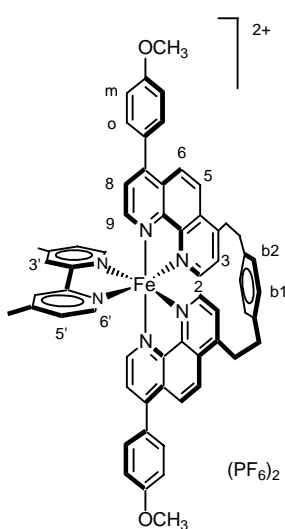


**Ion-pair Mediated Asymmetric Synthesis of a Configurationally Stable Mononuclear Tris(diimine)
Iron(II) Complex**

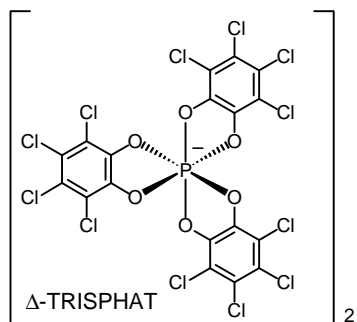
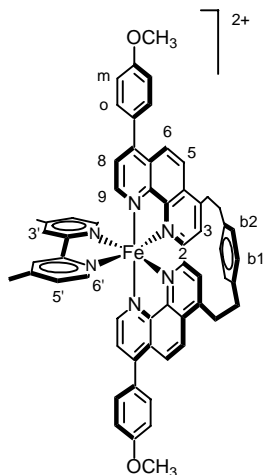
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General Information. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk lines techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use. Chloroform (Fluka) and CDCl_3 were filtered on basic alumina before use. Methanol, hexane and dichloromethane were distilled from calcium hydride. Deionized water was used. Purifications of reaction products were carried out by chromatography using J. T. Baker silica gel (30-60 μm). Thin layer chromatography was performed on Macherey-Nagel 0.25 mm silica gel plates. Visualization was accomplished with UV light. ^1H , ^{13}C and ^{31}P NMR spectra were recorded on Varian XL-200 (200 MHz) and Bruker AMX-400 (400 MHz) spectrometers. Chemical shifts are given in ppm. ^1H and ^{13}C chemical shifts were reported relative to Me_4Si , δ and J values correspond to the common ‘first order analysis’ of the spectra, multiplicity were determined by Dept 135° (C_q : quaternary carbon). Data are reported as: (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration; proton assignments). ^{31}P chemical shifts were reported relative to H_3PO_4 . Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer by using KBr disks. The absorption is indicated in wave numbers (cm^{-1}) and the intensities are represented as strong (s), medium (m) and weak (w). Optical rotations were determined on a Perkin Elmer 241 polarimeter in a thermostated (20°C) 10 cm long microcell with sodium or mercury lamps and are reported as follows: $[\alpha]_D^{20}$ (c g/100 mL, solvent). UV spectra were recorded on a UVIKON 860 spectrometer in a 1 cm quartz cell; λ_{max} were given in nm and molar adsorption coefficient ϵ in $\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$. Circular dichroism spectra were recorded on a JASCO J-715 spectropolarimeter in a 1 cm quartz cell; λ were given in nm and molar circular-dichroic absorption $\Delta\epsilon$ in $\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$. Electrospray mass spectra were obtained on a Finnigan SSQ 7000 spectrometer. Melting points (M.p.) were determined on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Dmbp stands for 4,4'-dimethyl-2,2'-bipyridine.



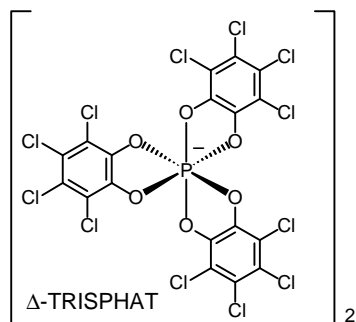
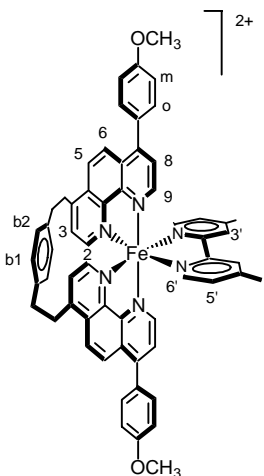
[FeL(dmbp)](PF₆)₂ [Fe(dmbp)₃](PF₆)₂ (0.129 g, 0.142 mmol) was dissolved in 50 mL of 1,2-dichloroethane under argon and transferred *via* canula to a refluxing solution of **L** (0.1 g, 0.142 mmol) in 1,2-dichloroethane under argon. After 24 hrs of reaction, the red violet solution was evaporated and chromatographed on silica, eluting with acetonitrile/water/sat. aqueous. KNO₃ (100:3:1). The collected fractions were combined and dissolved in acetonitrile. An aqueous solution of saturated potassium hexafluorophosphate (20 mL) was added and acetonitrile evaporated. Filtration under vacuum of the resulting precipitate afforded [Fe**L**(dmbp)](PF₆)₂ (0.109 g, 75%) as a violet solid. **¹H NMR** (300 MHz, CD₂Cl₂) : δ 2.62 (s, 6H, CH₃), 3.20 (m, 8H, CH₂), 3.94 (s, 6H, OCH₃), 6.27 (dd, 2H, H_{b2}, ³J = 7.8 Hz, ⁴J = 1.8 Hz), 6.57 (dd, 2H, H_{b1}, ³J = 7.8 Hz, ⁴J = 1.8 Hz), 6.84 (d, 2H, H₃, ³J = 5.5 Hz), 7.06 (d, 2H, H₂, ³J = 5.5 Hz), 7.18 (d, 4H, H_m, ³J = 8.8 Hz), 7.18 (d, 2H, H_{5'}, ³J = 5.9 Hz), 7.60 (d, 2H, H_{6'}, ³J = 6.0 Hz), 7.64 (d, 4H, H_o, ³J = 8.8 Hz), 7.68 (d, 2H, H₈, ³J = 5.5 Hz), 7.72 (d, 2H, H₉, ³J = 5.5 Hz), 8.23 (d, 2H, H₅, ³J = 9.6 Hz), 8.35 (d, 2H, H₆, ³J = 9.2 Hz), 8.36 (s, 2H, H₃).

Resolution of $[\text{FeL}(\text{dmbp})]^{2+}$ as $[\Delta\text{-TRISPHAT}]_2$ salts: A solution of [cinchonidinium][$\Delta\text{-TRISPHAT}$] (17.0 mg, 16.2 μmol , 2.5 equiv.) in acetone (2.5 mL) was added to a solution of the racemic $[\text{FeL}(\text{dmbp})][\text{PF}_6]_2$ complex (8.0 mg, 6.5 μmol , 1.0 equiv.) in CH_2Cl_2 (2.5 mL). The mixture was stirred for 10 minutes and concentrated *in vacuo* to a volume of 0.2 mL approximately. This solution was adsorbed on a TLC plate (SiO_2 , 20 x 20 cm, 0.25 mm), and the elution was performed with CH_2Cl_2 . Two bands appeared, which were abraded from the glass surface and suspended in CH_2Cl_2 . The resulting suspensions were filtered and concentrated *in vacuo*. The most eluted compound was identified as the *homochiral* salt $[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (7.7 mg, 3.1 μmol , 48%) and the least eluted as the *heterochiral* one $[\Lambda\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (7.2 mg, 2.9 μmol , 45%).



$[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$: $R_f = 0.94$ (SiO_2 , CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, 10% $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$): $\delta = 8.18$ (s broad, 2H, H_3); 8.14 (d, $J = 9.3$ Hz, 2H, H_6); 7.98 – 7.95 (m, 4H, $\text{H}_5 + \text{H}_9$); 7.74 (d, $J = 5.5$ Hz, 2H, H_8); 7.26 (d, $J = 5.5$ Hz, 2H, H_6); 7.18 (d, $J = 5.3$ Hz, 2H, H_5); 6.84 (d, $J = 8.8$ Hz, 4H, H_o); 6.74 (d, $J = 8.8$ Hz, 4H, H_m); 6.55 (d, $J = 6.0$ Hz, 2H, H_2); 6.37 (d, $J = 5.5$ Hz, 2H, H_3); 6.18 (dd, $J = 7.8, 1.5$ Hz, 2H, H_{b1}); 5.83 (dd, $J = 7.8, 1.5$ Hz, 2H, H_{b2}); 3.65 (s, 6H, CH_3); 3.47 – 3.43 (m, 2H, CH_2); 2.91 – 2.86 (m, 2H, CH_2); 2.72 – 2.47 (m, 4H, CH_2); 2.16 (s, 6H, CH_3); $^{31}\text{P NMR}$ (162 MHz, 10% $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$): $\delta = -80.11$; **IR** (KBr) $\tilde{\nu}$ 3436 (m), 2924 (w), 1636 (w), 1451 (s), 1261 (w), 1026 (m),

992 (m), 825 (s), 674 (m); **UV/Vis** (CH_2Cl_2 , $5.0 \cdot 10^{-6}$ M) λ_{max} (ϵ) 227.0 ($1.1 \cdot 10^5$), 297.0 ($4.6 \cdot 10^4$), 340.0 ($2.1 \cdot 10^4$), 534.0 ($1.0 \cdot 10^4$); **CD** (CH_2Cl_2 , $5.0 \cdot 10^{-6}$ M, 20.0°C) λ ($\Delta\epsilon$) = 239.5 (-122), 270.0 (73), 299.5 (-101), 479.0 (-16), 553.5 (18); $[\alpha]_D^{20} = 403$, $[\alpha]_{578}^{20} = 452$, $[\alpha]_{546}^{20} = -3097$, $[\alpha]_{436}^{20} = 468$ and $[\alpha]_{365}^{20} = -1839$ ($c = 0.006$, CH_2Cl_2); **ES-MS** m/z : (+) 1710.9 ($[\text{FeL}(\text{dmbp})]^{2+}[\text{TRISPHAT}]^-$), 471.2 ($[\text{FeL}(\text{dmbp})]^{2+}$), 379.2 ($[\text{Fe}(\text{L})]^{2+}$); (-) 768.7 ($[\text{TRISPHAT}]^-$).



$[\Lambda\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$: $R_f = 0.84$ (SiO_2 , CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, 10% $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$): $\delta = 8.28$ (s broad, 2H, H_3); 8.10 (d, $J = 9.3$ Hz, 2H, H_6); 7.97 (d, $J = 9.3$ Hz, 2H, H_5); 7.41 (d, $J = 5.3$ Hz, 2H, H_9); 7.37 (d, $J = 5.3$ Hz, 2H, H_8); 7.29 – 7.26 (m, 6H, $\text{H}_6 + \text{H}_o$); 6.89 – 6.87 (m, 6H, $\text{H}_m + \text{H}_5$); 6.74 (d, $J = 5.56$ Hz, 2H, H_2); 6.50 (d, $J = 5.3$ Hz, 2H, H_3); 6.26 (dd, $J = 7.8, 1.5$ Hz, 2H, H_{b1}); 5.96 (dd, $J = 7.8, 1.5$ Hz, 2H, H_{b2}); 3.65 (s, 6H, OCH_3); 3.65 – 3.59 (m, 2H, CH_2); 3.08 – 2.96 (m, 4H, CH_2); 2.81 – 2.73 (m, 2H, CH_2); 2.30 (s, 6H, CH_3); $^{31}\text{P NMR}$ (162 MHz, 10% $[\text{D}]_6\text{-DMSO}/\text{DCl}_3$): $\delta = -80.32$; **UV/Vis** (CH_2Cl_2 , $5.3 \cdot 10^{-6}$ M) λ_{max} (ϵ) 227.0 ($1.1 \cdot 10^5$), 297.0 ($4.4 \cdot 10^4$), 340.0 ($2.0 \cdot 10^4$), 529.0 ($1.0 \cdot 10^4$); **CD** (CH_2Cl_2 , $5.3 \cdot 10^{-6}$ M, 20.0°C) λ ($\Delta\epsilon$)

244.5 (-87), 269.0 (-74), 297.5 (85), 468.0 (13), 550.0 (-20); $[\alpha]_D^{20} = -985$, $[\alpha]_{578}^{20} = -1091$, $[\alpha]_{546}^{20} = 1849$, $[\alpha]_{436}^{20} = -1364$ and $[\alpha]_{365}^{20} = -379$ ($c = 0.007$, CH_2Cl_2); **ES-MS** m/z : (+) 1710.3 ($[\text{FeL}(\text{dmbp})]^{2+}[\text{TRISPHAT}]^-$), 471.3 ($[\text{FeL}(\text{dmbp})]^{2+}$), 379.2 ($[\text{Fe}(\text{L})]^{2+}$); (-) 768.7 ($[\text{TRISPHAT}]^-$).

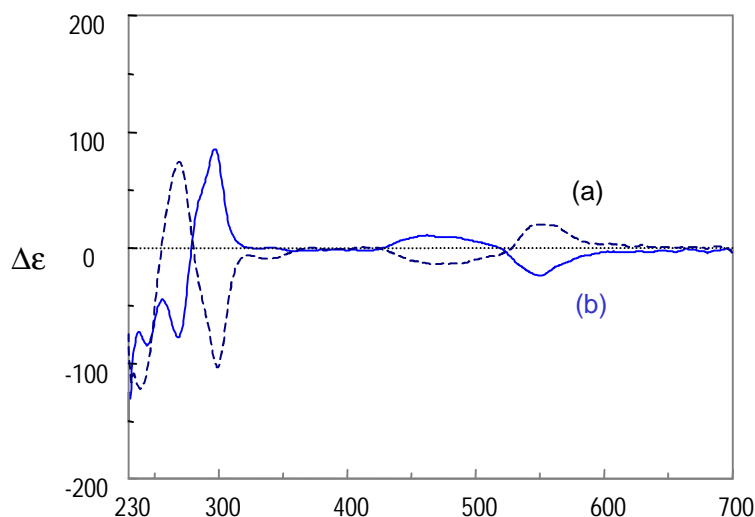


Figure 1. Circular dichroism spectra of solutions (CH_2Cl_2 , $\sim 5 \cdot 10^{-6}$ M) of the most eluted (a, - - -) and least eluted (b, —) diastereomers corresponding to compounds $[\Delta\text{-}2][\Delta\text{-}3]_2$ and $[\Lambda\text{-}2][\Delta\text{-}3]_2$ respectively.

Asymmetric synthesis of $[\text{FeL}(\text{dmbp})]^{2+}$ complex: Ligand **L** (1.23 mg, 1.75 μmol , 0.94 equiv.) and $[\text{Fe}(\text{dmbp})_3][\Delta\text{-TRISPHAT}]_2$ (4.01 mg, 1.86 μmol , 1.0 equiv.) were dissolved in CH_2Cl_2 (1.0 mL). The mixture was stirred for 60 hours at 40 °C under inert atmosphere. After concentration *in vacuo*, ^1H NMR analysis of the crude product was performed in 600 μL of 10 % $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$. Purification by column chromatography (SiO_2 , 0,5 x 1,5 cm, CH_2Cl_2) afforded the $[\text{FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ salt as a red solid (4.48 mg). Traces of persistent and unknown impurities in the aliphatic region (1.36 – 0.81 and 0.58 – 0.52 ppm) were observed which can account for the slight excess of mass (103 %). This solid was analyzed and contained essentially the homochiral ion pair $[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (d.e. > 96 %).

Thermodynamic equilibration of $[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$: A solution of the homochiral ion pair (2.3 mg, 0.93 μmol (d.e. > 90 %)) in CH_2Cl_2 (0.5 mL) was heated at 40 °C for 18 hours under argon atmosphere. After concentration *in vacuo*, ^1H NMR (10 % $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$, 600 μL) analysis that the crude reaction mixture contained essentially the homochiral ion pair $[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (d.e. > 96 %).

Thermodynamic equilibration of $[\Lambda\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$: A solution of the heterochiral ion pair (1.8 mg, 0.72 μmol (d.e. > 95 %)) in CH_2Cl_2 (0.5 mL) was heated at 40 °C for 18 hours under argon atmosphere. After concentration *in vacuo*, ^1H NMR (10 % $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$, 600 μL) analysis that the crude reaction mixture contained essentially the homochiral ion pair $[\Delta\text{-FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (d.e. > 96 %).

Asymmetric synthesis of $[\text{FeL}(\text{dmbp})]^{2+}$ complex under kinetic control: Ligand **L** (1.48 mg, 2.10 μmol , 0.99 equiv.) and $[\text{Fe}(\text{dmbp})_3][\Delta\text{-TRISPHAT}]_2$ (4.53 mg, 2.11 μmol , 1.0 equiv.) were dissolved in CH_2Cl_2 (1.0 mL). The mixture was stirred for 44 hours at 20 °C under inert atmosphere. After concentration *in vacuo*, ^1H NMR analysis of the crude product was performed in 600 μL of 10 % $[\text{D}]_6\text{-DMSO}/\text{CDCl}_3$ and showed that it contained both homochiral and heterochiral ion pairs $[\text{FeL}(\text{dmbp})][\Delta\text{-TRISPHAT}]_2$ (d.e. 0-5%).