

Supporting Information

5-Ferrocenyl-2,2'-bipyridine Ligands: synthesis,
palladium(II) and copper(I) complexes, optical and
electrochemical properties.

Synøve Ø. Scottwell,^a Karl J. Shaffer,^a C. John McAdam,^a and James D. Crowley^{a}*

^aDepartment of Chemistry, University of Otago, PO Box 56, Dunedin,

New Zealand; Fax: +64 3 479 7906; Tel: +64 3 479 7731.

***jcrowley@chemistry.otago.ac.nz**

Contents

1	Experimental Procedures	3
1.1	General	3
1.2	Ligand Synthesis.....	4
1.2.1	Synthesis of 5-bromo-2,2'-bipyridine (2a)	4
1.2.2	Synthesis of 5-bromo-5'-methyl-2,2'-bipyridine (2b)	5
1.2.3	Synthesis of 5-ferrocenyl-2,2'-bipyridine (3a)	6
1.2.4	Synthesis of 5-ferrocenyl-5'-methyl-2,2'-bipyridine (3b)	7
1.2.5	Synthesis of 6,6'-dimesityl-2,2'-bipyridine (10)	8
1.3	Palladium(II) Complexation	9
1.3.1	Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine)Cl ₂] (4a)	9
1.3.2	Synthesis of [Pd(5-ferrocenyl-5'-methyl-2,2'-bipyridine)Cl ₂] (4b)	9
1.3.3	Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine)(pyridine) ₂](SbF ₆) ₂ (5a)	10
1.3.4	Synthesis of [Pd(5-ferrocenyl-5'-methyl-2,2'-bipyridine)(pyridine) ₂](SbF ₆) ₂ (5b)	11
1.3.5	Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine)(DMAP) ₂](SbF ₆) ₂ (6a)	12
1.3.6	Synthesis of [Pd(5-ferrocenyl-5'-methyl-2,2'-bipyridine)(DMAP) ₂](SbF ₆) ₂ (6b)	13
1.3.7	Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine) ₂](SbF ₆) ₂ (9a)	14
1.4	Copper(I) Complexation.....	15
1.4.1	[Cu(6,6'-dimesityl-2,2'-bipyridine)(MeCN) ₂]PF ₆ (10Cu)	15
1.4.2	[Cu(6,6'-dimesityl-2,2'-bipyridine)(5-ferrocenyl-2,2'-bipyridine)]PF ₆ (11a)	16
1.4.3	[Cu(6,6'-dimesityl-2,2'-bipyridine)(5-ferrocenyl-5'-methyl-2,2'-bipyridine)]PF ₆ (11b)	17
2	Pertinent ¹ H NMR Stackplots	18
3	Representative Mass Spectra	21
4	UV-Vis Spectra	26
5	Electrochemistry	28
5.1	Representative Voltammograms	28
6	X-ray Data	30
6.1	Crystallographic Data Tables	30
6.2	Crystal Structures and Relevant Notes	33
7	References	37

1 Experimental Procedures

1.1 General

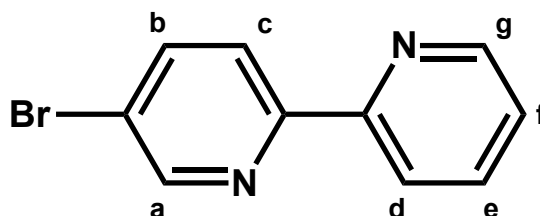
Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. The solvents used were laboratory grade, with petrol referring to the fraction of petroleum ether boiling in the range 40-60 °C, and ether referring to diethyl ether. Dry tetrahydrofuran (THF), acetonitrile (CH₃CN), dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) were obtained by passing them through an activated alumina column using a PureSolv™ solvent purification system (Innovative Technologies Inc., MA). Ammonium hydroxide/ethylenediaminetetraacetic acid (NH₄OH/EDTA) solution was made up by dissolving 30 g EDTA with 900 mL water and 100 mL NH₄OH. Microwave-assisted reactions were performed in a CEM Focused Microwave Synthesis System, Discover S-Class (CEM Corporation, NC), at 300 W.

¹H and ¹³C NMR spectra were recorded on either a 400 MHz Varian/Agilent 400-MR or Varian 500 MHz AR spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual solvent peaks (CDCl₃: ¹H δ 7.26 ppm, ¹³C δ 77.16 ppm; *d*₆-acetone: ¹H δ 2.05 ppm; ¹³C δ 29.84 & 206.26 ppm; CD₃CN: ¹H δ 1.94 ppm, ¹³C δ 1.32 & 118.26 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, t = triplet, dt = double triplet, d = doublet, dd = double doublet, s = singlet. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module, and band intensities are reported as strong (s), medium (m), or weak (w). Microanalyses were conducted at the Campbell Microanalytical Laboratory at the University of Otago. Electrospray mass spectra (ESMS) were collected on a Bruker micrOTOF-Q spectrometer. Melting points were determined using a Leica VMHB melting bar. UV-visible absorption spectra were acquired with a Jasco V550 UV/VIS spectrophotometer.

1.2 Ligand Synthesis

1.2.1 Synthesis of 5-bromo-2,2'-bipyridine (2a)

The synthesis of this compound has previously been reported by Rieke in 72% yield.¹



Under a nitrogen atmosphere, a solution of 2-pyridylzinc(II) bromide (THF, 0.5 M, 50 mL, 25.0 mmol, 1.10 eq.) was added to a solution of THF (20 mL) containing 2,5-dibromopyridine (5.38 g, 22.7 mmol, 1.00 eq.) and *tetrakis*(triphenylphosphine)palladium(0) (0.53 g, 0.46 mmol, 0.02 eq.). The resulting suspension was refluxed for five hours, before stirring at room temperature overnight (16 hours). $\text{NH}_4\text{OH}/\text{EDTA}$ (200 mL) and CH_2Cl_2 (150 mL) were added and the mixture allowed to stir for four hours. The organic phase was washed with water (2 × 50 mL) and saturated aqueous NaCl (2 × 50 mL), then dried over Na_2SO_4 and excess solvent removed under reduced pressure. Column chromatography (silica gel, gradient 100% petrol, then 1:1 petrol / CH_2Cl_2 , then 95:5 CH_2Cl_2 /acetone) was used to obtain a colourless solid. The solid residue was dissolved in CH_3CN and vapour diffused diethyl ether to provide colourless crystals. Yield: 3.84 g, 72%. Mp 82 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.72 (dd, $J = 2.4, 0.7$ Hz, 1H, H_a), 8.67 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 1H, H_g), 8.37 (dt, $J = 8.0, 1.1$ Hz, 1H, H_c), 8.32 (dd, $J = 8.5, 0.7$ Hz, 1H, H_d), 7.93 (dd, $J = 8.5, 2.4$ Hz, 1H, H_b), 7.81 (ddd, $J = 8.1, 7.5, 1.8$ Hz, 1H, H_f), 7.33 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H, H_e); ^{13}C NMR (125 MHz, CDCl_3) δ 155.3, 154.8, 150.3, 149.4, 139.6, 137.2, 124.1, 122.5, 121.3, 121.1; IR (ATR): ν (cm^{-1}) 3089 (w), 1549 (m), 1431 (m), 1363 (m), 1001 (s), 786 (s), 733 (s), 631 (s); HRESI-MS (MeOH): $m/z = 234.9870$ [$\mathbf{2a}+\text{H}$]⁺ (calc. for $\text{C}_{10}\text{H}_7\text{BrN}_2\text{H}$ 234.9865), $m/z = 256.9684$ [$\mathbf{2a}+\text{Na}$]⁺ (calc. for $\text{C}_{10}\text{H}_7\text{BrN}_2\text{Na}$ 256.9685); Anal. Calc. for $\text{C}_{10}\text{H}_7\text{BrN}_2$: C, 51.09; H, 3.00; N, 11.92. Found: C, 51.09; H, 2.93; N, 11.65.

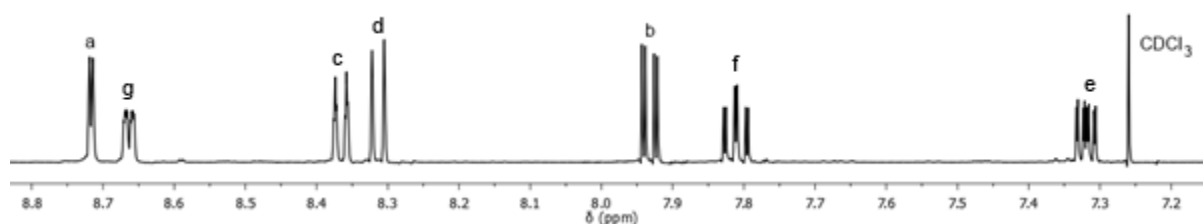


Figure S1 ^1H NMR spectrum (400 MHz, CDCl_3) of **2a**.

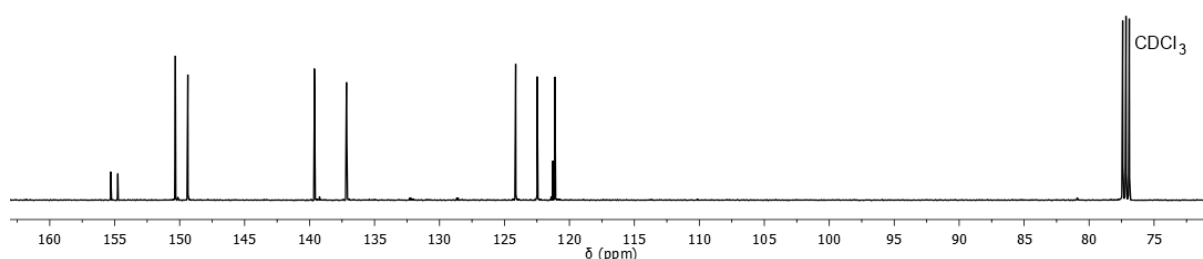
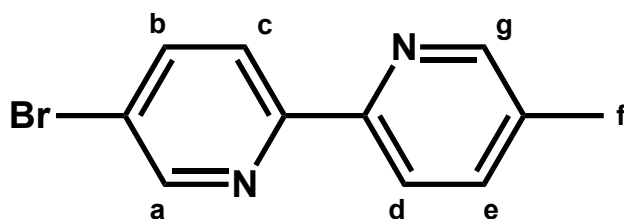


Figure S2 ^{13}C NMR spectrum (125 MHz, CDCl_3) of **2a**.

1.2.2 Synthesis of 5-bromo-5'-methyl-2,2'-bipyridine (2b)

The synthesis of this compound has previously been reported by Rieke in 63% yield.¹



Under a nitrogen atmosphere, a solution of 5-methyl-2-pyridylzinc(II) bromide (THF, 0.5 M, 50 mL, 25.0 mmol, 1.20 eq.) was added to a solution of THF (20 mL) containing 2,5-dibromopyridine (5.00 g, 21.1 mmol, 1.00 eq.) and *tetrakis*(triphenylphosphine)palladium(0) (0.45 g, 0.39 mmol, 0.02 eq.). The resulting suspension was refluxed for five hours, before stirring at room temperature overnight (16 hours). NH_4OH /EDTA (200 mL) and CH_2Cl_2 (150 mL) were added and the mixture allowed to stir for four hours. The organic phase was washed with water (2×50 mL) and saturated aqueous NaCl (2×50 mL), then dried over MgSO_4 and excess solvent removed under reduced pressure. The crude product was slurried with ether, filtered and washed with additional ether. Column chromatography (silica gel, gradient 100% CH_2Cl_2 to 9:1 CH_2Cl_2 /acetone) was used to obtain a colourless solid. The solid residue was dissolved in CH_3CN and vapour diffused diethyl ether to provide colourless crystals. Yield: 4.73 g, 90%. Mp 102 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.70 (dd, $J = 2.4, 0.7$ Hz, 1H, H_a), 8.49 (dd, $J = 2.3, 0.7$ Hz, 1H, H_g), 8.29 - 8.24 (m, 2H, $\text{H}_{c/d}$), 7.92 (dd, $J = 8.5, 2.4$ Hz, 1H, H_b), 7.62 (ddq, $J = 8.0, 2.2, 0.7$ Hz, 1H, H_e), 2.39 (s, 3H, H_f); ^{13}C NMR (125 MHz, CDCl_3) δ 154.9, 152.8, 150.1, 149.8, 139.5, 137.6, 133.9, 122.1, 120.8, 120.6, 18.5; IR (ATR): ν (cm^{-1}) 2918 (m), 1544 (m), 1456 (m), 1360 (m), 818 (s); HRESI-MS (MeOH): $m/z = 270.9804$ [$2b + \text{Na}$] $^+$ (calc. for $\text{C}_{11}\text{H}_9\text{BrN}_2\text{Na}$ 270.9841); Anal. Calc. for $\text{C}_{11}\text{H}_9\text{BrN}_2$: C, 53.04; H, 3.64; N, 11.25. Found: C, 53.11; H, 3.61; N, 11.22.

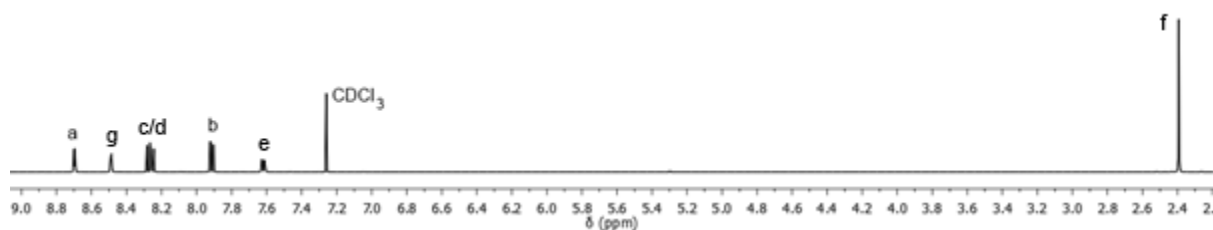


Figure S3 ^1H NMR spectrum (400 MHz, CDCl_3) of **2b**.

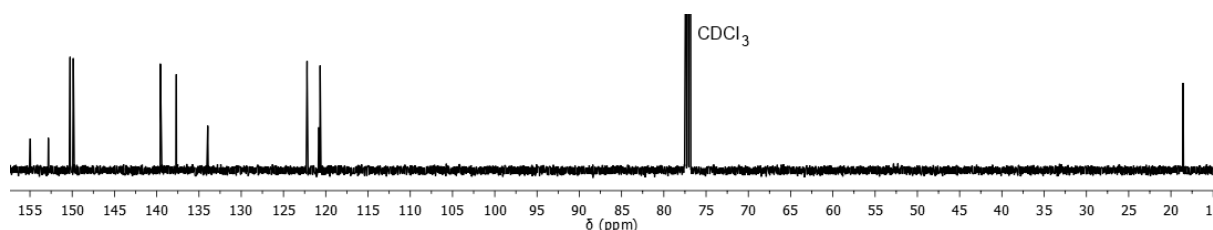
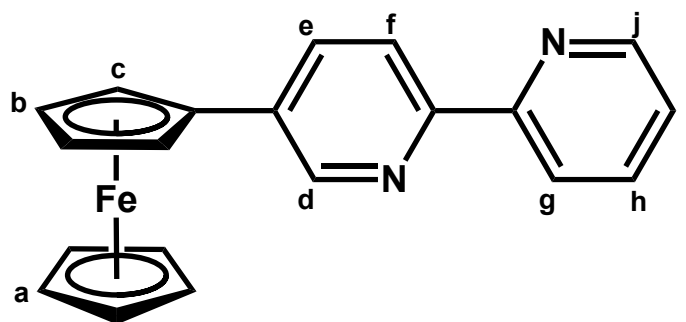


Figure S4 ^{13}C NMR spectrum (125 MHz, CDCl_3) of **2b**.

1.2.3 Synthesis of 5-ferrocenyl-2,2'-bipyridine (3a)



1,4-Dioxane (4.0 mL), 1,2-dimethoxyethane (4.0 mL), 1 M Na₂CO₃ (3.0 mL, 3.00 mmol, 1.50 eq.) and 3 M NaOH (1.5 mL, 1.50 mmol, 0.75 eq.) were added to a 35 mL microwave vial equipped with a stirrer bar and degassed with N₂ for 10 minutes. Ferroceneboronic acid (0.454 g, 1.98 mmol, 1.00 eq.), 5-bromo-2,2'-bipyridine (0.464 g, 1.98 mmol, 1.00 eq.) and [PdCl₂(1,1'-bis(diphenylphosphino)ferrocene)] (0.081 g, 0.10 mmol, 0.05 eq.) were added to the vial which was sealed then flushed with N₂. The vial was shaken to ensure homogeneity then heated via microwave irradiation for 30 minutes at 110 °C (300 W). The reaction mixture was added to aqueous NH₄Cl (200 mL) and CH₂Cl₂ (200 mL) and after a second extraction with CH₂Cl₂ (200 mL), the combined organic layers were filtered and dried over Na₂SO₄. The solvent was removed *in vacuo* and the product purified by column chromatography (silica gel, gradient 100:0 to 99:1 to 98:2 CH₂Cl₂/acetone). The product was isolated as an orange solid (0.419 g, 62%). Mp 142 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.81 (s, 1H, H_d), 8.69 (d, *J* = 5.5 Hz, 1H, H_j), 8.40 (d, *J* = 8.0 Hz, 1H, H_f), 8.33 (d, *J* = 8.3 Hz, 1H, H_g), 7.87 (dd, *J* = 8.2, 2.3 Hz, 1H, H_e), 7.82 (t, *J* = 7.6 Hz, 1H, H_i), 7.32 – 7.29 (m, 1H, H_h), 4.75 (s, 2H, H_c), 4.42 (s, 2H, H_b), 4.08 (s, 5H, H_a); ¹³C NMR (125 MHz, CDCl₃) δ 156.3, 153.6, 149.3, 146.8, 137.0, 136.0, 133.9, 123.5, 120.8, 120.8, 81.41, 69.9, 69.8, 66.7; IR (ATR): ν (cm⁻¹) 1571 (m), 1462 (m), 1431 (s), 1376 (m), 1105 (m), 889 (s), 815 (s), 799 (s), 751 (s), 508 (s), 491 (s), 460 (s); HRESI-MS (MeOH) *m/z* = 341.0722 [**3a**+H]⁺ (calc. for C₂₀H₁₆FeN₂H 341.0736). UV-Vis (acetone) λ_{max} (ε/ L mol⁻¹ cm⁻¹): 369 (4000), 456 (1400); Anal. Calc. for C₂₀H₁₆FeN₂: C, 70.61; H, 4.74; N, 8.23. Found: C, 70.57; H, 4.84; N, 8.40.

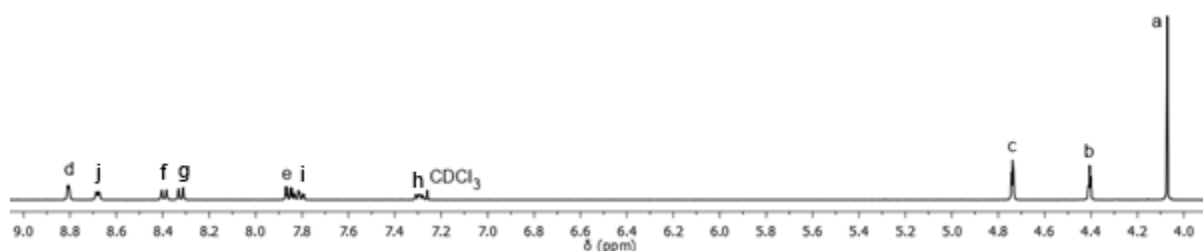


Figure S5 ¹H NMR spectrum (400 MHz, CDCl₃) of **3a**.

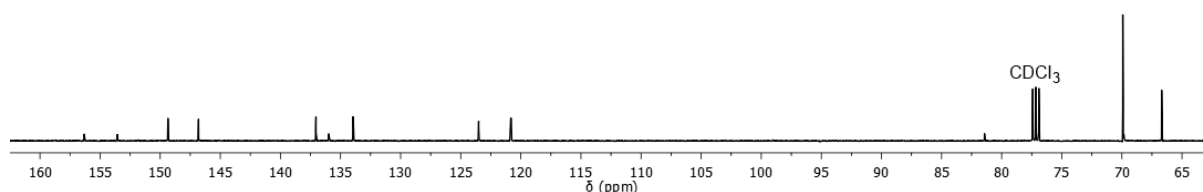
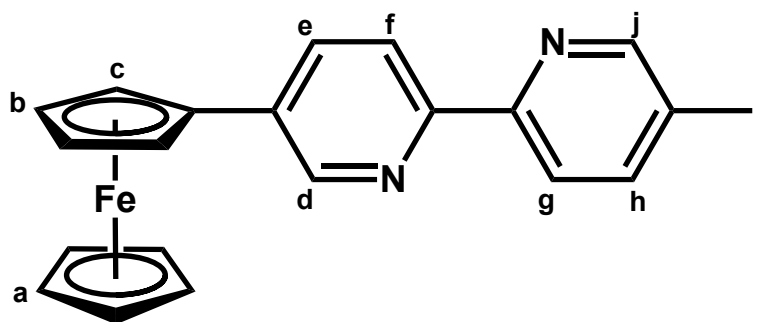


Figure S6 ¹³C NMR spectrum (125 MHz, CDCl₃) of **3a**.

1.2.4 Synthesis of 5-ferrocenyl-5'-methyl-2,2'-bipyridine (**3b**)



1,4-Dioxane (4.0 mL), 1,2-dimethoxyethane (4.0 mL), 1 M Na₂CO₃ (3.0 mL, 3.00 mmol, 1.81 eq.) and 3 M NaOH (1.5 mL, 1.50 mmol, 0.91 eq.) were added to a 35 mL microwave vial equipped with a stirrer bar and degassed with N₂ for 10 minutes. Ferroceneboronic acid (0.380 g, 1.65 mmol, 1.00 eq.), 5-bromo-5'-methyl-2,2'-bipyridine (0.412 g, 1.65 mmol, 1.00 eq.) and [PdCl₂(1,1'-bis(diphenylphosphino)ferrocene)] (0.068 g, 0.08 mmol, 0.05 eq.) were added to the vial which was sealed then flushed with N₂. The vial was shaken to ensure homogeneity then heated via microwave irradiation for 30 minutes at 110 °C (300 W). The reaction mixture was added to aqueous NH₄Cl (200 mL) and CH₂Cl₂ (200 mL) and after a second extraction with CH₂Cl₂ (200 mL) the combined organic layers were filtered and dried over Na₂SO₄. The solvent was removed *in vacuo* and the product purified by column chromatography (silica gel, gradient 100:0 to 99:1 to 98:2 CH₂Cl₂/acetone). The product was isolated as an orange solid (0.426 g, 73%). Mp 165 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.79 (s, 1H, H_d), 8.51 (s, 1H, H_j), 8.28 (d, *J* = 8.2 Hz, 2H, H_{f/g}), 7.85 (dd, *J* = 8.2, 2.2 Hz, 1H, H_e), 7.63 (d, *J* = 8.2 Hz, 1H, H_h), 4.73 (t, *J* = 1.7 Hz, 2H, H_c), 4.40 (t, *J* = 1.7 Hz, 2H, H_b), 4.08 (s, 5H, H_a), 2.40 (s, 3H, H_i); ¹³C NMR (125 MHz, CDCl₃) δ 153.8, 153.7, 149.8, 146.7, 137.6, 135.5, 134.0, 133.2, 120.5, 120.4, 81.6, 69.9, 69.8, 66.7, 18.5; IR (ATR): ν (cm⁻¹) 1573 (w), 1475 (m), 1374 (m), 1103 (m), 1090 (m), 1027 (m), 886 (m), 825 (s), 739 (m), 649 (m), 510 (s), 492 (s); HRESI-MS (MeOH): *m/z* = 355.0871 [**3b**+H]⁺ (calc. for C₂₁H₁₈FeN₂H 355.0892); UV-Vis (acetone) λ_{max} (ε/ L mol⁻¹ cm⁻¹): 364 (4100), 450 (1200); Anal. Calc. for C₂₁H₁₈FeN₂: C, 71.20; H, 5.12; N, 7.91. Found: C, 70.81; H, 5.14; N, 7.99.

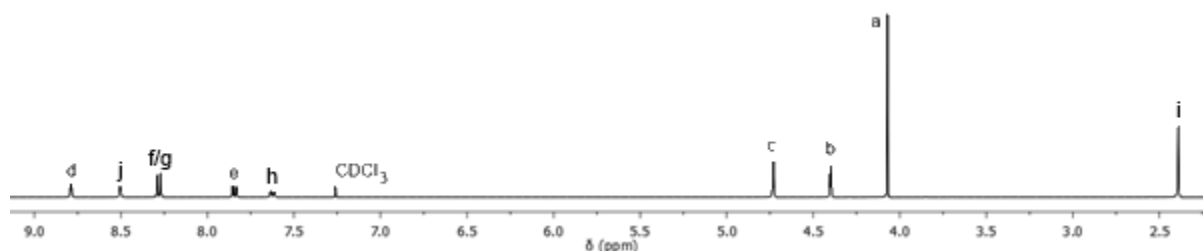


Figure S7 ¹H NMR spectrum (400 MHz, CDCl₃) of **3b**.

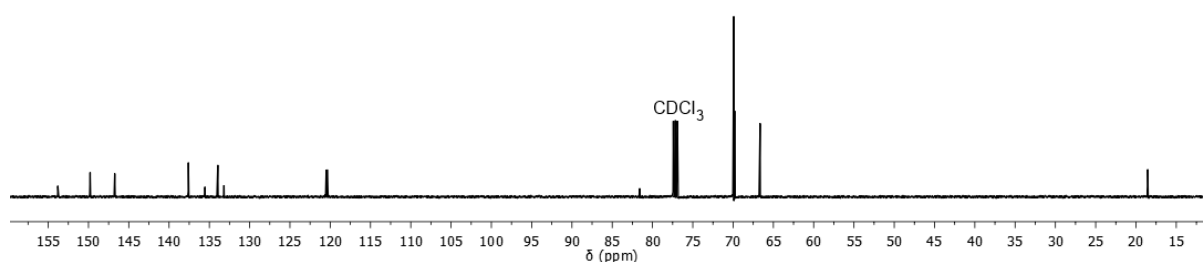
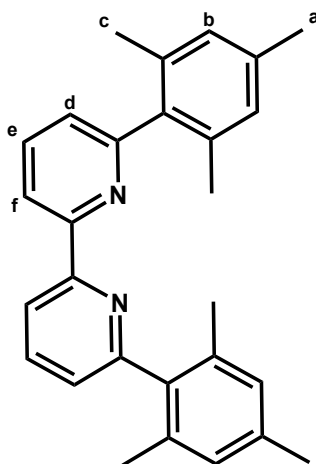


Figure S8 ¹³C NMR spectrum (125 MHz, CDCl₃) of **3b**.

1.2.5 Synthesis of 6,6'-dimesityl-2,2'-bipyridine (10)

The synthesis of this compound has previously been reported by Schmittl in 72% yield.²



Under a nitrogen atmosphere, 6,6'-dibromo-2,2'-bipyridine (0.20 g, 0.64 mmol, 1.00 eq.) and *tetrakis*(triphenylphosphine)palladium(0) (0.006 g, 5.2 μ mol, 0.008 eq.) were dissolved in degassed boiling toluene. A solution of mesitylboronic acid (0.25 g, 1.52 mmol, 2.40 eq.) in methanol (5 mL) and 2 M Na_2CO_3 (8 mL, 16.0 mmol, 25.1 eq.) were added, and the mixture refluxed for four hours. An additional 0.1 g of mesitylboronic acid was then added, and heating was continued for a further three days. After cooling, the solvent layers were separated, and the organic layer washed with a saturated aqueous solution of Na_2CO_3 containing a small amount of ammonia. The aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL), which in turn was washed with the Na_2CO_3 solution. The organic layers were combined, dried over Na_2SO_4 and the solvent removed *in vacuo*. Column chromatography (silica, CH_2Cl_2) was used to isolate the white product (0.199 g, 80%). Mp 211 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 7.9$ Hz, 2H, H_f), 7.80 (t, $J = 7.8$ Hz, 2H, H_e), 7.21 (d, $J = 7.6$ Hz, 2H, H_d), 6.98 (s, 4H, H_b), 2.35 (s, 6H, H_a), 2.12 (s, 12H, H_c); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 156.4, 138.2, 137.6, 137.0, 136.1, 128.6, 124.8, 119.3, 21.3, 20.6; IR: ν (cm^{-1}) 2915 (w), 1561 (s), 1438 (s), 851 (s), 815 (s), 631 (s); HRESI-MS (MeOH): $m/z = 393.2329$ [$\mathbf{10}+\text{H}$] $^+$ (calc. for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{H}$ 393.23), $m/z = 415.2158$ [$\mathbf{10}+\text{Na}$] $^+$ (calc. for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{Na}$ 415.53); Anal. Calc. for $\text{C}_{28}\text{H}_{28}\text{N}_2$: C, 85.67; H, 7.19; N, 7.14. Found: C, 85.43; H, 7.28; N, 7.28.

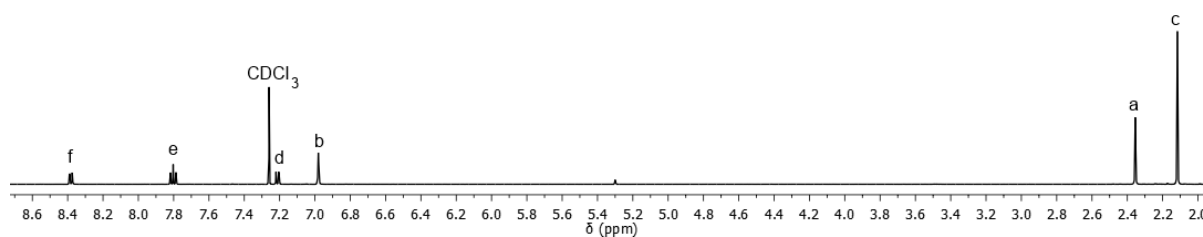


Figure S9 ^1H NMR spectrum (400 MHz, CDCl_3) of **10**.

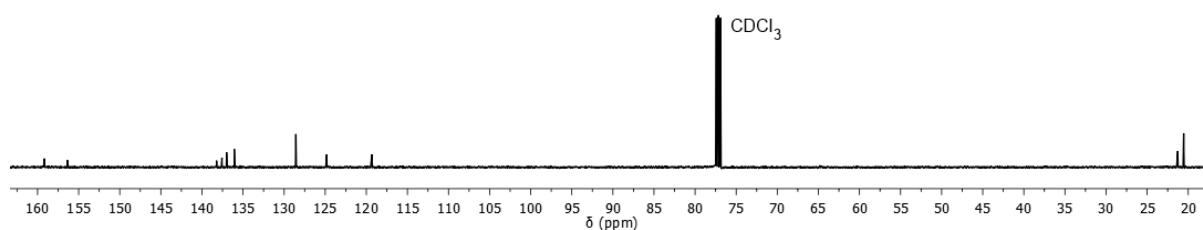
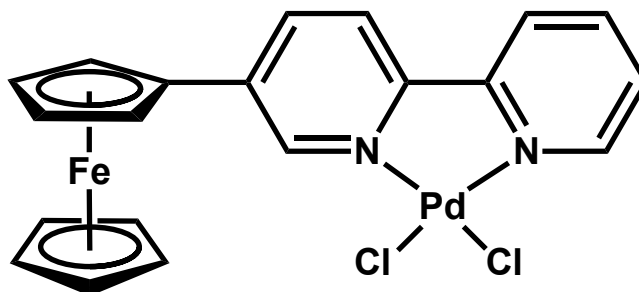


Figure S10 ^{13}C NMR spectrum (125 MHz, CDCl_3) of **10**.

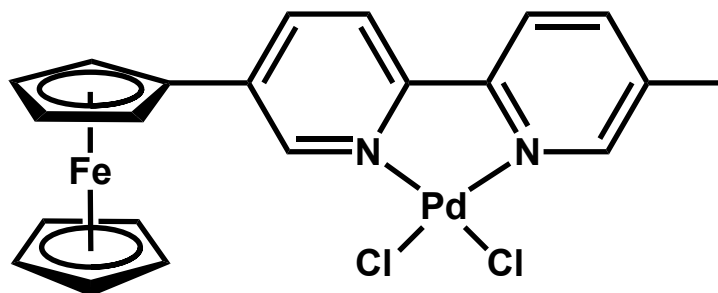
1.3 Palladium(II) Complexation

1.3.1 Synthesis of $[\text{Pd}(\text{5-ferrocenyl-2,2'-bipyridine})\text{Cl}_2]$ (**4a**)



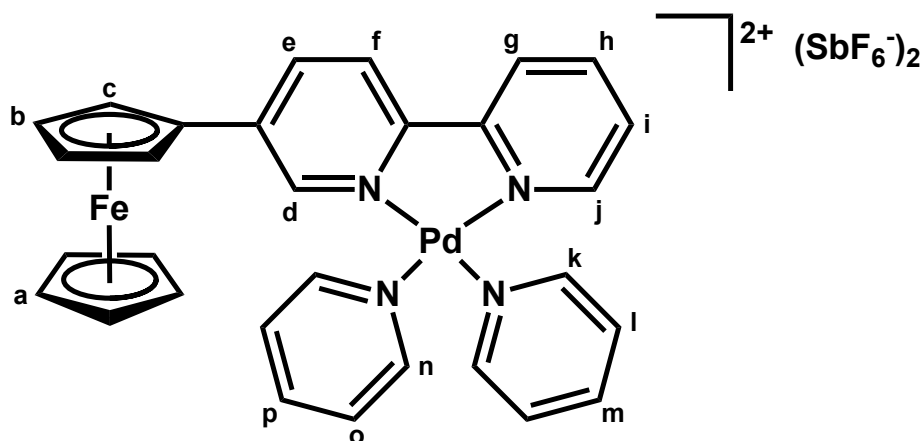
$[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ (15 mg, 0.059 mmol, 1.00 eq.) was added to a solution of **3a** (20 mg, 0.059 mmol, 1.00 eq.) in acetone (10 mL) and stirred for 30 minutes at room temperature, briefly sonicating during this time. The insoluble product precipitated and after addition of petroleum ether (10 mL) was isolated by filtration to give an orange solid (29 mg, 97%). Mp >230 °C; IR: ν (cm^{-1}) 3098 (w), 1603 (m), 1480 (m), 1439 (m), 1174 (s), 841 (s), 811 (s), 779 (s), 740 (s), 717 (s); Anal. Calc. for $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{FeN}_2\text{Pd}$: C, 46.42; H, 3.12; N, 5.41. Found: C, 46.67; H, 3.23; N, 5.40.

1.3.2 Synthesis of $[\text{Pd}(\text{5-ferrocenyl-5'-methyl-2,2'-bipyridine})\text{Cl}_2]$ (**4b**)



$[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ (15 mg, 0.028 mmol, 1.00 eq.) in acetone (2 mL) was layered over a solution of CH_2Cl_2 (2 mL) containing **3b** (20 mg, 0.028 mmol, 1.00 eq.) and allowed to slowly diffuse together. The insoluble product formed as X-ray quality orange crystals (27 mg, 90%). Mp >230 °C; IR: ν (cm^{-1}) 3076 (w), 1604 (w), 1489 (m), 1408 (m), 1377 (m), 1160 (m), 827 (s), 803 (s), 714 (m), 494 (s); Anal. Calc. for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{FeN}_2\text{Pd}$: C, 47.45; H, 3.41; N, 5.27. Found: C, 47.50; H, 3.35; N, 5.27.

1.3.3 Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine)(pyridine)₂](SbF₆)₂ (5a)



A solution of pyridine (24 μ L, 0.294 mmol, 2.00 eq.) in acetone (5 mL) was added to a suspension of [Pd(MeCN)₂Cl₂] (38 mg, 0.147 mmol, 1.00 eq.) in acetone (5 mL) and stirred for 30 minutes. AgSbF₆ (101 mg, 0.294 mmol, 2.00 eq.) in acetone (5 mL) was added and the solution was stirred for a further 30 minutes before the AgCl precipitate was removed via filtration. **3a** (50 mg, 0.147 mmol, 1.00 eq.) in acetone (5 mL) was added and the solution was stirred for 30 minutes. The crude product was obtained by precipitation upon addition of diethyl ether then purified by re-crystallisation from acetone via vapour diffusion of diethyl ether. Finally, after physical separation from a [Pd(pyridine)₄](SbF₆)₂ impurity \sim 5 mg, the product was isolated as purple needles (99 mg, 63%). Mp >230 $^{\circ}$ C; ¹H NMR (400 MHz, *d*₆-acetone) δ 9.57 (d, *J* = 5.5 Hz, 2H, H_k), 9.45 (d, *J* = 5.5 Hz, 2H, H_n), 8.68 (d, *J* = 8.1 Hz, 1H, H_j), 8.56 (s, 1H, H_o), 8.58 – 8.50 (m, 2H, H_{f/g}), 8.48 (t, *J* = 7.8 Hz, 1H, H_m), 8.34 (t, *J* = 7.8 Hz, 1H, H_p), 8.08 (t, *J* = 7.5 Hz, 2H, H_l), 7.94 (t, *J* = 7.6 Hz, 2H, H_o), 7.76 – 7.70 (m, 2H, H_{h/i}), 7.36 (s, 1H, H_e), 4.64 (s, 2H, H_c), 4.56 (s, 2H, H_b), 4.06 (s, 5H, H_a); ¹³C NMR (125 MHz, *d*₆-acetone) δ 157.6, 152.8, 152.6, 151.2, 146.9, 144.1, 143.8, 143.2, 142.8, 138.9, 129.6, 129.5, 128.7, 128.6, 125.3, 124.9, 78.1, 72.6, 71.1, 68.1; IR: ν (cm⁻¹) 1594 (w), 1476 (m), 1454 (m), 1290 (w), 1247 (w), 1074 (w), 1020 (w), 788 (m), 762 (m), 698 (m), 653 (s); HRESI-MS (MeOH/acetone) *m/z* = 761.9091 [**5a**-Pyr-SbF₆]⁺ (calc. for C₂₅H₂₁F₆FeN₃PdSb 761.9071), *m/z* = 559.9831 [**5a**+Cl-Pyr-2SbF₆]⁺ (calc. for C₂₅H₂₁ClFeN₃Pd 559.9813); UV-Vis (acetone) λ_{max} (ϵ / L mol⁻¹ cm⁻¹): 348 (31100), 550 (5200); Anal. Calc. for C₃₀H₂₆FeN₄PdSb₂F₁₂: C, 33.48; H, 2.43; N, 5.21. Found: C, 3.83; H, 2.48; N, 5.14.

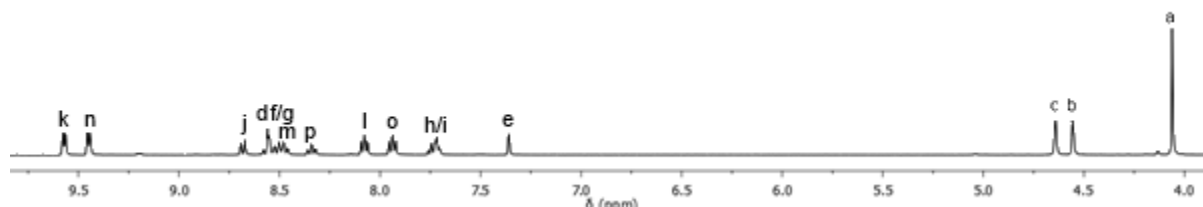


Figure S11 ¹H NMR spectrum (400 MHz, *d*₆-acetone) of **5a**.

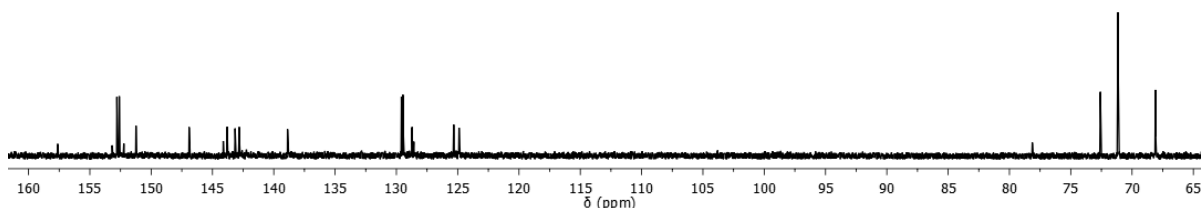
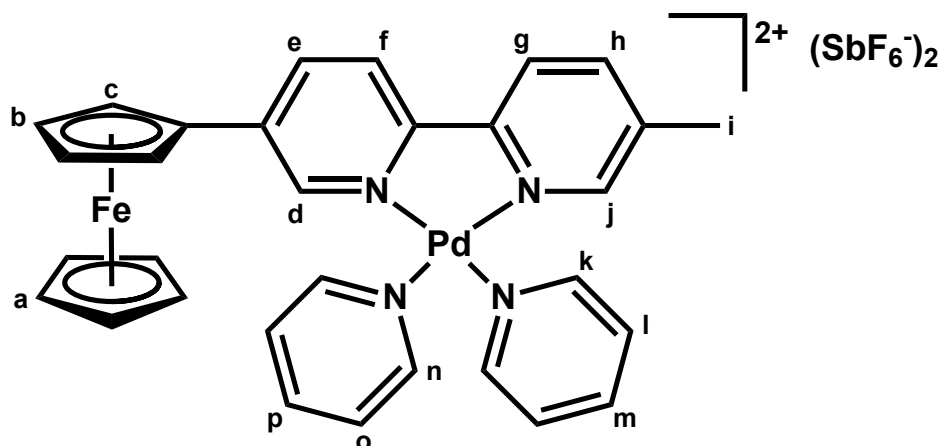


Figure S12 ^{13}C NMR spectrum (125 MHz, d_6 -acetone) of **5a**.

1.3.4 Synthesis of $[\text{Pd}(\text{5-ferrocenyl-5'-methyl-2,2'-bipyridine})(\text{pyridine})_2](\text{SbF}_6)_2$ (**5b**)



A solution of pyridine (23 μL , 0.282 mmol, 2.00 eq.) in acetone (5 mL) was added to a suspension of $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ (37 mg, 0.141 mmol, 1.00 eq.) in acetone (5 mL) and stirred for 30 minutes. AgSbF_6 (97 mg, 0.282 mmol, 2.00 eq.) in acetone (5 mL) was added and the solution was stirred for a further 30 minutes before the AgCl precipitate was removed via filtration. **3b** (50 mg, 0.141 mmol, 1.00 eq.) in acetone (5 mL) was added and the solution was stirred for 30 minutes. The crude product was obtained by precipitation upon addition of diethyl ether then purified by re-crystallisation from acetone via vapour diffusion of diethyl ether. Finally, after physical separation from a $[\text{Pd}(\text{pyridine})_4](\text{SbF}_6)_2$ impurity ~ 5 mg, the product was isolated as purple needles (111 mg, 70%). Mp >230 $^\circ\text{C}$; ^1H NMR (400 MHz, d_6 -acetone) δ 9.57 (d, $J = 6.3$ Hz, 2H, H_k), 9.43 (d, $J = 6.3$ Hz, 2H, H_n), 8.58 (d, $J = 8.2$ Hz, 2H, $\text{H}_{f/g}$), 8.52 (s, 1H, H_d), 8.48 (t, $J = 7.8$ Hz, 1H, H_m), 8.35 (s, 1H, H_j), 8.33 (t, $J = 7.7$ Hz, 1H, H_p), 8.07 (t, $J = 7.6$ Hz, 2H, H_l), 7.92 (t, $J = 7.6$ Hz, 2H, H_o), 7.55 (s, 1H, H_h), 7.32 (s, 1H, H_e), 4.62 (s, 2H, H_c), 4.54 (s, 2H, H_b), 4.05 (s, 5H, H_a), 2.33 (s, 3H, H_i); ^{13}C NMR (125 MHz, d_6 -acetone) δ 155.1, 152.9, 152.7, 151.0, 146.8, 144.2, 143.6, 143.2, 142.9, 140.3, 139.0, 129.7, 129.5, 129.5, 125.0, 124.4, 72.5, 71.2, 71.10, 68.1, 18.7; IR: ν (cm^{-1}) 1606 (w), 1486 (m), 1454 (m), 1291 (w), 1247 (w), 841 (m), 762 (m), 694 (m), 653 (s); HRESI-MS (MeOH/acetone) $m/z = 775.9209$ [**5b**-Pyr- SbF_6] $^+$ (calc. for $\text{C}_{26}\text{H}_{23}\text{F}_6\text{FeN}_3\text{PdSb}$ 775.9228), $m/z = 573.9945$ [**5b**+Cl-Pyr-2 SbF_6] $^+$ (calc. for $\text{C}_{26}\text{H}_{23}\text{ClFeN}_3\text{Pd}$ 573.9973); UV-Vis (acetone) λ_{max} ($\epsilon/\text{L mol}^{-1}\text{ cm}^{-1}$): 349 (34900), 547 (5200); Anal. Calc. for $\text{C}_{31}\text{H}_{28}\text{FeN}_4\text{PdSb}_2\text{F}_{12}$: C, 34.15; H, 2.59; N, 5.14. Found: C, 34.40; H, 2.69; N, 5.00.

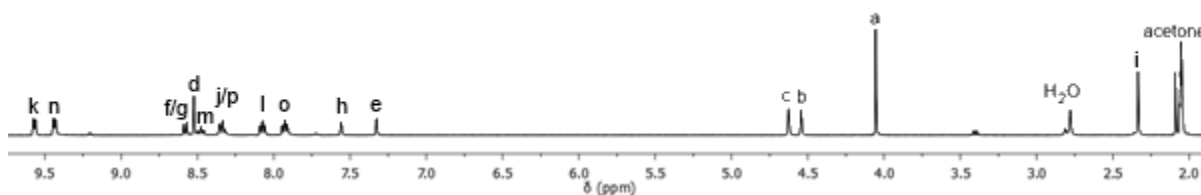


Figure S13 ^1H NMR spectrum (400 MHz, d_6 -acetone) of **5b**.

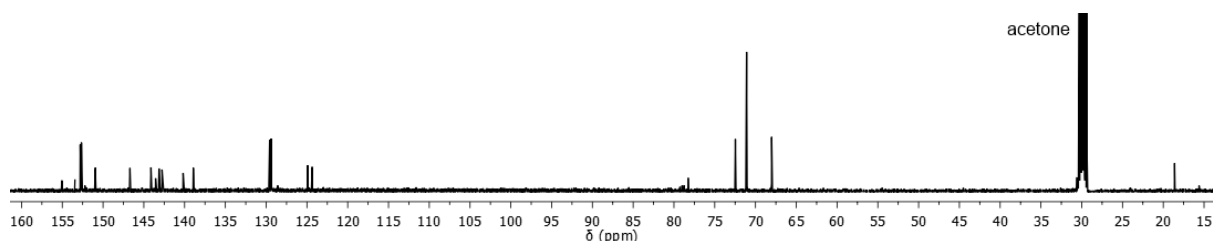
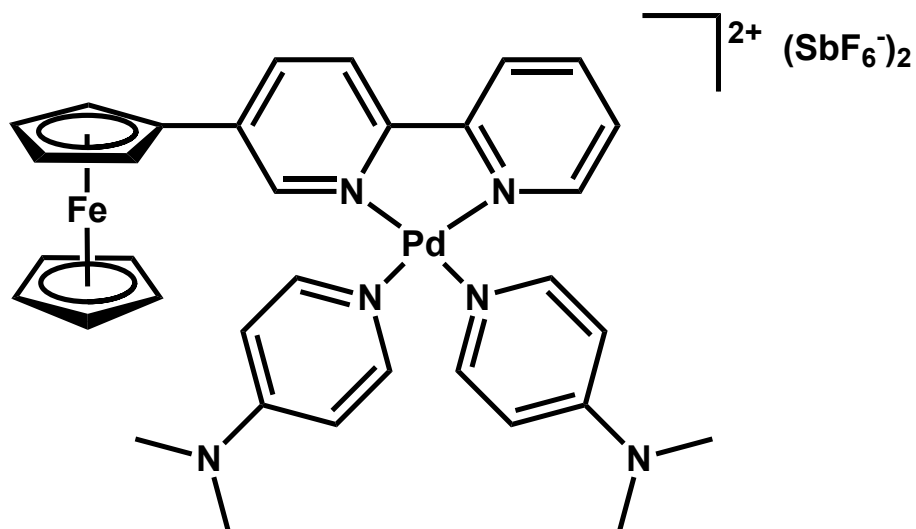


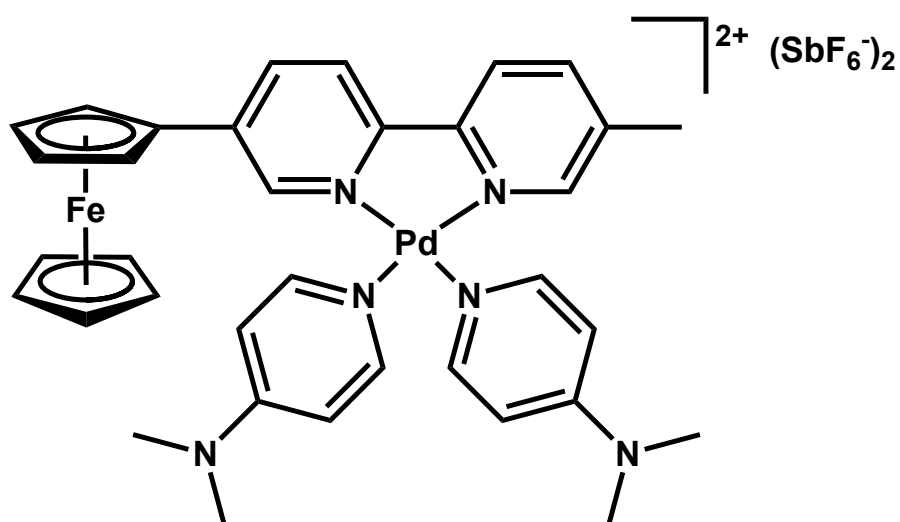
Figure S14 ^{13}C NMR spectrum (125 MHz, d_6 -acetone) of **5b**.

1.3.5 Synthesis of $[\text{Pd}(\text{5-ferrocenyl-2,2'}$ -bipyridine) $(\text{DMAP})_2](\text{SbF}_6)_2$ (**6a**)



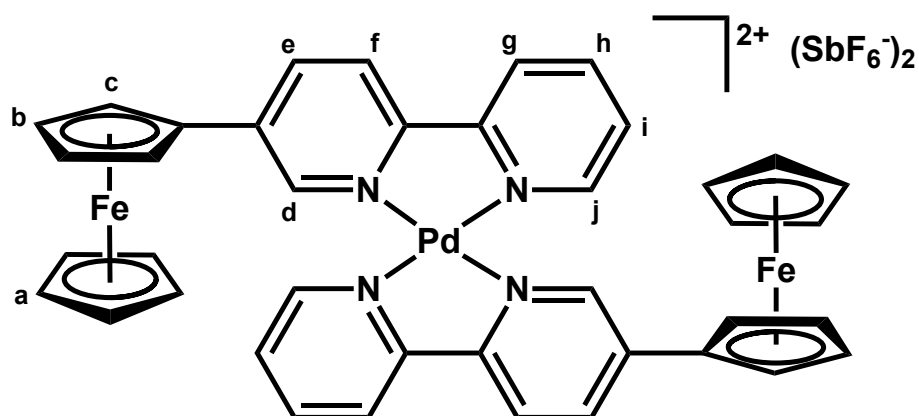
A solution of DMAP (14 mg, 0.118 mmol, 2.00 eq.) in acetone (5 mL) was added to a suspension of $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$ (15 mg, 0.059 mmol, 1.00 eq.) in acetone (5 mL) and stirred for 30 minutes. AgSbF_6 (40 mg, 0.118 mmol, 2.0 equiv.) in acetone (5 mL) was added and the solution was stirred for a further 30 minutes before the AgCl precipitate was removed via filtration. **3a** (20 mg, 0.059 mmol, 1.0 equiv.) in acetone (5 mL) was added and the solution was stirred for 30 minutes. The crude product was obtained by precipitation upon addition of petroleum ether then purified by re-crystallisation from acetone via vapour diffusion of diethyl ether. Finally, after physical separation from a $[\text{Pd}(\text{DMAP})_4](\text{SbF}_6)_2$ impurity ~ 5 mg, the product was isolated as purple blocks (48 mg, 71%). Mp >230 °C; IR: ν (cm^{-1}) 1619 (m), 1547 (m), 1475 (m), 1441 (m), 1394 (m), 1223 (m), 1077 (m), 1026 (m), 818 (m), 786 (m), 652 (s); HRESI-MS (MeOH/acetone) $m/z = 927.0359$ [**6a**- SbF_6] $^+$ (calc. for $\text{C}_{34}\text{H}_{36}\text{F}_6\text{FeN}_6\text{PdSb}$ 927.0327); Anal. Calc. for $\text{C}_{34}\text{H}_{36}\text{FeN}_6\text{PdSb}_2\text{F}_{12}$: C, 35.13; H, 3.12; N, 7.23. Found: C, 35.24; H, 3.26; N, 7.84.

1.3.6 Synthesis of [Pd(5-ferrocenyl-5'-methyl-2,2'-bipyridine)(DMAP)₂](SbF₆)₂ (**6b**)



A solution DMAP (14 mg, 0.113 mmol, 2.00 eq.) in acetone (5 mL) was added to a suspension of [Pd(MeCN)₂Cl₂] (15 mg, 0.056 mmol, 1.00 eq.) in acetone (5 mL) and stirred for 30 minutes. AgSbF₆ (40 mg, 0.113 mmol, 2.00 eq.) in acetone (5 mL) was added and the solution was stirred for a further 30 minutes before the AgCl precipitate was removed via filtration. **3b** (20 mg, 0.056 mmol, 1.00 eq.) in acetone (5 mL) was added and the solution was stirred for 30 minutes. The crude product was obtained by precipitation upon addition of petroleum ether then purified by re-crystallisation from acetone via vapour diffusion of diethyl ether. Finally, after physical separation from a [Pd(DMAP)₄](SbF₆)₂ impurity ~5 mg, the product was isolated as purple needles (51 mg, 77%). Mp >230 °C; IR: ν (cm⁻¹) 1618 (m), 1549 (m), 1485 (m), 1443 (m), 1394 (m), 1221 (m), 1073 (m), 1025 (m), 815 (m), 652 (s); HRESI-MS (MeOH/acetone) m/z = 617.0312 [**6b**+Cl-DMAP-2SbF₆]⁺ (calc. for C₂₈H₂₈ClFeN₄Pd 617.0392); Anal. Calc. for C₃₅H₃₈F₁₂FeN₆PdSb₂: C, 35.73; H, 3.26; N, 7.14. Found: C, 35.92; H, 3.33; N, 7.41.

1.3.7 Synthesis of [Pd(5-ferrocenyl-2,2'-bipyridine)]₂(SbF₆)₂ (9a)



3a (20 mg, 0.059 mmol, 2.00 eq.), [Pd(MeCN)₂Cl₂] (6 mg, 0.029 mmol, 1.00 eq.) and AgSbF₆ (20 mg, 0.059 mmol, 2.00 eq.) were combined in acetone (5 mL) and the resulting solution stirred for 30 minutes. The AgCl precipitate was removed via filtration before the purple product was recovered via precipitation upon addition of ether (34 mg, 92%). Mp >230 °C; ¹H NMR (500 MHz, *d*₆-acetone) δ 9.03-8.99 (m, 1H, H_j), 8.96 (s, 1H, H_d), 8.73-8.69 (m, 1H, H_f), 8.68-8.63 (m, 1H, H_e), 8.62-8.59 (m, 1H, H_g), 8.55-8.49 (m, 1H, H_h), 8.03-7.98 (m, 1H, H_i), 5.10 (s, 2H, H_c), 4.64 (s, 2H, H_b), 4.18 (s, 5H, H_a); ¹³C NMR (125 MHz, *d*₆-acetone) δ 160.5, 155.9, 153.3, 152.1, 148.1, 143.1, 138.6, 128.3, 124.9, 124.6, 78.9, 72.4, 71.2, 68.3; IR: ν (cm⁻¹) 1603 (w), 1440 (w), 787 (m), 655 (s); HRESI-MS (MeOH) *m/z* = 1022.9277 [**9a**-SbF₆]⁺ (calc. for C₄₀H₃₂F₆Fe₂N₄PdSb 1022.9316), *m/z* = 445.9719 [**9a**-FcBipy-2SbF₆]⁺ (calc. for C₂₀H₁₆FeN₂Pd 445.9703); UV-Vis (acetone) λ_{max} (ε/ L mol⁻¹ cm⁻¹): 333 (35700), 542 (6000); Anal. Calc. for C₄₀H₃₂Fe₂N₄PdSb₂F₁₂: C, 38.18; H, 2.56; N, 4.45. Found: C, 39.94; H, 2.20; N, 4.49.

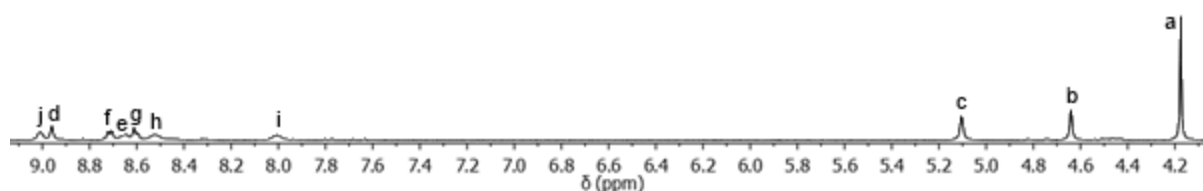


Figure S15 ¹H NMR spectrum (500 MHz, *d*₆-acetone) of **9a**.

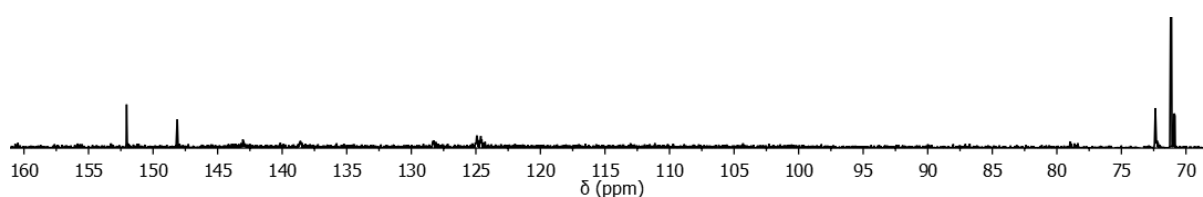
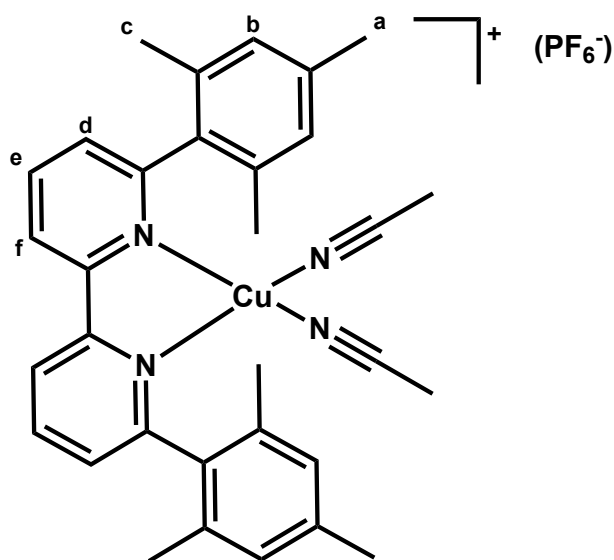


Figure S16 ¹³C NMR spectrum (125 MHz, *d*₆-acetone) of **9a**.

1.4 Copper(I) Complexation

1.4.1 [Cu(6,6'-dimesityl-2,2'-bipyridine)(MeCN)₂](PF₆) (10Cu)

The synthesis of this compound has previously been reported by Schmittl in quantitative yield.²



To a solution of [Cu(MeCN)₄](PF₆) (24 mg, 0.064 mmol, 1.00 eq.) in CD₃CN (0.75 mL) was added a solution of **7** (25 mg, 0.064 mmol, 1.00 eq.) in CD₃CN (0.75 mL). The mixture was stirred for 15 minutes, the resulting yellow solution subjected to ¹H NMR spectroscopy and mass spectrometry, and the complex was found to form in quantitative yield. ¹H NMR (400 MHz, CD₃CN) δ 8.34 (d, *J* = 8.1 Hz, 2H, H_f), 8.15 (t, *J* = 7.8 Hz, 2H, H_e), 7.52 (d, *J* = 7.6 Hz, 2H, H_d), 6.94 (s, 4H, H_b), 2.28 (s, 6H, H_a), 1.91 (s, 12H, H_c). HRESI-MS (MeOH): *m/z* = 496.1739 [**10Cu**-MeCN-PF₆]⁺ (calc. for C₃₀H₃₁CuN₃ 496.1809), *m/z* = 473.1610 [**10Cu**-2MeCN-PF₆+H₂O]⁺ (calc. for C₂₈H₃₀OCuN₂ 473.1649), *m/z* = 455.1491 [**10Cu**-MeCN-PF₆]⁺ (calc. for C₂₈H₂₈CuN₂ 455.1543).

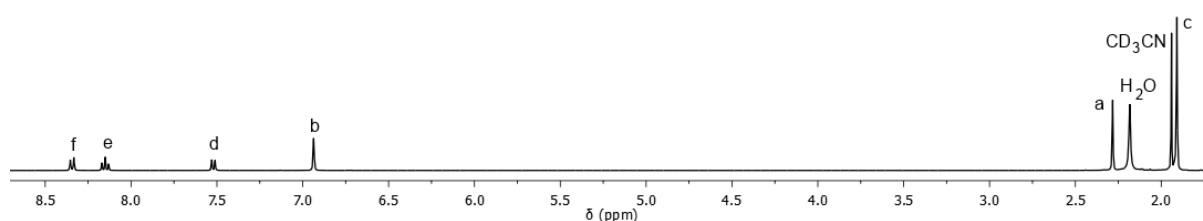
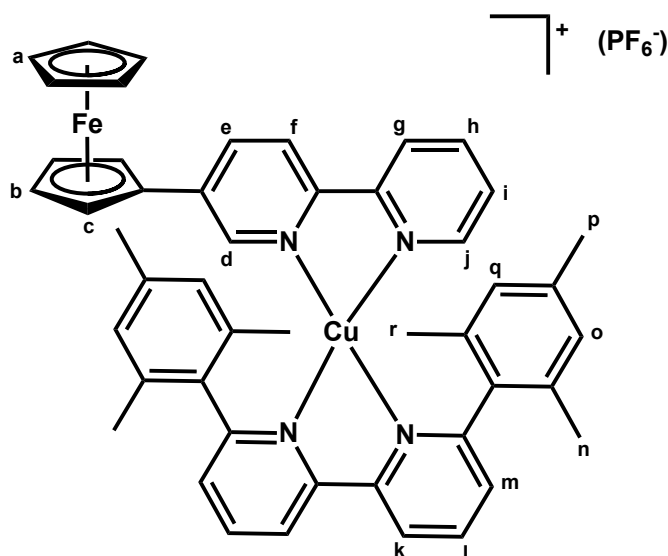


Figure S17 ¹H NMR spectrum (400 MHz, CD₃CN) of **10Cu**.

1.4.2 [Cu(6,6'-dimesityl-2,2'-bipyridine)(5-ferrocenyl-2,2'-bipyridine)]PF₆ (**11a**)



[Cu(MeCN)₄]PF₆ (22 mg, 0.059 mmol, 1.00 eq.) was dissolved in acetone (3 mL) and **10** (23 mg, 0.059 mmol, 1.00 eq.), also dissolved in acetone (3 mL), was added. The mixture was stirred for 15 minutes to give a yellow solution. **3a** (20 mg, 0.059 mmol, 1.00 eq.) was dissolved in acetone (3 mL) and added to this solution. The mixture was stirred for a further 15 minutes, then filtered through a cotton wool plug and vapour diffused (acetone/petrol) in order to obtain dark orange crystals (45 mg, 82%). Mp >230 °C; ¹H NMR (400 MHz, CDCl₃) 8.49 (d, *J* = 8.1 Hz, 2H, H_k), 8.23 (t, *J* = 7.8 Hz, 2H, H_l), 8.06 (s, 1H, H_d), 8.05 (d, *J* = 7.9 Hz, 1H, H_j), 7.98 (dd, *J* = 8.5, 1.9 Hz, 1H, H_e), 7.93 – 7.76 (m, 3H, H_{f/g/h}), 7.48 (d, *J* = 7.5 Hz, 2H, H_m), 7.33 (t, *J* = 6.0 Hz, 1H, H_i), 6.13 (s, 2H, H_q or H_o), 6.12 (s, 2H, H_q or H_o), 4.69 (s, 2H, H_c), 4.47 (s, 2H, H_b), 4.10 (s, 5H, H_a), 1.85 (s, 6H, H_p), 1.75 (s, 6H, H_r or H_n), 1.71 (s, 6H, H_r or H_n); ¹³C NMR (125 MHz, *d*₆-acetone) δ 159.3, 153.3, 152.2, 149.3, 149.1, 145.9, 139.5, 139.4, 138.5, 138.1, 138.0, 135.6, 135.5, 134.5, 128.1, 128.0, 127.9, 125.8, 121.3, 121.1, 121.0, 80.5, 71.2, 10.6, 67.5, 20.8, 20.6, 20.4; IR: ν (cm⁻¹) 2917 (w), 1592 (m), 1559 (m), 829 (s), 555 (s); HRESI-MS (MeOH): *m/z* = 795.2176 [**11a**-PF₆]⁺ (calc. for C₄₈H₄₄CuFeN₄ 795.2208); UV-Vis (acetone) λ_{max} (ε/ L mol⁻¹ cm⁻¹): 327 (29800), 394 (4900), 479 (7500); Anal. Calc. for C₄₈H₄₄CuFeN₄PF₆: C, 61.25; H, 4.71; N, 5.95. Found: C, 61.07; H, 4.70; N, 5.88.

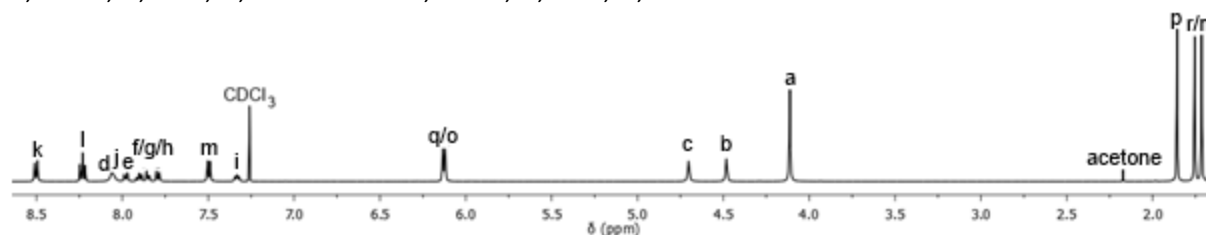


Figure S18 ¹H NMR spectrum (400 MHz, CDCl₃) of **11a**.

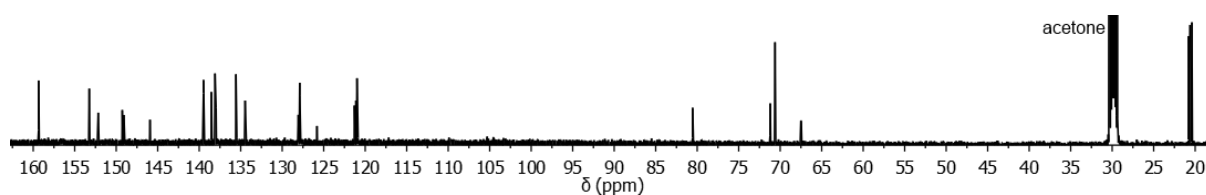
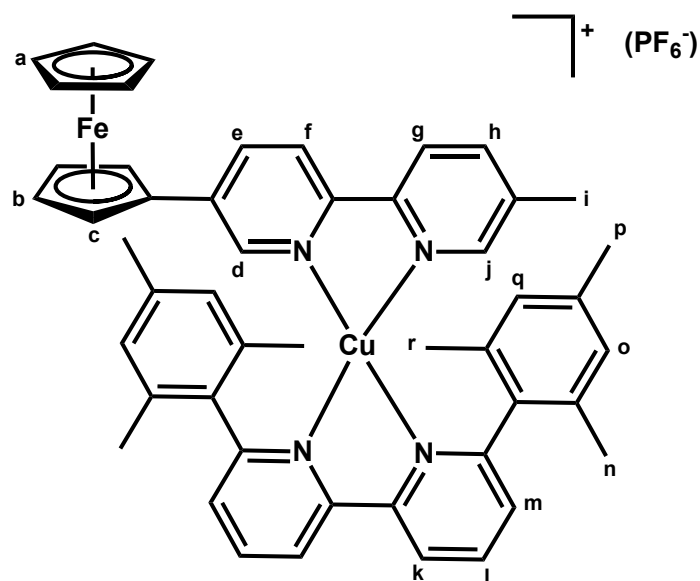


Figure S19 ¹³C NMR spectrum (125 MHz, *d*₆-acetone) of **11a**.

1.4.3 [Cu(6,6'-dimesityl-2,2'-bipyridine)(5-ferrocenyl-5'-methyl-2,2'-bipyridine)]PF₆ (**11b**)



[Cu(MeCN)₄]PF₆ (21 mg, 0.056 mmol, 1.00 eq.) was dissolved in acetone (3 mL) and **10** (22 mg, 0.056 mmol, 1.00 eq.), also dissolved in acetone (3 mL), was added. The mixture was stirred for 15 minutes to give a yellow solution. **3b** (20 mg, 0.056 mmol, 1.00 eq.) was dissolved in acetone (3 mL) and added to this solution. The mixture was stirred for 15 minutes, then filtered through a cotton wool plug and vapour diffused (acetone/petrol) in order to obtain dark orange crystals (44 mg, 82%). Mp >230 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, *J* = 7.8 Hz, 2H, H_k), 8.23 (t, *J* = 7.8 Hz, 2H, H_l), 8.05 (s, 1H, H_d), 7.94 (d, *J* = 7.8 Hz, 1H, H_e), 7.88 (s, 1H, H_i), 7.76 – 7.67 (m, 3H, H_{f/g/h}), 7.50 (d, *J* = 7.2 Hz, 2H, H_m), 6.13 (s, 4H, H_{q/o}), 4.70 (s, 2H, H_c), 4.48 (s, 2H, H_b), 4.11 (s, 5H, H_a), 2.36 (s, 3H, H_i), 1.86 (s, 6H, H_p), 1.77 (s, 6H, H_r or H_n), 1.72 (s, 6H, H_r or H_n); ¹³C NMR (125 MHz, *d*₆-acetone) δ 159.3, 153.2, 149.8, 149.4, 149.3, 145.8, 139.4, 138.9, 138.5, 138.2, 138.1, 136.0, 135.6, 135.5, 134.4, 128.0, 127.9, 127.9, 121.0, 120.9, 120.7, 80.7, 71.1, 70.6, 67.4, 20.8, 20.6, 20.3, 18.1; IR: ν (cm⁻¹) 2921 (w), 1482 (m), 1408 (m), 834 (s), 759 (m), 731 (m); HRESI-MS (MeOH): *m/z* = 809.2398 [**11b**-PF₆]⁺ (calc. for C₄₉H₄₆CuFeN₄ 809.2364); UV-Vis (acetone) λ_{max} (ε/ L mol⁻¹ cm⁻¹): 329 (25200), 394 (5700), 473 (8600); Anal. Calc. for C₄₉H₄₆CuFeN₄PF₆: C, 61.61; H, 4.85; N, 5.66. Found: C, 61.61; H, 5.04; N, 5.68.

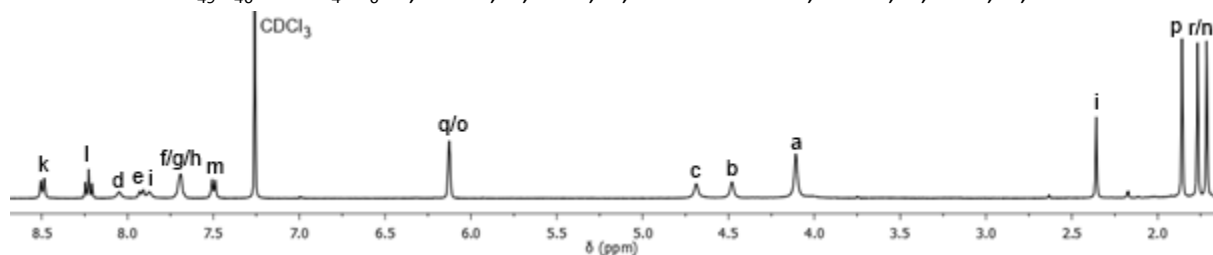


Figure S20 ¹H NMR spectrum (400 MHz, CDCl₃) of **11b**.

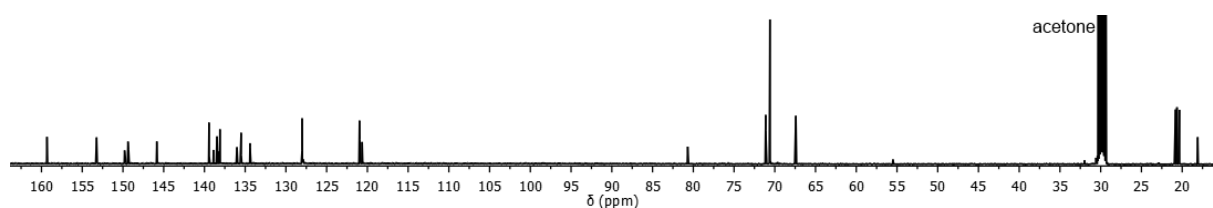


Figure S21 ¹³C NMR spectrum (125 MHz, *d*₆-acetone) of **11b**.

2 Pertinent ^1H NMR Stackplots

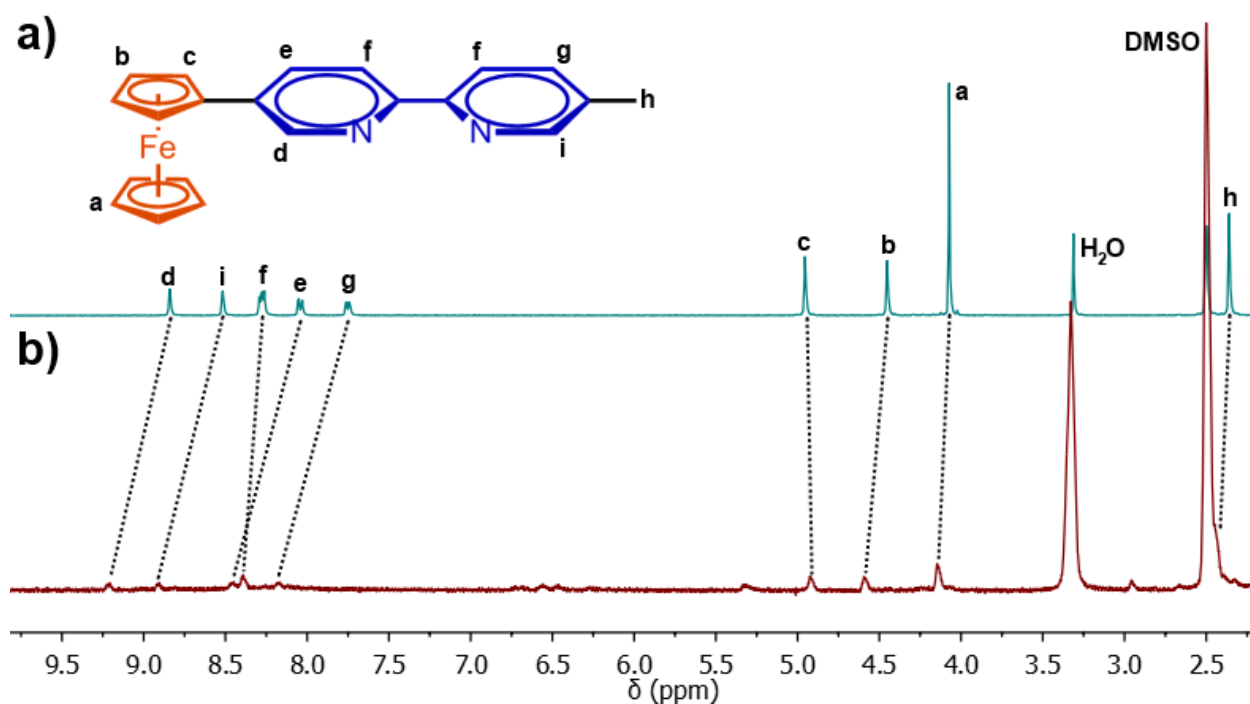


Figure S22 Stacked ^1H NMR spectra (d_6 -DMSO, 298 K) of a) the free ligand **3b** and b) the PdCl_2 complex **4b**.

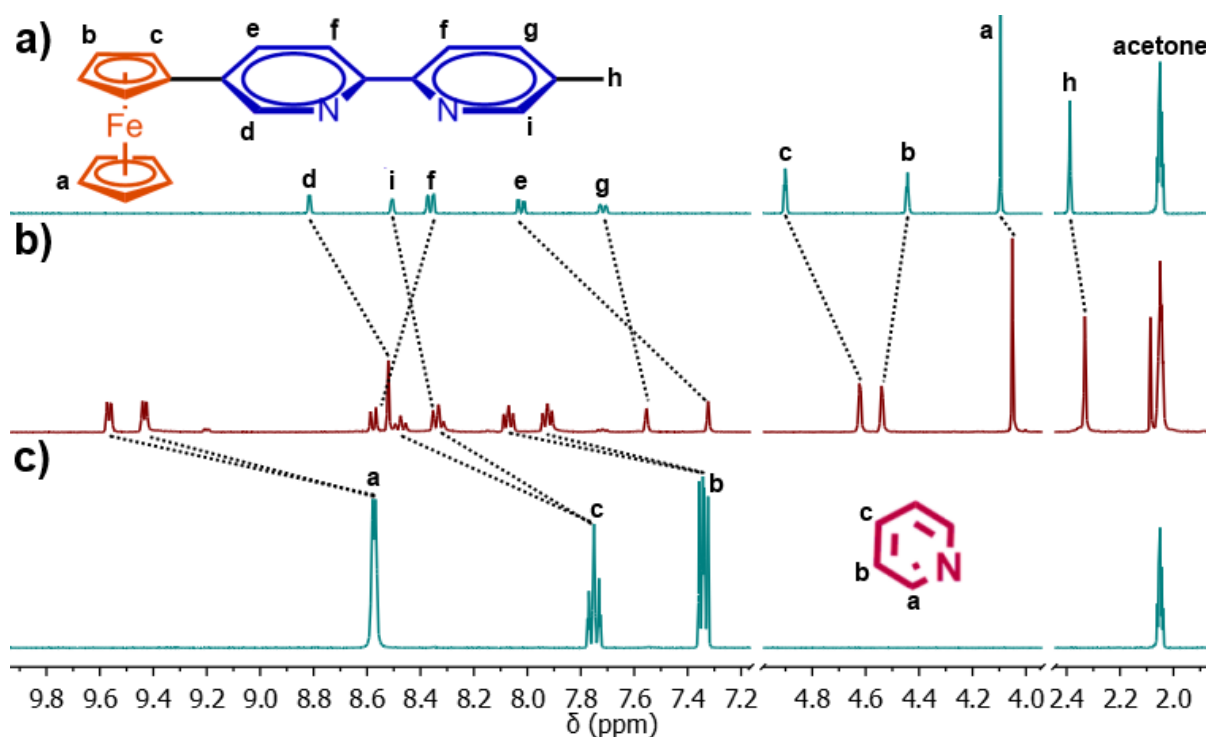


Figure S23 Stacked ^1H NMR spectra (d_6 -acetone, 298 K) of a) the free ligand **3b**, b) the PdPy_2 complex **5b**, and c) pyridine.

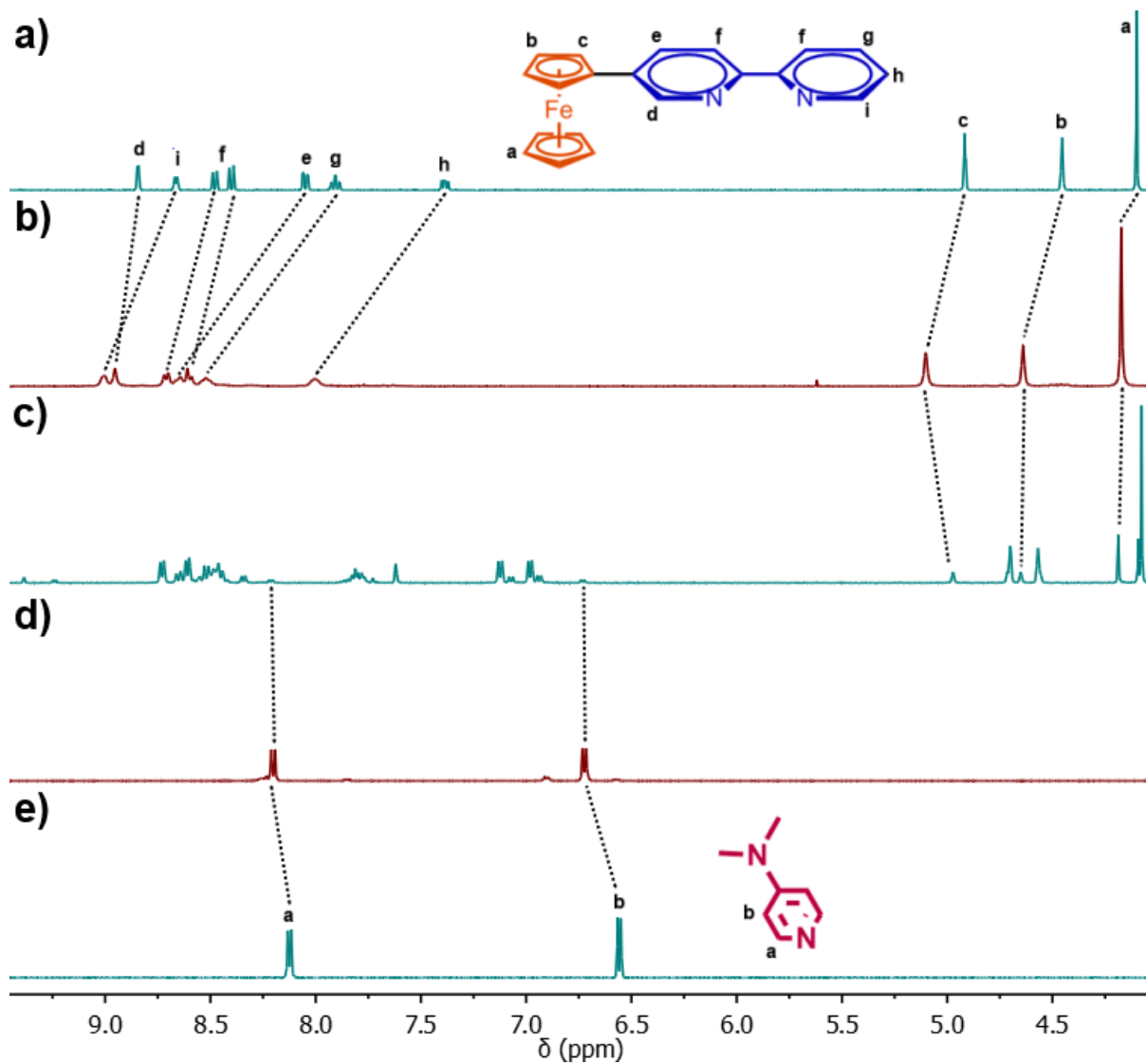


Figure S24 Stacked ^1H NMR spectra (d_6 -acetone, 298 K) of a) **3a**, b) $[\text{Pd}(\text{FcBipy})_2](\text{SbF}_6)_2$ (**9a**), c) the mixture of products resulting from the dissolution of **6a**, d) $[\text{Pd}(\text{DMAP})_4](\text{SbF}_6)_2$ (**8**), and e) DMAP.

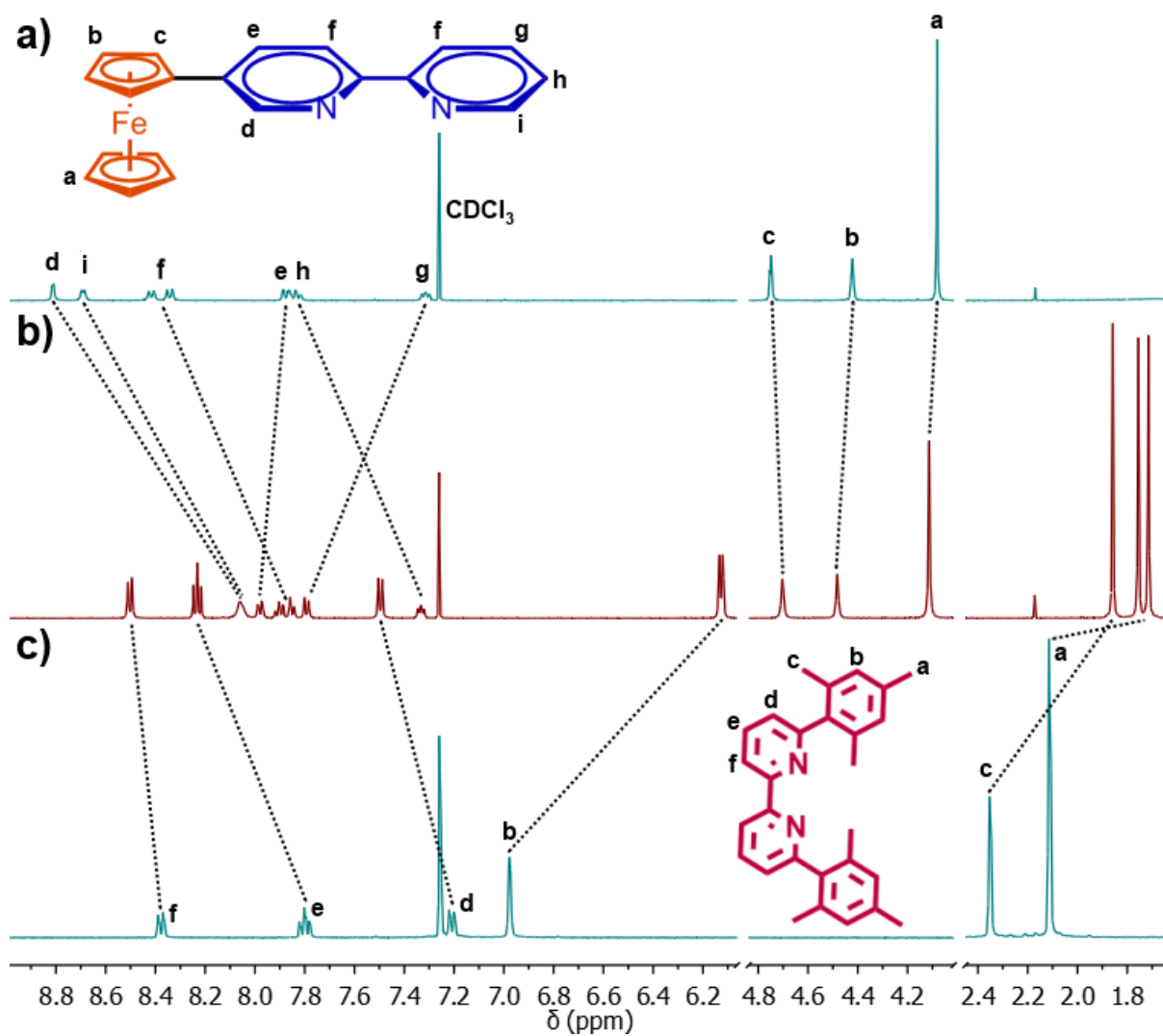


Figure S25 Stacked ^1H NMR spectra (CDCl₃, 298 K) of a) the free ligand **3a**, b) the Cu(I) complex **11b**, and c) the ligand **10**.

3 Representative Mass Spectra

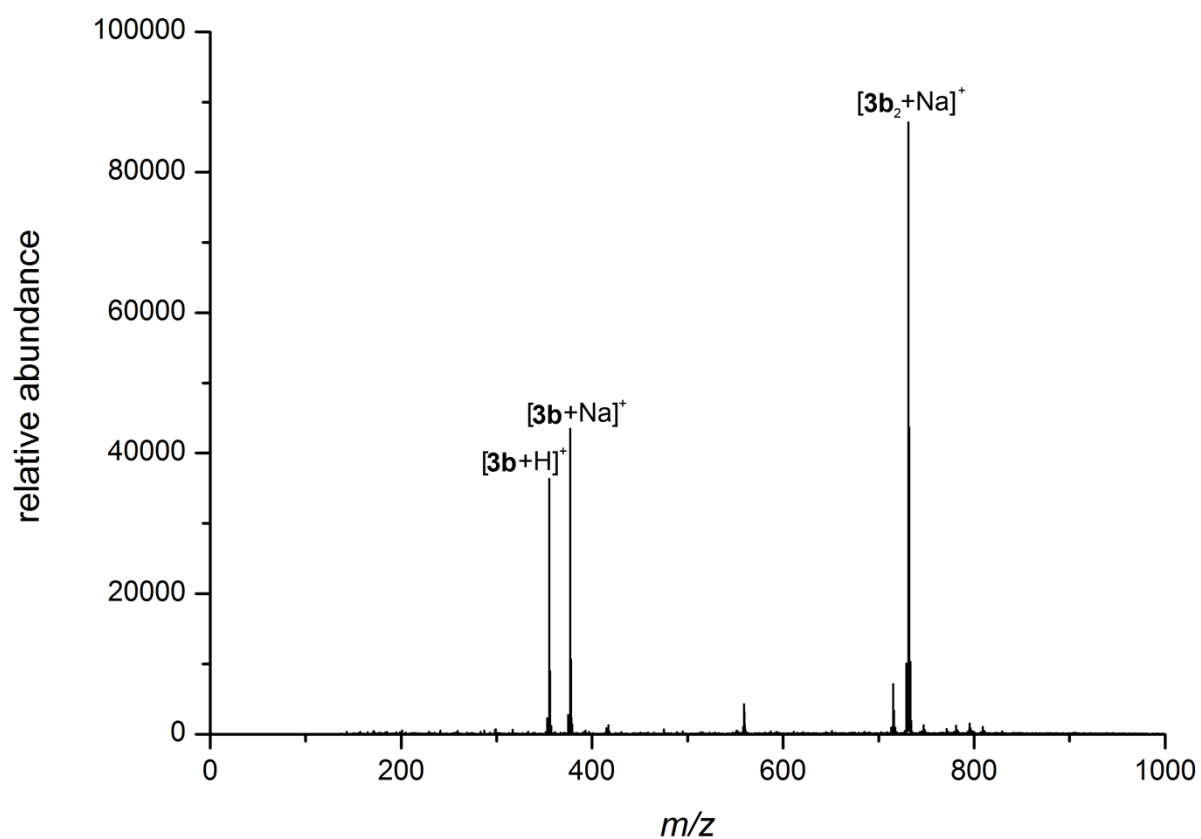


Figure S26 Full mass spectrum (MeOH) of ligand **3b** with relevant peaks annotated.

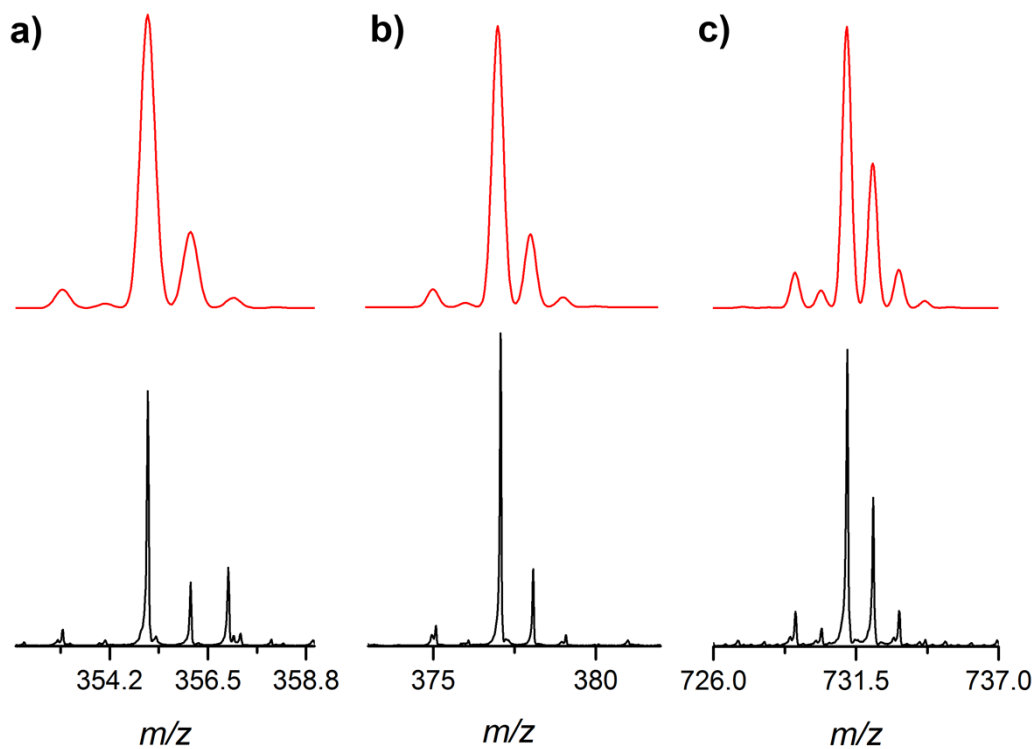


Figure S27 The calculated (red trace) and experimental (black trace) isotope patterns for a) $[3b+H]^+$, b) $[3b+Na]^+$, and c) $[3b_2+Na]^+$.

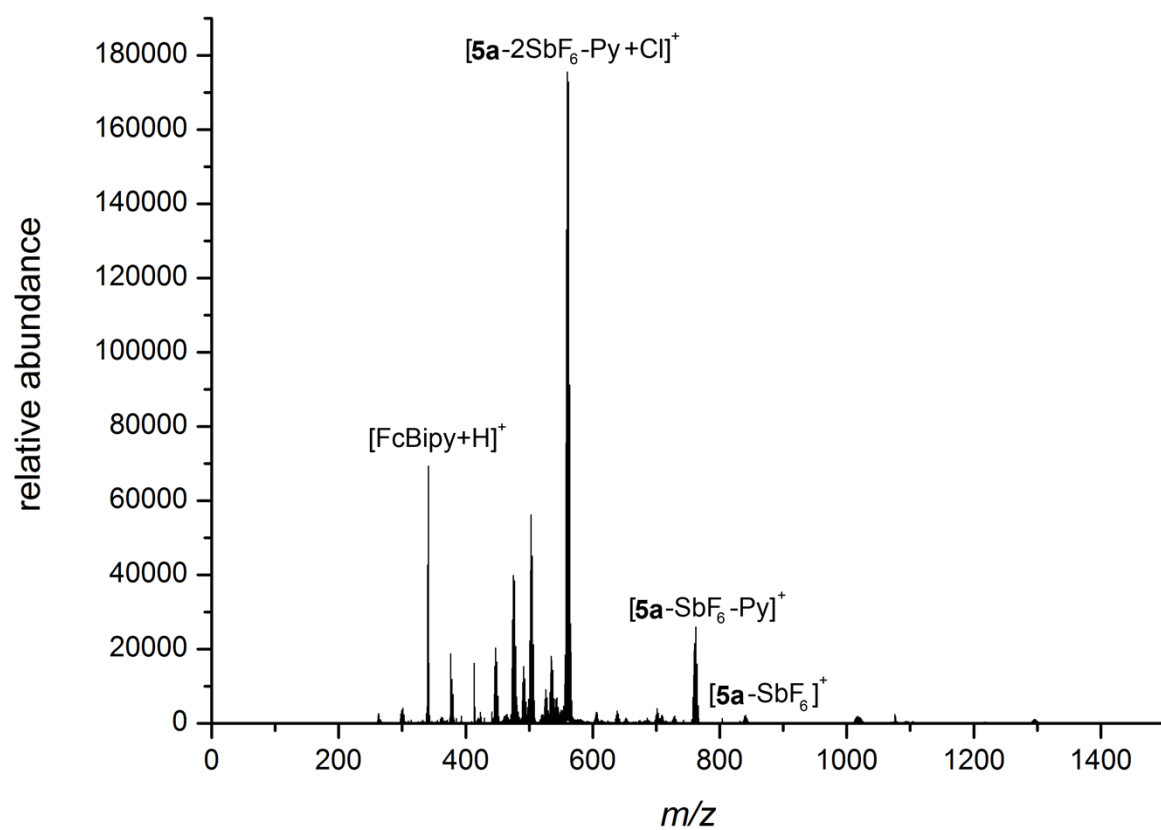


Figure S28 Full mass spectrum (MeOH/acetone) of complex **5a** with relevant peaks annotated.

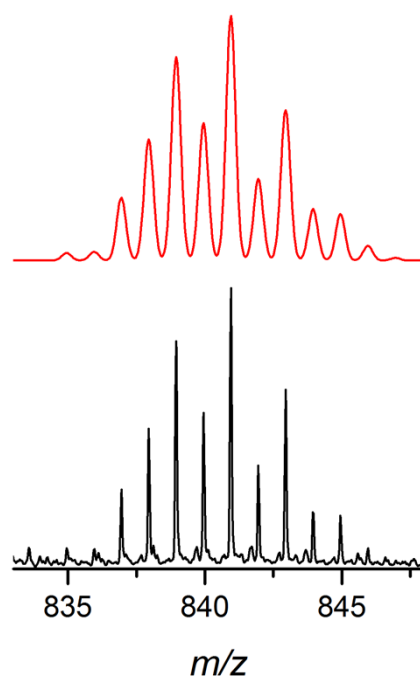


Figure S29 The calculated (red trace) and experimental (black trace) isotopic pattern of $[5a-SbF_6]^+$.

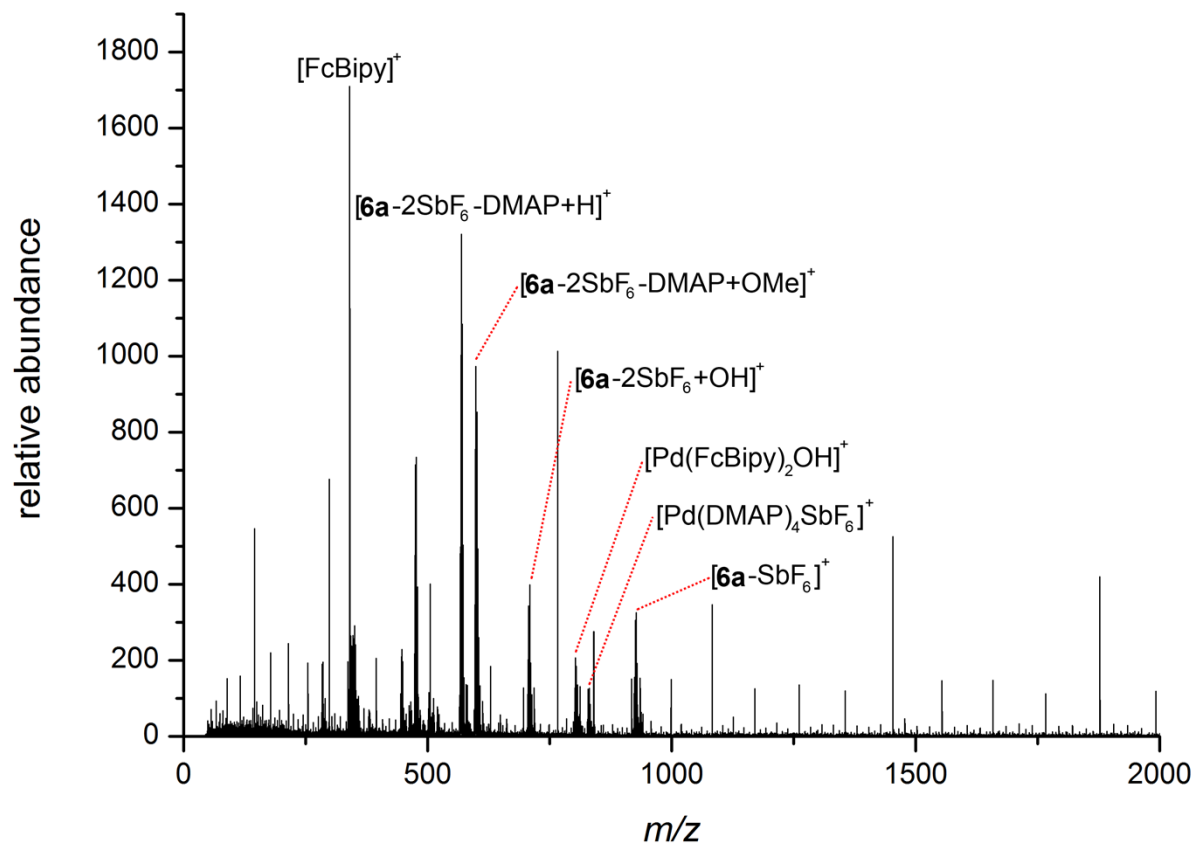


Figure S30 Full mass spectrum (MeOH/acetone) of complex **6a** with relevant peaks annotated.

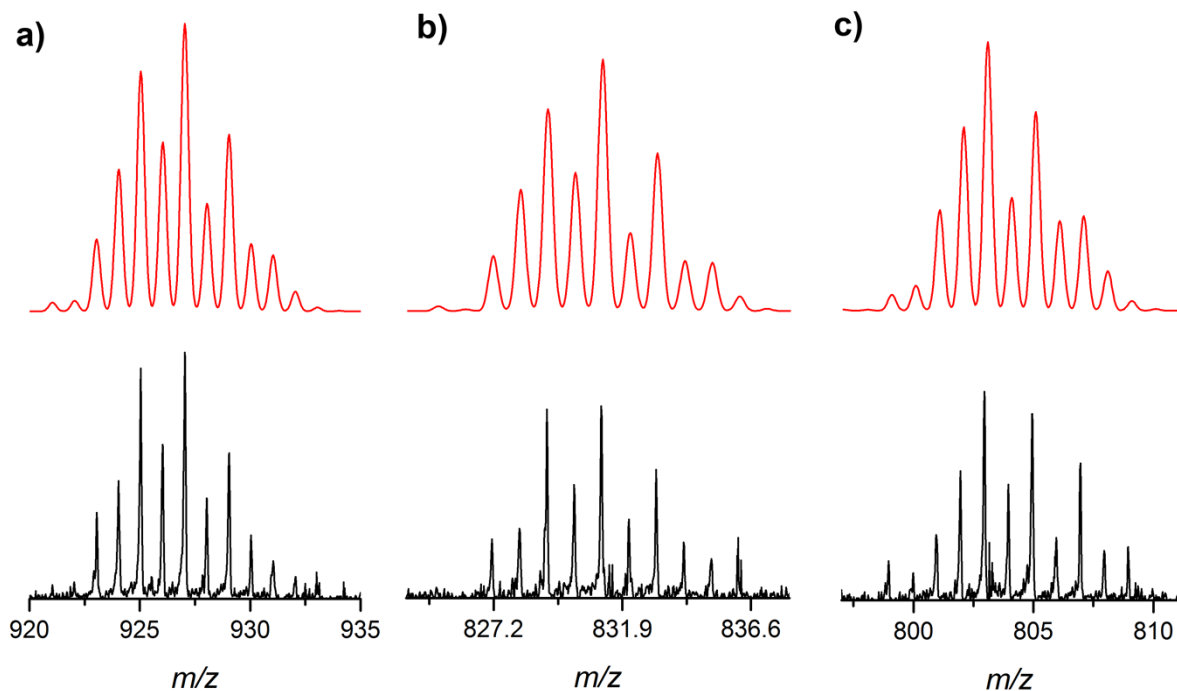


Figure S31 The calculated (red trace) and experimental (black trace) isotope patterns for a) $[6a-SbF_6]^+$, b) $[Pd(DMAP)_4SbF_6]^+$, and c) $[Pd(FcBipy)_2OH]^+$.

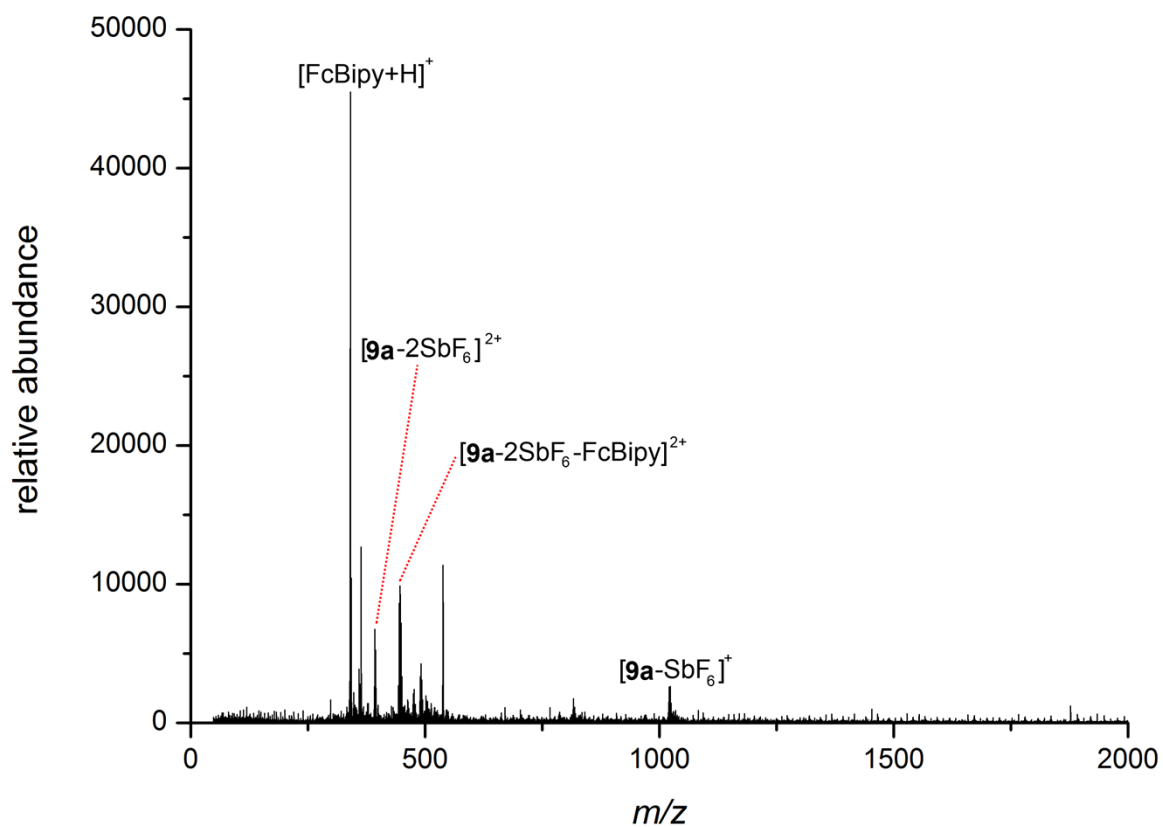


Figure S32 Full mass spectrum (MeOH/acetone) of complex **9a** with relevant peaks annotated.

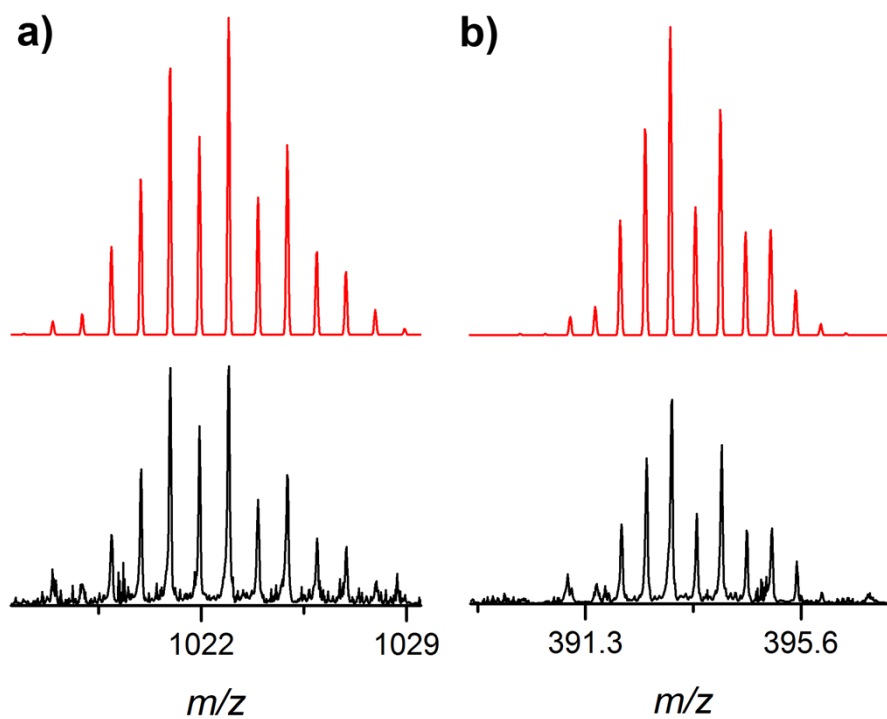


Figure S33 The calculated (red trace) and experimental (black trace) isotope patterns for a) $[\mathbf{9a}-\text{SbF}_6]^+$, and b) $[\mathbf{9a}-2\text{SbF}_6]^{2+}$.

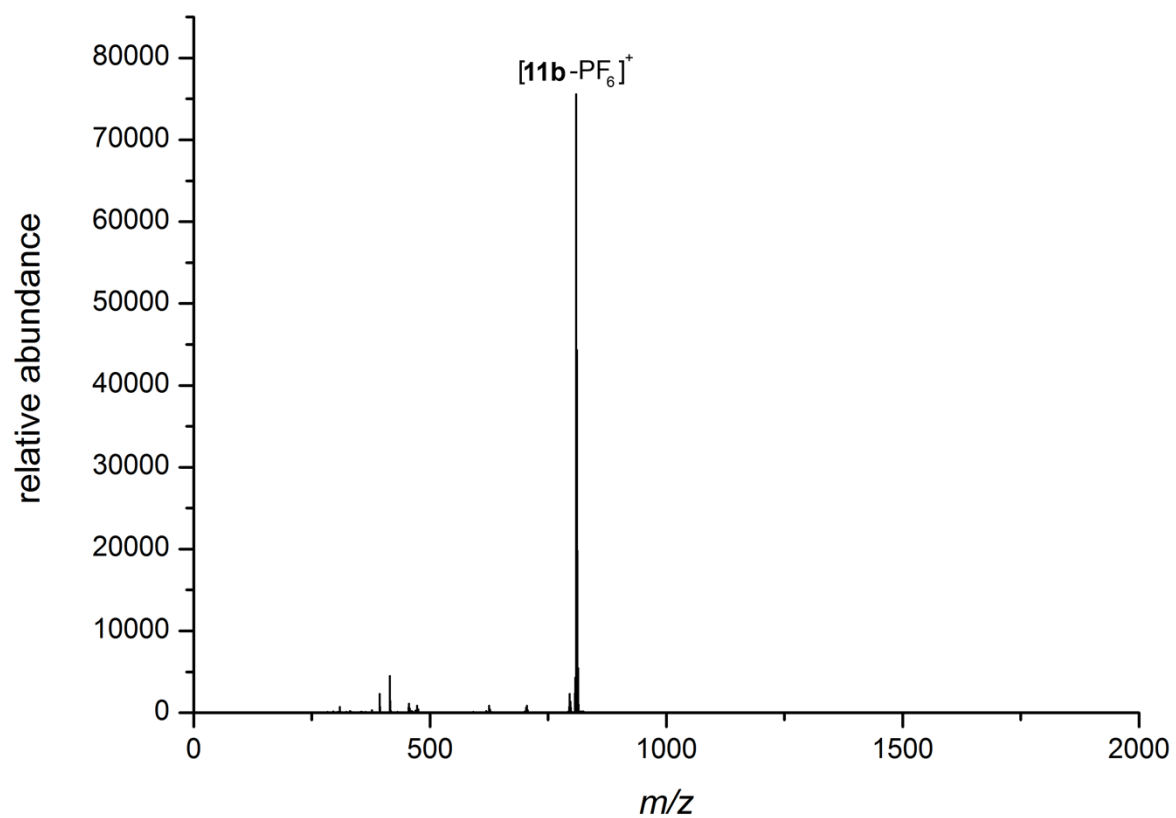


Figure S34 Full mass spectrum (MeOH) of complex **11b** with relevant peaks annotated.

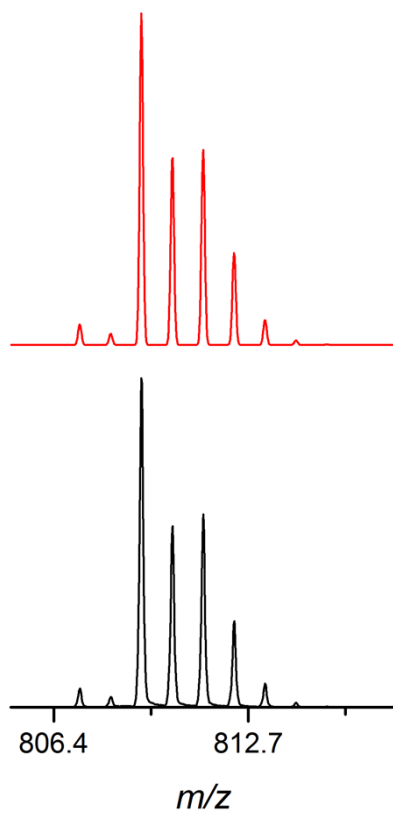


Figure S35 The calculated (red trace) and experimental (black trace) isotopic pattern of $[11b-PF_6]^+$.

4 UV-Vis Spectra

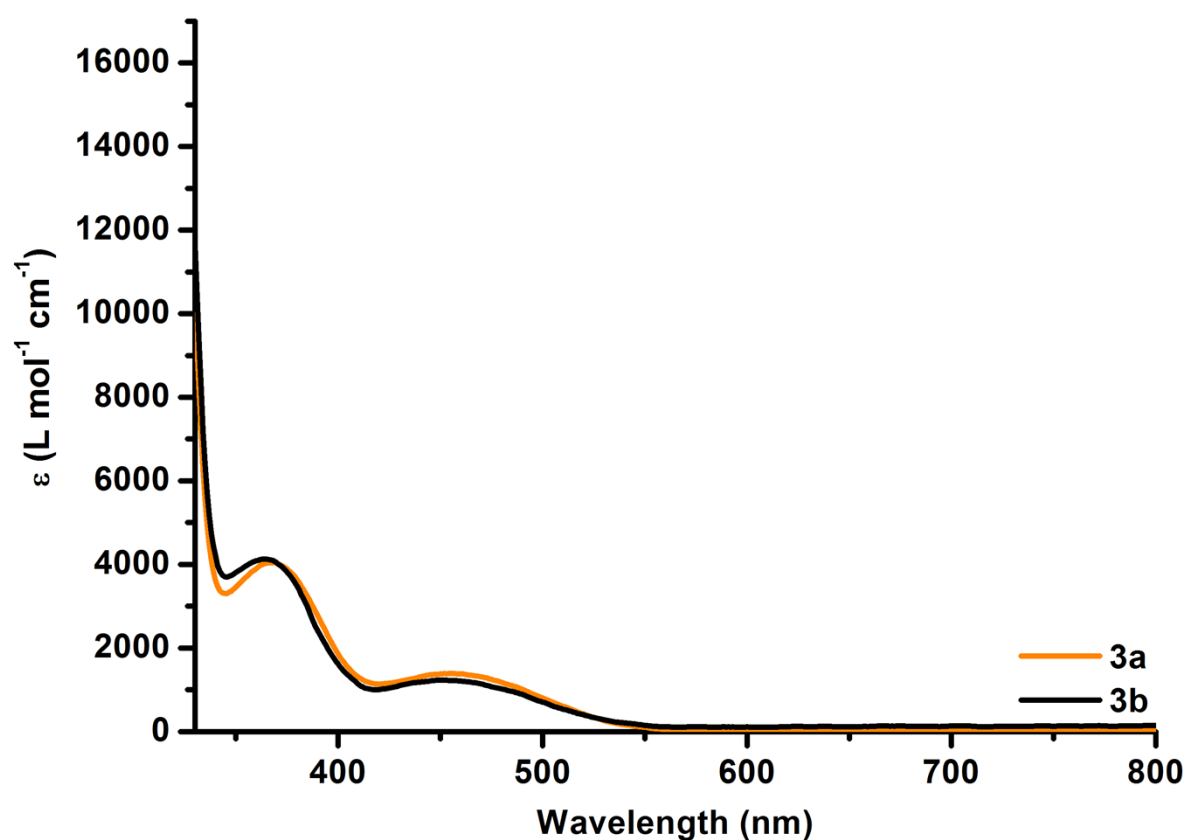


Figure S36 UV-Vis spectra of the FcBipy ligands **3a** and **3b** in acetone ($\sim 1 \times 10^{-5}$ M).

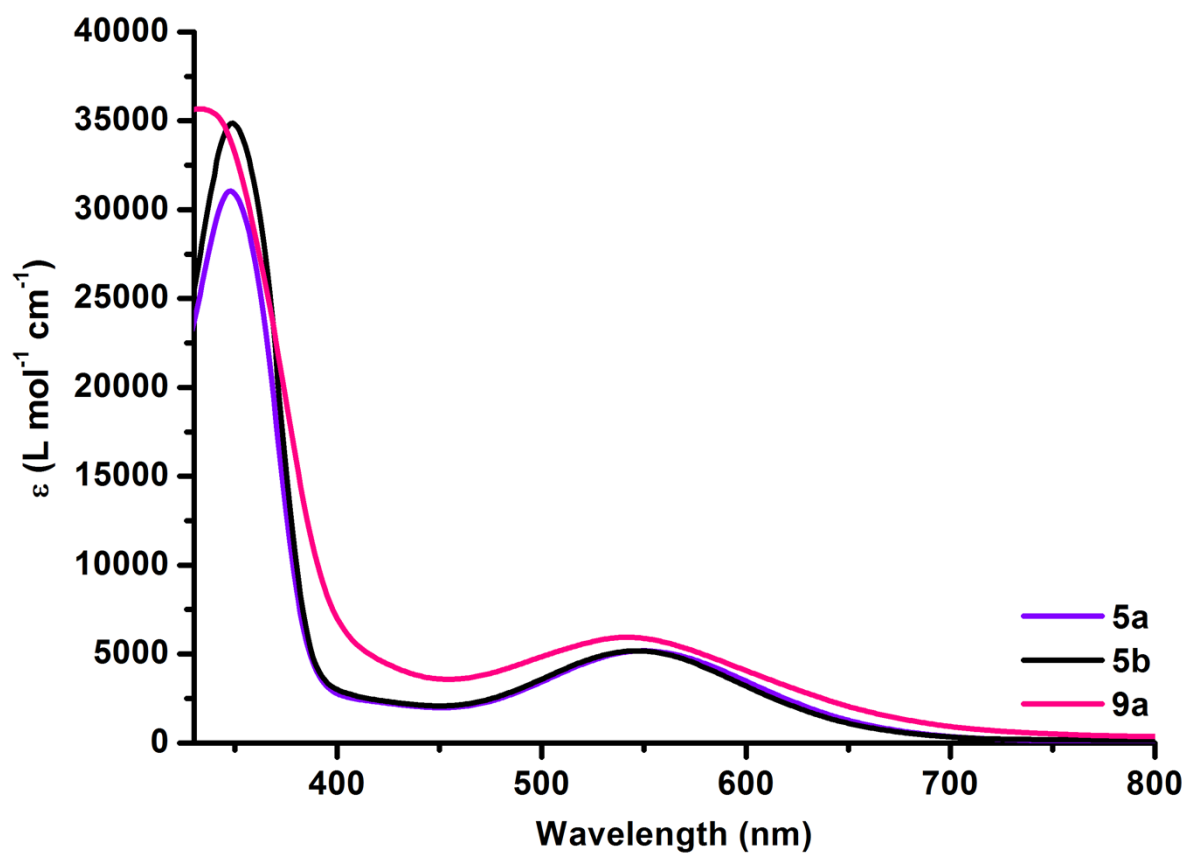


Figure S37 UV-Vis spectra of the Pd(II) complexes **5a**, **5b**, and **9a** in acetone ($\sim 1 \times 10^{-5}$ M).

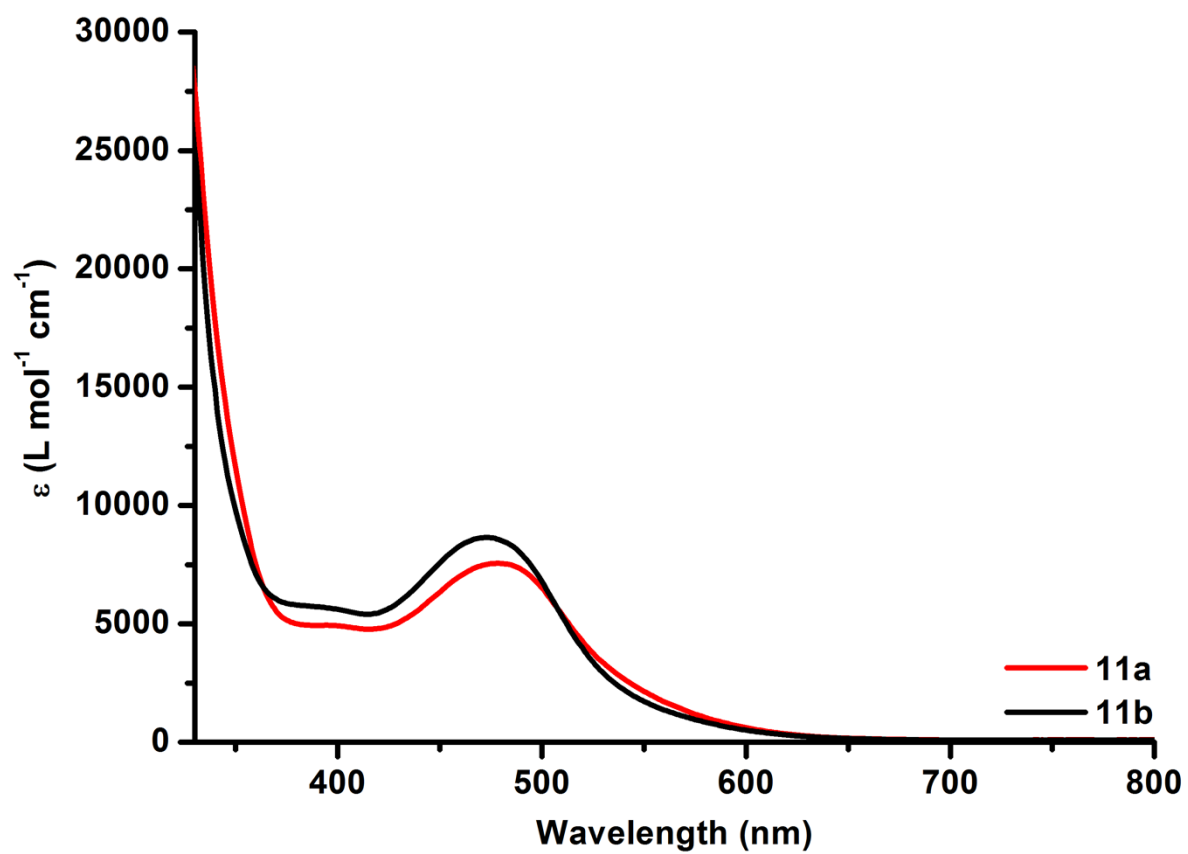


Figure S38 UV-Vis spectra of the Cu(I) complexes **11a** and **11b** in acetone ($\sim 1 \times 10^{-5}$ M).

5 Electrochemistry

Cyclic voltammetric (CV) experiments on 3-ferrocenylpyridine³ and selected bipyridyl complexes in acetone were performed at 20 °C on solutions degassed with argon. A three-electrode cell was used with Cypress Systems 1.4 mm diameter glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The solution was $\sim 10^{-3}$ M in electroactive material and contained 0.1 M Bu₄NPF₆ as the supporting electrolyte. Voltammograms were recorded with the aid of a Powerlab/4sp computer-controlled potentiostat. Potentials are referenced to the reversible formal potential (taken as $E^\circ = 0.00$ V) for the decamethylferrocene [Fc*]⁺⁰ process.⁴ Under the same conditions, E° calculated for [Fch]⁺⁰ was 0.49 V.⁵

Table S1 Additional electrochemical data for **3a-11b**.

Compounds	E° (V) (MeCN) ^a		E° (V) (CH ₂ Cl ₂) ^a	
	Cu ^{II/I}	Fc ⁺⁰	Cu ^{II/I}	Fc ⁺⁰
3-Fcpy	-	0.58(5) ³	-	0.64 ³
3a	-	0.59	-	0.64
3b	-	0.58(5)	-	0.63(5)
5a	-	0.73	-	insol.
5b	-	0.72	-	insol.
11a	0.56	0.73	0.71	0.78
11b	0.55	0.72	0.71	0.77
[Cu(bipy(Mes) ₂ bipy)]BF ₄	-	-	0.73 ⁶	-

^a 1×10^{-3} M in analyte, 0.1 M Bu₄NPF₆, referenced to [Fc*]⁺⁰ = 0.00 V.

5.1 Representative Voltammograms

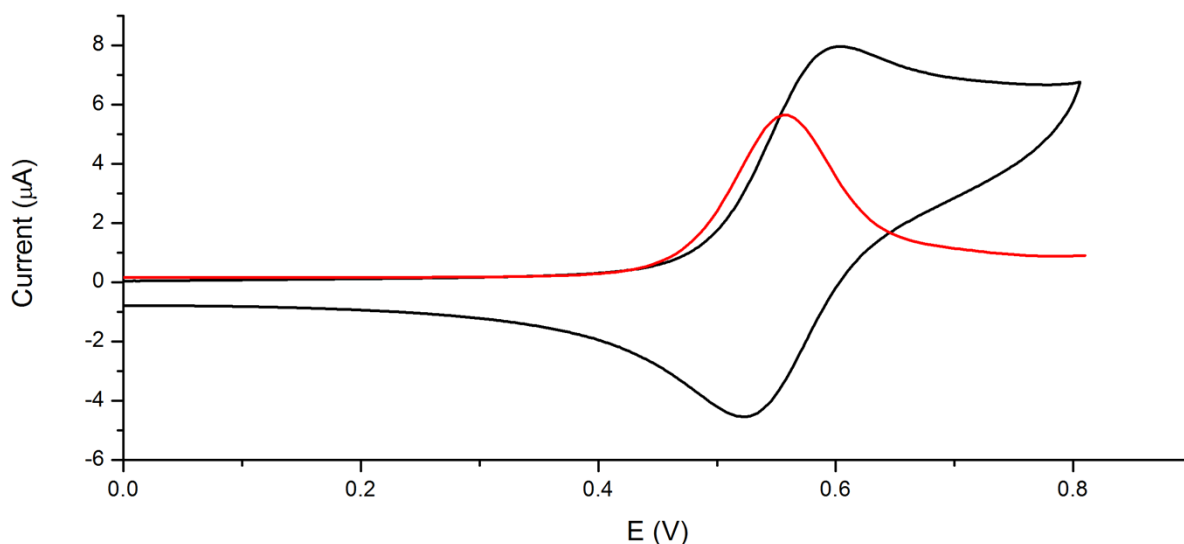


Figure S39 CV (black trace, 100 mV s⁻¹) and DPV (red trace) of the ligand **3b** in acetone.

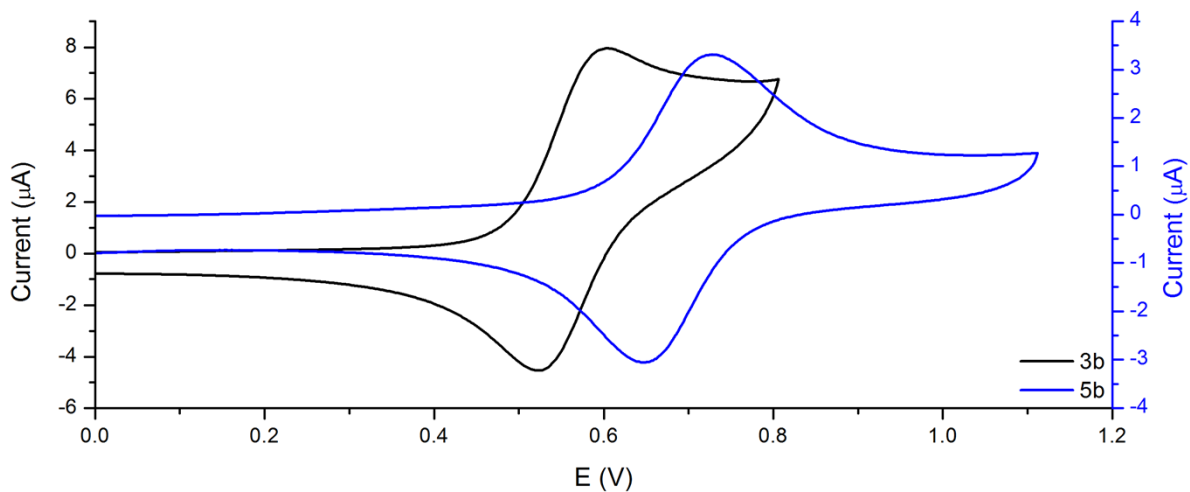


Figure S40 CVs (100 mV s^{-1}) of the ligand **3b** and the Pd(II) complex **5b** in acetone.

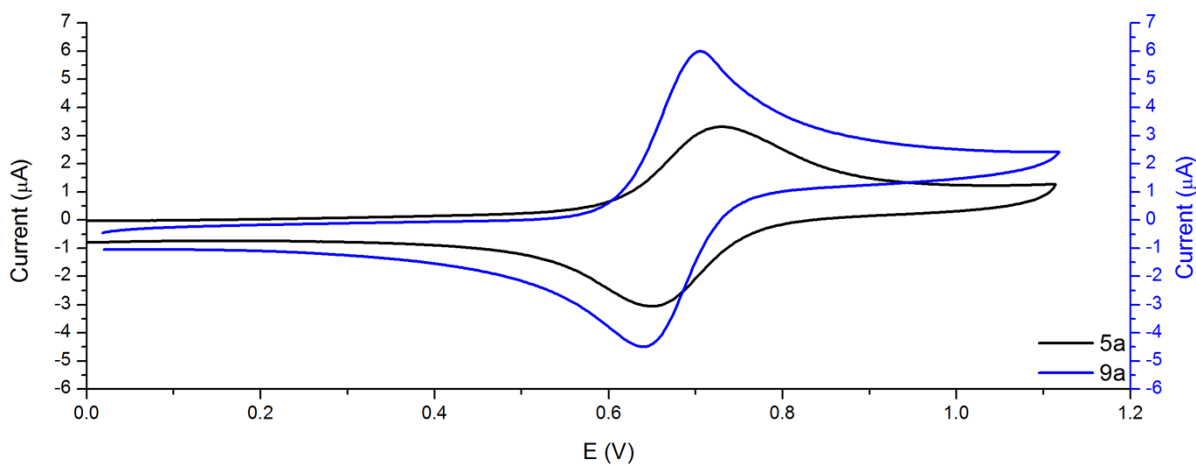


Figure S41 CVs (100 mV s^{-1}) of the Pd(II) complex **5a** and the Pd(II) complex **9a** in acetone.

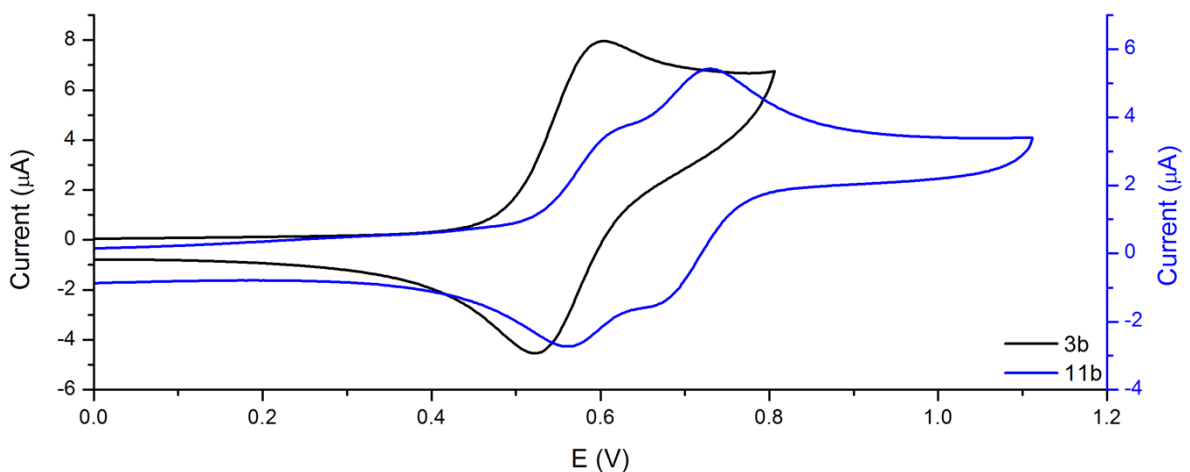


Figure S42 CVs (100 mV s^{-1}) of the ligand **3b** and the Cu(I) complex **11b** in acetone.

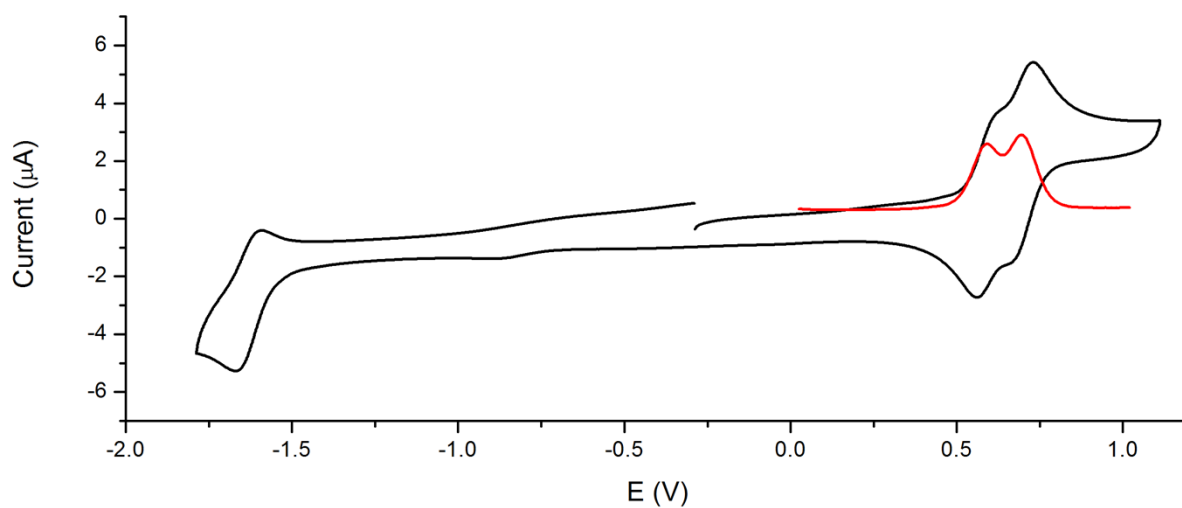


Figure S43 Full sweep CV (100 mV s^{-1}) of the Cu(I) complex **11b** (black trace) and the DPV of the oxidation area of interest (red trace) in acetone.

6 X-ray Data

6.1 Crystallographic Data Tables

Compound	3a	3a	4b
Empirical formula	C ₂₀ H ₁₆ FeN ₂	C ₂₀ H ₁₆ FeN ₂	C ₂₁ H ₁₈ Cl ₂ FeN ₂ Pd
Formula weight	340.20	340.20	531.55
Temperature	93(2) K	90(2) K	89(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P2₁/c</i>	<i>Pccn</i>	<i>P2₁/c</i>
Unit cell dimensions	a = 10.186(2) Å α = 90° b = 12.531(3) Å β = 92.469(7)° c = 11.828(2) Å γ = 90°	a = 13.0963(23) Å α = 90° b = 20.1531(35) Å β = 90° c = 11.7129(24) Å γ = 90°	a = 16.5082(5) Å α = 90° b = 7.4003(2) Å β = 113.5980(10)° c = 16.7660(5) Å γ = 90°
Volume	1508.3(5) Å ³	3091.4(9) Å ³	1876.95(9) Å ³
Z	4	8	4
Density (calculated)	1.498 Mg/m ³	1.462 Mg/m ³	1.888 Mg/m ³
Absorption coefficient	1.000 mm ⁻¹	0.975 mm ⁻¹	2.024 mm ⁻¹
F(000)	704	1408	1056
Crystal size	0.41 x 0.24 x 0.08 mm ³	0.39 x 0.26 x 0.09 mm ³	0.34 x 0.24 x 0.20 mm ³
Theta range for data collection	3.05 to 22.89°	2.54 to 22.25°	1.35 to 26.46°
Index ranges	-11<=h<=11, -13<=k<=13, -10<=l<=12	-13<=h<=12, -21<=k<=21, -12<=l<=12	-20<=h<=20, -9<=k<=6, -21<=l<=20
Reflections collected	11348	12480	13161
Independent reflections	2057 [R(int) = 0.0510]	1959 [R(int) = 0.0518]	3844 [R(int) = 0.0340]
Completeness	99.2% (theta = 22.89°)	99.8% (theta = 22.25°)	99.2% (theta = 26.46°)
Max. and min. transmission	0.9243 and 0.6847	0.92 and 0.6469	0.6876 and 0.5461
Data / restraints / parameters	2057 / 0 / 208	1959 / 0 / 208	3844 / 0 / 245
Goodness-of-fit on F ²	1.124	1.087	1.218
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1847	R1 = 0.0320, wR2 = 0.0840	R1 = 0.0271, wR2 = 0.0752
R indices (all data)	R1 = 0.0660, wR2 = 0.1929	R1 = 0.0369, wR2 = 0.0885	R1 = 0.0337, wR2 = 0.0922
Largest diff. peak and hole	1.700 and -0.480 e.Å ⁻³	0.262 and -0.422 e.Å ⁻³	0.570 and -0.556 e.Å ⁻³

Compound	5a	6a	6b
Empirical formula	C ₃₀ H ₂₆ F ₁₂ FeN ₄ PdSb ₂	C ₃₈ H ₄₂ F ₁₂ FeN ₈ PdSb ₂	C ₃₇ H ₄₁ F ₁₂ FeN ₇ PdSb ₂
Formula weight	1076.30	1244.55	1217.52
Temperature	89(2) K	89(2) K	90(2) K
Wavelength	0.71073 Å	0.71069 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>C2/c</i>	<i>P-1</i>	<i>P-1</i>
Unit cell dimensions	a = 31.201(4) Å α = 90° b = 11.3669(11) Å β = 95.873(4)° c = 19.088(2) Å γ = 90°	a = 11.635(2) Å α = 67.083(7)° b = 13.391(2) Å β = 84.398(7)° c = 15.929(2) Å γ = 82.022(7)°	a = 10.353(7) Å α = 73.09(3)° b = 14.768(9) Å β = 73.84(3)° c = 15.121(10) Å γ = 74.59(3)°
Volume	6734.2(12) Å ³	2261.2(6) Å ³	2081(2) Å ³
Z	8	2	2
Density (calculated)	2.123 Mg/m ³	1.828 Mg/m ³	1.943 Mg/m ³
Absorption coefficient	2.631 mm ⁻¹	1.975 mm ⁻¹	2.143 mm ⁻¹
F(000)	4128	1216	1188
Crystal size	0.22 x 0.21 x 0.05 mm ³	0.78 x 0.24 x 0.08 mm ³	0.20 x 0.17 x 0.05 mm ³
Theta range for data collection	1.31 to 26.51°	2.64 to 25.5°	1.44 to 21.92°
Index ranges	-39<=h<=38, 0<=k<=14, 0<=l<=23	-14<=h<=14, -16<=k<=16, -17<=l<=19	-10<=h<=10, -15<=k<=14, -15<=l<=15
Reflections collected	13014	32184	17648
Independent reflections	13014 [R(int) = 0.0000]	8362 [R(int) = 0.0322]	4754 [R(int) = 0.0693]
Completeness	99.0% (theta = 26.51°)	99.4% (theta = 25.5°)	94.0% (theta = 21.9°)
Max. and min. transmission	0.8841 and 0.5952	0.857 and 0.578	0.9004 and 0.6739
Data / restraints / parameters	13014 / 0 / 452	8362 / 30 / 609	4754 / 0 / 547
Goodness-of-fit on F ²	1.011	1.03	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0603, wR2 = 0.1565	R1 = 0.0246, wR2 = 0.056	R1 = 0.0471, wR2 = 0.1182
R indices (all data)	R1 = 0.0866, wR2 = 0.1693	R1 = 0.0287, wR2 = 0.0589	R1 = 0.0687, wR2 = 0.1282
Largest diff. peak and hole	1.046 and -1.007 e.Å ⁻³	0.515 and -0.638 e.Å ⁻³	0.882 and -1.014 e.Å ⁻³

Compound	11a	11b	7
Empirical formula	C ₄₈ H ₄₄ CuF ₆ FeN ₄ P	C ₄₉ H ₄₆ CuF ₆ FeN ₄ P•5.5H ₂ O	C ₂₆ H ₃₂ F ₁₂ N ₄ O ₂ PdSb ₂
Formula weight	941.23	1054.34	1010.46
Temperature	90(2) K	90(2) K	90(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71069 Å
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> 4 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	a = 12.6769(12) Å α = 90° b = 17.8460(16) Å β = 98.382(5)° c = 18.8833(16) Å γ = 90°	a = 39.118(3) Å α = 90° b = 39.118(3) Å β = 90° c = 12.8349(11) Å γ = 90°	a = 8.745(5) Å α = 90° b = 19.021(5) Å β = 98.519(5)° c = 10.628(5) Å γ = 90°
Volume	4226.4(7) Å ³	19640(3) Å ³	1748.3(14) Å ³
Z	4	16	2
Density (calculated)	1.479 Mg/m ³	1.426 Mg/m ³	1.919 Mg/m ³
Absorption coefficient	0.951 mm ⁻¹	0.835 mm ⁻¹	2.137 mm ⁻¹
F(000)	1936	7927	976
Crystal size	0.82 x 0.49 x 0.08 mm ³	0.90 x 0.60 x 0.43 mm ³	0.51 x 0.32 x 0.19 mm ³
Theta range for data collection	1.58 to 26.42°	1.04 to 26.46°	2.21 to 25.50°
Index ranges	-15<=h<=15, -22<=k<=22, -23<=l<=23	-48<=h<=48, -48<=k<=48, -16<=l<=15	-10<=h<=10, -23<=k<=23, -12<=l<=12
Reflections collected	97906	136258	42952
Independent reflections	8666 [R(int) = 0.0676]	10065 [R(int) = 0.0731]	3257 [R(int) = 0.0412]
Completeness	99.6% (theta = 26.42°)	99.3% (theta = 26.46°)	99.8% (theta = 25.50°)
Max. and min. transmission	0.7454 and 0.6340	0.7195 and 0.5258	0.7464 and 0.5749
Data / restraints / parameters	8666 / 0 / 556	10065 / 0 / 566	3257 / 0 / 216
Goodness-of-fit on F ²	1.071	1.141	1.182
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1078	R1 = 0.0552, wR2 = 0.1278	R1 = 0.0375, wR2 = 0.0995
R indices (all data)	R1 = 0.0577, wR2 = 0.1142	R1 = 0.0712, wR2 = 0.1331	R1 = 0.0406, wR2 = 0.1013
Largest diff. peak and hole	0.555 and -0.465 e.Å ⁻³	0.348 and -0.386 e.Å ⁻³	2.385 and -0.784 e.Å ⁻³

6.2 Crystal Structures and Relevant Notes

The structures were collected on a Bruker Kappa Apex II area detector diffractometer using monochromated Mo K α radiation at low temperature (89-93 K). SADABS⁷ was used for absorption correction. The structures were solved by direct methods using SIR-97⁸ or X-Seed⁹ and refined against F² using anisotropic thermal displacement parameters for all non-hydrogen atoms using SHELXL-97¹⁰ software. Hydrogen atoms were placed in calculated positions and refined using a riding model.

The structure for **5a** was found to be a two-component non-merohedral twin, thus the TWINABS function within PLATON was used to give multi-component absorption corrections.

Due to the extent of disordered solvent molecules in the crystal lattice of **11b**, the SQUEEZE routine within PLATON was implemented. SQUEEZE details are listed below, beneath the relevant structure, as well as in the relevant CIF.

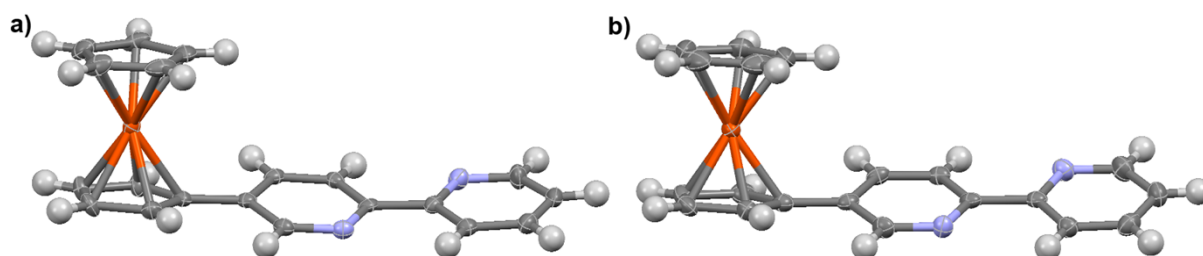


Figure S44 Mercury ellipsoid plots of **3a** in a) monoclinic and b) orthorhombic polymorphs. Ellipsoids are shown at the 50% probability level.

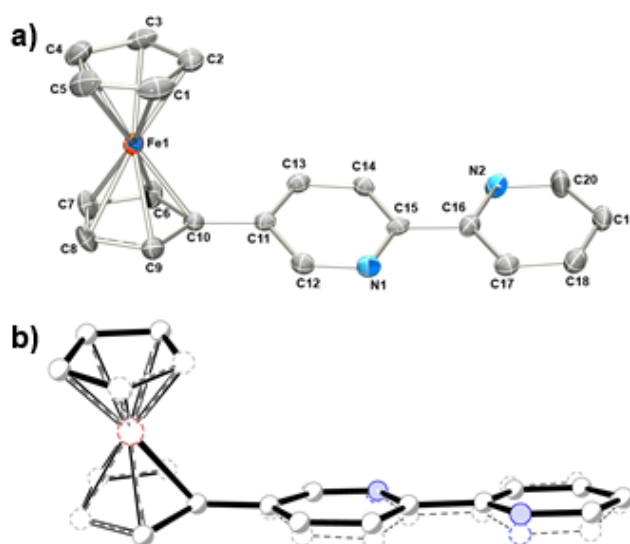


Figure S45 a) One of two collected crystal structures of ligand **3a** showing ellipsoids at the 50% probability level, and b) the two structures of **3a** overlaid to show the 5.62° difference in torsion angle between the ferrocene and the bipyridine.

Hydrogens are omitted for clarity.

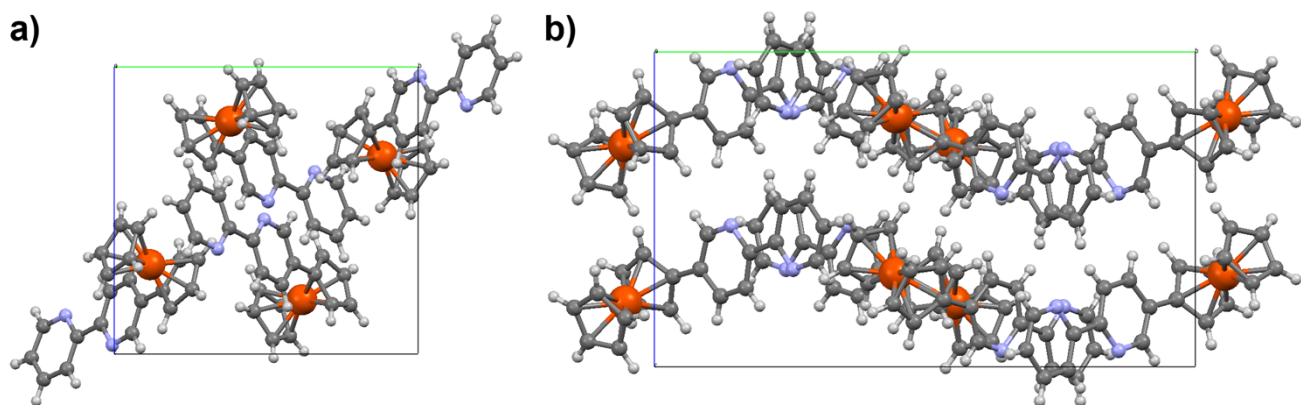


Figure S46 Crystal packing of ligand **3a** seen down the 'a' axis in the a) monoclinic, and b) orthorhombic crystal structures.

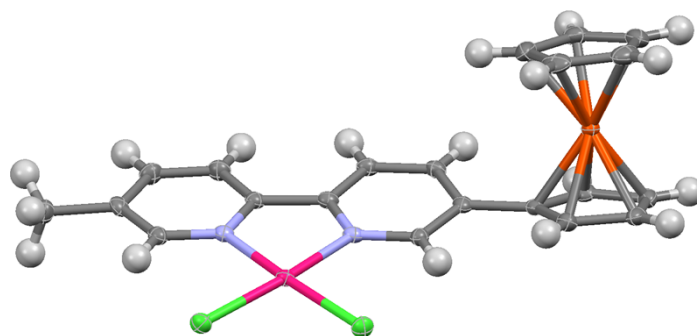


Figure S47 Mercury ellipsoid plot of **4b**. Ellipsoids are shown at the 50% probability level.

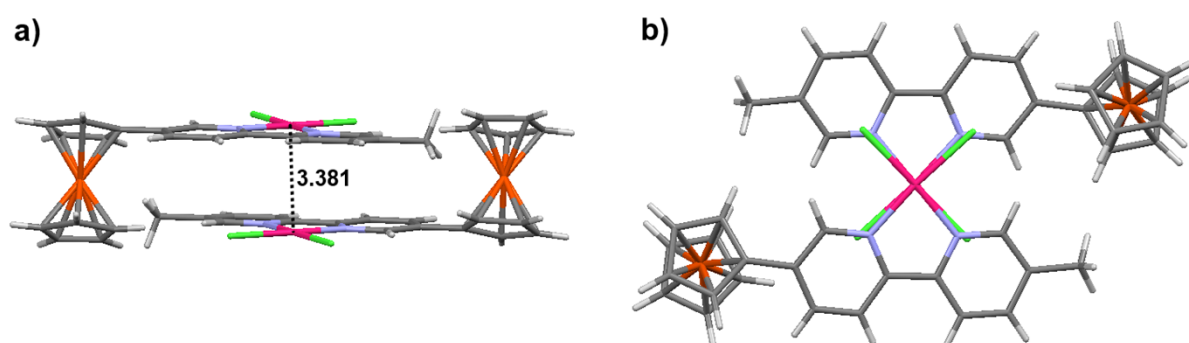


Figure S48 a) Side view of the head-to-tail **4b** dimer with the Pd-Pd metal interaction measured in Å, and b) the top-down view along the Pd-Pd interaction.

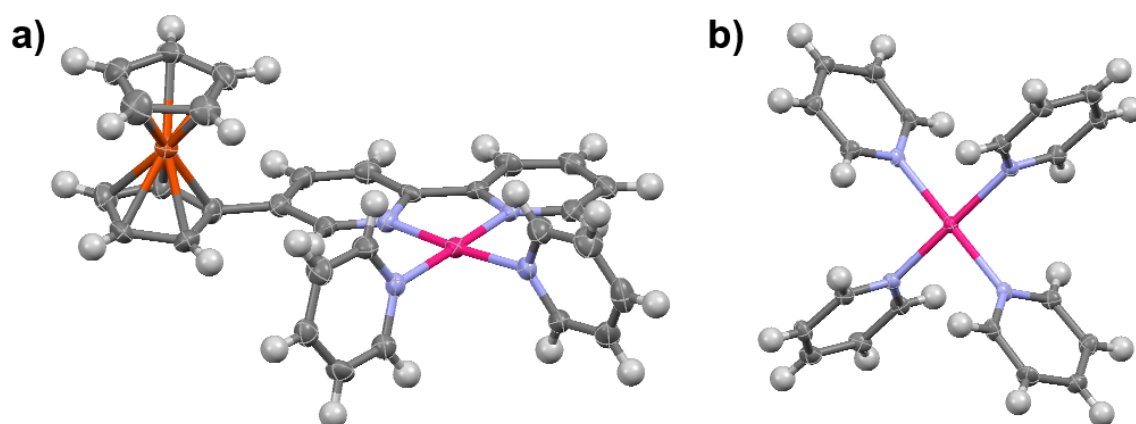


Figure S49 Mercury ellipsoid plots of a) **5a** and b) the $[\text{Pd}(\text{Py})_4]^{2+}$ side product **7**. Solvent and counterions are omitted for clarity. Ellipsoids are shown at the 50% probability level. **5a** was a two-component non-merohedral twin wherein TWINABS was used to give multi-component absorption corrections.

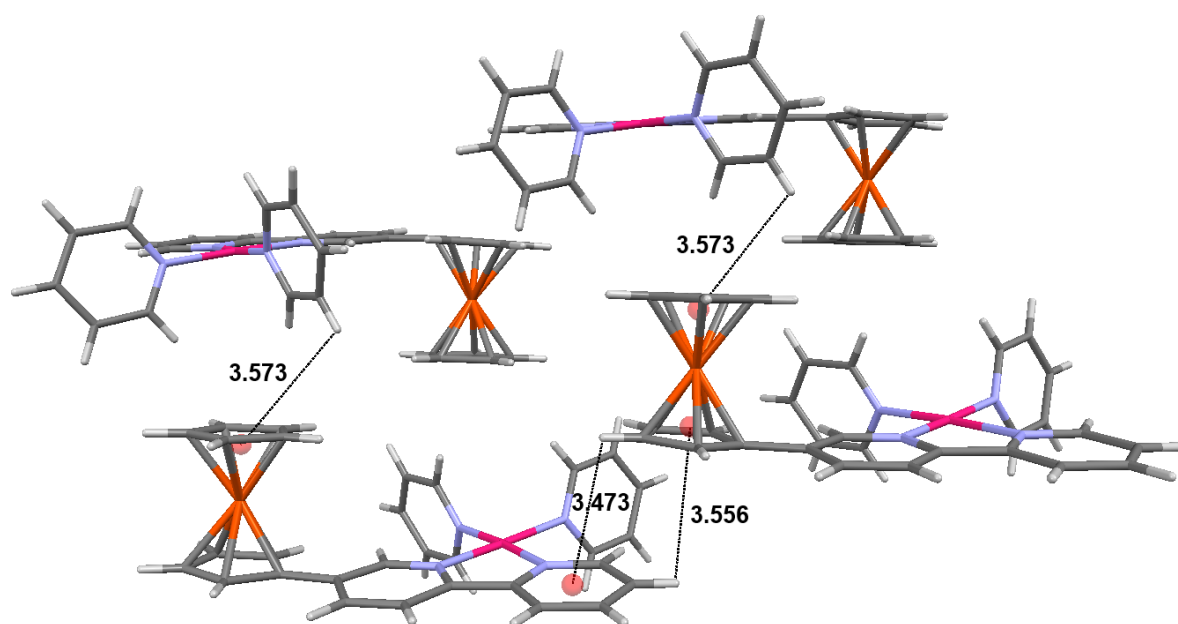


Figure S50 π -stacking interactions within the extended solid state structure of **5a**, with H-centroid distances shown in Å. Solvent and counterions are omitted for clarity.

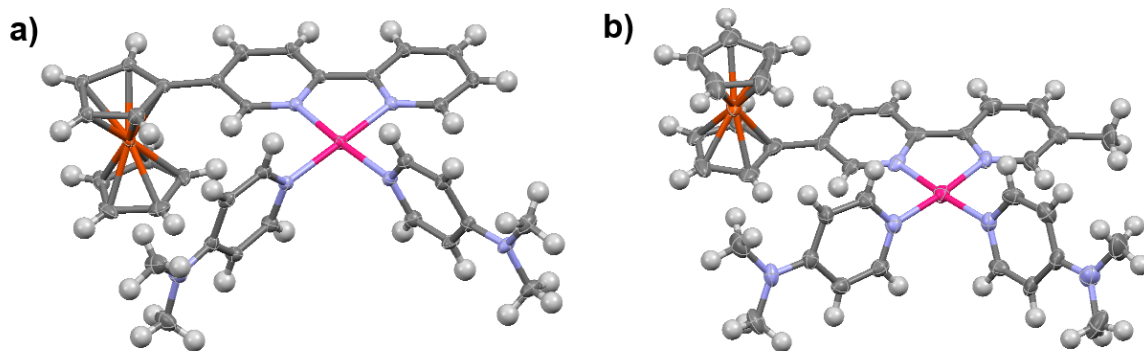


Figure S51 Mercury ellipsoid plots of a) **6a** and b) **6b**. Solvent and counterions are omitted for clarity. Ellipsoids are shown at the 50% probability level.

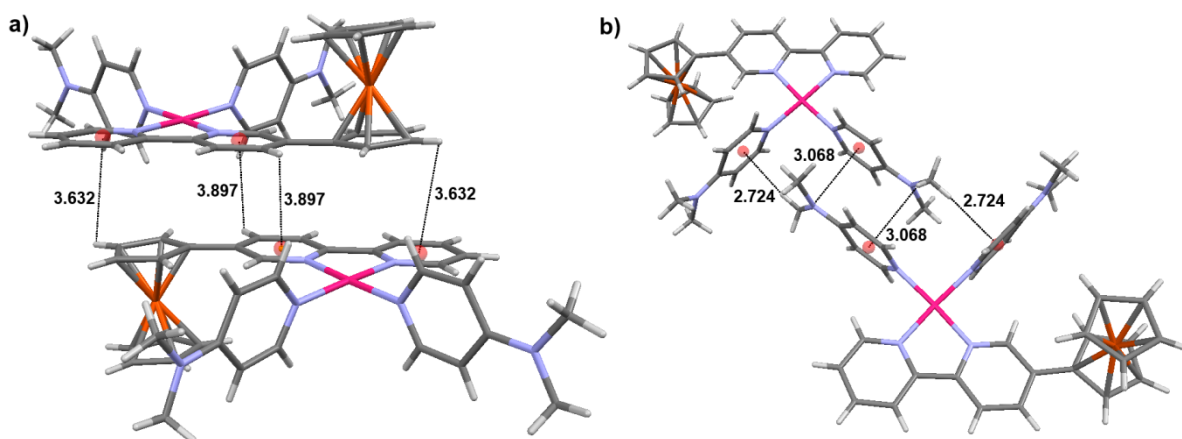


Figure S52 π -stacking interactions of a) the FcBipy ligand π -surfaces, and b) the interdigitating DMAP ligands within the extended solid state structure of **6a**, with H-centroid distances shown in Å. Solvent and counterions are omitted for clarity.

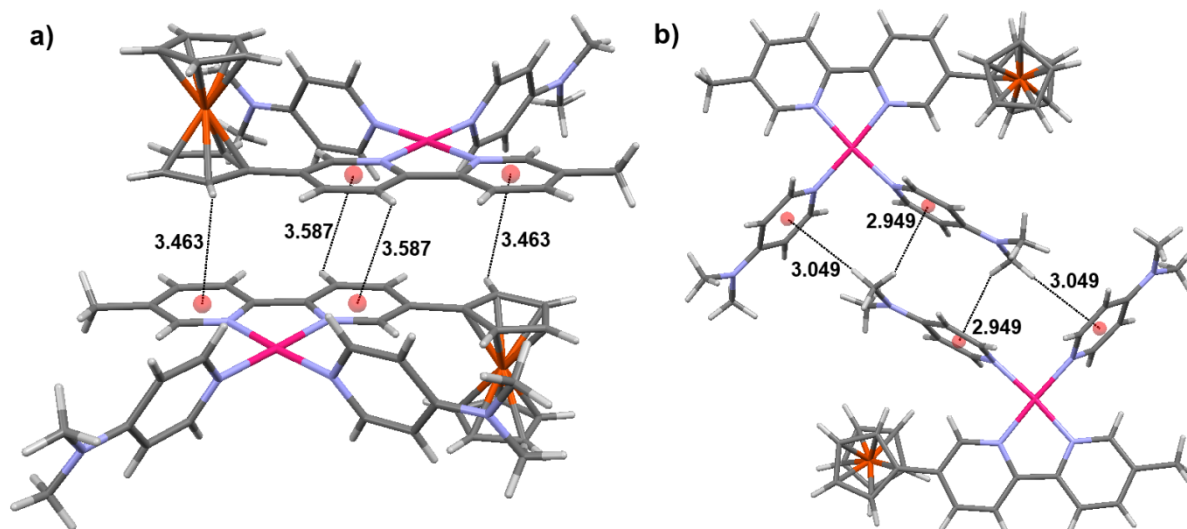


Figure S53 π -stacking interactions of a) the FcBipy ligand π -surfaces, and b) the interdigitating DMAP ligands within the extended solid state structure of **6b**, with H-centroid distances shown in Å. Solvent and counterions are omitted for clarity.

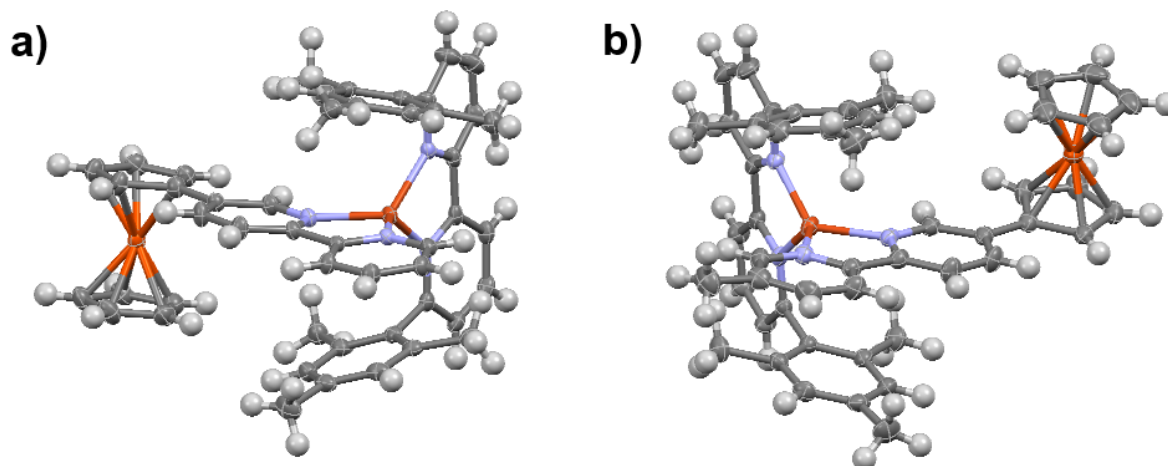


Figure S54 Mercury ellipsoid plots of a) **11a** and b) **11b**. Solvent and counterions omitted for clarity. Ellipsoids are shown at the 50% probability level. **11b** was subject to Platon Squeeze, details of which follow.

PLATON SQUEEZE details for **11b**

Void number	1	2	3	4	5	6	7	8
Average x	0.000	0.000	0.250	0.250	0.500	0.500	0.750	0.750
Average y	0.250	0.750	0.000	0.500	0.250	0.750	0.000	0.500
Average z	0.625	0.375	0.800	0.191	0.875	0.125	0.690	0.303
Volume	36.8	36.8	771.4	771.4	36.7	36.7	771.3	771.4
Electron count	-3.8	-4.0	220.3	220.1	-4.0	-3.8	220.1	220.3

The packing of the crystal shows sizeable solvent channels containing significant amounts of diffuse electron density, accounted for by disordered solvent which could not be modelled as discrete molecules. As such, PLATON SQUEEZE was employed to calculate the contribution to the diffraction from the solvent channels and thereby produced a set of solvent-free diffraction intensities.

Details

SQUEEZE estimated four 'voids' containing 220 electrons each. This gives a total of 880 electrons. Due to this being a tetragonal space group with 16 asymmetric units per unit cell, this amounts to $880/16 = 55$ electrons per asymmetric unit. This can be accounted for by 5.5 water molecules per asymmetric unit.

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