first attempt at exploiting low pressure outer-sphere asymmetric hydrogenation of quinolines using an iridium complex bearing a chiral monodentate NHC ligand. A number of future directions may be considered for improvement of this process. In particular, we are investigating the synthesis of bidentate NHC ligands based on related ferrocenyl ligand motifs as a means to enhance the observed enantioselectivity and yield of hydrogenation. Results in this area of research will be reported in due course.

Experimental Section

General

All reagents were purchased from commercial sources and used as received unless otherwise indicated. Tetrahydrofuran (THF) was freshly dried and distilled over sodium/benzophenone ketyl under an atmosphere of nitrogen. All alkyllithium and lithium amide bases were titrated against *N*-benzylbenzamide[23] to a blue endpoint. All reactions were performed under argon in flame- or oven-dried glassware using syringe-septum cap techniques unless otherwise indicated. The syntheses of metal complexes were conducted under argon using dry, degassed solvents. 2-Propylquinoline and 2-phenylquinoline were prepared according to reported procedures.[24] Column chromatography was performed on silica gel 60 (70–230 mesh). NMR spectra were obtained on a Bruker Avance 300 or 600 MHz instrument and are referenced to TMS or to the residual proton signal of the deuterated solvent for ^1H spectra, and to the carbon multiplet of the deuterated solvent for ^{13}C spectra according to published values. Enantiomeric ratios were determined on an Agilent 1100 series HPLC system at $\lambda = 254$ nm on a Chiralcel OD-H column. FT-IR spectra were obtained on an ATI Mattson Research Series spectrometer as KBr pellets for solids or on KBr discs for liquids. Optical rotations were measured on a Rudolph Research Autopol III automatic polarimeter. Mass spectra were obtained on an MSI/Kratos Concept 1S Mass Spectrometer. Combustion analyses were performed by Atlantic Microlab Inc., Norcross, GA, USA. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Synthesis of *anti*- and *syn*-10

A solution of **9**[15a] (212 mg, 0.34 mmol) and *p*-toluenesulfonic acid (129 mg, 0.68 mmol) in $CHCl_3$ (4 mL) was stirred at room temperature for 5 min. A distinct colour change from orange to brown was observed. The solution was worked up with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a 4:1 mixture of *anti*/*syn* epimers; yield: 117 mg (70%). Flash column chromatography (silica gel, 3:7 EtOAc/hexane) gave, sequentially, *syn*-**10** (yield: 21 mg, 13%, $R_f = 0.43$) and *anti*-**10** (yield: 96 mg, 57%, $R_f = 0.23$).

Data for *syn*-10 [(+)-(6a*R*,6b*S*)-5,5-diphenyl-6b,7,8,9-tetrahydro-5*H*-(S_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazin-11(6a*H*)-one]: Orange glassy solid; $[\alpha]_D^{20}$: +70.3 (*c* 0.85, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 80:20 hexanes/*i*-PrOH, 1.0 mL min^{-1}): >99:1 *er*, >98% *ee* [t_R(minor) = 5.59 min, t_R(major) = 10.77 min]; IR (KBr): ν_{max} = 3085, 3058, 3026, 2954, 1714, 1504, 1402 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.49 (d, 2H, *J* = 7.5 Hz), 7.43–7.37 (t, 2H, *J* = 7.5 Hz), 7.32–7.30 (d, 1H, *J* = 6.9 Hz), 7.25–7.22 (m, 3H), 7.17–7.14 (m, 2H), 4.93 (d, 1H, *J* = 7.5 Hz), 4.69 (s, 1H), 4.16–4.07 (m, 2H), 3.87–3.74 (m, 7H), 3.19–3.11 (m, 1H), 2.36–2.28 (m, 1H), 2.18–2.12 (m, 2H), 1.98–1.93 (m, 1H); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 159.8, 146.3, 145.1, 128.0, 127.9, 127.8, 127.7, 126.7, 125.6, 94.1, 82.2, 80.5, 77.6, 69.8, 63.4, 62.7, 61.1, 56.0, 45.7, 25.4, 25.0; EI-MS: *m*/*z* (%) = 490 (M^+, 16), 105 (100), 84 (48), 77 (33), 49 (58); HR-MS (EI): *m*/*z* = 490.1345, calcd. for $C_{29}H_{26}N_2O_2{}^{56}Fe$: 490.1343.

Data for *anti*-10 [(+)-(6a*S*,6b*S*)-5,5-diphenyl-6b,7,8,9-tetrahydro-5*H*-(S_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazin-11(6a*H*)-one]: Orange solid; mp 251–252 °C (CH_2Cl_2/hexane); $[\alpha]_D^{20}$: +168.0 (*c* 0.50, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 80:20 hexanes/*i*-PrOH, 1.0 mL min^{-1}): >99:1 *er*, >98% *ee* [t_R(minor) = 8.64 min, t_R(major) = 10.09 min]; IR (KBr): ν_{max} = 3085, 3058, 2968, 2896, 1712, 1502, 1392, 1028, 1001 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74–7.73 (d, 2H, *J* = 7.8 Hz), 7.54–7.52 (t, 2H, *J* = 7.2 Hz), 7.44–7.42 (t, 1H, *J* = 7.2 Hz), 7.15–7.10 (m, 3H), 6.88–6.87 (m, 2H), 5.46 (s, 1H), 5.17 (s, 1H), 4.12–4.11 (t, 1H, *J* = 2.7 Hz), 3.90–3.85 (m, 2H), 3.70 (s, 5H), 3.68–3.63 (m, 1H), 3.18–3.14 (m, 1H), 2.23–2.18 (m, 1H), 2.11–2.07 (m, 1H), 1.99–1.94 (m, 1H), 1.58–1.52 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 158.7, 146.6, 144.9, 127.9, 127.7, 127.6, 127.5, 127.3, 126.4, 92.5, 83.1, 82.8, 80.7, 69.9, 64.2, 64.1, 63.5, 60.5, 45.3, 28.4, 25.7; EI-MS: *m*/*z* (%) = 490 (M^+, 8), 86 (64), 84 (100), 49 (17), 47 (19); HR-MS (EI): *m*/*z* = 490.1336, calcd. for $C_{29}H_{26}N_2O_2Fe$: 490.1343; anal. calcd. for $C_{29}H_{26}N_2O_2{}^{56}Fe$: C 71.03, H 5.34; found: C 70.51, H 5.14.

***Scale-up*:** Repetition of the above procedure using a solution of **9** (1.2 g, 1.9 mol) and *p*-toluenesulfonic acid (716 mg, 3.76 mmol) in $CHCl_3$ (20 mL), stirred at room temperature for 20 min, gave only *anti*-**10** after work-up. The crude mixture was dissolved in a minimum amount of CH_2Cl_2, and hexane was added to precipitate the product. Recrystallization from CH_2Cl_2/hexane afforded *anti*-**10** as an orange solid (*vide supra*); yield: 645 mg (70%).

(+)-(6a*S*,6b*S*)-5,5-Diphenyl-6a,6b,7,8,9,11-hexahydro-5H-(S_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*]-[1,3]oxazine (11)

A solution of *anti*-**10** (610 mg, 1.24 mmol) in THF (60 mL) at −78 °C under argon was treated with DIBAL-H (5 mL, 1 M in hexanes, 4.98 mmol). The reaction mixture was allowed to warm slowly to room temperature (*ca.* 5 h). After 16 h, the mixture was cooled to 0 °C, diluted with EtOAc, and worked up with a solution of saturated aqueous potassium sodium tartrate (2 mL). It was then stirred gently for 15 min until the organic and aqueous layers separated. The organic layer was isolated, washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography (silica gel, 50:45:5 EtOAc/hexane/Et_3N, $R_f = 0.23$) gave **11** as an orange crystalline solid that was stable indefinitely in a freezer under argon; yield: 470 mg (79%); mp 203–204 °C; $[\alpha]_D^{20}$: +312 (*c* 0.50, $CHCl_3$); IR (KBr): ν_{max} = 3085, 3023, 2958, 2937, 2861, 2848, 1490, 1469, 1360, 1136, 1105 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.74 (d, 2H, *J* = 7.2 Hz), 7.52–7.47 (t, 2H, *J* = 7.2 Hz), 7.40–7.39 (t, 1H, *J* = 7.5 Hz), 7.12–7.09 (m, 3H), 6.96–6.93 (m, 2H), 4.89 (s, 1H), 4.45 (s, 1H), 3.99–3.97 (m, 1H), 3.91–3.88 (dd, 2H, *J* = 12.3, 6.9 Hz), 3.84–3.80 (m, 2H), 3.68 (s, 5H), 3.22–3.21 (m, 1H), 2.88–2.87 (m, 1H), 2.25–2.24 (m, 1H), 1.86–1.77 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.8, 146.0, 127.7, 127.5, 127.4, 127.1, 126.9, 126.6, 100.2, 91.2, 81.7, 81.4, 75.2, 70.2, 70.0, 63.9, 63.3, 61.9, 56.0, 20.6, 26.7; EI-MS: *m*/*z* (%) = 476 (M^+, 44), 83 (100), 55 (12); HR-MS (EI): *m*/*z* = 476.1554, calcd. for $C_{29}H_{28}N_2O_1Fe$: 476.1551; anal. calcd. for $C_{29}H_{26}N_2O_2{}^{56}Fe$: C 73.11, H 5.92; found: C 72.81, H 6.05.

(−)-Chloro[η^4-1,5-cyclooctadiene][(6a*S*,6b*S*)-5,5-diphenyl-5,6a,6b,7,8,9-hexahydro(S_p-ferroceno)[*d*]-pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazinylidene]-iridium (12)

A solution of **11** (200 mg, 0.42 mmol) and triphenylcarbenium tetrafluoroborate (139 mg, 0.42 mmol) in CH_2Cl_2 (4 mL) was stirred in a Schlenk flask at room temperature under argon, protected from light. After 5 h, the solvent was evaporated under reduced pressure and the crude solid was washed with dry diethyl ether (3 × 5 mL) under argon, then dried under vacuum. In a glovebox, the crude imidazolinium salt was treated with $[Ir(COD)Cl]_2$ (141 mg, 0.21 mmol) and degassed THF (14 mL). After removal from the glovebox, the solution was cooled to −78 °C and KO-*t*-Bu (47 mg, 0.42 mmol) was added under an increased flow of argon. After 1 h, the reaction mixture was warmed to room temperature and the volatiles were removed under reduced pressure. Flash column chromatography (silica gel, 2:8 EtOAc/hexane) gave a 4:1 mixture of coordination isomers. The minor isomer was found to convert to the major isomer in CH_2Cl_2 solution after 16 h at room temperature to afford **12** as a crystalline orange solid; yield: 194 mg (57%); R_f = 0.25 (2:8 EtOAc/hexane). Data for **12**: mp 222–223 °C (CH_3CN); $[\alpha]_D^{20}$: −245 (*c* 0.50, $CHCl_3$); X-ray diffractometry [CCDC 1030224] was performed on an orange crystal (0.16 × 0.05 × 0.04 mm^3): $C_{37}H_{38}ClFeIrN_2O$: M = 810.19 g mol^{-1}, triclinic, *P*1, *a* = 9.6609(9) Å, *b* = 11.9882(12) Å, *c* = 14.7752(14) Å, *V* = 1614.8(3) Å^3, α =

74.139(2)°, $\beta = 89.285(2)°$, $\gamma = 79.066(2)°$, $Z = 2$, $\rho_{cald} = 1.666\ g\,cm^{-3}$, F(000) = 804, $T = 147(2)$ K; 26631 data were collected. The structure was solved by Direct Methods (SHELXTL) and refined by full-matrix least squares on F^2 resulting in final R, Rw and GOF [for 13430 data with $F > 2\sigma(F)$] of 0.0395, 0.0804 and 0.965, respectively, for solution using the *S*p enantiomer model [Flack parameter = −0.024(5)]; IR (KBr): $\nu_{max} = 2956$, 2922, 2873, 2828, 1699, 1518, 1413 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.71$–7.68 (d, 2H, $J = 7.5$ Hz), 7.55–7.50 (t, 2H, $J = 7.2$ Hz), 7.45–7.40 (t, 1H, $J = 7.2$ Hz), 7.16–7.11 (m, 3H), 6.88–6.84 (m, 2H), 6.28–6.27 (m, 1H), 5.74–5.73 (d, 1H, $J = 4.2$ Hz), 4.85–4.80 (m, 1H), 4.69–4.63 (m, 1H), 4.48–4.39 (m, 1H), 4.20–4.19 (t, 1H, $J = 2.7$ Hz), 4.05–3.98 (m, 1H), 3.93–3.91(m, 1H), 3.78 (s, 5H), 3.54–3.46 (m, 1H), 3.24–3.20 (m, 1H), 2.87–2.81(m, 1H), 2.36–2.15 (m, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$ 206.4, 146.4, 144.8, 127.8, 127.7, 127.6, 127.4, 126.1, 93.9, 89.4, 86.5, 86.3, 83.6, 81.4, 70.63, 68.5, 64.6, 64.0, 63.0, 54.7, 51.1, 46.3, 34.0, 32.8, 29.6, 28.9, 28.5, 25.5; FAB-MS: *m/z* (%) = 810 (M^+, 2), 95 (50), 91 (36), 67 (70), 55 (100), 43 (99), 39 (54), 29 (73); HR-MS (FAB): *m/z* = 810.1619, calcd. for $C_{37}H_{38}N_2OClFeIr$: 810.1651; anal. calcd. for $C_{37}H_{38}N_2OCl^{56}FeIr$: C 54.85, H 4.73; found: C 54.57, H 4.75.

(−)-[η⁴-1,5-Cyclooctadiene][triphenylphosphine][(6a*S*,6b*S*)-5,5-diphenyl-5,6a,6b,7,8,9-hexahydro(*S*$_p$-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]-oxazinylidene]iridium Hexafluorophosphate (13)

A solution of **12** (100 mg, 0.12 mmol) in CH_2Cl_2 (1 mL) was treated with a solution of triphenylphosphine (32 mg, 0.12 mmol) in CH_2Cl_2 (1 mL). The resulting red solution was stirred at room temperature under argon for 3 h and then concentrated under reduced pressure. The residue was dissolved in a minimum amount of CH_3CN and a solution of KPF_6 (29 mg, 0.16 mmol) in a minimum amount of CH_3CN was added. The mixture was stirred at room temperature under argon for 1 h, and then passed through Celite, rinsing thoroughly with CH_2Cl_2. The volatiles were removed under reduced pressure to give a red solid that was triturated with pentane to afford **13** as a red crystalline solid; yield: 131 mg (90%); mp 189–190 °C; $[\alpha]_D^{20}$: −71.6 (*c* 0.50, $CHCl_3$); IR (KBr): $\nu_{max} = 2918$, 2880, 2850, 1500, 1436, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$–7.41 (m, 20H), 7.33–7.32 (m, 2H), 7.16–7.14 (m, 3H), 6.92–6.90 (d, 2H, $J =$ 6.3 Hz), 5.77 (s, 1H), 5.24 (s, 1H), 4.74 (m, 1H), 4.35 (s, 1H), 4.24 (m, 2H), 4.01 (m, 1H), 3.75 (m, 1H), 3.55–3.46 (m, 7H), 3.29–3.28 (m, 1H), 2.42–2.35 (m, 1H), 2.29–2.17 (m, 3H), 1.97–1.91 (m, 6H), 1.60–1.49 (m, 1H), 1.15–1.12 (m, 1H); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 16.2$, −144.2 (septet, $J = 713.2$ Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$): $\delta =$ −73.5 (d, $J = 711.6$ Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$ 202.9, 145.7–145.6 (d, $J_{C,P} = 6.8$ Hz), 133.7 (d, $J_{C,P} = 19$ Hz), 131.8, 129.2 (d, $J_{C,P} = 9.8$ Hz), 128.7, 128.4, 128.2, 127.9 (d, $J_{C,P} = 9.1$ Hz), 127.6, 125.5, 94.0, 90.6–90.5 (d, $J_{C,P} = 8.3$ Hz), 86.5, 85.1, 83.1, 81.4, 81.2, 80.7, 71.4, 70.2, 65.4, 64.1, 62.4, 45.2, 33.2, 32.2, 29.2, 29.0, 25.9, 24.8; FAB-MS: *m/z*(%) = 1037 (M^+, 8), 83 (29), 71 (30), 69 (60), 67 (38), 55 (100), 43 (94); HR-MS (FAB): *m/z* = 1037.2830, calcd. for $C_{55}H_{53}N_2OPFeIr$: 1037.2874; anal. calcd. for $C_{55}H_{53}N_2OP^{56}FeIr^+PF_6^-$: C 55.89, H 4.52; found: C 55.72, H 4.66.

(−)-2-[(2R_p-(Diphenylhydroxymethyl)ferrocenyl]-1*S*-triethylsilyloxy-7a*S*-hexahydropyrrolo[1,2-*c*]imidazol-3-one (14)

A solution of *anti*-**8** (809 mg, 1.84 mmol) in THF (15 mL) at −78 °C under argon was treated with *t*-BuLi (4.0 mL, 1.04 M, 4.16 mmol). After stirring for 30 min, a distinct colour change from orange to orange-red was observed. The reaction mixture was quenched with a solution of Ph_2CO (837 mg, 4.59 mmol) in THF (5 mL) and stirred for 30 min at that temperature. Work-up was conducted by addition of water (0.5 mL) and, after warming to room temperature, the reaction mixture was extracted with diethyl ether (2 × 40 mL). The combined organic extract was washed with water, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography (silica gel, 2:8 EtOAc/hexane, $R_f = 0.43$) gave **14** as a diastereomerically enriched crystalline orange solid; yield: 1.06 g (93%); mp 181–182 °C (EtOH/H_2O); $[\alpha]_D^{20}$: −67.0 (*c* 1.0, $CHCl_3$); IR (KBr): $\nu_{max} = 3221$, 3086, 3054, 2954, 2909, 1686, 1460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.74$ (d, 2H, $J =$ 7.2 Hz), 7.46 (d, 2H, $J = 6.9$ Hz), 7.31–7.29 (m, 1H), 7.23–7.14 (m, 5H), 5.37 (s, 1H), 4.40 (s, 5H), 4.31- 4.29 (m, 1H), 4.02 (t, 1H, $J = 2.7$ Hz), 3.45–3.43 (m, 1H), 3.38–3.29 (m, 1H), 3.23–3.18 (m, 1H), 2.96–2.90 (m, 1H), 1.82–1.81 (m, 1H), 1.74–1.66 (m, 2H), 0.97 (t, 10H, $J = 7.8$ Hz), 0.67 (q, 6H, $J = 7.8$ Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 161.5$, 147.5, 145.9, 127.6, 127.3, 127.2, 127.1, 126.3, 126.2, 92.0, 90.8, 87.2, 76.1, 70.4, 70.1, 66.4, 66.0, 63.5, 45.3, 28.3, 24.9, 6.8, 5.2; EI-MS: *m/z* (%) = 622 (M^+, 3), 490 (56), 105 (58), 103 (100), 75 (79); HR-MS (EI): *m/z* = 622.2285, calcd, for $C_{35}H_{42}N_2O_3Si^{56}Fe$: 622.2314; anal. calcd. for $C_{35}H_{42}N_2O_3SiFe$: C 67.51, H 6.80; found: C 67.25, H 6.72.

Synthesis of *anti*- and *syn*-15

A solution of **14** (1.10 g, 2.00 mmol) and *p*-toluenesulfonic acid (761 mg, 4.00 mmol) in $CHCl_3$ (20 mL) was stirred for 5 min at room temperature. A distinct colour change from orange to brown was observed. The mixture was worked up with saturated aqueous $NaHCO_3$ solution. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a 1.4:1 mixture of *syn*/*anti* epimers; yield: 650 mg (1.33 mmol, 66%). Flash column chromatography (silica gel, 3:7 EtOAc/hexanes, R_f (*anti*) = 0.32, R_f (*syn*) = 0.29) gave, sequentially *anti*-**15** (yield: 270 mg, 0.55 mmol, 27%) and *syn*-**15** (yield: 380 mg, 39%).

Data for *anti*-15 [(−)-(6a*S*,6b*S*)-5,5-diphenyl-6b,7,8,9-tetrahydro-5*H*-(*R*$_p$-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazin-11(6a*H*)-one]: Orange solid; mp 119–120 °C; $[\alpha]_D^{20}$: −230 (*c* 2.0, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 90:10 hexanes/*i*-PrOH, 1.0 mL min^{-1}): > 99:1 *er*, > 98% *ee* [t_R(major) = 6.13 min, t_R(minor) = 9.88 min]; IR (KBr): $\nu_{max} = 3085$, 3058, 3006, 2970, 2920, 1714, 1489, 1392, 1329 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (d, 2H, $J =$ 7.5 Hz), 7.40 (t, 2H, $J = 7.2$ Hz), 7.32–7.28 (m, 1H), 7.23–7.19 (m, 3H), 7.17–7.14 (m, 2H), 4.60 (d, 1H, $J = 1.5$ Hz), 4.59–4.57 (m, 1H), 4.11 (t, 1H, $J = 8.4$ Hz), 4.07 (t, 1H, $J =$ 2.7 Hz), 3.97–3.92 (m, 1H), 3.84 (s, 5H), 3.66–3.58 (m, 1H), 3.25–3.16 (m, 1H), 2.05–1.86 (m, 3H), 1.26 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 160.5$, 145.9, 145.1, 128.4, 127.9, 127.8, 127.7, 126.8, 125.7, 93.1, 82.5, 82.3, 81.5, 69.9,

63.7, 62.8, 57.2, 46.3, 45.4, 28.7, 25.6; EI-MS: m/z (%) = 490 (M^+, 83), 86 (65), 84 (96), 51 (44), 49 (100), 47 (20), 47 (18); HR-MS (EI): m/z = 490.1348, calcd. for $C_{29}H_{26}N_2O_2{}^{56}Fe$: 490.1343.

Data for *syn*-15 [(−)-(6a*R*,6b*S*)-5,5-diphenyl-6b,7,8,9-tetrahydro-5*H*-(R_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazin-11(6a*H*)-one]: Orange solid; mp 97–98 °C; $[\alpha]_D^{20}$: −303 (*c* 1.0, $CHCl_3$); CSP HPLC analysis (Chiralcel OD-H; eluent: 60:40 hexanes/*i*-PrOH, 0.5 mL min^{-1}): >99:1 *er*, >98% *ee* [t_R(minor) = 10.85 min, t_R(major) = 11.56 min]; IR (KBr): ν_{max} = 3086, 3057, 3026, 2924, 2853, 1713, 1504, 1492, 1398 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, 2H, J = 7.2 Hz), 7.52 (t, 2H, J = 7.8 Hz), 7.42 (t, 1H, J = 7.2 Hz), 7.14–7.08 (m, 3H), 6.87–6.84 (m, 2H), 5.58 (d, 1H, J = 6.6 Hz), 5.08–5.06 (m, 1H), 4.21–4.15 (m, 1H), 4.09 (t, 1H, J = 2.7 Hz), 3.81–3.79 (m, 1H), 3.75 (s, 5H), 3.73–3.67 (m, 1H), 3.14–3.06 (m, 1H), 2.14–2.08 (m, 1H), 1.91–1.83 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.1, 146.9, 144.8, 127.7, 127.7, 127.6, 127.4, 127.3, 125.6, 93.1, 82.6, 80.9, 80.5, 70.0, 64.0, 60.4, 60.3, 46.2, 45.6, 26.5, 24.3; EI-MS: m/z (%) = 490 (M^+, 4), 87 (12), 85 (59), 83 (100), 47 (18); HR-MS (EI): m/z = 490.1342, calcd. for $C_{29}H_{26}N_2O_2Fe$: 490.1343; anal. calcd. for $C_{29}H_{26}N_2O_2Fe$: C 71.03, H 5.34; found: C 70.75, H 5.53.

(−)-(6a*S*,6b*S*)-5,5-Diphenyl-6a,6b,7,8,9,11-hexahydro-5*H*-(R_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*]-[1,3]oxazine (*anti*-16)

To a solution of *anti*-**15** (195 mg, 0.40 mmol) in THF (20 mL) at −78 °C was added DIBAL-H (1.80 mL, 1.00 M solution in hexanes, 1.60 mmol). The reaction mixture was allowed to warm to room temperature (*ca.* 5 h). After 16 h, the solution was cooled to 0 °C and worked up with aqueous potassium sodium tartrate. It was then stirred for 15 min until separate aqueous and organic layers were visible. The organic layer was isolated, washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography (silica gel, 50:45:5 EtOAc/hexanes/Et_3N, R_f = 0.40) afforded aminal *anti*-**16** as an orange solid; yield: 114 mg (60%); mp 88–90 °C; $[\alpha]_D^{20}$: −343 (*c* 1.0, $CHCl_3$); IR (KBr): ν_{max} = 3084, 3026, 2954, 2919, 2865, 1491, 1473 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, 2H, J = 7.5 Hz), 7.37 (t, 2H, J = 7.2 Hz), 7.28–7.23 (m, 6H), 4.32 (d, 1H, J = 7.5 Hz), 4.21 (d, 1H, J = 7.5 Hz), 4.12–4.11 (m, 1H), 4.06 (t, 1H, J = 2.7 Hz), 3.98 (d, 1H, J = 2.7 Hz), 3.87–3.82 (m, 1H), 3.80–3.79 (m, 1H), 3.77 (s, 5H), 3.20–3.13 (m, 1H), 2.72–2.64 (m, 1H), 2.15–2.07 (m, 1H), 1.79–1.68 (m, 2H), 1.61–1.55 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 146.7, 145.5, 128.1, 127.8, 127.6, 127.3, 126.4, 125.6, 102.6, 88.7, 84.2, 81.0, 78.6, 70.2, 68.8, 63.0, 62.3, 54.9, 54.0, 29.4, 25.7; EI-MS: m/z (%) = 476 (M^+, 84), 83 (100), 56 (76), 57 (46), 41 (40); HR-MS (EI): m/z = 476.1544, calcd. for $C_{29}H_{28}N_2O^{56}Fe$: 476.1551.

(−)-(6a*R*,6b*S*)-5,5-Diphenyl-6a,6b,7,8,9,11-hexahydro-5*H*-(R_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*]-[1,3]oxazine (*syn*-16)

To a solution of *syn*-**15** (150 mg, 0.31 mmol) in THF (15 mL) at −78 °C was added DIBAL-H (1.40 mL, 1.00 M solution in hexanes, 1.60 mmol). The reaction mixture was allowed to warm to room temperature (*ca.* 5 h). After 16 h, the solution was cooled to 0 °C and worked up with aqueous potassium sodium tartrate. It was then stirred for 15 min until separate aqueous and organic layers were visible. The organic layer was isolated, washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Flash column chromatography (silica gel, 50:45:5 EtOAc/hexanes/Et_3N, R_f = 0.23) afforded *syn*-**16** as an orange solid; yield: 115 mg (0.24 mmol, 78%); mp 56–57 °C; $[\alpha]_D^{20}$: −318 (*c* 1.5, $CHCl_3$); IR (KBr): ν_{max} = 3085, 3056, 2954, 2917, 2867, 1508, 1490, 1473 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, 2H, J = 7.5 Hz), 7.48 (t, 2H, J = 7.2 Hz), 7.40–7.37 (m, 1H), 7.14–7.12 (m, 3H), 6.99–6.96 (m, 2H), 5.07 (d, 1H, J = 4.5 Hz), 4.33 (s, 1H), 4.19 (d, 1H, J = 4.8 Hz), 4.04–3.99 (m, 2H), 3.89–3.88 (m, 1H), 3.72 (s, 5H), 3.56 (d, 1H, J = 4.8 Hz), 3.05–3.00 (m, 1H), 2.58–2.54 (m, 1H), 2.30–2.26 (m, 1H), 1.87–1.76 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.7, 146.1, 127.6, 127.5, 127.5, 127.0, 126.9, 126.4, 102.9, 86.3, 81.9, 81.7, 77.4, 74.7, 69.6, 67.0, 63.7, 63.0, 59.6, 55.2, 26.9, 24.5; EI-MS: m/z (%) = 476 (M^+, 78), 83 (100), 56 (63), 41 (34), 43 (31); HR-MS (EI): m/z = 476.1547, calcd. for $C_{29}H_{28}N_2O^{56}Fe$: 476.1551.

(−)-Chloro[η^4-1,5-cyclooctadiene][(6a*R*,6b*S*)-5,5-diphenyl-5,6a,6b,7,8,9-hexahydro(R_p-ferroceno)[*d*]-pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]oxazinylidene]-iridium (17)

A solution of *syn*-**16** (60 mg, 0.13 mmol) and triphenylcarbenium tetrafluoroborate (42 mg, 0.13 mmol) in CH_2Cl_2 (2 mL) was stirred in a Schlenk flask at room temperature under argon, protected from light. After 5 h, the solvent was removed under reduced pressure, and the crude solid was washed with diethyl ether (3 × 5 mL) under argon and dried under vacuum. The crude material was transferred to a glovebox, and treated with $[Ir(COD)Cl]_2$ (42 mg, 0.06 mmol) and degassed THF (4 mL). The mixture was removed from the glovebox, cooled to −78 °C and, with an increased flow of argon, KO-*t*-Bu (14 mg, 0.13 mmol) was added. The reaction mixture was allowed to warm to room temperature. After 16 h, the volatiles were removed under reduced pressure. Flash column chromatography (silica gel, 3:7 EtOAc/hexane, R_f = 0.40) gave **17** as a crystalline orange solid; yield: 26 mg (25%); mp 157–158 °C; $[\alpha]_D^{20}$: −49.0 (*c* 0.5, $CHCl_3$); IR (KBr): ν_{max} = 3132, 2954, 2924, 2873, 1734, 1519, 1400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, 2H, J = 7.5 Hz), 7.53 (t, 2H, J = 7.2 Hz), 7.45 (t, 1H, J = 7.2 Hz), 7.12–7.10 (m, 3H), 6.95–6.92 (m, 2H), 6.13 (s, 1H), 5.69 (d, 1H, J = 7.8 Hz), 4.80–4.75 (m, 1H), 4.68–4.61 (m, 1H), 4.57–4.52 (m, 1H), 4.21–4.13 (m, 2H), 3.80–3.75 (s, 6H), 3.55–3.51 (m, 1H), 3.28–3.26 (m, 1H), 3.08–3.06 (m, 1H), 2.45–2.33 (m, 3H), 2.20–2.13 (m, 2H), 2.03–1.98 (m, 3H), 1.89–1.81 (m, 2H), 1.74–1.68 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 206.8, 146.6, 143.9, 128.2, 127.9, 127.7, 127.6, 127.5, 126.9, 94.4, 86.9, 86.6, 84.9, 83.1, 82.7, 70.2, 65.9, 65.0, 64.6, 61.7, 54.9, 49.6, 48.3, 34.7, 32.5, 30.4, 28.4, 25.9, 23.9; FAB-MS: m/z (%) = 810 (M^+, 2), 95 (50), 91 (36), 67 (70), 55 (100), 43 (99), 39 (54), 29 (73); HR-MS (FAB): m/z = 810.1613, calcd. for $C_{37}H_{38}N_2OCl^{56}FeIr$: 810.1651.

(−)-[η⁴-1,5-Cyclooctadiene][triphenylphosphine][(6a*R*,6b*S*)-5,5-diphenyl-5,6a,6b,7,8,9-hexahydro(R_p-ferroceno)[*d*]pyrrolo[1′,2′:3,4]imidazo[5,1-*b*][1,3]-oxazinylidene]iridium Hexafluorophosphate (18)

A solution of **17** (13 mg, 0.02 mmol) in CH_2Cl_2 (0.5 mL) was treated with a solution of triphenylphosphine (4 mg, 0.02 mmol) in CH_2Cl_2 (0.5 mL) under argon. The resulting red solution was stirred at room temperature for 3 h and concentrated under reduced pressure. The residue was dissolved in a minimum amount of CH_3CN, and a solution of KPF_6 (3.5 mg, 0.02 mmol) in a minimum amount of CH_3CN was added. After stirring at room temperature for 1 h, the reaction mixture was passed through Celite, rinsing with CH_2Cl_2. Removal of the solvent under reduced pressure gave a red solid that was triturated with pentane to afford **18** as a red crystalline solid; yield: 17 mg (90%); mp 138–140 °C; $[\alpha]_D^{20}$: −319 (*c* 0.4, $CHCl_3$); IR (KBr): ν_{max} = 3061, 2929, 2887, 1493, 1436, 1096, 847 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6): δ = 7.68–7.58 (m, 2H), 7.56–7.49 (m, 3H), 7.46–7.39 (m, 4H), 7.37–7.29 (m, 6H), 7.26–7.14 (m, 5H), 7.04 (t, 1H, *J* = 7.2 Hz), 6.87 (t, 2H, *J* = 7.8 Hz), 6.57 (d, 2H, *J* = 7.5 Hz), 6.16 (d, 1H, *J* = 7.8 Hz), 5.85–5.84 (m, 1H), 4.87–4.86 (m, 1H), 4.66–4.53 (m, 3H), 4.51–4.45 (m, 1H), 4.37–4.36 (m, 1H), 3.80 (s, 5H), 3.59–3.47 (m, 1H), 3.40–3.36 (m, 1H), 3.00–2.93 (m, 2H), 2.80–2.78 (m, 3H), 2.62–2.50 (m, 4H), 1.95–1.75 (m, 3H), 1.70 (m, 1H), 1.58–1.51 (m, 1H); ^{31}P NMR (242.9 MHz, $CDCl_3$): δ = 18.9 (s), −144.3 (septet, *J* = 714.1 Hz); ^{19}F NMR (564.7 MHz, $CDCl_3$): δ = −73.6 (d, *J* = 711.6 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 198.3 (d, *J* = 7.5 Hz), 146.9, 146.0, 134.0 (d, *J* = 12.1 Hz), 131.5 (d, *J* = 15.1 Hz), 128.6 (t, *J* = 10.6 Hz), 128.3, 127.9, 127.8, 127.7, 127.6, 95.2, 92.2, 85.6, 85.0, 84.1 (d, *J* = 13.6 Hz), 83.6, 80.2, 79.8, 70.8, 67.2, 65.7, 63.8, 63.1, 45.0, 35.1, 34.7, 28.1, 27.2, 25.7, 21.2; FAB-MS: *m/z* (%) = 1037 (M^+, 17), 81 (42), 67 (41), 55 (100), 43 (93); HR-MS (FAB): *m/z* = 1037.2682, calcd. for $C_{55}H_{53}N_2OP^{56}FeIr$: 1037.2874.

(−)-(*S*)-2-Methyl-l,2,3,4-tetrahydroquinoline (20a)[25,26]

A vial containing a solution of 2-methylquinoline **19a** (0.07 mL, 0.51 mmol), triphenylphosphine (1.3 mg, 1 mol%) and iridium complex **13** (6 mg, 1 mol%) in toluene (2 mL) was sealed in a Parr bomb. The vessel was evacuated and back-filled with hydrogen three times, then pressurized to 5 atm. The mixture was stirred at room temperature for 6 h, after which the pressure was carefully released. The reaction mixture was concentrated under reduced pressure and passed through a short column of silica gel, eluting with 2:94:4 EtOAc/hexane/Et_3N. Evaporation of the solvent under vacuum gave **20a** as a colourless oil; yield: 69 mg (94%); $[\alpha]_D^{20}$: −53.0 (*c* 3.0, $CHCl_3$) {lit[27] (*R*)-**20a**: $[\alpha]_D^{20}$: +84.3 (*c* 0.20, $CHCl_3$, 99% *ee*)}; CSP HPLC analysis (Chiralcel OD-H; eluent: 98:2 hexanes/*i*-PrOH, 0.5 mL min^{-1}): 79:21 *er*, 58% *ee* [t_R(minor) = 14.16 min, t_R(major) = 16.17 min]; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.01–6.97 (m, 2H), 6.63 (t, 1H, *J* = 7.6 Hz), 6.51–6.48 (m, 1H), 3.45–3.39 (m, 1H), 2.90–2.71 (m, 2H), 1.99–1.91 (m, 1H), 1.68–1.55 (m, 1H), 1.23 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.7, 129.2, 126.6, 121.0, 116.9, 113.9, 47.1, 30.0, 26.5, 22.5.

(−)-(*S*)-6-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (20b)[25,26]

A vial containing a solution of 6-methoxy-2-methylquinoline **19b** (87 mg, 0.50 mmol), triphenylphosphine (1.3 mg, 1 mol%) and iridium complex **13** (6 mg, 1 mol%) in toluene (2 mL) was sealed in a Parr bomb. The vessel was evacuated and back-filled with hydrogen three times, then pressurized to 5 atm. The mixture was stirred at room temperature for 24 h, after which the pressure was carefully released. The reaction mixture was concentrated under reduced pressure and passed through a short column of silica gel, eluting with 10:86:4 EtOAc/hexane/Et_3N. Evaporation of the solvent under vacuum gave **20b** as a yellow oil that solidified on standing; yield: 69 mg (78%); $[\alpha]_D^{20}$: −59.7 (*c* 1.0, $CHCl_3$) {lit[27] (*R*)-**20b**: $[\alpha]_D^{20}$: +80.3 (*c* 0.19, $CHCl_3$, >99% *ee*)}; CSP HPLC analysis (Chiralcel OD-H; eluent: 98:2 hexanes/*i*-PrOH, 0.5 mL min^{-1}): 79:21 *er*, 58% *ee* [t_R(minor) = 19.58 min, t_R(major) = 22.85 min]; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.62–6.58 (m, 2H), 6.47–6.44 (m, 1H, *J* = 8.1 Hz), 3.73 (s, 3H), 3.33 (bs, 1H), 2.85–2.69 (m, 2H), 1.96–1.88 (m, 1H), 1.65–1.51 (m, 1H), 1.22–1.20 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 151.8, 138.8, 122.5, 115.5, 114.6, 112.8, 55.8, 47.4, 30.3, 26.9, 22.5.

(−)-(*S*)-6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (20c)[25,26]

A vial containing a solution of 6-fluoro-2-methylquinoline **19c** (81 mg, 0.51 mmol), triphenylphosphine (1.3 mg, 1 mol%) and iridium complex **13** (6 mg, 1 mol%) in toluene (2 mL) under argon was sealed in a Parr bomb. The vessel was evacuated and back-filled with hydrogen three times, then pressurized to 5 atm. The mixture was stirred at room temperature for 10 h, after which the pressure was carefully released. The reaction mixture was concentrated under reduced pressure and passed through a short column of silica gel, eluting with 2:94:4 EtOAc/hexane/Et_3N. Evaporation of the solvent under vacuum gave **20c** as a colourless solid; yield: 77 mg (93%); $[\alpha]_D^{20}$: −77.5 (*c* 0.65, $CHCl_3$) {lit[27] (*R*)-**20c**: $[\alpha]_D^{20}$: +80.3 (*c* 0.19, $CHCl_3$, 98% *ee*)}; CSP HPLC analysis (Chiralcel OD-H; eluent: 98:2 hexanes/*i*-PrOH, 0.5 mL min^{-1}): 90:10 *er*, 80% *ee* [t_R(minor) = 12.55 min, t_R(major) = 16.66 min]; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.71–6.65 (m, 2H), 6.43–6.38 (m, 1H), 3.40–3.32 (m, 2H), 2.83–2.67 (m, 2H), 1.95–1.88 (m, 1H), 1.63–1.50 (m, 1H), 1.21 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.0, 153.9, 140.9, 122.5, 122.4, 115.5, 115.2, 114.7, 114.6, 113.3, 113.0, 47.3, 29.8, 26.7, 22.4.

(−)-(*S*)-2-Propyl-l,2,3,4-tetrahydroquinoline (20d)[25,26]

A vial containing a solution of 2-propylquinoline **19d** (0.08 mL, 0.50 mmol), triphenylphosphine (1.3 mg, 1 mol%) and iridium complex **13** (6 mg, 1 mol%) in toluene (2 mL) was sealed in a Parr bomb. The vessel was evacuated and back-filled with hydrogen three times, then pressurized to 5 atm. The mixture was stirred at room temperature for 24 h, after which the pressure was carefully released. The reaction mixture was concentrated under reduced pressure and passed through a short column of silica gel, eluting with 2:94:4 EtOAc/hexane/Et_3N. Evaporation of the solvent under vacuum gave **20d** as a colourless oil; yield: 68 mg

(78%); $[\alpha]_D^{20}$: −48.0 (*c* 1.1, $CHCl_3$) {lit[27] (*R*)-**20d**: $[\alpha]_D^{20}$: +80.3 (*c* 0.19, $CHCl_3$, 99% *ee*)}; CSP HPLC analysis (Chiralcel OD-H; eluent: 98:2 hexanes/*i*-PrOH, 0.5 mL min^{-1}): 69:31 *er*, 38% *ee* [t_R(minor) = 12.46 min, t_R(major) = 14.84 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98 (t, 2H, *J* = 6.6 Hz), 6.61 (t, 1H, *J* = 7.8 Hz), 6.50 (d, 1H, *J* = 8.1 Hz), 3.80 (bs, 1H) 3.29–3.25 (m, 1H), 2.84–2.75 (m, 2H), 2.01–1.95 (m, 1H), 1.66–1.59 (m, 1H), 1.54–1.42 (m, 4H), 0.98 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.6, 129.2, 126.6, 121.4, 116.9, 114.0, 51.3, 38.8, 28.1, 26.4, 18.9, 14.2.

(+)-(*R*)-2-Phenyl-1,2,3,4-tetrahydroquinoline (20e)[25,26,27,28]

A vial containing a solution of 2-phenylquinoline **19e** (103 mg, 0.50 mmol), triphenylphosphine (1.3 mg, 1 mol%) and iridium complex **13** (6 mg, 1 mol%) in toluene (2 mL) was sealed in a Parr bomb. The vessel was evacuated and back-filled with hydrogen three times, then pressurized to 5 atm. The mixture was stirred at room temperature for 24 h, after which the pressure was carefully released. The reaction mixture was concentrated under reduced pressure. Purification by preparative TLC on silica gel, eluting with 5:95 EtOAc/hexane, gave **20e** as a yellow solid; yield: 26 mg (25%); $[\alpha]_D^{20}$: +18.0 (*c* 0.4, $CHCl_3$) {lit[29] (*R*)-**20e**: $[\alpha]_D^{20}$: +41.9 (*c* 1.0, $CHCl_3$, 98% *ee*)}; CSP HPLC analysis (Chiralcel OD-H; eluent: 95:5 hexanes/*i*-PrOH, 0.6 mL min^{-1}): 75:25 *er*, 50% *ee* [t_R(minor) = 17.68 min, t_R(major) = 22.35 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 5H), 7.01 (t, 2H, *J* = 6.9 Hz), 6.65 (t, 1H, *J* = 7.5 Hz), 6.54 (d, 1H, *J* = 8.1 Hz), 4.45 (dd, 1H, *J* = 9.3, 3.3 Hz), 4.07 (bs, 1H), 2.99–2.90 (m, 1H), 2.74 (dt, 1H, *J* = 16.5, 4.8 Hz), 2.17–2.03 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.8, 144.7, 129.3, 128.5, 127.4, 126.9, 126.5, 120.8, 117.1, 113.9, 56.2, 30.9, 26.4.

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