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Supporting Information

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Iron-Catalyzed Asymmetric Olefin *cis*-Dihydroxylation with 97% Enantiomeric Excess

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Contents

Synthetic procedures and characterization of complexes

Bis(2-pyridylmethyl)-(*R*,*R*)-2,2'bipyrrolidine (**BPBP**)

Bis(2-quinolinylmethyl)-(*R*,*R*)-2,2'bipyrrolidine (**BQBP**)

Bis(6-methyl-2-pyridylmethyl)-(*R*,*R*)-2,2'bipyrrolidine **(6-Me$_2$-BPBP)**

2-aminomethylpyridine was obtained from Aldrich. 6-Methyl-2-aminomethylpyridine and quinolin-2-ylmethanamine were prepared according to literature procedures.[1,2] Published procedure was then followed, using this aminomethylpyridine synthon, to form *N*,*N*-bis(2-pyridylmethyl)-(*R*,*R*)-4,5-diamino-1,7-octadiene, *N*,*N*-bis(2-quinolinylmethyl)-(*R*,*R*)-4,5-diamino-1,7-octadiene, and *N*,*N*-bis(6-methyl-2-pyridylmethyl)-(*R*,*R*)-4,5-diamino-1,7-octadiene,[3] and the final bipyrrolidine ligand.[4]

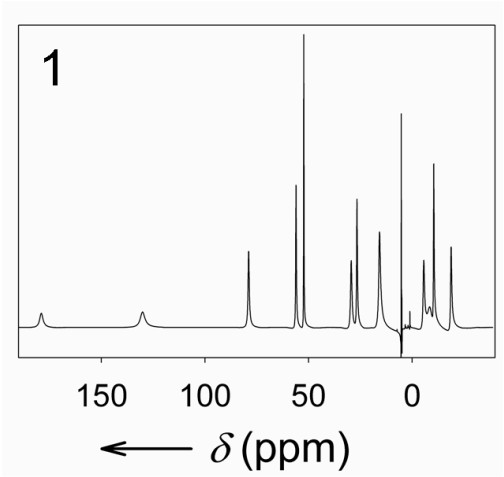
[Fe^{II}(BPBP)(OTf)$_2$] (**1**)

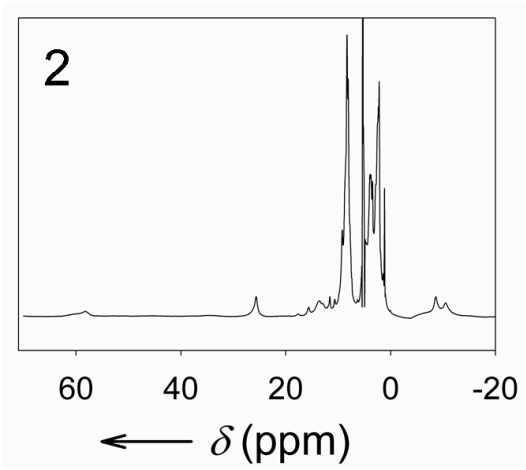
[Fe^{II}(BQBP)(OTf)$_2$] (**2**)

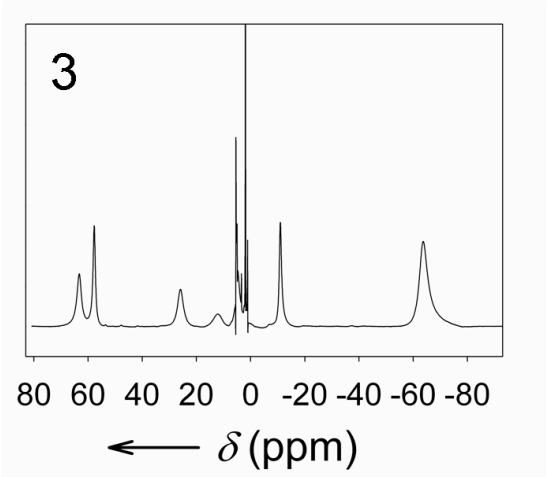
[Fe^{II}(6-Me$_2$-BPBP)(OTf)$_2$] **(3)**

Under a nitrogen atmosphere, a solution of either BPBP, BQBP, or 6-Me$_2$-BPBP (96.7 mg, 0.3 mmol) in dichloromethane (2 mL) was added to a suspension of Fe(OTf)$_2$•2MeCN[5] (130.8 mg, 0.3 mmol) in dichloromethane (2 mL) at room temperature with stirring. The mixture was stirred overnight and the solvent removed *in vacuo* to give a light brown powder, which was recrystallized from dichloromethane and ether to afford pale yellow crystals in 72% yield for **1**, 60% yield for **2** and 75% yield for **3**, which were suitable for X-ray crystallographic analysis. Characterization data for **1**: Anal. Calcd. (found) for $C_{22}H_{26}F_6FeN_4O_6S_2$•$H_2O$: C, 38.05 (38.10); H, 4.06 (4.15); N, 8.07 (8.04); S, 9.23 (9.26). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): see Figure S1. Characterization data for **2**: Anal. Calcd. (found) for $C_{30}H_{30}F_6FeN_4O_6S_2$•$H_2O$: C, 45.35 (45.41); H, 4.06 (4.02); N, 7.05 (6.95); S, 8.07 (7.96). ^{1}H NMR (500 MHz, CD_3CN, 25 °C): See Figure S1. Characterization data for **3**: Anal. Calcd. (found) for $C_{24}H_{30}F_6FeN_4O_6S_2$•0.5$CH_2Cl_2$: C, 39.40 (39.83); H, 4.18 (4.38); N, 7.50 (7.54); S, 8.59 (8.64). ^{1}H NMR (500 MHz, CD_3CN, 25 °C): see Figure S1.

Figure S1. ^{1}H NMR of **1** in CD_2Cl_2, of **2** in CD_2Cl_2, and of **3** in CD_3CN.







X-ray crystallographic data

A crystal of **1** (approximate dimensions 0.45 x 0.11 x 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 110 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30º steps in ω at four different φ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[6] Final cell constants were calculated 2414 strong reflections from the actual data collection after integration (SAINT).[7] Please refer to Table S1 for additional crystal and refinement information.

The structure of **1** was solved using Bruker SHELXTL[8] and refined using Bruker SHELXTL. The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0438$ and $wR2 = 0.1057$ (F^2, all data).

A crystal of **2** (approximate dimensions 0.38 x 0.19 x 0.05 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 144 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30º steps in ω at four different φ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[6] Final cell constants were calculated from 2565 strong reflections from the actual data collection after integration (SAINT).[7] Please refer to Table S2 for additional crystal and refinement information.

The structure of **2** was solved using Bruker SHELXTL[8] and refined using Bruker SHELXTL. The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0457$ and $wR2 = 0.1261$ (F^2, all data).

A crystal of **3** (approximate dimensions 0.35 x 0.17 x 0.12 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a CCD area detector diffractometer for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 268 reflections. The data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 20 seconds and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 Å. Four major sections of frames were collected with 0.30º steps in ω at four different φ settings and a detector position of -28º in 2θ. The intensity data were corrected for absorption and decay (SADABS).[6] Final cell constants were calculated from 2816 strong reflections from the actual data collection after integration (SAINT).[7] Please refer to Table S3 for additional crystal and refinement information.

The structure of **3** was solved using Bruker SHELXTL[8] and refined using Bruker SHELXTL. The space group $P2_12_12_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0297$ and $wR2 = 0.0610$ (F^2, all data).

Table S1. Crystal data and structure refinement for **1**.

Identification code	04130a	
Empirical formula	C_{22} H_{26} F_6 Fe N_4 O_6 S_2	
Formula weight	676.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.1835(9) Å	α = 90°
	b = 28.648(3) Å	β = 90.950(2)°
	c = 10.6141(10) Å	γ = 90°
Volume	2792.1(5) $Å^3$	
Z	4	
Density (calculated)	1.609 Mg/m^3	
Absorption coefficient	0.774 mm^{-1}	
F(000)	1384	
Crystal color, morphology	Yellow, Block	
Crystal size	0.45 x 0.11 x 0.10 mm^3	
Theta range for data collection	1.92 to 27.50°	
Index ranges	$-11 \le h \le 11$, $-36 \le k \le 36$, $0 \le l \le 13$	
Reflections collected	25318	
Independent reflections	12444 [R(int) = 0.0435]	
Observed reflections	10271	
Completeness to theta = 27.50°	99.3%	
Max. and min. transmission	0.9266 and 0.7220	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12444 / 1 / 739	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	$R1$ = 0.0438, $wR2$ = 0.0971	
R indices (all data)	$R1$ = 0.0595, $wR2$ = 0.1057	
Absolute structure parameter	-0.002(11)	
Largest diff. peak and hole	0.626 and -0.487 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2**.

Identification code	04132b	
Empirical formula	$C_{33}H_{38}Cl_2F_6FeN_4O_7S_2$	
Formula weight	907.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.4974(10) Å	α = 90°
	b = 12.3425(14) Å	β = 92.008(2)°
	c = 16.6426(18) Å	γ = 90°
Volume	1949.7(4) $Å^3$	
Z	2	
Density (calculated)	1.546 Mg/m^3	
Absorption coefficient	0.711 mm^{-1}	
F(000)	932	
Crystal color, morphology	Yellow, Plate	
Crystal size	0.38 x 0.19 x 0.05 mm^3	
Theta range for data collection	2.05 to 27.51°	
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $0 \le l \le 21$	
Reflections collected	17596	
Independent reflections	7722 [R(int) = 0.0346]	
Observed reflections	6895	
Completeness to theta = 27.51°	99.3%	
Max. and min. transmission	0.9653 and 0.7740	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7722 / 9 / 510	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	$R1$ = 0.0457, $wR2$ = 0.1200	
R indices (all data)	$R1$ = 0.0529, $wR2$ = 0.1261	
Absolute structure parameter	0.023(16)	
Largest diff. peak and hole	0.750 and -0.599 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **3**.

Identification code	04221a	
Empirical formula	C_{25} H_{32} Cl_2 F_6 Fe N_4 O_6 S_2	
Formula weight	789.42	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 12.6183(13) Å	α = 90°
	b = 14.6618(16) Å	β = 90°
	c = 17.6780(19) Å	γ = 90°
Volume	3270.6(6) $Å^3$	
Z	4	
Density (calculated)	1.603 Mg/m^3	
Absorption coefficient	0.832 mm^{-1}	
F(000)	1616	
Crystal color, morphology	Colorless, Block	
Crystal size	0.35 x 0.17 x 0.12 mm^3	
Theta range for data collection	1.80 to 27.52°	
Index ranges	$-16 \le h \le 16$, $0 \le k \le 19$, $0 \le l \le 22$	
Reflections collected	38917	
Independent reflections	7510 [R(int) = 0.0338]	
Observed reflections	6950	
Completeness to theta = 27.52°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9068 and 0.7595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7510 / 0 / 417	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	$R1$ = 0.0297, $wR2$ = 0.0597	
R indices (all data)	$R1$ = 0.0340, $wR2$ = 0.0610	
Absolute structure parameter	0.033(10)	
Largest diff. peak and hole	0.426 and -0.358 $e.Å^{-3}$	

Materials, physical measurements, and catalytic procedures

Materials: All reagents were purchased from Aldrich and used as received unless noted otherwise. Purifications of olefin substrates were completed by passing them through neutral alumina oxide. Prior to their use as solvents, both CH_3CN and CH_2Cl_2 were distilled from CaH_2 under an argon atmosphere. All other chemicals were utilized without further purification.

Physical measurements: ^1H NMR spectra were recorded on a Varian Unity 500 MHz spectrometer at ambient temperature. Chemical shifts (ppm) were referenced to the residual protic solvent peaks. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Oxidation product analyses were performed on a PerkinElmer AutoSystem gas chromatograph (AT-1701 column, 30 m) with flame-ionization detection. The ee analysis of diol product was performed on a PerkinElmer AutoSystem XL gas chromatograph (Chiraldex G-TA column, 30 m) with flame-ionization detection. GC mass spectral analyses were performed on an HP 6890 gas chromatograph (HP-5 column, 30 m) with an Agilent 5973 mass detector. A 4% NH_3/CH_4 mixture was used as the ionization gas for chemical ionization analyses.

Substrate oxidation studies for **3**: Solutions of H_2O_2 (diluted from 35% H_2O_2 solution with CH_3CN resulting in a 70 mM concentration) and catalyst/substrate in CH_3CN were separately degassed via three freeze, pump, thaw cycles and held under an Ar atmosphere. Following this degassing procedure, 10 equiv of H_2O_2 were delivered by syringe pump over a period of 20 min at 25 ^oC to the vigorously stirred CH_3CN solution containing iron catalyst and 1000 equiv olefin substrate. The final concentrations were 0.7 mM iron catalyst, 7.0 mM H_2O_2, and 0.35 M olefin. The solution was stirred for an additional 5 min after syringe pump addition, after which organic products were esterified by 1 mL acetic anhydride together with 0.1 mL 1-methylimidazole and extracted with $CHCl_3$. An internal standard (naphthalene) was added and the solution was washed with 1 M H_2SO_4, sat. $NaHCO_3$, and H_2O. The organic layer was dried with $MgSO_4$ or Na_2SO_4 and subjected to GC analysis. Products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds. The reported results are the average of at least three trials.

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