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Ferrosalen and Ferrosalen-Type Ligands: Structural Modulation and Applications in Asymmetric Catalysis

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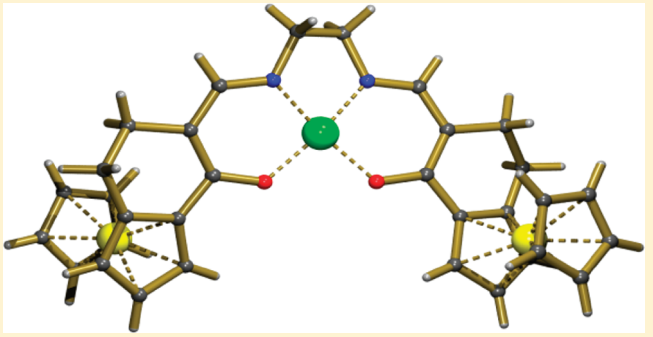
Supporting Information

ABSTRACT: Several ferrosalen and ferrosalen-type ligands, **1**−**10**, were prepared and fully characterized. The structure of one of these ligands ligated to Cu(II) was determined by single-crystal X-ray diffraction analysis. In comparison with the parent ligand **1**, the two six-membered rings of ligand **2** are not aromatized and the synthesis was more facile. Diastereoisomers **3** and **4**, containing substituents on the ethylene chain, were synthesized. The aromatized versions of **3** and **4**, namely **5** and **6**, were also prepared. Further modulation of the ethylene backbone produced ligands **7** and **8**. Replacing the Cp ligands with Cp* and Cp^{Ph5} gave ligands **9** and **10**, respectively. All these ligands were tested for catalytic asymmetric reactions, including the Co(III)-catalyzed carbonyl-ene reaction, Al(III)-catalyzed Strecker reaction, and Al(III)-catalyzed silylcyanation of aldehyde.



INTRODUCTION

Salen and salen-type ligands have been widely used in asymmetric catalysis. Most of these ligands were rendered chiral by introduction of two central chiral centers at the 8- and 8′-positions in their backbone. To solve certain selected problems such as enantioselective epoxidation of conjugated *cis*-olefins and unfunctionalized olefins, Katsuki's group designed and synthesized salen ligands that contain central or axial chiral centers at the 3- and 3′-positions.[1] Recently, salen and salen-type ligands that contain the planar chiral ferrocenyl moieties were also reported in the literature. For example, Ballistreri and co-workers used ferrocene-containing diamines for salen-type ligand synthesis. The resulting ligands contained one or more ferrocenyl groups in their backbone.[2] Bildstein's group incorporated one or more ferrocenyl groups into the front part of salen-type ligands.[3] Erker's group used hydroxyferrocene as the building block for salen-type ligand synthesis. In this case, the bulky FeCp groups are very close to the catalytic center, which may be beneficial for stereocontrol.[4]

Three years ago, we started to develop a new class of chiral ferrocenyl ligands based on two common structural motifs (Figure 1). Our preliminary results showed that such ligands are chemically and configurationally stable and are compatible with several catalytic reaction conditions.[5] More recently, we have successfully developed a stereoselective method to access this class of ligands such as **1** (Figure 2). As a result, we no longer need to rely on chiral HPLC resolution to obtain them in enantiopure form, and gram-sized quantities can be synthesized conveniently.[6] In addition, this synthetic route provided an opportunity to modulate the steric hindrance at the ethylene backbone and at the FeCp groups. In this paper, we wish to report the synthesis and characterization of ligands **2**−**10** (Figure 2) and their use for the Co(III)-catalyzed carbonyl-ene reaction, Al(III)-catalyzed Strecker reaction, and Al(III)-catalyzed silylcyanation of aldehyde.

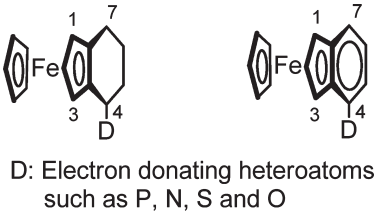


Figure 1. The two structural motifs of a new class of chiral ligands.

RESULTS AND DISCUSSION

The synthesis of ligand **1** (both enantiomers are accessible) has been reported previously.[6] Ligand **2** is the unaromatized version of **1**. As the synthesis of **2** is several steps shorter, it was prepared to evaluate usefulness in asymmetric catalysis. This unaromatized ligand may also display useful electronic and steric properties in catalysis. As shown in Scheme 1, enantiopure **11** (both enantiomers are accessible; the *R* enantiomer was used)[6] was condensed with 1,2-diaminoethane in anhydrous methanol at room temperature.[7] Ligand **2** was obtained in quantitative yield as a red foam. Stirring **2** with cupric acetate in a solvent mixture of ethanol and water at room temperature gave the Cu(II) complex **12** in 75% yield (Scheme 1).[8] Compound **12** is paramagnetic and was not characterized by NMR, but HRMS contained a peak equal to the calculated molecular

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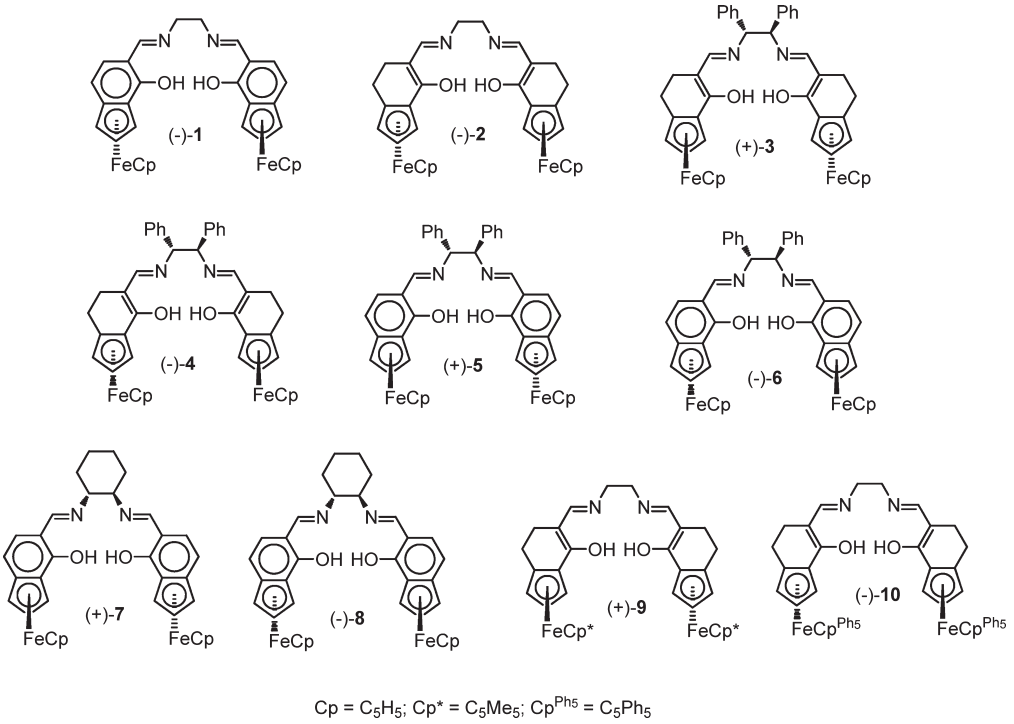
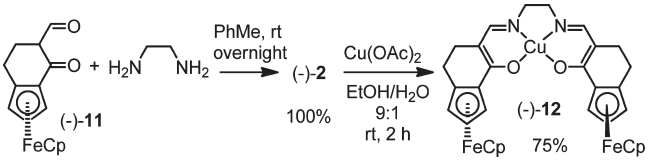


Figure 2. Ferrosalen and ferrosalen-type ligands.

Scheme 1. Synthesis of Ligand 2 and the Cu(II) Complex 12



weight. We were also successful in growing crystals for X-ray diffraction analysis (Figure 3). In the solid-state structure, like most metallosalen complexes in the absence of multidentate ancillary ligands, **12** adopts a trans configuration. Although there is no substituent at the ethylenediamine backbone, the five-membered ring containing Cu(II) and two nitrogen atoms are in a half-chair conformation. This produces an overall stepped conformation for the metallosalen complex.[9]

Ligands **3** and **4** are diastereoisomers. In catalytic applications, they should display different efficiencies in stereocontrol. Their syntheses were achieved by condensing the commercially available enantiopure **13** with (+)- and (−)-**11** in anhydrous methanol, respectively (Scheme 2). Good isolated yields were obtained. Ligands **5** and **6** are also diastereoisomers. They are the aromatized version of compounds **3** and **4**. Their syntheses were accomplished under similar conditions for the synthesis of **3** and **4** using (+)-**13** and the two enantiomers of compound **14** (Scheme 2).[6] The ethylenediamine backbone of ferrosalen **5** and **6** was changed to 1,2-diaminocyclohexane (**15**) to give ligands **7** and **8** (Scheme 2) utilizing similar synthetic conditions. Ligands **3**−**8** were fully characterized by ^{1}H and ^{13}C NMR and HRMS. They are stable deep red crystalline solids, and in solution, they are stable under inert atmospheres. Upon exposure to air, the solutions turn green, indicating oxidation occurred; this is typical for ferrocenyl compounds. One would predict that the aromatized compounds (**5**−**8**) would be less stable than the unaromatized ones (**2**−**4**) due to the reduced aromaticity of their ferrocenyl units. However, we did not observe any obvious difference in their stabilities in the solid state as well in solution. Our attempts to obtain crystals of these ligands chelating to metal centers such as Cu(II), Co(II), and Ru(II) complexes for X-ray diffraction analysis have not been successful so far.

A significant advantage of using the FeCp group in ligands to control stereoselectivity of catalytic reactions is the ability to modulate its size. For example, the Cp group can be changed to Cp* (C_5Me_5) and Cp^{Ph5} (C_5Ph_5). With these more bulky groups, the apical positions of the catalytic center of the ferrosalen-metal complex may be shielded to varying degrees, which may only allow substrates to react through one specific pathway. In order to evaluate this, enantiopure **9** and **10** were synthesized (Scheme 3). For the synthesis of **9**, compound **16a**[11] was reacted with succinic anhydride in the presence of $AlCl_3$ to give the ferrocenyl ketone **17a**. Reduction of the ketone with Zn/$HgCl_2$ resulted in compound **18a**. Compound **18a** was cyclized through an intramolecular Friedel−Crafts reaction using trifluoroacetic anhydride as the activation agent to give the racemic ferrocenyl cyclohexanone **19a**. To resolve the enantiomers, commercially available enantiopure (+)-**20** was deprotonated with *n*-BuLi and the resulting anion reacted with ketone **19a** to give diastereoisomers **21xa** and **21ya**. These isomers could be resolved on TLC with R_f values being 0.55 and 0.40, respectively, when the developing solvent mixture was hexanes/ether (1/1). However, we only obtained **21xa** in pure form. During flash column chromatography, **21xa** and **21yb** slowly decomposed to give **20** and the parent ketones (+)- and (−)-**19**; the other diastereoisomer **21ya** was contaminated with ketones and could not be purified. Pure **21xa** was decomposed in refluxing toluene to give enantiopure (+)-**19a**.[6,12] Formylation of **19a** with ethyl

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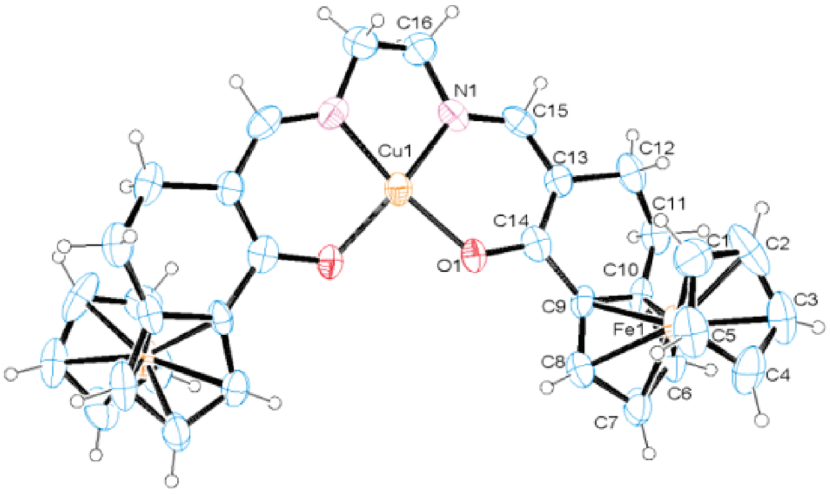
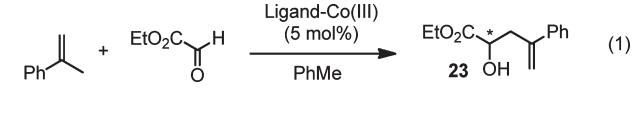


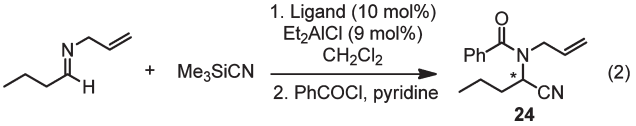
Figure 3. ORTEP-3[10] structure of **12**. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary radii. Selected bond lengths (Å) and angles (deg) for **12**: Fe1−C1 = 2.012(12), Fe1−C2 = 2.041(14), Fe1−C3 = 2.006(14), Fe1−C4 = 2.024(11), Fe1−C5 = 2.028(11), Fe1−C6 = 2.023(11), Fe1−C7 = 2.009(12), Fe1−C8 = 2.037(11), Fe1−C9 = 2.067(10), Fe1−C10 = 2.082(11), Cu1−O1 = 1.927(7), Cu1−N1 = 1.936(8), N1−C15 = 1.326(14), N1−C16 = 1.453(13); O1−Cu1−O1′ = 91.8(4), O1−Cu1−N1′ = 165.6(3), O1−Cu1−N1 = 93.9(4), N1′−Cu1−N1 = 83.7(6). Equivalent atoms (denoted by a prime) generated by $-x+2$, $-x+y+1$, $-z+{}^{1}/_{3}$.

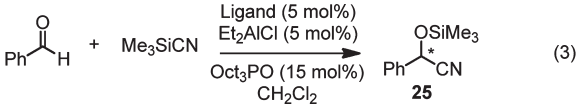
formate in the presence of sodium hydride gave **22a**, which was condensed with 1,2-diaminoethane in anhydrous methanol to give ligand (+)-**9**.

For the synthesis of **10**, compound **16b** was prepared according to a modified literature procedure.[13] This compound was converted to racemic **19b** following the same sequence of reactions used for the preparation of **19a**. Racemic **19b** was then resolved using (+)-**20** according to the procedure described for resolution of **19a**. The two diastereoisomers **21xb** and **21yb** have R_f values of 0.35 and 0.20, respectively, when the developing solvent mixture was hexanes/ether (2/1). Similar to compounds **21xa** and **21ya**, these two diastereoisomers were not stable; they decompose slowly, resulting in **20** and the parent ketones (+)- and (−)-**19**. Because **21xb** has an R_f value similar to that of ketone **19**, we were only able to obtain pure **21yb**. Removal of the chiral auxiliary **20** from **21yb** in refluxing toluene gave enantiopure (−)-**19b** (Scheme 3). At this time, we were not able to obtain enantiopure (+)-**19b**. With enantiopure (−)-**19b** in hand, the synthesis of (−)-**10** was straightforward, even though the highly bulky FeCp^{Ph5} group could have hindered the synthesis during the formylation and imine formation reactions. For formylation, compound **22b** was obtained in 77% yield. Condensation of **22b** with 1,2-diaminoethane gave ligand (−)-**10** in 68% yield (Scheme 3).

All the ligands (**1**−**10**) were tested in the Co(III)-catalyzed carbonyl-ene reaction (eq 1), Al(III)-catalyzed Strecker reaction (eq 2; for ease of isolation, the product was acylated with benzoyl chloride), and Al(III)-catalyzed silylcyanation of aldehyde (eq 3). Under the conditions we have investigated, all reactions resulted in good yields but unsatisfactory enantioselectivity. The best selectivity we achieved for the carbonyl-ene reaction was 29% using (−)-**8**-Co(III) as the catalyst with a 5 mol % loading and with a 78% yield. The major enantiomer has an *R* configuration. Using (+)-**7**, a diastereoisomer of (−)-**8**, as the ligand, under the same conditions, the ee was 10% but the yield was higher at 99%. In this case, the major enantiomer had an *S* configuration. For the Strecker reaction, the best ee we obtained was 20%. The catalyst used was (−)-**1**-AlCl generated in situ with 10 mol % ligand and 9 mol % Et_2AlCl. Under these conditions, the yield was quantitative. For the aldehyde silylcyanation reaction, the best ee was 26% in an 89% yield. This was achieved using (+)-**3**-AlCl as the catalyst at a loading of 5 mol %. The configuration of the major enantiomer is *S*.[14] With (+)-**5**-AlCl as catalyst and under similar conditions, the selectivity and yield were lowered to 18% ee and 84%, respectively. We believe that the low ee's obtained with ligands **1**−**10** can be attributed in part to the lack of steric hindrance at the 5- and 5′-positions. Without any bulky groups at these positions, a large area at the side opposite to the FeCp group is open. Assuming that there are no secondary interactions between the substrates and the catalysts, the conformations of the transition states are flexible.







In conclusion, we have synthesized and fully characterized nine enantiopure ferrosalen ligands and investigated their applications in enantioselective carbonyl-ene, Strecker, and silylcyanation of aldehyde reactions. All the ligands are compatible with these reaction conditions, and high yields were obtained. However, the enantionselectivity was low under the conditions we tested. The low selectivity may be a result of the lack of steric hindrance at the 5- and 5′-positions of the ligands. Future work will be directed to the modulation of steric hindrance at these

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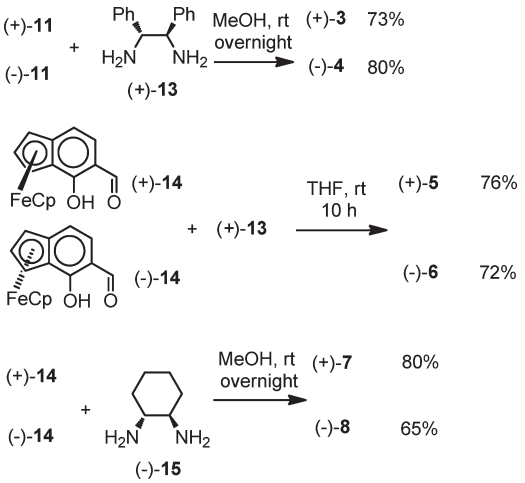
positions and to the evaluation of the resulting new ligands for catalytic enantioselective reactions.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed in oven-dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Reagents and solvents available from commercial sources were used as received unless otherwise noted. THF was distilled from Na/benzophenone ketyl. MeOH, CH_2Cl_2, and toluene were distilled over CaH_2. Thin-layer chromatography (TLC) was performed using plates with silica gel 60F-254 over glass support, 0.25 μm thickness. Flash column chromatography was performed using silica gel with a particle size of 32−63 μm.

Scheme 2. Synthesis of Ligands 3−8

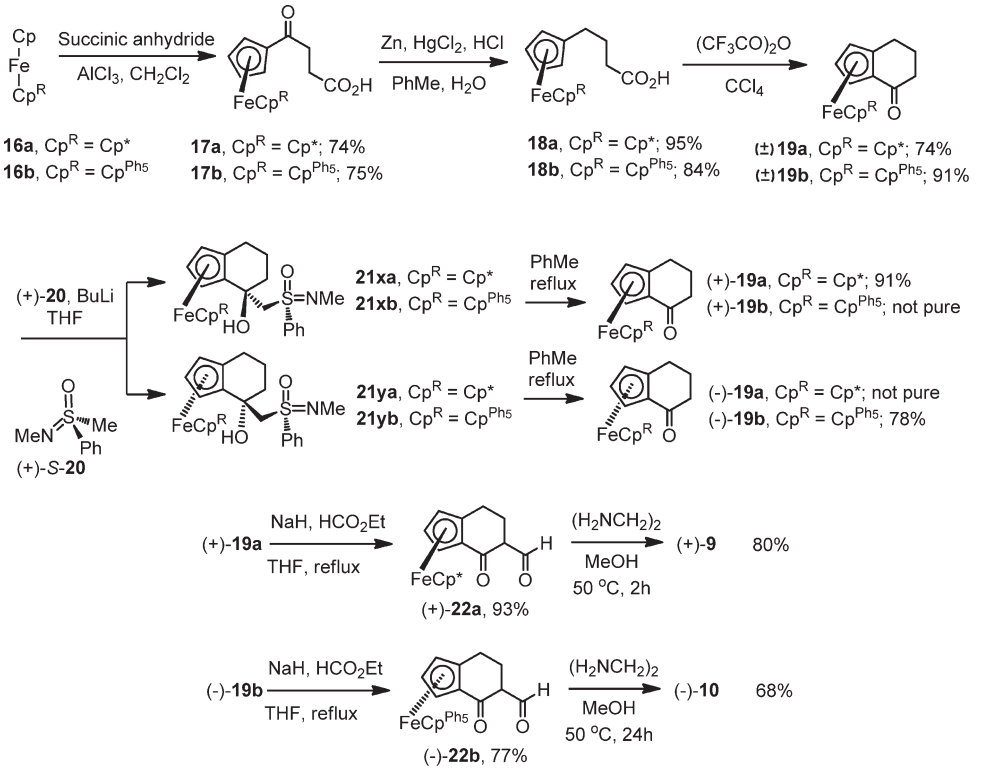


^{1}H and ^{13}C NMR spectra were measured at 400 and 100 MHz, respectively; chemical shifts (δ) were reported in reference to solvent peaks (residue $CHCl_3$ at δ 7.24 ppm for ^{1}H and $CDCl_3$ at δ 77.00 ppm for ^{13}C, C_6D_5H at δ 7.16 ppm for ^{1}H and C_6D_6 at δ 128.4 ppm for ^{13}C). GC-MS were measured on a Shimadzu GCMS-QP5050A instrument: column, DB-5MS; thickness, 0.25 μm; diameter, 0.25 mm; length, 25 m; MS, positive EI. HPLC was performed on a JASCO LC-2000Plus System: pump, PU-2089Plus Quaternary Gradient; detector, UV-2075Plus; chiral analytical column, Chiracel AS-H (5 μm diameter, 100 Å, 250 × 4.6 mm). All profiles were generated by detection of UV absorbance at 260 nm using a linear gradient solvent system: 1−10% 2-propanol in hexanes over 30 min at a flow rate of 1 mL/min.

Ferrosalen (−)-2. A solution of enantiopure (−)-**11** (213 mg, 0.755 mmol) and 1,2-diaminoethane (22.7 mg, 0.378 mmol) in dry toluene (5 mL) was stirred under a nitrogen atmosphere at room temperature overnight. The solvent was removed under reduced pressure. Pure product (−)-**2** was given as a red foam (222 mg, 0.376 mmol, 100%): R_f = 0.1 (hexanes/CH_2Cl_2/Et_3N 1/1/0.05); $[\alpha]^{21}_D$ = −308.2° (c = 0.0036, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 9.54 (br s, 2H), 6.48 (s, 1H), 6.45 (s, 1H), 4.67 (br s, 2H), 4.31 (t, J = 2.4 Hz, 2H), 4.23 (br s, 2H), 4.12 (s, 10H), 3.34−3.10 (m, 4H), 2.94−2.82 (m, 2H), 2.39−2.02 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 193.0, 149.8, 101.8, 91.6, 78.7, 69.5, 69.2, 68.8, 63.8, 50.0, 28.5, 23.6; HRMS (FAB) m/z calcd for $C_{32}H_{32}Fe_2N_2O_2$ $[M]^+$ 588.1163, found 588.1160.

Ferrosalen (+)-3. Following the procedure for the preparation of (−)-**2**, (+)-**11** (176 mg, 0.624 mmol) and (+)-**13** (66.3 mg, 0.312 mmol) in MeOH (6 mL) were stirred at room temperature overnight. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03), and (+)-**3** was obtained as a red foam (168 mg, 0.227 mmol, 73%): R_f = 0.25 (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03); $[\alpha]^{21}_D$ = +105.6° (c = 0.011, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 10.50 (br s, 2H), 7.20−7.10 (m, 6H), 7.02−6.92 (m, 4H), 6.71 (s, 1H), 6.68 (s, 1H), 4.74 (br s, 2H), 4.36 (t, J = 2.4 Hz, 2H), 4.28 (br s, 2H), 4.21 (s, 10H), 4.15 (s, 1H), 4.14 (s, 1H), 3.10−2.98 (m, 2H), 2.47−2.16 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 193.4, 148.7, 138.4, 128.5, 127.7, 127.4,

Scheme 3. Synthesis of Ligands 9 and 10



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102.7, 91.9, 78.9, 69.8, 69.6, 69.4, 69.0, 63.9, 28.8, 23.6; HRMS (ESI) m/z calcd for $C_{44}H_{40}Fe_2N_2O_2$ $[M + H]^+$ 741.1861, found 741.1840.

Ferrosalen (−)-4. Following the procedure for the preparation of (−)-**2**, (−)-**11** (359 mg, 1.27 mmol) and (+)-**13** (108 mg, 0.508 mmol) in MeOH (15 mL) were stirred at room temperature overnight. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03), and (−)-**4** was obtained as a red foam (300 mg, 0.405 mmol, 80%): R_f = 0.25 (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03); $[\alpha]^{21}{}_D = -541.3°$ (c = 0.009, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 10.32 (br s, 2H), 7.22−6.97 (m, 10H), 6.58 (s, 1H), 6.55 (s, 1H), 4.71 (br s, 2H), 4.33 (t, J = 2.4 Hz, 2H), 4.21 (br s, 2H), 4.14 (s, 1H), 4.13 (s, 1H), 4.09 (s, 10H), 2.85−2.72 (m, 2H), 2.26−2.09 (m, 4H), 1.92−1.79 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 193.1, 148.3, 138.1, 128.4, 127.6, 127.0, 102.5, 91.7, 78.8, 70.7, 69.6, 69.5, 69.3, 68.7, 63.7, 28.3, 23.4; HRMS (ESI) m/z calcd for $C_{44}H_{40}Fe_2N_2O_2$ $[M + H]^+$ 741.1846, found 741.1846.

Ferrosalen (+)-5. Following the procedure for the preparation of (−)-**2**, (+)-**14** (107 mg, 0.382 mmol) and (+)-**13** (36.9 mg, 0.174 mmol) in THF (5 mL) were stirred at room temperature for 10 h. The product was purified with flash column chromatography (SiO_2, hexanes/EtOAc 2/3), and (+)-**5** was obtained as a red foam (53 mg, 0.072 mmol, 76%; recovered 54 mg of ferrocenyl aldehyde): R_f = 0.20 (SiO_2, hexanes/EtOAc 2/3); $[\alpha]^{21}{}_D = +2380°$ (c = 0.002, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.41 (s, 1H), 7.38 (s, 1H), 7.23−7.08 (m, 10H), 6.28 (d, J = 8.8 Hz, 2H), 6.24 (d, J = 8.8 Hz, 2H), 5.11 (br s, 2H), 4.65 (br s, 2H), 4.61 (br s, 1H), 4.60 (br s, 1H), 4.34 (t, J = 2.4 Hz, 2H), 3.98 (br s, 10H); ^{13}C NMR ($CDCl_3$) δ 191.7, 154.7, 136.8, 129.1, 128.6, 127.5, 126.3, 113.8, 108.0, 89.4, 78.1, 71.2, 70.9, 70.5, 66.6, 64.5; HRMS (ESI) m/z calcd for $C_{44}H_{36}Fe_2N_2O_2$ $[M]^+$ 736.1470, found 736.1455.

Ferrosalen (−)-6. Following the procedure for the preparation of (−)-**2**, (−)-**14** (96 mg, 0.343 mmol) and (+)-**13** (33.1 mg, 0.156 mmol) in THF (5 mL) were stirred at room temperature for 10 h. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03), and (−)-**6** was obtained as a red foam (53 mg, 0.072 mmol, 72%; 40 mg of (−)-**14** was recovered): R_f = 0.25 (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03); $[\alpha]^{21}{}_D = -2635°$ (c = 0.003, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.30−7.09 (m, 12H), 6.12 (d, J = 9.2 Hz, 2H), 6.07 (d, J = 8.8 Hz, 2H), 5.09 (br s, 2H), 4.62 (br s, 2H), 4.54 (br s, 1H), 4.52 (br s, 1H), 4.32 (t, J = 2.4 Hz, 2H), 3.86 (s, 10H); ^{13}C NMR (C_6D_6) δ 191.4, 154.3, 136.5, 128.8, 128.3, 127.2, 125.9, 113.4, 108.0, 89.2, 77.8, 70.8, 70.0, 66.2, 64.1; HRMS (ESI) m/z calcd for $C_{44}H_{36}Fe_2N_2O_2$ $[M]^+$ 736.1470, found 736.1463.

Ferrosalen (+)-7. Following the procedure for the preparation of (−)-**2**, (+)-**14** (275 mg, 0.983 mmol) and (−)-**15** (56 mg, 0.492 mmol) in MeOH (10 mL) were stirred at room temperature overnight. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH/Et_3N 10/10/1/1), and (+)-**7** was obtained as a red foam (252 mg, 0.394 mmol, 80%): R_f = 0.20−0.25 (SiO_2, hexanes/Et_2O/MeOH/Et_3N 10/10/1/1); $[\alpha]^{21}{}_D = +5605°$ (c = 0.005, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.25 (d, J = 11.2 Hz, 1H), 7.09 (d, J = 12.0 Hz, 1H), 6.22 (d, J = 9.2 Hz, 1H), 6.18 (d, J = 9.2 Hz, 1H), 6.09 (d, J = 9.2 Hz, 1H), 6.01 (d, J = 9.2 Hz, 1H), 5.07 (br s, 1H), 5.04 (br s, 1H), 4.63 (br s, 1H), 4.62 (br s, 1H), 4.32 (t, J = 2.4 Hz, 1H), 4.30 (t, J = 2.4 Hz, 1H), 3.92 (s, 5H), 3.90 (s, 5H), 3.14−2.94 (m, 2H), 2.31−2.10 (m, 2H), 1.96−1.76 (m, 2H), 1.66−1.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 191.5, 191.4, 155.2, 126.5, 126.4, 113.3, 113.1, 107.3, 107.0, 89.7, 89.5, 78.3, 71.1, 70.9, 70.3, 70.2, 66.4, 66.2, 64.9, 64.6, 64.3, 64.1, 32.6, 32.3, 24.7, 24.5; HRMS (ESI) m/z calcd for $C_{36}H_{34}Fe_2N_2O_2$ $[M]^+$ 638.1314, found 638.1308.

Ferrosalen (−)-8. Following the procedure for the preparation of (−)-**2**, (−)-**14** (404 mg, 1.443 mmol) and (−)-**15** (82.4 mg, 0.722 mmol) in MeOH (15 mL) were stirred at room temperature overnight. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03), and (−)-**8** was obtained as a red foam (302 mg, 0.473 mmol, 65%): R_f = 0.25 (SiO_2, hexanes/Et_2O/MeOH 1/1/0.03); $[\alpha]^{21}{}_D = -3861°$ (c = 0.007, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.23 (d, J = 12.0 Hz, 1H), 7.06 (d, J = 12.0 Hz, 1H), 6.20 (d, J = 9.6 Hz, 1H), 6.15 (d, J = 9.2 Hz, 1H), 6.07 (d, J = 9.2 Hz, 1H), 5.98 (d, J = 8.8 Hz, 1H), 5.04 (br s, 1H), 5.01 (br s, 1H), 4.60 (br s, 1H), 4.58 (br s, 1H), 4.28 (t, J = 2.0 Hz, 1H), 4.26 (t, J = 1.6 Hz, 1H), 3.89 (s, 5H), 3.85 (s, 5H), 3.09−2.92 (m, 2H), 2.24−1.20 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 191.1, 154.9, 126.2, 126.1, 112.9, 112.7, 106.9, 106.6, 89.4, 77.9, 70.7, 70.5, 69.9, 69.8, 66.0, 65.9, 64.4, 64.1, 63.9, 63.7, 32.2, 32.0, 24.2, 24.1; HRMS (ESI) m/z calcd for $[M]^+$ 638.1314, found 638.1302.

Table 1. Crystal Data and Data Collection and Structure Refinement Details for 12.

empirical formula	$C_{32}H_{30}CuFe_2N_2O_2$
M_r	649.83
cryst syst	trigonal
space group	$P3_121$ (No. 152)
a, b, c/Å	11.314(3), 11.314(3), 17.897(4)
V/Å^3	1984.0(8)
μ/mm^{-1}	1.913
D_{calcd}/g cm^{-3}	1.632
cryst size/mm	0.15 × 0.25 × 0.40
Z	3
T/K	291
$2\theta_{max}$/deg	50
total, unique no. of data; R_{int}	1471, 1353; 0.067
no. of params/restraints	177/0
R1($I \geq 2\sigma(I)$), wR2, S^a	0.0554, 0.1175, 1.08
min/max resid density/e Å^{-3}	−0.35, 0.42

^{a} $w = 1/[\sigma^2(F_o{}^2) + (0.0384P)^2 + 1.9441P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Ferrosalen−Cu(II) Complex (−)-12. A two-necked round-bottom flask was charged with (−)-**2** (33.6 mg, 0.057 mmol) and the solvent mixture EtOH/H_2O (9/1, 3.3 mL). Cupric acetate (11.44 mg, 0.057 mmol) was added under positive N_2 pressure. After the mixture was stirred at room temperature for 2 h, volatile components were removed under reduced pressure. The deep red mixture was suspended in EtOH (2 mL) and poured onto a pad of Celite. The solid on the Celite was further washed with cold EtOH (1 mL × 2). Then, to the filter cake was added CH_2Cl_2 (3 mL). The red solid was dissolved and was filtered into a clean round-bottom flask. The Celite was further washed with CH_2Cl_2 (3 mL × 2). The combined red filtrate was evaporated under reduced pressure, giving compound (−)-**12** as a red crystalline solid (28.0 mg, 75%): $[\alpha]^{22}{}_D = -1564.7°$ (c = 0.002, CH_2Cl_2); HRMS (ESI) m/z calcd for $C_{32}H_{30}CuFe_2N_2O_2$ $[M]^+$ 649.0302, found 649.0275. This compound is paramagnetic and was not characterized with NMR. The structure of this complex was further confirmed with single-crystal X-ray diffraction analysis. A crystal suitable for the analysis was grown by slowly diffusing pentane into a solution of (−)-**12** in CH_2Cl_2 at room temperature. Crystal data collection and processing parameters are given in Table 1. All calculations were performed using the SHELXL-97 program suite[15] under the GUI WinGX.[16] The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. All details of the structure solution and refinements are given in the Supporting Information (CIF data). As is evident in a packing diagram supplied as Supporting Information, the molecules are arranged so that the cyclopentadiene ligands are involved in $\pi-\pi$ stacking with opposite sides of the salen moiety. These packing interactions may be responsible for the slight twist away from planarity of the salen ligand. Full listings of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures have been deposited at the

Cambridge Crystallographic Data Centre (deposition number: CCDC 816340).

Ferrocenyl Ketocarboxylic Acid 17a. An oven-dried two-necked round-bottom flask was flushed with argon. $AlCl_3$ (3.195 g, 23.96 mmol) and CH_2Cl_2 (30 mL) were added. Compound **16a**[11] (5.113 g, 19.97 mmol) in CH_2Cl_2 (50 mL) was then added dropwise via a cannula. The solution turned dark brown. After addition, succinic anhydride (2.398 g, 23.96 mmol) was added under positive argon pressure. The mixture was stirred at room temperature overnight. The reaction flask was cooled with an ice bath. Ice water (80 mL) was added to the mixture slowly over about 5 min. The contents were transferred to a separation funnel. The organic and aqueous phases were separated. The organic phase was washed with water (50 mL × 3), dried over anhydrous Na_2SO_4, and filtered. Solvents were removed under reduced pressure. The residue was purified with flash column chromatography (SiO_2, hexanes/Et_2O/CH_2Cl_2 2/1/1), giving **17a** as a red solid (5.23 g, 74%): R_f = 0.20 (SiO_2, hexanes/Et_2O/CH_2Cl_2 2/1/1); mp 135 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.24 (br s, 1H), 3.99 (br s, 2H), 2.90 (br s, 2H), 2.61 (br s, 2H), 1.76 (s, 15H); ^{13}C NMR ($CDCl_3$) δ 202.7, 178.6, 81.5, 80.0, 76.5, 71.7, 35.4, 29.5, 10.6; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}FeO_3$ $[M]^+$ 356.1080, found 356.1071.

Ferrocenyl Carboxylic Acid 18a. In a two-necked round-bottom flask containing **17a** (3.80 g, 10.67 mmol) and toluene (100 mL) was added Zn dust (20.90 g, 319.6 mmol) and $HgCl_2$ (1.94 g, 7.143 mmol) sequentially under positive argon pressure. The mixture was stirred vigorously while H_2O (100 mL) and then HCl (12.1 M, 100 mL) were added via syringe. After addition, the mixture was heated to reflux for about 3 h. TLC indicated that **17a** was completely consumed. The reaction mixture was cooled to room temperature. Some solids were formed, which were removed by filtration. The mother liquor was transferred into a separation funnel. The aqueous phase was removed. The organic phase was washed with brine (80 mL × 2), dried over anhydrous Na_2SO_4, and filtered. Solvents were evaporated under reduced pressure, giving pure **18a** as a red solid (3.47 g, 95%): R_f = 0.45 (short SiO_2 column, hexanes/Et_2O/CH_2Cl_2 2/1/1); mp 61−64 °C; ^{1}H NMR ($CDCl_3$) δ 3.69 (br s, 2H), 3.59 (br s, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.95 (s, 15H), 1.87−1.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 180.2, 86.7, 79.8, 71.6, 70.8, 33.5, 27.0, 26.5, 10.9; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{26}FeO_2$ $[M]^+$ 342.1288, found 342.1276.

Racemic Ferrocenyl Cyclohexanone (±)-19a. A two-necked round-bottom flask was charged with **18a** (3.470 g, 10.14 mmol) and CCl_4 (100 mL), and wrapped with aluminum foil. The solution was bubbled with argon for 10 min. After the solution was cooled to 0 °C, trifluoroacetic anhydride (5.60 mL, 40.30 mmol) was added via a syringe. The mixture was stirred on an ice bath and warmed to room temperature gradually. TLC indicated that the reaction was complete in 3 h. The contents were transferred into a separation funnel and partitioned between 10% NaOH (120 mL) and CH_2Cl_2 (80 mL). The organic phase was washed with brine (100 mL × 2), dried over anhydrous Na_2SO_4, and filtered. Volatiles were removed under reduced pressure. Purification with flash column chromatography (SiO_2, hexanes/Et_2O 2/1) gave (±)-**19a** as a red solid (2.44 g, 74%): R_f = 0.30 (SiO_2, hexanes/Et_2O 1/1); mp 102 °C; ^{1}H NMR (C_6D_6) δ 4.28−4.26 (m, 1H), 3.63 (t, *J* = 2.4 Hz, 1H), 3.58−3.56 (m, 1H), 2.28−2.20 (m, 1H), 2.17−2.09 (m, 1H), 2.04−1.77 (m, 4H), 1.56 (s, 15H); ^{13}C NMR (C_6D_6) δ 201.2, 90.6, 80.6, 77.1, 75.6, 73.7, 69.7, 39.5, 23.9, 21.7, 10.3; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}FeO$ $[M]^+$ 324.1182, found 324.1172.

Enantiopure Ferrocenyl Cyclohexanone (+)-19a. To a solution of (+)-(*S*)-*N*,*S*-dimethyl-S-phenylsulfoximine (**20**; 2.80 g, 16.5 mmol) in dry THF (40 mL) at 0 °C was added a solution of *n*-butyllithum in hexane (2.0 M, 8.30 mL). After it was stirred for 15 min at this temperature, the mixture was cooled to −78 °C. The racemic (±)-**19a** (2.44 g, 7.53 mmol) in dry THF (60 mL) was added via cannula dropwise over 10 min. The mixture was stirred for an additional 3 h while being warmed to −20 °C gradually. Saturated ammonium chloride (50 mL) was then added. The mixture was diluted with water (50 mL) and extracted with ether (50 mL × 3). The ether phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure at room temperature. The two diastereoisomers **21xa** and **21ya** were not very stable; they lose their chiral auxiliary slowly even at room temperature. A quick separation with flash column chromatography (SiO_2, hexanes/Et_2O 2/1) gave pure **21xa**, as indicated by TLC (R_f = 0.55, SiO_2, hexanes/Et_2O 1/1). However, **21ya** was found to be contaminated with (±)-**19a**. Because **21ya** and (±)-**19a** have similar R_f values (R_f = 0.45, SiO_2, hexanes/Et_2O 1/1), attempts to separate them were not successful. The pure **21xa** was dissolved in dry toluene (30 mL), and the solutions were heated to reflux for 12 h. After the solution was cooled to room temperature, volatiles were removed. The residue was purified with flash chromatography (SiO_2, hexanes/Et_2O 2/1). Enantiopure (+)-**19a** was obtained as a red solid (1.11 g, 91%): R_f = 0.45 (SiO_2, hexanes/Et_2O 1/1); mp 110 °C; $[\alpha]^{23}_D$ = +532° (*c* = 0.018, CH_2Cl_2); ^{1}H NMR (C_6D_6) δ 4.32 (br s, 1H), 3.63 (t, *J* = 2.4 Hz, 1H), 3.56 (br s, 1H), 2.30−2.22 (m, 1H), 2.16−2.08 (m, 1H), 2.03−1.76 (m, 4H), 1.57 (s, 15H); ^{13}C NMR (C_6D_6) δ 201.2, 90.6, 80.6, 77.2, 75.5, 73.7, 69.8, 39.5, 23.9, 21.7, 10.3; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{24}FeO$ $[M]^+$ 324.1182, found 324.1173. The impure **21ya** was also heated in toluene to give (−)-**19a**, which was contaminated with (+)-**19a** (totally 1.20 g). The chiral auxiliary **20** was recovered without losing any optical purity. The combined yield of **20** from **21xa** and **21ya** was 89% (2.50 g).

Ferrocenyl Ketoformaldehyde (+)-22a. In a two-necked round-bottom-flask was charged (+)-**19a** (124.0 mg, 0.380 mmol) and NaH (153.0 mg, 3.82 mmol) under nitrogen. THF (15 mL) and ethyl formate (0.308 mL, 3.82 mmol) were added via syringe sequentially. The mixture was heated to reflux for 3 h. TLC indicated that the reaction was complete. After the mixture was cooled to room temperature, water (30 mL) was added, and the contents were transferred into a separation funnel. The mixture was extracted with ether (15 mL × 3). The combined ether extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification with flash column chromatography (SiO_2, hexanes/Et_2O 4/1) gave (+)-**22a** as a red solid (125.0 mg, 93%): R_f = 0.60 (SiO_2, hexanes/Et_2O 1/1); mp 130 °C (dec); $[\alpha]^{23}_D$ = +659° (*c* = 0.018, CH_2Cl_2); ^{1}H NMR (C_6D_6) δ 7.21 (br s, 1H), 4.29 (m, 1H), 3.72 (t, *J* = 2.8 Hz, 1H), 3.58 (m, 1H), 2.33−2.23 (m, 1H), 2.12−1.92 (m, 4H), 1.54 (s, 15H); ^{13}C NMR (C_6D_6) δ 195.4, 164.6, 109.2, 90.4, 81.2, 76.4, 74.2, 68.9, 24.6, 20.9, 10.3; HRMS (ESI) *m*/*z* calcd for $C_{20}H_{24}FeO_2$ $[M]^+$ 352.1131, found 352.1117.

Ferrosalen (+)-9. Following the procedure for the preparation of (−)-**2**, (+)-**22a** (122.0 mg, 0.345 mmol) and 1,2-diaminoethane (11.5 μL, 0.172 mmol) in MeOH (5 mL) were stirred at 50 °C for 2 h. The product was purified with flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.08), and (+)-**9** was obtained as a red solid (101 mg, 80%): R_f = 0.35 (SiO_2, hexanes/Et_2O/MeOH 1/1/7.5%); mp 82 °C dec; $[\alpha]^{23}_D$ = +120° (*c* = 0.015, CH_2Cl_2); ^{1}H NMR (C_6D_6) δ 9.72 (br s, 2H), 6.12 (s, 1H), 6.09 (s, 1H), 4.50 (br s, 2H), 3.70 (t, *J* = 2.4 Hz, 2H), 3.57 (br s, 2H), 2.70−2.57 (m, 2H), 2.50−2.11 (m, 10H), 1.71 (s, 30H); ^{13}C NMR (C_6D_6) δ 192.3, 148.9, 102.3, 89.9, 80.5, 79.8, 74.7, 72.6, 69.0, 49.9, 28.5, 22.0, 10.5; HRMS (ESI) *m*/*z* calcd for $C_{42}H_{52}Fe_2N_2O_2$ $[M]^+$ 728.2733, found 728.2730.

Ferrocene 16b. This compound was synthesized using a modified literature procedure.[13] To a solution of 1-bromopentaphenylcyclopentadiene (132 mg, 0.25 mmol) in benzene (5 mL) was added $Fe(CO)_5$ (59.0 mg, 0.30 mmol) under nitrogen. The mixture was heated to reflux for 3 h. After this mixture was cooled to room temperature, a solution of CpNa (0.263 mL of 2.0 M in THF, 0.525 mmol) was added via syringe. The mixture was stirred at room temperature for 18 h. The resulting orange mixture was filtered through Celite. The filtrate was collected,

and solvents were removed under reduced pressure. The orange residue was heated to 160 °C under vacuum for 3 h. After it was cooled to room temperature, the remaining mixture was suspended in toluene and filtered through Celite. The filtrate was collected, and solvents were removed. Purification by recrystallization in hot toluene gave **16b** as a red crystalline solid (115 mg, 81%).

Ferrocenyl Ketocarboxylic Acid 17b. Following a procedure similar to that for the preparation of **17a**, the reaction of **16b** (1.882 g, 3.325 mmol), $AlCl_3$ (0.935 g, 7.012 mmol), and succinic anhydride (0.332 g, 3.323 mmol) in CH_2Cl_2 at reflux temperature in 24 h gave **17b** as a red foam after purification with flash column chromatography (SiO_2, hexanes/Et_2O 1/1; 1.65 g, 75%): R_f = 0.15 (SiO_2, hexanes/Et_2O 1/1); ^1H NMR ($CDCl_3$) δ 7.18−7.01 (m, 25H), 4.88 (br s, 2H), 4.50 (br s, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 201.9, 178.3, 134.7, 132.1, 127.2, 126.6, 88.2, 83.1, 79.0, 74.8, 36.2, 27.9; HRMS (ESI) m/z calcd for $C_{44}H_{34}FeO_3$ $[M + H]^+$ 667.1936, found 667.1948.

Ferrocenyl Carboxylic Acid 18b. Following a procedure similar to that for the preparation of **18a**, the reduction of **17b** (1.65 g, 2.477 mmol) with Zn dust (4.860 g, 74.31 mmol) and $HgCl_2$ (0.450 g, 1.657 mmol) in toluene (20 mL), H_2O (20 mL), and HCl (12.1 M, 20 mL) at reflux temperature in 24 h gave **18b** as a red solid after purification with flash column chromatography (short SiO_2 column, hexanes/Et_2O 2/1; 1.35 g, 84%): R_f = 0.30 (SiO_2, hexanes/Et_2O 1/1); mp 192 °C; ^1H NMR ($CDCl_3$) δ 7.15−7.01 (m, 25H), 4.15 (br s, 2H), 4.12 (br s, 2H), 2.30−2.18 (m, 4H), 1.79−1.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 179.1, 135.9, 132.4, 127.1, 126.1, 90.5, 87.6, 75.0, 74.1, 33.2, 26.7, 26.5; HRMS (ESI) m/z calcd for $C_{44}H_{36}FeO_2$ $[M]^+$ 652.2065, found 652.2075. The compound may decompose slowly at room temperature, and storing at −20 °C is suggested.

Racemic Ferrocenyl Cyclohexanone (±)-19b. Following a procedure similar to that for the preparation of (±)-**19a**, cyclization of **18b** (424.0 mg, 0.650 mmol) to give (±)-**19b** was achieved with trifluoroacetic anhydride (1.0 mL, 7.195 mmol) in CCl_4 (15 mL) at 50 °C overnight. Purification with flash column chromatography (SiO_2, hexanes/CH_2Cl_2/Et_2O 20/20/1) gave the product as a red solid (375.0 mg, 91%): R_f = 0.30 (hexanes/CH_2Cl_2/Et_2O 20/20/1); mp 220 °C dec; ^1H NMR ($CDCl_3$) δ 7.16−6.98 (m, 25H), 4.84−4.82 (m, 1H), 4.45−4.43 (m, 1H), 4.37 (t, J = 2.4 Hz, 1H), 2.65−2.55 (m, 1H), 2.44−2.28 (m, 3H), 2.02−1.94 (m, 1H), 1.77−1.64 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 203.9, 134.5, 132.2, 127.2, 126.5, 94.4, 87.7, 78.4, 77.8, 77.2, 72.8, 39.5, 24.9, 21.8; HRMS (ESI) m/z calcd for $C_{44}H_{34}FeO$ $[M]^+$ 634.1965, found 634.1959.

Enantiopure Ferrocenyl Cyclohexanone (−)-19b. Following a procedure similar to that for the resolution of (±)-**19a**, (±)-**19b** (437.0 mg, 0.688 mmol) was first converted to **21xb** and **21yb** using (+)-(*S*)-**20** (349.0 mg, 2.065 mmol) and *n*-butyllithum in hexane (2.0 M, 1.032 mL) in THF. Because the two diastereoisomers **21xb** and **21yb** slowly lose the chiral auxiliary even at room temperature, they were quickly separated with flash column chromatography (short SiO_2 column, hexanes/CH_2Cl_2/EtOAc 20/10/1). TLC analysis indicated that **21xb** was still contaminated with (±)-**19b**. Because their R_f values were very close (R_f = 0.35, SiO_2, hexanes/Et_2O 2/1), attempts to separate them were not successful. However, the other diastereoisomer **21yb**, which had an R_f value of 0.20 (SiO_2, hexanes/Et_2O 2/1), was obtained in pure form. The solution of **21yb** in dry toluene (10 mL) was then heated to reflux overnight. Enantiopure (−)-**19b** was obtained as a red solid (171 mg, 78%): R_f = 0.35 (SiO_2, hexanes/CH_2Cl_2/EtOAc 20/10/1); mp 220 °C dec; $[\alpha]^{23}_D$ = −311° (c = 0.0095, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.17−6.96 (m, 25H), 4.83 (br s, 1H), 4.44 (br s, 1H), 4.38 (br s, 1H), 2.66−2.55 (m, 1H), 2.45−2.28 (m, 3H), 2.02−1.93 (m, 1H), 1.79−1.64 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 204.0, 134.5, 132.2, 127.2, 126.5, 94.4, 87.7, 78.4, 77.8, 77.2, 72.8, 39.5, 24.9, 21.8; HRMS (ESI) m/z calcd for $C_{44}H_{34}FeO$ $[M]^+$ 634.1965, found 634.1956. The impure **21xb** was also heated in toluene to give (+)-**19b**, which was contaminated with (−)-**19b** (total 262 mg). The chiral auxiliary **20** was recovered without losing any optical purity. The combined yield of **20** from **21xb** and **21yb** was 86% (300 mg).

Ferrocenyl Ketoaldehyde (−)-22b. A procedure similar to that for the synthesis of (+)-**22a** was followed. Compound (−)-**19b** 171.0 mg, 0.269 mmol), NaH (214.0 mg, 5.380 mmol), and ethyl formate (0.434 mL, 5.380 mmol) in THF (20 mL) were heated to reflux overnight. After the mixture was cooled to room temperature, saturated NH_4Cl (30 mL) was added. The mixture was extracted with EtOAc (15 mL × 2). The organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography (short SiO_2 column, hexanes/CH_2Cl_2/EtOAc 40/10/1) gave (−)-**22b** as a red solid (138.0 mg, 77%). The product may decompose slowly on silica gel. Enantiopure (−)-**22b**: R_f = 0.25 (SiO_2, hexanes/Et_2O 5/1); mp 210 °C dec; $[\alpha]^{22}_D$ = −197° (c = 0.009, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.50−7.43 (br s, 1H), 7.20−6.96 (m, 25H), 4.86 (t, J = 2.0 Hz, 1H), 4.42 (br s, 1H), 4.41 (br s, 1H), 2.68−2.58 (m, 1H), 2.44−2.24 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 194.7, 165.4, 134.6, 132.5, 127.4, 126.7, 111.1, 91.4, 88.3, 78.7, 78.4, 77.7, 73.2, 25.6, 21.4; HRMS (ESI) m/z calcd for $C_{45}H_{34}FeO_2$ $[M]^+$ 662.1914, found 662.1904.

Ferrosalen (−)-10. Following the procedure for the preparation of (−)-**2**, (−)-**22b** (40.0 mg, 0.0604 mmol) and 1,2-diaminoethane (1.68 μL, 0.0251 mmol) in MeOH (5 mL) were stirred at 50 °C for 24 h. Purification by flash column chromatography (SiO_2, hexanes/Et_2O/MeOH 1/1/0.02) gave (−)-**10** as a red solid (23.0 mg, 68%): R_f = 0.10 (SiO_2, hexanes/Et_2O 1/1); mp 124−127 °C; $[\alpha]^{22}_D$ = −69° (c = 0.0225, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 9.38 (br s, 2H), 7.14−6.96 (m, 50H), 6.46 (s, 1H), 6.43 (s, 1H), 4.75 (br s, 2H), 4.24 (br s, 4H), 3.32−3.20 (br s, 2H), 3.14−3.00 (br s, 2H), 2.58−2.06 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 192.0, 149.1, 135.2, 132.7, 127.2, 126.3, 103.9, 91.3, 87.9, 82.0, 77.0, 76.6, 72.7, 50.4, 29.2, 22.2; HRMS (ESI) m/z calcd for $C_{92}H_{72}Fe_2N_2O_2$ $[M]^+$ 1348.4293, found 1348.4292; calcd for $[M + H]^+$ 1349.4365, found 1349.4360.

Enantioselective Carbonyl-Ene Reaction Catalyzed with Ferrosalen-Co(III) Complexes.[17] Ligand (−)-**8** is used as an example. In a round-bottom flask containing (−)-**8** (190 mg, 0.298 mmol) and MeOH (10 mL) was added $Co(OAc)_2 \cdot 4H_2O$ (74.2 mg, 0.298 mmol) in MeOH (5 mL) via a cannula. The mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure on a rotary evaporator. The flask, which contained the residue, was then wrapped with an aluminum foil. CH_2Cl_2 (15 mL) was added via syringe, which was followed by addition of $AgSbF_6$ (205 mg, 0.596 mmol). The mixture was stirred at room temperature overnight. The resulting black suspension was poured onto a pad of Celite, which was washed with CH_2Cl_2. The filtrate was discarded. The Celite pad was then washed with acetone. The filtrate was concentrated to dryness under reduced pressure to give the (−)-**8**−Co(III) complex. The compound was used directly as a catalyst for the carbonyl-ene reaction without further purification. Ethyl glyoxylate (50% in toluene; 250.9 mg, 1.23 mmol) was heated to reflux under nitrogen for 1 h to crack its dimer. After it was cooled to room temperature, the solution was added to a round-bottom flask containing (−)-**8**−Co(III) (19.0 mg, 0.02 mmol) in dry toluene (3 mL). The mixture was stirred at room temperature for 10 min. α-Methylstyrene (48.2 mg, 0.41 mmol) was then added via syringe in one portion. The reaction was allowed to proceed at room temperature, and the progress was monitored with GC-MS. After 16 h, the mixture was passed through a pad of Celite, which was washed with CH_2Cl_2 (3 mL × 3). Volatiles were removed under reduced pressure. The residue was purified with flash column chromatography (SiO_2, hexanes/Et_2O 4/1). The product **23**[17] was obtained as a colorless oil (70.0 mg, 78%). The ee was determined with chiral HPLC using the conditions described in General Considerations. The enantiomers *S*-**23** and

R-**23** were eluted at 17.0 and 21.0 min, respectively. The ee was 29%, with *R* being the major enantiomer. In addition to ligand (−)-**8**, all other ligands, including (−)-**1**, (−)-**2**, (+)-**3**, (−)-**4**, (+)-**5**, (−)-**6**, (+)-**7**, (+)-**9**, and (−)-**10**, were also tested for the reaction. The yields ranged from 20% to 99%. The ee's ranged from 0% to 10%.

Enantioselective Strecker Reaction Catalyzed with Ferrosalen-Al(III) Complexes.[18]**.** Ligand (−)-**1** is used as an example. In a round-bottom flask containing ligand (−)-**1** (18.0 mg, 0.031 mmol) and dry CH_2Cl_2 (5 mL) was added Et_2AlCl (1.0 M solution in hexanes, 27.8 μL, 0.028 mmol) via syringe. The mixture was stirred at room temperature for 2 h under nitrogen. (*E*)-*N*-Butylideneprop-2-en-1-amine (34.5 mg, 0.31 mmol) was added via syringe. After the mixture was cooled to −78 °C, the solution of TMSCN (62 μL, 0.456 mmol) in CH_2Cl_2 (2 mL) was added via a cannula dropwise. The reaction mixture was warmed to room temperature gradually over 12 h. Pyridine (2 mL) was added, which was followed by benzoyl chloride (0.5 mL). The mixture was stirred for 1 h. Solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, hexanes/Et_2O 10/1 to 5/1) to give pure product **24** as a colorless oil (77.9 mg, 100%).[18] The ee was determined with chiral HPLC using the conditions described in General Considerations. The enantiomers (−)-**24** and (+)-**24** were eluted at 19.1 and 20.0 min, respectively. The ee was 20%, with (+)-**24** being the major enantiomer. In addition to ligand (−)-**1**, all other ligands, including (−)-**2**, (+)-**3**, (−)-**4**, (+)-**5**, (−)-**6**, (+)-**7**, (−)-**8**, (+)-**9**, and (−)-**10**, were also tested for the reaction. The yields were all quantitative. The ee's ranged from 0% to 18%.

Enantioselective Silylcyanation of Aldehyde.[4b]**.** Ligand (+)-**3** is used as an example. In a round-bottom flask under nitrogen was charged (+)-**3** (15.2 mg, 0.0205 mmol) and CH_2Cl_2 (1 mL). Et_2AlCl (20.5 uL of 1.0 M solution in hexanes, 0.0205 mmol) was added via syringe. The mixture was stirred at room temperature for 5 h. Oct_3PO (23.8 mg, 0.0616 mmol) in CH_2Cl_2 (1 mL) was then added via cannula. After the mixture was cooled to −20 °C, freshly distilled benzaldehyde (43.6 mg, 0.41 mmol) and trimethylsilyl cyanide (136 μL, 1.025 mmol) were added via syringe sequentially. The reaction was allowed to proceed at −20 °C, monitored with GC-MS, and and found complete in 24 h. Volatiles were removed under reduced pressure. The residue was suspended in ether and passed through a 1 in. pad of silica gel to remove the catalyst. The filtrate was concentrated to dryness. Purification with flash column chromatography (SiO_2, hexanes/Et_2O 10/1) gave product **25**[4b] as a colorless liquid (76.0 mg, 89%). The ee was determined with chiral HPLC using the conditions described in General Considerations. The enantiomers *S*-**25** and *R*-**25** were eluted at 4.9 and 6.0 min, respectively. The ee was 26%, with *R* being the major enantiomer. In addition to ligand (+)-**3**, all other ligands, including (−)-**1**, (−)-**2**, (−)-**4**, (+)-**5**, (−)-**6**, (+)-**7**, (−)-**8**, (+)-**9**, and (−)-**10**, were also tested for the reaction. The yields ranged from 63% to 99%. The ee's ranged from 0% to 26%.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving ^1H and ^{13}C NMR spectra and MS of all new compounds, chiral HPLC profiles, and a crystal packing diagram and a CIF file giving X-ray crystallographic data for the structure determination of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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