Supplementary Information

Self-Assembling Optically Pure Fe(A-B)$_3$ Chelates

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General Considerations

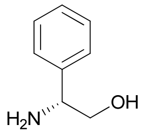
All glassware and cannulae was stored in an oven (>373 K) prior to use. Most reagents and solvents were purchased from commercial sources, such as Sigma Aldrich, and used without further purification. Tetrahydrofuran was dried by refluxing for three days under dinitrogen over potassium and was degassed before use. The dry solvent was then stored in glass ampoules under argon.

NMR spectra were recorded on Bruker Spectrospin DPX300 and DPX400 spectrometers. Routine NMR assignments were confirmed by ^{1}H-^{1}H (COSY) and ^{13}C-^{1}H (HMQC) correlation experiments where necessary. The spectra were internally referenced using the residual protio solvent ($CDCl_3$, CD_3CN etc.) resonance relative to tetramethylsilane (δ = 0 ppm). ESI mass spectra were measured on a Bruker Esquire 2000 spectrometer. Infra-Red spectra were measured using a Perkin-Elmer FTIR spectrometer. Elemental analyses were performed by Warwick Analytical Services, Coventry, UK and MEDAC Ltd, Surrey, UK.

Synthesis

(*R*)-2-Phenylglycinol

(Adapted from prep for (*S*)-*tert*-Leucinol)[1]



A dry three-necked round-bottom flask charged with sodium borohydride (31.21 g, 0.83 mol) and (*R*)-2-phenylglycine (50.00 g, 0.33 mol) was flushed with argon and dry THF (400 ml) was added. The flask was cooled to 0°C using an ice-water bath before iodine (83.75 g, 0.33 mol) in dry THF (150 ml) was added dropwise to the solution. A reflux condenser was fitted and the reaction was stirred at ambient temperature for 2 h, before heating to reflux (80°C) overnight. Methanol (400 ml) was added slowly until the solution became clear. All solvents were then removed on the rotary evaporator to leave a white paste, which was then dissolved in aqueous 20% potassium hydroxide solution (600 ml) and stirred at ambient temperature overnight. The product was extracted into dichloromethane (5 × 250 ml), dried over sodium sulfate and the solvent removed to leave the crude product (crude yield = 48.00 g). The product was recrystallised from hot toluene. Yield = 23.33 g, 0.17 mol, 52%.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ_H 7.30-7.18 (5H, m, Ph), 3.97 (1H, dd, $^3J_{HH}$ = 4 Hz, 8 Hz, CH), 3.66 (^{1}H, dd, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 4 Hz, CH_2), 3.48 (1H, dd, $^2J_{HH}$ = 11 Hz , $^3J_{HH}$ = 8 Hz, CH_2), 2.05 (2H, s, NH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, 298K, $CDCl_3$) δ_C 142.7 (Ph), 128.7 (Ph), 127.5 (Ph), 126.5 (Ph), 68.0 (CH_2), 57.4 (CH).

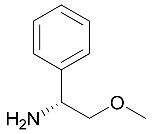
MS (ESI) 138.0 $[M+H]^+$, 121.0 $[M-NH_2]^+$.

IR *ν* cm^{-1}: 2835 m, 1604 m, 1497 m, 1453 m, 1361 w, 1197 w, 1077 m, 1047 m, 978 m, 882 m, 755 s, 700 s.

Elemental Analysis found (Calculated for $C_8H_{11}NO$) % C 69.79 (70.04), H 8.08 (8.08), N 10.18 (10.21).

Melting Point 76-78°C (Lit. mp 76-79°C).[2]

2-Methoxy-1-phenylethanamine[3]



(*R*)-2-Phenylglycinol (2.00 g, 14.6 mmol) was dissolved in dry THF (20 ml) and was added dropwise to a stirred suspension of sodium hydride (0.72 g, 30.0 mmol, 2.05 eq) in dry THF (10 ml). The solution was stirred for 1 h at ambient temperature. Iodomethane (0.96 ml, 15.4 mmol) was added dropwise and the solution was stirred for 1 h at ambient temperature. At this point, the solution was heated to reflux (65°C) under partial vacuum for a further 2 h before cooling to ambient temperature, followed by the addition of brine (40 ml). The product was extracted with diethyl ether (4 × 60 ml), dried over sodium sulfate and the solvent was removed to leave a clear oil (crude yield = 1.80 g). This crude product was purified by Kügelrohr distillation to give a clear oil (bp 70°C under high vacuum). Purified yield = 1.38 g, 9.1 mmol, 63%.

^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ_H 7.33-7.16 (5H, m, Ph), 4.12 (1H, dd, $^3J_{HH}$ = 4 Hz, 9 Hz, CH), 3.43 (1H, dd, $^2J_{HH}$ = 5 Hz , $^3J_{HH}$ = 4 Hz, CH_2), 3.32-3.26 (4H, m, CH_2, CH_3), 1.67 (2H, s, NH_2).

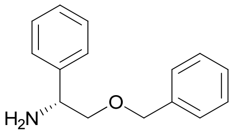
$^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δ_C 142.6 (Ph), 128.4 (Ph), 127.4 (Ph), 126.8 (Ph), 79.0 (CH_2), 58.9 (CH_3), 55.4 (CH).

MS (ESI) 135.0 $[M-NH_2]^+$.

IR *ν* cm^{-1}: 3028 w, 2888 m, 1603 w, 1493 m, 1453 m, 1355 w, 1194 m, 1111 s, 968 m, 844 m, 758/700 s.

Elemental Analysis found (Calculated for $C_9H_{13}NO$) % C 71.01 (71.49), H 8.65 (8.67), N 8.92 (9.26).

2-(Benzyloxy)-1-phenylethanamine[4]



(*R*)-2-Phenylglycinol (1.00 g, 7.3 mmol) was dissolved in dry THF (15 ml) and was added dropwise to a stirred suspension of sodium hydride (0.36 g, 14.9 mmol, 2.05 eq.) in dry THF (10 ml). The solution was stirred for 1 h at ambient temperature. Benzyl bromide (0.91 ml, 7.7 mmol, 1.05 eq.) was added dropwise over 10 minutes and the solution was stirred for 1 h at ambient temperature. At this point, the solution was heated to reflux (65°C) under partial vacuum for a further 3 h before cooling to ambient temperature, followed by the addition of brine (40 ml). The product was extracted with diethyl ether (4 × 60 ml), dried over sodium sulfate and the solvent was removed to leave a yellow oil (crude yield = 1.42 g). This crude product was purified by two Kügelrohr distillations, the first at 125°C (under high vacuum) to remove unreacted benzyl bromide and (*R*)-2-phenylglycinol, and the second to give the product, a slightly yellow liquid (bp 165°C under high vacuum). Purified yield = 0.93 g, 4.1 mmol, 56%.

^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ_H 7.33-7.16 (10H, m, Ph), 4.49 (2H, s, CH_2Ph), 4.18 (1H, dd, $^3J_{HH}$ = 4 Hz, 9 Hz, CH), 3.54 (1H, dd, $^2J_{HH}$ = 9 Hz , $^3J_{HH}$ = 4 Hz, CH_2), 3.38 (1H, pseudo t, $^2J_{HH}$ / $^3J_{HH}$ = 9 Hz, CH_2), 1.69 (2H, s, NH_2).

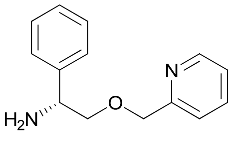
$^{13}C\{^1H\}$ NMR (75 MHz, 298 K, $CDCl_3$) δC 142.5 (Ph), 138.2 (Ph), 128.5 (Ph), 127.8 (Ph), 127.7 (Ph), 127.6 (Ph), 127.4 (Ph), 126.9 (Ph), 76.7 (CH_2), 73.3 (CH_2Ph), 55.6 (CH).

MS (ESI) 228.0 $[M+H]^+$, 250.0 $[M+Na]^+$.

IR *v* cm^{-1}: 3029 w, 2857 w, 1603 w, 1494 m, 1453 m, 1355 w, 1206 w, 1090 s, 1027 m, 843 m, 735s, 697 s.

Elemental Analysis found (Calculated for $C_{15}H_{17}NO$) % C 78.88 (79.26), H 7.58 (7.54), N 6.09 (6.16).

2-(Pyridinoxy)-1-phenylethanamine



2-(Bromomethyl)-pyridine hydrobromide (3.50 g, 13.9 mmol, 0.95 eq.) was added as a solid to a stirred suspension of sodium hydride (0.43 g, 18.0 mmol, 1.3 eq.) in dry THF (20 ml). The solution was stirred for 30 min at ambient temperature and then heated to 55°C for 45 min. (*R*)-2-Phenylglycinol (2.00 g, 14.6 mmol) was dissolved in dry THF (10 ml) and was added dropwise to a stirred suspension of sodium hydride

(0.70 g, 29.2 mmol, 2.0 eq.) in dry THF (20 ml). The solution was stirred for 1 h at ambient temperature. The (*R*)-2-phenylglycinol/NaH solution was added to the 2-(bromomethyl)-pyridine hydrobromide/NaH solution via a cannula and the solution was stirred for 1 h at ambient temperature. At this point, the solution was heated to reflux (65°C) under partial vacuum overnight. The solution was cooled to ambient temperature and brine (100 ml) was added slowly. The product was extracted with diethyl ether (3 × 150 ml), dried over sodium sulfate and the solvent was removed to leave a dark yellow oil (crude yield = 2.89 g), which contained product and (*R*)-2-phenylglycinol in a ratio of 1:0.15. This crude product was purified by two Kügelrohr distillations, the first at 125°C (under high vacuum) to remove the unreacted (*R*)-2-phenylglycinol, and the second to give the product, a slightly yellow liquid (bp 195°C under high vacuum). Purified yield = 2.25 g, 9.8 mmol, 68%.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ_H 8.56 (1H, d, $^3J_{HH}$ = 5 Hz, Py), 7.69 (1H, td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, Py), 7.42-7.18 (7H, m, Ph/Py), 4.70 (2H, s, CH_2Py), 4.31 (1H, dd, $^3J_{HH}$ = 4 Hz, 9 Hz, CH), 3.71 (1H, dd, $^2J_{HH}$ = 9 Hz , $^3J_{HH}$ = 4 Hz, CH_2), 3.38 (1H, pseudo t, $^2J_{HH}$ / $^3J_{HH}$ = 9 Hz, CH_2), 1.83 (2H, s, NH_2).

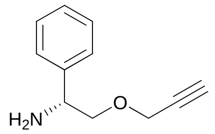
^{13}C{^{1}H} NMR (100 MHz, 298 K, $CDCl_3$) δ_C 158.4 (Py), 149.2 (Py), 142.4 (Ph/Py), 136.6 (Ph/Py), 128.5 (Ph/Py), 127.5 (Ph/Py), 126.9 (Ph/Py), 122.4 (Ph/Py), 121.4 (Ph/Py), 77.3 (CH_2), 74.1 (CH_2Py), 55.6 (CH).

MS (ESI) 212.0 $[M-NH_2]^+$, 229.0 $[M+H]^+$, 251.0 $[M+Na]^+$.

IR *ν* cm^{-1}: 3027 w, 2858 w, 1591 m, 1571 m, 1435 m, 1355 m, 1113 s, 755 s, 700 s.

Elemental Analysis found (Calculated for $C_{14}H_{16}N_2O$) % C 73.76 (73.66), H 7.15 (7.06), N 12.21 (12.27).

2-(Propargyloxy)-1-phenylethanamine



(*R*)-2-Phenylglycinol (0.50 g, 3.6 mmol) was dissolved in dry THF (15 ml) and was added dropwise to a stirred suspension of sodium hydride (0.17 g, 7.3 mmol, 2.0 eq.) in dry THF (10 ml). The solution was stirred for 1 h at ambient temperature. Propargyl bromide 80% wt. in toluene (0.43 ml, 3.8 mmol, 1.05 eq.) was added dropwise and the solution was stirred for 1 h at ambient temperature. At this point, the solution was heated to reflux (65°C) under partial vacuum overnight before cooling to ambient temperature, followed by the addition of brine (30 ml). The product was extracted with diethyl ether (4 × 50 ml), dried over sodium sulfate and the solvent was removed to leave a yellow oil (crude yield = 0.52 g). This crude product was purified by Kügelrohr distillation to give the product as a clear liquid (bp 95°C under high vacuum). Purified yield = 0.45 g, 2.6 mmol, 71%.

^{1}H NMR (300 MHz, 298 K, $CDCl_3$) δ_H 7.33-7.16 (5H, m, Ph), 4.17-4.10 (3H, m, CH_2-C≡C and CHPh), 3.60 (1H, dd, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 4 Hz, C*H₂*CHPh), 3.39 (1H, pseudo t, $^2J_{HH}$ / $^3J_{HH}$ = 9 Hz, C*H₂*CHPh), 2.36 (1H, t, $^4J_{HH}$ = 2 Hz, C≡CH), 1.70 (2H, s, NH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$) δ_C 142.3 (Ph), 128.5 (Ph), 127.5 (Ph), 126.9 (Ph), 79.6 (*C*≡CH), 76.3 (*C*H_2CHPh), 74.6 (C≡*C*H), 58.5 (*C*H_2-C≡C), 55.4 (*C*HPh).

MS (ESI) 159.0 $[M-NH_2]^+$, 176.0 $[M+H]^+$, 198.0 $[M-Na]^+$, 214.0 $[M+K]^+$.

IR *v* cm^{-1}: 3289 w, 2857 w, 1604 w, 1493 w, 1453 m, 1356 m, 1088 s, 1020 m, 860 m, 759 s, 699 s.

Elemental Analysis found (Calculated for $C_{11}H_{13}NO$) % C 75.46 (75.40), H 7.56 (7.48), N 7.95 (7.99).

General procedure for $[FeL_3][ClO_4]_2$ Complexes

2-Pyridinecarboxaldehyde (3 equivalents) and $Fe(ClO_4)_2 \cdot 6H_2O$ (1 equivalent) were dissolved in acetonitrile to form a red solution containing the iron(II) tris 2-pyridinecarboxaldehyde complex. The appropriate amine (3 equivalents) was added and immediately the solution turned purple. This was stirred overnight before ethyl acetate/diethyl ether was added dropwise until signs of crystallisation. The purple crystals were filtered and dried under vacuum. If necessary, the product $[FeL_3][ClO_4]_2$, was recrystallised from acetonitrile and ethyl acetate. Yields are unoptimised – analysis of crude reaction mixtures indicates that reactions are essentially complete.

$[FeL^1_3][ClO_4]_2 \cdot ½CH_3CN$

Yield = 0.22 g, 26%.

Ratio *fac*:*mer* is 1:2

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 9.08 (1H, s, CH=N *mer*), 8.49 (3H, s, CH=N *fac*), 8.38 (1H, s, CH=N *mer*), 8.30 (2H, m, Py *mer*), 8.22 (1H, s, CH=N, *mer*), 8.17 (1H, t, $^3J_{HH}$ = 7 Hz, Py *mer*), 8.02 (1H, t, $^3J_{HH}$ = 7 Hz, Py *mer*), 7.98-6.80 (50H, m, Py/Ph *mer* and *fac*), 5.48 (3H, d, $^3J_{HH}$ = 13 Hz, CH_2 *fac*), 5.38 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*), 5.06 (3H, d, $^3J_{HH}$ = 13 Hz, CH_2 *fac*), 4.94 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*), 4.81 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*), 4.49 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*), 4.38 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*), 4.07 (1H, d, $^3J_{HH}$ = 13 Hz, CH_2 *mer*).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 174.00 (C=N), 153.7 (Py/Ph), 138.2 (Py/Ph), 128.9 (Py/Ph), 128.9 (Py/Ph), 128.7 (Py/Ph), 128.6 (Py/Ph), 128.1 (Py/Ph), 127.9 (Py/Ph), 126.9 (Py/Ph), 65.2 (CH_2), 64.4 (CH_2), 63.6 (CH_2), 62.6 (CH_2). Many peaks due to the same carbon in the *fac*/*mer* isomers overlap.

MS (ESI positive) m/z 322.1 $[Fe\mathbf{L}^1_3]^{2+}$.

IR ν cm^{-1}: 1614 w, 1590 w, 1556 w, 1496 m, 1471 m, 1444 m, 1297 w, 1239 w, 1072 s, 741 s, 698 s, 622 s.

Elemental Analysis found (Calculated for $C_{80}H_{75}Cl_4Fe_2N_{13}O_{16}$) % C 55.22 (55.60), H 4.39 (4.37), N 10.59 (10.54).

Λ-*fac*-[FeL$^2_3$][ClO$_4$]$_2$·CH$_3$COOC$_2$H$_5$
Yield = 64 %.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 8.75 (3H, s, HC=N), 7.83 (3H, t, $^3J_{HH}$ = 7 Hz, Py), 7.47 (3H, d, $^3J_{HH}$ = 7 Hz, Py), 7.33 (3H, t, $^3J_{HH}$ = 7 Hz, Py), 7.12 (3H, t, $^3J_{HH}$ = 8 Hz, Ph), 6.99 (6H, t, $^3J_{HH}$ = 8 Hz, Ph), 6.74 (3H, d, $^3J_{HH}$ = 7 Hz, Py), 6.59 (6H, d, $^3J_{HH}$ = 8 Hz, Ph), 5.36 (3H, quartet, $^3J_{HH}$ = 4 Hz, CH), 1.98 (9H, d, $^3J_{HH}$ = 4 Hz, CH_3).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 170.8 (C=N), 158.2 (Py), 153.6 (Py), 139.5 (Ph), 138.3 (Py), 129.1 (Py), 129.0 (Ph), 127.8 (Py), 127.3 (Ph), 124.4 (Ph), 69.1 (CH), 25.4 (CH_3).

MS (ESI) m/z 343.14 [Fe**L**$^2_3$]$^{2+}$.

IR ν cm^{-1}: 1706 m, 1614 w, 1444 m, 1386 w, 1070 s, 757 s, 701 s.

Elemental Analysis found (Calculated for $C_{46}H_{50}O_{10}Cl_2FeN_6$) % C 56.64 (56.74), H 5.14 (5.18), N 8.80 (8.63).

Δ-*fac*-[FeL$^3_3$][ClO$_4$]$_2$·½CH$_3$CN·½H$_2$O
Yield = 47 %.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 8.97 (3H, s, HC=N), 7.73 (3H, t, $^3J_{HH}$ = 7 Hz, Py), 7.42 (3H, d, $^3J_{HH}$ = 7 Hz, Py), 7.21 (3H, t, $^3J_{HH}$ = 7 Hz, Py), 7.11 (3H, t, $^3J_{HH}$ = 9 Hz, Ph), 7.00 (6H, t, $^3J_{HH}$ = 9 Hz, Ph), 6.82 (9H, m, Py/Ph), 5.77 (3H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 1 Hz, CH), 4.26 (3H, m, CH_2), 4.10 (3H, s, OH), 3.92 (3H m, CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 171.4 (C=N), 158.6 (Py), 153.4 (Py), 138.2 (Py), 135.1 (Ph), 128.7 (Py), 128.5 (Ph), 127.6 (Ph), 127.4 (Py), 125.7 (Ph), 73.3 (CH), 64.6 (CH_2).

MS (ESI) m/z 607.10 [(Fe**L**$^3_2$)(ClO_4)]$^+$.

IR ν cm^{-1}: 3463 w, 1614 w, 1473 m, 1452 m, 1241 w, 1080 s, 757 s, 701 s.

Elemental Analysis found (Calculated for $C_{89}H_{89}O_{23}Cl_4Fe_2N_{13}$) % C 53.30 (53.62), H 4.57 (4.66), N 9.34 (9.45).

Δ-*fac*-[FeL$^4_3$][ClO$_4$]$_2$·½CH$_3$CN·½H$_2$O
Yield = 75 %.

^{1}H NMR (400 MHz, 298 K, CD_3CN). δ_H 8.89 (3H, s, HC=N), 7.69 (3H, td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, Py), 7.38 (3H, d, $^3J_{HH}$ = 8 Hz, Py), 7.17 (3H, m, Py), 7.09 (3H, t, $^3J_{HH}$ = 7 Hz, Ph), 6.98 (6H, t, $^3J_{HH}$ = 7 Hz, Ph), 6.77 (3H, d, $^3J_{HH}$ = 5 Hz, Py), 6.71 (6H, d, $^3J_{HH}$ = 7 Hz, Ph), 5.81 (3H, dd, $^3J_{HH}$ = 3 Hz, 11 Hz, CH), 4.23 (3H, pseudo t, $^2J_{HH}$ / $^3J_{HH}$ = 11 Hz, CH_2), 3.67 (9H, s, CH_3), 3.55 (3H, dd, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 3 Hz, CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 171.1 (C=N), 158.5 (Py), 153.5 (Py), 138.3 (Py), 134.7 (Ph), 129.0 (Py), 128.9 (Ph), 127.8 (Ph), 127.5 (Py), 125.6 (Ph), 74.0 (CH_2), 70.9 (CH), 58.2 (CH_3).

MS (ESI) m/z 388.16 $[Fe\mathbf{L}^4{}_3]^{2+}$, 635.14 $[(Fe\mathbf{L}^4{}_2)(ClO_4)]^+$.

IR ν cm^{-1}: 1613 w, 1473 m, 1451 m, 1236 w, 1078 s, 758 s, 699 s.

Elemental Analysis found (Calculated for $C_{49}H_{54}Cl_2FeN_8O_{11}$) % C 55.29 (55.64), H 4.89 (5.15), N 10.12 (10.59).

Δ-*fac*-$[FeL^5{}_3][ClO_4]_2\cdot CH_3CN$
Yield = 36 %.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H. 8.88 (3H, s, HC=N), 7.68-7.61 (9H, m, Py/Ph), 7.42-7.31 (12H, m, Py/Ph), 7.12 (3H, t, $^3J_{HH}$ = 6 Hz, Py), 7.02 (3H, t, $^3J_{HH}$ = 7 Hz, Ph), 6.86 (6H, t, $^3J_{HH}$ = 7 Hz, Ph), 6.68 (3H, d, $^3J_{HH}$ = 6 Hz, Py), 6.53 (6H, $^3J_{HH}$ = 7 Hz, Ph), 5.74 (6H, dd, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 3 Hz, CH), 4.77 (6H, s, $^2J_{HH}$ = 12 Hz, CH_2Ph), 4.14 (3H, pseudo t, $^2J_{HH}$ / $^3J_{HH}$ = 10 Hz, CH_2), 3.28 (3H, dd, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 3 Hz, CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 171.0 (C=N), 158.5 (Ph/Py), 153.4 (Py), 138.3 (Ph/Py), 137.5 (Ph/Py), 134.6 (Ph/Py), 128.9 (Ph/Py), 128.8 (Ph/Py), 128.6 (Ph/Py), 128.4 (Ph/Py), 128.2 (Ph/Py), 127.8 (Ph/Py), 127.4 (Ph/Py), 125.8 (Ph), 73.5 (CH_2Ph), 72.1 (CH_2), 71.1 (CH).

MS (ESI) 502.20 $[Fe\mathbf{L}^5{}_3]^{2+}$.

Elemental Analysis found (Calculated for $C_{65}H_{63}Cl_2FeN_7O_{11}$) % C 62.71 (62.85), H 4.99 (5.10), N 7.67 (7.88).

IR ν cm^{-1}: 1613 w, 1454 m, 1362 w, 1241 w, 1084 s, 758 s, 701 s.

Δ-*fac*-$[FeL^6{}_3][ClO_4]_2\cdot {}^3/_2CH_3OH$
Yield = 29 %.

^{1}H NMR (400 MHz, 298 K, CD_3CN). δ_H 9.03 (3H, s, HC=N), 8.60 (3H, d, $^3J_{HH}$ = 5 Hz, Py), 7.77 (3H, td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, Py), 7.68 (3H, td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, Py), 7.61 (3H, d, $^3J_{HH}$ = 8 Hz, Py), 7.40 (3H, d, $^3J_{HH}$ = 8 Hz, Py), 7.28 (3H, t, $^3J_{HH}$ = 6 Hz, Py), 7.16 (3H, td, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, Py), 7.03 (3H, t, $^3J_{HH}$ = 7 Hz, Ph), 6.86 (6H, t, ${}^3J_{HH}$ = 7 Hz, Ph), 6.75 (3H, d, ${}^3J_{HH}$ = 6 Hz, Py), 6.65 (6H, d, ${}^3J_{HH}$ = 7 Hz, Ph), 5.85 (3H, dd, ${}^3J_{HH}$ = 10 Hz, ${}^3J_{HH}$ = 3 Hz, CH), 4.95 (3H, d, ${}^2J_{HH}$ = 13 Hz, CH_2Py), 4.89 (3H, d, ${}^2J_{HH}$ = 13 Hz, CH_2Py), 4.35 (3H, pseudo t, ${}^2J_{HH}$ / ${}^3J_{HH}$ = 11 Hz, CH_2), 3.50 (3H, dd, ${}^2J_{HH}$ = 11 Hz, ${}^3J_{HH}$ = 3 Hz, CH_2).

${}^{13}C\{{}^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 171.56 (C=N), 158.50 (Py/Ph), 157.21 (Py/Ph), 153.42 (Py), 149.38 (Py), 138.31 (Py), 136.87 (Py), 134.60 (Py/Ph), 128.97 (Py), 128.84 (Ph), 127.83 (Ph), 127.46 (Py), 125.83 (Ph), 122.98 (Py), 122.43 (Py), 74.162 (CH_2Py), 72.47 (CH_2), 71.14 (CH).

MS (ESI) 503.70 $[Fe\mathbf{L}^{\mathbf{6}}_3]^{2+}$.

IR ν cm^{-1}: 1733 m, 1590 m, 1473 m, 1353 w, 1245 m, 1077 s, 760 s, 700 s.

Elemental Analysis found (Calculated for $C_{246}H_{252}Cl_8Fe_4N_{36}O_{50}$) % C 59.17 (58.86), H 4.88 (5.06), N 9.92 (10.04).

Δ-*fac*-$[FeL^7_3][ClO_4]_2{\cdot}H_2O$

${}^1H$ NMR (400 MHz, 298 K, CD_3CN) δ_H 8.93 (3H, s, HC=N), 7.70 (3H, td, ${}^3J_{HH}$ = 8 Hz, ${}^4J_{HH}$ = 1 Hz, Py), 7.40 (3H, d, ${}^3J_{HH}$ = 7 Hz, Py), 7.18 (3H, td, ${}^3J_{HH}$ = 7 Hz, ${}^4J_{HH}$ = 1 Hz, Py), 7.10 (3H, t, ${}^3J_{HH}$ = 7 Hz, Ph), 6.99 (6H, t, ${}^3J_{HH}$ = 7 Hz, Ph), 6.78 (9H, m, Py/Ph), 5.81 (3H, dd, ${}^3J_{HH}$ = 11 Hz, ${}^3J_{HH}$ = 3 Hz, CHPh), 4.60 (3H, dd, ${}^2J_{HH}$ = 16 Hz, ${}^4J_{HH}$ = 2 Hz, CH_2-C≡C), 4.51 (3H, dd, ${}^2J_{HH}$ = 16 Hz, ${}^4J_{HH}$ = 2 Hz, CH_2-C≡C), 4.38 (3H, pseudo t, ${}^2J_{HH}$ / ${}^3J_{HH}$ = 11 Hz, C*H₂*CHPh), 3.70 (3H, dd, ${}^2J_{HH}$ = 11 Hz, ${}^3J_{HH}$ = 3 Hz, C*H₂*CHPh), 2.95 (3H, t, ${}^4J_{HH}$ = 2 Hz, C≡CH).

${}^{13}C\{{}^1H\}$ NMR (75 MHz, 298 K, CD_3CN) δ_C 170.9 (C=N), 158.1 (Py/Ph), 153.3 (Ph), 138.2 (Py), 134.1 (Py/Ph), 128.8 (Py/Ph), 128.8 (Py/Ph), 127.8 (Py/Ph), 127.4 (Py/Ph), 125.6 (Py/Ph), 78.7 (*C*≡CH), 76.0 (C≡*C*H), 70.9 (*C*H_2CHPh), 70.4 (*C*HPh), 58.0 (*C*H_2-C≡C).

MS (ESI) m/z 424.16 $[Fe\mathbf{L}^7_3]^{2+}$.

IR ν cm^{-1}: 3259 w, 1732 w, 1613 w, 1474 m, 1452 m, 1356 w, 1240 m, 1076 s, 758 s, 699 s.

Elemental Analysis found (Calculated for $C_{51}H_{50}Cl_2FeN_6O_{12}$) % C 57.36 (57.48), H 4.65 (4.73), N 7.69 (7.89).

$[FeL^8_3][ClO_4]_2{\cdot}H_2O$

Yield = 24 %.

Ratio *fac*:*mer* is 2.8:1

${}^1H$ NMR (400 MHz, 298 K, CD_3CN) δ_H 9.32 (1H, s, HC=N, *mer*), 9.25 (1H, s, HC=N, *mer*), 9.00 (1H, s, HC=N, *mer*), 8.91 (3H, s, HC=N, *fac*), 8.43-7.45 (21H, m, Py *mer*/*fac*), 6.85 (3H, d, $^3J_{HH}$ = 6 Hz, Py, *fac*), 3.89 (3H, m, CH, *fac*), 3.59 (1H, m, CH *mer*), 3.45 (1H, m, CH *mer*), 3.27 (1H, m, CH *mer*), 1.66-0.54 (84H, m, CH_3/Cy, *mer*/*fac*).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3CN) δ_C 170.3 (C=N), 159.3 (Py), 154.6 (Py), 138.9 (Py), 129.8 (Py), 128.3 (Py), 69.2 (CH), 40.5 (CH_3), 30.8 (Cy), 26.3 (Cy), 25.6 (Cy), 23.4 (Cy).

All peaks on $^{13}C\ \{^1H\}$ NMR are due to the major isomer (*fac*). The peaks for the *mer*-isomer are too small to be observed.

MS (ESI) m/z 352.21 $[Fe\mathbf{L}^{\mathbf{8}}_3]^{2+}$.

IR νcm^{-1}: 1731 w, 1612 w, 1445 m, 1395 w, 1241 m, 1077 s, 766 m.

Elemental Analysis found (Calculated for $C_{42}H_{62}O_9Cl_2FeN_6$) % C 55.03 (54.73), H 6.67 (6.78), N 8.89 (9.12).

$[\mathbf{FeL^9_2}][\mathbf{ClO_4}]_2$

The same reaction conditions resulted in a red paramagnetic bis-complex. Yield = 63%.

MS (ESI) m/z 207.15 $[\mathbf{L}^{\mathbf{9}}+H]^+$.

IR νcm^{-1}: 3225 w, 1600 m, 1481 m, 1370 m, 1225 m, 1046 s, 786 s.

Elemental Analysis found (Calculated for $C_{24}H_{36}Cl_2FeN_4O_{10}$) % C 43.48 (43.20), H 5.46 (5.44), N 8.59 (8.40).

1. D. A. Evans, G. S. Peterson, J. S. Johnson, D. M. Barnes, K. R. Campos and K. A. Woerpel, *J. Org. Chem.*, 1998, **63**, 4541-4544.
2. J. M. Janey, T. Iwama, S. A. Kozmin and V. H. Rawal, *J. Org. Chem.*, 2000, **65**, 9059-9068.
3. R. N. Bream, S. V. Ley, B. McDermott and P. A. Procopiou, *J. Chem. Soc., Perkin Trans. 1*, 2002, 2237-2242.
4. Z. Y. Chang and R. M. Coates, *J. Org. Chem.*, 1990, **55**, 3475-3483.