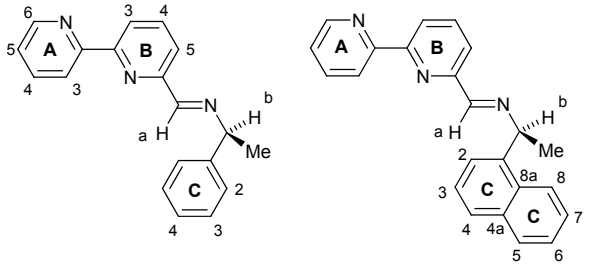
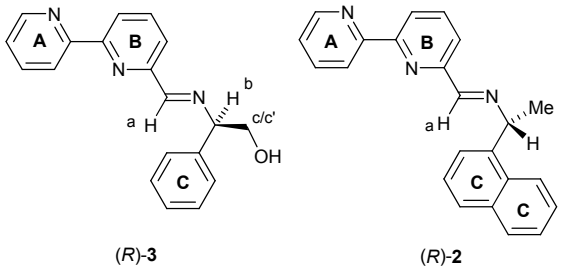
Supplementary data

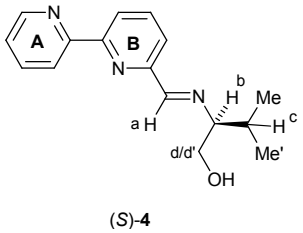
Experimental section

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 = δ0 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]







[Fe{(*S*)-1}$_2$][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 $FeCl_2 \cdot 4H_2O$ (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 NH_4PF_6 (163 mg, 1.00 mmol, 5.0 cm^3) 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/H_2O (3.0 cm^3, 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 P_2O_5. $[Fe\{(S)\text{-}\mathbf{1}\}_2][PF_6]_2$ 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, CD_3CN) δ / ppm 8.80 (s, 2H, H^a), 8.74 (d, J = 7.8 Hz, 2H, H^{B5}), 8.53 (t, J = 8.0 Hz, 2H, H^{B4}), 8.26 (d, J = 8.1 Hz, 2H, H^{B3}), 7.65 (d, J = 7.9 Hz, 2H, H^{A3}), 7.56 (t, J = 7.7 Hz, 2H, H^{A4}), 6.96 (m, 2H, H^{C4}), 6.94 (m, 2H, H^{A5}), 6.70 (t, J = 7.6 Hz, 4H, H^{C3}), 6.38 (d, J = 7.5 Hz, 2H, H^{A6}), 6.03 (d, J = 7.7 Hz, 4H, H^{C2}), 3.91 (quartet, J = 6.2 Hz, 2H, H^b), 1.32 (d, J = 6.6 Hz, 6H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN): δ / ppm 168.4 (C^a), 161.6 (C^{A2}), 161.0 (C^{B2}), 158.3 (C^{B6}), 153.1 (C^{A6}), 139.9 (C^{A4}), 139.4 (C^{C1}), 138.5 (C^{B4}), 130.3 (C^{B5}), 129.9 (C^{C3}), 129.6 (C^{C4}), 128.7 (C^{A5}), 126.4 (C^{C2}), 124.8 (C^{A3}), 123.8 (C^{B3}), 67.5 (C^b), 23.9 (C^{Me}). Minor diastereoisomer: ^1H NMR (500 MHz, CD_3CN) δ / ppm 8.58 (overlapping, 6H, $H^{B3+B4+B5}$), 8.57 (s, 2H, H^a), 8.00 (d, J = 7.9 Hz, 2H, H^{A3}), 7.73 (t, J = 7.8 Hz, 2H, H^{A4}), 7.13 (t, J = 7.3 Hz, 2H, H^{C4}), 7.02 (t, J = 6.6 Hz, 2H, H^{A5}), 6.93 (overlapping, 4H, H^{C3}), 6.44 (d, J = 5.5 Hz, 2H, H^{A6}), 6.39 (overlapping, 4H, H^{C2}), 4.11 (quartet, J = 6.9 Hz, 2H, H^b), 0.87 (d, J = 6.9 Hz, 6H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN): δ 170.2 (C^a), 162.4 (C^{B6}), 161.9 (C^{B2}), 158.0 (C^{A2}), 153.3 (C^{A6}), 140.4 (C^{A4}), 139.1 (C^{B4}), 138.4 (C^{C1}), 130.5 (C^{B5}), 130.0 (C^{C3}), 129.1 (C^{C4}), 128.9 (C^{A5}), 128.1 (C^{C2}), 125.2 (C^{A3}), 124.7 (C^{B3}), 70.5 (C^b), 20.9 (C^{Me}).

For the mixture of diastereoisomers: IR (solid, cm^{-1}): 1609w, 1456m, 1400w, 1381w, 1178w, 835s, 764s, 739m, 702m, 667w, 555s. UV/VIS λ_{max}/nm (2.5×10^{-5} mol dm^{-3}, CH_3CN) 267 ($\varepsilon/10^3$ dm^3 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 $[M - PF_6]^+$ (calc. 775.2), 315.2 $[M - 2PF_6]^{2+}$ (base peak, calc. 315.1). Found C 48.83, H 3.85, N 9.06; $C_{38}H_{34}F_{12}FeN_6P_2 \cdot 0.5H_2O$ requires C 49.58, H 3.72, N 9.13%.

$[Fe\{(S)\text{-}\mathbf{2}\}_2][PF_6]_2$

(*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 cm^{-3}). Solid $FeCl_2 \cdot 4H_2O$ (19.8 mg, 0.100 mmol) was added and the purple violet solution was stirred for 1 h. Excess aqueous NH_4PF_6 (163 mg, 1.00 mmol, 8.0 cm^3) 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/H_2O (3.0 cm^3, v/v 1:5). The resulting solid was redissolved in CH_3CN and the mixture filtered. The filtrate was concentrated to dryness, and the solid dried *in vacuo* over P_2O_5. [Fe{(*S*)-**2**}$_2$][PF_6]$_2$ was isolated as a red-brown solid (82.2 m, 80.6%). The reaction was fully diastereoselective. ^{1}H NMR (500 MHz, CD_3CN) δ / ppm 8.96 (s, 2H, H^a), 8.56 (d, J = 7.8 Hz, 2H, H^{B5}), 7.93 (t, J = 7.6 Hz, 2H, H^{B4}), 7.86 (d, J = 8.2 Hz, 2H, H^{C4}), 7.57 (m, 2H, H^{C3}), 7.56 (overlapping, 4H, H^{C8+C7}), 7.53 (m, 2H, H^{A4}), 7.49 (d, J = 8.2, 2H, H^{B3}), 7.43 (m, 2H, H^{C2}), 7.42 (d, J = 7.9, 2H, H^{A3}), 6.89 (t, J = 6.1 Hz, 2H, H^{A5}), 6.41 (t, J = 7.2 Hz, 2H, H^{C6}), 1H), 6.33 (d, J = 5.5 Hz, 2H, H^{A6}), 5.82 (d, J = 6.3 Hz, 2H, H^{C5}), 4.77 (quartet, J = 6.3 Hz, 2H, H^b), 1.54 (d, J = 6.5 Hz, 6H, H^{Me}); ^{13}C NMR (126 MHz, CD_3CN): δ 169.1 (C^a), 161.1 (C^{B2}), 160.8 (C^{B6}), 157.7 (C^{A2}), 153.2 (C^{A6}), 139.9 (C^{A4}), 138.3 (C^{B4}), 135.6 (C^{C1}), 134.8 (C^{C4a}), 130.6 (C^{C8a}), 130.3 (C^{B5}), 130.2 (C^{C4}), 129.3 (C^{C8}), 128.7 (C^{A5}), 128.5 (C^{C3}), 127.4 (C^{C2}), 126.4 (C^{C6}), 124.5 (C^{A3}), 123.9 (C^{C5}), 123.1 (C^{C7}), 122.5 (C^{B3}), 63.4 (C^b), 23.1 (C^{Me}). IR (solid, cm^{-1}): 1607w, 1558w, 1456w, 1383w, 1178w, 831s, 766s, 739m, 667w, 611w, 555s. UV/VIS λ_{max}/nm (2.5 × 10^{-5} mol dm^{-3}, CH_3CN) 270 ($\varepsilon/10^3$ dm^3 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 – PF_6]$^+$ (calc. 875.2), 365.3 [M – 2PF_6]$^{2+}$ (base peak, calc. 365.1). Found C 54.23, H 3.99, N 8.32; $C_{46}H_{38}F_{12}FeN_6P_2$ requires C 54.13, H 3.75, N 8.23%.

[Fe{(*R*)-2}$_2$][PF_6]$_2$

The complex was prepared as for [Fe{(*S*)-**2**}$_2$][PF_6]$_2$ 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 $FeCl_2$·$4H_2O$ (19.8 mg, 0.100 mmol). [Fe{(*R*)-**2**}$_2$][PF_6]$_2$ was isolated as red-brown microcrystals (78.0 mg, 75.7%). ^{1}H NMR spectroscopic data matched those of [Fe{(*S*)-**2**}$_2$][PF_6]$_2$. Found C 54.34, H 3.96, N 8.28; $C_{46}H_{38}F_{12}FeN_6P_2$ requires C 54.13, H 3.75, N 8.23%.

[Fe{(*R*)-3}$_2$][PF_6]$_2$

(*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 cm^3). $FeCl_2$·$4H_2O$ (19.8 mg, 0.100 mmol) was added while the reaction mixture was stirrred at room temperature. The purple solution was allowed to stir for 1 h, after which time, excess aqueous NH_4PF_6 (163 mg, 1.00 mmol, 8.0 cm^3) 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/H_2O (3.0 cm^3, v/v 1:5). The resulting solid was redissolved in MeCN, the the mixture was filtered. The filtrate was collected and concentrated to dryness. After drying *in vacuo* over P_2O_5, [Fe{(*R*)-**3**}$_2$][PF_6]$_2$ was isolated as a purple solid (81.9 mg, 80.6%). ^{1}H NMR (500 MHz, CD_3CN) δ / ppm 8.92 (s, 2H, H^a), 8.80 (d, *J* = 7.8 Hz, 2H, H^{B5}), 8.54 (t, *J* = 8.0 Hz, 2H, H^{B4}), 8.27 (d, *J* = 8.1 Hz, 2H, H^{B3}), 7.63 (d, *J* = 7.9 Hz, 2H, H^{A3}), 7.55 (t, *J* = 7.7 Hz, 2H, H^{A4}), 6.99 (m, 2H, H^{C4}), 6.96 (t, *J* = 7.7 Hz, 2H, H^{A5}), 6.73 (t, *J* = 7.7 Hz, 4H, H^{C3}), 6.48 (d, *J* = 5.5 Hz, 2H, H^{A6}), 6.10 (d, *J* = 7.5 Hz, 4H, H^{C2}), 3.79 (m, 2H, H^c) overlapping with 3.78 (s, 2H, H^b), 3.51 (m, 2H, $H^{c'}$), 3.47 (m, 2H, H^{OH}); ^{13}C NMR (126 MHz, CD_3CN): δ / ppm 170.2 (C^a), 161.8 (C^{B2}), 160.8 (C^{B6}), 158.0 (C^{A2}), 153.4 (C^{A6}), 140.0 (C^{A4}), 138.5 (C^{B4}), 134.8 (C^{C1}), 130.6 (C^{B5}), 129.7 (C^{C3}), 129.5 (C^{C4}), 128.7 (C^{A5}), 127.6 (C^{C2}), 124.6 (C^{A3}), 123.6 (C^{B3}), 72.9 (C^b), 64.3 (C^c). IR (solid, cm^{-1}): 3311w, 1609w, 1456m, 1400w, 1180w, 1057w, 1020w, 835s, 766s, 739m, 704m, 613w, 555s. UV/VIS λ_{max}/nm (2.5×10^{-5} mol dm^{-3}, CH_3CN) 267 ($\varepsilon/10^3$ dm^3 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 $[M - PF_6]^+$ (calc. 807.2), 662.2 $[M - 2PF_6]^+$ (calc. 662.2). Found C 46.72, H 3.80, N 8.94; $C_{38}H_{34}F_{12}FeN_6O_2P_2 \cdot H_2O$ requires C 47.03, H 3.74, N 8.66%.

[Fe{(*S*)-4}$_2$][PF_6]$_2$

(*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 cm^3). Solid $FeCl_2 \cdot 4H_2O$ (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 NH_4PF_6 (163 mg, 8.0 cm^3) 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/H_2O (3.0 cm^3, v/v 1:5), then dissolved in MeCN. The solution was filtered and the filtrate evaporated to dryness. Crude [Fe{(*S*)-**4**}$_2$][PF_6]$_2$ (55.1 mg) was dried *in vacuo* and a ^{1}H NMR spectrum showed the presence of two diastereisomers in a ratio of ≈5 : 1. These were separated by plate TLC (silica, MeCN/aqueous KNO_3/H_2O, 7:1:0.5). The fraction containing the major diastereoisomer was treated with excess aqueous NH_4PF_6. Volatile solvents were removed under reduced pressure, and the resulting aqueous solution was extracted twice with CH_2Cl_2/MeCN (9:1, v:v). The organic phases were combined and dried over Na_2SO_4, filtered and concentrated to dryness, and further dried *in vacuo* overnight. The major diastereoisomer of [Fe{(*S*)-**4**}$_2$][PF_6]$_2$ was isolated as a purple solid (35.6 mg, 40.3%). Major diastereoisomer: ^{1}H NMR (500 MHz, CD_3CN) δ / ppm 8.81 d, *J* = 7.7 Hz, 2H,

H^{B3}), 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^{OH}), 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, $H^{Me/Me'}$), –0.37 (d, J = 6.5 Hz, 6H, $H^{Me/Me'}$). ^{13}C NMR (126 MHz, CD_3CN): 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^{c}), 18.5 ($C^{Me/Me'}$), 18.4 ($C^{Me/Me'}$). IR (solid, cm^{-1}): 3628w, 1684w, 1653w, 1607w, 1558w, 1456m, 1400w, 1373w, 1177w, 1057w, 1034w, 831s, 768s, 739m. UV/VIS λ_{max}/nm (2.5 × 10^{-5} mol dm^{-3}, MeCN) 267 ($\varepsilon/10^3$ dm^3 mol^{-1} cm^{-1} 33.1), 315 (24.7), 489 (5.20), 587 (8.64). FAB-MS (NOBA) *m/z* 739.2 $[M - PF_6]^+$ (calc. 739.2), 594.3 $[M - 2PF_6]^+$ (calc. 594.2). Found C 42.73, H 4.18, N 9.62; $C_{32}H_{38}F_{12}FeN_6O_2P_2 \cdot H_2O$ 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/SCALEPACK[4] and CRYSTALS,[5] or Stoe IPDS software[6] and SHELXL97.[7]

1 F. R. Heirtzler, M. Neuburger, M. Zehnder and E. C. Constable, *Liebigs Ann. Recueil*, 1997, 297.
2 COLLECT Software, Nonius BV 1997-2001.
3 A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*., 1994, **27**, 435.
4 Z. Otwinowski and W. Minor, *Methods in Enzymology*, Vol. 276, ed. by C.W. Carter, Jr and R.M. Sweet, 1997, Academic Press, New York, pp. 307.
5 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.
6 Stoe & Cie, IPDS software v 1.26, Stoe & Cie, Darmstadt, Germany, 1996.
7 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.