

Electronic Supplementary Information (ESI) for Monovalent Chiral-at-Copper Complexes: Halide-controlled Diastereoselectivity

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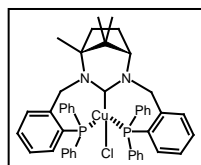
Experimental

General considerations

The synthesis of the ligand precursor **1**·HPF₆ is discussed elsewhere (Dalton Trans., manuscript currently being submitted). All procedures for the synthesis of the copper(I) complexes were performed under N₂ using standard Schlenk techniques. THF was distilled over sodium/benzophenone under N₂ before use. Toluene and CH₂Cl₂ were dried using a MBraun SPS-800 solvent purification system. The resultant complexes **2a**, **2b** and **2c** are air-stable in the solid state but show some very slow aerial decomposition in solution. NMR spectra were obtained on a Jeol Eclipse 300 MHz spectrometer or a Bruker 500 MHz spectrometer. Electronic and circular dichroism spectra were obtained on an Applied Photophysics Chirascan spectrometer. The authors are grateful to Dr Robert Mart for his assistance in obtaining the electronic and CD spectra. Mass spectra were obtained on a Waters LCT Premier XE mass spectrometer and microanalytical data were performed by Stephen Boyer at London Metropolitan University elemental analysis services.

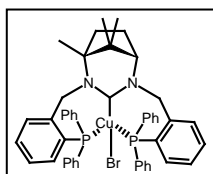
Synthesis and characterisation of complexes **2a**, **2b** and **2c**.

[Cu(κ^3 -P,C,P-**1**)Cl], **2a**



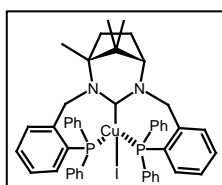
To a solution of **1**·HPF₆ (190 mg, 2.24 x 10⁻⁴ mol) in THF (10 ml) was added KO^tBu (35 mg, 3.14 x 10⁻⁴ mol) and the mixture stirred for 10 mins. CuCl (31 mg, 3.13 x 10⁻⁴ mol) was then added, the mixture stirred overnight and subsequently filtered to remove some fine solid. The volatiles were removed in *vacuo* and the cream residue taken into CH₂Cl₂ (5 ml) and filtered to remove a slight solid. The volatiles were removed at the pump and the residue triturated with toluene to give the desired product as a cream solid which was isolated by filtration under nitrogen and recrystallised from THF/toluene in air. Yield = 129 mg (72%, based on **1**·HPF₆). ¹H NMR (CDCl₃, 300 MHz) δ 7.7 – 6.8 (28H, m), 5.29 (1H, d, *J* 14.8 Hz), 4.88 (1H, d, *J* 15.8 Hz), 4.47 (1H, d, *J* 15.8 Hz), 4.14 (1H, d, *J* 14.8 Hz), 3.40 (1H, d, *J* 4.0 Hz), 2.15 (2H, m), 1.99 (2H, m), 1.52 (3H, s), 1.04 (3H, s), 0.38 (3H, s) ppm. ¹³C{¹H} DEPT NMR (CDCl₃, 125.8 MHz) δ 200.2 (t, ²J_{C-P} 31.5 Hz), 142.7 (d, *J* 5.0 Hz), 140.8 (d, *J* 17.6 Hz), 137.9, 134.1, 134 – 128 (aromatics), 125.3, 69.1, 67.6, 58.0, 52.5 (d, *J* 8.8 Hz), 41.3, 40.2, 31.8, 21.9, 18.0, 17.8 ppm. ³¹P (CDCl₃, 121.6 MHz): δ -3.2 (AB, ²J_{P-P} 80.4 Hz), -5.8 (AB, ²J_{P-P} 80.4 Hz) ppm. MS: 798 ([M⁺], 20%). *Anal.*: Calc. for C₄₇H₄₆N₂P₂ClCu: C, 70.57; H, 5.81; N, 3.50%. Found: C, 70.5; H, 5.7; N, 3.4%.

[Cu(κ^3 -P,C,P-**1**)Br], **2b**



Prepared as detailed for **2a** above except using 100 mg of **1·HPF₆**. Yield = 68 mg (68%). ¹H NMR (CDCl₃, 300 MHz) δ 8.0 – 6.5 (28H, m br), 5.32 (1H, br), 4.86 (0.5H, d br, *J* 15.2 Hz), 4.42 (0.5H, d br, *J* 17.1 Hz), 4.34 (1H, br), 4.13 (0.5H, d br, 15.2 Hz), 3.67 (1H, br), 3.39 (0.5H, br), 3.02 (0.5H, br), 2.1 – 1.1 (4H, br), 1.00 (1.5H, s br), 0.89 (1.5H, s br), 0.88 (1.5H, s obs), 0.69 (1.5H, s br), 0.35 (1.5H, s br), -0.60 (1.5H, s br) ppm. ³¹P (CDCl₃, 223K, 121.6 MHz): δ -3.2 (AB, ²*J*_{P-P} 80.4 Hz), -6.5 (AB, ²*J*_{P-P} 80.4 Hz), -11.7 (AB, ²*J*_{P-P} 47.7 Hz) -16.3 (AB, ²*J*_{P-P} 47.7 Hz) ppm. MS: 845 ([M⁺], 75%). *Anal.*: Calc. for C₄₇H₄₆N₂P₂BrCu: C, 66.85; H, 5.50; N, 3.32%. Found: C, 66.5; H, 5.3; N, 3.3%.

[Cu(κ³-P,C,P-1)I], **2c**



Prepared as detailed for **2a** above. Recrystallised from toluene in air. Yield = 177 mg (89%). ¹H NMR (d₈-THF, 213K, 300 MHz) δ (major isomer) 8.0 – 6.7 (28H, m), 5.08 (1H, d, *J* 14.5 Hz), 4.43 (1H, d, *J* 15.8 Hz), 3.83 (1H, d, *J* 14.5 Hz), 3.28 (1H, s br), 2.36 (1H, m), 1.97 (1H, m), 1.78 (2H, m), 0.87 (3H, s), 0.70 (3H, s), -0.67 (3H, s) ppm; δ (minor isomer) 8.0 – 6.7 (28H, m), 5.30 (1H, d, *J* 14.5 Hz), 3.91 (1H, d, *J* 14.5 Hz), 3.33 (1H, s br), 1.30 (3H, s br), 0.93 (3H, s), 0.83 (3H, s) ppm (all other resonances obscured). ¹³C{¹H} NMR (CDCl₃, 293K, 125.8 MHz) δ 213.2 (br), 145.0, 141.5, 137.9, 136.0, 135 – 126 (aromatics), 69.1, 61.9 (br), 59.3, 58.3, 41.1, 40.6, 37.8, 31.9, 30.4, 22.6, 22.2, 18.4, 17.8, 16.5 ppm. ³¹P (CDCl₃, 121.6 MHz): δ -13.9 (AB, ²*J*_{P-P} 41 Hz), -16.0 (AB, ²*J*_{P-P} 41 Hz) ppm. ³¹P (CDCl₃, 223K, 121.6 MHz): δ (major isomer) -13.6 (AB, ²*J*_{P-P} 44.7 Hz), -16.4 (AB, ²*J*_{P-P} 44.7 Hz) ppm; δ (minor isomer) -3.6 (AB, ²*J*_{P-P} 77.4 Hz), -6.9 (AB, ²*J*_{P-P} 77.4 Hz) ppm. MS: 891 ([M⁺], 5%; [M – I⁻]⁺, 30%). *Anal.*: Calc. for C₄₇H₄₆N₂P₂I Cu: C, 70.57; H, 5.81; N, 3.50%. Found: C, 70.4; H, 5.8; N, 3.5%.

Representative spectra

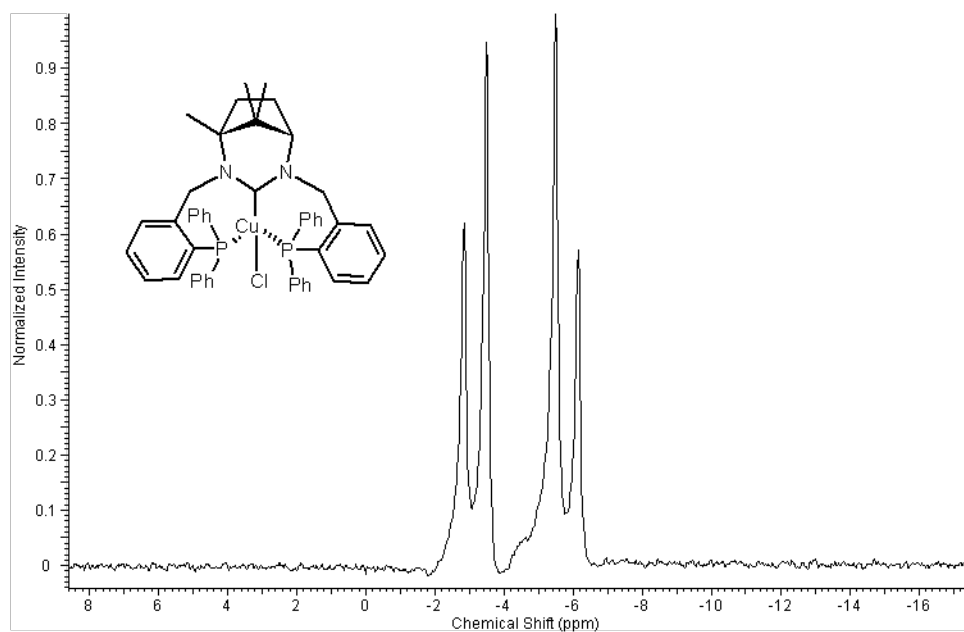


Fig. S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** at 293K in CDCl_3 .

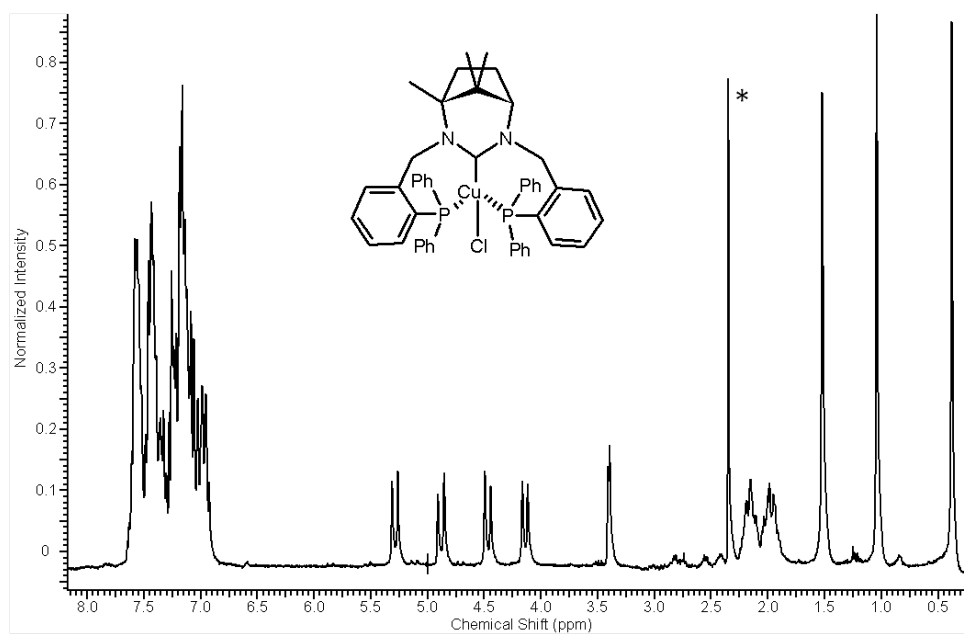


Fig. S2. ^1H NMR spectrum of **2a** at 293K in CDCl_3 (* solvent impurity).

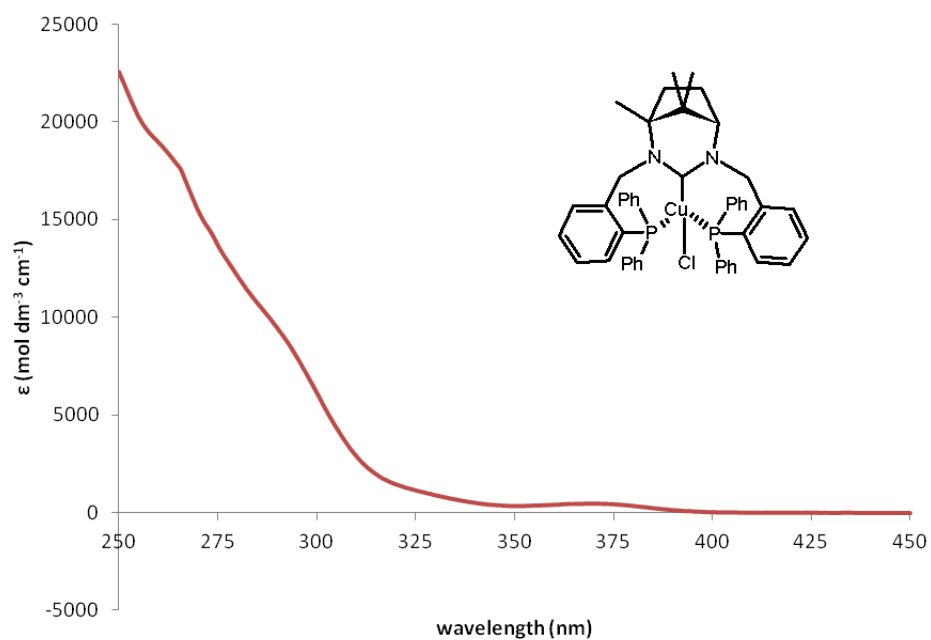


Fig S3. Electronic spectrum of **2a** ($1 \times 10^{-3} \text{ mol dm}^{-3} \text{ cm}^{-1}$) recorded in CDCl_3 at 298K.

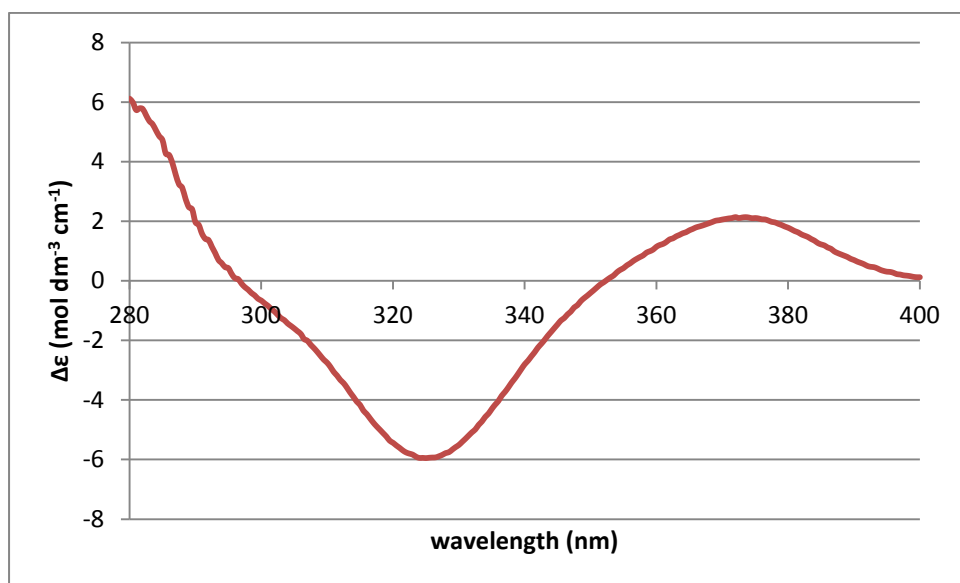


Fig S4. Circular dichroism spectrum of **2a** ($1 \times 10^{-3} \text{ mol dm}^{-3} \text{ cm}^{-1}$) recorded in CDCl_3 at 298K.

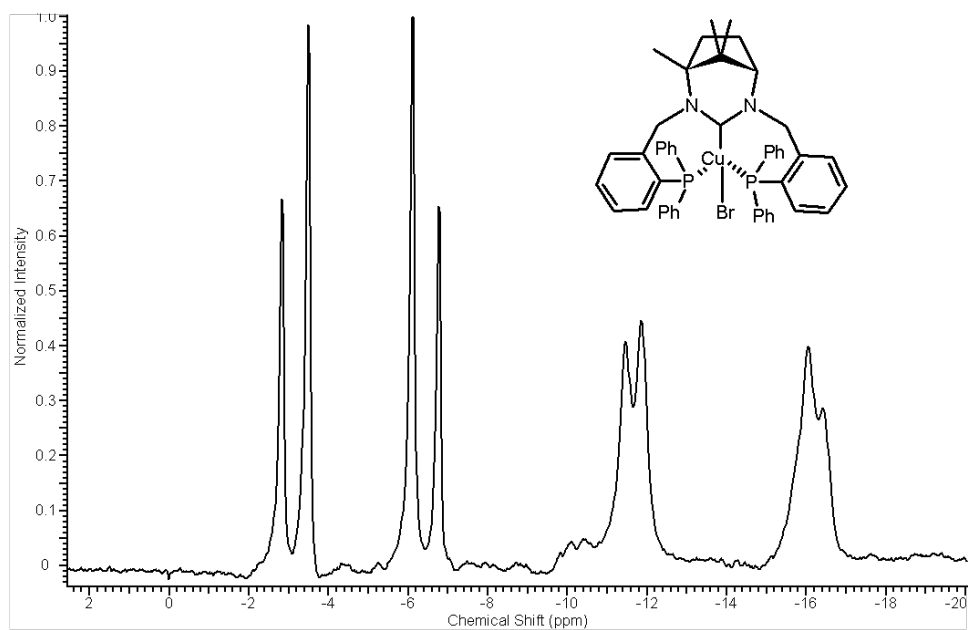


Fig. S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2b** at 223K in CDCl_3 .

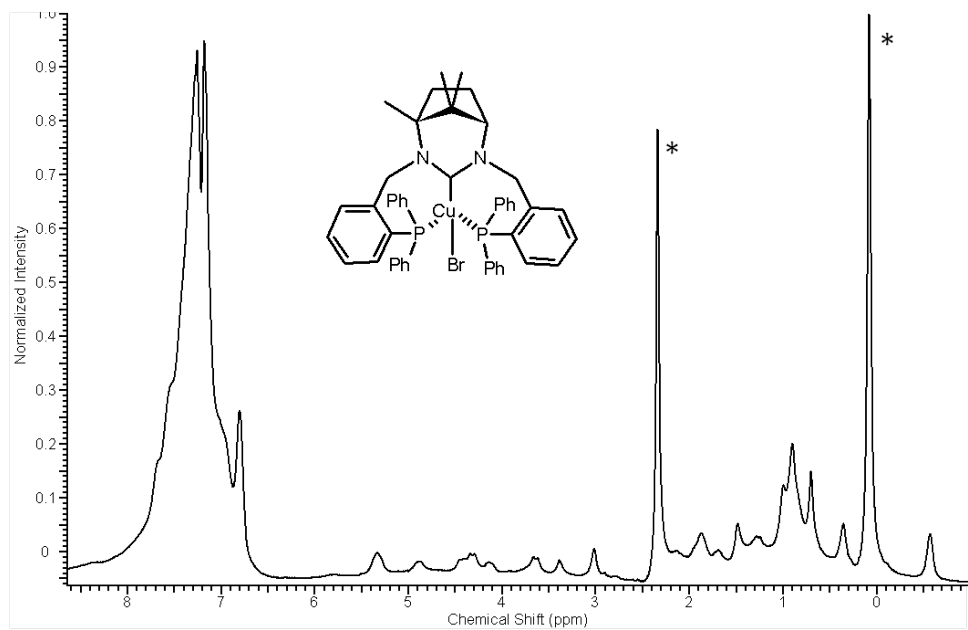


Fig. S6. ^1H NMR spectrum of **2b** at 293K in CDCl_3 (* solvent impurity).

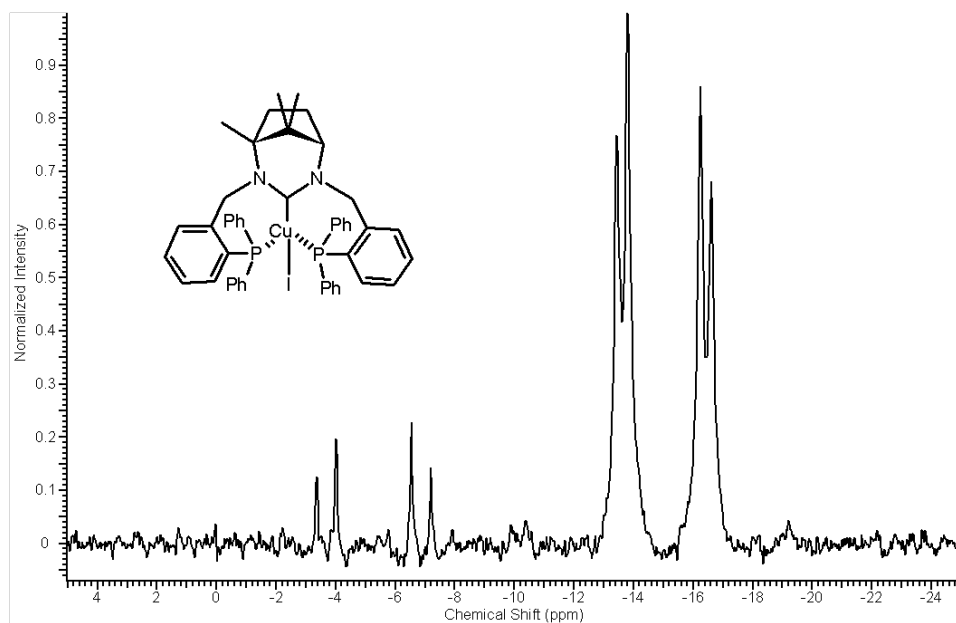


Fig. S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2c** at 223K in CDCl_3 .

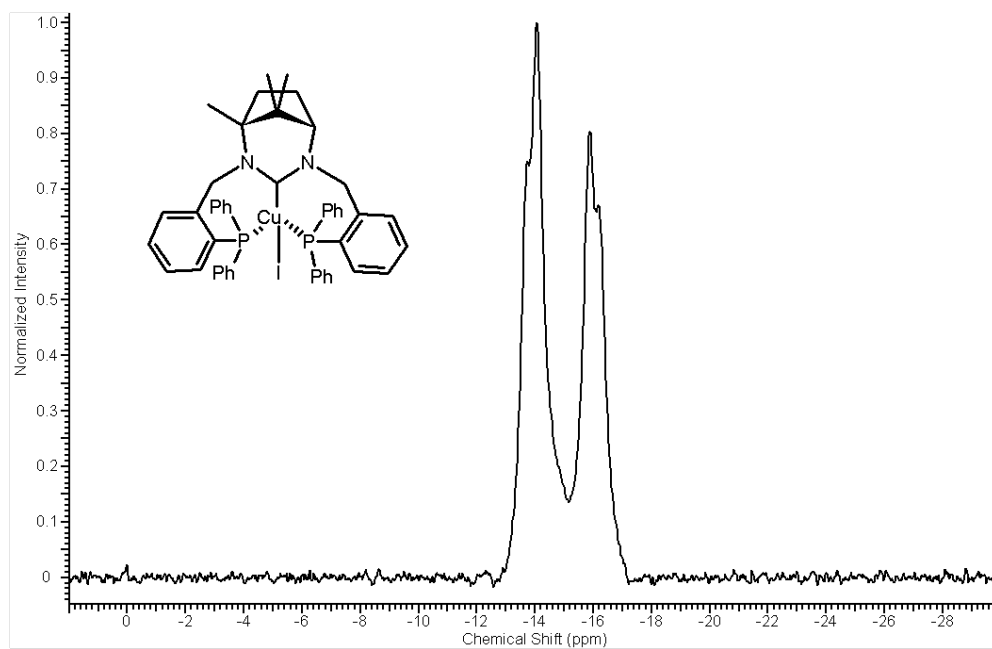


Fig. S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2c** at 293K in CDCl_3 .

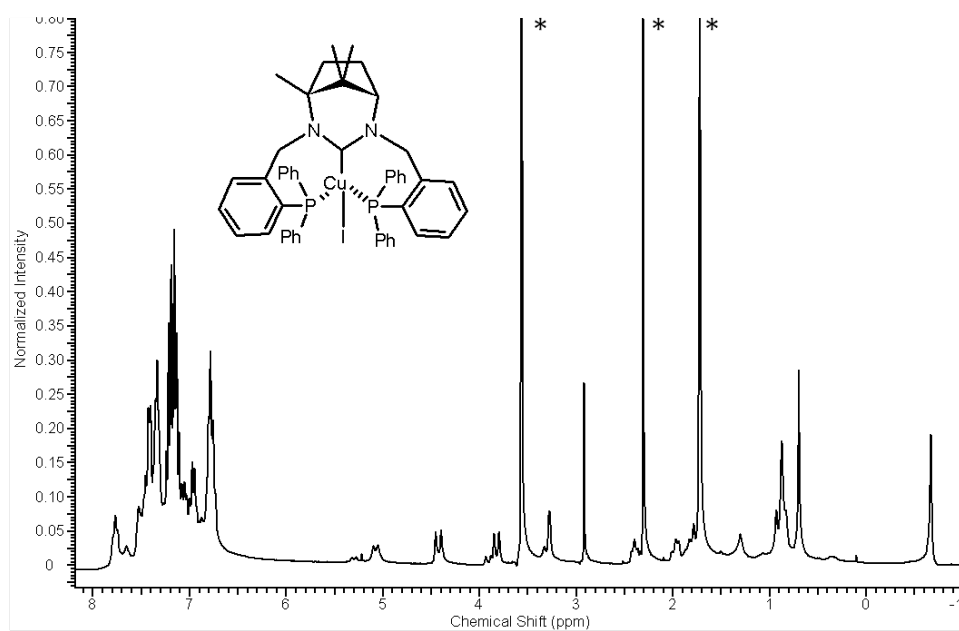


Fig. S9. ^1H NMR spectrum of **2c** at 213K in d_8 -THF (* solvent impurity).

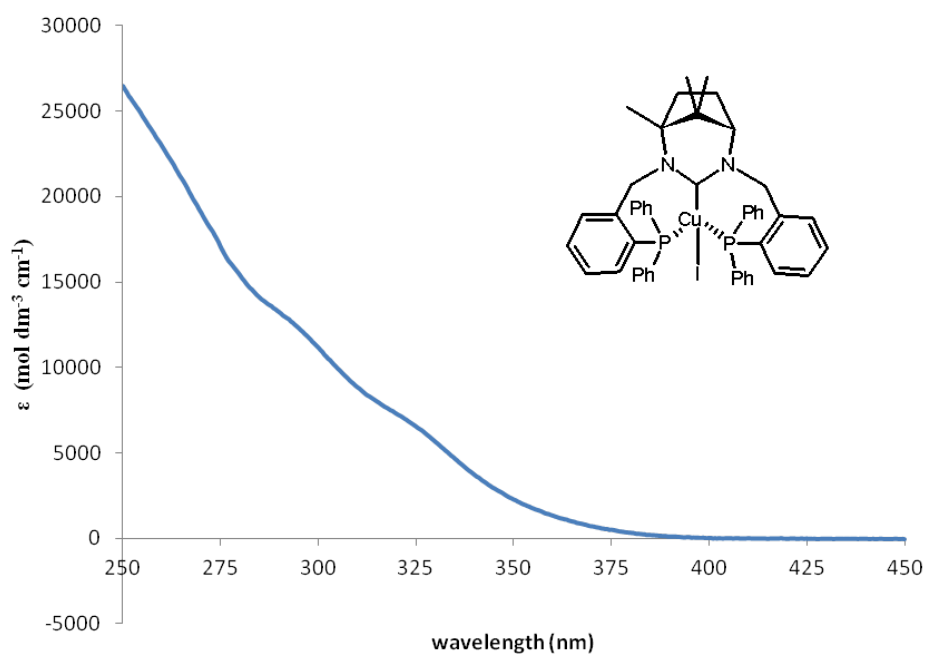


Fig S10. Electronic spectrum of **2c** ($1 \times 10^{-3} \text{ mol dm}^{-3} \text{ cm}^{-1}$) recorded in CDCl_3 at 298K.

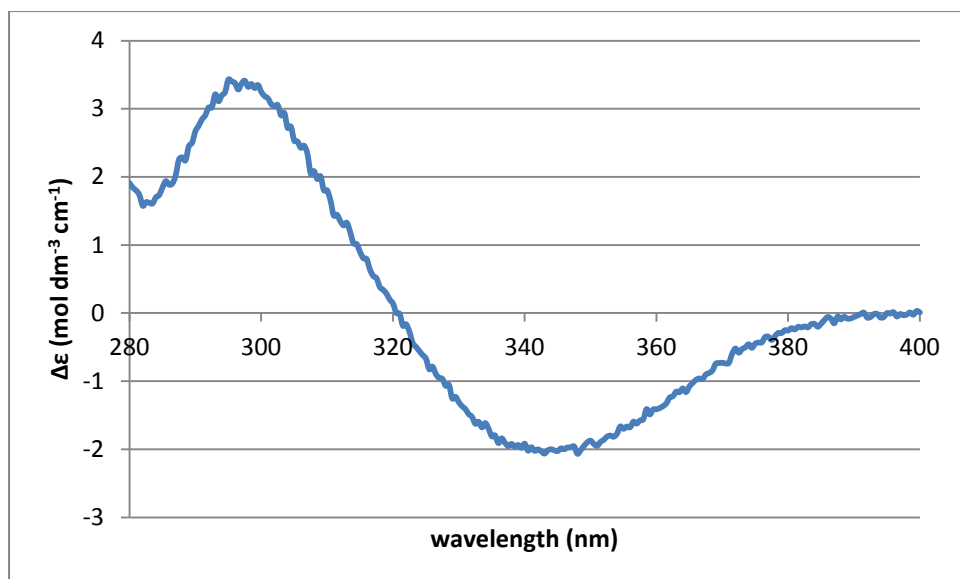


Fig S11. Circular dichroism spectrum of **2c** ($1 \times 10^{-3} \text{ mol dm}^{-3} \text{ cm}^{-1}$) recorded in CDCl_3 at 298K.

X-ray data collection, solution and refinement for **2c**

The data were collected at 150 K on a Nonius Kappa CCD diffractometer using graphite-monochromated $\text{Mo-K}\alpha$, ($\alpha = 0.71073 \text{ \AA}$) radiation equipped with an Oxford Cryosystems sample cooler. The structures were solved by direct methods using SHELXS-96ⁱ and refined with all data on F^2 full-matrix least squares using SHELXL-97.ⁱⁱ All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were generally located from difference Fourier maps and a riding model with atomic displacement parameters 1.2 times (1.5 times for methyl groups) those of the atom to which they are bonded was used for subsequent refinements.

Crystallographic details for **2c**

Empirical Formula	$\text{C}_{54}\text{H}_{52}\text{CuIN}_2\text{P}_2 \cdot \text{C}_7\text{H}_8$
Formula weight	981.36
Crystal System	Triclinic
Space group	P1
Unit cell dimensions	10.5163(5) Å
	12.2376(6) Å

	18.5565(6) Å
	$\beta = 94.095(2)^\circ$
Volume	2292.79(17) Å ³
Z	2
Density (calculated)	1.421 g cm ⁻³
F(000)	1004
Theta range for data collection	2.17 to 23.21°
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 12, -20 ≤ l ≤ 19
Reflections collected	10672
Independent reflections	7699
Data / restraints / parameters	10672 / 1351 / 829
Goodness of fit on F ²	1.085
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0713, wR2 = 0.1441
R indices (all data)	R1 = 0.1118, wR2 = 0.1642
Largest diff peak and hole	0.810, -1.405 e Å ³
Flack parameter	0.26(5)

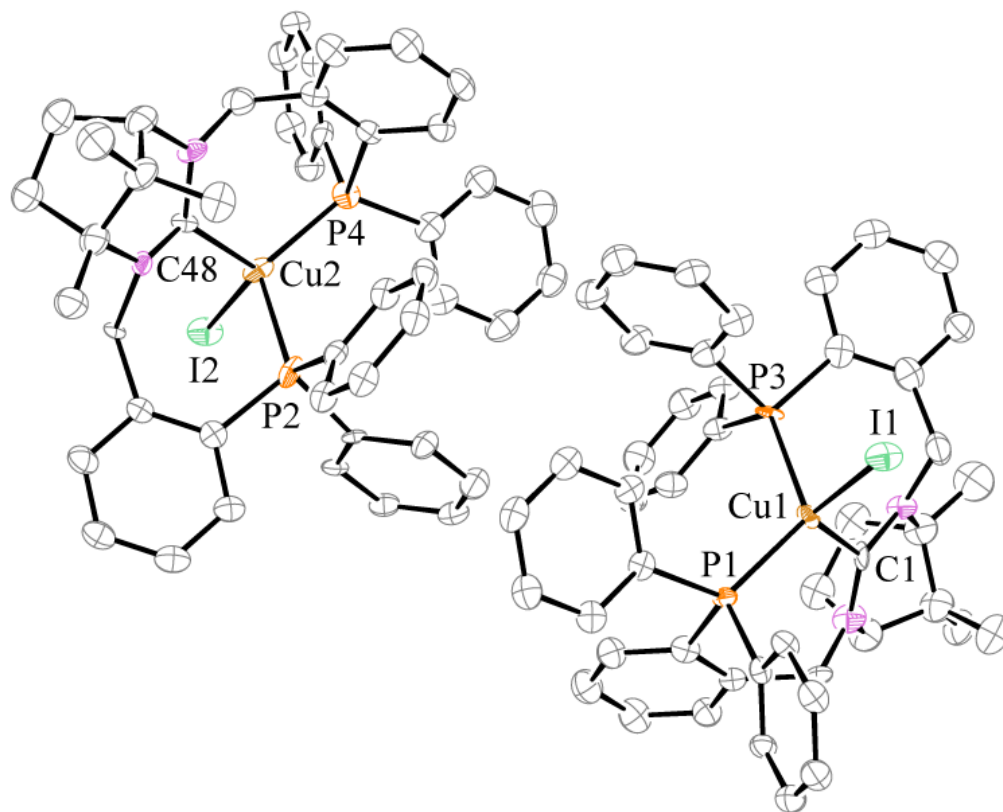


Figure S12. Ellipsoid plot of the two diastereomers of **2c**.

ⁱ G.M. Sheldrick, *Acta Crystallogr., Sect. A.*, 1990, **46**, 467.

ⁱⁱ G.M. Sheldrick, Program for Crystal Structure Refinement, Universitat Gottingen, 1997.