Supplementary data

Experimental section

General: $^1$H and $^{13}$C NMR spectra were recorded on Bruker DRX-500 or DPX-400 MHz spectrometers; chemical shifts for $^1$H and $^{13}$C NMR spectra are referenced to residual solvent peaks with respect to TMS = $\delta$0 ppm. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with solid samples on a Golden Gate diamond ATR accessory. Electrospray mass spectra were recorded using a Finnigan MAT LCQ mass spectrometer. Electronic absorption spectra were recorded using a Varian-Cary 5000 spectrophotometer.

2,2'-Bipyridine-6-carbaldehyde was prepared by a reported method.$^1$

$[\text{Fe}\{(\text{S})-1\}_2][\text{PF}_6]_2$

(S)-(-)-1-Phenylethanamine (24.2 mg, 0.200 mmol) and 2,2'-bipyridine-6-carbaldehyde (36.8 mg, 0.200 mmol) were dissolved in MeOH (3.0 cm$^3$). Solid FeCl$_2$·4H$_2$O (19.8 mg, 0.100 mmol) was added at room temperature while the mixture was stirred. The resulting purple
solution was stirred for 1 h. Aqueous NH₄PF₆ (163 mg, 1.00 mmol, 5.0 cm³) was then added dropwise while the reaction mixture was stirred and a purple precipitate formed. The suspension was allowed to stand for another one hour, and was then filtered by suction, and the solid washed with MeOH/H₂O (3.0 cm³, v/v 1:5). The purple solid was redissolved in MeCN. After filtration, the filtrate was concentrated to dryness, and then dried *in vacuo* over P₂O₅. [Fe{(S)-1}₂][PF₆]₂ was isolated as a purple solid (60.2 mg, 76.0%). The diastereoisomeric ratio was determined as 1.2 : 1 from the ¹H NMR spectrum. Major diastereoisomer: ¹H NMR (500 MHz, CD₃CN) δ / ppm 8.80 (s, 2H, Hₐ), 8.74 (d, J = 7.8 Hz, 2H, H₈), 8.53 (t, J = 8.0 Hz, 2H, H₄), 8.26 (d, J = 8.1 Hz, 2H, H₃), 7.65 (d, J = 7.9 Hz, 2H, H₅), 7.56 (t, J = 7.7 Hz, 2H, H₆), 6.96 (m, 2H, H₇), 6.94 (m, 2H, H₈), 6.70 (t, J = 7.6 Hz, 4H, H₉), 6.38 (d, J = 7.5 Hz, 2H, H₁₀), 6.03 (d, J = 7.7 Hz, 4H, H₁₁), 3.91 (quartet, J = 6.2 Hz, 2H, H₁₂), 1.32 (d, J = 6.6 Hz, 6H, H₁₃); ¹³C NMR (126 MHz, CD₃CN): δ / ppm 168.4 (C₉), 161.6 (C₈), 161.0 (C₇), 158.3 (C₆), 153.1 (C₅), 139.9 (C₄), 139.4 (C₃), 138.5 (C₂), 130.3 (C₁), 129.9 (C₀), 129.6 (C₀), 128.7 (C₀), 126.4 (C₀), 124.8 (C₀), 123.8 (C₀), 67.5 (C₀), 23.9 (C₀). Minor diastereoisomer: ¹H NMR (500 MHz, CD₃CN) δ / ppm 8.58 (overlapping, 6H, H₈), 8.57 (s, 2H, H₉), 8.00 (d, J = 7.9 Hz, 2H, H₁₀), 7.73 (t, J = 7.8 Hz, 2H, H₁₁), 7.13 (t, J = 7.3 Hz, 2H, H₁₂), 7.02 (t, J = 6.6 Hz, 2H, H₁₃), 6.93 (overlapping, 4H, H₁₄), 6.44 (d, J = 5.5 Hz, 2H, H₁₅), 6.39 (overlapping, 4H, H₁₆), 4.11 (quartet, J = 6.9 Hz, 2H, H₁₇), 0.87 (d, J = 6.9 Hz, 6H, H₁₈); ¹³C NMR (126 MHz, CD₃CN): δ 170.2 (C₀), 162.4 (C₀), 161.9 (C₀), 158.0 (C₀), 153.3 (C₀), 140.4 (C₀), 139.1 (C₀), 138.4 (C₀), 130.5 (C₀), 130.0 (C₀), 129.1 (C₀), 128.9 (C₀), 128.1 (C₀), 125.2 (C₀), 124.7 (C₀), 70.5 (C₀), 20.9 (C₀). For the mixture of diastereoisomers: IR (solid, cm⁻¹): 1609w, 1456m, 1400w, 1381w, 1178w, 835s, 764s, 739m, 702m, 667w, 555s. UV/VIS λmax/nm (2.5 × 10⁻⁵ mol dm⁻³, CH₃CN) 267 (ε/10⁴ dm³ mol⁻¹ cm⁻¹ 26.2), 318 (22.2), 363sh (2.20), 483 (4.96), 585 (8.16). ESI-MS (MeOH) m/z 775.2 [M – PF₆]⁺ (calc. 775.2), 315.2 [M – 2PF₆]²⁺ (base peak, calc. 315.1). Found C 48.83, H 3.85, N 9.06; C₃₈H₃₄F₁₂FeN₆P₂·0.5H₂O requires C 49.58, H 3.72, N 9.13%.

[Fe{(S)-2}₂][PF₆]₂

{(S)-1-(Naphthalen-1-yl)ethanamine (34.2 mg, 0.200 mmol) and 2,2'-bipyridine-6-carbaldehyde (36.8 mg, 0.200 mmol) were dissolved in MeOH (3.0 cm³). Solid FeCl₂·4H₂O (19.8 mg, 0.100 mmol) was added and the purple violet solution was stirred for 1 h. Excess aqueous NH₄PF₆ (163 mg, 1.00 mmol, 8.0 cm³) was added dropwise while the mixture was
stirred and resulted in the formation of a red-brown precipitate. The suspension was allowed to stand for 1 h, and was then filtered under suction, and the solid washed with MeOH/H2O (3.0 cm³, v/v 1:5). The resulting solid was redissolved in CH3CN and the mixture filtered. The filtrate was concentrated to dryness, and the solid dried in vacuo over P2O5. [Fe{((S)-2)}2][PF6]2 was isolated as a red-brown solid (82.2 m, 80.6%). The reaction was fully diastereoselective. ¹H NMR (500 MHz, CD3CN) δ / ppm 8.96 (s, 2H, Ha), 8.56 (d, J = 7.8 Hz, 2H, Hb), 7.93 (t, J = 7.6 Hz, 2H, H4), 7.86 (d, J = 8.2 Hz, 2H, H6), 7.57 (m, 2H, H3), 7.56 (overlapping, 4H, H8+C7), 7.53 (m, 2H, H4), 7.49 (d, J = 8.2, 2H, HB3), 7.43 (m, 2H, H2), 7.42 (d, J = 7.9, 2H, HA3), 6.89 (t, J = 6.1 Hz, 2H, HA5), 6.41 (t, J = 7.2 Hz, 2H, HB6), 1H), 6.33 (d, J = 5.5 Hz, 2H, HB6), 5.82 (d, J = 6.3 Hz, 2H, HC5), 4.77 (quartet, J = 6.3 Hz, 2H, Hb), 1.54 (d, J = 6.5 Hz, 6H, HMe); ¹³C NMR (126 MHz, CD3CN): δ 169.1 (Ca), 161.1 (CB2), 160.8 (CB6), 157.7 (CA2), 153.2 (CA6), 139.9 (CA4), 138.3 (CB4), 135.6 (CA1), 134.8 (CA8a), 130.6 (CA8b), 130.3 (CB5), 130.2 (CA4), 129.3 (CA8), 128.7 (CA5), 128.5 (CA3), 127.4 (CB2), 126.4 (CA6), 124.5 (CA5), 123.9 (CA3), 123.1 (CA7), 122.5 (CB5), 63.4 (Cb), 23.1 (CMe). IR (solid, cm⁻¹): 1607w, 1558w, 1456w, 1383w, 1178w, 831s, 766s, 739m, 667w, 611w, 555s. UV/VIS λmax/nm (2.5 × 10⁻⁵ mol dm⁻³, CH3CN) 270 (ε/10³ dm³ mol⁻¹ cm⁻¹ 29.1), 315 (21.8), 357sh (6.16), 483 (4.92), 585 (8.04). ESI-MS (MeOH) m/z 875.3 [M – PF6]⁺ (calc. 875.2), 365.3 [M – 2PF6]²⁺ (base peak, calc. 365.1). Found C 54.23, H 3.99, N 8.32; C₄₆H₃₈F₁₂FeN₆P₂ requires C 54.13, H 3.75, N 8.23%.

[Fe{((R)-2)}₂][PF₆]₂

The complex was prepared as for [Fe{(S)-2}₂][PF₆]₂ starting with (R)-1-(naphthalen-1-yl)ethanamine (34.2 mg, 0.200 mmol), 2,2'-bipyridine-6-carbaldehyde (36.8 mg, 0.200 mmol) and FeCl₂·4H₂O (19.8 mg, 0.100 mmol). [Fe{(R)-2}₂][PF₆]₂ was isolated as red-brown microcrystals (78.0 mg, 75.7%). ¹H NMR spectroscopic data matched those of [Fe{(S)-2}₂][PF₆]₂. Found C 54.34, H 3.96, N 8.28; C₄₆H₃₈F₁₂FeN₆P₂ requires C 54.13, H 3.75, N 8.23%.

[Fe{(R)-3}₂][PF₆]₂

(R)-2-Amino-2-phenylethanol (27.4 mg, 0.200 mmol) and 2,2'-bipyridine-6-carbaldehyde (36.8 mg, 0.200 mmol) were dissolved in MeOH (3.0 cm³). FeCl₂·4H₂O (19.8 mg, 0.100 mmol) was added while the reaction mixture was stirred at room temperature. The purple solution was allowed to stir for 1 h, after which time, excess aqueous NH₄PF₆ (163 mg, 1.00 mmol, 8.0 cm³) was added causing a red-brown precipitate to form. The suspension was
allowed to stand for 1 h, was filtered by suction, and was washed with MeOH/H2O (3.0 cm³, v/v 1:5). The resulting solid was redissolved in MeCN, the mixture was filtered. The filtrate was collected and concentrated to dryness. After drying in vacuo over P2O5, [Fe{(R)-3}]2[PF6]2 was isolated as a purple solid (81.9 mg, 80.6%). 1H NMR (500 MHz, CD3CN) \( \delta / \text{ppm} \) 8.92 (s, 2H, Ha), 8.80 (d, \( J = 7.8 \) Hz, 2H, Hb), 8.54 (t, \( J = 8.0 \) Hz, 2H, H3), 8.27 (d, \( J = 8.1 \) Hz, 2H, H1), 7.63 (d, \( J = 7.9 \) Hz, 2H, H2), 7.55 (t, \( J = 7.7 \) Hz, 2H, H4), 6.99 (m, 2H, H5), 6.69 (t, \( J = 7.7 \) Hz, 2H, HA3), 6.73 (t, \( J = 7.7 \) Hz, 4H, Hc), 6.48 (d, \( J = 5.5 \) Hz, 2H, H6), 6.10 (d, \( J = 7.5 \) Hz, 4H, Hc2), 3.79 (m, 2H, Hb) overlapping with 3.78 (s, 2H, Hb), 3.51 (m, 2H, Hc), 3.47 (m, 2H, HC3); 13C NMR (126 MHz, CD3CN): \( \delta / \text{ppm} \) 170.2 (Ca), 161.8 (CB2), 160.8 (C2), 158.0 (C2), 153.4 (CA6), 140.0 (CA4), 138.5 (CB4), 134.8 (CA3), 130.6 (CB5), 129.7 (C3), 129.5 (CA2), 128.7 (CA5), 127.6 (CA4), 124.6 (CA4), 123.6 (CB3), 72.9 (Ca), 64.3 (Cb). IR (solid, cm⁻¹): 3311w, 1609w, 1456m, 1400w, 1180w, 1057w, 1020w, 835s, 766s, 739m, 704m, 613w, 555s. UV/VIS \( \lambda_{\text{max}}/\text{nm} \) (2.5 × 10⁻⁵ mol dm⁻³, CH3CN) 267 (\( \varepsilon / 10^3 \) dm³ mol⁻¹ cm⁻¹ 25.8), 318 (21.4), 364sh (2.24), 485 (5.00), 588 (7.60). FAB-MS (NOBA) \( m/z \) 807.2 [M – PF6]⁺ (calc. 807.2), 662.2 [M – 2PF6]⁺ (calc. 662.2). Found C 46.72, H 3.80, N 8.94; C38H34F12FeN6O2P2·H2O requires C 47.03, H 3.74, N 8.66%.

[S]-2-Amino-3-methylbutan-1-ol (20.6 mg, 0.200 mmol) and 2,2'-bipyridine-6-carbaldehyde (36.8 mg, 0.200 mmol) were dissolved in MeOH (3.0 cm³). Solid FeCl₂·4H₂O (19.8 mg, 0.100 mmol) was added to the stirring solution. The purple solution was stirred for 1 h, after which time, excess aqueous NH₄PF₆ (163 mg, 8.0 cm³) was added. The resulting suspension was allowed to stand for an hour, and was then filtered under suction. The purple-black solid was washed with MeOH/H₂O (3.0 cm³, v/v 1:5), then dissolved in MeCN. The solution was filtered and the filtrate evaporated to dryness. Crude [Fe{(S)-4}]2[PF6]2 (55.1 mg) was dried in vacuo and a 1H NMR spectrum showed the presence of two diastereoisomers in a ratio of ≈5 : 1. These were separated by plate TLC (silica, MeCN/aqueous KNO₃/H₂O, 7:1:0.5). The fraction containing the major diastereoisomer was treated with excess aqueous NH₄PF₆. Voltatile solvents were removed under reduced pressure, and the resulting aqueous solution was extracted twice with CH₂Cl₂/MeCN (9:1, v:v). The organic phases were combined and dried over Na₂SO₄, filtered and concentrated to dryness, and further dried in vacuo overnight. The major diastereoisomer of [Fe{(S)-4}]2[PF6]2 was isolated as a purple solid (35.6 mg, 40.3%). Major diastereoisomer: 1H NMR (500 MHz, CD₃CN) \( \delta / \text{ppm} \) 8.81 d, \( J = 7.7 \) Hz, 2H,
HB₃), 8.63 (d, J = 7.9 Hz, 2H, H'B₅), 8.60 (d, J = 7.9 Hz, 2H, H'B₄), 8.44 (d overlapping, 2H, H'A₃), 8.42 (s, 2H, H'a), 7.92 (t, J = 7.7 Hz, 2H, H'A₄), 7.14 (m, 2H, H'A₅), 6.95 (d, J = 5.4 Hz, 2H, H'A₆), 3.35 (m, 2H, H'd/d'), 3.27 (m, 2H, H'DOH), 2.69 (m, 2H, H'd/d'), 1.73 (s, 2H, H'b), 1.67 (m, 2H, H'c), 0.49 (d, J = 6.4 Hz, 6H, H'Me/M'e'), –0.37 (d, J = 6.5 Hz, 6H, H'Me/M'e'). ¹³C NMR (126 MHz, CD₃CN): δ / ppm 170.2 (C a), 160.85 (C'B²/B₆), 160.8 (C'B²/B₆), 158.2 (C'A₂), 154.1 (C'A₆), 140.4 (C'A₄), 138.4 (C'B₄), 129.9 (C'B₅), 129.1 (C'A₅), 124.8 (C'A₃), 124.3 (C'B₃), 75.3 (C'b), 59.1 (C'd), 28.1 (C'e), 18.5 (C'Me/M'e'), 18.4 (C'Me/M'e'). IR (solid, cm⁻¹): 3628w, 1684w, 1653w, 1607w, 1558w, 1456w, 1400w, 1373w, 1177, 1057w, 1034w, 831s, 768s, 739m. UV/VIS λmax/nm (2.5 × 10⁻⁵ mol dm⁻³, MeCN) 267 (ε/10³ dm⁻³ mol⁻¹ cm⁻¹ 33.1), 315 (24.7), 489 (5.20), 587 (8.64). FAB-MS (NOBA) m/z 739.2 [M – PF₆]+ (calc. 739.2), 594.3 [M – 2PF₆]+ (calc. 594.2). Found C 42.73, H 4.18, N 9.62; C₃₂H₃₈F₁₂FeN₆O₂P₂·H₂O requires C 42.59, H 4.47, N 9.31%.

Crystallography: general
Data were collected on a Bruker-Nonius Kappa CCD or Stoe IPDS instrument; data reduction, solution and refinement used the programs COLLECT,² SIR92,³ DENZO/SCALEPACK⁴ and CRYSTALS,⁵ or Stoe IPDS software⁶ and SHELXL97.⁷

6 Stoe & Cie, IPDS software v 1.26, Stoe & Cie, Darmstadt, Germany, 1996.