# Supporting information

## Exploring Asymmetric Electrochemical Atom Transfer Radical Addition with Chiral Copper Complexes.

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# Experimental section

## Reagents

1,2,3,4-Tetrahydroisoquinoline (**4**), 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine (**10**), ammonium *D*-(+)-α-bromocamphor-2-sulfonate (**8**), bromoacetonitrile, 2-bromopropionitrile, styrene and copper(II) perchlorate hexahydrate were obtained from commercial sources. Anhydrous acetonitrile and tetrahydrofuran (THF) were distilled from $CaH_2$ and sodium/benzophenone, respectively, under an Ar atmosphere. All moisture-sensitive reactions were performed with oven-dried glassware. $Et_4N(ClO_4)$ was prepared, and purified, as previously described.[1] were purchased from Ambeed with the latter necessitating separation from its stabilisers using an alumina plug.

## Instrumentation

### *Nuclear Magnetc Resonance*

NMR spectra were recorded with a Bruker AS500 (500 MHz, 125 MHz), AV500 (500 MHz, 125 MHz) or AV400 (400 MHz, 101 MHz) spectrometer at 25 °C in deuterated solvent solutions ($CDCl_3$) and referenced against solvent resonances ($CHCl_3$, $^1H$ 7.26 ppm, $^{13}C\{^1H\}$ 77.16 ppm). The signal multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, ddd = doublet of doublet of doublet, m = multiplet.

### *Mass Spectrometry and Chiral Gas Chromatography*

High-resolution mass spectrometry (HRMS) was conducted using a Bruker MicroOTOF-Q spectrometer HCT 3D Ion Trap spectrometer, and a Shimadzu GCMS-QP5000 spectrometer. Chiral gas chromatography (GC) analyses were performed on a Shimadzu Nexis GC-2030 instrument equipped with an RT-bDEXcst chiral capillary column.

### *Crystallography*

Crystallographic data were acquired either an Oxford Diffraction Gemini Ultra S dual source (Mo/Cu) diffractometer at 190 K (cooling with an Oxford Cryosystems Desktop Cooler) or a Bruker D8 Venture dual source (Mo/Cu) diffractometer at 150 K (Oxford Cryosystems Cobra cooling unit). Structures were solved with SHELXT and refined with SHELXL.[2] Thermal ellipsoid diagrams were generated with Mercury.[3] All

calculations were carried out within the WinGX user interface.[4] All non-H atoms were refined anisotropically except minor contributors to disorder (perchlorate O-atoms and solvent molecules (MeCN, $Et_2O$), which were modelled with partial occupancies where appropriate. H atoms were included at calculated positions using a riding model. Crystal and refinement data are given in Table S1. Data collected with Mo radiation (λ = 0.71073 Å) were cut off at 2θ = 55°, while data collected with Cu radiation (λ = 1.54184 Å) were cut off at 2θ = 126°.

### *UV-Vis Spectroscopy and Spectroelectrochemistry*

A Shimadzu UV−2600 UV-visible spectrophotometer was used for all accurate solution UV-Vis spectroscopy. For spectroelectrochemistry, an Agilent 8453 Diode Array UV–Vis Spectrometer was used with a Pine Instruments honeycomb spectroelectrochemical electrode and cell (path length 1.6 mm) comprising a platinum working electrode and a separate platinum auxiliary electrode. A nonaqueous $Ag^{0/+}$ in MeCN (0.1 M $Et_4N(ClO_4)$) reference electrode was used, calibrated externally relative to the $Fc^{0/+}$ couple. The applied potential was set using a Gamry Interface 1010E potentiostat in constant-potential electrolysis mode. All measurements were conducted under a blanket of $N_2$ introduced by a fine needle into the top of the cell.

### *Cyclic voltammetry*

Cyclic voltammograms were recorded with an Epsilon Eclipse potentiostat. The configuration for cyclic voltammetry experiments consisted of a Pt (1.6 mm diam.) working electrode, a nonaqueous $Ag^{+/0}$ reference electrode (0.1 M $Et_4N(ClO_4)$ in anhydrous MeCN), and a Pt wire counter electrode. All experiments were performed at room temperature, and the data are referenced versus the $Fc^{0/+}$ couple.

## Ligand Syntheses

The syntheses of N,N'-dimethyl-bis(2'-pyridylmethyl(R,R-cyclohexane-1,2-diamine) (**BPCDA**)[5] and N,N'-dibenzyl-bis(2'-pyridylmethyl(R,R-cyclohexane-1,2-diamine) (**BNBPCDA**)[6] have been published.

*3,4-dihydroisoquinoline* ***5.***

This reaction was conducted following the modified procedure reported by Pelletier et al.[7] In an oven dried, argon flushed, two necked round bottom flask equipped

with a stirrer bar, 1,2,3,4-tetrahydroisoquinoline (**4**, 10.0 g, 75.2 mmol) and $CH_2Cl_2$ (200 mL) were added and stirred at room temperature. The reaction flask was covered in aluminium foil and freshly recrystallised, dry, N-bromosuccinimide (14.7 g, 82.7 mmol) was added in regular portions over the course of 40 to 50 min. The solution turned orange at the end of the addition, and the mixture was let stir for an additional 1.5 h. The solution was cooled at 0°C and $NaOH_{(aq)}$ (200 mL , 40 wt%) was added slowly before the mixture was allowed to warm to room temperature over 5h. Workup was conducted immediately after. Water (100 mL) was added and the two layers were separated. The organic layer was extracted with $HCl_{(aq)}$ (2 × 100 mL, 10 wt%) and the combined acidic layers were washed with $CH_2Cl_2$ (100 mL). $NaOH_{(aq)}$ (70 mL, 40 wt%) was added and the aqueous suspension was allowed to cool room temperature before $CH_2Cl_2$ extraction (3 × 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated to dryness to yield a viscous light orange oil crude. Purification was performed using a Kügelrohr apparatus (0.97-1.0 mm Hg, 70-80°C) and yielded a colourless viscous oil (8.6 g, 86% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.34 (dt, J = 2.6, 1.3 Hz, 1H), 7.36 (td, J = 7.1, 2.1 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.16 (ddt, J = 7.3, 1.5, 0.8 Hz, 1H), 3.78 (qd, J = 2.2, 1.4 Hz, 2H), 2.78 – 2.73 (m, 2H). Note: adequate storage conditions are required (i.e. freezer, inert atmosphere) to prevent degradation.

*1,1',2,2',3,3',4,4'-octahydrobiisoquinoline meso/rac mixture* ***6.***

This followed a slightly modified procedure by Alexakis et al.[8] In an oven dried, argon flushed, two necked round bottom flask equipped with a stirrer bar and reflux condenser was added ground magnesium turnings (3.1 g, 130 mmol,) and 3,4-dihydroisoquinoline (8.5 g, 64 mmol) with dry THF (30 mL). TMSCl (16 mL, 130 mmol) was initially added slowly to temper fuming before completing the addition. The mixture was then heated to reflux for 2h before cooling to 0°C. $NH_{3(aq)}$ (35 mL, 25 wt%) was added extremely slowly before saturated $NH_4Cl_{(aq)}$ (35 mL) was poured in the reaction flask. Vacuum filtration was performed and the solid was washed with $Et_2O$ and discarded. The filtrate was extracted with $Et_2O$ (100 mL) and $CH_2Cl_2$ (2 × 100 mL), the organic layers were combined, dried over anhydrous $K_2CO_3$, and evaporated to dryness to yield the

stereoisomer mixture **6** (8.11 g, 82 %) and **4** (0.84 g, 8 %)[‡] as a crude yellow to orange wet solid (8.95 g 90 % mass recovery).

*Rac-1,1',2,2',3,3',4,4'-octahydrobiisoquinoline* ***7/7'.***

This step was adapted from a procedure reported by Elliott et al.[9] In a round bottomed flask, the partially reduced octahydro-1,1'-biisoquinoline crude mixture **6** (8.85 g) was carefully mixed with concentrated HBr (30 mL, 48 wt%). The mixture was stirred at room temperature for 1h before the suspension was filtered under vacuum, yielding an off-white paste. This was redissolved in boiling HBr (200 mL, 10 wt%) for an additional 16 h. After complete dissolution, the solution was cooled to room temperature and bromide salts **7**·2HBr rand **7'**·2HBr were recovered as an off-white solid (4.18 g). The salts were dissolved in a mixture of $Et_2O$ (100 mL) and $NaOH_{(aq)}$ (100 mL, 20 wt%) under vigorous stirring. The organic layer was separated, dried over anhydrous $K_2CO_3$, filtered and evaporated to dryness to afford the racemic mixture as a colourless solid (2.31 g, 26 % yield over two steps). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.17 (td, *J* = 7.4, 1.4 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.70 (s, 1H), 3.20 (ddd, *J* = 11.8, 5.0, 2.2 Hz, 1H), 2.99 – 2.88 (m, 1H), 2.82 (td, *J* = 11.5, 3.0 Hz, 1H), 2.66 – 2.57 (m, 1H).

*(S,S)-1,1',2,2',3,3',4,4'-octahydrobiisoquinoline* ***7.***

This step was adapted from a procedure reported by Elliott et al.[9] In a round bottomed flask racemic 1,1',2,2',3,3',4,4'-octahydro-1,1'-biisoquinoline **7**/**7'** (2.31 g, 8.7 mmol) and ammonium *d*-(+)-3-bromocamphor-8-sulfonic acid **(+)-8** (2.86 g, 8.7 mmol) were added with EtOH (24 mL). The mixture was refluxed until full dissolution was achieved. The mixture was cooled to room temperature which afforded large crystals of **(+)-8** which were filtered off. The EtOH filtrate was then evaporated to dryness, and the mixture of **7**/**7'** and **(+)-8**) was stirred in hot EtOH (12 mL) until dissolution. The mixture was again cooled to room temperature before it was transferred to a refrigerator for crystallisation. Crystals of the salt **9** (from **7** and **(+8)**) were collected and redissolved in a mixture of $CH_2Cl_2$ (50 mL) and $NaOH_{(aq)}$ (50 mL, 20 wt%) under vigorous stirring. The two

[‡] Yields determined from $^1$H NMR integrations with the following signals: $^1$H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 2H) *rac*-**7/7'.**, 4,64 (s, 2H) *meso* isomer, 4.02 (s, 0.95H).

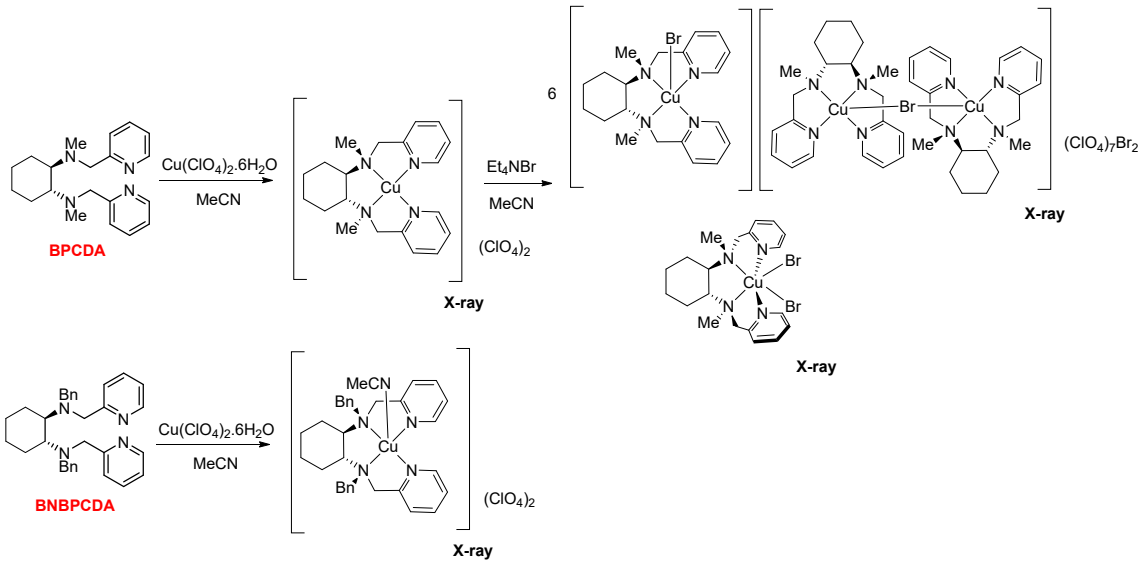
layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (50 mL). The organic layers were combined, dried over NaOH pellets and evaporated to dryness under reduced pressure to yield (1*S*,1'*S*)- 1,1',2,2',3,3',4,4'-octahydro-1,1'-biisoquinoline **7** as a colourless solid (1.09 g, 47% yield) after reprecipitation in $Et_2O$. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 (td, J = 7.4, 1.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 4.70 (s, 1H), 3.20 (ddd, J = 11.8, 5.0, 2.2 Hz, 1H), 2.98 – 2.89 (m, 1H), 2.83 (td, J = 11.5, 3.0 Hz, 1H), 2.66 – 2.57 (m, 1H).

*N,N'-bis(4-methoxy-3,5-dimethylpyridylmethyl)-1,1',2,2',3,3',4,4'-octahydrobiisoquinoline* ***$^{MeO}$Ohq.***

This procedure was adapted from work conducted by Clarosó et al.[10] In an oven dried, argon flushed, two necked round bottomed flask, **7** (1.09 g, 4.1 mmol), 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine (1.52 g, 8.2 mmol), anhydrous sodium carbonate (7.0 g, 66 mmol) and $Et_4NBr$ (0.1 g, 0.29 mmol) were added with MeCN (75 mL). The mixture was then stirred under reflux for 20 h. The reaction mixture was cooled to room temperature before it was transferred in a round bottomed flask and evaporated to dryness under vacuum. $NaOH_{(aq)}$ (100 mL, 4 wt%) and $CH_2Cl_2$ (100 mL) were added and the layers separated. The aqueous layer was subsequently extracted with $CH_2Cl_2$ (2 × 50 mL) and the organic layers were collectively dried over NaOH pellets before removal of the solvent. A light brown solid was obtained after $Et_2O$ reprecipitation. This was then recrystallised in MeCN (5 mL) and cold MeCN washes yielded the ligand **$^{MeO}$Ohq** as a white crystalline solid (1.67 g, 72% yield). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 6.94 – 6.91 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.77 (dq, *J* = 8.2, 4.1 Hz, 1H), 4.12 (s, 1H), 3.71 (d, *J* = 12.2 Hz, 1H), 3.62 (s, 3H), 3.50 (ddd, *J* = 12.5, 10.0, 4.4 Hz, 1H), 2.89 (ddd, *J* = 15.6, 10.1, 5.1 Hz, 1H), 2.73 (dt, *J* = 12.6, 4.6 Hz, 1H), 2.49 (dt, *J* = 16.2, 4.2 Hz, 1H), 2.19 (d, *J* = 0.7 Hz, 3H), 2.01 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.93, 157.32, 148.02, 136.63, 135.98, 128.57, 128.22, 126.62, 125.26, 125.08, 124.96, 77.42, 77.36, 77.16, 76.91, 65.98, 60.35, 59.88, 45.88, 24.86, 13.38, 10.74. m/z (ESI) 563.3374 (cation $[M - H]^+$, 100%), $[\alpha]^D$ = 7.97 (c 0.01, EtOH).

The same procedure was followed for the racemic ligand ***rac*-$^{MeO}$Ohq** starting from racemic mixture **7/7'**.

## Cu Complex Syntheses




**Scheme S1.** Syntheses of Cu complexes of BPCDA and BNBPCDA.

***Caution.*** Perchlorate salts are potentially explosive, and special care should be taken when handling them. They should never be heated in the solid state or scraped from sintered glass frits.

***[Cu(BPCDA)](ClO$_4$)$_2$***

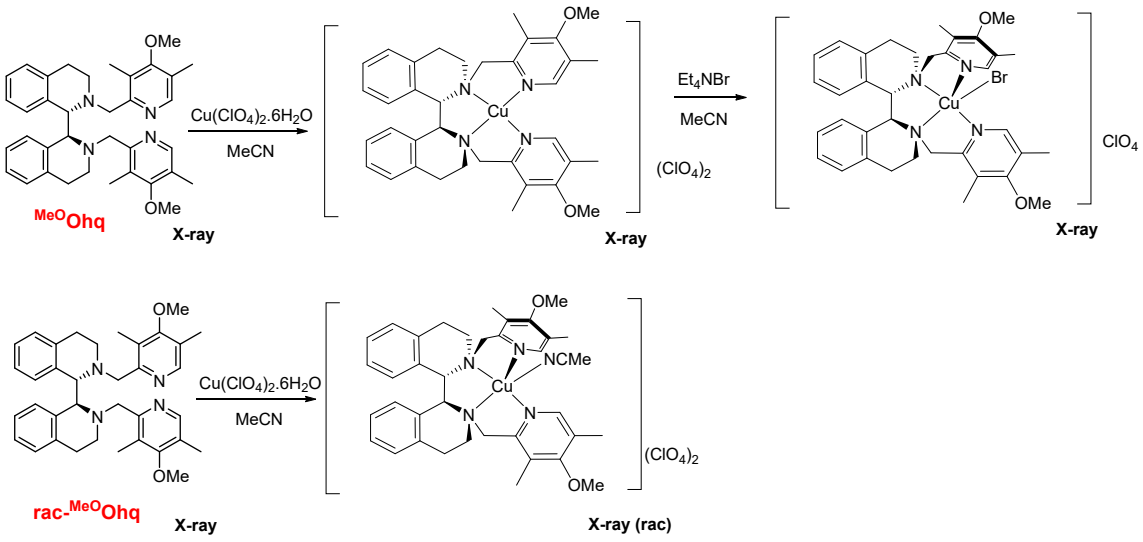
A solution of BPCDA (0.88 g, 2.71 mmol) in MeCN (10 mL) was added dropwise to a solution of Cu(ClO$_4$)$_2$·6H$_2$O (1.00 g, 2.71 mmol) in MeCN (30 mL). The reaction mixture was stirred at 40 °C to obtain a deep blue solution. After 4 h, the reaction mixture was cooled to room temperature and the product crystallised by vapour diffusion of diethyl ether into the MeCN solution to afford purple crystals (1.35 g, 80%) of [Cu(BPCDA)](ClO$_4$)$_2$.

***[{Cu(BPCDA)}$_2$(μ-Br)]·6[Cu(BPCDA)Br](ClO$_4$)$_7$Br$_2$·2MeCN·3H$_2$O and [Cu(BPCDA)Br$_2$]***

Crystals of the halido complexes for X-ray crystallography were obtained by the addition of 6 equivalents of Et$_4$NBr to a MeCN solution of [Cu(BPCDA)](ClO$_4$)$_2$. The colour of the solution changed to green, and vapor diffusion of Et$_2$O afforded crystals suitable for single-crystal X-ray diffraction. Different forms crystallised from the same solution and these were identified based on their habit and analysed separately.

### *[Cu(BNBPCDA)(NCMe)](ClO$_4$)$_2$·MeCN*

A solution of BNBPCDA (1.643 g, 3.45 mmol) in MeCN (20 mL) was added dropwise to a solution of Cu(ClO$_4$)$_2$·6H$_2$O (1.278 g, 3.45 mmol) in MeCN (10 mL). The reaction mixture was stirred at 40 °C to obtain a deep blue solution. After 4 h, the reaction mixture was cooled to room temperature and the product crystallised by vapour diffusion of diethyl ether into the MeCN solution to afford blue crystals (1.44 g, 54%) of [Cu(BNBPCDA)(NCMe)](ClO$_4$)$_2$.MeCN.




**Scheme S2.** Syntheses of Cu complexes of $^{MeO}$Ohq and rac-$^{MeO}$Ohq.

### *[Cu($^{MeO}$Ohq)](ClO$_4$)$_2$·0.5Et$_2$O*

In a two necked round bottomed flask equipped with a stirrer bar, a solution of copper(II) perchlorate hexahydrate (370 mg, 1.0 mmol, 1 equiv) in EtOH (10 mL) was added and stirred at room temperature while a solution of $^{MeO}$Ohq (570mg, 1.0 mmol, 1 equiv) in 10 mL EtOH (10 mL) was added dropwise. The now indigo solution was heated to reflux for 3h or until no dark blue tar was found at the bottom of the flask. The solution was then poured into a conical flask, allowed to cool at room temperature and then slowly topped with n-pentane (20 to 30 mL) and placed in a refrigerator for 24 to 48h. Purple thin needles were recovered from the solution through vacuum filtration before being dried under vacuum for 24 additional hours. To obtain crystals suitablefor X-ray diffraction, 20 mg (0.024 mmol) of the purple powder was added to a 20 mL vial and dissolved in a

minimum amount of MeCN. Vapour diffusion of diethyl ether into the MeCN solution, gave purple crystals.

***[Cu($^{MeO}$Ohq)Br](ClO$_4$)·EtOH***

In a 20 mL vial, [Cu($^{MeO}$Ohq)](ClO$_4$)$_2$·½Et$_2$O (20 mg, 0.024 mmol), 1 equiv) and Et$_4$NBr (5.0 mg, 0.11 mmol, 2 equiv) were dissolved in EtOH (2 mL) to give a cyan coloured solution. The vial was then placed inside a larger glass jar containing Et$_2$O (15 mL). Vapor diffusion afforded crystals suitable for X-ray work.

***[Cu(rac-$^{MeO}$Ohq)](ClO$_4$)$_2$***

In a two-necked round bottomed flask equipped with a stirrer bar, a solution of copper(II) perchlorate hexahydrate (370 mg, 1.0 mmol) in EtOH (10 mL) was added and stirred at room temperature while a solution of *rac*-$^{MeO}$Ohq (570mg, 1.0 mmol) in EtOH (10 mL) was added dropwise. The ensuing indigo solution was heated to reflux for 3 h until no dark blue tar was found at the bottom of the flask. The solution was then poured in a conical flask, allowed to cool at room temperature and then slowly topped with *n*-pentane (20 to 30 mL) for layer diffusion crystallisation. The conical flask was then placed in a refridgerator for 24 to 48 h. Purple needles were then recovered from the solution through vacuum filtration before being dried under vacuum for 24 h.

***[Cu(rac-$^{MeO}$Ohq)(NCMe)](ClO$_4$)$_2$***

In a two necked round bottomed flask equipped with a stir bar, a solution of copper (II) perchlorate hexahydrate (370 mg, 1.0 mmol) in EtOH (10 mL) was added and stirred at room temperature while a solution of *rac*-$^{MeO}$Ohq (570 mg, 1.0 mmol in EtOH (10 mL) was added dropwise. The now blue solution was heated to reflux for 3h. The solution was then poured in a vial, allowed to cool at room temperature and n-pentane was then added until full precipitation of the complex. The light blue solid was filtered off. Vapour diffusion of Et$_2$O into a concentrated MeCN solution of the complex afforded crystals suitable for X-ray work.

## *e*ATRA Synthesis

The bulk electrolysis setup consisted of an “H-Cell” with each compartment 10 cm (height) × 2.5 cm (diameter) and separated by a sintered glass frit. In the working

electrode compartment a Pt basket (2.7 × 4.8 × 0.1 cm), and a nonaqueous $Ag^{+/0}$ (MeCN) reference electrode were installed, and a smaller Pt basket (2.7 × 3.5 × 0.1 cm) or Pt mesh electrode was added to the counter electrode compartment. The Pt electrodes and glassware used for bulk electrolysis were cleaned before each use with piranha solution (4:1 mixture of $H_2SO_4$:$H_2O_2$, caution!). A typical bulk electrolysis procedure is as follows.

An oven-dried H-cell set up was cooled under argon. Styrene (100 mg, 0.96 mmol, 1 equiv), organic bromide (1.92 mmol, 2 equiv) and $[Cu^{II}L](ClO_4)_2$ (L = BPCDA or $^{MeO}$Ohq) were dissolved in 10 mL of a 0.1 M $Et_4N(ClO_4)$ solution in MeCN and placed into the working electrode compartment while 10 mL of a 0.1 M $Et_4N(ClO_4)$ solution in MeCN was added simultaneously to the counter electrode compartment. During electrolysis at potential $E_{appl}$ (from cyclic voltammetry, see Fig. S2) a constant stream of argon was maintained to both cell compartments.

The solution in the working electrode compartment was transferred to a beaker with $CH_2Cl_2$. The mixture was thoroughly washed with distilled water (3 × 100 mL). The $CH_2Cl_2$ layer containing the product was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (230-400 mesh size), with *n*-hexane/EtOAc solvent mixtures in varying proportions for each product (usually gradient from 0 to 40% EtOAc). Isolated yields are reported (Table 2). The NMR data (below) agree with the spectra published for **11** and **12**.[11, 12]

**11** $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 5.10 – 4.98 (m, 1H), 2.63 – 2.37 (m, 4H).
**12** (2 diastereomers) $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 8H), 5.14 (dd, J = 11.0, 3.8 Hz, 1H), 5.08 (dd, J = 9.2, 6.7 Hz, 1H), 3.10 (dqd, J = 10.5, 7.1, 4.8 Hz, 1H), 2.64 (ddd, J = 13.5, 9.0, 6.7 Hz, 1H), 2.52 – 2.32 (m, 3H), 2.26 (ddd, J = 14.5, 10.5, 3.8 Hz, 1H), 1.42 (d, J = 7.1 Hz, 3H), 1.33 (d, J = 6.9 Hz, 3H).

## Crystallography

### **Table S1.** Crystal and Refinement Data

| | $^{MeO}$**Ohq** | ***rac*-$^{MeO}$Ohq** | **[Cu(BPCDA)](ClO$_4$)$_2$** | **[Cu(BPCDA)Br$_2$]** |
|---|---|---|---|---|
| formula | $C_{36}H_{42}N_4O_2$ | $C_{36}H_{42}N_4O_2$ | $C_{20}H_{28}Cl_2CuN_4O_8$ | $C_{20}H_{28}Br_2CuN_4$ |
| F.W. | 562.73 | 562.73 | 586.90 | 547.82 |
| WL (Å) | 1.54184 | 0.71073 | 1.54184 | 1.54184 |
| Cryst. sys. | tetragonal | monoclinic | monoclinic | tetragonal |
| Sp. Gr. | $P4_12_12$ | $C2/c$ | $P2_1$ | $P4_12_12$ |
| $a$ (Å) | 11.1967(3) | 16.438(3) | 8.2035(3) | 9.2340(1) |
| $b$ (Å) | 11.1967(3) | 6.906(1) | 10.3285(4) | 9.2340(1) |
| $c$ (Å) | 25.1270(7) | 27.092(5) | 14.0427(5) | 24.0323(4) |
| $\beta$ (°) | | 104.848(5) | 90.891(3) | |
| $V$ (Å$^3$) | 3150.1(2) | 2972.7(9) | 1189.69(8) | 2049.16(6) |
| $T$ (K) | 150 | 150 | 190 | 190 |
| $Z$ | 4 | 4 | 2 | 4 |
| $R_1$ (obs.) | 0.0341 | 0.0731 | 0.0462 | 0.0332 |
| $wR_2$ (all) | 0.0908 | 0.1619 | 0.1173 | 0.0847 |
| GOF | 1.055 | 1.125 | 1.03 | 1.068 |
| CCDC | 2493586 | 2493587 | 2493588 | 2493589 |

| | **[{Cu(BPCDA)}$_2$(μ–Br)] ·6[Cu(BPCDA)Br](ClO$_4$)$_7$Br$_2$ ·2MeCN·3H$_2$O** | **[Cu(BNBPCDA)(NCMe)](ClO$_4$)$_2$·MeCN** |
|---|---|---|
| formula | $C_{164}H_{236}Br_9Cl_7Cu_8N_{34}O_{31}$ | $C_{36}H_{42}Cl_2CuN_6O_8$ |
| F.W. | 4655.51 | 821.19 |
| WL (Å) | 1.54184 | 1.54184 |
| Cryst. Syst. | monoclinic | Orthorhombic |
| Sp. Gr. | $P2$ | $P2_12_12_1$ |
| $a$ (Å) | 15.884(2) | 11.1760(5) |
| $b$ (Å) | 11.778(1) | 14.4703(7) |
| $c$ (Å) | 26.135(3) | 23.124(1) |
| $\beta$ (°) | 90.854(3) | |
| $V$ (Å$^3$) | 4888.7(8) | 3739.5(3) |
| $T$ (K) | 150 | 150 |
| $Z$ | 1 | 4 |
| $R_1$ (obs.) | 0.0652 | 0.0531 |
| $wR_2$ (all) | 0.1950 | 0.1320 |
| GOF | 1.038 | 1.111 |
| CCDC | 2493590 | 2493591 |

## Table S1 (continued).

| | [Cu($^{MeO}$Ohq)](ClO$_4$)$_2$·½Et$_2$O | [Cu($^{MeO}$Ohq)Br](ClO$_4$)·EtOH | [Cu(*rac*-$^{MeO}$Ohq)(NCMe)](ClO$_4$)$_2$ |
|---|---|---|---|
| formula | $C_{36}H_{42}Cl_2CuN_4O_{10}$ | $C_{38}H_{48}BrClCuN_4O_7$ | $C_{38}H_{45}Cl_2CuN_5O_{10}$ |
| F.W. | 825.17 | 851.70 | 866.23 |
| WL (Å) | 1.54184 | 1.54184 | 0.71073 |
| Cryst. Syst. | monoclinic | monoclinic | monoclinic |
| Sp. Gr. | $P2_1$ | $P2_1$ | $P2_1/n$ |
| *a* (Å) | 13.3913(5) | 11.9722(4) | 14.2914(6) |
| *b* (Å) | 9.9980(4) | 13.7073(5) | 17.1771(6) |
| *c* (Å) | 15.3739(6) | 13.1598(6) | 16.8454(7) |
| *β* (°) | 91.828(2) | 115.539(1) | 113.355(1) |
| *V* (Å$^3$) | 2057.3(1) | 1948.60(13) | 3796.5(3) |
| *T* (K) | 150 | 150 | 150 |
| *Z* | 2 | 2 | 4 |
| $R_1$ (obs.) | 0.0608 | 0.0310 | 0.0401 |
| $wR_2$ (all) | 0.1823 | 0.0741 | 0.1021 |
| GOF | 1.136 | 1.033 | 1.024 |
| CCDC | 2493592 | 2493593 | 2493594 |

## Unusual features

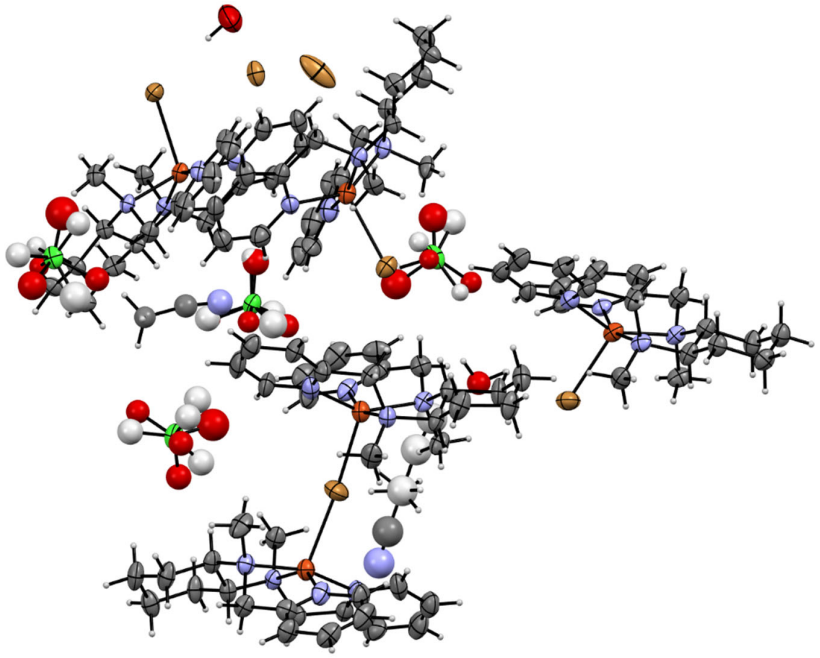


**Figure S1.** ORTEP view of the structure of [{Cu(BPCDA)}$_{2(}$μ–Br)]·6[Cu(BPCDA)Br](ClO$_4$)$_7$Br$_2$·2MeCN·3H$_2$O. Minor contributors to disorder in light grey.

**[{Cu(BPCDA)}$_{2(}$μ–Br)]·6[Cu(BPCDA)Br](ClO$_4$)$_7$Br$_2$·2MeCN·3H$_2$O** (Figure S1): This structure comprises a large asymmetric unit (> 120 non-H atoms, with a Br-bridged dimeric complex occupying a 2-fold axis while the three other independent monomeric Cu complexes are on general positions. All $ClO_4^-$ anions in the asymmetric unit and the MeCN molecule are disordered. For the $ClO_4^-$ ions, the O-atom positional parameters of each contributor were refined with geometric restraints and complementary occupancies, as were the C/N atoms of the MeCN molecule. Also, the atoms Br2 ($Br^-$ anion) and Cl4 (from a $ClO_4^-$ anion) are disordered and were refined with constrained complementary occupancies of 50% which results in some residual positive and negative electron density near Cl4 and Br2. Other non-stoichiometric $ClO_4^-$/Br ratios were not pursued.

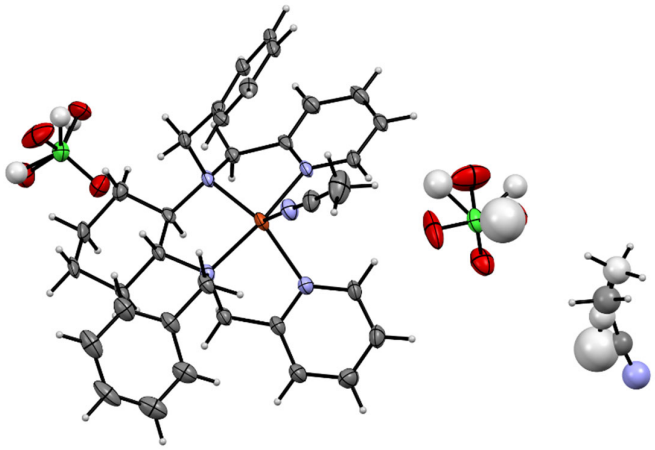


**Figure S2.** ORTEP view of the structure of [Cu(BNBPCDA)(NCMe)]$(ClO_4)_2$·MeCN. Minor contributors to disorder in light grey.

**[Cu(BNBPCDA)(NCMe)]$(ClO_4)_2$·MeCN** (Figure S2): both the $ClO_4^-$ anions and the non-coordinated MeCN molecule are disordered. For the $ClO_4^-$ ions, the O-atom positional parameters of each contributor were refined with geometric restraints (SHELX SAME) and complementary occupancies, as were the C/N atoms of the MeCN molecule.

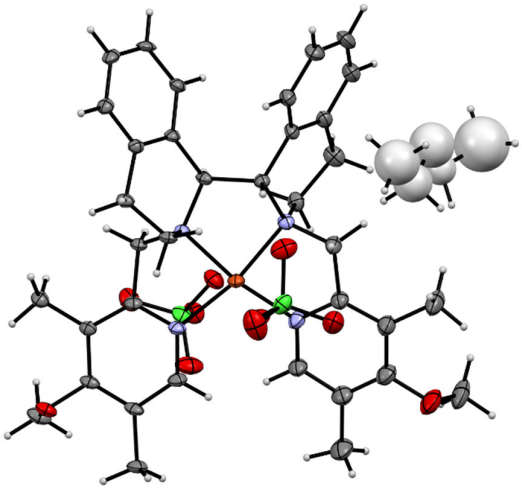


**Figure S3.** ORTEP view of the structure of [Cu($^{MeO}$Ohq)]$(ClO_4)_2$·½$Et_2O$. Partially occupied diethyl ether molecule in light grey.

**[Cu($^{MeO}$Ohq)]$(ClO_4)_2$·½$Et_2O$** (Figure S3): disordered diethyl ether molecules occupy channels parallel to the *b* axis. The $Et_2O$ molecues were modelled at 50% occupancy.

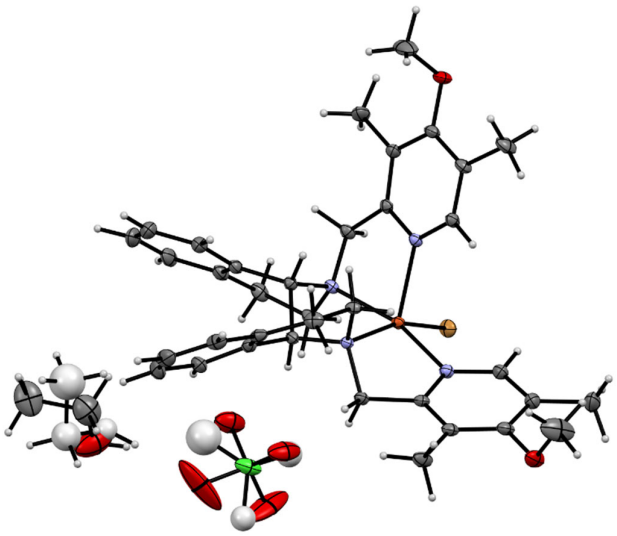


**Figure S4.** ORTEP view of the structure of [Cu($^{MeO}$Ohq)Br]($ClO_4$)·EtOH. Minor contributors to disorder in light grey.

**[Cu($^{MeO}$Ohq)Br]($ClO_4$)·EtOH** (Figure S4) : The $ClO_4^-$ anion and EtOH molecule are disordered and were modelled with complementary occupancies and with geometric restraints and isotropic thermal parameters for the minor contributors.

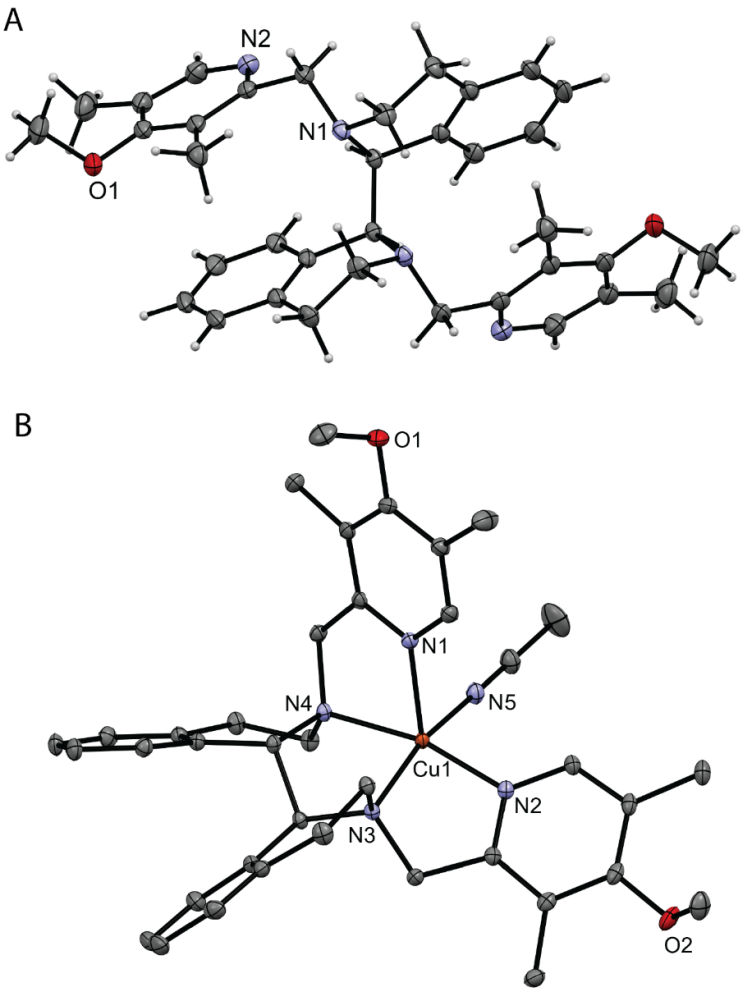



**Figure S5.** ORTEP images (30% probability ellipsoids) from the crystal structures of (A) *rac*-$^{MeO}$OHq (*S,S* enantiomer) (B) [Cu(*rac*-$^{MeO}$OHq)(NCMe)]$(ClO_4)_2$ (*S,S* enantiomer shown). For (B) H-atoms, solvent molecules and counter anions omitted for clarity.

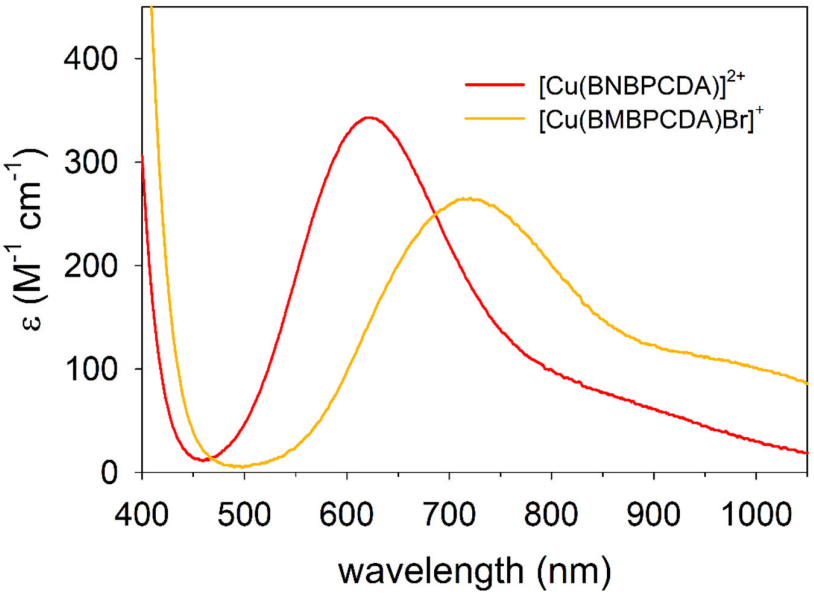



**Figure S6.** Solvent and anion dependent UV-vis spectra of $[Cu(BNBPCDA)]^{2+}$.

## Electrochemical Data

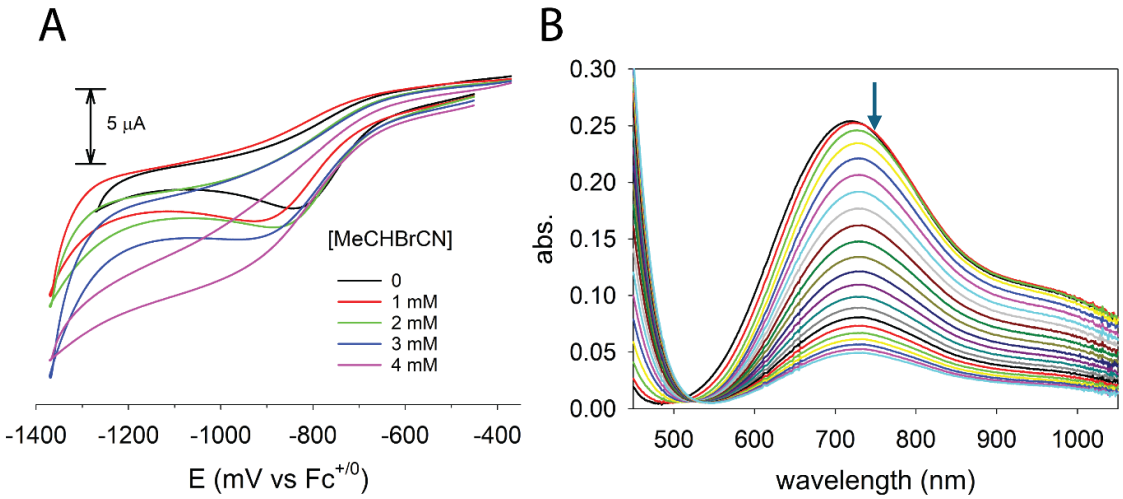



**Figure S7.** (A) Cyclic voltammetry of $[Cu(BNBPCDA)Br]^+$ (1 mM) with the sequential addition of 2-bromoproprionitrile (0.1 M $Et_4N(ClO_4)$ as supporting electrolyte in MeCN, scan rate 20 mV $s^{-1}$). - (B) Spectroelectrochemistry of $[Cu(BNBPCDA)Br]^+$ (6 mM in MeCN, 0.1 M $Et_4N(ClO_4)$ and $BrCH_2CN$ (18 mM) with the potential poised at −700 mV vs $Fc^{+/0}$). The spectra were measured at 3 s intervals.

## NMR data

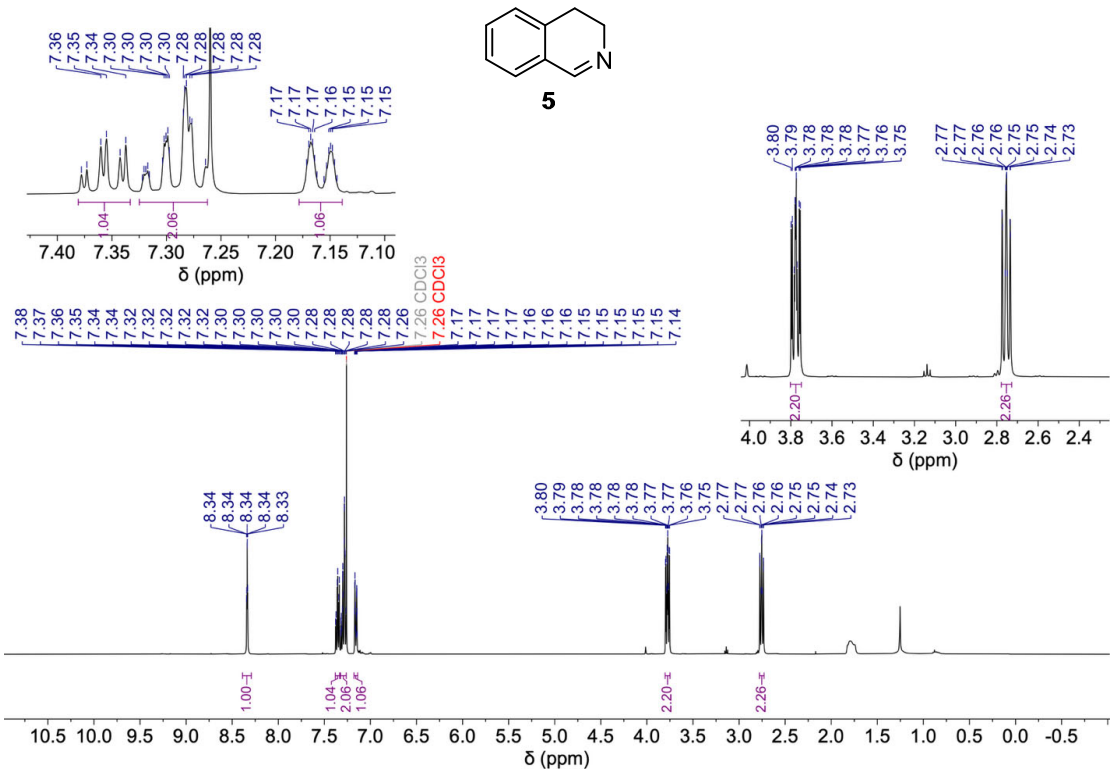



**Figure S8.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **5.**

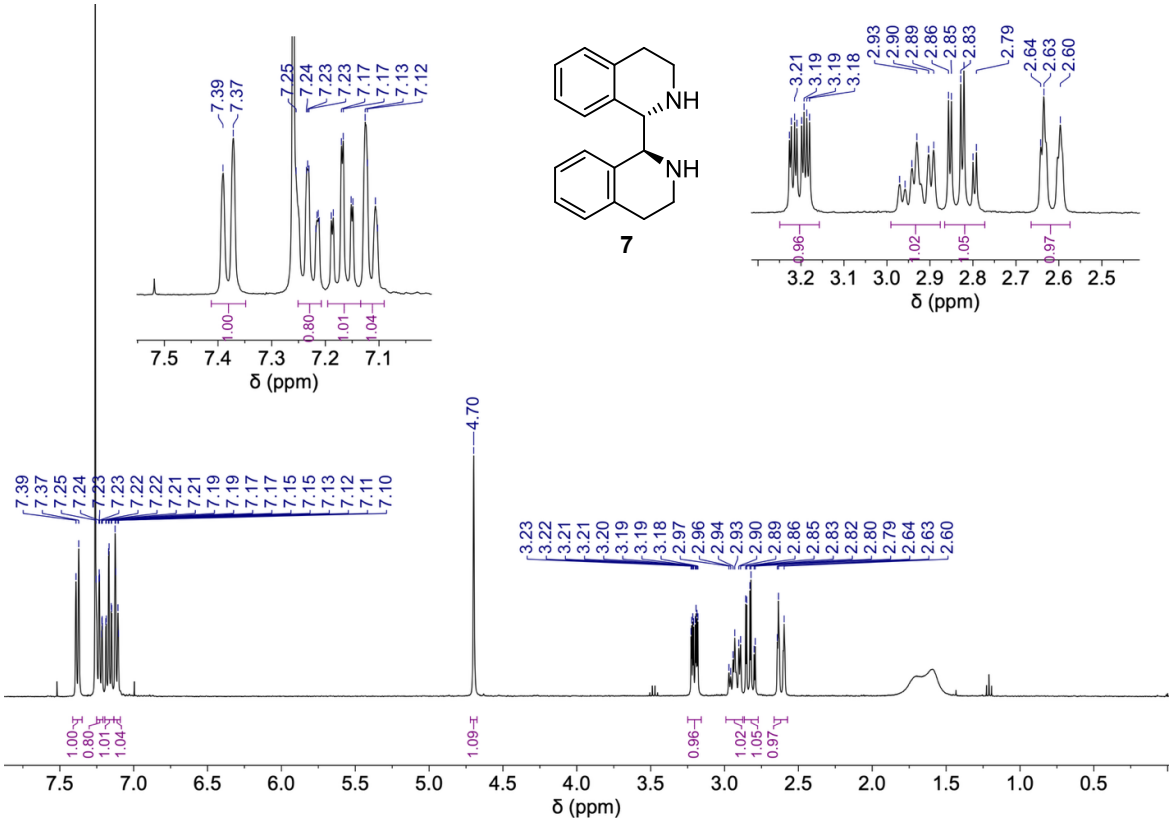



**Figure S9.** $^{1}$H-NMR (400 MHz, $CDCl_3$) of **7.**

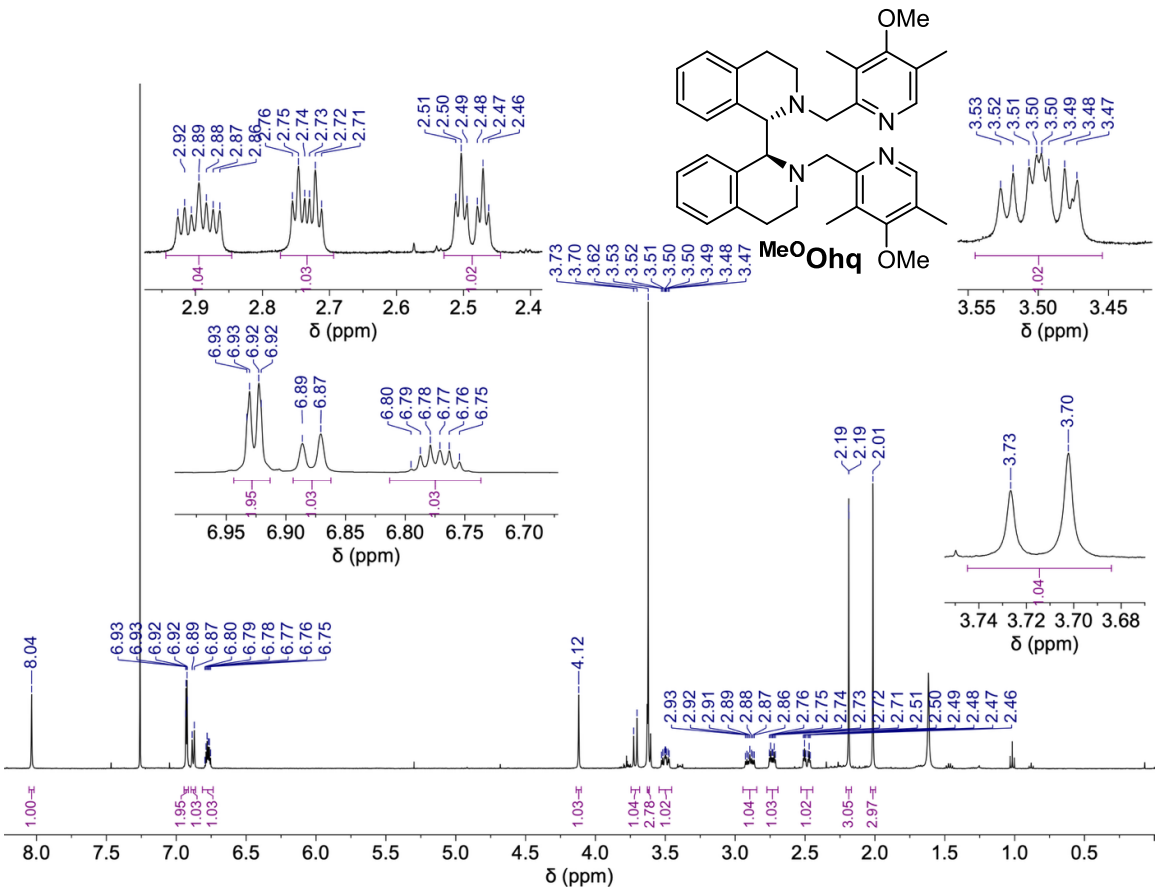



**Figure S10.** $^{1}$H-NMR (500 MHz, $CDCl_3$) of $^{MeO}$**Ohq**.

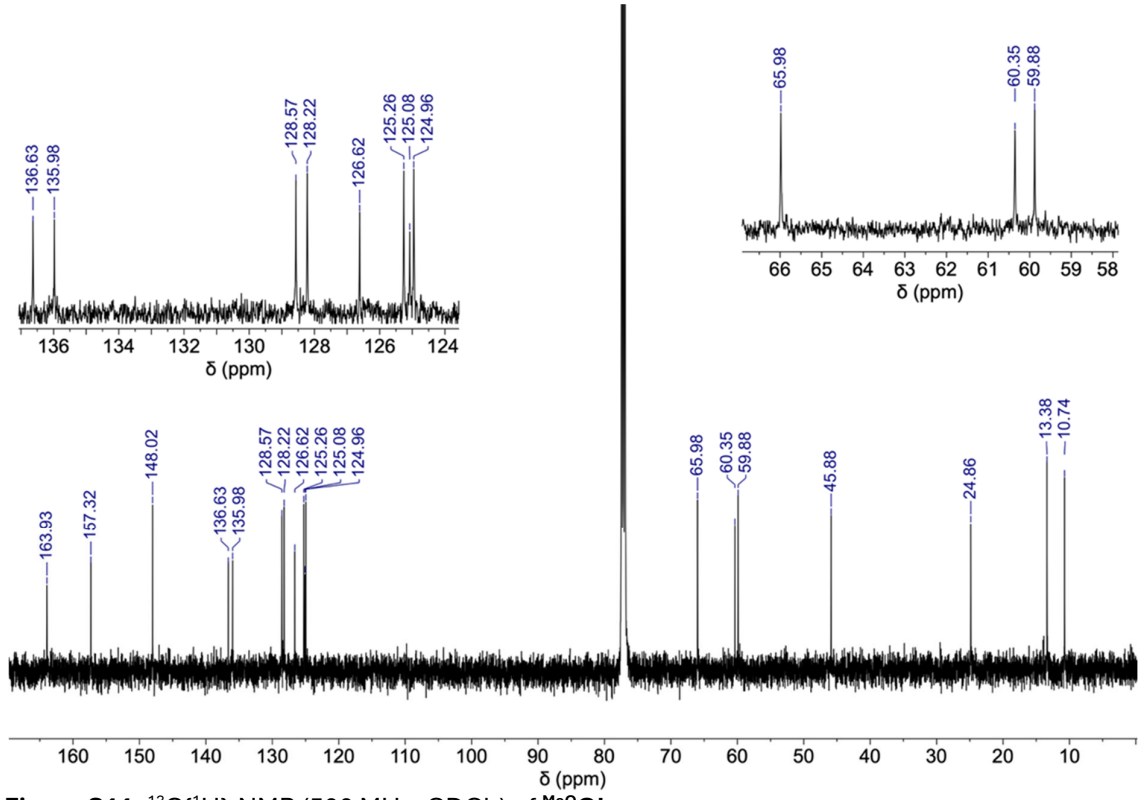



**Figure S11.** $^{13}C\{^{1}H\}$-NMR (500 MHz, $CDCl_3$) of $^{MeO}$**Ohq**.

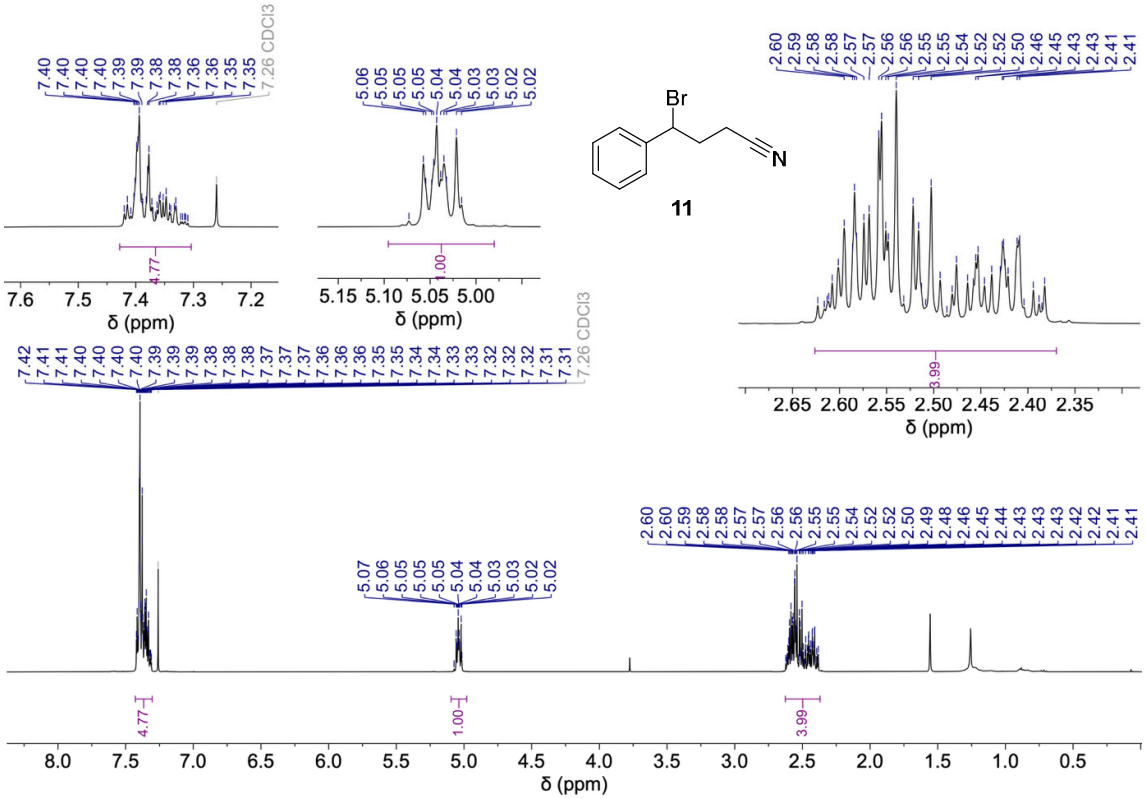



**Figure S12.** $^{1}$H-NMR (500 MHz, $CDCl_3$) of **11**.

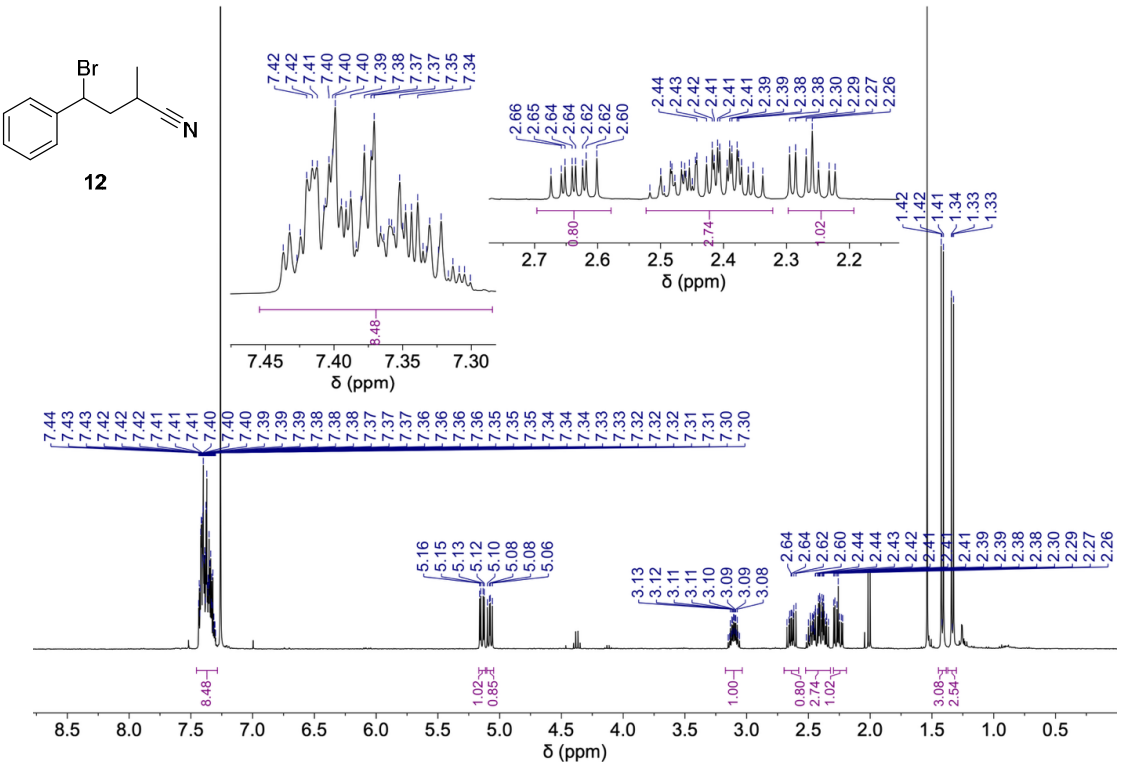



**Figure S13.** $^{1}$H-NMR (500 MHz, $CDCl_3$) of **12** (2 diastereomers).

## Chiral Gas Chromatography

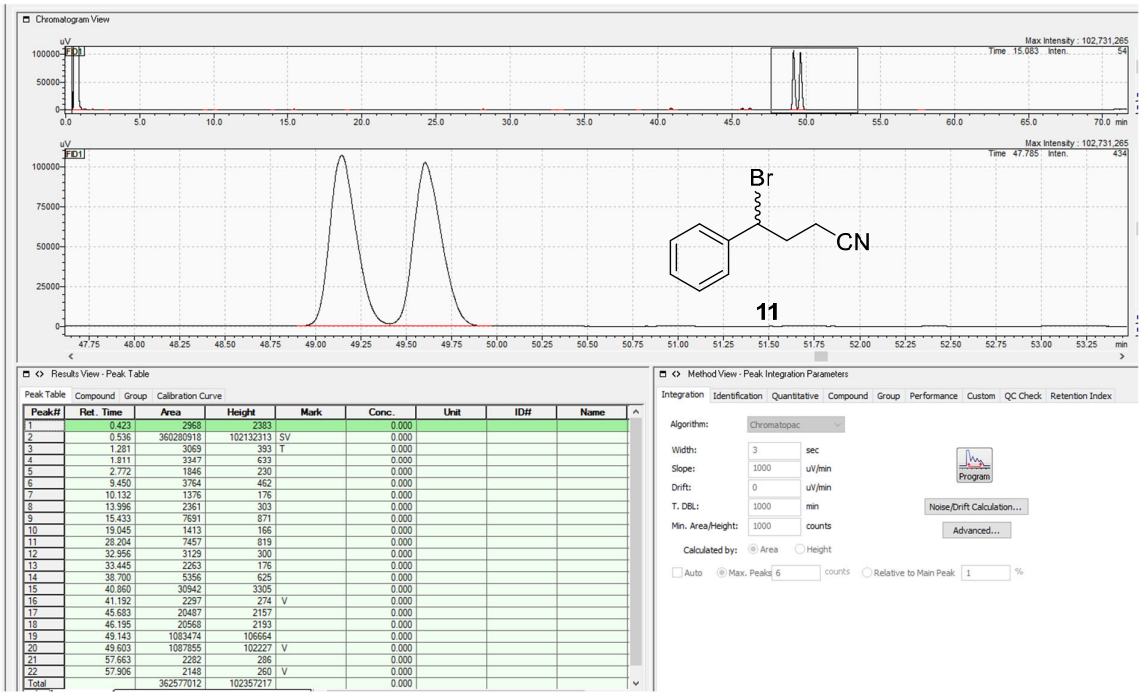
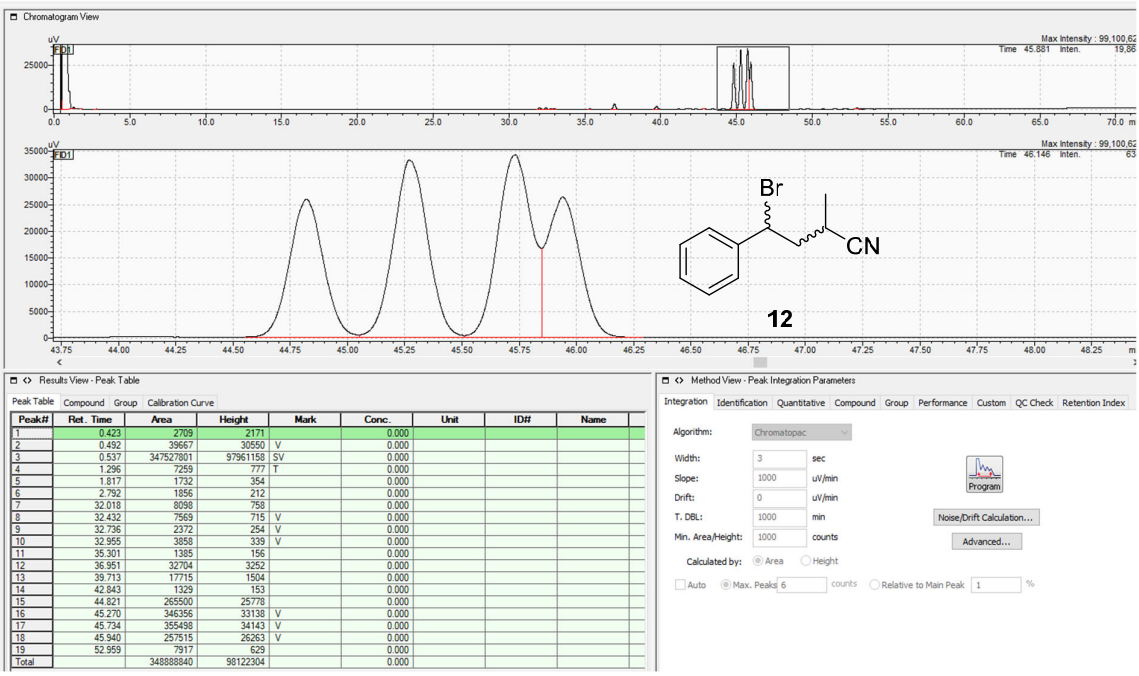



**Figure S14.** Chiral GC for the reaction between styrene and bromoacetonitrile catalysed by $[Cu(BPCDA)]^{2+}$ under *e*ATRA condition giving compound **11.** The analysis was carried out under the following conditions: RT-bDEXcst chiral capillary column (30 m length × 0.25 mm film thickness and 0.25 ⍰m inner diameter), analysed by GC-FID (gas chromatography with flame-ionization detector), separation was achieved using the following program started at 40 °C for 5 min, heating 1.5 C°/min up to 100 °C, then holding for 10 min, heating 1.5 C°/min up to 200°C and holding for 10 min. The two enantiomers of **11** are present at equal amounts.




| Peak# | Ret. Time | Area | Height | Mark | Conc. | Unit | ID# | Name |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.423 | 2709 | 2171 | | 0.000 | | | |
| 2 | 0.492 | 39667 | 30550 | V | 0.000 | | | |
| 3 | 0.537 | 347527801 | 97961158 | SV | 0.000 | | | |
| 4 | 1.296 | 7259 | 777 | T | 0.000 | | | |
| 5 | 1.817 | 1732 | 354 | | 0.000 | | | |
| 6 | 2.792 | 1856 | 212 | | 0.000 | | | |
| 7 | 32.018 | 8098 | 758 | | 0.000 | | | |
| 8 | 32.432 | 7569 | 715 | V | 0.000 | | | |
| 9 | 32.736 | 2372 | 254 | V | 0.000 | | | |
| 10 | 32.955 | 3858 | 339 | V | 0.000 | | | |
| 11 | 35.301 | 1385 | 156 | | 0.000 | | | |
| 12 | 36.951 | 32704 | 3252 | | 0.000 | | | |
| 13 | 39.713 | 17715 | 1504 | | 0.000 | | | |
| 14 | 42.843 | 1329 | 153 | | 0.000 | | | |
| 15 | 44.821 | 265500 | 25778 | | 0.000 | | | |
| 16 | 45.270 | 346356 | 33138 | V | 0.000 | | | |
| 17 | 45.734 | 355498 | 34143 | V | 0.000 | | | |
| 18 | 45.940 | 257515 | 26263 | V | 0.000 | | | |
| 19 | 52.959 | 7917 | 629 | | 0.000 | | | |
| Total | | 348888840 | 98122304 | | 0.000 | | | |

**Figure S15.** Chiral GC for the reaction between styrene and 2-bromopropionitrile catalysed by $[Cu(BPCDA)]^{2+}$ giving compound **12**. The analysis was carried out under the following conditions: RT-bDEXcst chiral capillary column (30 m length × 0.25 mm film thickness and 0.25 □m inner diameter), analysed by GC-FID (gas chromatography with flame-ionization detector), separation was achieved using following program started at 40 °C for 5 min, heating 1.5 C°/min up to 100 °C, then holding for 10 min, heating 1.5 C°/min up to 200°C and holding for 10 min. 4 isomers were separated comprising two pairs of diastereomers (dr 1.3:1) with no enantiomeric excess for either enantiomeric pair.

## References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